ON THE EWALD METHOD AND THE QUARTIC HELMHOLTZ FREE ENERGY OF AN ANHARMONIC METALLIC CRYSTAL

by

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Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

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December 1977

To my wife, Ayşe

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ABSTRACT

A mathematical expression for the quartic term of the Helmholtz free energy of an anharmonic crystal (F_4) is derived which is more appropriate for the long range oscillatory potentials in metals. All the fourth rank tensor sums required in the calculation of F_4 have been obtained by the Ewald's summation technique for the long range asymptotic potentials of the form $r^{-n} \cos(2k_F r)$ and $r^{-(n+1)} \sin(2k_F r)$, where n is an odd integer. The long range contributions (corrections) to each of the various physical properties such as F_4, F_4^E (in Einstein approximation), U(Energy), $\langle\omega^2\rangle$(average ω^2) and the phonon frequencies $\omega_{\underset{\sim}{q}j}$ for a model of Na at 90°K (Shukla and Taylor, 1974) are found to be small.

ACKNOWLEDGEMENT

The analytical and numerical calculations reported in this thesis were suggested and supervised by Dr. R.C. Shukla. I would like to express my gratitude to him for his constant encouragement and personal help.

I would also like to thank Mr. Martin VanderSchans for giving me the long range potential constants.

I should like to thank the National Research Council of Canada and the Department of Physics of Brock University for their financial assistance.

Lastly, I would like to express my appreciation to Mrs. J. Cowan for typing this manuscript and Brock University Computing Center for their excellent services throughout the course of this thesis.

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1. INTRODUCTION

In the theory of the lattice vibrations accurate calculations of anharmonicity have aroused considerable theoretical interest since Mie (1903) and Grüneisen (1908) developed their equation of state assuming a temperature dependent lattice constant. For the first time using classical statistical mechanics, Born and Brody (1921) investigated the effect of anharmonicity on the caloric equation of state. Born and co-workers (1939) studied the temperature dependent elastic constants in the high temperature limit. Stern (1958) discussed the anharmonic deviation of the specific heat from the Dulong-Petit law (3R) at high temperatures. Apparently, the first quantum mechanical perturbation treatment of anharmonic Helmholtz free energy, which is based on the expansion of the crystal potential energy in terms of an ordering parameter, λ, defined by the ratio of a typical atomic displacement and nearest neighbour distance, was given by Ludwig (1958). Expressions for the two lowest order terms in the Helmholtz free energy of $O(\lambda^2)$ arising from the cubic and quartic terms in the Hamiltonian were derived by Ludwig and these are valid for all temperatures. Numerical calculation of the anharmonic Helmholtz free energy was carried out by Maradudin et al (1961) in the high temperature limit for the case of nearest neighbour central force interaction in the leading term approximation where one takes into account in the calculation only the highest order radial derivative of interatomic potential. Horton (1968) has reviewed the anharmonic calculations of the Helmholtz free energy for ideal rare gas crystals. In these crystals it is sufficient to take into account the nearest neighbour interaction in the anharmonic calculations because the potential is of short-range nature. On the contrary, in many simple metals, the potential consists of two parts; the short-range and the oscillatory-long-range. The latter contribution to the potential arises from the effect of the singularity in the dielectric function in the effective ion-ion interaction. For large distances the oscillatory asymptotic potential behaves as $r^{-3}\,\mathrm{Cos}(2k_F r)$ (Harrison, 1966). Thus, for metals, any calculation of a potential dependent physical quantity will end up with an oscillatory result, and will create a convergence problem. For example, Shukla and Taylor (1974) have computed the lowest order cubic (F_3) and quartic (F_4) anharmonic contributions to the Helmholtz free energy for Na and K. In their calculations, (F_3) was found to be rapidly convergent sum, but (F_4) oscillated wildly and turned out to be a function of the shell contributions. This last mentioned quantity (F_4) can be expressed as a sum of potential derivatives over the real-space lattice vectors and certain functions involving Brillouin zone sums for each real-lattice vector. They performed the Brillouin zone sums first and the real space vector summations last, examining the contributions to (F_4) up to 23 real-lattice vector shells, and did not get a convergent answer. On the other hand, for oscillatory asymptotic long range potentials if we perform the real-space summations first and the Brillouin zone summations last, the real-space sums then can be evaluated as rapidly convergent sums with the aid of Ewald's method. Consequently, these convergent sums can be used to calculate long range contributions to many physical quantities such as the quartic term of the Helmholtz free energy, the phonon frequencies, the elastic constants, the Grüneisen constant, thermal expansion, etc. Cohen et al (1976) have studied the long-range contributions to the Grüneisen parameter and the elastic constants. To the best of our knowledge the calculation of the fourth-rank tensor sums for oscillatory asymptotic potentials of the form $r^{-n} \cos(2k_F r)$ and $r^{-(n+1)} \sin(2k_F r)$ (n is odd) by Ewald's method have not previously been reported in the literature. This is one of the main objectives of this thesis.

In Section 2 the quartic anharmonic contribution to the Helmholtz free energy has been expressed in terms of the wave-vector dependent direct lattice sums more suitable for the application of Ewald method. In Section 3 we have given the analytical form of the interionic potential for large distances which yields correct representations of the first, second, third and fourth derivatives of potential when compared with the actual potential derivatives. The method and formalism of Ewald's sums have been given in Section 4. In Section 5 we have presented the numerical calculations for the long-range contributions to the exact quartic term (F_4) in the Helmholtz free energy and the Einstein quartic term (F_4^E). Since the simplest quantities such as the long-range contributions to the energy and the phonon frequencies can also be calculated as another application of Ewald's method we have also computed these quantities in this section. Numerical results have been discussed in Section 6, and finally the conclusions drawn from the results obtained in this thesis are presented in Section 7.

2. QUARTIC ANHARMONIC CONTRIBUTION TO THE HELMHOLTZ FREE ENERGY

The potential energy of vibrating lattice may be expanded in terms of the small displacements

$$\phi = \phi(|\underset{\sim}{r} + \underset{\sim}{u}|)$$
$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \phi_4 + \cdots \tag{2.1}$$

where

$$\phi_n = \frac{1}{2}\frac{N}{n!}\sum_{\ell}{}' \sum_{\alpha\beta\gamma\delta\ldots t} \phi_{\alpha\beta\gamma\delta\ldots t}(|\underset{\sim}{r}^{\ell}|)\, u_\alpha^{\ell} u_\beta^{\ell} u_\gamma^{\ell} u_\delta^{\ell} \cdots u_t^{\ell} \tag{2.2}$$

the prime over the ℓ sum indicates the omission of the origin from the sum, $\underset{\sim}{r}^{\ell}$ are the real lattice vectors $\phi_{\alpha\beta\gamma\delta\ldots t}$ are the anharmonic force constants, and the indices $\alpha, \beta, \gamma, \delta, \ldots, t$ each take the values x, y, z in the summation. u_α the α-component of displacement operator, is given by

$$u_\alpha^{\ell} = \left(\frac{\hbar}{2NM}\right)^{1/2} \sum_{\underset{\sim}{q} j} \frac{e_\alpha(\underset{\sim}{q} j)}{\omega(\underset{\sim}{q} j)^{1/2}}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}^{\ell}} \left(a_{\underset{\sim}{q} j} + a^{\dagger}_{-\underset{\sim}{q} j}\right) \tag{2.3}$$

where N is the number of unit cells in the crystal, M is atomic mass, $e_\alpha(\underset{\sim}{q} j)$ is the α-component of the eigenvector, $\omega(\underset{\sim}{q} j)$ is the angular frequency of the dynamical matrix, $a_{\underset{\sim}{q} j}$ and $a^{\dagger}_{\underset{\sim}{q} j}$ are annihilation and creation operators for the wave vector $(\underset{\sim}{q})$ and branch index (j).

In the first order perturbation theory the quartic anharmonic contribution to the Helmholtz free energy arising from ϕ_4 term in Eq(2.1) is given by (Shukla & Taylor, 1974)

$$F_4 = \langle \phi_4 \rangle \tag{2.4}$$

where the angular bracket denotes the thermal average of ϕ_4 which for any operator $\mathcal{O}$ is defined by

$$\langle \mathcal{O} \rangle_T = \mathrm{Tr}\, e^{-\beta H_o} \mathcal{O} / \mathrm{Tr}\, e^{-\beta H_o} \tag{2.5}$$

where H_o is the harmonic hamiltonian, $k_B T = \beta^{-1}$, k_B is the Boltzmann constant, T is the temperature, Tr denotes the trace of the operators. Substituting ϕ_4 from Eq(2.2) in Eq(2.4) we get

$$E_4 = \frac{1}{2}\frac{N}{4!} \sum_{\ell}{}' \sum_{\alpha\beta\gamma\delta} \phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|) \langle u_\alpha u_\beta u_\gamma u_\delta \rangle \tag{2.6}$$

Anharmonic force constants $\phi_{\alpha\beta\gamma\delta}$ in Eq(2.6) are given by

$$\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|) = \frac{\partial^4}{\partial u_\alpha \partial u_\beta \partial u_\gamma \partial u_\delta} \phi(|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|)\Big|_{\underset{\sim}{u}=0} \tag{2.6)'$$

$$\begin{aligned}
\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|) = {} & (r_\alpha^\ell - u_\alpha)(r_\beta^\ell - u_\beta)(r_\gamma^\ell - u_\gamma)(r_\delta^\ell - u_\delta)|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|^{-4} C(|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|) \\
& + [(r_\alpha^\ell - u_\alpha)(r_\beta^\ell - u_\beta)\delta_{\gamma\delta} + (r_\beta^\ell - u_\beta)(r_\gamma^\ell - u_\gamma)\delta_{\alpha\delta} + (r_\gamma^\ell - u_\gamma)(r_\alpha^\ell - u_\alpha)\delta_{\beta\delta} \\
& + (r_\alpha^\ell - u_\alpha)(r_\delta^\ell - u_\delta)\delta_{\beta\gamma} + (r_\beta^\ell - u_\beta)(r_\delta^\ell - u_\delta)\delta_{\alpha\gamma} + (r_\gamma^\ell - u_\gamma)(r_\delta^\ell - u_\delta)\delta_{\alpha\beta}]|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|^{-3} B(|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|) \\
& + (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\delta\alpha} + \delta_{\alpha\gamma}\delta_{\beta\delta})|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|^{-2} A(|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|)\Big|_{\underset{\sim}{u}=0}
\end{aligned} \tag{2.6a}$$

where

$$C(r) = \left(\frac{d^4}{dr^4} - 6r^{-1}\frac{d^3}{dr^3} + 15r^{-2}\frac{d^2}{dr^2} - 15r^{-3}\frac{d}{dr}\right)\phi(r) \tag{2.6b}$$

$$B(r) = \left(\frac{d^3}{dr^3} - 3r^{-1}\frac{d^2}{dr^2} + 3r^{-2}\frac{d}{dr}\right)\phi(r) \tag{2.6c}$$

$$A(r) = \left(\frac{d^2}{dr^2} - r^{-1}\frac{d}{dr}\right)\phi(r) \tag{2.6d}$$

$\phi(r)$ is a potential function for a given distance.

In Eq(2.6), decoupling the quantity inside the angular bracket, two at a time in all possible ways and taking into account the symmetry of $\phi_{\alpha\beta\gamma\delta}$ in all indices, we can write

$$F_4' = \frac{1}{2}\,\frac{3N}{4!}\sum_{\ell}{}'\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|)\,\langle u_\alpha u_\beta\rangle^{\ell}\langle u_\gamma u_\delta\rangle^{\ell} \tag{2.7}$$

In terms of u_α and u_β, the correlation functions $\langle u_\alpha\ u_\beta\rangle^{\ell}$ can be expressed as

$$\langle u_\alpha u_\beta\rangle^{\ell} = \frac{\hbar}{NM}\sum_{\underset{\sim}{q}j}\frac{e_\alpha(\underset{\sim}{q}j)\,e_\beta(\underset{\sim}{q}j)}{\omega(\underset{\sim}{q}j)}\left[1-\cos(\underset{\sim}{q}\cdot\underset{\sim}{r}^{\ell})\right]\coth\left[\frac{\hbar}{2}\beta\omega(\underset{\sim}{q}j)\right] \tag{2.8}$$

Substitution of Eq(2.8) in Eq(2.7) gives

$$F_4' = \frac{\hbar^2}{16NM^2}\sum_{\ell}{}'\Big\{\sum_{\alpha\beta\gamma\delta}\sum_{\underset{\sim}{q}_1 j_1}\sum_{\underset{\sim}{q}_2 j_2}\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|)\cdot\frac{e_\alpha(\underset{\sim}{q}_1 j_1)\,e_\beta(\underset{\sim}{q}_1 j_1)\,e_\gamma(\underset{\sim}{q}_2 j_2)\,e_\delta(\underset{\sim}{q}_2 j_2)}{\omega(\underset{\sim}{q}_1 j_1)\,\omega(\underset{\sim}{q}_2 j_2)}$$
$$\cdot\left[1-\cos(\underset{\sim}{q}_1\cdot\underset{\sim}{r}^{\ell})\right]\left[1-\cos(\underset{\sim}{q}_2\cdot\underset{\sim}{r}^{\ell})\right]\coth\left(\frac{\hbar}{2}\beta\omega(\underset{\sim}{q}_1 j_1)\right)\coth\left(\frac{\hbar}{2}\beta\omega(\underset{\sim}{q}_2 j_2)\right)\Big\} \tag{2.9}$$

It is obvious from Eq(2.9) that one method of performing the summation for a fixed direct lattice vector r^{ℓ} over the wave vectors and branch indices $(\underset{\sim}{q}j)$ would be to define first the functions $S_{\alpha\beta}(\underset{\sim}{r}^{\ell})$ by

$$S_{\alpha\beta}(\underset{\sim}{r}^{\ell}) = \sum_{\underset{\sim}{q}j}\frac{e_\alpha(\underset{\sim}{q}j)\,e_\beta(\underset{\sim}{q}j)}{\omega(\underset{\sim}{q}j)}\coth\left(\frac{\hbar}{2}\beta\omega(\underset{\sim}{q}j)\right)\left[1-\cos(\underset{\sim}{q}\cdot\underset{\sim}{r}^{\ell})\right] \tag{2.10}$$

and then express Eq(2.9) in terms of $S_{\alpha\beta}$; i.e.

$$F_4' = \frac{\hbar^2}{16NM^2}\sum_{\ell}{}'\sum_{\alpha\beta\gamma\delta}\phi_{\alpha\beta\gamma\delta}(|\underset{\sim}{r}^{\ell}|)\,S_{\alpha\beta}(\underset{\sim}{r}^{\ell})\,S_{\gamma\delta}(\underset{\sim}{r}^{\ell}) \tag{2.11}$$

At this stage one can carry out the summation over $\alpha, \beta, \gamma, \delta$ in Eq(2.11) for a fixed value of $\underset{\sim}{r}^{\ell}$ and this yields altogether 81 terms. Since the fourth-rank tensor $\phi_{\alpha\beta\gamma\delta}$ is completely symmetric and $S_{\alpha\beta}$ is a symmetric tensor, Eq(2.9) really contains 15 distinct terms with different coefficients. The final expression for F_4 is

$$
\begin{aligned}
F_4 = \frac{\hbar^2}{16NM^2}\sum_{\ell}{}' \Big\{ & \phi_{xxxx}(r^{\ell})S_{xx}^2(r^{\ell}) + \phi_{yyyy}(r^{\ell})S_{yy}^2(r^{\ell}) + \phi_{zzzz}(r^{\ell})S_{zz}^2(r^{\ell}) \\
& + \phi_{xxyy}(r^{\ell})\left[2S_{xx}(r^{\ell})S_{yy}(r^{\ell}) + 4S_{xy}^2(r^{\ell})\right] + \phi_{xxzz}(r^{\ell})\left[2S_{xx}(r^{\ell})S_{zz}(r^{\ell}) + 4S_{xz}^2(r^{\ell})\right] \\
& + \phi_{yyzz}(r^{\ell})\left[2S_{yy}(r^{\ell})S_{zz}(r^{\ell}) + 4S_{yz}^2(r^{\ell})\right] + \phi_{xxxy}(r^{\ell})\left(4S_{xx}(r^{\ell})S_{xy}(r^{\ell})\right) + \phi_{xxxz}(r^{\ell})\left(4S_{xx}(r^{\ell})S_{xz}(r^{\ell})\right) \\
& + \phi_{yyyx}(r^{\ell})\left[4S_{yy}(r^{\ell})S_{xy}(r^{\ell})\right] + \phi_{yyyz}(r^{\ell})\left[4S_{yy}(r^{\ell})S_{yz}(r^{\ell})\right] + \phi_{zzzx}(r^{\ell})\left[4S_{zz}(r^{\ell})S_{xz}(r^{\ell})\right] \\
& + \phi_{zzzy}(r^{\ell})\left[4S_{zz}(r^{\ell})S_{yz}(r^{\ell})\right] + \phi_{xxyz}(r^{\ell})\left[4S_{xx}(r^{\ell})S_{yz}(r^{\ell}) + 8S_{xy}(r^{\ell})S_{yz}(r^{\ell})\right] \\
& + \phi_{yyxz}(r^{\ell})\left[4S_{yy}(r^{\ell})S_{xz}(r^{\ell}) + 8S_{xy}(r^{\ell})S_{yz}(r^{\ell})\right] \\
& + \phi_{zzxy}(r^{\ell})\left[4S_{zz}(r^{\ell})S_{xy}(r^{\ell}) + 8S_{xz}(r^{\ell})S_{yz}(r^{\ell})\right]\Big\}
\end{aligned}
\tag{2.12}
$$

or

$$F_4 = \frac{\hbar^2}{16NM^2}\sum_{\ell}{}' f_{\ell} \tag{2.13}$$

where f_{ℓ} is the quantity inside the curly bracket in Eq(2.12). This procedure of calculating F_4 as a function of direct lattice vectors was followed by Shukla and Taylor (1974), which clearly would be useful if f_{ℓ} drops rapidly in magnitude as the $|\underset{\sim}{r}^{\ell}|$ increases. For short range potentials, where the ℓ summation is extended to a few neighbours only, the above method of Shukla and Taylor (1974) would give a rapid convergence. For metals, where the potential is not only long range but oscillatory in nature, F_4 can never be summed satisfactorily by the above method. This was demonstrated by Shukla and Taylor (1974) in their calculation of Na and K. F_4 really never converged, although the summation was extended out to 23 neighbour shells. Since this method did not give a convergent answer for F_4 from Eq(2.9), it was necessary to introduce a different method to get a convergent result for F_4. In this procedure we perform the real lattice vector summations first and the wave vector summations last. Combining the two cosine terms in Eq(2.9) and defining the fourth-rank tensor sums for a fixed value of wave vector $\underset{\sim}{Q}$, as

$$F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q}) = \sum_{\ell}{}' \phi_{\alpha\beta\gamma\delta}(r^{\ell}) \cos(\underset{\sim}{Q}.\underset{\sim}{r}^{\ell}) \tag{2.14}$$

we can express Eq(2.9) in terms of $F_{\alpha\beta\gamma\delta}$; i.e.

$$F_4 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} \sum_{\underset{\sim}{q}_1\underset{\sim}{q}_2 j_1 j_2} \frac{e_\alpha(q_1 j_1) e_\beta(q_1 j_1)}{\omega(\underset{\sim}{q}_1 j_1)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_1 j_1)\right) \cdot \frac{e_\gamma(\underset{\sim}{q}_2 j_2) e_\delta(\underset{\sim}{q}_2 j_2)}{\omega(\underset{\sim}{q}_2 j_2)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_2 j_2)\right)$$

$$\cdot \Big[F_{\alpha\beta\gamma\delta}(0) - F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1) - F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_2) + \frac{1}{2} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{q}_2) + \frac{1}{2} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 - \underset{\sim}{q}_2) \Big] \tag{2.15}$$

Eq(2.15) can be written in terms of only three distinct terms.

On interchanging $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ the second and third terms in Eq(2.15) are found to be equivalent. Since $\underset{\sim}{q}_2$ takes all possible values in the summation, changing $\underset{\sim}{q}_2$ to $-\underset{\sim}{q}_2$ the fourth term is equivalent to the fifth, and finally F_4 can be written as

$$F_4 = F_4^0 - 2F_4^1 + F_4^3 \tag{2.16}$$

where

$$F_4^0 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta}(0) \sum_{\underset{\sim}{q}_1 j_1} \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)}{\omega(\underset{\sim}{q}_1 j_1)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_1 j_1)\right) \sum_{\underset{\sim}{q}_2 j_2} \frac{e_\gamma(\underset{\sim}{q}_2 j_2)\, e_\delta(\underset{\sim}{q}_2 j_2)}{\omega(\underset{\sim}{q}_2 j_2)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_2 j_2)\right) \tag{2.17}$$

$$F_4^1 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} \sum_{\underset{\sim}{q}_1 j_1} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1) \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)}{\omega(\underset{\sim}{q}_1 j_1)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_1 j_1)\right) \sum_{\underset{\sim}{q}_2 j_2} \frac{e_\gamma(\underset{\sim}{q}_2 j_2)\, e_\delta(\underset{\sim}{q}_2 j_2)}{\omega(\underset{\sim}{q}_2 j_2)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_2 j_2)\right) \tag{2.18}$$

$$F_4^3 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} \sum_{\substack{\underset{\sim}{q}_1 \underset{\sim}{q}_2 \\ j_1 j_2}} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{q}_2) \frac{e_\alpha(\underset{\sim}{q}_1 j_1)\, e_\beta(\underset{\sim}{q}_1 j_1)}{\omega(\underset{\sim}{q}_1 j_1)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_1 j_1)\right) \frac{e_\gamma(\underset{\sim}{q}_2 j_2)\, e_\delta(\underset{\sim}{q}_2 j_2)}{\omega(\underset{\sim}{q}_2 j_2)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}_2 j_2)\right) \tag{2.19}$$

2.1 SIMPLIFICATION OF F_4^o, F_4^1, F_4^3

In this section we will simplify the terms F_4^o, F_4^1 and F_4^3 arising in the expression for the quartic term (F_4) in the Helmholtz free energy. Using all the 48 point group operations of a cube for a general wave vector $\underset{\sim}{q}$ with positive components satisfying the condition $q_x \neq q_y \neq q_z \neq 0$ and recalling the fact that

$$\omega(-\underset{\sim}{q}j) = \omega(\underset{\sim}{q}j) \tag{2.20}$$

the wave vector sum appearing in Eq(2.17) can be simplified as

$$\sum_{\underset{\sim}{q}j} \frac{e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j)}{\omega(\underset{\sim}{q}j)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}j)\right) = D\delta_{\alpha\beta} \tag{2.21}$$

Summing the diagonal term of Eq(2.21) over the index α, where α =x,y,z, and using the normalization condition on the eigenvectors, $\sum_\alpha e_\alpha^2(\underset{\sim}{q}j) = 1$ the quantity D is expressed as

$$D = \frac{1}{3}\sum_{\underset{\sim}{q}j} \omega^{-1}(\underset{\sim}{q}j) \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}j)\right) \tag{2.22}$$

Substituting Eq(2.21) in Eq(2.17), we obtain

$$F_4^o = \frac{\hbar^2 D^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta}(0)\, \delta_{\alpha\beta}\, \delta_{\gamma\delta}$$

$$= \frac{\hbar^2 D^2}{16NM^2} \sum_{\alpha\gamma} F_{\alpha\alpha\gamma\gamma}(0) \tag{2.23}$$

Summation over α and γ gives

$$F_4^0 = \frac{\hbar^2 D^2}{16NM^2}\Big\{F'_{xxxx}(0) + F'_{yyyy}(0) + F'_{zzzz}(0) + 2\big[F'_{xxyy}(0) + F'_{xxzz}(0) + F'_{yyzz}(0)\big]\Big\} \tag{2.24}$$

Introducing

$$t_{\alpha\beta}(\underset{\sim}{q}j) = \frac{e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j)}{\omega(\underset{\sim}{q}j)} \coth\left(\frac{\hbar}{2}\beta\,\omega(\underset{\sim}{q}j)\right) \tag{2.25}$$

and using Eq(2.21),Eq(2.18) can be written as

$$F_4^1 = \frac{\hbar^2 D}{16NM^2}\sum_{\underset{\sim}{q}_1 j_1}\sum_{\alpha\beta\gamma\delta} t_{\alpha\beta}(\underset{\sim}{q}_1 j_1)\, F'_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1)\,\delta_{\gamma\delta}$$

$$= \frac{\hbar^2 D}{16NM^2}\sum_{\underset{\sim}{q}_1 j_1}\sum_{\alpha\beta\gamma} t_{\alpha\beta}(\underset{\sim}{q}_1 j_1)\, F'_{\alpha\beta\gamma\gamma}(\underset{\sim}{q}_1) \tag{2.26}$$

or summation over α, β and γ gives for F_4^1

$$\begin{aligned} F_4^1 = \frac{\hbar^2 D}{16NM^2}\sum_{\underset{\sim}{q}_1 j_1}\Big\{ & t_{xx}(\underset{\sim}{q}_1 j_1)\big[F'_{xxxx}(\underset{\sim}{q}_1) + F'_{xxyy}(\underset{\sim}{q}_1) + F'_{xxzz}(\underset{\sim}{q}_1)\big] \\ & + t_{yy}(\underset{\sim}{q}_1 j_1)\big[F'_{yyyy}(\underset{\sim}{q}_1) + F'_{xxyy}(\underset{\sim}{q}_1) + F'_{yyzz}(\underset{\sim}{q}_1)\big] \\ & + t_{zz}(\underset{\sim}{q}_1 j_1)\big[F'_{zzzz}(\underset{\sim}{q}_1) + F'_{xxzz}(\underset{\sim}{q}_1) + F'_{yyzz}(\underset{\sim}{q}_1)\big] \\ & + 2\, t_{xy}(\underset{\sim}{q}_1 j_1)\big[F'_{xxxy}(\underset{\sim}{q}_1) + F'_{yyyx}(\underset{\sim}{q}_1) + F'_{zzxy}(\underset{\sim}{q}_1)\big] \\ & + 2\, t_{xz}(\underset{\sim}{q}_1 j_1)\big[F'_{xxxz}(\underset{\sim}{q}_1) + F'_{zzzx}(\underset{\sim}{q}_1) + F'_{yyxz}(\underset{\sim}{q}_1)\big] \\ & + 2\, t_{yz}(\underset{\sim}{q}_1 j_1)\big[F'_{yyyz}(\underset{\sim}{q}_1) + F'_{zzzy}(\underset{\sim}{q}_1) + F'_{xxyz}(\underset{\sim}{q}_1)\big]\Big\} \end{aligned} \tag{2.27}$$

With the aid of Eq(2.25), Eq(2.19) can be written as

$$F_4^3 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} \sum_{\underset{\sim}{q}_1 j_1} \sum_{\underset{\sim}{q}_2 j_2} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q}_1 + \underset{\sim}{q}_2)\, t_{\alpha\beta}(\underset{\sim}{q}_1 j_1)\, t_{\gamma\delta}(\underset{\sim}{q}_2 j_2) \tag{2.28}$$

For simplicity, we introduce

$$\underset{\sim}{Q} = \underset{\sim}{q}_1 + \underset{\sim}{q}_2$$

and we rewrite Eq(2.28) as

$$F_4^3 = \frac{\hbar^2}{16NM^2} \sum_{\alpha\beta\gamma\delta} \sum_{\underset{\sim}{Q}} F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q}) \sum_{\underset{\sim}{q}_1 j_1 j_2} t_{\alpha\beta}(\underset{\sim}{q}_1 j_1)\, t_{\gamma\delta}(\underset{\sim}{Q} - \underset{\sim}{q}_1, j_2) \tag{2.29}$$

Summation over α, β, γ, δ gives

$$\begin{aligned} F_4^3 = \frac{\hbar^2}{16NM^2} \sum_{\underset{\sim}{Q}} \Big\{ & F_{xxxx}(\underset{\sim}{Q}) T_{xxxx}(\underset{\sim}{Q}) + F_{yyyy}(\underset{\sim}{Q}) T_{yyyy}(\underset{\sim}{Q}) + F_{zzzz}(\underset{\sim}{Q}) T_{zzzz}(\underset{\sim}{Q}) \\ & + F_{xxyy}(\underset{\sim}{Q}) T_{xxyy}(\underset{\sim}{Q}) + F_{xxzz}(\underset{\sim}{Q}) T_{xxzz}(\underset{\sim}{Q}) + F_{yyzz}(\underset{\sim}{Q}) T_{yyzz}(\underset{\sim}{Q}) \\ & + F_{xxxy}(\underset{\sim}{Q}) T_{xxxy}(\underset{\sim}{Q}) + F_{xxxz}(\underset{\sim}{Q}) T_{xxxz}(\underset{\sim}{Q}) + F_{yyyx}(\underset{\sim}{Q}) T_{yyyx}(\underset{\sim}{Q}) \\ & + F_{yyyz}(\underset{\sim}{Q}) T_{yyyz}(\underset{\sim}{Q}) + F_{zzzx}(\underset{\sim}{Q}) T_{zzzx}(\underset{\sim}{Q}) + F_{zzzy}(\underset{\sim}{Q}) T_{zzzy}(\underset{\sim}{Q}) \\ & + F_{xxyz}(\underset{\sim}{Q}) T_{xxyz}(\underset{\sim}{Q}) + F_{yyxz}(\underset{\sim}{Q}) T_{yyxz}(\underset{\sim}{Q}) + F_{zzxy}(\underset{\sim}{Q}) T_{zzxy}(\underset{\sim}{Q}) \Big\} \end{aligned} \tag{2.30}$$

where

$$T_{xxxx}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q}_1 j_1 j_2} t_{xx}(\underset{\sim}{q}_1 j_1)\, t_{xx}(\underset{\sim}{Q} - \underset{\sim}{q}_1, j_2) \tag{2.31}$$

$$T_{yyyy}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q_1} j_1 j_2} t_{yy}(\underset{\sim}{q_1}, j_1)\, t_{yy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) \tag{2.32}$$

$$T_{zzzz}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q_1} j_1 j_2} t_{zz}(\underset{\sim}{q_1}, j_1)\, t_{zz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) \tag{2.33}$$

$$T_{xxyy}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{xx}(\underset{\sim}{q_1} j_1)\, t_{yy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{xx}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{yy}(\underset{\sim}{q_1} j_1) + 4\, t_{xy}(\underset{\sim}{q_1} j_1)\, t_{xy}(\underset{\sim}{Q} - \underset{\sim}{q_1}) \Big] \tag{2.34}$$

$$T_{xxzz}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{xx}(\underset{\sim}{q_1} j_1)\, t_{zz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{xx}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{zz}(\underset{\sim}{q_1} j_1) + 4\, t_{xz}(\underset{\sim}{q_1} j_1)\, t_{xz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) \Big] \tag{2.35}$$

$$T_{yyzz}(\underset{\sim}{Q}) = \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{yy}(\underset{\sim}{q_1} j_1)\, t_{zz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{yy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{zz}(\underset{\sim}{q_1} j_1) + 4\, t_{yz}(\underset{\sim}{q_1} j_1)\, t_{yz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) \Big] \tag{2.36}$$

$$T_{xxxy}(\underset{\sim}{Q}) = 2 \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{xx}(\underset{\sim}{q_1} j_1)\, t_{xy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{xx}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{xy}(\underset{\sim}{q_1} j_1) \Big] \tag{2.37}$$

$$T_{xxxz}(\underset{\sim}{Q}) = 2 \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{xx}(\underset{\sim}{q_1} j_1)\, t_{xz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{xx}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{xz}(\underset{\sim}{q_1} j_1) \Big] \tag{2.38}$$

$$T_{yyyx}(\underset{\sim}{Q}) = 2 \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{yy}(\underset{\sim}{q_1} j_1)\, t_{xy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{yy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{xy}(\underset{\sim}{q_1} j_1) \Big] \tag{2.39}$$

$$T_{yyyz}(\underset{\sim}{Q}) = 2 \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{yy}(\underset{\sim}{q_1} j_1)\, t_{yz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{yy}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{yz}(\underset{\sim}{q_1} j_1) \Big] \tag{2.40}$$

$$T_{zzzx}(\underset{\sim}{Q}) = 2 \sum_{\underset{\sim}{q_1} j_1 j_2} \Big[t_{zz}(\underset{\sim}{q_1} j_1)\, t_{xz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2) + t_{zz}(\underset{\sim}{Q} - \underset{\sim}{q_1}, j_2)\, t_{xz}(\underset{\sim}{q_1} j_1) \Big] \tag{2.41}$$

$$T_{zzzy}(\underset{\sim}{Q})=2\sum_{\underset{\sim}{q}_1 j_1 j_2}\left[t_{zz}(\underset{\sim}{q}_1 j_1)\,t_{yz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{zz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{yz}(\underset{\sim}{q}_1 j_1)\right] \tag{2.42}$$

$$\begin{aligned}T_{xxyz}(\underset{\sim}{Q})=2\sum_{\underset{\sim}{q}_1 j_1 j_2}\Big[&t_{xx}(\underset{\sim}{q}_1 j_1)\,t_{yz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{xx}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{yz}(\underset{\sim}{q}_1 j_1)\\&+2\left(t_{xy}(\underset{\sim}{q}_1 j_1)\,t_{xz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{xy}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{xz}(\underset{\sim}{q}_1 j_1)\right)\Big]\end{aligned} \tag{2.43}$$

$$\begin{aligned}T_{yyxz}(\underset{\sim}{Q})=2\sum_{\underset{\sim}{q}_1 j_1 j_2}\Big[&t_{yy}(\underset{\sim}{q}_1 j_1)\,t_{xz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{yy}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{xz}(\underset{\sim}{q}_1 j_1)\\&+2\left(t_{xy}(\underset{\sim}{q}_1 j_1)\,t_{yz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{xy}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{yz}(\underset{\sim}{q}_1 j_1)\right)\Big]\end{aligned} \tag{2.44}$$

$$\begin{aligned}T_{zzxy}(\underset{\sim}{Q})=2\sum_{\underset{\sim}{q}_1 j_1 j_2}\Big[&t_{zz}(\underset{\sim}{q}_1 j_1)\,t_{xy}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{zz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{xz}(\underset{\sim}{q}_1 j_1)\\&+2\left(t_{xz}(\underset{\sim}{q}_1 j_1)\,t_{yz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)+t_{xz}(\underset{\sim}{Q}-\underset{\sim}{q}_1, j_2)\,t_{yz}(\underset{\sim}{q}_1 j_1)\right)\Big]\end{aligned} \tag{2.45}$$

2.2 THE QUARTIC ANHARMONIC CONTRIBUTION TO THE HELMHOLTZ FREE ENERGY IN THE EINSTEIN MODEL (F_4^E) AND THE AVERAGE ω^2

The simplest calculation of any thermal vibrational property of solids can be performed in the Einstein model where every phonon frequency $\omega(\underset{\sim}{q}j)$ is replaced by the Einstein frequency $\omega_E = \langle \omega^2 \rangle^{1/2}$. Since we are interested in the calculation of F_4 in the Einstein approximation (F_4^E) and average ω^2, in this section we will derive analytical expressions for these quantities.

In the Einstein approximation the frequency dependent term can be taken out of the wave vector sum in Eq(2.8) and the correlation function can be written as

$$\langle u_\alpha u_\beta \rangle^\ell = \frac{\hbar}{NM}\, \omega_E^{-1} \coth\left(\frac{\hbar}{2}\beta\omega_E\right) \sum_{\underset{\sim}{q} j} e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j) \left[1 - \cos(\underset{\sim}{q}.\underset{\sim}{\ell})\right] \tag{2.46}$$

where for simplicity we have substituted $\underset{\sim}{\ell}$ in place of the direct lattice vector $\underset{\sim}{r}^\ell$.

The Eq(2.46) can be simplified using the orthonormality condition of the eigenvectors

$$\sum_j e_\alpha(\underset{\sim}{q}j)\, e_\beta(\underset{\sim}{q}j) = \delta_{\alpha\beta} \tag{2.47}$$

and the sum over the wave vectors $\underset{\sim}{q}$, viz

$$\sum_{\underset{\sim}{q}} \cos(\underset{\sim}{q}.\underset{\sim}{\ell}) = N\,\Delta(\underset{\sim}{\ell}) \tag{2.48}$$

where

$$\Delta(\underset{\sim}{\ell}) = 1 \quad \text{if} \quad \underset{\sim}{\ell} = 0$$
$$= 0 \quad \text{otherwise}$$

The final result is

$$\langle u_\alpha u_\beta \rangle = C_E \delta_{\alpha\beta} \tag{2.49}$$

where

$$C_E = \hbar (M\omega_E)^{-1} \coth\left(\frac{\hbar}{2}\beta\omega_E\right) \tag{2.50}$$

(a) Expression for F_4^E

Substituting Eq(2.49) in Eq(2.7), we get

$$F_4^E = \frac{1}{2}\frac{3N}{4!} C_E^2 \sum_{\alpha\beta\gamma\delta} \sum_{\underset{\sim}{l}}' \phi_{\alpha\beta\gamma\delta}(l\underset{\sim}{l}1)\, \delta_{\alpha\beta}\delta_{\gamma\delta}$$

$$= \frac{1}{2}\frac{3N}{4!} C_E^2 \sum_{\alpha\gamma} \sum_{\underset{\sim}{l}}' \phi_{\alpha\alpha\gamma\gamma}(l\underset{\sim}{l}1) \tag{2.51}$$

Using Eqs(2.6b), (2.6c), (2.6d) in Eq(2.6a) and substituting the resulting expressions in Eq(2.51) then summing over α and γ we obtain the following expression for F_4^E

$$F_4^E = \frac{1}{2}\frac{3N}{4!} C_E^2 \sum_{\underset{\sim}{l}}' \left[\phi''''(l\underset{\sim}{l}1) + 4|\underset{\sim}{l}|^{-1} \phi'''(l\underset{\sim}{l}1) \right] \tag{2.52}$$

(b) Expression for $\langle \omega^2 \rangle$

The average ω^2, $\langle \omega^2 \rangle$, is defined by

$$\langle \omega^2 \rangle = (3N)^{-1} \sum_{\underset{\sim}{q}j} \omega^2(\underset{\sim}{q}j) \tag{2.53}$$

The eigenvalue equation is given by

$$\omega^2(\underset{\sim}{q}j)\, e_\alpha(\underset{\sim}{q}j) = \sum_\beta D_{\alpha\beta}(\underset{\sim}{q})\, e_\beta(\underset{\sim}{q}j) \tag{2.54}$$

where the elements of the dynamical matrix, $D_{\alpha\beta}$, are defined by

$$D_{\alpha\beta}(\underset{\sim}{q}) = M^{-1} \sum_{\underset{\sim}{\ell}}' \phi_{\alpha\beta}(|\underset{\sim}{\ell}|)\left(1 - e^{-i\underset{\sim}{q}\cdot\underset{\sim}{\ell}}\right) \tag{2.55}$$

Multiplying both sides of Eq(2.54) by $e_\alpha(\underset{\sim}{q}j)$ and summing over the index α, we get

$$\sum_\alpha e_\alpha(\underset{\sim}{q}j)\,\omega^2(\underset{\sim}{q}j)\,e_\alpha(\underset{\sim}{q}j) = \sum_{\alpha\beta} e_\alpha(\underset{\sim}{q}j)\,D_{\alpha\beta}(\underset{\sim}{q})\,e_\beta(\underset{\sim}{q}j) \tag{2.56}$$

Using the normalization condition

$$\sum_\alpha e_\alpha(\underset{\sim}{q}j)\,e_\alpha(\underset{\sim}{q}j) = 1 \tag{2.57}$$

in Eq(2.56) and summing both sides of this equation over $\underset{\sim}{q}$ and j, we get

$$\begin{aligned}\sum_{\underset{\sim}{q}j} \omega^2(\underset{\sim}{q}j) &= \sum_{\underset{\sim}{q}j}\sum_{\alpha\beta} e_\alpha(\underset{\sim}{q}j)\,D_{\alpha\beta}(\underset{\sim}{q})\,e_\beta(\underset{\sim}{q}j)\\ &= \sum_{\underset{\sim}{q}}\sum_{\alpha\beta} D_{\alpha\beta}(\underset{\sim}{q})\sum_j e_\alpha(\underset{\sim}{q}j)\,e_\beta(\underset{\sim}{q}j)\end{aligned} \tag{2.58}$$

Using Eq(2.47), we can write Eq(2.58) as

$$\begin{aligned}\sum_{\underset{\sim}{q}j} \omega^2(\underset{\sim}{q}j) &= \sum_{\underset{\sim}{q}}\sum_{\alpha\beta} D_{\alpha\beta}(\underset{\sim}{q})\,\delta_{\alpha\beta}\\ &= \sum_{\underset{\sim}{q}}\sum_{\alpha} D_{\alpha\alpha}(\underset{\sim}{q})\\ &= \sum_{\underset{\sim}{q}} \mathrm{Tr}\, D(\underset{\sim}{q})\end{aligned} \tag{2.59}$$

and finally the expression for $\langle\omega^2\rangle$ can be obtained by combining Eqs(2.53) and (2.59) in the form

$$\langle\omega^2\rangle = (3N)^{-1}\sum_{\underset{\sim}{q}} \mathrm{Tr}\, D(\underset{\sim}{q}) \tag{2.60}$$

Substituting Eq(2.55) in Eq(2.60) we get

$$\langle\omega^2\rangle = (3MN)^{-1} \sum_{\underset{\sim}{\ell}}' \sum_{\underset{\sim}{q}} \sum_{\alpha} \phi_{\alpha\alpha}(1\underset{\sim}{\ell}1)\left(1 - e^{-i\underset{\sim}{q}\cdot\underset{\sim}{\ell}}\right)$$

$$= (3MN)^{-1} \sum_{\underset{\sim}{\ell}}' \sum_{\alpha} \phi_{\alpha\alpha}(1\underset{\sim}{\ell}1)\left[N - N\Delta(\underset{\sim}{\ell})\right]$$

$$= (3M)^{-1} \sum_{\underset{\sim}{\ell}}' \left[\phi_{xx}(1\underset{\sim}{\ell}1) + \phi_{yy}(1\underset{\sim}{\ell}1) + \phi_{zz}(1\underset{\sim}{\ell}1)\right] \qquad (2.61)$$

where in obtaining Eq(2.61) we have used Eq(2.48). The harmonic force constants appearing in the above equation are defined by

$$\phi_{\alpha\beta}(1\underset{\sim}{\ell}1) = \left(\frac{\partial^2}{\partial u_\alpha \partial u_\beta}\phi(1\underset{\sim}{\ell} - \underset{\sim}{u}1)\right|_{\underset{\sim}{u}=0}$$

$$= \Big((\ell_\alpha - u_\alpha)(\ell_\beta - u_\beta)|\underset{\sim}{\ell} - \underset{\sim}{u}|^{-2}\left[\phi''(1\underset{\sim}{\ell} - \underset{\sim}{u}1) - |\underset{\sim}{\ell} - \underset{\sim}{u}|^{-1}\right.$$

$$\left.\cdot\,\phi'(1\underset{\sim}{\ell} - \underset{\sim}{u}1)\right] + \delta_{\alpha\beta}|\underset{\sim}{\ell} - \underset{\sim}{u}|^{-1}\phi'(1\underset{\sim}{\ell} - \underset{\sim}{u}1)\Big|_{\underset{\sim}{u}=0} \qquad (2.62)$$

With the aid of Eq(2.62), Eq(2.61) is reduced to the following form

$$\langle\omega^2\rangle = (3M)^{-1} \sum_{\underset{\sim}{\ell}}' \left[\phi''(1\underset{\sim}{\ell}1) + 2|\underset{\sim}{\ell}|^{-1}\phi'(1\underset{\sim}{\ell}1)\right] \qquad (2.63)$$

3. INTERIONIC POTENTIAL

For simple metals like Na,K (tightly bound cores) the interionic potential can be written as

$$U(r) = (Z'e)^2 r^{-1} + U_{Ie} \qquad (3.1)$$

where Z' is the ionic valence and U_{Ie} is the ion-electron interaction which comes from the screening of the ion motion by the conduction electrons.

$$U_{Ie} = -\pi^{-1} 2(Z'e)^2 \int_0^{\infty} dq\, F(q)\, (qr)^{-1} \sin(qr) \qquad (3.2)$$

where

$$F(q) = (Z')^2 M(q) \left[(q^2 + Q(q))^{-1} Q(q) \right] \qquad (3.3)$$

M(q) is the bare electron-ion matrix element, Q(q) is the static electron gas screening function related to the dielectric function by the equation

$$Q(q) = q^2 \left[\epsilon(q) - 1 \right] \qquad (3.4)$$

where

$$\epsilon(q) = 1 + (2\pi k_F \hbar^2 \eta^2)^{-1} m e^2 \left[(2\eta)^{-1} (1-\eta^2) \ln \left| \frac{1+\eta}{1-\eta} \right| + 1 \right] \qquad (3.5)$$

and $\eta = q/2k_F$, q is the wave vector, k_F is the Fermi wave number, m and e are the electronic mass and charge respectively.
For large distances, the effect of the logarithmic singularity at $|\underset{\sim}{q}| = 2k_F$ in $\epsilon(q)$ given by Eq(3.5) gives rise to an asymptotic representation of the potential function of the

form (Harrison, 1966)

$$r^{-3}\, \mathrm{Cos}(2k_F r)$$

This oscillatory behavior of the potential creates the convergence problem for the potential and potential derivative dependent sums over the real lattice vectors(r), such as the quartic term (F_4) in the Helmholtz free energy, the phonon frequencies, etc. In the numerical calculation, the oscillatory convergence of (F_4) has been indicated by Shukla and Taylor (1974). In Figures 1 and 2 we have plotted (F_4) and $\langle\omega^2\rangle$ calculated from the interionic potential given by Eq(3.1) (Shukla & Taylor (1974)). To compute the long-range contribution to the energy, Basinski et al. (1970) introduced the four-term asymptotic potential

$$\sum_{i=1}^{2}\left[\alpha_{2i-1}(2k_F)^{-(2i+1)}\mathrm{Cos}(2k_F r)+\alpha_{2i+1}(2k_F)^{-(2i+2)}\mathrm{Sin}(2k_F r)\right] \tag{3.6}$$

But Eq(3.6) does not give/the correct representation of the third and fourth derivatives obtained from the actual potential (Shukla and Taylor, 1974), thus we have chosen the 8-term pair potential as

$$\phi(r^{\ell})=\sum_{i=1}^{4}\left[A_i(2k_F r^{\ell})^{-(2i+1)}\mathrm{Cos}(2k_F r^{\ell})+B_i(2k_F r^{\ell})^{-(2i+2)}\mathrm{Sin}(2k_F r^{\ell})\right] \tag{3.7}$$

The potential constants A_i and B_i presented in Table 1 have been determined from the four inflection points of the actual potential function.

The first, second, third and fourth derivatives obtained from the above potential Eq(3.7), for Na at 90^{o}K are in reasonable agreement at larger distances in terms of magnitude and sign with those of the actual potential of Shukla and Taylor (1974). We have presented in Table 2 the first four derivatives calculated by Shukla and Taylor (1974) and from Eq(3.7) respectively.

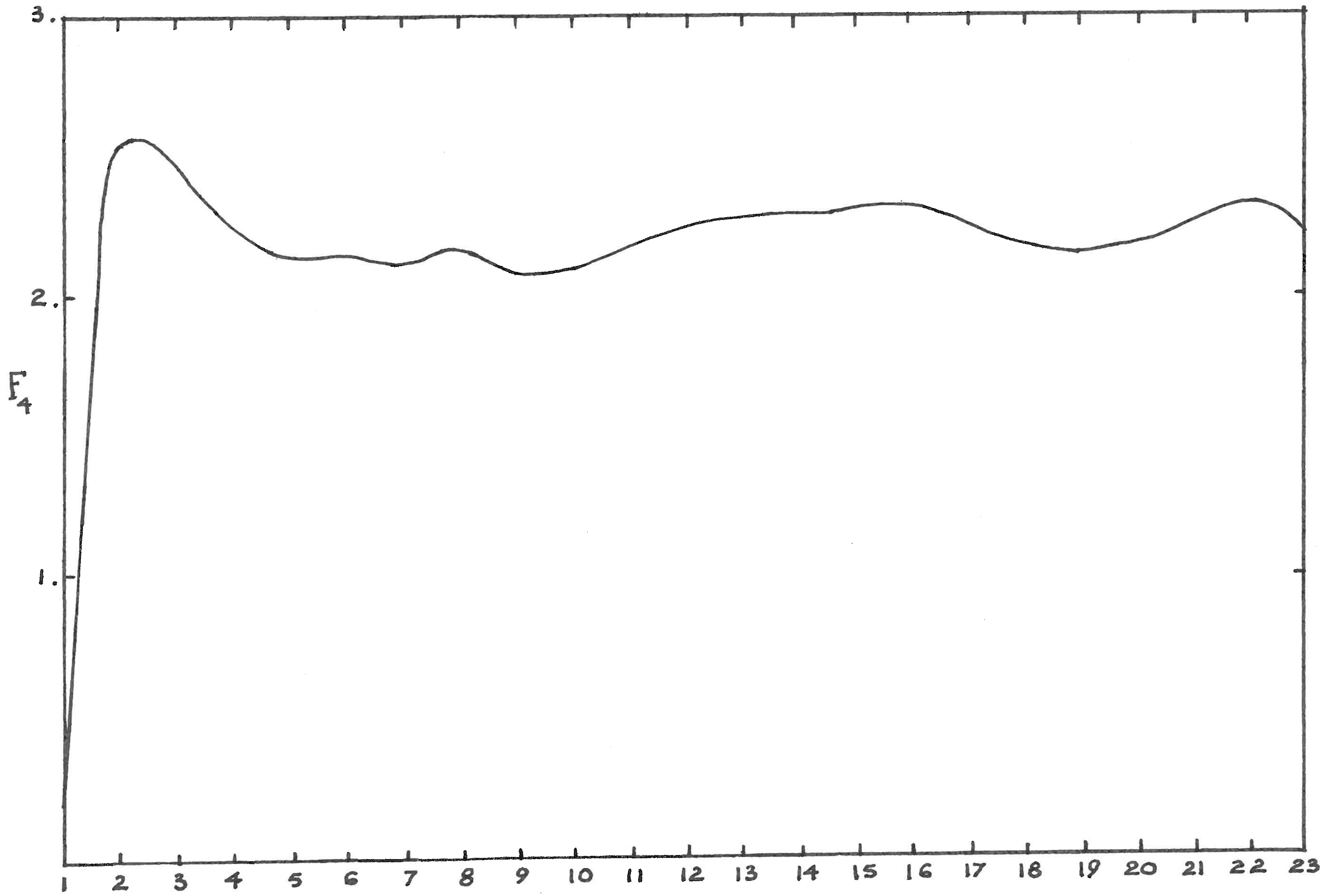

Figure 1. F_4, in units of $10^{12} N(k_B T)^2 erg^{-1}$ as a function of shell number, for actual potential. $a = 4.234$ Å.

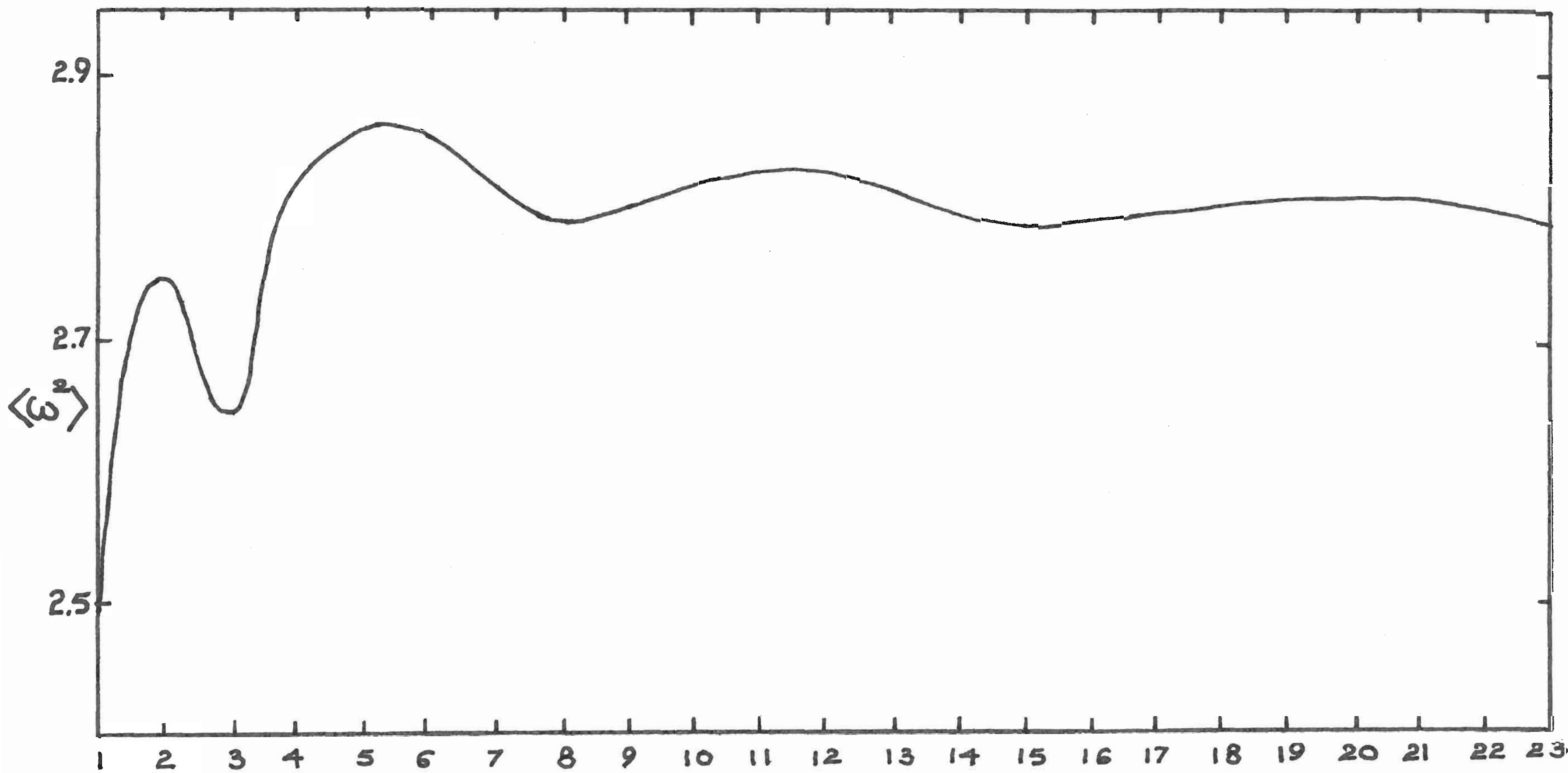

Figure 2. $\langle \omega^2 \rangle$, in units of 10^{26} rad^{2}sec^{-2} as a function of shell number for actual potential and lattice parameter $a = 4.234$ Å.

TABLE 1. Long range potential constants.

The units are eV for $a = 4.234$ Å.

A_1	$-.528305137$
B_1	$-.397123867 \times 10$
A_2	$-.416975194 \times 10^{2}$
B_2	$-.319156322 \times 10^{4}$
A_3	$-.103945142 \times 10^{4}$
B_3	$-.125589463 \times 10^{6}$
A_4	$.718540782 \times 10^{6}$
B_4	$.568556732 \times 10^{7}$

TABLE 2. Actual and long range potential derivatives as a function of $\underset{\sim}{r}^s = (a/2)(n_x^s, n_y^s, n_z^s)$. The units are $erg.cm^{-2}$, $erg.cm^{-2}$, $erg.cm^{-3}$, $erg.cm^{-4}$. $a = 4.234 \times 10^{-8}$ cm. for Na at 90° K.

	$d\phi/dr^s/r^s/10^2$		$d^2\phi/d(r^s)^2/10^3$		$d^3\phi/d(r^s)^3/10^{11}$		$d^4\phi/d(r^s)^4/10^{20}$	
$\underset{\sim}{n}^s$	AP	LRP	AP	LRP	AP	LRP	AP	LRP
111	-1.3335	-4.4371	3.7627	5.5220	-9.8008	-7.0953	1.8343	-2.2853
200	1.2083	.4976	.3498	1.2203	-3.4268	-5.3266	.7047	1.0760
220	-.1349	-.0867	-.0783	-.0807	.4246	.3977	-.0493	-.0500
311	-.0343	-.0238	.0922	.0700	-.0511	-.0448	-.0071	-.0200
222	.0023	.0029	.0699	.0488	-.1031	-.0839	-.0245	-.0056
400	.0212	.0110	-.0219	-.0204	-.0610	-.0113	.0069	.0091
331	-.0034	-.0045	-.0193	-.0102	.0312	.0237	-.0044	.0007
420	-.0073	-.0062	-.0125	-.0036	.0287	.0263	.0028	-.0015
422	-.0050	-.0015	.0123	.0085	.0066	-.0016	-.0062	-.0030
333	.0013	.0022	.0065	.0033	-.0121	-.0120	.0043	-.0002
511	.0013	.0022	.0065	.0033	-.0121	-.0120	.0043	-.0002
440	.0030	.0008	-.0047	-.0043	-.0141	-.0007	.0054	.0016
531	.0002	-.0008	-.0055	-.0027	.0055	.0057	.0007	.0006
442	-.0004	-.0011	-.0044	-.0016	.0064	.0064	.0003	.0002
600	-.0004	-.0011	-.0044	-.0016	.0064	.0064	.0003	.0002
620	-.0016	-.0009	-.0003	.0020	.0073	.0030	.0015	-.0009
533	-.0010	.00002	.0032	.0024	.0010	-.0014	-.0043	-.0008
622	-.0006	.0003	.0028	.0021	-.0046	-.0026	-.0022	-.0006
444	.0003	.0007	.0025	-.0001	.0025	-.0036	-.0030	.0002
551	.0008	.0004	-.0004	-.0014	-.0110	-.0017	.0017	.0006
711	.0008	.0004	-.0004	-.0014	-.0110	-.0017	.0017	.0006
640	.0006	.0003	-.0017	-.0016	-.0059	-.0008	.0047	.0006
624	.0001	-.0003	-.0002	-.0011	.0026	.0020	-.0021	.0003

4. METHOD OF OBTAINING WAVE-VECTOR DEPENDENT TENSOR SUMS

We have introduced the oscillatory asymptotic form of the interionic potential in section 3. As pointed out before in section 1, this potential creates oscillatory wave vector dependent direct lattice sums which arise in the calculation of the various physical properties. Thus, in this section we turn our attention to the development of a technique for evaluating these sums.

The simplest property we can calculate is the potential energy.

$$U = \frac{1}{2} \sum_{\ell}{}' \phi(|\underset{\sim}{r}^{\ell}|) \tag{4.1}$$

where r^{ℓ} is the ℓ th neighbour distance and $\phi(r^{\ell})$ is the 8-term asymptotic potential

$$\phi(r^{\ell}) = \sum_{i=1}^{4} \left[a_i (r^{\ell})^{-(2i+1)} \mathrm{Cos}(2k_F r^{\ell}) + b_i (r^{\ell})^{-(2i+2)} \mathrm{Sin}(2k_F r^{\ell}) \right] \tag{4.2}$$

where

$$a_i = A_i (2k_F)^{-(2i+1)} \quad , \quad b_i = B_i (2k_F)^{-(2i+2)} \tag{4.3}$$

After substituting Eq(4.2) in Eq(4.1) and introducing the sums (tensors of zero rank)

$$C_n(2k_F, \underset{\sim}{Q}, \underset{\sim}{u}) = \sum_{\ell}{}' |\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|^{-n} \mathrm{Cos}(2k_F |\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|) \, \mathrm{Cos}(\underset{\sim}{Q} \cdot \underset{\sim}{r}^{\ell}) \tag{4.4}$$

$$S_n(2k_F, \underset{\sim}{Q}, \underset{\sim}{u}) = \sum_{\ell}{}' |\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|^{-n} \mathrm{Sin}(2k_F |\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|) \cdot \mathrm{Cos}(\underset{\sim}{Q} \cdot \underset{\sim}{r}^{\ell}) \tag{4.5}$$

the interionic potential energy can be written as

$$U = \frac{1}{2}\sum_{i=1}^{4}\left[a_i C_{2i+1}(2k_F,0,0) + b_i S_{2i+2}(2k_F,0,0)\right] \tag{4.6}$$

The other wave vector dependent direct lattice sums arise in the expression of the dynamical matrix elements defined by

$$M D_{\alpha\beta}(\underset{\sim}{Q}) = \sum_{\ell}' \phi_{\alpha\beta}(r^{\ell})\left[1 - \cos(\underset{\sim}{Q}\cdot\underset{\sim}{r}^{\ell})\right] \tag{4.7}$$

where the force constants $\phi_{\alpha\beta}$ are given by

$$\phi_{\alpha\beta}(r^{\ell}) = \frac{\partial^2}{\partial u_\alpha \partial u_\beta}\,\phi(|\underset{\sim}{r}^{\ell} - \underset{\sim}{u}|)\Big|_{\underset{\sim}{u}=0} \tag{4.8}$$

Substituting ϕ from Eq(4.2) in Eq(4.8) the resulting expression for Eq(4.7) can be expressed in terms of the following second rank tensor sums:

$$C_n^{\alpha\beta}(2k_F,\underset{\sim}{Q}) = \frac{\partial^2}{\partial u_\alpha \partial u_\beta}\,C_n(2k_F,\underset{\sim}{Q},\underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{4.9}$$

$$S_m^{\alpha\beta}(2k_F,\underset{\sim}{Q}) = \frac{\partial^2}{\partial u_\alpha \partial u_\beta}\,S_n(2k_F,\underset{\sim}{Q},\underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{4.10}$$

as

$$M D_{\alpha\beta}(\underset{\sim}{Q}) = \sum_{i=1}^{4}\Big\{a_i\left[C_{2i+1}^{\alpha\beta}(2k_F,0) - C_{2i+1}^{\alpha\beta}(2k_F,\underset{\sim}{Q})\right]$$

$$+ b_i\left[S_{2i+2}^{\alpha\beta}(2k_F,0) - S_{2i+2}^{\alpha\beta}(2k_F,\underset{\sim}{Q})\right]\Big\} \tag{4.11}$$

In section 2 the quartic term (F_4) in the free energy was expressed in terms of the wave vector dependent lattice sums defined by

$$F'_{\alpha\beta\gamma\delta}(\underset{\sim}{Q}) = \sum_{\ell}' \phi_{\alpha\beta\gamma\delta}(r^{\ell}) \,\mathrm{Cos}(\underset{\sim}{Q}\cdot\underset{\sim}{r}^{\ell}) \tag{4.12}$$

Substituting ϕ from Eq(4.2) in Eq(2.6)$'$ and defining the following two different fourth rank tensor sums

$$C_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{Q}) = \frac{\partial^4}{\partial u_\alpha \partial u_\beta \partial u_\gamma \partial u_\delta} C_n(2k_F, \underset{\sim}{Q}, \underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{4.13}$$

$$S_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{Q}) = \frac{\partial^4}{\partial u_\alpha \partial u_\beta \partial u_\gamma \partial u_\delta} S_n(2k_F, \underset{\sim}{Q}, \underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{4.14}$$

Eq(4.12) can be expressed as

$$F'_{\alpha\beta\gamma\delta}(\underset{\sim}{Q}) = \sum_{i=1}^{4} \left[a_i\, C_{2i+1}^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{Q}) + b_i\, S_{2i+2}^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{Q}) \right) \tag{4.15}$$

Therefore, in the calculations of the long range contributions to the quartic term (F_4) in the free energy, energy (U), and phonon frequencies $\omega(\underset{\sim}{q}j)$, we need to evaluate six types of oscillatory slowly convergent "infinite" direct lattice sums viz.

$$C_n, \; S_n, \; C_n^{\alpha\beta}, \; C_n^{\alpha\beta\gamma\delta}, \; S_n^{\alpha\beta\gamma\delta}, \; S_n^{\alpha\beta}$$

One of the most useful methods of evaluating slowly convergent lattice sums was introduced by Ewald (1921). First we apply Ewald's method to C_n and then we generate all other cosine sums by differentiating this basic sum with respect to u_α, u_β, u_γ, u_δ. All sine sums are also generated from the cosine sums from the following equation

$$S_n(2k_F, \underset{\sim}{Q}, \underset{\sim}{u}) = -\frac{d}{d(2k_F)} C_{n+1}(2k_F, \underset{\sim}{Q}, \underset{\sim}{u})$$

According to Ewald's procedure, the term $|\underset{\sim}{r}-\underset{\sim}{u}|^{-n}$ in the direct lattice sum is replaced by the Gaussian integral, then the integral is split into two parts over the dummy variable. This creates two direct lattice sums. Using the Theta function transformation, the slowly convergent direct lattice sum is replaced by the reciprocal sum. (For further details see Appendix A2). The sum C_n is independent of the choice of the splitting point, namely the Ewald parameter (α). α is chosen in such a manner that the two sums over the direct and the reciprocal lattice vectors converge rapidly.

Following Born and Huang notation we find (see Appendix A2)

$$C_n(2k_F,\underset{\sim}{q},\underset{\sim}{u})=\frac{2}{\Gamma(n/2)}\Big[\sum_{\underset{\sim}{\ell}}{}' \operatorname{Cos}(2k_F|\underset{\sim}{\ell}-\underset{\sim}{u}|)\operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})\int_{\alpha}^{\infty}dy\, y^{n-1}e^{-\ell^2y^2}\Big]$$
$$+\sum_{\underset{\sim}{G}}E_n^c(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,\underset{\sim}{u})-\frac{2}{\Gamma(n/2)}\int_0^{\alpha}dy\, y^{n-1}e^{-u^2y^2} \tag{4.16}$$

$$S_n(2k_F,\underset{\sim}{q},\underset{\sim}{u})=\frac{2}{\Gamma(\frac{n+1}{2})}\sum_{\underset{\sim}{\ell}}{}'|\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n}\operatorname{Sin}(2k_F|\underset{\sim}{\ell}-\underset{\sim}{u}|)\operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})\int_{\alpha}^{\infty}dy\, y^{n}e^{-\ell^2y^2} \tag{4.17}$$
$$+\sum_{\underset{\sim}{G}}E_n^s(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,\underset{\sim}{u})$$

where

$$E_n^c(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,\underset{\sim}{u})=\frac{\pi^{3/2}\operatorname{Cos}(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}}{v_c\Gamma(n/2)}\int_0^{\alpha}dy\, y^{n-4}$$
$$\cdot\Big[(1+|\underset{\sim}{G}+\underset{\sim}{q}|^{-1}\zeta)\exp[-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)/4y^2] \tag{4.18}$$
$$+(1-|\underset{\sim}{G}+\underset{\sim}{q}|^{-1}\zeta)\exp[-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)/4y^2]\Big]$$

$$E_n^S(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,\underset{\sim}{u})=\frac{\pi^{3/2}\cos[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}]}{2v_c\Gamma\left(\frac{n+1}{2}\right)}\Big\{|\underset{\sim}{G}+\underset{\sim}{q}|^{-1}\Big[\int_0^\alpha dy$$

$$\Big(\exp[-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2]\cdot[(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2y^{n-5}-2y^{n-3}]$$

$$-\exp[-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2][(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2y^{n-5}-2y^{n-3}]\Big)\Big]\Big\} \qquad (4.19)$$

and v_c is the volume of the direct lattice unit cell and $\zeta=2k_F$. With the help of two sums $C_n(2k_F,0,0)$ and $S_n(2k_F,0,0)$ we can now calculate $\langle\omega^2\rangle$ and the Einstein quartic term (F_4^E) in the free energy. To obtain these particular sums we have to take the limit of the direct and the reciprocal lattice sums in Eqs(4.16) and (4.17) as vector $\underset{\sim}{q}$ tends to zero for $\underset{\sim}{u}=0$. The direct lattice sum does not create any problem, however the reciprocal lattice sum must be examined more carefully because of the singular nature of the term $|\underset{\sim}{G}+\underset{\sim}{q}|^{-1}$. This term diverges for $\underset{\sim}{G}=0$ and $\underset{\sim}{q}=0$. Isolating this term in the reciprocal sum and taking the limit as $|\underset{\sim}{G}+\underset{\sim}{q}|$ tends to zero, we find

$$C_n(2k_F,0,0)=\frac{2}{\Gamma(n/2)}\Big[{\sum_{\underset{\sim}{\ell}}}'\cos(2k_F|\underset{\sim}{\ell}|)\int_\alpha^\infty dy\,y^{n-1}e^{-\ell^2y^2}-\frac{\alpha^n}{n}\Big] \qquad (4.20)$$

$$+{\sum_{\underset{\sim}{G}}}' E_n^C(2k_F,|\underset{\sim}{G}|,0)$$

$$+\frac{2\pi^{3/2}}{v_c\Gamma(n/2)}\int_0^\alpha dy\Big[y^{n-4}-\frac{(2k_F)^2}{2}y^{n-6}\Big]\exp\Big[-\frac{(2k_F)^2}{4y^2}\Big]$$

$$S_n(2k_F,0,0)=\frac{2}{\Gamma(\frac{n+1}{2})}\sum_{\underset{\sim}{\ell}}{}' |\underset{\sim}{\ell}| \operatorname{Sin}(2k_F|\underset{\sim}{\ell}|)\int_{\alpha}^{\infty}dy\, y^n e^{-\ell^2y^2}$$

$$+\sum_{\underset{\sim}{G}}{}' E_n^S(2k_F,|\underset{\sim}{G}|,0)$$

$$+\frac{\pi^{3/2}(2k_F)}{2v_c\Gamma(\frac{n+1}{2})}\left[6\int_0^{\alpha}dy\left(y^{n-5}-(2k_F)^2y^{n-7}\right)\exp\left[-\frac{(2k_F)^2}{4y^2}\right]\right] \tag{4.21}$$

The second rank tensor sums required in the calculation of the dynamical matrix elements can be obtained similarly by substituting Eqs(4.16) and (4.17) in Eqs(4.9) and (4.10) respectively. We get

$$C_n^{\alpha\beta}(2k_F,\underset{\sim}{q})=\sum_{\underset{\sim}{\ell}}{}'\left[\ell^{-2}\ell_\alpha\ell_\beta A_n^c(2k_F,\ell)+\delta_{\alpha\beta}\ell^{-1}D_n^c(2k_F,\ell)\right]\operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$-\sum_{\underset{\sim}{G}}(G_\alpha+q_\alpha)(G_\beta+q_\beta)\,E_n^c(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,0)$$

$$+\frac{2\delta_{\alpha\beta}}{\Gamma(n/2)}\left[(2k_F)^2\frac{\alpha^n}{n}+2\frac{\alpha^{n+2}}{(n+2)}\right] \tag{4.22}$$

$$S_n^{\alpha\beta}(2k_F,\underset{\sim}{q})=\sum_{\underset{\sim}{\ell}}{}'\left[\ell^{-2}\ell_\alpha\ell_\beta A_n^S(2k_F,\ell)+\delta_{\alpha\beta}\ell^{-1}D_n^S(2k_F,\ell)\right]\operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$-\sum_{\underset{\sim}{G}}(G_\alpha+q_\alpha)(G_\beta+q_\beta)\,E_n^S(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,0)-\frac{4\delta_{\alpha\beta}(2k_F)\,\alpha^{n+1}}{\Gamma(\frac{n+1}{2})\,(n+1)} \tag{4.23}$$

where

$$A_n^c(\mathcal{C},|\underset{\sim}{\ell}|)=\frac{2}{\Gamma(n/2)}\left\{\int_{\alpha}^{\infty}dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{2}y^{n-1+2\nu}a_{\nu+1}^c(\mathcal{C},\ell)\right]\right\} \tag{4.24}$$

$$D_n^c(\mathcal{C},|\underset{\sim}{\ell}|)=-\frac{2}{\Gamma(n/2)}\left\{\int_{\alpha}^{\infty}dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{1}y^{n-1+2\nu}d_{\nu+1}^c(\mathcal{C},\ell)\right]\right\} \tag{4.25}$$

$$a_1^c(\zeta,\ell) = -\zeta^2 \mathrm{Cos}(\zeta\ell) + \zeta\ell^{-1}\mathrm{Sin}(\zeta\ell)$$

$$a_2^c(\zeta,\ell) = 4\zeta\ell\,\mathrm{Sin}(\zeta\ell)$$

$$a_3^c(\zeta,\ell) = 4\ell^2\mathrm{Cos}(\zeta\ell)$$

$$d_1^c(\zeta,\ell) = \zeta\,\mathrm{Sin}(\zeta\ell)$$

$$d_2^c(\zeta,\ell) = 2\ell\,\mathrm{Cos}(\zeta\ell)$$

$$A_n^s(\zeta,\ell) = \frac{2}{\Gamma(\frac{n+1}{2})}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{2} y^{n+2\nu} a_{\nu+1}^s(\zeta,\ell)\right]\right\}$$

$$D_n^s(\zeta,\ell) = \frac{2}{\Gamma(\frac{n+1}{2})}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{1} y^{n+2\nu} d_{\nu+1}^s(\zeta,\ell)\right]\right\}$$

$$a_1^s(\zeta,\ell) = -\zeta^2\ell\,\mathrm{Sin}(\zeta\ell) + \zeta\,\mathrm{Cos}(\zeta\ell) - \ell^{-1}\mathrm{Sin}(\zeta\ell)$$

$$a_2^s(\zeta,\ell) = -4\left[\zeta\ell^2\mathrm{Cos}(\zeta\ell) + \ell\,\mathrm{Sin}(\zeta\ell)\right]$$

$$a_3^s(\zeta,\ell) = 4\ell^3\mathrm{Sin}(\zeta\ell)$$

$$d_1^s(\zeta,\ell) = \zeta\ell\,\mathrm{Cos}(\zeta\ell) + \mathrm{Sin}(\zeta\ell)$$

$$d_2^s(\zeta,\ell) = -2\ell^2\mathrm{Sin}(\zeta\ell)$$

To evaluate the sums $C_n^{\alpha\beta}$ and $S_n^{\alpha\beta}$ for $\underset{\sim}{q}=0$, we again take the limit of direct and reciprocal lattice sums in the Eqs (4.22) and (4.23). In this case the reciprocal sum does not create any difficulty because the quantity $(G_\alpha + q_\alpha)(G_\beta + q_\beta) \cdot |\underset{\sim}{G}+\underset{\sim}{q}|^{-1}$ tends to zero as $\underset{\sim}{G} \to 0$ and $\underset{\sim}{q} \to 0$, hence in the numerical computation we replace $\sum_{\underset{\sim}{G}}$ by $\sum_{\underset{\sim}{G}}'$ for the sums $C_n^{\alpha\beta}(2k_F,0)$ and $S_n^{\alpha\beta}(2k_F,0)$.

The calculation of the quartic term (F_4) in the free energy requires tensor sums of the type given by Eq(4.15), viz, $C_n^{\alpha\beta\gamma\delta}$ and $S_n^{\alpha\beta\gamma\delta}$. Substituting Eqs(4.16) and (4.17) in Eqs(4.13) and (4.14) respectively we obtain the fourth rank cosine and sine tensor sums. These are given by

$$
\begin{aligned}
C_n^{\alpha\beta\gamma\delta}(2k_F,\underset{\sim}{q}) = {\sum_{\underset{\sim}{\ell}}}' \Big[& \ell^{-4}\ell_\alpha \ell_\beta \ell_\gamma \ell_\delta \, C_n^c(2k_F,\ell) \\
& + \ell^{-3}(\delta_{\gamma\delta}\ell_\alpha \ell_\beta + \delta_{\alpha\delta}\ell_\beta \ell_\gamma + \delta_{\beta\delta}\ell_\gamma \ell_\alpha + \delta_{\beta\gamma}\ell_\alpha \ell_\delta + \delta_{\alpha\gamma}\ell_\beta \ell_\delta + \delta_{\alpha\beta}\ell_\gamma \ell_\delta)\, B_n^c(2k_F,\ell) \\
& + \ell^{-2}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\delta\alpha} + \delta_{\alpha\gamma}\delta_{\beta\delta})\, A_n^c(2k_F,\ell)\Big] \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) \quad + \mathcal{E}_n^c(2k_F,\alpha) \\
& + \sum_{\underset{\sim}{G}} (G_\alpha + q_\alpha)(G_\beta + q_\beta)(G_\gamma + q_\gamma)(G_\delta + q_\delta)\, E_n^c(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,0)
\end{aligned}
$$

$$
\begin{aligned}
S_n^{\alpha\beta\gamma\delta}(2k_F,\underset{\sim}{q}) = {\sum_{\underset{\sim}{\ell}}}' \Big[& \ell^{-4}\ell_\alpha \ell_\beta \ell_\gamma \ell_\delta \, C_n^s(2k_F,\ell) \\
& + \ell^{-3}(\delta_{\gamma\delta}\ell_{\alpha\beta} + \delta_{\alpha\delta}\ell_\beta \ell_\gamma + \delta_{\beta\delta}\ell_\gamma \ell_\alpha + \delta_{\beta\gamma}\ell_\alpha \ell_\delta + \delta_{\alpha\gamma}\ell_\beta \ell_\delta + \delta_{\alpha\beta}\ell_\gamma \ell_\delta)\, B_n^s(2k_F,\ell) \\
& + \ell^{-2}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\delta\alpha} + \delta_{\alpha\gamma}\delta_{\beta\delta})\, A_n^s(2k_F,\ell)\Big] \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) \quad + \mathcal{E}_n^s(2k_F,\alpha) \\
& + \sum_{\underset{\sim}{G}} (G_\alpha + q_\alpha)(G_\beta + q_\beta)(G_\gamma + q_\gamma)(G_\delta + q_\delta)\, E_n^s(2k_F,|\underset{\sim}{G}+\underset{\sim}{q}|,0)
\end{aligned}
$$

The expressions for the functions C_n^c, C_n^s, B_n^c, B_n^s, $\mathcal{E}_n^c$ and $\mathcal{E}_n^s$ are

$$C_n^c(\zeta,\ell)=\frac{2}{\Gamma(n/2)}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{4} y^{\,n-1+2\nu}\, c^c_{\nu+1}(\zeta,\ell)\right]\right\}$$

$$B_n^c(\zeta,\ell)=\frac{2}{\Gamma(n/2)}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{3} y^{\,n-1+2\nu}\, b^c_{\nu+1}(\zeta,\ell)\right]\right\}$$

$$\mathcal{R}_n^c(\zeta,\ell)=\frac{2}{\Gamma(n/2)}\left[\zeta^4\frac{\alpha^n}{3n}+4\zeta^2\frac{\alpha^{n+2}}{(n+2)}+4\frac{\alpha^{n+4}}{(n+4)}\right]$$

where

$$c_1^c(\zeta,\ell)=\zeta^4\cos(\zeta\ell)-6\zeta^3\ell^{-1}\sin(\zeta\ell)-15\zeta^2\ell^{-2}\cos(\zeta\ell)+15\zeta\ell^{-3}\sin(\zeta\ell)$$

$$c_2^c(\zeta,\ell)=-8\zeta^3\ell\sin(\zeta\ell)-24\zeta^2\cos(\zeta\ell)+24\zeta\ell^{-1}\sin(\zeta\ell)$$

$$c_3^c(\zeta,\ell)=24\left[-\zeta^2\ell^2\cos(\zeta\ell)+\zeta\ell\sin(\zeta\ell)\right]$$

$$c_4^c(\zeta,\ell)=32\ell^3\zeta\sin(\zeta\ell)$$

$$c_5^c(\zeta,\ell)=16\ell^4\cos(\zeta\ell)$$

$$b_1^c(\zeta,\ell)=\zeta^3\sin(\zeta\ell)+3\zeta^2\ell^{-1}\cos(\zeta\ell)-3\zeta\ell^{-2}\sin(\zeta\ell)$$

$$b_2^c(\zeta,\ell)=6\left[\zeta^2\ell\cos(\zeta\ell)-\zeta\sin(\zeta\ell)\right]$$

$$b_3^c(\zeta,\ell)=-12\zeta\ell^2\sin(\zeta\ell)$$

$$b_4^c(\zeta,\ell)=-8\ell^3\cos(\zeta\ell)$$

$$C_n^s(\zeta,\ell)=\frac{2}{\Gamma\left(\frac{n+1}{2}\right)}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{4} y^{\,n+2\nu}\, c^s_{\nu+1}(\zeta,\ell)\right]\right\}$$

$$B_n^s(\zeta,\ell)=\frac{2}{\Gamma\left(\frac{n+2}{2}\right)}\left\{\int_\alpha^\infty dy\,\exp(-\ell^2y^2)\left[\sum_{\nu=0}^{3} y^{\,n+2\nu}\, b^s_{\nu+1}(\zeta,\ell)\right]\right\}$$

$$\mathcal{R}_n^s(\zeta,\ell)=-\frac{8}{\Gamma\left(\frac{n+1}{2}\right)}\left[\zeta^3\frac{\alpha^{n+1}}{3(n+1)}+2\zeta\frac{\alpha^{n+3}}{(n+3)}\right]$$

$$c_1^s(\zeta,\ell) = \zeta^4 \ell \,\mathrm{Sin}(\zeta\ell) + 2\zeta^3 \mathrm{Cos}(\zeta\ell) + 3\zeta^2 \ell^{-1} \mathrm{Sin}(\zeta\ell)$$
$$+ 15\zeta \ell^{-1} \mathrm{Cos}(\zeta\ell) - 15\ell^{-3} \mathrm{Sin}(\zeta\ell)$$

$$c_2^s(\zeta,\ell) = 8\zeta^3 \ell^2 \mathrm{Cos}(\zeta\ell) + 24\zeta \,\mathrm{Cos}(\zeta\ell) - 24\ell^{-1} \mathrm{Sin}(\zeta\ell)$$

$$c_3^s(\zeta,\ell) = 24\left[-\zeta^2 \ell^3 \mathrm{Sin}(\zeta\ell) + \zeta\ell^2 \mathrm{Cos}(\zeta\ell) - \ell \,\mathrm{Sin}(\zeta\ell)\right]$$

$$c_4^s(\zeta,\ell) = -32\left[\zeta\ell^4 \mathrm{Cos}(\zeta\ell) + \ell^3 \mathrm{Sin}(\zeta\ell)\right]$$

$$c_5^s(\zeta,\ell) = 16\ell^5 \mathrm{Sin}(\zeta\ell)$$

$$b_1^s(\zeta,\ell) = -\zeta^3 \ell \,\mathrm{Cos}(\zeta\ell) - 3\ell^{-1}\zeta \,\mathrm{Cos}(\zeta\ell) + 3\ell^{-2} \mathrm{Sin}(\zeta\ell)$$

$$b_2^s(\zeta,\ell) = 6\left[\zeta^2 \ell^2 \mathrm{Sin}(\zeta\ell) - \zeta\ell \,\mathrm{Cos}(\zeta\ell) + \mathrm{Sin}(\zeta\ell)\right]$$

$$b_3^s(\zeta,\ell) = 12\left[\zeta\ell^3 \mathrm{Cos}(\zeta\ell) + \ell^2 \mathrm{Sin}(\zeta\ell)\right)$$

$$b_4^s(\zeta,\ell) = -8\ell^4 \,\mathrm{Sin}(\zeta\ell)$$

If we examine the sums $C_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{q})$ and $S_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{q})$ for $\underset{\sim}{q}=0$, it is obvious that $\underset{\sim}{G}=0$ vector does not create a singularity in the reciprocal sum because the term $(G_\alpha + q_\alpha)(G_\beta + q_\beta)(G_\gamma + q_\gamma)(G_\delta + q_\delta) \cdot |\underset{\sim}{G}+\underset{\sim}{q}|^{-1} \longrightarrow 0$ as $\underset{\sim}{q} \to 0$ and $\underset{\sim}{G} \to 0$; consequently in the numerical computation of $C_n^{\alpha\beta\gamma\delta}(2k_F, 0)$ and $S_n^{\alpha\beta\gamma\delta}(2k_F, 0)$ we replace $\sum_{\underset{\sim}{G}}$ by $\sum_{\underset{\sim}{G}}'$.

5. NUMERICAL CALCULATION

Our fundamental goal is to evaluate the contribution or correction from the oscillatory long range part of the potential function to the anharmonic term (F_4) in the Helmholtz free energy. Before we calculate the exact F_4 we will evaluate the long range contributions to much simpler physical quantities such as the Einstein quartic term (F_4^E) in the Helmholtz free energy, phonon frequencies $\omega(\underset{\sim}{q}j)$, and energy ($U$). F_4^E depends on $\langle\omega^2\rangle$, hence we need to evaluate this quantity separately.

The contribution or correction to a given physical property (P) from the long range potential can be obtained in the following manner.

First we compute this property from the δ-term potential given by Eq(3.7) employing the sums obtained from the Ewald method (P_∞). Then P is calculated once again from the same potential using a discrete real space lattice vector summation. The difference of these two calculations gives the necessary contribution or correction for that physical property (ΔP) from the long range part of the potential function. Symbolically we can state all this in terms of

$$\Delta P = (P)_\infty - (P)_n$$

We have pointed out earlier in Sec. 4 that with the help of two sums, $C_n(2k_F,0,0)$ and $S_n(2k_F,0,0)$, one can calculate $\langle\omega^2\rangle$, $\vec{F}_4^E$ and U. These sums are given by the Eqs(4.20) and (4.21), respectively. The Ewald's parameter (α) appearing in these expressions is to be chosen in such a way that the real and the reciprocal lattice sums converge simultaneously and rapidly. The choice of α by Born and Huang (1954) was $\alpha=1/a$, Shukla (unpublished result) chose $\alpha=1.25/a$ Cohen and Keffer (1955) selected $\alpha=\pi^{1/2}/a$.

In the numerical calculation we will follow Cohen and Keffer (1955) and choose $\alpha=\pi^{1/2}/a$ and replace the integrals appearing in Eq(4.20) and (4.21) by the φ-functions introduced by Misra (1941)

$$\varphi_{\frac{1}{2}n-1}(\tau\pi\ell^2)=2(\pi\tau)^{-n/2}\int_{\sqrt{\tau\pi}}^{\infty}dy\,y^{n-1}e^{-\ell^2y^2} \tag{5.1}$$

$$\varphi_{\frac{1}{2}-\frac{1}{2}n}\left[(2k_F+G)^2/4\pi\tau\right]=2(\pi\tau)^{(3-n)/2}\int_{0}^{\sqrt{\tau\pi}}dy\,y^{n-4}e^{-(2k_F+G)^2/4y^2} \tag{5.2}$$

where $\tau=\frac{1}{a^2}$, $\alpha=(\tau\pi)^{1/2}$, $\varphi_m=\int_1^{\infty}dy\,y^m e^{-xy}$

These functions satisfy the recurrence relations

$$\varphi_m(x) = e^{-x}/x + (m/x)\,\varphi_{m-1}(x) \qquad , \quad m>0$$

$$\varphi_{-m}(x) = [1/(m-1)][e^{-x} - x\,\varphi_{-(m-1)}(x)] \ , \quad m>0$$

$$\frac{\partial}{\partial x}\varphi_m(x) = -\varphi_{m+1}(x)$$

and reduce for $m=0,-1/2,-1$ to the well-known tabulated functions

$$\varphi_0(x) = e^{-x}/x$$

$$\varphi_{-1/2}(x) = (\pi/x)^{1/2}[1-\phi(x^{1/2})]$$

$$\varphi_{-1}(x) = -Ei(-x)$$

where $Ei(-x)$ is the exponential integral, and $\phi(x)$ is Gauss' error function.

We have presented in Table 3 the dimensionless sums CC_n and SS_n defined by

$$CC_n = (2k_F)^{-n} C_n(2k_F,0,0) \tag{5.3}$$

$$SS_n = (2k_F)^{-n} S_n(2k_F,0,0) \tag{5.4}$$

We have found that for an accuracy of 8 significant figures the summation over $\underset{\sim}{\ell}$ and $\underset{\sim}{G}$ in Eq.(4.20) and (4.21) from which CC_n and SS_n are obtained can be restricted to the 9th shell.

TABLE 3. Dimensionless infinite sums CC_n and SS_n for BCC lattice .

CC_3	$.34162860 \times 10^{-1}$
SS_4	$.25356562 \times 10^{-2}$
CC_5	$.59164169 \times 10^{-3}$
SS_6	$.59384309 \times 10^{-4}$
CC_7	$.11800645 \times 10^{-4}$
SS_8	$.12318190 \times 10^{-5}$
CC_9	$.25097378 \times 10^{-6}$
SS_{10}	$.25200346 \times 10^{-7}$
CC_{11}	$.54470766 \times 10^{-8}$
SS_{12}	$.51823362 \times 10^{-9}$
CC_{13}	$.11896291 \times 10^{-9}$
SS_{14}	$.10761030 \times 10^{-10}$
CC_{15}	$.26036681 \times 10^{-11}$
SS_{16}	$.22573867 \times 10^{-12}$
CC_{17}	$.57035565 \times 10^{-13}$
SS_{18}	$.47793358 \times 10^{-14}$

5.1 LONG RANGE CONTRIBUTIONS TO THE EINSTEIN QUARTIC TERM (F_4^E), $\langle\omega^2\rangle$, AND ENERGY (U).

(a) Corrections to $\langle\omega^2\rangle$:

Differentiating the 8-term asymptotic potential, Eq(3.7), with respect to $|\underset{\sim}{r}^{\ell}|$ and substituting the resulting derivatives in Eq(2.63), then using the sums CC_n and SS_n defined by the Eqs(5.3), (5.4) respectively, $\langle\omega^2\rangle$ can be written as

$$\langle\omega^2\rangle = \frac{(2k_F)^2}{3M}\sum_{i=1}^{4}\Big\{A_i\big[-CC_{2i+1}+4SS_{2i+2}+2i(2i+1)CC_{2i+3}\big]$$
$$+B_i\big[-SS_{2i+2}-2i(2i+1)CC_{2i+3}+(2i+1)(2i+2)SS_{2i+4}\big]\Big\} \qquad (5.5)$$

The calculated discrete cumulative 23-shell and infinite sums for $\langle\omega^2\rangle$ and the corresponding corrections $\Delta\langle\omega^2\rangle=(\langle\omega^2\rangle)_\infty-(\langle\omega^2\rangle)_n$ for different shells(n) are presented in Table 4. $(\langle\omega^2\rangle)_\infty$ is evaluated simply by substituting the values of CC_n and SS_n from Table 3 in Eq(5.5), and we find

$$(\langle\omega^2\rangle)_\infty = 3.9594480 \times 10^{26}\ \text{rad}^2\text{sec}^{-2}.$$

The minimum correction to $\langle\omega^2\rangle$ appears when the discrete sums are truncated at the 23rd shell, which is

$$\Delta\langle\omega^2\rangle = -0.0003188 \times 10^{26}\ \text{rad}^2\text{sec}^{-2}.$$

To get the total $\langle\omega^2\rangle$ we perform the summation in Eq(2.63) up to the 23rd shell for actual potential(AP) which is found to be

$$(\langle\omega^2\rangle_{23})_{AP} = 2.8001527 \times 10^{26} \ \mathrm{rad}^2.\mathrm{sec}^{-2}.$$

and then we add the minimum correction to it . i.e.

$$(\langle\omega^2\rangle)_{Total} = (\langle\omega^2\rangle_{23})_{AP} + (\Delta\langle\omega^2\rangle)_{LRP}$$

$$= 2.799833 \times 10^{26} \ \mathrm{rad}^2.\mathrm{sec}^{-2} \ .$$

TABLE 4. $\langle\omega^2\rangle$, F_4 and (U) as a function of shell vectors $\underset{\sim}{l}=(a/2)(n_x^s,n_y^s,n_z^s)$, where $a=4.234\times10^{-8}$cm, and corresponding corrections $\Delta\langle\omega^2\rangle$, ΔF_4^E and $\Delta(U)$ for 8-term potential. $(\langle\omega^2\rangle, \Delta\langle\omega^2\rangle)$, $(F_4^E, \Delta F_4^E)$, $(U, \Delta U)$ are in units of $10^{26}\,\mathrm{rad}^2.\mathrm{sec}^{-2}$, $10^{12}\,N(k_BT)^2.\mathrm{erg}^{-1}$, 10^{-14} ergs respectively.

$\underset{\sim}{n}^s$	$(\langle\omega^2\rangle)_n$	$\Delta\langle\omega^2\rangle$	$(F_4^E)_n$	ΔF_4^E	$(U)_n$	ΔU
111	3.2362	.7232	-5.3558	.5681	.1556	-6.6876
200	3.9276	.0318	-4.6037	-.1840	-8.2041	1.3614
220	3.8249	.1346	-4.6652	-.1225	-5.9024	-.9403
311	3.9616	-.0021	-4.7838	-.0039	-7.0935	.2508
222	3.9961	-.0367	-4.8018	.0140	-7.5743	.7317
400	3.9866	-.0271	-4.7904	.0027	-7.5081	.6654
331	3.9634	-.0039	-4.7804	-.0074	-7.0745	.2318
420	3.9532	.0062	-4.7822	-.0055	-6.7887	-.0540
422	3.9705	-.0110	-4.7982	.0105	-7.0066	.1639
333	3.9731	-.0136	-4.7994	.0116	-7.0612	.2186
511	3.9810	-.0215	-4.8028	.0150	-7.2252	.3251
531	3.9647	-.0052	-4.7906	.0029	-6.9526	.1100
441	3.9609	-.0014	-4.7887	.0010	-6.8723	.0296
600	3.9599	-.0005	-4.7883	.0006	-6.8522	.0096
620	3.9639	-.0044	-4.7926	.0049	-6.8971	.0544
533	3.9689	-.0095	-4.7969	.0092	-6.9762	.1335
622	3.9734	-.0139	-4.8004	.0127	-7.0511	.2084
444	3.9734	-.0139	-4.8001	.0124	-7.0553	.2126
551	3.9707	-.0112	-4.7974	.0096	-7.0196	.1769
711	3.9679	-.0085	-4.7946	.0069	-6.9839	.1412
640	3.9648	-.0053	-4.7916	.0039	-6.9385	.0958
642	3.9598	-.0003	-4.7878	.0001	-6.8497	.0071
∞	3.9594		-4.7877		-6.8427	

(b) Corrections to the Einstein quartic term (F_4^E) in the Helmholtz free energy:

In the numerical evaluation of F_4^E or F_4 it was convenient to take the high temperature limit, which affects only the hyperbolic cotangent function, $\coth(\frac{\hbar}{2}\beta\omega)$, in their expressions. Expanding this function in the high temperature limit and taking the first term in the expansion, we have

$$\coth\left(\frac{\hbar}{2}\frac{\omega}{k_BT}\right) = \frac{2k_BT}{\hbar\omega} + \cdots \tag{5.6}$$

Substituting Eq(5.6) in Eq(2.50), C_E which arises in the expression for F_4^E can be written as

$$C_E = \frac{2k_BT}{M\omega_E^2} \tag{5.7}$$

where $$\omega_E^2 = \langle\omega^2\rangle_{Total}$$

Substituting Eq(5.7) in Eq(2.52), the Einstein quartic term(F_4^E) can be written as

$$F_4^E = \frac{N(k_BT)^2}{4M^2(\langle\omega^2\rangle_{Total})^2}\sum_{\underset{\sim}{\ell}}{}' \left[\phi''''(|\underset{\sim}{\ell}|) + 4|\underset{\sim}{\ell}|^{-1}\phi'''(|\underset{\sim}{\ell}|)\right] \tag{5.8}$$

Differentiating the 8-term potential given by Eq(3.7) and substituting the derivatives in Eq(5.8), and then using the sums CC_n, SS_n, as defined by the Eqs(5.3),(5.4) respectively and given in Table 3, F_4^E can be written as

$$F_4^E = \frac{N(k_B T)^2 (2k_F)^4}{4M^2(\langle\omega^2\rangle_{Total})^2} \sum_{i=1}^{4} \{ A_i [CC_{2i+1} - 8i SS_{2i+2}$$

$$-12i(2i+1) CC_{2i+3} + 8i(2i+1)(2i+2) SS_{2i+4}$$

$$+2i(2i+1)(2i+2)(2i+3) CC_{2i+5}]$$

$$+ B_i [SS_{2i+2} + 4(2i+1) CC_{2i+3} - 6(2i+1)(2i+2) SS_{2i+4}$$

$$-4(2i+1)(2i+2)(2i+3) CC_{2i+5}$$

$$+(2i+1)(2i+2)(2i+3)(2i+4) SS_{2i+6}] \} \quad (5.9)$$

The discrete cumulative 23-shell and infinite sums for F_4^E and the related corrections $\Delta F_4^E = (F_4^E)_\infty - (F_4^E)_n$ for different shells are presented in Table 4. The smallest correction arises when the discrete sum over the shells is truncated at the 23rd shell, we find

$$\Delta F_4^E = 0.0001137 \times 10^{12} N(k_B T)^2 \text{ erg}^{-1}.$$

To evaluate the total F_4^E for this particular shell, first the summation is performed in Eq(5.8) up to the 23rd shell using the actual potential(AP), and we obtain

$$((F_4^E)_{23})AP = 1.6968875 \times 10^{12} N(k_B T)^2 \text{ erg}^{-1}.$$

then we add the corresponding correction to $((F_4^E)_{23})AP$ to obtain

$$(F_4^E)_{Total} = ((F_4^E)_{23})AP + (\Delta(F_4^E))_{LRP}$$

$$= 1.6970006 \times 10^{12} N(k_B T)^2 \text{ erg}^{-1}.$$

(c) Corrections to Energy (U) :

Substituting the 8-term asymptotic potential i.e. Eq(3.7) in Eq(4.1) and using the sums CC_n and SS_n , we express the energy as

$$U = \frac{1}{2}\sum_{i=1}^{4}\left(A_i\, CC_{2i+1} + B_i\, SS_{2i+2}\right) \tag{5.10}$$

The finite cumulative 23-shell and infinite sums for U and the corresponding corrections $\Delta U = (U)_\infty - (U)_n$, where $(U)_n$ represents the truncated sum at the n^{th} shell, are presented in Table 4 . $(U)_\infty$ is evaluated substituting the values of CC_n and SS_n from Table 3 in Eq(5.10), and we find

$$(U)_\infty = -6.8426812 \times 10^{-14} \text{ ergs.}$$

The smallest correction arises when the finite sums are truncated at the 23rd shell .

5.2 LONG RANGE CONTRIBUTIONS TO THE PHONON FREQUENCIES FOR Na AT 90° K IN THREE FUNDAMENTAL DIRECTIONS $[\zeta 00]$, $[\zeta\zeta 0]$, $[\zeta\zeta\zeta]$.

The calculation of the long range corrections to the phonon frequencies from the 8-term potential requires the computation of the dynamical matrix elements, Eq(4.7). Numerical accuracy of these elements can be checked deriving the following sum rule

$$M\sum_{\alpha\beta} D_{\alpha\beta}(\underset{\sim}{q})\,\delta_{\alpha\beta} = M\sum_{\alpha} D_{\alpha\alpha}(\underset{\sim}{q})$$

$$= \sum_{\underset{\sim}{\ell}}{}' \left[A(|\underset{\sim}{\ell}|) + 3|\underset{\sim}{\ell}|^{-1} D(|\underset{\sim}{\ell}|)\right]\left[1 - \mathrm{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})\right]$$

$$= d^{\circ} \qquad (5.11)$$

To derive this sum rule, first we substitute Eq(2.62) in Eq(4.7) and get

$$M D_{\alpha\beta}(\underset{\sim}{q}) = \sum_{\underset{\sim}{\ell}}{}' \left[\ell^{-2}\ell_\alpha \ell_\beta A(\ell) + \delta_{\alpha\beta} D(\ell)\right]\left[1 - \mathrm{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})\right] \qquad (5.12)$$

where $A(\ell)$ is given by Eq(2.6d), $D(\ell) = \frac{d}{d\ell}\,\phi(\ell)$ and $\phi(\ell)$ is the potential function, then use Eq(5.12) in (5.11) and sum over index α.

The LHS of Eq(5.11) can be computed independently with the help of the second rank tensor sums $C_n^{\alpha\beta}(2k_F, \underset{\sim}{q})$, $S_n^{\alpha\beta}(2k_F, \underset{\sim}{q})$ given by Eq(4.11) and the RHS is also computed independently using the zeroth rank tensor sums from the Eqs(4.4), (4.5). The terms appearing on the RHS are then written as

$$\sum_{\underset{\sim}{\ell}}' A(\ell)\left[1-\mathrm{Cos}(\underset{\sim}{q}.\underset{\sim}{\ell})\right]=\sum_{i=1}^{4}\Big\{-(2k_F)^2 a_i\left[C_{2i+1}(2k_F,0,0)-C_{2i+1}(2k_F,\underset{\sim}{q},0)\right.$$

$$+\left[(2k_F)(4i+3)a_i-(2k_F)^2 b_i\right]\left[S_{2i+2}(2k_F,0,0)-S_{2i+2}(2k_F,\underset{\sim}{q},0)\right]$$

$$+\left[(2i+1)(2i+3)a_i-(2k_F)(4i+5)b_i\right]\left[C_{2i+3}(2k_F,0,0)-C_{2i+3}(2k_F,\underset{\sim}{q},0)\right]$$

$$+(2i+2)(2i+4)b_i\left[S_{2i+4}(2k_F,0,0)-S_{2i+4}(2k_F,\underset{\sim}{q},0)\right]\Big\} \tag{5.13}$$

$$\sum_{\underset{\sim}{\ell}}' \ell^{-1} D(\ell)\left[1-\mathrm{Cos}(\underset{\sim}{q}.\underset{\sim}{\ell})\right]=\sum_{i=1}^{4}\Big\{-(2k_F)^2 a_i\left[S_{2i+2}(2k_F,0,0)-S_{2i+2}(2k_F,\underset{\sim}{q},0)\right]$$

$$+\left[-(2i+1)a_i+(2k_F)b_i\right]\left[C_{2i+3}(2k_F,0,0)-C_{2i+3}(2k_F,\underset{\sim}{q},0)\right]$$

$$-(2i+2)b_i\left[S_{2i+4}(2k_F,0,0)-S_{2i+4}(2k_F,\underset{\sim}{q},0)\right]\Big\} \tag{5.14}$$

Letting $d_{\alpha\beta}(\underset{\sim}{q}) = M\, D_{\alpha\beta}(\underset{\sim}{q})$, we have presented in Tables 5a,5b,5c the functions $d_{\alpha\beta}(\underset{\sim}{q})$ and the term d^0 which represents the RHS of Eq(5.11), in three fundamental directions $[\zeta 00]$, $[\zeta\zeta 0]$, $[\zeta\zeta\zeta]$, where $\underset{\sim}{q} = (2\pi/a)\underset{\sim}{\zeta}$.

After solving the eigen-value equation of dynamical matrix,

$\underset{\sim}{D}(\underset{\sim}{q})\underset{\sim}{e}(\underset{\sim}{q}j) = \omega^2(\underset{\sim}{q}j)\underset{\sim}{e}(\underset{\sim}{q}j)$, as we indicated before in Section 5 the long range corrections(contributions) to the phonon frequencies, $\nu_j(\underset{\sim}{q}) = \omega(\underset{\sim}{q}j)/2\pi$, is obtained from the equation

$$\Delta \nu_j(\underset{\sim}{q}) = \left(\nu_j(\underset{\sim}{q})\right)_{\infty} - \left(\nu_j(\underset{\sim}{q})\right)_n$$

where $(\nu_j(\underset{\sim}{q}))_{\infty}$ is calculated from the Ewald's method and $(\nu_j(\underset{\sim}{q}))_n$ from discrete summation.

We have presented in Tables 6a,6b,6c $(\nu_j(\underset{\sim}{q}))_{\infty}$, $(\nu_j(\underset{\sim}{q}))_n$, $\Delta(\nu_j(\underset{\sim}{q}))$ for three basic directions $\lfloor\zeta 00\rfloor$, $\lfloor\zeta\zeta 0\rfloor$, and $\lfloor\zeta\zeta\zeta\rfloor$ in their FBZ's taking different shells (n = 5,8,12,16,23).

TABLE 5a Second rank tensor sums and sum rules for LRP. $\underset{\sim}{q}=(2\pi/a)\underset{\sim}{\zeta}$

$d_{\alpha\beta}$ and d^{o} are in units of eV/A^{o2}.

$\underset{\sim}{\zeta}=[\zeta 00]$ direction, $d_{yy}=d_{zz}$, $d_{\alpha\beta}=0$ for $\alpha\neq\beta$; $0.2\leqslant\zeta\leqslant 1.0$.

ζ	d_{xx}	d_{yy}	d^{o}
0.2	0.2664	0.1502	0.5668
0.4	0.8267	0.5574	1.9416
0.6	1.2672	1.0496	3.3664
0.8	1.5091	1.4444	4.3979
1.0	1.5949	1.5949	4.7848

TABLE 5b $\underset{\sim}{\zeta}=[\zeta\zeta 0]$ direction. $0.1\leqslant\zeta\leqslant 0.5$, $d_{xx}=d_{yy}$,

$d_{xz}=d_{yz}=0$, $d_{xy}\neq 0$.

ζ	d_{xx}	d_{zz}	d_{xy}	d^{o}
0.1	0.10799	0.0739	0.0973	0.2899
0.2	0.3919	0.2674	0.3534	1.0512
0.3	0.7278	0.5069	0.6548	1.9628
0.4	0.9914	0.7036	0.8888	2.6866
0.5	1.0897	0.7774	0.9765	2.9569

TABLE 5c $\underset{\sim}{\zeta}=[\zeta\zeta\zeta]$ direction. $0.1\leqslant\zeta\leqslant 0.5$, $d_{xx}=d_{yy}=d_{zz}$

$d_{xy}=d_{xz}=d_{yz}$.

ζ	d_{xx}	d_{xy}	d^{o}
0.1	0.1429	0.0916	0.4287
0.2	0.4951	0.2780	1.4854
0.3	0.8536	0.3723	2.5607
0.4	1.0765	0.2669	3.2295
0.5	1.1372	0.0	3.4116

TABLE 6a. Frequency table and phonon corrections for LRP in $\zeta = [\zeta 00]$ direction, where $q = 2\pi/a\ \zeta$, $0.2 \leq \zeta \leq 1.0$. $\nu_j(q)$ and corrections $\Delta\nu_j(q) = (\nu_j(q))_\infty - (\nu_j(q))_n$ are in units of 10^{12} cps.

ζ	Shell →	5	8	12	16	23	∞
0.2	L	1.7276	1.6826	1.7078	1.6920	1.6862	1.6827
	Δ	-0.0428	0.0002	-0.0250	-0.0093	-0.0034	
	T	1.2902	1.2669	1.2841	1.2697	1.2679	1.2638
	Δ	-0.0265	-0.0031	-0.0203	-0.0060	-0.0041	
0.4	L	2.9832	2.9593	2.9681	2.9652	2.9638	2.9644
	Δ	-0.0187	0.0052	-0.0036	-0.0007	0.0007	
	T	2.4392	2.4194	2.4384	2.4316	2.4342	2.4343
	Δ	-0.0049	0.0149	-0.0041	0.0026	0.0001	
0.6	L	3.6749	3.6669	3.6773	3.6710	3.6704	3.6702
	Δ	-0.0047	0.0033	-0.0071	-0.0008	-0.0002	
	T	3.3437	3.3345	3.3489	3.3440	3.3422	3.3404
	Δ	-0.0033	0.0058	-0.0086	-0.0036	-0.0018	
0.8	L	4.0167	4.0006	4.0074	4.0062	4.0037	4.0053
	Δ	-0.0114	0.0046	-0.0022	-0.0009	0.0015	
	T	3.9292	3.9186	3.9270	3.9215	3.9181	3.9185
	Δ	-0.0108	-0.0001	-0.0085	-0.0030	0.0004	
1.0	L,T	4.1337	4.1195	4.1260	4.1186	4.1185	4.1176
	Δ	-0.0161	-0.0019	-0.0084	-0.0010	-0.0008	

TABLE 6b. Frequency table and phonon corrections for LRP in $\xi=[\xi\xi 0]$ direction, where $q = 2\pi/a\ \xi$, $0.1 \leq \xi \leq 0.5$. $\nu_j(q)$ and corrections $\Delta\nu_j(q) = (\nu_j(q)) - (\nu_j(q))_n$ are in units of 10^{12} cps.

ξ	Shell →	5	8	12	16	23	∞
0.1	L	1.5073	1.4775	1.4990	1.4855	1.4793	1.4774
	Δ	-0.0299	-0.0001	-0.0216	-0.0081	-0.0019	
	T_1	0.3900	0.3318	0.3659	0.3502	0.3318	0.3366
	Δ	-0.0531	0.0047	-0.0293	-0.0137	0.0047	
	T_2	0.9129	0.9836	0.9061	0.8925	0.8870	0.8866
	Δ	-0.0263	-0.0070	-0.0195	-0.0060	-0.0004	
0.2	L	2.8372	2.8053	2.8243	2.8173	2.8161	2.8146
	Δ	-0.0225	0.0094	-0.0097	-0.0026	-0.0015	
	T_1	0.7192	0.6376	0.6777	0.6574	0.6456	0.6398
	Δ	-0.0794	0.0021	-0.0380	-0.0176	-0.0058	
	T_2	1.7256	1.6984	1.7107	1.6975	1.6907	1.6860
	Δ	-0.0395	-0.0123	-0.0247	-0.0114	-0.0046	
0.3	L	3.8537	3.8363	3.8397	3.8362	3.8335	3.8340
	Δ	-0.0197	-0.0023	-0.0057	-0.0023	0.0005	
	T_1	0.9510	0.8812	0.9137	0.8935	0.8918	0.8817
	Δ	-0.0693	0.0005	-0.0320	-0.0118	-0.0100	
	T_2	2.3564	2.3322	2.3390	2.3313	2.3276	2.3214
	Δ	-0.0350	-0.0108	-0.0176	-0.0100	-0.0062	

TABLE 6b continued

ß	Shell →	5	8	12	16	23	∞
0.4	L	4.4808	4.4705	4.4749	4.4704	4.4717	4.4707
	Δ	-0.0102	0.0001	-0.0042	0.0003	-0.0013	
	T_1	1.0797	1.0321	1.0671	1.0463	1.0418	1.0443
	Δ	-0.0354	0.0123	-0.0227	-0.0020	0.0026	
	T_2	2.7523	2.7333	2.7405	2.7353	2.7328	2.7348
	Δ	-0.0175	0.0015	-0.0057	-0.0005	0.0020	
0.5	L	4.9614	4.6809	4.6928	4.6900	4.6857	4.6867
	Δ	-0.0047	0.0058	-0.0061	-0.0034	0.0010	
	T_1	1.1195	1.0820	1.1219	1.1009	1.9111	1.0971
	Δ	-0.0224	0.0151	-0.0238	-0.0038	0.0060	
	T_2	2.8870	2.8699	2.8793	2.8747	2.8706	2.8748
	Δ	-0.0120	0.0049	-0.0045	0.00009	0.0042	

TABLE 6c. Frequency table and phonon corrections for LRP in $\underset{\sim}{\zeta} = [\zeta\zeta\zeta]$ direction, where $\underset{\sim}{q} = 2\pi/a\,\underset{\sim}{\zeta}$, $0.1 \leq \zeta \leq 0.5$. $\Delta\nu_j(\underset{\sim}{q}) = (\nu_j(\underset{\sim}{q}))_\infty - (\nu_j(\underset{\sim}{q}))_n$ are in units of 10^{12} cps.

ζ	Shell→	5	8	12	16	23	∞
0.1	L	1.8963	1.8650	1.8854	1.8716	1.8655	1.8622
	Δ	-0.0341	-0.0028	-0.0233	-0.0095	-0.0033	
	T	0.7697	0.7336	0.7583	0.7458	0.7398	0.7383
	Δ	-0.0314	0.0046	-0.0200	-0.0075	-0.0016	
0.2	L	3.3599	3.3349	3.3462	3.3430	3.3431	3.3427
	Δ	-0.0172	0.0078	-0.0035	-0.0003	-0.0004	
	T	1.5345	1.4978	1.5266	1.5190	1.5208	1.5192
	Δ	-0.0153	0.0215	-0.0073	0.0002	-0.0016	
0.3	L	4.1300	4.1205	4.1282	4.1237	4.1224	4.1218
	Δ	-0.0082	0.0013	-0.0065	-0.0019	-0.0006	
	T	2.2764	2.2550	2.2730	2.2673	2.2646	2.2618
	Δ	-0.0145	0.0068	-0.0112	-0.0056	-0.0027	
0.4	L	4.1476	4.1345	4.1429	4.1400	4.1370	4.1374
	Δ	-0.0102	0.0029	-0.0055	-0.0025	0.0004	
	T	2.9513	2.9361	2.9437	2.9363	2.9333	2.9336
	Δ	-0.0176	-0.0025	-0.0101	-0.0026	0.0003	
0.5	L,T	3.4959	3.4801	3.4840	3.4761	3.47693	3.47691
	Δ	-0.0190	-0.0032	-0.0070	0.0008	-0.00002	

5.3 LONG RANGE CONTRIBUTION TO THE ANHARMONIC QUARTIC TERM (F_4) OF THE HELMHOLTZ FREE ENERGY FOR Na AT 90°K.

The exact calculation of F_4, Eqs(2.16), (2.17), (2.18), (2.19), involves the summation over the Brillouin zone wave vectors. The wave vectors $\underset{\sim}{q} = L^{-1}(2\pi/a)\underset{\sim}{p}$ are generated from the boundaries of the first B.Z. defined by $p_x + p_y \leq L$, $p_y + p_z \leq L$ $p_z + p_x \leq L$, $0 \leq p_z \leq p_y \leq p_x$, where p_x, p_y, p_z are integers and L denotes the step length. For a given step length L, this procedure will generate $2L^3$ points in the whole zone.

The long range contribution to F_4 from the 8-term asymptotic potential, Eq(3.7), requires the computation of the fourth rank wave vector dependent tensor sums $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ given by Eq(4.15). In order to get a realistic answer for F_4, the density of points in q-space must be reasonable. Usually this requires a large number of points distributed uniformly in the first B.Z. We have found that for a given step length L, the major contribution to a B.Z. sum comes from those components of $\underset{\sim}{p}$ which are either, all odd or all even (Shukla, unpublished results) viz. Good Wave Vectors (GWV) and L = 2,4,6.... This generates ($L^3/4$) points in the whole zone.

All sums over the first B.Z. were computed over the irreducible sector (1/48th) and by suitable weighting the results were obtained for the whole zone. We have presented in Table 7 the number of even good wave vectors in the 1/48th portion of FBZ. The number of odd good wave vectors can be obtained from this table, since the number of odd good wave vectors in 1/48 portion of FBZ for step length (L) is equal to the number of even good wave vectors in 1/48 portion of FBZ for step length (L+2).

In order to assess the numerical accuracy of the function $F^{1}_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ we derive the following sum rule

$$\sum_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} = \sum_{\alpha\gamma} F_{\alpha\alpha\gamma\gamma}(\underset{\sim}{q})$$

$$= \sum_{\underset{\sim}{\ell}}{}' \left[C(\ell) + 10\,\ell^{-1} B(\ell) + 15\,\ell^{-2} A(\ell) \right] \cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$= f^{0} \tag{5.15}$$

To derive this sum rule we substitute the expression for $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ from Eq(2.14) and sum over α, γ indices and use Eqs(2.6a), (2.6b), (2.6c), (2.6d). Now the LHS can be computed independently from the Eq(4.15) with the help of $C_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{q})$ and $S_n^{\alpha\beta\gamma\delta}(2k_F, \underset{\sim}{q})$. The RHS can also be computed independently with the help of zero rank tensor sums which can be obtained from the Eqs(4.4) and (4.5). The expressions for these terms are

$$\sum_{\underset{\sim}{\ell}}{}' \ell^{-1} B(\ell) \cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) = \sum_{i=1}^{4} \Big\{ (2k_F)^3 a_i \, S_{2i+2}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \left[3(2k_F)^2 (2i+2) a_i - (2k_F)^3 b_i \right] C_{2i+3}(2k_F, \underset{\sim}{q}, 0)$$

$$+ 3\left[-(2k_F)(4i^2+10i+5) a_i + (2k_F)^2 (2i+3) b_i \right] S_{2i+4}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \big[-(2i+1)(4i^2+16i+15) a_i$$

$$+ 3(2k_F)(4i^2+14i+11) b_i \big] C_{2i+5}(2k_F, \underset{\sim}{q}, 0)$$

$$- (2i+2)(2i+4)(2i+6) b_i \, S_{2i+6}(2k_F, \underset{\sim}{q}, 0) \Big\} \tag{5.16}$$

$$\sum_{\underset{\sim}{\ell}}{}' C(\ell) \cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) = \sum_{i=1}^{4} \Big\{ (2k_F)^2 a_i \, C_{2i+1}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \left[-2(2k_F)^3 (4i+5) a_i + (2k_F)^4 b_i \right] S_{2i+2}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \left\{ -(2k_F)^2 \left[6(2i+1)(2i+5) \right] a_i + 2(2k_F)^3 (4i+7) b_i \right\} C_{2i+3}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \big\{ (2k_F) \left[2(2i+1)(2i+2)(4i+15) + 15(4i+3) \right] a_i$$

$$- (2k_F)^2 \left[6(2i+2)(2i+6) + 15 \right] b_i \big\} S_{2i+4}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \big\{ \left[(2i+1)(2i+2)(2i+3)(2i+10) + 15(2i+1)(2i+3) \right] a_i$$

$$- (2k_F) \left[2(2i+2)(2i+3)(4i+17) + 15(4i+5) \right] b_i \big\} C_{2i+5}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \big[(2i+2)(2i+3)(2i+4)(2i+11)$$

$$+ 15(2i+2)(2i+4) \big] b_i \, S_{2i+6}(2k_F, \underset{\sim}{q}, 0) \Big\} \tag{5.17}$$

$$\sum_{\underset{\sim}{\ell}}^{\prime} \ell^{-2} A(\ell) \cos(\underset{\sim}{q} \cdot \underset{\sim}{\ell}) = \sum_{i=1}^{4} \Big\{ -(2k_F)^2 a_i\, C_{2i+3}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \left[(2k_F)(4i+3) a_i - (2k_F)^2 b_i \right] S_{2i+4}(2k_F, \underset{\sim}{q}, 0)$$

$$+ \left[(2i+1)(2i+3) a_i - (2k_F)(4i+5) b_i \right] C_{2i+5}(2k_F, \underset{\sim}{q}, 0)$$

$$+ (2i+2)(2i+4) b_i\, S_{2i+6}(2k_F, \underset{\sim}{q}, 0) \Big\} \qquad (5.18)$$

We have presented in Table 8 all distinct $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ functions and the term f^o which corresponds to the RHS of Eq(5.15). This table not only shows the numerical verification of the sum rule, Eq(5.15), for every wave vector $\underset{\sim}{q}$, but also displays the symmetry of $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ for we know that the transformation properties of $F_{\alpha\beta\gamma\delta}(\underset{\sim}{q})$ are decided by those of the vector $\underset{\sim}{q}$.

We have derived the expression for F_4^E in Section (2.2) and computed it in Section (5.1). To test our computer program of F_4 further, we set all phonon frequencies equal to a constant, ω_E , and expect our program to produce the answer for F_4^E. Indeed for the step length L = 32 we have obtained exactly the same numerical result as calculated from Eq(2.52).

Finally as pointed out in Section 5 the long range correction (contribution) to exact F_4 is obtained from the equation

$$\Delta F_4 = (F_4)_{\infty} - (F_4)_{23}$$

where $(F_4)_\infty$ is calculated from the Ewald's method and $(F_4)_{23}$ is calculated from discrete summation (using the simplifications outlined in Appendix A1). In both methods of evaluations of $(F_4)_\infty$ and $(F_4)_{23}$ the eigenvalues $\omega^2(\underset{\sim}{q}j)$ and the corresponding eigenvectors $\underset{\sim}{e}(\underset{\sim}{q}j)$ in Eq(2.15) or Eqs (2.7), (2.18), (2.19) have been obtained from the actual potential (Shukla and Taylor, 1974).

We have presented in Table 9 the total F_4 as well as its three separate contributions viz F_4^0, F_4^1, F_4^3 and the corresponding corrections $\Delta F_4'$ as a function of step length (L).

TABLE 7. Number of Even Good Wave Vectors (NEGWV) of BCC lattice in 1/48 portion of FBZ as a function of step length (L).

L	NEGWV	L	NEGWV	L	NEGWV	L	NEGWV
2	2	36	385	70	2280	104	690
4	5	38	440	72	2470	106	7308
6	8	40	506	74	2660	108	7714
8	14	42	572	76	2870	110	8120
10	20	44	650	78	3080	112	8555
12	30	46	728	80	3311	114	8990
14	40	48	819	82	3542	116	9455
16	55	50	910	84	3795	118	9920
18	70	52	1015	86	4048	120	10416
20	91	54	1120	88	4324	122	10912
22	112	56	1240	90	4600	124	11440
24	140	58	1360	92	4900	126	11968
26	168	60	1496	94	5200	128	12529
28	204	62	1632	96	5525		
30	240	64	1785	98	5850		
32	285	66	1938	100	6201		
34	330	68	2109	102	6552		

TABLE 8. Fourth rank tensor sums and sum rules for LRP. $q = (2\pi / aL)\ell$ all sums are units of $eV/A^{\circ 4}$ .Even good wave vectors are generated from $L = 8$.

ℓ	000	200	220	222	400	420	422
F_{xxxx}	-1.5437	-1.9316	-1.3763	-0.9867	-1.2681	-1.3035	-1.3323
F_{yyyy}	-1.5437	-0.6960	-1.3763	-0.9867	1.3779	-0.0181	-0.0368
F_{zzzz}	-1.5437	-0.6960	-0.1206	-0.9867	1.3779	1.3399	-0.0368
F_{xxyy}	-1.5042	-0.9500	-0.5436	-0.3868	-0.0540	0.1700	0.1726
F_{xxzz}	-1.5042	-0.9500	-0.7365	-0.3868	0.0540	0.0413	0.1726
F_{yyzz}	-1.5042	-1.1916	-0.7365	-0.3868	-0.4077	-0.1919	-0.0055
F_{xxxy}	0.0	0.0	-0.9918	0.7049	0.0	1.3247	0.9348
F_{xxxz}	0.0	0.0	0.0	0.7049	0.0	0.0	0.9348
F_{yyyx}	0.0	0.0	-0.9918	0.7049	0.0	1.3459	0.9481
F_{yyyz}	0.0	0.0	0.0	0.7049	0.0	0.0	0.0264
F_{zzzx}	0.0	0.0	0.0	0.7049	0.0	0.0	0.9481
F_{zzzy}	0.0	0.0	0.0	0.7049	0.0	0.0	0.0264
F_{xxyz}	0.0	0.0	0.0	0.2717	0.0	0.0	-0.0082
F_{yyxz}	0.0	0.0	0.0	0.2717	0.0	0.0	0.3960
F_{zzxy}	0.0	0.0	0.3996	0.2717	0.0	0.5687	0.3960
f^{0}	-13.6561	-9.5070	-6.9064	-5.2808	0.8881	0.05700	-0.7266

TABLE 8 cont.

ℓ	440	442	444	600	620	622	800
F_{xxxx}	-1.3374	-1.3612	-1.3870	2.0120	1.4014	0.9645	4.2860
F_{yyyy}	-1.3374	-1.3612	-1.3870	3.4339	1.4014	0.9644	4.2860
F_{zzzz}	1.3100	-0.0589	-1.38700	3.4339	2.8153	0.9644	4.2860
F_{xxyy}	0.2990	0.3080	0.3150	0.6372	0.5593	0.3880	0.7716
F_{xxzz}	0.0306	0.1737	0.3150	0.6372	0.3871	0.3880	0.7716
F_{yyzz}	0.0306	0.1737	0.3150	0.4176	0.3871	0.3880	0.7716
F_{xxxy}	1.8619	1.3130	0.0	0.0	0.9206	0.6465	0.0
F_{xxxz}	0.0	0.0	0.0	0.0	0.0	0.6465	0.0
F_{yyyx}	1.8619	1.3130	0.0	0.0	0.9206	0.6465	0.0
F_{yyyz}	0.0	0.0	0.0	0.0	0.0	-0.6465	0.0
F_{zzzx}	0.0	0.0	0.0	0.0	0.0	0.6465	0.0
F_{zzzy}	0.0	0.0	0.0	0.0	0.0	-0.6465	0.0
F_{xxyz}	0.0	0.0	0.0	0.0	0.0	-0.2933	0.0
F_{yyxz}	0.0	0.0	0.0	0.0	0.0	0.2933	0.0
F_{zzxy}	0.7950	0.5562	0.0	0.0	0.4115	0.2933	0.0
f^{o}	-0.6440	-1.4705	-2.2708	12.2640	8.2851	5.2209	17.4877

TABLE 9. Long range correction ($\Delta = (P)_{\infty} - (P)_n$) to F_4^0, F_4^1, F_4^3, Anharmonic quartic term(F_4) as a function of step length (L), where $F_4 = F_4^0 - 2F_4^1 + F_4^3$ and n is shell number. F_4^0, F_4^1, F_4^3, F_4 and Δ are in units of $N(k_B T)^2$ erg^{-1}.

L	n	F_4^0	F_4^1	F_4^3	F_4
	∞	-10.7808	-4.0536	-15.4142	-18.0877
4	23	-10.7811	-4.0447	-37.2598	-39.9514
	Δ	0.0002	-0.0089	21.8456	21.8637
	∞	-15.4315	-7.6870	-3.8092	-3.8687
6	23	-15.4319	-7.6848	-15.2199	-15.2822
	Δ	0.0004	-0.0022	11.4107	11.4154
	∞	-18.3410	-10.0756	-4.9810	-3.1718
8	23	-18.3414	-10.0742	-4.9791	-3.1721
	Δ	0.0004	-0.0014	-0.0019	0.0013
	∞	-20.1759	-11.5959	-5.8183	-2.8025
10	23	-20.1764	-11.5948	-5.8180	-2.8048
	Δ	0.3335	-0.0011	-0.0004	0.0023
	∞	-21.4067	-12.6153	-6.4219	-2.5980
12	23	-21.4072	-12.6158	-6.4221	-2.5978
	Δ	0.0005	0.0005	0.0002	-0.0003

TABLE 9. continued

L	n	F_4^0	F_4^1	F_4^3	F_4
	∞	-22.2797	-13.3372	-6.6891	-2.4745
14	23	-22.2802	-13.3380	-6.8695	-2.4737
	Δ	0.0005	0.0008	0.0004	-0.0007
	∞	-22.9276	-13.8725	-7.2110	-2.3937
16	23	-22.9272	-13.8722	-7.2108	-2.3945
	Δ	0.0005	-0.0003	-0.0003	0.0008
	∞	-22.4264	-14.2823	-7.4784	-2.3403
18	23	-23.4270	-14.2824	-7.4783	-2.3406
	Δ	1.0006	0.0001	-0.0001	0.0002
	∞	-23.8220	-14.6066	-7.6932	-2.3021
20	23	-23.8226	-14.6069	-7.6931	-2.3018
	Δ	0.0006	0.0003	-0.0001	-0.0003
	∞	-24.1435	-14.8720	-7.8695	-2.2726
22	23	-24.1440	-14.7802	-7.8691	-2.2727
	Δ	0.0006	0.0001	-0.0003	0.0001
	∞	-24.4099	-15.0882	-8.0159	-2.2494
24	23	-24.4105	-15.0883	-8.0159	-2.2498
	Δ	0.0006	0.0001	-0.0000	0.0004

TABLE 9. continued

L	n	F_4^0	F_4^1	F_4^3	F_4
	∞	-24.6343	-15.2716	-8.1400	-2.2312
26	23	-24.6349	-15.2718	-8.1400	-2.2314
	Δ	0.0006	0.0002	0.0000	0.0002
	∞	-24.8260	-15.4282	-8.2464	-2.2160
28	23	-24.8266	-15.4283	-8.2464	-2.2162
	Δ	0.0006	0.0001	0.0000	0.0001
	∞	-24.9917	-15.5635	-8.3385	-2.2032
30	23	-24.9923	-15.5638	-8.3386	-2.2033
	Δ	0.0006	0.0002	0.0001	0.0001
	∞	-25.1364	-15.6817	-8.4192	-2.1921
32	23	-25.1370	-15.6819	-8.4192	-2.1923
	Δ	0.0006	0.0002	-0.0000	0.0002
	∞	-25.2637	-15.7857	-8.4903	-2.1826
34	23	-25.2643	-15.7859	-8.4903	-2.1828
	Δ	0.0006	0.0002	0.0000	-0.0002
	∞	-25.3768	-15.8779	-8.5534	-2.1743
36	23	-25.3774	-15.8782	-8.5535	-2.1744
	Δ	0.0006	0.0003	0.0001	0.0001

TABLE 9. continued

L	n	F_4^0	F_4^1	F_4^3	F_4
	∞	-25.4777	-15.9604	-8.6100	-2.1669
38	23	-25.4783	-15.9606	-8.6100	-2.1670
	Δ	0.0006	0.0002	0.0000	0.0001
	∞	-25.5685	-16.0346	-8.6609	-2.1603
40	23	-25.5691	-16.0348	-8.6608	-2.1604
	Δ	0.0006	0.0002	-0.0001	0.0001
	∞	-25.6505	-16.1015	-8.7069	-2.1544
42	23	-25.6512	-16.1016	-8.7069	-2.1545
	Δ	0.0006	0.0002	0.0000	0.0001
	∞	-25.7251	-16.1623	-8.7487	-2.1491
44	23	-25.7257	-16.1626	-8.7487	-2.1492
	Δ	0.0006	0.0003	0.0000	0.0001
	∞	-25.7930	-16.2178	-8.7869	-2.1442
46	23	-25.7937	-16.2181	-8.7869	-2.1444
	Δ	0.0006	0.0002	-0.0000	0.0001
	∞	-25.8553	-16.2687	-8.8219	-2.1398
48	23	-25.8559	-16.2690	-8.8219	-2.1399
	Δ	0.0006	0.0002	-0.0000	0.0001
	∞	-25.9126	-16.3155	-8.8541	-2.1358
50	23	-25.9132	-16.3157	-8.8541	-2.1359
	Δ	0.0006	0.0002	0.0000	0.0001

6. DISCUSSION

In order to calculate the long range contribution (correction) to the quartic term of the Helmholtz free energy (F_4 and F_4^E), phonon frequencies $(\omega(\underset{\sim}{q}j))$ and energy (U) it is necessary to select a long range potential as given by Eq(3.7). As shown in Table 2 the first, second, third and fourth derivatives obtained from this potential are in reasonable agreement with the actual potential at large distances. It is easily seen from Table 2 that the magnitude and sign of the derivatives from the two potentials are very close for many shells: for example, at the 18th shell, $\phi''_{AP} = .0028$ and $\phi''_{LRP} = .0021$

The corrections to $\langle\omega^2\rangle$, F_4^E, and U for different shells as obtained from the 8-term potential are presented in Table 4. After the third shell and except for the 8th shell, all corrections are negative for $\langle\omega^2\rangle$. If we ignore the first few shells where the asymptotic potential has no validity, the smallest correction is obtained when the discrete sums are truncated at the 23rd shell. All corrections for F_4^E are positive after the 7th shell. Except for the first, third, and eighth shells, all corrections to U from the LRP are positive.

Tables 6a, 6b, 6c show the long range corrections to the phonon frequencies in the three principle symmetry directions $[\zeta 0 0]$, $[\zeta\zeta 0]$, $[\zeta\zeta\zeta]$.

In $[\zeta 0 0]$ direction the magnitude of the smallest correction is found for the longitudinal mode beyond the 8th shell for $\zeta = .2$ and the 23rd shell for $\zeta = .6$. These are the same as the smallest transverse mode correction beyond the 23rd shell for $\zeta = .4$.

In $[\zeta\zeta 0]$ direction the smallest correction is found beyond the 23rd shell for the longitudinal mode.

In $[\zeta\zeta\zeta]$ direction the smallest correction for the longitudinal and transverse modes is found beyond the 23rd shell at the BZ boundary.

Since the smallest corrections for $\langle \omega^2 \rangle$, F_4^E, and U are found beyond the 23rd shell, we have examined the correction to the exact F_4 beyond this shell. We have presented in Table 9 the three terms of F_4, viz. F_4^0, F_4^1, F_4^3 arising in the expression of F_4, Eq(2.16). This table also contains the corresponding corrections to each of these 3 terms and total F_4 beyond the 23rd shell as a function of the step length (L). It is clear from this table that the numerical magnitude of F_4^0, F_4^1, F_4^3 and the total F_4 change rather rapidly with the number of points in the whole zone but the correction to F_4 is unchanged as the step length is increased from L = 38 to L = 50. This correction is found to be 0.0001 $N(k_B T)^2 \mathrm{erg}^{-1}$.

7. CONCLUSION

We have developed the theory and performed the calculations for the long range contributions (corrections) to the anharmonic quartic term (F_4) in the Helmholtz free energy, the Einstein quartic term (F_4^E), average $\langle \omega^2 \rangle$ Energy (U) and phonon frequencies $\omega_{\underset{\sim}{q}j}$ from the 8-term asymptotic potential with the help of several tensor lattice sums of rank zero, two and four obtained by the Ewald's method. The long range corrections to the above mentioned properties are found to be negligible beyond the 23rd shell.

APPENDIX A1 SIMPLIFICATION OF THE WAVE VECTOR DEPENDENT FOURTH RANK DISCRETE TENSOR SUMS

In order to evaluate the fourth rank discrete tensor sum, Eq(2.14), which requires the summation over the discrete lattice vectors $\underset{\sim}{r}^{\ell}$, the most practical method of reducing the computer time is to use all the 48 point group operations of a cube for a general direct lattice vector $\underset{\sim}{r}^{\ell}$ with positive components satisfying the condition $r_x^{\ell} \neq r_y^{\ell} \neq r_z^{\ell}$. This procedure reduces the ℓ summation to shell(s) summation and thus $F_{\alpha\beta\gamma\delta}(\underset{\sim}{Q})$ needs to be computed for only one representative point in that shell. There are four distinct types of tensor sums and their expressions can be obtained by the method outlined in Shukla and Wilk (1974).

$$F_{xxxx}(\underset{\sim}{Q}) = \sum_{s}{}' (n_s/6)\Big[\phi_{xxxx}\, c_{xx}(c_{yy}c_{zz} + c_{yz}c_{zy}) + \phi_{yyyy}\, c_{xy}(c_{yx}c_{zz} + c_{yz}c_{zx}) + \phi_{zzzz}\, c_{xy}(c_{yy}c_{zx} + c_{yx}c_{zy})\Big] \tag{A1.1}$$

$$F_{xxyy}(\underset{\sim}{Q}) = \sum_{s}{}' (n_s/6)\Big[\phi_{xxyy}\, c_{zz}(c_{xx}c_{yy} + c_{xy}c_{yx}) + \phi_{xxzz}\, c_{zy}(c_{xx}c_{yz} + c_{xz}c_{yx}) + \phi_{yyzz}\, c_{zx}(c_{xz}c_{yy} + c_{xy}c_{yz})\Big] \tag{A1.2}$$

$$F_{xxxy}(\underset{\sim}{Q}) = \sum_s{}' (-n_s/6)\Big[s_{xx}(\phi_{xxxy}\, s_{yy}\, c_{zz} + \phi_{xxxz}\, s_{yz}\, c_{zy})$$

$$+ s_{xy}(\phi_{yyyx}\, s_{yx}\, c_{zz} + \phi_{yyyz}\, s_{yz}\, c_{zx})$$

$$+ s_{xz}(\phi_{zzzx}\, s_{yx}\, c_{zy} + \phi_{zzzy}\, s_{yy}\, c_{zx})\Big] \qquad \text{(A1.3)}$$

$$F_{xxyz}(\underset{\sim}{Q}) = \sum_s{}' (-n_s/6)\Big[\phi_{xxyz}\, c_{xx}(s_{yy}\, s_{zz} + s_{yz}\, s_{zy})$$

$$+ \phi_{yyxz}\, c_{xy}(s_{yx}\, s_{zz} + s_{yz}\, s_{zx})$$

$$+ \phi_{zzxy}\, c_{xz}(s_{yy}\, s_{zx} + s_{yx}\, s_{zy})\Big]$$

(A1.4)

where $c_{\alpha\beta} = \mathrm{Cos}(Q_\alpha r^s_\beta)$, $s_{\alpha\beta} = \mathrm{Sin}(Q_\alpha r^s_\beta)$; $\alpha, \beta = x, y, z$
$\underset{\sim}{r}^s = \frac{a}{2}(n^s_x, n^s_y, n^s_z)$; s is the shell index, $\underset{\sim}{r}^s$ is the real lattice shell vector; n^s_x, n^s_y, n^s_z are three positive integers with $n^s_x \geqslant n^s_y \geqslant n^s_y$, n_s is the number of points in s^{th} shell, and

$$\phi_{xxxx}(r^s) = r_x^4 r^{-4} C(r) + 6 r_x^2 r^{-3} B(r) + 3 r^{-2} A(r)\Big|_{r=r^s} \qquad \text{(A1.5)}$$

$$\phi_{xxyy}(r^s) = r_x^2 r_y^2 r^{-4} C(r) + (r_x^2 + r_y^2) r^{-3} B(r) + r^{-2} A(r)\Big|_{r=r^s} \qquad \text{(A1.6)}$$

$$\phi_{xxxy}(r^s) = r_x^3 r_y r^{-4} C(r) + 3 r_x r_y r^{-3} B(r)\Big|_{r=r^s} \qquad \text{(A1.7)}$$

$$\phi_{xxyz}(r^s) = r_x^2 r_y r_z r^{-4} C(r) + r_y r_z r^{-3} B(r)\Big|_{r=r^s} \qquad \text{(A1.8)}$$

where $C(r)$, $B(r)$ and $A(r)$ are given by Eqs(2.6b), (2.6c), (2.6d).

The other eleven fourth rank tensor sums, indicated in the square brackets viz.

$$\left[F_{yyyy}(\underset{\sim}{Q}), F_{zzzz}(\underset{\sim}{Q})\right], \left[F_{xxzz}(\underset{\sim}{Q}), F_{yyzz}(\underset{\sim}{Q})\right],$$
$$\left[F_{xxxz}(\underset{\sim}{Q}), F_{yyyx}(\underset{\sim}{Q}), F_{yyyz}(\underset{\sim}{Q}), F_{zzzx}(\underset{\sim}{Q}), F_{zzzy}(\underset{\sim}{Q})\right],$$
$$\left[F_{yyxz}(\underset{\sim}{Q}), F_{zzxy}(\underset{\sim}{Q})\right]$$

can be obtained from Eqs(A1.1), (A1.2), (A1.3) and (A1.4) respectively by cyclic permutation of x, y, z indices.

APPENDIX A2. WAVE VECTOR DEPENDENT LATTICE SUMS AND EWALD'S METHOD

In this appendix we will evaluate slowly convergent lattice sums $C_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$, $C_n^{\alpha\beta}(\zeta, \underset{\sim}{q})$, $C_m^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q})$, $S_m(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$, $S_m^{\alpha\beta}(\zeta, \underset{\sim}{q})$, $S_m^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q})$

CALCULATION OF $C_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$ AND $S_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$

The zeroth rank tensor cosine lattice sum is defined by

$$C_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u}) = \sum_{\underset{\sim}{\ell}}{}' |\underset{\sim}{\ell} - \underset{\sim}{u}|^{-n} \cos(\zeta |\underset{\sim}{\ell} - \underset{\sim}{u}|) \cos(\underset{\sim}{q} \cdot \underset{\sim}{\ell}) \tag{A2.1}$$

The summation over the direct lattice vectors $\underset{\sim}{\ell}$ converges slowly. However, for numerical calculations we need to convert this sum by a rapidly convergent sum. This can be easily done by the following Ewald's method.

Using integral representation of $|\underset{\sim}{\ell} - \underset{\sim}{u}|^{-n}$ we can write

$$\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell} - \underset{\sim}{u}|^{-n} e^{i\zeta|\underset{\sim}{\ell} - \underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell} - \underset{\sim}{u})} = \frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}} e^{i\zeta|\underset{\sim}{\ell} - \underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell} - \underset{\sim}{u})} \int_0^\infty dy\, y^{n-1} e^{-|\underset{\sim}{\ell} - \underset{\sim}{u}|^2 y^2} \tag{A2.2}$$

Since the summation in Eq(A2.2) is over discrete values of $\underset{\sim}{\ell}$, the sequence of the integration and summation are interchangeable, and we rewrite Eq(A2.2) as

$$\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell} - \underset{\sim}{u}|^{-n} e^{i\zeta|\underset{\sim}{\ell} - \underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell} - \underset{\sim}{u})} = \frac{2}{\Gamma(n/2)} \int_0^\infty dy \sum_{\underset{\sim}{\ell}} e^{i\zeta|\underset{\sim}{\ell} - \underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell} - \underset{\sim}{u})} e^{-|\underset{\sim}{\ell} - \underset{\sim}{u}|^2 y^2} y^{n-1} \tag{A2.3}$$

The RHS of this equation will converge quickly for a fixed value of the parameters ζ, $\underset{\sim}{q}$, and $\underset{\sim}{\ell}$ for large values of y but for small values of y there is a convergence problem. Therefore we split the integration over the dummy variable y into two parts at some arbitrary point α .

$$\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} e^{i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})} = \frac{2}{\Gamma(n/2)} \int_0^{\alpha} dy \sum_{\underset{\sim}{\ell}} y^{n-1} e^{i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2}$$

$$+\frac{2}{\Gamma(n/2)} \int_{\alpha}^{\infty} dy \sum_{\underset{\sim}{\ell}} y^{n-1} e^{i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2} \tag{A2.4}$$

If α is not very small the second integral in Eq(A2.4) converges rapidly. On the other hand, the dummy variable y which is in the range $0 \leqslant y \leqslant \alpha$ may be very small for the first integral and cause slow convergence, since exponential term will not be able to control the term y^{n-1}, we must find a transformation to convert the term $e^{-x^2 y^2}$ to e^{-z^2/y^2} ; this conversion can be done by the Fourier transformation.

The sum $C_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})$ can be trivially obtained from the two following sums defined by

$$F^1(\underset{\sim}{u},y) = \frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}} y^{n-1} e^{i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2} \tag{A2.5}$$

$$F^2(\underset{\sim}{u},y) = \frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}} y^{n-1} e^{-i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|} e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2} \tag{A2.6}$$

where each of these functions are periodic in $\underset{\sim}{u}$ with the periodicity of the lattice. We expand them in Fourier series.

For Eq(A2.5) we have

$$F^1(\underset{\sim}{u}, y) = \sum_{\underset{\sim}{G}} F^1_{\underset{\sim}{G}}\, e^{i\underset{\sim}{G}\cdot\underset{\sim}{u}} \tag{A2.7}$$

where

$$F^1_{\underset{\sim}{G}} = V^{-1}\int F^1(\underset{\sim}{u}, y)\, e^{-i\underset{\sim}{G}\cdot\underset{\sim}{u}}\, d^3\underset{\sim}{u} \tag{A2.8}$$

$\underset{\sim}{G}$ is the reciprocal lattice vector, V is the volume of the crystal. Noting that $\exp(i\,\underset{\sim}{G}\cdot\underset{\sim}{\ell}) = 1$ and substituting Eq(A2.5) in Eq(A2.8), we get

$$F^1_{\underset{\sim}{G}} = \frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}} y^{n-1} \int e^{i\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|}\, e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2}\, e^{i\underset{\sim}{G}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})}\, e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})}\, d^3\underset{\sim}{u} \tag{A2.9}$$

letting $\underset{\sim}{r} = \underset{\sim}{\ell} - \underset{\sim}{u}$, we rewrite Eq(A2.9) as,

$$F^1_{\underset{\sim}{G}} = \frac{2}{v_c\,\Gamma(n/2)}\, y^{n-1} \int e^{-r^2y^2}\, e^{i\zeta r}\, e^{i\underset{\sim}{G}'\cdot\underset{\sim}{r}}\, d^3\underset{\sim}{r} \tag{A2.10}$$

where $\underset{\sim}{G}' = \underset{\sim}{q} + \underset{\sim}{G}$, $v_c = N^{-1}V$, v_c is the volume of the real space unit cell, and N is the number of unit cells.

The triple integration in Eq(A2.10) reduces to the following one dimensional integral

$$F^1_{\underset{\sim}{G}} = \frac{4\pi\, y^{n-1}}{i v_c G' \Gamma(n/2)} \int_0^\infty dr\, r\, e^{-r^2y^2}\left[e^{i(\zeta+G')r} - e^{i(\zeta-G')r}\right] \tag{A2.11}$$

Similarly if we repeat the same procedure for Eq(A2.6) we obtain the corresponding Fourier coefficient as

$$F^2_{\underset{\sim}{G}} = \frac{4\pi\, y^{n-1}}{i v_c G' \Gamma(n/2)} \int_0^\infty dr\, r\, e^{-r^2y^2}\left[e^{-i(\zeta-G')r} - e^{-i(\zeta+G')r}\right] \tag{A2.12}$$

Combining Eqs(A2.11) and (A2.12) we find

$$F^{1}_{\underset{\sim}{G}}+F^{2}_{G}=\frac{8\pi\, y^{n-1}}{v_c\, G'\,\Gamma(n/2)}\int_0^{\infty} dr\, r\, e^{-r^2y^2}\left\{\sin[(\zeta+G')r]-\sin[(\zeta-G')r]\right\} \tag{A2.13}$$

But

$$\int_0^{\infty} dx\, x\, e^{-ax^2}\sin bx=\frac{b}{4}\left(\frac{\pi}{a^3}\right)^{1/2} e^{-b^2/4a} \quad ; \quad a,b>0 \tag{A2.14}$$

Hence, Eq(A2.13) can be simplified with the help of Eq(A2.14) and we get

$$F^{1}_{\underset{\sim}{G}}+F^{2}_{\underset{\sim}{G}}=\frac{2\pi^{3/2}\, y^{n-4}}{v_c\, G'\,\Gamma(n/2)}\left\{(\zeta+G')\, e^{-(\zeta+G')^2/4y^2}-(\zeta-G')\, e^{-(\zeta-G')^2/4y^2}\right\} \tag{A2.15}$$

From Eqs(A2.5) and (A2.6) the cosine sum can be written as

$$\frac{2}{\Gamma(n/2)}\sum_{\underset{\sim}{\ell}} y^{n-1}\cos(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|)\, e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2y^2}\, e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})}=\frac{1}{2}\left[F^{1}(\underset{\sim}{u},y)+F^{2}(\underset{\sim}{u},y)\right]$$

$$=\frac{1}{2}\sum_{\underset{\sim}{G}}\left(F^{1}_{\underset{\sim}{G}}+F^{2}_{\underset{\sim}{G}}\right)e^{i\underset{\sim}{G}\cdot\underset{\sim}{u}} \tag{A2.16}$$

Substituting for $F^{1}_{\underset{\sim}{G}} + F^{2}_{\underset{\sim}{G}}$ from Eq(A2.15) in Eq(A2.16), we get

$$\frac{2}{\Gamma(n/2)}\sum_{\underset{\sim}{\ell}} y^{n-1}\cos(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|)\, e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2y^2}\, e^{i\underset{\sim}{q}\cdot(\underset{\sim}{\ell}-\underset{\sim}{u})}=\frac{\pi^{3/2}}{v_c\,\Gamma(n/2)}$$

$$\cdot\sum_{\underset{\sim}{G}} e^{i\underset{\sim}{G}\cdot\underset{\sim}{u}}\, y^{n-4}\left[\left(1+\frac{\zeta}{G'}\right)e^{-(\zeta+G')^2/4y^2}+\left(1-\frac{\zeta}{G'}\right)e^{-(\zeta-G')^2/4y^2}\right] \tag{A2.17}$$

The expression given by Eq(A2.17) is the well known Theta function transformation of crystal physics.

From Eq(A2.4) we can write the cosine sum

$$\sum_{\boldsymbol{\ell}} |\boldsymbol{\ell}-\boldsymbol{u}|^{-n} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|)\, e^{i\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{u})} = \frac{2}{\Gamma(n/2)} \int_0^{\alpha} dy \sum_{\boldsymbol{\ell}} y^{n-1} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|)\, e^{i\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{u})} e^{-|\boldsymbol{\ell}-\boldsymbol{u}|^2 y^2}$$

$$+\frac{2}{\Gamma(n/2)} \int_{\alpha}^{\infty} dy \sum_{\boldsymbol{\ell}} y^{n-1} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|)\, e^{i\boldsymbol{q}\cdot(\boldsymbol{\ell}-\boldsymbol{u})} e^{-|\boldsymbol{\ell}-\boldsymbol{u}|^2 y^2} \qquad \text{(A2.18)}$$

First we substitute Eq(A2.17) into the first integral of Eq(A2.18) and then we multiply both sides of the resulting equation by $e^{i\boldsymbol{q}\cdot\boldsymbol{u}}$ to get

$$\sum_{\boldsymbol{\ell}} |\boldsymbol{\ell}-\boldsymbol{u}|^{-n} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|)\, e^{i\boldsymbol{q}\cdot\boldsymbol{\ell}} = \frac{\pi^{3/2}}{v_c \Gamma(n/2)} \sum_{\boldsymbol{G}} e^{i(\boldsymbol{G}+\boldsymbol{q})\cdot\boldsymbol{u}}$$

$$\cdot \left\{ \int_0^{\alpha} dy\, y^{n-4} \left[\left(1+\frac{\zeta}{|\boldsymbol{q}+\boldsymbol{G}|}\right) e^{-(\zeta+|\boldsymbol{G}+\boldsymbol{q}|)^2/4y^2} + \left(1-\frac{\zeta}{|\boldsymbol{q}+\boldsymbol{G}|}\right) e^{-(\zeta-|\boldsymbol{G}+\boldsymbol{q}|)^2/4y^2} \right] \right\}$$

$$+\frac{2}{\Gamma(n/2)} \sum_{\boldsymbol{\ell}} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|)\, e^{i\boldsymbol{q}\cdot\boldsymbol{\ell}} \int_{\alpha}^{\infty} dy\, y^{n-1} e^{-|\boldsymbol{\ell}-\boldsymbol{u}|^2 y^2} \qquad \text{(A2.19)}$$

In order to evaluate $C_n(\zeta, \boldsymbol{q}, \boldsymbol{u})$ given by Eq(A2.1) we first evaluate the sum

$$\sum_{\boldsymbol{\ell}} |\boldsymbol{\ell}-\boldsymbol{u}|^{-n} \cos(\zeta|\boldsymbol{\ell}-\boldsymbol{u}|) \cos(\boldsymbol{q}\cdot\boldsymbol{\ell})$$

which can be expressed as

$$\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \mathrm{Cos}(G|\underset{\sim}{\ell}-\underset{\sim}{u}|) \mathrm{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) = \frac{1}{2}\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \mathrm{Cos}(G|\underset{\sim}{\ell}-\underset{\sim}{u}|)\left(e^{i\underset{\sim}{q}\cdot\underset{\sim}{\ell}} + e^{-i\underset{\sim}{q}\cdot\underset{\sim}{\ell}}\right)$$

$$= \frac{1}{2}\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \mathrm{Cos}(G|\underset{\sim}{\ell}-\underset{\sim}{u}|)\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{\ell}}$$

$$+ \frac{1}{2}\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \mathrm{Cos}(G|\underset{\sim}{\ell}-\underset{\sim}{u}|)\, e^{-i\underset{\sim}{q}\cdot\underset{\sim}{\ell}} \qquad \text{(A2.20)}$$

The first term of this equation is given by Eq(A2.19) whereas the second term can be obtained from Eq(A2.19) by changing $\underset{\sim}{q}$ to $-\underset{\sim}{q}$. The change $\underset{\sim}{q} \to -\underset{\sim}{q}$ will not affect the sum over $\underset{\sim}{\ell}$ but the reciprocal sum should be examined more carefully. For this, we consider the following reciprocal sum which has the same structure as the sum we are interested in

$$\xi(\underset{\sim}{q}) = \sum_{\underset{\sim}{G}} \eta(|\underset{\sim}{G}+\underset{\sim}{q}|)\, e^{i(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}} \qquad \text{(A2.21)}$$

If we replace $\underset{\sim}{q}$ by $-\underset{\sim}{q}$ in Eq(A2.21), we get

$$\xi(-\underset{\sim}{q}) = \sum_{\underset{\sim}{G}} \eta(|\underset{\sim}{G}-\underset{\sim}{q}|)\, e^{i(\underset{\sim}{G}-\underset{\sim}{q})\cdot\underset{\sim}{u}} \qquad \text{(A2.22)}$$

but $\underset{\sim}{G}$ takes all possible values in the summation, hence Eq(A2.22) can be written as

$$\xi(-\underset{\sim}{q}) = \sum_{\underset{\sim}{G}} \eta(|\underset{\sim}{G}+\underset{\sim}{q}|)\, e^{-i(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}} \qquad \text{(A2.23)}$$

Combining Eqs(A2.23) and (A2.21) we get

$$\frac{1}{2}\left[\xi(\underset{\sim}{q})+\xi(-\underset{\sim}{q})\right] = \sum_{\underset{\sim}{G}} \eta(|\underset{\sim}{G}+\underset{\sim}{q}|)\, \mathrm{Cos}\left[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}\right] \qquad \text{(A2.24)}$$

With the help of Eq(A2.24), we can write Eq(A2.20) as

$$\sum_{\underset{\sim}{\ell}} |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \operatorname{Cos}(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|) \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) = \frac{\pi^{3/2}}{v_c\Gamma(n/2)} \sum_{\underset{\sim}{G}} \operatorname{Cos}[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}]$$

$$\cdot\left\{\int_0^{\alpha} dy\, y^{n-4}\left[\left(1+\frac{\zeta}{|\underset{\sim}{G}+\underset{\sim}{q}|}\right)e^{-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}+\left(1-\frac{\zeta}{|\underset{\sim}{G}+\underset{\sim}{q}|}\right)e^{-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}\right]\right\}$$

$$+\frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}} \operatorname{Cos}(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|) \int_{\alpha}^{\infty} dy\, y^{n-1} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2} \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) \qquad \text{(A2.25)}$$

The real lattice sum in Eq(A2.25) contains a singularity when $\underset{\sim}{u} \to 0$ for $\underset{\sim}{\ell}=0$. To remove this singularity we subtract the corresponding $\underset{\sim}{\ell}=0$ term from both sides of this equation and obtain

$$C_n(\zeta,\underset{\sim}{q},\underset{\sim}{u}) = \sum_{\underset{\sim}{\ell}}{}' |\underset{\sim}{\ell}-\underset{\sim}{u}|^{-n} \operatorname{Cos}(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|) \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$= \frac{\pi^{3/2}}{v_c\Gamma(n/2)} \sum_{\underset{\sim}{G}} \operatorname{Cos}[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}]$$

$$\cdot\left\{\int_0^{\alpha} dy\, y^{n-4}\left[\left(1+\frac{\zeta}{|\underset{\sim}{q}+\underset{\sim}{G}|}\right)e^{-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}+\left(1-\frac{\zeta}{|\underset{\sim}{q}+\underset{\sim}{G}|}\right)e^{-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}\right]\right\}$$

$$+\frac{2}{\Gamma(n/2)} \sum_{\underset{\sim}{\ell}}{}' \operatorname{Cos}(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|) \int_{\alpha}^{\infty} dy\, y^{n-1} e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2 y^2} \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$-\frac{2}{\Gamma(n/2)} \operatorname{Cos}(\zeta|\underset{\sim}{u}|) \int_0^{\alpha} dy\, y^{n-1} e^{-|\underset{\sim}{u}|^2 y^2} \qquad \text{(A2.26)}$$

The derivation of sum $S_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})$ is straightforward, since

$$S_n(\zeta,\underset{\sim}{q},\underset{\sim}{u}) = -\frac{d}{d\zeta} C_{n+1}(\zeta,\underset{\sim}{q},\underset{\sim}{u}) \qquad \text{(A2.27)}$$

using this equation we can obtain $S_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$ from Eq(A2.26) and write it as

$$S_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})=\frac{\pi^{3/2}}{2v_c\Gamma\left(\frac{n+1}{2}\right)}\sum_{\underset{\sim}{G}}\cos[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}]|\underset{\sim}{G}+\underset{\sim}{q}|^{-1}\Bigg\{\int_0^{\alpha}dy\,y^{n-5}$$
$$\cdot\left[(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2 e^{-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2 e^{-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}\right]$$
$$+2\int_0^{\alpha}dy\,y^{n-3}\left[e^{-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}-e^{-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}\right]\Bigg\}$$
$$+\frac{2}{\Gamma\left(\frac{n+1}{2}\right)}\sum_{\underset{\sim}{\ell}}{}'\,|\underset{\sim}{\ell}-\underset{\sim}{u}|\,\sin(\zeta|\underset{\sim}{\ell}-\underset{\sim}{u}|)\int_{\alpha}^{\infty}dy\,y^n e^{-|\underset{\sim}{\ell}-\underset{\sim}{u}|^2y^2}\cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) \qquad \text{(A2.28)}$$

Eqs(A2.26) and (A2.28) still contain the singularity as $\underset{\sim}{G}\to 0$ for $\underset{\sim}{q}=0$. Hence, the reciprocal lattice sum in $C_n(\zeta,0,0)$ and $S_n(\zeta,0,0)$ has to be split into two parts as $\sum_{\underset{\sim}{G}}{}'$ + ($\underset{\sim}{G}=0$ term). To find the $\underset{\sim}{G}=0$ term for $\underset{\sim}{q}=0$, we have to examine the Fourier coefficients given by Eqs(A2.11) and (A2.12). From Eq(A2.11) we get

$$\lim_{\underset{\sim}{G}\to 0} F^1_{\underset{\sim}{G}}=\frac{8\pi y^{n-1}}{v_c\Gamma(n/2)}\int_0^{\infty}dr\,r^2 e^{-r^2y^2}e^{i\zeta r}\left[\lim_{G\to 0}\frac{\sin(Gr)}{(Gr)}\right] \qquad \text{(A2.29)}$$

or

$$\lim_{\underset{\sim}{G}\to 0} F^1_{G}=\frac{8\pi y^{n-1}}{v_c\Gamma(n/2)}\int_0^{\infty}dr\,r^2 e^{-r^2y^2}e^{i\zeta r} \qquad \text{(A2.30)}$$

and similarly from Eq(A2.12) we have

$$\lim_{\underset{\sim}{G}\to 0} F^2_{G}=\frac{8\pi y^{n-1}}{v_c\Gamma(n/2)}\int_0^{\infty}dr\,r^2 e^{-r^2y^2}e^{-i\zeta r} \qquad \text{(A2.31)}$$

Combining the two previous equations, we get

$$\lim_{\underset{\sim}{G}\to 0}\left(F^{\prime 1}_{\underset{\sim}{G}}+F^{\prime 2}_{\underset{\sim}{G}}\right)=\frac{16\pi\, y^{n-1}}{v_c\Gamma(n/2)}\int_0^\infty dr\, r^2 e^{-r^2y^2}\cos(\zeta r) \tag{A2.32}$$

But

$$\begin{aligned}\int_0^\infty dr\, r^2 e^{-r^2y^2}\cos(\zeta r)&=\frac{d}{d\zeta}\int_0^\infty dr\, r\, e^{-y^2r^2}\sin(\zeta r)\\ &=\frac{\pi^{1/2}}{4y^3}\left(1-\frac{\zeta^2}{2y^2}\right)e^{-\zeta^2/4y^2}\end{aligned} \tag{A2.33}$$

Therefore the substitution of Eq(A2.33) in Eq(A2.32) gives

$$\lim_{\underset{\sim}{G}\to 0}\left(F^{\prime 1}_{\underset{\sim}{G}}+F^{\prime 2}_{\underset{\sim}{G}}\right)=\frac{4\pi^{3/2}}{v_c\Gamma(n/2)}\left(y^{n-4}-\frac{\zeta^2}{2}y^{n-6}\right)e^{-\zeta^2/4y^2} \tag{A2.34}$$

and finally the $\underset{\sim}{G}=0$ and $\underset{\sim}{q}=0$ term is

$$\int_0^\alpha dy \lim_{\underset{\sim}{G}\to 0}\left\{\frac{1}{2}\left(F^{\prime 1}_{\underset{\sim}{G}}+F^{\prime 2}_{\underset{\sim}{G}}\right)\right\}=\frac{2\pi^{3/2}}{v_c\Gamma(n/2)}\int_0^\alpha dy\left(y^{n-4}-\frac{\zeta^2}{2}y^{n-6}\right)e^{-\zeta^2/4y^2} \tag{A2.35}$$

The final expression for $C_n(\zeta,0,0)$ is given by

$$\begin{aligned}C_n(\zeta,0,0)=&\frac{\pi^{3/2}}{v_c\Gamma(n/2)}\left\{\sum_{\underset{\sim}{G}}{}'\left\{\int_0^\alpha dy\, y^{n-4}\left[\left(1+\frac{\zeta}{|\underset{\sim}{G}|}\right)e^{-(\zeta+|\underset{\sim}{G}|)^2/4y^2}\right.\right.\right.\\ &\left.\left.\left.+\left(1-\frac{\zeta}{|\underset{\sim}{G}|}\right)e^{-(\zeta-|\underset{\sim}{G}|)^2/4y^2}\right]\right\}+2\int_0^\alpha dy\left(y^{n-4}-\frac{\zeta^2}{2}y^{n-6}\right)e^{-\zeta^2/4y^2}\right\}\\ &+\frac{2}{\Gamma(n/2)}\left\{\sum_{\underset{\sim}{\ell}}{}'\left[\cos(\zeta|\underset{\sim}{\ell}|)\int_\alpha^\infty dy\, y^{n-1}e^{-|\underset{\sim}{\ell}|^2y^2}\right]-\frac{\alpha^n}{n}\right\}\end{aligned} \tag{A2.36}$$

and with the help of Eq(A2.27) $S_n(\zeta,0,0)$ can be obtained from $C_n(\zeta,0,0)$. The final expression is

$$
\begin{aligned}
S_n(\zeta,0,0) = \frac{\pi^{3/2}}{2v_c\,\Gamma\left(\frac{n+1}{2}\right)} \Bigg(\sum_{\underset{\sim}{G}}{}' |\underset{\sim}{G}|^{-1} \Bigg\{ & \int_0^{\alpha} dy\, y^{n-5} \Big[(\zeta + |\underset{\sim}{G}|)^2 e^{-(\zeta+|\underset{\sim}{G}|)^2/4y^2} \\
& \qquad - (\zeta - |\underset{\sim}{G}|)^2 e^{-(\zeta-|\underset{\sim}{G}|)^2/4y^2} \Big] \\
& + 2\int_0^{\alpha} dy\, y^{n-3} \Big[e^{-(\zeta-|\underset{\sim}{G}|)^2/4y^2} - e^{-(\zeta+|\underset{\sim}{G}|)^2/4y^2} \Big] \Bigg\} \\
& + \zeta \Big[\int_0^{\alpha} dy \left(6\, y^{n-5} - \zeta^2 y^{n-7} \right) e^{-\zeta^2/4y^2} \Big] \Bigg) \\
& + \frac{2}{\Gamma\left(\frac{n+1}{2}\right)} \sum_{\underset{\sim}{\ell}}{}' |\underset{\sim}{\ell}| \sin(\zeta |\underset{\sim}{\ell}|) \int_{\alpha}^{\infty} dy\, y^{n} e^{-|\underset{\sim}{\ell}|^2 y^2} \qquad \text{(A2.37)}
\end{aligned}
$$

CALCULATION OF $C_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$ AND $S_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$.

The second rank cosine and sine tensor sums are obtained from the two following equations:

$$C_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = \frac{\partial^2}{\partial u_\alpha \partial u_\beta} C_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{A2.38}$$

$$S_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = \frac{\partial^2}{\partial u_\alpha \partial u_\beta} S_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{A2.39}$$

where the sine tensor sum $S_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$ can also be obtained from the cosine tensor sum $C_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$ with the help of Eq(A2.27) as

$$S_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = -\frac{d}{d\zeta} C_{n+1}^{\alpha\beta}(\zeta,\underset{\sim}{q}) \tag{A2.40}$$

Substituting $C_n(\zeta,\underset{\sim}{q},\underset{\sim}{u})$ from Eq(A2.26) into Eq(A2.38), and letting $\underset{\sim}{l}'=\underset{\sim}{l}-\underset{\sim}{u}$, $l=|\underset{\sim}{l}|$, $u=|\underset{\sim}{u}|$, $l'=|\underset{\sim}{l}-\underset{\sim}{u}|$ we get

$$\begin{aligned} C_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = & \sum_{\underset{\sim}{l}}{}' \left[l'^{-2} l'_\alpha l'_\beta A_n^c(\zeta,l') + \delta_{\alpha\beta} l'^{-1} D_n^c(\zeta,l) \right] \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{l}) \\ & - \sum_{\underset{\sim}{G}} (G_\alpha+q_\alpha)(G_\beta+q_\beta)\, E_n^c(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,\underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \\ & + \left(W_n^c(\zeta,\alpha)\right)_{\alpha\beta} \end{aligned} \tag{A2.41}$$

Here we note that the argument α in the function $\left(W_n(\zeta,\alpha)\right)_{\alpha\beta}$ is the Ewald parameter and should not be confused with the tensor indices α, β etc., and

$$A_n^c(\zeta, \xi) = \left(\frac{d^2}{d\xi^2} - \xi^{-1}\frac{d}{d\xi}\right)\phi(\zeta, \xi) \tag{A2.42}$$

$$D_n^c(\zeta, \xi) = \frac{d}{d\xi}\phi(\zeta, \xi) \tag{A2.43}$$

$$E_n^c(\zeta, |\underset{\sim}{G}+\underset{\sim}{q}|, \underset{\sim}{u}) = \frac{\pi^{3/2}\cos[(\underset{\sim}{G}+\underset{\sim}{q})\cdot\underset{\sim}{u}]}{v_c\,\Gamma(n/2)}\int_0^{\alpha} dy\, y^{n-4}$$

$$\cdot\left[\left(1+\frac{\zeta}{|\underset{\sim}{G}+\underset{\sim}{q}|}\right)e^{-(\zeta+|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2} + \left(1-\frac{\zeta}{|\underset{\sim}{G}+\underset{\sim}{q}|}\right)e^{-(\zeta-|\underset{\sim}{G}+\underset{\sim}{q}|)^2/4y^2}\right] \tag{A2.44}$$

$$\left(W_n^c(\zeta,\alpha)\right)_{\alpha\beta} = \lim_{\underset{\sim}{u}\to 0}\left\{-\left(u^{-2}u_\alpha u_\beta A_n^c(\zeta,u) + \delta_{\alpha\beta}\,u^{-1}D_n^c(\zeta,u)\right)\right\} \tag{A2.45}$$

where the dummy variable ξ can assume different values such as l, l' or u arising in the following ϕ function.

$$\phi(\zeta, l') = \cos(\zeta l')\int_{\alpha}^{\infty} dy\, y^{n-1}\, e^{-l'^2 y^2} \tag{A2.46}$$

Letting $\xi = \ell'$ in Eqs.(A2.42) and (A2.43) and then substituting for $\phi(\xi,\ell')$ from Eq.(A2.46) into these equations, we can express $A_n^c(\zeta,\ell')$ and $D_n^c(\zeta,\ell')$ in the following form.

$$A_n^c(\zeta,\ell') = \frac{2}{\Gamma(n/2)}\Big\{\left[-\zeta^2\cos(\zeta\ell') + \zeta\ell'^{-1}\sin(\zeta\ell')\right]\int_\alpha^\infty dy\, y^{n-1} e^{-\ell'^2 y^2}$$
$$+ 4\zeta\ell'\sin(\zeta\ell')\int_\alpha^\infty dy\, y^{n+1} e^{-\ell'^2 y^2}$$
$$+ 4\ell'^2\cos(\zeta\ell')\int_\alpha^\infty dy\, y^{n+3} e^{-\ell'^2 y^2}\Big\} \tag{A2.47}$$

$$D_n^c(\zeta,\ell') = -\frac{2}{\Gamma(n/2)}\Big\{\zeta\sin(\zeta\ell')\int_\alpha^\infty dy\, y^{n-1} e^{-\ell'^2 y^2} + 2\ell'\cos(\zeta\ell')\int_\alpha^\infty dy\, y^{n+1} e^{-\ell'^2 y^2}\Big\} \tag{A2.48}$$

The calculation of $(W_n^c(\zeta,\alpha))_{\alpha\beta}$ involves taking limits of some functions of u such as $A_n^c(\zeta,u)$ and $D_n^c(\zeta,u)$ which can be obtained in a similar manner as the functions $A_n^c(\zeta,\ell')$ and $D_m^c(\zeta,\ell')$ except that now the limit of all integrals in Eqs(A2.47) and (A2.48) is from 0 to α instead of α to ∞. The final expressions are

$$A_n^c(\zeta,u) = \frac{2}{\Gamma(n/2)}\Big\{\left[-\zeta^2\cos(\zeta u) + \zeta u^{-1}\sin(\zeta u)\right]\int_0^\alpha dy\, y^{n-1} e^{-u^2 y^2}$$
$$+ 4\zeta u\sin(\zeta u)\int_0^\alpha dy\, y^{n+1} e^{-u^2 y^2}$$
$$+ 4u^2\cos(\zeta u)\int_0^\alpha dy\, y^{n+3} e^{-u^2 y^2}\Big\} \tag{A2.49}$$

$$D_n^c(\zeta,u) = -\frac{2}{\Gamma(n/2)}\Big\{\zeta\sin(\zeta u)\int_0^\alpha dy\, y^{n-1} e^{-u^2 y^2} + 2u\cos(\zeta u)\int_0^\alpha dy\, y^{n+1} e^{-u^2 y^2}\Big\} \tag{A2.50}$$

Now we can examine Eq(A2.45) for $\underset{\sim}{u} \to 0$. The term $u^{-2} u_\alpha u_\beta A_n^c(\zeta,u)$

for $\underset{\sim}{u} \to 0$ can be written as

$$\lim_{\underset{\sim}{u}\to 0} u^{-2} u_\alpha u_\beta A_n^c(\zeta, u) = \frac{2}{\Gamma(n/2)} \lim_{\underset{\sim}{u}\to 0} \Big\{ u^{-1} u_\alpha u_\beta \Big[\zeta^3 j_1(\zeta u) \cdot \int_0^\alpha dy\, y^{n-1} e^{-u^2y^2} + 4\zeta \operatorname{Sin}(\zeta u) \int_0^\alpha dy\, y^{n+1} e^{-u^2y^2} + 4u \operatorname{Cos}(\zeta u) \int_0^\alpha dy\, y^{n+3} e^{-u^2y^2} \Big] \Big\} \tag{A2.51}$$

where

$$j_1(x) = \frac{\operatorname{Sin} x}{x^2} - \frac{\operatorname{Cos} x}{x} \tag{A2.52}$$

is the first order Spherical Bessel function of the first kind, and $\lim_{x\to 0} j_1(x) \to 0$, $\lim_{\underset{\sim}{u}\to 0} u^{-1} u_\alpha u_\beta \to 0$, thus

$$\lim_{\underset{\sim}{u}\to 0} u^{-2} u_\alpha u_\beta A_n^c(\zeta, u) \longrightarrow 0 \tag{A2.53}$$

The term $u^{-1} D_n^c(\zeta, u)$ as $\underset{\sim}{u} \to 0$ can be written as

$$\lim_{\underset{\sim}{u}\to 0} u^{-1} D_n^c(\zeta, u) = -\frac{2}{\Gamma(n/2)} \lim_{\underset{\sim}{u}\to 0} \Big\{ \zeta^2 \frac{\operatorname{Sin}(\zeta u)}{(\zeta u)} \cdot \int_0^\alpha dy\, y^{n-1} e^{-u^2y^2} + 2 \operatorname{Cos}(\zeta u) \int_0^\alpha dy\, y^{n+1} e^{-u^2y^2} \Big\} \tag{A2.54}$$

Since $\lim_{x\to 0} x^{-1} \operatorname{Sin} x \to 1$, Eq(A2.54) can be simplified after interchanging the process of integration and limit, we get

$$\lim_{\underset{\sim}{u}\to 0} u^{-1} D_n^c(\zeta, u) = -\frac{2}{\Gamma(n/2)} \Big[\zeta^2 \frac{\alpha^n}{n} + 2 \frac{\alpha^{n+2}}{(n+2)} \Big] \tag{A2.55}$$

Substituting Eqs(A2.53) and (A2.55) in (A2.45) we get

$$\left(W_n^c(\zeta,\alpha)\right)_{\alpha\beta\gamma\delta} = \frac{2\delta_{\alpha\beta}}{\Gamma(n/2)}\left[\zeta^2\frac{\alpha^n}{n} + 2\frac{\alpha^{n+2}}{(n+2)}\right] \tag{A2.56}$$

Now the second rank cosine tensor sum, $C_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$ given by Eq(A2.41), can be written as

$$C_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = \sum_{\underset{\sim}{\ell}}{}' \left[\ell^{-2}\ell_\alpha\ell_\beta A_n^c(\zeta,\ell) + \delta_{\alpha\beta}\ell^{-1}D_n^c(\zeta,\ell)\right]\cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$-\sum_{\underset{\sim}{G}}(G_\alpha+q_\alpha)(G_\beta+q_\beta)E_n^c(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,0)$$

$$+\frac{2}{\Gamma(n/2)}\delta_{\alpha\beta}\left[\zeta^2\frac{\alpha^n}{n} + 2\frac{\alpha^{n+2}}{(n+2)}\right] \tag{A2.57}$$

To derive the second rank sine tensor sum $S_n^{\alpha\beta}(\zeta,\underset{\sim}{q})$, we substitute Eq(A2.57) in Eq(A2.40) and obtain

$$S_n^{\alpha\beta}(\zeta,\underset{\sim}{q}) = \sum_{\underset{\sim}{\ell}}{}' \left[\ell^{-2}\ell_\alpha\ell_\beta A_n^s(\zeta,\ell) + \delta_{\alpha\beta}\ell^{-1}D_n^s(\zeta,\ell)\right]\cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$-\sum_{\underset{\sim}{G}}(G_\alpha+q_\alpha)(G_\beta+q_\beta)E_n^s(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,0)$$

$$-\frac{4\delta_{\alpha\beta}}{\Gamma\left(\frac{n+1}{2}\right)}\zeta\,\frac{\alpha^{n+1}}{(n+1)} \tag{A2.58}$$

where

$$A_n^s(\zeta,\ell)=\frac{2}{\Gamma\left(\frac{n+1}{2}\right)}\left\{\left[-\zeta^2\ell\,\mathrm{Sin}(\zeta\ell)+\zeta\,\mathrm{Cos}(\zeta\ell)-\ell^{-1}\mathrm{sin}(\zeta\ell)\right]\int_\alpha^\infty dy\; y^n e^{-\ell^2y^2}\right.$$
$$-4\left[\zeta\ell^2\,\mathrm{Cos}(\zeta\ell)+\ell\,\mathrm{Sin}(\zeta\ell)\right]\int_\alpha^\infty dy\; y^{n+2}e^{-\ell^2y^2}$$
$$\left.+4\ell^3\,\mathrm{Sin}(\zeta\ell)\int_\alpha^\infty dy\; y^{n+4}e^{-\ell^2y^2}\right\} \tag{A2.59}$$

$$D_n^s(\zeta,\ell)=\frac{2}{\Gamma\left(\frac{n+1}{2}\right)}\left\{\left[\zeta\ell\,\mathrm{Cos}(\zeta\ell)+\mathrm{Sin}(\zeta\ell)\right]\int_\alpha^\infty dy\; y^n e^{-\ell^2y^2}\right.$$
$$\left.-2\ell^2\,\mathrm{Sin}(\zeta\ell)\int_\alpha^\infty dy\; y^{n+2}e^{-\ell^2y^2}\right\} \tag{A2.60}$$

$$E_n^s(\zeta,|\mathbf{G}+\mathbf{q}|,0)=\frac{\pi^{3/2}}{2v_c\Gamma\left(\frac{n+1}{2}\right)}\left\{|\mathbf{G}+\mathbf{q}|^{-1}\left[(\zeta+|\mathbf{G}+\mathbf{q}|)^2\int_0^\alpha dy\; y^{n-5}e^{-(\zeta+|\mathbf{G}+\mathbf{q}|)^2/4y^2}\right.\right.$$
$$-2\int_0^\alpha dy\; y^{n-3}e^{-(\zeta+|\mathbf{G}+\mathbf{q}|)^2/4y^2}$$
$$-(\zeta-|\mathbf{G}+\mathbf{q}|)^2\int_0^\alpha dy\; y^{n-5}e^{-(\zeta-|\mathbf{G}+\mathbf{q}|)^2/4y^2}$$
$$\left.\left.+2\int_0^\alpha dy\; y^{n-3}e^{-(\zeta-|\mathbf{G}+\mathbf{q}|)^2/4y^2}\right]\right\} \tag{A2.61}$$

CALCULATION OF $C_n^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q})$ AND $S_n^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q})$.

The fourth rank cosine and sine tensor sums are given by

$$C_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q}) = \frac{\partial^4}{\partial u_\alpha \partial u_\beta \partial u_\gamma \partial u_\delta} C_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{A2.62}$$

$$S_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q}) = \frac{\partial^4}{\partial u_\alpha \partial u_\beta \partial u_\gamma \partial u_\delta} S_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \tag{A2.63}$$

To evaluate $S_n^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q})$ once again we use Eq(A2.27), which allows us to obtain the sine tensor sum from the cosine tensor.

$$S_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q}) = -\frac{d}{d\zeta} C_{n+1}^{\alpha\beta\gamma\delta}(\zeta, \underset{\sim}{q}) \tag{A2.64}$$

Substituting $C_n(\zeta, \underset{\sim}{q}, \underset{\sim}{u})$ from Eq(A2.26) into Eq(A2.62), we find

$$\begin{aligned} C_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q}) = {} & \sum_{\underset{\sim}{\ell}}{}' \Big[\ell'^{-4} \ell'_\alpha \ell'_\beta \ell'_\gamma \ell'_\delta \, C_n^c(\zeta, \ell') \\ & + \ell'^{-3} \left(\delta_{\gamma\delta} \ell'_\alpha \ell'_\beta + \delta_{\alpha\delta} \ell'_\beta \ell'_\gamma + \delta_{\beta\delta} \ell'_\gamma \ell'_\alpha + \delta_{\beta\gamma} \ell'_\alpha \ell'_\delta + \delta_{\alpha\gamma} \ell'_\beta \ell'_\delta + \delta_{\alpha\beta} \ell'_\gamma \ell'_\delta \right) B_n^c(\zeta, \ell') \\ & + \ell'^{-2} \left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\delta\alpha} + \delta_{\alpha\gamma}\delta_{\beta\delta} \right) A_n^c(\zeta, \ell') \Big] \operatorname{Cos}(\underset{\sim}{q}\cdot\underset{\sim}{\ell}) \\ & + \sum_{\underset{\sim}{G}} (G_\alpha + q_\alpha)(G_\beta + q_\beta)(G_\gamma + q_\gamma)(G_\delta + q_\delta) \, E_n^c(\zeta, |\underset{\sim}{G} + \underset{\sim}{q}|, \underset{\sim}{u})\Big|_{\underset{\sim}{u}=0} \\ & + \left(R_n^c(\zeta, \alpha)\right)_{\alpha\beta\gamma\delta} \end{aligned} \tag{A2.65}$$

where

$$C_n^c(\zeta,\xi)=\mathscr{D}_4(\xi)\,\phi(\zeta,\xi) \qquad \text{(A2.66)}$$

$$B_n^c(\zeta,\xi)=\mathscr{D}_3(\xi)\,\phi(\zeta,\xi) \qquad \text{(A2.67)}$$

$$A_n^c(\zeta,\xi)=\mathscr{D}_2(\xi)\,\phi(\zeta,\xi) \qquad \text{(A2.68)}$$

and the differential operators appearing in Eqs(A2.66), (A2.67), (A2.68) are defined by

$$\mathscr{D}_4(\xi)=\frac{d^4}{d\xi^4}-6\xi^{-1}\frac{d^3}{d\xi^3}+15\xi^{-2}\frac{d^2}{d\xi^2}-15\xi^{-3}\frac{d}{d\xi} \qquad \text{(A2.69)}$$

$$\mathscr{D}_3(\xi)=\frac{d^3}{d\xi^3}-3\xi^{-1}\frac{d^2}{d\xi^2}+3\xi^{-2}\frac{d}{d\xi} \qquad \text{(A2.70)}$$

$$\mathscr{D}_2(\xi)=\frac{d^2}{d\xi^2}-\xi^{-1}\frac{d}{d\xi} \qquad \text{(A2.71)}$$

The function $E_n^c(\zeta,|\underset{\sim}{\xi}+\underset{\sim}{q}|,\underset{\sim}{u})$ is defined previously in Eq(A2.44). The full expression for the last term in Eq(A2.65), $\left(R_n^c(\zeta,\alpha)\right)_{\alpha\beta\gamma\delta}$, is

$$\begin{aligned}\left(R_n^c(\zeta,\alpha)\right)_{\alpha\beta\gamma\delta}=\lim_{\underset{\sim}{u}\to 0}\Big(&u^{-4}u_\alpha u_\beta u_\gamma u_\delta\, C_n^c(\zeta,u)\\ &+u^{-3}\left(\delta_{\gamma\delta}u_\alpha u_\beta+\delta_{\alpha\delta}u_\beta u_\gamma+\delta_{\beta\delta}u_\gamma u_\alpha+\delta_{\beta\gamma}u_\alpha u_\delta+\delta_{\alpha\gamma}u_\beta u_\delta+\delta_{\alpha\beta}u_\gamma u_\delta\right)B_n^c(\zeta,u)\\ &+u^{-2}\left(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\delta\alpha}+\delta_{\alpha\gamma}\delta_{\beta\delta}\right)A_n^c(\zeta,u)\Big)\end{aligned} \qquad \text{(A2.72)}$$

Explicit expressions for $C_n^c(\zeta,\ell')$ etc. can be obtained following the procedure outlined in the section of the calculation of $C_n^{\alpha\beta}(\zeta, \underset{\sim}{q})$ etc. The final results are

$$
\begin{aligned}
C_n^c(\zeta,\ell') = \frac{2}{\Gamma(n/2)} \Big\{ & \Big[\zeta^4 \cos(\zeta\ell') - 6\zeta^3 \ell'^{-1} \sin(\zeta\ell') + 15\zeta^2 \ell'^{-2} \cos(\zeta\ell') \\
& + 15\zeta \ell'^{-3} \sin(\zeta\ell')\Big] \int_\alpha^\infty dy\, y^{n-1} e^{-\ell'^2 y^2} \\
& + \Big[-8\zeta^3 \ell' \sin(\zeta\ell') - 24\zeta\ell'^{-1} \sin(\zeta\ell')\Big] \int_\alpha^\infty dy\, y^{n+1} e^{-\ell'^2 y^2} \\
& + 24\Big[-\zeta^2 \ell'^2 \cos(\zeta\ell') + \zeta\ell' \sin(\zeta\ell')\Big] \int_\alpha^\infty dy\, y^{n+3} e^{-\ell'^2 y^2} \\
& + 32\zeta\ell'^3 \sin(\zeta\ell') \int_\alpha^\infty dy\, y^{n+5} e^{-\ell'^2 y^2} \\
& + 16\ell'^4 \cos(\zeta\ell') \int_\alpha^\infty dy\, y^{n+7} e^{-\ell'^2 y^2} \Big\}
\end{aligned}
\tag{A2.73}
$$

$$
\begin{aligned}
B_n^c(\zeta,\ell') = \frac{2}{\Gamma(n/2)} \Big\{ & \Big[\zeta^3 \sin(\zeta\ell') + 3\zeta^2 \ell'^{-1} \cos(\zeta\ell') - 3\zeta\ell'^{-2} \sin(\zeta\ell')\Big] \int_\alpha^\infty dy\, y^{n-1} e^{-\ell'^2 y^2} \\
& + 6\Big[\zeta^2 \ell' \cos(\zeta\ell') - \zeta \sin(\zeta\ell')\Big] \int_\alpha^\infty dy\, y^{n+1} e^{-\ell'^2 y^2} \\
& - 12\zeta\ell'^2 \sin(\zeta\ell') \int_\alpha^\infty dy\, y^{n+3} e^{-\ell'^2 y^2} \\
& - 8\ell'^3 \cos(\zeta\ell') \int_\alpha^\infty dy\, y^{n+5} e^{-\ell'^2 y^2} \Big\}
\end{aligned}
\tag{A2.74}
$$

$(R_n^c(\zeta,\alpha))_{\alpha\beta\gamma\delta}$ is evaluated as follows. The contributions from the functions $u^{-4} u_\alpha u_\beta u_\gamma u_\delta C_n^c(\zeta, u)$ and $u^{-3}(\delta_{\gamma\delta} u_\alpha u_\beta + \ldots) B_n^c(\zeta, u)$ as $\underset{\sim}{u} \to 0$ is zero. The proof is similar to the calculation outlined in Eqs(A2.51) and (A2.52). The nonzero contribution arises from $u^{-2}(\delta_{\alpha\beta}\delta_{\gamma\delta}+\cdots)A_n^c(\zeta,u)$. Substituting for $A_n^c(\zeta,u)$ from Eq(A2.49), we get

$$\left(R_n^c(\zeta,\alpha)\right)_{\alpha\beta\gamma\delta}=\frac{2}{\Gamma(n/2)}\left(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\delta\alpha}+\delta_{\alpha\gamma}\delta_{\beta\delta}\right)$$
$$\cdot\lim_{\underset{\sim}{u}\to 0}\Big\{\zeta^4(\zeta u)^{-1}j_1(\zeta u)\int_0^\alpha dy\, y^{n-1}e^{-u^2y^2}$$
$$+4\zeta^2\frac{\sin(\zeta u)}{(\zeta u)}\int_0^\alpha dy\, y^{n+1}e^{-u^2y^2}$$
$$+4\cos(\zeta u)\int_0^\alpha dy\, y^{n+3}e^{-u^2y^2}\Big\} \qquad \text{(A2.75)}$$

But

$$\lim_{z\to 0} z^{-1}\sin z \to 1$$

and

$$\lim_{z\to 0} z^{-1}j_1(z)\to\frac{1}{3} \quad \text{(Handbook of Mat.-Funct.; p.437, 1970, Abromowitz)}$$

Thus, Eq(A2.75) is reduced to the following form

$$\left(R_n^c(\zeta,\alpha)\right)_{\alpha\beta\gamma\delta}=\frac{2}{\Gamma(n/2)}\left(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\delta\alpha}+\delta_{\alpha\gamma}\delta_{\beta\delta}\right)$$
$$\cdot\left[\zeta^4\frac{\alpha^n}{3n}+4\zeta^2\frac{\alpha^{n+2}}{(n+2)}+4\frac{\alpha^{n+4}}{(n+4)}\right] \qquad \text{(A2.76)}$$

Combining Eqs(A2.64), (A2.65) and (A2.76) we can evaluate the sine tensor sum $S_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q})$. The final expression is

$$S_n^{\alpha\beta\gamma\delta}(\zeta,\underset{\sim}{q})=\sum_{\underset{\sim}{\ell}}{}' \Big[\ell^{-4}\ell_\alpha\ell_\beta\ell_\gamma\ell_\delta\, C_n^s(\zeta,\ell)$$

$$+\ell^{-3}(\delta_{\gamma\delta}\ell_\alpha\ell_\beta+\delta_{\alpha\delta}\ell_\beta\ell_\gamma+\delta_{\beta\delta}\ell_\gamma\ell_\alpha+\delta_{\beta\gamma}\ell_\alpha\ell_\delta+\delta_{\alpha\gamma}\ell_\beta\ell_\delta+\delta_{\alpha\beta}\ell_\gamma\ell_\delta)\,B_n^s(\zeta,\ell)$$

$$+\ell^{-2}(\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\delta\alpha}+\delta_{\alpha\gamma}\delta_{\beta\delta})\,A_n^s(\zeta,\ell)\Big]\cos(\underset{\sim}{q}\cdot\underset{\sim}{\ell})$$

$$+\sum_{\underset{\sim}{G}}(G_\alpha+q_\alpha)(G_\beta+q_\beta)(G_\gamma+q_\gamma)(G_\delta+q_\delta)\,E_n^s(\zeta,|\underset{\sim}{G}+\underset{\sim}{q}|,0)$$

$$-\frac{2}{\Gamma(\frac{n+1}{2})}\left[\zeta^3\frac{4\alpha^{n+1}}{3(n+1)}+8\zeta\frac{\alpha^{n+3}}{(n+3)}\right](\delta_{\alpha\beta}\delta_{\gamma\delta}+\delta_{\beta\gamma}\delta_{\delta\alpha}+\delta_{\alpha\gamma}\delta_{\beta\delta}) \qquad \text{(A2.77)}$$

where $C_n^s(\zeta,\ell)$ and $B_n^s(\zeta,\ell)$ are given by

$$C_n^s(\zeta,\ell)=\frac{2}{\Gamma(\frac{n+1}{2})}\Big\{\Big[\zeta^4\ell\sin(\zeta\ell)+2\zeta^3\cos(\zeta\ell)+3\zeta^2\ell^{-1}\sin(\zeta\ell)$$

$$+15\zeta\ell^{-1}\cos(\zeta\ell)-15\ell^{-3}\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^n e^{-\ell^2y^2}$$

$$+\Big[8\zeta^3\ell^2\cos(\zeta\ell)+24\zeta\cos(\zeta\ell)-24\ell^{-1}\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^{n+2}e^{-\ell^2y^2}$$

$$+24\Big[-\zeta^2\ell^3\sin(\zeta\ell)+\zeta\ell^2\cos(\zeta\ell)-\ell\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^{n+4}e^{-\ell^2y^2}$$

$$-32\Big[\zeta\ell^4\cos(\zeta\ell)+\ell^3\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^{n+6}e^{-\ell^2y^2}$$

$$+16\ell^5\sin(\zeta\ell)\int_\alpha^\infty dy\, y^{n+8}e^{-\ell^2y^2}\Big\} \qquad \text{(A2.78)}$$

$$B_n^s(\zeta,\ell)=\frac{2}{\Gamma(\frac{n+1}{2})}\Big\{\Big[-\zeta^3\ell\cos(\zeta\ell)-3\zeta\ell^{-1}\cos(\zeta\ell)+3\ell^{-2}\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^n e^{-\ell^2y^2}$$

$$+6\Big[\zeta^2\ell^2\sin(\zeta\ell)-\zeta\ell\cos(\zeta\ell)+\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^{n+2}e^{-\ell^2y^2}$$

$$+12\Big[\zeta\ell^3\cos(\zeta\ell)+\ell^2\sin(\zeta\ell)\Big]\int_\alpha^\infty dy\, y^{n+4}e^{-\ell^2y^2}$$

$$-8\ell^4\sin(\zeta\ell)\int_\alpha^\infty dy\, y^{n+6}e^{-\ell^2y^2}\Big\} \qquad \text{(A2.79)}$$

and the quantities $A_n^s(\zeta, \ell)$ and $E_n^s(\zeta, |\underset{\sim}{G}+\underset{\sim}{q}|, 0)$ have been defined by Eqs(A2.59) and (A2.61), respectively.

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