Chapter 3

Physical Properties

In the present chapter we summarise the relevant equations for different physical properties along with brief theory, if needed.

3.1 Binding Energy

The binding energy is defined as sum of the five terms representing the uniform electron gas energy \(E_0\), the first order correction to energy \(E_1\), the electrostatic energy \(E_{es}\), the band structure energy \(E_{bs}\) and the repulsive (Born-Mayer) energy \(E_R\), also containing the effect of local field correction in a phenomenological manner [Onwuagba (1983)].

The total energy per atom can be written as,

\[
E_{total} = E_0 + E_1 + E_{es} + E_{bs} + E_R
\]  

(3.1)

The free electron gas energy \(E_o\) is given by

\[
E_o = Z^* \left[ \frac{2.21}{R_s^2} - \frac{0.916}{R_s} - 0.115 - 0.031 \ln R_s \right]
\]  

(3.2)

Writing \(\frac{3}{5} e_f = \frac{2.21}{R_s^2}, e_x = -\frac{0.916}{R_s}\) and \(e_c = -(0.115 - 0.031 \ln R_s)\), we have \(E_o = Z^* \left(\frac{3}{5} e_f + e_x + e_c\right). R_s\) is the radius of the sphere containing one electron. \(Z^*\)
is the effective charge of ion.

\[ R_s = \left[ \frac{3\Omega}{4\pi Z^*} \right]^{1/3} \]  \hspace{1cm} (3.3)

\( \Omega \) is the volume per atom.

The second term of [3.1], \( E_1 \), is the first order correction to the energy or the average value of the electron-ion interaction. It is given by,

\[ E_1 = \lim_{q \to 0} \left[ \frac{4\pi Z^* e^2}{\Omega q^2} + Z^* v_{ion}(q) \right] \]  \hspace{1cm} (3.4)

\( v_{ion}(q) \) is the bare-ion pseudopotential.

In the case of our model pseudopotential \( E_1 \) takes the following form

\[ E_1 = \frac{4\pi Z^* e^2 R^2_s}{\Omega} + \frac{\beta Z^*}{\Omega} \]  \hspace{1cm} (3.5)

The third term of [3.1] is the electrostatic energy of point ions in the uniform gas of valence electrons. It is given by,

\[ E_{es} = -\frac{\alpha Z^*}{R_s} \]  \hspace{1cm} (3.6)

\( \alpha \) is known as Madelung's constant. The value of \( \alpha \) for f.c.c. structure is 1.79172, for b.c.c. structure 1.19186 and 1.67085 for diamond structure. For h.c.p. structure, when \( \xi/\alpha \) ratio equals to 1.632, the value of \( \alpha \) is 1.78997.

\( R_s \) is the radius of Weigner-Seitz sphere.

\[ R_s = \left[ \frac{3\Omega}{4\pi} \right]^{1/3} \]  \hspace{1cm} (3.7)

\( E_{es} \) can also be written as [Wallace (1972)]

\[ E_{es} = \sum_Q \frac{2\pi Z^2 e^2}{\Omega Q^2} e^{-Q^2/4\sigma^2} + \frac{1}{2} \sum_R Z^2 e^2 R^{-1} \text{erf}((\eta R) - \frac{1}{2} Z^* e^2 \left[ \frac{2\eta}{\sqrt{\pi}} + \frac{\pi}{\eta^2 \Omega} \right] \]  \hspace{1cm} (3.8)
$Q$ denotes reciprocal lattice vector and $R$ denotes direct lattice vector. The summation $\Sigma'$ excludes $Q = 0$ and $R = 0$.

The complimentary error function is defined by

$$
erfc(y) = \frac{2}{\sqrt{\pi}} \int_y^\infty e^{-x^2} dx$$

(3.9)

Here $\eta$ is a parameter so adjusted that both the sums over $Q$ and $R$ can be converged conveniently. In the present work $\eta$ is taken as $\frac{1}{R}$. 

The fourth term of (3.1) is the band-structure energy. It is given by

$$E_{bs} = \sum_{Q} F(Q)$$

(3.10)

$F(Q)$ is the energy-wave number characteristic, given by,

$$F(Q) = -\frac{Q^2 \Omega}{8 \pi e^2} \frac{[\sigma(Q)]^2 [H(Q) - 1]}{1 + [H(Q) - 1][1 - Y(Q)]}$$

(3.11)

where $[H(Q) - 1]$ is the Hartree dielectric function given by

$$H(Q) - 1 = \frac{2me^2 K_F}{\pi \hbar^2 Q^2} \left[ 1 + \frac{1 - t^2}{2t} \ln \left| \frac{1 + t}{1 - t} \right| \right]$$

(3.12)

with $t = \frac{Q}{2K_F}$.

$K_F$ is Fermi wave vector given by

$$K_F = \left[ \frac{3\pi^2 Z^*}{\Theta} \right]^{1/3}$$

(3.13)

$Y(Q)$ is the exchange and correlation. For $Y(Q)$, we use the form suggested by Vashistha and Singwi [1972]

$$Y(Q) = A \left[ 1 - e^{-B \left( \frac{Q}{K_F} \right)^2} \right]$$

(3.14)

where $A$ and $B$ are constants depending on the electron gas density.
The fifth term of (3.1) is the repulsive energy given by

$$E_R = \frac{1}{2} \sum_{R} \alpha_B \cdot e^{-\gamma_B R}$$  \hspace{1cm} (3.15)

\(\alpha_B\) and \(\gamma_B\) are adjustable parameters which take into account the local field correction also in a phenomenological manner.

In evaluating (3.15) we have taken sum over nearest and next-nearest neighbours.

Considering all such contributions, the total energy \(E_{\text{total}}\) becomes,

$$E_{\text{total}} = Z^* \left[ \frac{2}{3} e_f + e_x + e_c + \left( \frac{E_1}{2} \right) \right]$$

$$+ \sum_{Q} 2\pi Z^* e^2 e^{-Q^2/4\eta^2} + \frac{1}{2} \sum_{R} Z^* e^2 R^{-1} \text{erfc} (\eta R)$$

$$- \frac{1}{2} Z^* e^2 \left[ \frac{2\pi}{\sqrt{\pi}} + \frac{\pi}{\eta^2} \right] + \sum_{Q} F(Q)$$

$$+ \frac{1}{2} \sum_{R} \alpha_B e^{-\gamma_B R}$$  \hspace{1cm} (3.16)

Collecting \(Q\)-dependent terms, we define \(G(Q)\) as follows:

$$G(Q) = \frac{2\pi Z^* e^2}{\Omega Q^2} e^{-Q^2/4\eta^2} + F(Q)$$  \hspace{1cm} (3.17)

Collecting \(R\)-dependent terms, we define \(\phi(R)\),

$$\phi(R) = Z^* e^2 R^{-1} \text{erfc}(\eta R) + \alpha_B e^{-\gamma_B R}$$  \hspace{1cm} (3.18)

With the help of eqs. (3.16), (3.17) and (3.18), total energy becomes

$$E_{\text{total}} = Z^* \left[ \frac{2}{3} e_f + e_x + e_c + \left( \frac{E_1}{2} \right) \right]$$

$$+ \sum_{Q} G(Q) + \frac{1}{2} \sum_{R} \phi(R)$$

$$- \frac{1}{2} Z^* e^2 \left[ \frac{2\pi}{\sqrt{\pi}} + \frac{\pi}{\eta^2} \right]$$  \hspace{1cm} (3.19)
### 3.2 Pressure

The volume derivative of $E_{\text{total}}$ gives pressure ($P$).

$$ P = -\frac{dE_{\text{total}}}{dV} $$

$$ P = \frac{1}{\Omega} \left[ \sum_{Q} \left\{ G(Q) + \frac{2}{3} Q^2 G'(Q) + \Delta_1(Q) \right\} - \frac{1}{3} \sum_{R} \phi'(R) \right] $$

where $G'(Q)$ is the partial derivatives of $G(Q)$ with respect to $Q^2$, where

$$ \Delta_1(Q) = \frac{1}{3} \frac{\partial F(Q)}{\partial Q^2} $$

$$ G'(Q) = \frac{\partial G}{\partial Q^2} = \frac{\partial F(Q)}{\partial Q^2} - \frac{2\pi Z^* e^2}{\Omega Q^2} \left\{ \frac{1}{4\eta^2} + \frac{1}{Q^2} \right\} e^{-Q^2/4\eta^2} $$

$$ \phi'(R) = \frac{\partial \phi(R)}{\partial R^2} $$

$$ \phi'(R) = -\frac{2\pi Z^* e^2}{\sqrt{\pi} R^2} \left[ e^{-\eta^2 R^2} - \frac{e^{2\eta^2 R^2}}{2\eta R} \right] $$

### 3.3 Bulk Modulus

The bulk modulus is given by

$$ B = \frac{\partial^2 E_{\text{total}}}{\partial \Omega^2} $$

$$ B = \frac{1}{\Omega} \left[ \sum_{Q} \{ 2G(Q) + \frac{22}{9} Q^2 G'(Q) + \frac{4}{9} Q^4 G''(Q) + \Delta_2(Q) \} \right] $$

$$ B = \frac{1}{\Omega} \left[ \sum_{R} \left\{ -R^2 \phi'(R) + 2R^4 \phi''(R) \right\} \right] $$

where,

$$ G''(Q) = \frac{\partial^2 G(Q)}{\partial (Q^2)^2} $$

$$ G''(Q) = \frac{\partial F(Q)}{\partial (Q^2)^2} + \frac{2\pi Z^* e^2}{\Omega Q^2} \left[ \left\{ \frac{1}{\eta^2} + \frac{1}{Q^2} \right\}^2 + \frac{1}{Q^4} \right] e^{-Q^2/4\eta^2} $$
\[ \phi''(R) = \frac{\partial^2 \phi(R)}{\partial R^2} \]
\[ = Z^2 e^2 \left[ \left( \frac{1}{\sqrt{\pi}} \right) (\eta^2 R^{-2} + 3/2 \eta R^{-4}) e^{-\eta^2 R^2} + \frac{3}{4} R^{-5} e^{-\gamma B R} \right] \] (3.25)

\[ + \frac{1}{4} \alpha_B \gamma_B (\gamma B R^{-2} + R^{-3}) e^{-\gamma B R} \]

and

\[ \Delta_2(Q) = \frac{1}{9} \left\{ 10 K_F \left[ \frac{\partial F(Q)}{\partial K} \right] + K_F^2 \left[ \frac{\partial^2 F(Q)}{\partial K^2} \right] + 2 Q K_F \left[ \frac{\partial^2 F(Q)}{\partial Q \partial K} \right] \right\} \] (3.26)

The above equations give the pressure and bulk modulus to second order in pseudopotential at 0°K.

### 3.4 Elastic Constants

Using the homogeneous deformation method [Wallace (1972)], we have the difference between stress-strain coefficients \( B_{11} \) and \( B_{12} \) as given by,

\[ B_{11} - B_{12} = \frac{1}{2} \frac{d^2 E_{\text{total}}}{d e_{zz}^2} \]
\[ = \frac{1}{\pi} \sum Q \left[ \frac{1}{3} Q^2 G'(Q) + \left( Q_z^2 - Q_x^2 Q_y^2 \right) G''(Q) \right] \]
\[ + \frac{2}{\pi} \sum R \left[ \frac{1}{3} R^2 \phi'(R) + \left( R_z^2 - R_x^2 R_y^2 \right) \phi''(R) \right] \] (3.27)

The elastic constant \( B_{44} \) is given by

\[ B_{44} = \frac{1}{\pi} \frac{d^2 E_{\text{total}}}{d e_{xy}^2} \]
\[ B_{44} = \frac{1}{\pi} \sum Q \left[ \frac{1}{3} Q^2 G'(Q) + 2 Q_x^2 Q_y^2 G''(Q) \right] \]
\[ + \frac{1}{\pi} \sum R \left[ \frac{1}{3} R^2 \phi'(R) + 2 R_x^2 R_y^2 \phi''(R) \right] \] (3.28)

Also,

\[ B = \frac{1}{3} \left( B_{11} + 2 B_{12} \right) \] (3.29)
3.5 Third Order Correction to the Energy

The third order short-range energy is given by [Brovman and Kagan (1967, 1968, 1970), Lloyd and Sholl (1968)]

\[
E^{(3)} = \Omega \sum_{\vec{Q}_1, \vec{Q}_2, \vec{Q}_3 \neq 0} \left[ \frac{\nu_{\text{sen}}(\vec{Q}_1) \nu_{\text{sen}}(\vec{Q}_2) \nu_{\text{sen}}(\vec{Q}_3)}{c(\vec{Q}_1)c(\vec{Q}_2)c(\vec{Q}_3)} S(\vec{Q}_1) S(\vec{Q}_2) S(\vec{Q}_3) \times \right] \\
\wedge^{(3)}(\vec{Q}_1, \vec{Q}_2, \vec{Q}_3) \Delta \left( \vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3 \right) \right]
\]

In the above equation \( \Delta \left( \vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3 \right) \) is a delta function describing the momentum conservation law.

For the present case,

\[
\Delta \left( \vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3 \right) = \begin{cases} 1 & \text{for } \vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3 = 0 \\ 0 & \text{for } \vec{Q}_1 + \vec{Q}_2 + \vec{Q}_3 \neq 0 \end{cases} \quad (3.31)
\]

\( S(Q) \) is the structure factor and \( \wedge^{(3)}(\vec{Q}_1, \vec{Q}_2, \vec{Q}_3) \) is given by [Brovman and Kagan (1967, 1968)]

\[
\wedge^{(3)}(\vec{Q}_1, \vec{Q}_2, \vec{Q}_3) = \frac{2m^2}{3\pi^2 \hbar^4} \cdot \frac{Q_h^2}{Q_1 Q_2 Q_3} \sum_{m=1}^{3} \cos \theta_m \ell_n \left| \frac{2KE + Q_m}{2K_F - Q_m} \right| \times \\
-\Delta \left( \ell_n \left| \frac{(1-\Delta A)}{1+\Delta A} \right| \text{ for } \frac{KE}{QR} < 1 \\
2 \arctan \Delta A \text{ for } \frac{KE}{QR} > 1 \right) \quad (3.32)
\]

In this expression \( Q_R \) is the radius of the circle inscribed in the triangle with sides \( Q_1, Q_2 \) and \( Q_3 \).

\[
2Q_R = \frac{Q_m}{\sin \theta_m} = \frac{Q_1}{\sin \theta_1} = \frac{Q_2}{\sin \theta_2} = \frac{Q_3}{\sin \theta_3} \quad (3.33)
\]

\[
\cos \theta_{nm} = -\frac{Q_n Q_m}{|Q_n||Q_m|} \quad (3.34)
\]

The area of the triangle is,

\[
A = \frac{Q_1 Q_2 Q_3}{(2K_F)^3} \left[ 1 - \frac{1}{2} \left( \frac{Q_1^2 + Q_2^2 + Q_3^2}{(2K_F)^2} \right) \right]^{-1} \\
= \frac{\sin \theta_1 \sin \theta_2 \sin \theta_3}{X^2 - X \left( 1 + \cos \theta_1 \cos \theta_2 \cos \theta_3 \right)} \text{ with } X = \frac{K_F}{Q_R} \quad (3.35)
\]
$\Delta$ is given by

$$\Delta = \left[ 1 - \left( \frac{K_F}{Q_R} \right)^2 \right]^{1/2} \quad (3.37)$$

$\epsilon(Q)$ is the dielectric constant given by

$$\epsilon(Q) = 1 + \frac{4\pi\varepsilon^2}{Q^2}\pi(Q) \quad (3.38)$$

where,

$$\pi(Q) = \frac{H(Q) - 1}{\left[ 1 - \frac{4\pi\varepsilon^2}{Q^2}\left[H(Q) - 1\right] Y(Q) \right]} \quad (3.39)$$

### 3.6 Dynamical Matrix - Second and Third Order (Reciprocal-Space Analysis)

The lattice dynamics of metals has been discussed in complete detail by several authors [Wallace (1972), Yastrebov and Katsnelson (1987), Brovman and Kagan (1974)].

To obtain the vibrational frequency $\omega_{q,\lambda}$ for $\vec{q}, \lambda$ mode, one essentially requires to diagonalize the dynamical matrix for different values of $\vec{q}$.

The total dynamical matrix $D_{\alpha\beta}(q)$ will consist of three terms

$$D_{\alpha\beta}(q) = D_{\alpha\beta}^C(q) + D_{\alpha\beta}^E(q) + D_{\alpha\beta}^R(q) \quad (3.40)$$

Here superscripts stand for Coulombic, electronic and repulsive contributions respectively. Here,

$$D_{\alpha\beta}^C(q) = \frac{2}{M} \left[ \sum_q G_1 \left[ |\vec{Q} + \vec{q}| \right] \left( \vec{Q} + \vec{q} \right)_\alpha \left( \vec{Q} + \vec{q} \right)_\beta - \sum_q G_1 \left[ |\vec{Q}| \right] Q_\alpha Q_\beta + \sum_r \left\{ \phi^*_r(R)\delta_{\alpha\beta} + 2\phi^*_r(R)R_\alpha R_\beta \left( 1 - \cos \left( \vec{q} \cdot \vec{R} \right) \right) \right\} \right] \quad (3.41)$$
$M$ is the mass of ion.

\[ G_1 (|\vec{Q}|) = \frac{2\pi Z^* e^2}{\Omega Q^2} e^{-Q^2/4r^2} \]  
(3.42)

\[ \phi_1 (R) = Z^* e^2 R^{-1} \text{erfc}(\eta R) \]  
(3.43)

\[ \phi'_1 (R) = \frac{d\phi_1 (R)}{dR^2} = -Z^* e^2 \left[ \frac{1}{\sqrt{\pi}} \frac{\eta}{R^2} e^{-\eta^2 R^2} + \frac{1}{2} \frac{\eta}{R^2} \text{erfc}(\eta R) \right] \]  
(3.44)

and

\[ \phi''_1 (R) = \frac{d^2 \phi_1 (R)}{d (R^2)^2} = Z^* e^2 \left[ \frac{1}{\sqrt{\pi}} \left( \frac{\eta^3}{R^2} + \frac{3\eta}{2R^4} \right) e^{-\eta^2 R^2} + \frac{3}{4R^5} \text{erfc}(\eta R) \right] \]  
(3.45)

\[ D_{\alpha\beta}^{(2)E}(q) = D_{\alpha\beta}^{(2)E}(q) + D_{\alpha\beta}^{(3)E}(q) \]  
(3.46)

where

\[ D_{\alpha\beta}^{(2)E}(q) = \frac{2}{M} \left[ \sum_Q F \left( |\vec{Q} + \vec{q}| \right) (\vec{Q} + \vec{q})_\alpha (\vec{Q} + \vec{q})_\beta \right] \]  
(3.47)

\[ D_{\alpha\beta}^{(3)E}(q) = \frac{6\Omega}{M} \sum_{\vec{Q}_1, \vec{Q}_2, \vec{Q}_3} \left[ \left( \vec{q} + \vec{Q}_1 \right)_\alpha \left( \vec{q} + \vec{Q}_2 \right)_\beta \right] \times \Delta \left( \vec{Q}_1 - \vec{Q}_2 + \vec{Q}_3 \right) \]  
(3.48)

\[ \Delta \left( \vec{Q}_1 - \vec{Q}_2 + \vec{Q}_3 \right) = \begin{cases} 1 & \text{for } \vec{Q}_1 + \vec{Q}_3 = \vec{Q}_2 \\ 0 & \text{otherwise} \end{cases} \]  
(3.49)

\[ \Gamma^{(3)} \left( \vec{q} + \vec{Q}_1, -\vec{q} - \vec{Q}_2, \vec{Q}_3 \right) = \frac{\lambda^{(3)} \left( \vec{q} + \vec{Q}_1 - \vec{q} - \vec{Q}_2 - \vec{Q}_3 \right)}{\epsilon \left( |\vec{q} + \vec{Q}_1| \right) \epsilon \left( |\vec{q} + \vec{Q}_3| \right) \epsilon \left( |\vec{Q}_2| \right)} \]  
(3.49)

\[ D_{\alpha\beta}^{(R)}(q) = \frac{2}{M} \sum_R \left[ \left\{ \phi''_2 (R) \delta_{\alpha\beta} + 2\phi''_2 (R) R_\alpha R_\beta \right\} \times \left( 1 - \cos (\vec{q} \cdot \vec{R}) \right) \right] \]  
(3.50)

where

\[ \phi''_2 (R) = \frac{d^2 \phi_2 (R)}{d (R^2)^2} = \frac{1}{2} \frac{\alpha_B \gamma_B e^{-\gamma_B R}}{R} \]  
(3.51)

\[ \phi''_2 (R) = \frac{d^2 \phi_2 (R)}{d (R^2)^2} = \frac{1}{4} \frac{\alpha_B \gamma_B}{R^2} \left( \frac{\gamma_B}{R^2} + \frac{1}{R^3} \right) e^{-\gamma_B R} \]  
(3.52)
3.7 Frequency Spectra : Density of States

To generate a set of wave vectors, an irreducible sector of the Brillouin zone (1/48 portion) is defined for a f.c.c. lattice by the set of equations

\[
(q_x + q_y + q_z) \leq \frac{3}{2}
\]

\[
q_x \leq 1; \ q_y \leq 1; \ q_z \leq 1
\]

(3.53)

Dividing the \( q_x, q_y \) and \( q_z \) axes into \( z \) equal intervals and writing

\[
q_x = \frac{P_x}{z}; \ q_y = \frac{P_y}{z}; \ q_z = \frac{P_z}{z}
\]

Then eq. (3.53) becomes

\[
(P_x + P_y + P_z) \leq \frac{3}{2}z
\]

(3.54)

where \( P_x, P_y \) and \( P_z \) are integers which are either all even or all odd. This choice generates a b.c.c. net in the reciprocal space.

For a b.c.c. lattice the relations which correspond to eqs. (3.53) and (3.54) are

\[
(q_x + q_y) \leq 1; \ (q_y + q_z) \leq 1; \ (q_z + q_x) \leq 1
\]

\[
q_x \leq 1; \ q_y \leq 1; \ q_z \leq 1
\]

(3.55)

\[
(P_x + P_y) \leq z; \ (P_y + P_z) \leq z; \ (P_z + P_x) \leq z
\]

\[
P_x \leq z; \ P_y \leq z; \ P_z \leq z
\]

(3.56)

where \( P_x, P_y \) and \( P_z \) are integers such that \((P_x + P_y + P_z)\) is even. This choice generates a f.c.c. net in the reciprocal space.

Each point is weighed according to the number of points equivalent to it by symmetry. Care has to be taken in giving the proper weights to points lying on the surfaces, edges and corners of the Brillouin zone. The total number of points in the whole zone is \( z^3 \).
In the present work, we have taken \( z = 40 \). The total number of points in the whole zone was thus \((40)^3 = 6400\) and total number of frequencies are 1,97,000 approximately.

In order to calculate the frequency distribution function \( g(\omega) \), counts of the number of frequencies falling in the intervals of 100\(^{th}\) part of the maximum frequency was used to construct a frequency histogram.

The various physical properties can be obtained with the help of frequency spectrum \( g(\omega) \). In the following section we intend to study (1) the Debye-Waller factor, (2) X-rays characteristic-temperature, and (3) the mean square displacement.

### 3.8 Debye-Waller Factor

It has been shown experimentally that the intensity of X-ray diffraction maxima decreases with rising temperature on account of thermal vibrations. The effect of thermal vibrations of ions about their equilibrium positions on the intensity of scattered X-rays, neutrons and Mössbauer effect experiments were explained for the first time by Debye. Such explanation was modified by Waller. He showed that the scattered intensity decrease could be expressed by an exponential factor \( \exp[-2W] \), often referred to as the Debye-Waller factor. This factor is sometimes called temperature factor due to its strong temperature dependence. Moreover, due to the direct relation of this factor \( 2W \) to the mean square displacement of the atoms \( \langle \ddot{u}^2 \rangle \), it has provided a powerful tool to study several phenomena of solid state physics such as neutron scattering, electrical conductivity and melting of crystals.
Theory:

In the harmonic approximation, the Debye-Waller exponent $2W$ is directly related to the mean square displacement of the atoms, and following James [1964] it can be given as

$$2W = \left( | \vec{K} \cdot \vec{U}(n) |^2 \right)$$

where $\vec{U}(n)$ is the displacement of the $n^{th}$ atom and $\vec{K}$ is the difference of the initial and final wave vectors of X-rays.

From the knowledge of the time dependence of the atomic displacements and average energy of the phonon in mode $q$, the amplitude $\vec{U}_q$ of the mode $q$ can be written as,

$$|\vec{U}_q|^2 = \left( \bar{n}_{q,\lambda} + \frac{1}{2} \right) \frac{\hbar}{MN \omega_{q,\lambda}}$$

where $\bar{n}_{q,\lambda}$ is the average occupation number of $(q, \lambda)$ lattice mode and is given by

$$\bar{n}_{q,\lambda} = \left[ \exp \left( \frac{\hbar \omega_{q,\lambda}}{K_BT} \right) - 1 \right]^{-1}$$

where $T$ is the absolute temperature and $K_B$ is Boltzmann’s constant.

With the help of the above equations,

$$2W = \frac{\hbar}{MN} \sum_{q,\lambda} \frac{(\vec{K} \cdot \vec{e}_{q,\lambda})^2}{\omega_{q,\lambda}} \left\{ \frac{1}{2} + \frac{1}{\exp \left( \frac{\hbar \omega_{q,\lambda}}{K_BT} \right) - 1} \right\}$$

where $\vec{e}_{q,\lambda}$ is the polarisation vector of $(q, \lambda)$ lattice mode and summation extends over the normal modes of vibrations of the crystal. For a monoatomic
cubic crystal, the polarisation factor \((\vec{R} \cdot \vec{e}_{\perp,\lambda})^2\) can be replaced by its average value outside the summation so that eq. (3.60) can be written as

\[
2W = \frac{8\lambda^2 \hbar^2}{3MM} \left( \frac{\sin \theta}{\lambda'} \right)^2 \sum_{\xi,\omega,\lambda} \frac{1}{\omega_{\xi,\lambda}} \text{Coth} \left( \frac{\hbar \omega_{\xi,\lambda}}{2KB_T} \right)
\]

(3.61)

Here, \(\theta\) is the glancing angle of the incidence and \(\lambda'\) is the wavelength of the incident wave. In terms of \(g(\omega)\),

\[
2W = \frac{8\lambda^2 \hbar^2}{3MN} \left( \frac{\sin \theta}{\lambda'^2} \right) \int_0^{\omega_{\text{max}}} \frac{g(\omega)}{\omega} \text{Coth} \left( \frac{\hbar \omega}{2KB_T} \right) d\omega
\]

(3.62)

\(\omega_{\text{max}}\) is the maximum phonon frequency. The Debye-Waller factor is calculated with the help of (3.62) for different values of temperature.

### 3.9 X-Ray Characteristic Temperature \(\Theta_M\) and Mean Square Displacement

For a Debye model of the solid, the temperature dependence of the Debye-Waller exponent can be written as

\[
2W = \frac{48\lambda^2 \hbar^2 T}{MKB \Theta_M^2} \left\{ \Phi(x) + \frac{x}{4} \right\} \left( \frac{\sin \theta}{\lambda'} \right)^2
\]

(3.63)

Here \(\Theta_M\) is the effective X-ray characteristic temperature, \(\Phi(x)\) is the usual Debye integral function given by,

\[
\Phi(x) = \left( \frac{1}{x} \right) \int_0^x [\exp(y) - 1]^{-1} y dy
\]

(3.64)

with \(x = \frac{\Theta_M}{T}\) and \(y = \frac{\omega}{\omega_{\text{max}}}\).

#### Mean Square Displacement \(\bar{u}^2\)

In the harmonic approximation, the mean square displacement of the atoms \(\bar{u}^2\) is given by the following relation

\[
\bar{u}^2 = \frac{3}{8\lambda'^2} \left( \frac{\lambda'}{\sin \theta} \right)^2 W
\]

(3.65)
The comparison between theory and experiment is made in terms of temperature parameter $Y$ given by,

$$Y = \log_{10} \left( \frac{\lambda'}{\sin \theta} \right)^2 (2W_{T_0} - 2W_T)$$

(3.66)

where $W_T$ and $W_{T_0}$ are the values of the Debye-Waller exponents for temperatures $T$ and $T_0$ respectively. The quantity $Y$ is independent of $\lambda'$ and $\theta$, and is directly accessible from the measured intensity of Bragg reflection in X-ray diffraction experiments. If $I_T$ and $I_{T_0}$ are the measured integrated intensities of a certain diffraction line at temperature $T$ and $T_0$ respectively, we have

$$\frac{I_T}{I_{T_0}} = \frac{\exp \left[-2W_T\right]}{\exp \left[-2W_{T_0}\right]}$$

(3.67)

This yields,

$$Y = \left( \frac{\lambda'}{\sin \theta} \right)^2 \log_{10} \left[ \frac{I_T}{I_{T_0}} \right]$$

(3.68)

$$= \log_{10} \left( \frac{\lambda'}{\sin \theta} \right)^2 [2W_T - 2W_{T_0}]$$

### 3.10 Harmonic Contribution of Free Energy

The harmonic contribution to the free energy is given by,

$$E_H = \sum_{\vec{q}, \lambda} E (\vec{q}, \lambda)$$

(3.69)

Here $E (\vec{q}, \lambda)$ is the vibrational energy associated with vibrational mode $(\vec{q}, \lambda)$. It is given by

$$E (\vec{q}, \lambda) = \hbar \omega_{\vec{q}, \lambda} \left( \vec{n}_{\vec{q}, \lambda} + \frac{1}{2} \right)$$

(3.70)

With the help of eqs. (3.70) and (3.59), $E_H$ can be given as

$$E_H = \sum_{\vec{q}, \lambda} \hbar \omega_{\vec{q}, \lambda} \left\{ \frac{1}{\exp \left( \frac{\hbar \omega_{\vec{q}, \lambda}}{k_B T} \right) - 1} + \frac{1}{2} \right\}$$

(3.71)

In terms of frequency distribution function,

$$E_H = 3N \int_0^{\omega_{\text{max}}} g(\omega) \left\{ \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp \left( \frac{\hbar \omega}{k_B T} \right) - 1} \right\} d\omega$$

(3.72)

For the different values of $T$ we can find free energy as a function of temperature.
### 3.11 Lattice Heat Capacity : $C_v$

The specific heat associated with lattice vibration in harmonic approximation is defined as

$$C_v = \left( \frac{\partial E_H}{\partial T} \right)_{n=\Omega_o}$$  \hspace{1cm} (3.73)

Using equation for $E_H$

$$C_V \frac{k}{3R} = \int_o^{\omega_{max}} \left[ \left( \frac{\hbar \omega}{k_B T} \right)^2 \exp \left( \frac{\hbar \omega}{k_B T} \right) \right] \left[ \exp \left( \frac{\hbar \omega}{k_B T} \right) - 1 \right]^2 g(\omega) d\omega$$  \hspace{1cm} (3.74)

$R$ is gas constant.

### 3.12 Debye Temperature

The Debye temperature $\Theta_D$ at different temperatures can be found by using the standard tables of $\frac{C_V}{3k}$ versus $\frac{\Theta_D}{T}$ [Ghatak and Kothari (1972)].

The concept of Debye temperature $\Theta_D$, ever since its introduction, played an important role in the field of thermophysical properties of materials. It is basically a measure of the vibrational response of the material and, therefore, intimately connected with properties like specific heat, thermal expansion and vibrational entropy, etc. [Grimvall (1956)]. Debye temperature is not a strictly determined parameter and various estimates may be obtained through well established empirical or semi-empirical formulae, relating $\Theta_D$ with various macroscopic properties [Leadbetter (1983)].

In general, these diverse estimates do not agree with each other, mainly because of differing philosophies of estimating them. A non-empirical or \textit{ab initio} calculation of $\Theta_D$ is very difficult and at present only a few such
3.13 Thermal Pressure, Thermal Expansion, Isothermal Bulk Modulus

The thermal pressure arises from the vibrational part of the free energy. In harmonic approximation, thermal pressure

\[ P^* (\Omega, T) = - \left( \frac{\partial E_H}{\partial \Omega} \right) |_T \]  

(3.75)

In order to find \( P^* \), the volume derivatives of the phonon frequencies are required. These are related with what are known as Grüneisen parameters

\[ \gamma_{q,\lambda} = - \frac{\partial \ln \omega_{q,\lambda}}{\partial \ln V} \]

(3.76)

\[ = - \left( \frac{\omega_{q,\lambda}}{\omega^2} \right) \left( \frac{d \omega_{q,\lambda}}{d V} \right) \]

Here \( \gamma_{q,\lambda} \) is known as mode Grüneisen parameter associated with the mode \((q, \lambda)\).

\[ \xi_{q,\lambda} = \left( \frac{\omega^2}{\omega_{q,\lambda}} \right) \left( \frac{d^2 \omega_{q,\lambda}}{dV^2} \right) \]

(3.77)

Using above equations, \( P^* \) is given by,

\[ P^*(\Omega, T) = \frac{1}{\Omega} \sum_{q,\lambda} \hbar \omega_{q,\lambda} \gamma_{q,\lambda} \left\{ \bar{n}_{q,\lambda} + \frac{1}{2} \right\} \]

(3.78)

In terms of frequency distribution

\[ P^* (\Omega, T) = \frac{3N}{\Omega} \int_0^{\omega_{\text{max}}} \hbar \omega \gamma \left\{ \frac{1}{2} + \frac{1}{\exp \left( \frac{\hbar \omega}{K_B T} \right) - 1} \right\} g(\omega) d\omega \]  

(3.79)

\( N \) is the Avogadro number.

Using eqs. (3.20) and (3.79), total pressure corrected to third order is

\[ P(\Omega, T) = P_0(\Omega) + P^*(\Omega, T) \]  

(3.80)
where \( P_0(0) \) is the pressure at 0°C.

The bulk modulus at temperature \( T \) is defined as,

\[
B^*(\Omega, T) = \left( \frac{\partial^2 E_H}{\partial \Omega^2} \right) |_T
\]

\[
B^*(\Omega, T) = \frac{1}{\Omega} \sum_{\tilde{q}, \lambda} \hbar \omega_{\tilde{q}, \lambda} \left[ \xi_{\tilde{q}, \lambda} \left( \eta_{\tilde{q}, \lambda} + \frac{1}{2} \right) - \gamma_{\tilde{q}, \lambda}^2 \right]
\]

\[
\left( \frac{\hbar \omega_{\tilde{q}, \lambda}}{K_BT} \right) \left( \eta_{\tilde{q}, \lambda}^2 + \eta_{\tilde{q}, \lambda} \right)
\]

[3.81]

In terms of frequency distribution,

\[
B^*(\Omega, T) = \frac{3N}{\Omega} \int_0^{\omega_{\text{max}}} \hbar \omega \left[ \xi \left( \frac{1}{2} + \frac{1}{\exp \left( \frac{\hbar \omega}{K_BT} \right) - 1} \right) - \gamma^2 \left( \frac{\hbar \omega}{K_BT} \right) \right]
\]

\[
\times \left\{ \frac{1}{\exp \left( \frac{\hbar \omega}{K_BT} \right) - 1}^2 + \frac{1}{\exp \left( \frac{\hbar \omega}{K_BT} \right) - 1} \right\} g(\omega) d\omega
\]

[3.82]

Using eqs. (3.33) and (3.82) the isothermal bulk-modulus \( B_T \) corrected to fourth order is given by

\[
B_T(\Omega, T) = B_0(\Omega) + B^*(\Omega, T)
\]

[3.83]

Here \( B_0(\Omega) \) is the bulk modulus at 0°C.

The thermal expansion is defined as,

\[
\beta = \frac{1}{\Omega} \left( \frac{\partial \Omega}{\partial T} \right)_P
\]

[3.84]

\( \beta \) is calculated from the quantity \( \beta B_T \) given by,

\[
\beta B_T = - \left( \frac{\partial^2 E_H}{\partial \Omega^2} \right)_{TV}
\]

\[
= \frac{1}{\Omega} \sum_{\tilde{q}, \lambda} \hbar \omega_{\tilde{q}, \lambda} \gamma_{\tilde{q}, \lambda} \left( \frac{\partial \eta_{\tilde{q}, \lambda}}{\partial T} \right)_V
\]

[3.85]

with

\[
\left( \frac{\partial \eta_{\tilde{q}, \lambda}}{\partial T} \right)_V = \left( \frac{\hbar \omega_{\tilde{q}, \lambda}}{K_BT^2} \right) \left( \eta_{\tilde{q}, \lambda}^2 + \eta_{\tilde{q}, \lambda} \right)
\]

[3.86]

Using (3.85) in (3.86)

\[
\beta B_T = \frac{1}{\Omega} \sum_{\tilde{q}, \lambda} \hbar \omega_{\tilde{q}, \lambda} \gamma_{\tilde{q}, \lambda} \left( \frac{\hbar \omega_{\tilde{q}, \lambda}}{K_BT^2} \right) \left( \eta_{\tilde{q}, \lambda}^2 + \eta_{\tilde{q}, \lambda} \right)
\]

[3.87]
In terms of frequency distribution function

\[ \frac{\beta B_T}{3K_B} = \frac{3N}{\Omega} \int_{\omega_{min}}^{\omega_{max}} \gamma K_B \left( \frac{\hbar \omega}{K_B T} \right)^2 \left\{ \frac{1}{[\exp \left( \frac{\hbar \omega}{K_B T} \right) - 1]^2} + \frac{1}{[\exp \left( \frac{\hbar \omega}{K_B T} \right) - 1]} \right\} g(\omega) d\omega \]  

(3.88)

Above equation can be written in the dimensionless form

\[ \frac{\beta B_T}{3K_B} = \frac{1}{3N} \sum_{\eta, \lambda} \gamma_{\eta, \lambda} \left( \frac{\hbar \omega_{\eta, \lambda}}{K_B T} \right)^2 \left( n_{\eta, \lambda}^2 + \bar{n}_{\eta, \lambda} \right) \]  

(3.89)

In terms of frequency distribution,

\[ \frac{\beta B_T}{3K_B} = \frac{3N}{\Omega} \int_{\omega_{min}}^{\omega_{max}} \gamma \left( \frac{\hbar \omega}{K_B T} \right)^2 \left\{ \frac{1}{[\exp \left( \frac{\hbar \omega}{K_B T} \right) - 1]^2} + \frac{1}{[\exp \left( \frac{\hbar \omega}{K_B T} \right) - 1]} \right\} g(\omega) d\omega \]  

(3.90)

In the high temperature limit, eq. (3.90) reduces to the macroscopic Grüneisen parameter. With the help of (3.83) and (3.90) thermal expansion coefficient \( \beta \) can be studied for different temperature \( T \).

The mean value of all \( \gamma_{\eta, \lambda} \) for all vibrational modes is known as bulk Grüneisen parameter and it is obtained from

\[ \gamma_M = \frac{\sum_{\eta, \lambda} \gamma_{\eta, \lambda} E \left( \frac{\hbar \omega_{\eta, \lambda}}{K_B T} \right)}{\sum_{\eta, \lambda} E \left( \frac{\hbar \omega_{\eta, \lambda}}{K_B T} \right)} \]  

(3.91)

with \( x = \frac{\hbar \omega_{\eta, \lambda}}{K_B T} \); \( E(x) \) is given by

\[ E(x) = \frac{x^2 e^x}{(e^x - 1)^2} \]  

(3.92)

### 3.14 Interatomic Potential

In the study of various properties of solids, the knowledge of interaction energy between the ions or atoms is required.
Various empirical forms for interatomic potential have been suggested in the literature [Grüneisen (1912), Morse (1929), Esterling and Swaroop (1979), Harrison and Wills (1981), Wills and Harrison (1983), Singh (1999)].

For metals, the situation becomes complicated because of the presence of the conduction electrons, and consequently their effects on the interaction between ions.

The two-body pairwise effective interionic potential $V(R)$ may be composed of three contributions, Coulomb, band structure and Born-Mayer repulsive terms.

With all three contributions, interatomic potential can be written as

$$V(R) = \frac{Z^*e^2}{R} - \frac{2Z^*e^2}{\pi} \int C(q) \frac{\sin qR}{qR} dq + \alpha e^{-\gamma R}$$  \hspace{1cm} (3.93)

where

$$C(q) = \left( \frac{\Omega q^2}{4\pi Z^*e^2} \right)^2 \left[ v_{\text{ion}}(q) \right]^2 \frac{[H(q) - 1]}{1 + [H(q) - 1][1 - Y(q)]}$$  \hspace{1cm} (3.94)

At large value of $R$, the second term of (3.93) takes the form,

$$V_{\text{bs}}(R) \mid _{R \to \infty} = -\frac{Z^*e^2}{R} + \frac{\cos(2K_F R)}{(K_F R)^3}$$  \hspace{1cm} (3.95)

This shows that $V(R)$ oscillates at large $R$. These oscillations are known as Friedel oscillations.

### 3.15 Interatomic Force Constants

The interaction between different atoms may be thought of as springs with some values of force constants connecting them.
There are only two independent interionic (interatomic) force constants namely the radial \((R_L)\) and tangential \((T_L)\) between a pair of ions interacting through central interaction \(V(R)\).

The tangential force constants \((T_L)\) at \(0^\circ K\) is given by

\[
T_L (0^\circ K) = \frac{1}{R_L} \frac{\partial V(R)}{\partial R} |_{R = R_L}
\]

\[
T_L (0^\circ K) = -\frac{2\pi e^2}{R_L^2} - \frac{2Z^*e^2}{R_L^2} \int C(q) \left[ \cos qR_L - \frac{\sin qR_L}{qR_L} \right] dq - \frac{\alpha \gamma_\beta e^{-\gamma_\beta R_L}}{R_L}
\]

(3.96)

The radial force constant \((R_L)\) at \(0^\circ K\),

\[
R_L (0^\circ K) = \frac{\partial^2 V(R)}{\partial R^2} |_{R = R_L}
\]

\[
R_L (0^\circ K) = \frac{2\pi e^2}{R_L^2} - \frac{2Z^*e^2}{R_L^2} \int C(q) \left[ -\frac{q \sin qR_L}{qR_L} - \frac{2 \cos qR_L}{qR_L} + \frac{2 \sin qR_L}{qR_L} \right] dq + \alpha \gamma_\beta e^{-\gamma_\beta R_L}
\]

(3.97)

Radial and tangential force constants depend only upon the distance between the ions.

### 3.16 Temperature Dependent Interatomic Potential and Interatomic Force Constants

Within the framework of pseudopotential theory, Harrison [1973a,b] has given the leading term of multi-ion interaction using the one-electron Green’s function. Then Takanaka and Yamamoto [1977] have obtained the asymptotic expression for the temperature dependent Green’s function and the usual contour integral.

Their form gives a damping factor \(\exp \left[ -\frac{\pi K_B T R}{4\hbar \nu_f} \right]\) for the usual two body interaction. The Fermi velocity \(\nu_f = \frac{\hbar K_f}{m}\) and \(T\) is temperature.
The interaction potential at $T \ (°K)$ is given by

$$V_T(R) = V(R) \exp \left[ -\frac{\pi K_B T R}{\hbar \nu_f} \right]$$

(3.98)

At $(T°K)$, the tangential force constants can be written as

$$T_L (T°K) = \exp \left[ -\frac{\pi K_B T R_L}{\hbar \nu_f} \right] \left\{ T_L (0°K) - \left( \frac{\pi K_B T}{\hbar \nu_f} \right) \frac{V_R (0°K)}{R_L} \right\}$$

(3.99)

Also radial force constant $R_L (T°K)$ given by

$$R_L (T°K) = \exp \left[ -\frac{\pi K_B T R_L}{\hbar \nu_f} \right] \left[ R_L (0°K) + 2R_L T_L (0°K) \left( \frac{\pi K_B T}{\hbar \nu_f} \right) \right]$$

$$+ V_R (0°K) \left( \frac{\pi K_B T}{\hbar \nu_f} \right)^2$$

(3.100)

The vibrational frequencies $\omega_{q_{\lambda}}$ can be obtained by using radial and tangential force constants. The dynamical matrix in this method can be obtained as,

$$D_{\alpha\beta} (q) = \sum_{\ell} \left( 1 - e^{-\pi R_{\ell}} \right) \left[ T_L \delta_{\alpha\beta} + \frac{R_{\ell\alpha} R_{\ell\beta}}{R^2_{\ell}} (R_L - T_L) \right]$$

(3.101)

The phonon frequencies can be obtained from the three solutions of the secular determinantal equation

$$\det \left| D_{\alpha\beta} (q) - 4\pi^2 \nu^2 M \delta_{\alpha\beta} \right| = 0$$

(3.102)

The tensor force constants $K_{\alpha\beta}(R)$ can be obtained from radial and tangential force constants, using the following equations

$$K_{\alpha\beta}(R) |_{T°K} = \left[ \delta_{\alpha\beta} - \frac{R_{\alpha} R_{\beta}}{R^2} \right] T_L (T°K) + \frac{R_{\alpha} R_{\beta}}{R^2} R_L (T°K)$$

(3.103)

### 3.17 Dynamical Elastic Constants and Bulk Modulus

Three independent elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ for cubic crystal can also be obtained from long wavelength limit in the phonon dispersion curves. Thus dynamical elastic constants can be obtained in terms of
tensor force constants [Squires (1963), Soma and Satooh (1980)].

For b.c.c. crystal,

\[ C_{11} = \frac{1}{12a} \sum_n N(n) \left( x^2 K_{xx}^{(n)} + y^2 K_{yy}^{(n)} + z^2 K_{zz}^{(n)} \right) \]  

\( C_{44} = \frac{1}{24a} \sum_n \left[ (y^2 + z^2) + K_{xx}^{(n)} + (x^2 + x^2) + K_{yy}^{(n)} + (x^2 + y^2) K_{zz}^{(n)} \right] \)  

\[ C_{12} + C_{44} = \frac{1}{6a} \sum_n N(n) \left[ yz K_{yz}^{(n)} + zz K_{zz}^{(n)} + xy K_{xy}^{(n)} \right] \]  

For f.c.c. crystal such relationship is given by,

\[ C_{11} = \frac{1}{6a} \sum_n N(n) \left[ x^2 K_{xx}^{(n)} + y^2 K_{yy}^{(n)} + z^2 K_{zz}^{(n)} \right] \]  

\[ C_{44} = \frac{1}{12a} \sum_n N(n) \left[ (y^2 + z^2) \right. \left. \left( x^2 + x^2 \right) \right. + \left. K_{xx}^{(n)} \right. + \left. K_{yy}^{(n)} \right. + \left. (x^2 + y^2) K_{zz}^{(n)} \right] \)  

\[ C_{12} + C_{44} = \frac{1}{3a} \sum_n N(n) \left[ yz K_{yz}^{(n)} + zz K_{zz}^{(n)} + xy K_{xy}^{(n)} \right] \]  

where \( a \) is the lattice constant and \( N(n) \) is the number of atoms at the \( n^{th} \) neighbour separation.

The bulk modulus

\[ B = \frac{C_{11} + 2C_{12}}{3} \]  

Modulus of pure shear

\[ C' = \frac{|C_{11} - C_{12}|}{2} \]  

3.18 Deviation from Cauchy's Relation, Poisson Ratio and Young's Modulus

In fact, in a metal, the longitudinal elastic constants \( C_{11} \) and \( C_{12} \) have contributions arising from the volume dependent terms in the energy, whereas, the transverse elastic constant \( C_{44} \) does not. Since the difference
between \( C_{11} \) and \( C_{12} \) is proportional to \( C_{44} \), the absence of volume dependent term will bring ions in an equilibrium under the two-body central force and Cauchy relation would be satisfied. But it is a well established experimental fact that Cauchy’s relation is not obeyed in any metal [Brovman and Kagan (1974)]. We note here that the volume dependence, implicit in the effective interaction \( V(r) \), prevents the fulfilment of the Cauchy relation. The extent to which the interionic forces are non-pairwise can be studied by investigating the breakdown of the Cauchy relation.

The violation of the Cauchy relation is obtained by following equation

\[
C_{12} - C_{44} = \frac{1}{\Omega} \sum_n \left[ K_{zz}^n \cdot R_{nx} - K_{zy}^n \cdot R_{nx} \cdot R_{ny} \right]
\]  

\[3.112\]

The Cauchy ratio, defined by \( \frac{C_{12}}{C_{44}} \) is also predicted in the study.

In terms of the elastic constants of cubic crystal the Poisson ratio given by

\[
\sigma = \frac{C_{12}}{C_{11} + C_{12}}
\]  

\[3.113\]

From the calculated values of bulk modulus and Poisson’s ratio, we have also estimated the Young’s modulus

\[
Y = 3B \left[ 1 - 2\sigma \right]
\]  

\[3.114\]

### 3.19 Propagation of Elastic Waves

The theory of elasticity is based upon the continuum approximation and the corresponding frequency region. This wavelength region falls under the acoustic or the ultrasonic region and hence dealing with the sound or the acoustic waves in metals. The exploitation of these ultrasonic waves is generally made to study the lattice defects, the electronic structure of
metals, and many other properties.

In the cubic system, the propagation velocities for the longitudinal and transverse waves in the symmetry directions are given by

\[
V_L[100] = \left[ \frac{C_{11}}{\rho} \right]^{1/2} \tag{3.115}
\]

\[
V_T[100] = \left[ \frac{C_{44}}{\rho} \right]^{1/2} \tag{3.116}
\]

\[
V_L[110] = \left[ \frac{C_{11} + C_{12} + 2C_{44}}{\rho} \right]^{1/2} \tag{3.117}
\]

\[
V_{T1}[110] = \left[ \frac{C_{44}}{\rho} \right]^{1/2} \tag{3.118}
\]

\[
V_{T2}[110] = \left[ \frac{C_{11} - C_{12}}{2\rho} \right]^{1/2} \tag{3.119}
\]

\[
V_L[111] = \left[ \frac{C_{11} + 2C_{12} + 4C_{44}}{3\rho} \right]^{1/2} \tag{3.120}
\]

\[
V_T[111] = \left[ \frac{C_{11} - C_{12} + C_{44}}{3\rho} \right]^{1/2} \tag{3.121}
\]

\(\rho\) is the density of crystal.

### 3.20 Calculation of Second Moment

The second moment of the phonon spectrum can be found by taking trace of \(D_{\alpha\beta}(\bar{q})\).

The average phonon frequency squared is simply obtained from the average over \(\bar{K}\) of the trace of the dynamical matrices, Wallace (1968), and is given by

\[
3M \langle \omega^2 \rangle = \alpha_B \gamma_B \sum_{\bar{R}} \exp \left[ -\gamma_B R \left( \frac{2}{R} \right) \right] + 2 \sum_{\bar{Q}} \bar{Q}^2 F(Q) \left( N^{-1} - \delta_{\bar{q}, \bar{Q}} \right) \tag{3.122}
\]
In terms of real-space parameters $\langle \omega^2 \rangle$ has been given by Hartman and Milbrodt [1971].

$$\langle \omega^2 \rangle = (3M)^{-1} \sum_t (R_t + 2T_t) \quad (3.123)$$

$$= \left( \frac{2Z^* e^2}{3\pi M} \right) \int_0^\infty C(q) q^2 \sum_t \frac{\sin (qR_t)}{qR_t} dq \quad (3.124)$$

For actual calculations of $\langle \omega^2 \rangle$, convergence can be improved for large $R_L$ by adding a correction term calculated by approximating the sum (3.124) from radius $R_L$ to infinity with an integral. We find the correction term to simply

$$\Delta \langle \omega^2 \rangle = - \left( \frac{4\pi N}{3M \Omega} \right) R_L^3 T_L \quad (3.125)$$

### 3.21 Temperature Dependence of the Phonon Frequencies

The phonon frequencies $\omega_{\xi,\lambda}$ vary with volume and temperature because of the anharmonic character of the crystal lattice.

Of particular interest is the extent to which the anharmonic temperature dependence of the $\omega_{\xi,\lambda}$ contributes to the temperature dependence of various properties of metals. The temperature dependence of the $\omega_{\xi,\lambda}$ of metals have been carried out at constant (zero) pressure. However, from the theoretical point of view, there are distinct advantages in knowing the temperature dependence of $\omega_{\xi,\lambda}$ at constant volume. Such information would permit an analysis of the anharmonic contribution of $\omega_{\xi,\lambda}$ to the temperature dependent properties of a metal without the serious complication introduced by volume change.

In the present work phonon frequencies at a temperature $T (°K)$ have been calculated using temperature dependent force constants [eq. (3.99),...
The ratio $\Delta \omega_{q,\lambda} / \omega_{q,\lambda}$ can be found in the principal symmetry directions. $\Delta \omega_{q,\lambda}$ denotes the change in $\omega_{q,\lambda}$ as the temperature increases from $0^\circ K$ to $T^\circ K$ with lattice constant held fixed. Thus,

$$\frac{\Delta \omega_{q,\lambda}}{\omega_{q,\lambda}} = \frac{\omega_{q,\lambda}(T^\circ K) - \omega_{q,\lambda}(0^\circ K)}{\omega_{q,\lambda}(0^\circ K)}$$

(3.126)

### 3.22 Pressure (Volume) Dependence of the Melting Temperature of Metals

We follow the method used by Soma et al. [1983]. In Debye’s model simplifying contributions from the acoustical modes, the mean square displacement $\langle U^2 \rangle$ at temperature $T$ higher than Debye’s temperature $\theta_D$ is expressed as [for example, Ziman (1976)]

$$\langle U^2 \rangle = \frac{9h^2T}{MK_B\theta_D^2}$$

(3.127)

Lindeman [1910] proposed that the melting process occurs when the root mean square displacement of the lattice vibration $\sqrt{\langle U^2 \rangle}$ reaches a critical fraction of the nearest neighbour distance. We define Lindeman’s criterion for melting $x_m$ as the ratio of two times the root mean square displacement of the melting point to the nearest neighbour distance $R_1$,

$$x_m = 2\sqrt{\frac{\langle U^2 \rangle}{R_1}}$$

(3.128)

Combining eq. (3.127) and (3.128), we obtain

$$T_m = \frac{x_m^2}{36h^2} MK_B^2 \theta_D^2 R_1^2$$

(3.129)

Considering the volume dependence of Debye’s temperature $\theta_D$ and the nearest neighbour distance $R_1 \sim \Omega^{1/3}$ as a criterion for melting $x_m$, we obtain the following differential equation for $T_m$

$$\frac{d(\ln T_m)}{d(\ln \Omega)} = -2\gamma + \frac{2}{3}$$

(3.130)
where \( \gamma \) is volume-dependent Grüneisen parameter (which is taken as constant in Debye's model)

\[
\gamma = -\frac{d \ln \theta_D}{d \ln \Omega}
\]  

(3.131)

The differential equation (3.130) can be solved by satisfying the melting point \( T_m \left( \frac{\Omega}{\Omega_0} = 1 \right) \) under atmospheric pressure with the crystal volume \( \Omega_0 \)

\[
\frac{T_m(y)}{T_m(1)} = \exp \left[ 2 \int_y^1 \frac{\gamma(y) - \frac{1}{3}}{y} dy \right]
\]

(3.132)

where \( y = \frac{\Omega}{\Omega_0} \), \( T_m(y) = \) melting temperature at pressure \( P \) (at a volume \( \Omega \)) and \( T_m(1) = \) melting temperature at zero pressure (at a volume \( \Omega_0 \)).

In order to find \( T_m(y) \) it is also necessary to find volume dependence of Grüneisen parameter. To determine \( \gamma(y) \), we follow the following method [Leibfried and Ludwing (1969)]

\[
\gamma = -\frac{1}{2} \frac{d \ln \tilde{p}^2}{d \ln \Omega}
\]

(3.133)

where \( \tilde{p}^2 \) is the second moment of the frequency spectrum. \( \tilde{p}^2 \) is related to the coordinate derivative of the interatomic potential \( V(R) \). For the pairwise central interaction,

\[
\gamma = -\frac{1}{6} \left[ \sum_i C_i \left\{ -\frac{2}{R} V'(R) + 2 V''(R) + R V''(R) \right\} \right]_{R=R_i}
\]

(3.134)

Here \( C_i \) is the co-ordination number for \( i \)th coordination sphere of radius \( R_i \). \( V'(R), V''(R) \) and \( V'''(R) \) are first, second and third order derivatives w.r.t. \( R \) which can be evaluated using eq. (3.93). With the help of eq. (3.134), \( \gamma \) is calculated as a function of compressed volume and hence the melting temperature \( T_m(y) \).
3.23 Debye Temperature at $0^\circ K$

The Debye temperature is related to the maximum cut-off frequency ($\nu_D$) as follows [Hirschfelder et al. (1954)].

$$\theta_D = \frac{\hbar \nu_D}{K_B} \quad (3.135)$$

Assuming Debye frequency distribution, $\nu_D$ is related to the fundamental frequency $\nu$ in the following manner

$$\nu_D = \left( \frac{5}{3} \right)^{1/2} \nu \quad (3.136)$$

Therefore,

$$\theta_D = \left( \frac{5}{3} \right)^{1/2} \frac{\hbar \nu}{K_B} \quad (3.137)$$

$$\nu_D = \left[ \frac{5}{3} \right]^{1/2} \nu \quad (3.138)$$

Following the Hirschfelder et al. [1954], the square of the fundamental frequency $\nu^2$ for an atom of mass $M$ moving in a three dimensional potential well is given by

$$\nu^2 = \frac{1}{2\pi^2 M} \left[ \frac{1}{3} \sum_{i=1}^{n} n_i \left\{ \frac{V' (R_i)}{R_i} + \frac{V'' (R_i)}{2} \right\} \right] \quad (3.139)$$

where $n_i$ is the $i^{th}$ coordination number, $R_i$ is the corresponding inter-atomic distance. In terms of the radial and tangential force constants, the above expression takes the following form,

$$\nu^2 = \frac{1}{2\pi^2 M} \left[ \frac{1}{3} \sum_{i=1}^{n} n_i \left\{ T_i + \frac{R_i}{2} \right\} \right] \quad (3.140)$$

$$\theta_D^2 = \frac{5}{3} \left( \frac{\hbar}{K_B} \right)^2 \cdot \frac{1}{2\pi^2 M} \left[ \frac{1}{3} \sum_{i=1}^{n} \left\{ T_i + \frac{R_i}{2} \right\} \right] \quad (3.141)$$

3.24 Liquid Metal Resistivity

The topic was first considered in the work of Ziman [1961], Bardley et al. [1962], Feber and Ziman [1965] in which the expressions for electrical resistivity, thermo-emf etc. were derived using pseudopotential form factors
for both liquid and amorphous metals.

\[
\rho_{\text{Ziman}} = \frac{3\pi m^2}{4\pi e^2\hbar^3 n K_F^2} \int_0^\infty dq q^4 S(q) |V(q)|^2 \Theta (2K_F - q) \tag{3.142}
\]

Here, \( S(q) \) is the structure factor. In the present work, we have used the hard-sphere solution of the Percus-Yevick equation yields a satisfactory structure factor with the packing fraction \( \eta = 0.45 \).

The structure factor is given by Shimoji [1977]

\[
S(q) = \frac{1}{1 - \rho \tilde{C}(q)} \tag{3.143}
\]

In the above equation, \( \tilde{C}(q) \) is given by

\[
\tilde{C}(q) = -\frac{2\eta}{(qd)^2} \left\{ \begin{array}{l}
\alpha (qd)^3 \{ qd \sin(qd) - (qd \cos(qd)) \} \\
+ \beta (qd)^2 \{ 2qd \sin(qd) - (q^2d^2 - 2) \cos(qd) - 2 \} \\
+ \gamma \left\{ (4q^2d^2 - 24qd) \sin qd \\
- (q^4d^4 - 12q^2d^2 + 24) \cos qd + 24 \right\}
\end{array} \right. \tag{3.144}
\]

Now \( \rho \) is the number density given by

\[
\rho = \frac{1}{\Omega} = \frac{K_F^3}{3\pi^2 z} \tag{3.145}
\]

The packing fraction \( \eta \) is related to the hard-sphere diameter \( d \) by the following expression

\[
\eta = \frac{1}{6} \pi \rho d^3 \tag{3.146}
\]

The constants \( \alpha, \beta \) and \( \gamma \) given by

\[
\alpha = \frac{(1 + 2\eta)^2}{(1 - \eta)^4} \tag{3.147}
\]

\[
\beta = \frac{-6\eta (1 + \frac{1}{2}\eta)^2}{(1 - \eta)^4} \tag{3.148}
\]

\[
\gamma = \frac{1}{2} \eta \alpha = \frac{1}{2} \frac{\eta(1 + 2\eta)^2}{(1 - \eta)^4} \tag{3.149}
\]

Now, in eq. (3.142), \( V(q) \) is the electron-ion pseudopotential, \( n \) is the conduction electron density related to the Fermi wave number \( K_F = (3\pi^3 n)^{1/3} \).
The unit step function $\Theta$ which cuts off the integration at $2K_F$ corresponding to a perfectly sharp Fermi surface, is defined as

$$\Theta(2K_F - q) = 0 \text{ for } q > 2K_F$$
$$= 1 \text{ for } q \leq 2K_F$$ (3.150)

But the finite mean free path corresponds to a finite uncertainty in the electron position. This corresponds to a finite uncertainty in the electron momentum. Thus, the Fermi surface is not perfectly sharp as implied by Eq. (3.142) but it is blurred. The attempts to take this blurring into account in the formulation of resistivity is reviewed by McCaskill and March [1982]. Ferraz and March [1979] approach yields in place of eq. (3.142)

$$\rho_{sc} = \frac{3\pi^3 m^2}{4\pi e^2 h^3 n K_F^2} \int_0^\infty q^4 dq S(q) \mid V(q) \mid^2 \Gamma(q, K_F, \ell)$$ (3.151)

This equation must be solved self-consistently. Very few explicit approximations are proposed for the function $\Gamma(q, K_F, \ell)$ [McCaskill and March (1982)].

In this work we have used the form for $\Gamma(q, K_F, \ell)$ as used by Laakkonen and Nieminen [1983] and Khajil and Tomak [1986].

$$\Gamma(q, K_F, \ell) = \frac{2}{\pi q^2} \left[ \tan^{-1}(q\ell) - \frac{1}{2} \tan^{-1} \frac{2q\ell}{1+4(K_F \ell)^2 - (q\ell)^2} \right]$$ (3.152)

The step function which determines the upper limit of integration (3.151) is defined as,

$$\Theta \left( q - \left( \frac{1}{2\ell} + 4K_F^2 \right)^{1/2} \right) = 1 \text{ for } \left( \frac{1}{2\ell} + 4K_F^2 \right)^{1/2} \leq q$$
$$= 0 \text{ for } \left( \frac{1}{2\ell} + 4K_F^2 \right)^{1/2} > q$$ (3.153)

The mean free path is determined self-consistently as follows. The first step of the self-consistency loop is to calculate $\rho$ using eq. (3.142) i.e. with mean free path $'\ell'$ is infinity. A new $'\ell'$ (mean free path) is then calculated from the Drude relations

$$\rho_L = \frac{\hbar K_F}{ne^2 \ell}$$ (3.154)

The iterations are continued till $\rho_L$ converges.
3.25 Thermo-Electric Power

If we assume that thermo-emf $Q$ and electrical resistivity are related by [Ziman (1961)]

$$Q = -\frac{\pi^2 K_B T}{3eE_F} \left[ \frac{\partial \ln \rho_L(E)}{\partial \ln E} \right]_{E=E_F}$$  \hspace{1cm} (3.155)

This expression holds for any metal or alloy, whether crystalline or not. It can be shown that the dimensionless parameter

$$X = -\left[ \frac{\partial \ln \rho_L(E)}{\partial \ln E} \right]_{E=E_F}$$  \hspace{1cm} (3.156)

determines the dependence of thermo-emf on microscopic characteristic of the metal. Ziman and his coworkers expressed $X$ in terms of the structure factor and pseudopotential parameters

$$X = 3 - 2 \cdot g_o$$  \hspace{1cm} (3.157)

where

$$g_o = \frac{S(2K_F) \mid V(2K_F) \mid^2}{< S(q) \mid V(q) \mid^2>}$$  \hspace{1cm} (3.158)

The average function $< SV^2 >$ is defined by

$$< S(q) \mid V(q) \mid^2 > = 4 \int_0^1 S(q) \mid V(q) \mid^2 \eta^3 d\eta$$  \hspace{1cm} (3.159)

with $\eta = \frac{q}{2K_F}$. For local pseudopotential thermoelectric power $Q$ is given by

$$Q = -\frac{\pi^2 K_B T}{3eE_F} \left[ 3 - \frac{2S(2K_F) \mid V(2K_F) \mid^2}{< S(q) \mid V(q) \mid^2>} \right]$$  \hspace{1cm} (3.160)

The thermo-electric power $Q$ using eq. (3.160) can be evaluated at $T = T_M$ (melting temperature).

3.26 Monovacancy Resistivity

The defects are intrinsic to real crystals and determine or modify the properties of real materials. For example, the point defects such as vacancies
and interstitials modify the electrical properties because they contribute to the residual resistivity.

The resistance due to these static imperfections (and grain boundary) is called residual resistance. At low temperature, the residual resistance due to such imperfections can be significant while at high temperatures this contribution is very small compared to that due to the scattering of conduction electrons by phonons. Much attention has been drawn in recent years towards the study of properties of crystals containing point defects. In the present study we have used pseudopotential method to examine the contribution of monovacancy, which is one of the point defects, to the resistivity of metals. It is well known that lattice defects and impurities destroy the periodicity of the lattice. In many important cases the lattice distortion due to such defect can be neglected.

Within the framework of the pseudopotential formulation, for low vacancy concentration and neglecting lattice distortion, the formula for monovacancy resistivity can be derived using standard scattering theory with the missing pseudopotential associated with the vacancy as,

\[ \rho_V = \frac{3}{16\pi e^2 K_F^4} \int_\Omega q^3 |V(q)|^2 dq d\Omega' \]  

\( \Omega' \) is the solid angle in the scattering vector space.

### 3.27 Scattering and Phase Shift

We are concerned in this section with the scattering occurring in liquid metals. For example, a flux of electrons is incident on a scattering centre and it is important to know the number of electrons that are scattered in a definite direction. This problem is most conveniently discussed using
phase shift analysis. This analysis will throw much additional light on the use of pseudopotential.

The phase-shift $\eta$ of the $l^{th}$ partial wave related to the pseudopotential is given by,

$$
\eta_l = -\frac{mK_F\Omega_o}{4\pi\hbar^2} \int_0^2 V(y)yP_l(\cos \theta)dy
$$

(3.162)

with $y = \frac{2}{K_F}$; $P_l(\cos \theta)$ is a Legendre polynomial and $\cos \theta = 1 - \frac{9}{2}(\frac{q}{K_F})^2$.

Using the above equation phase shifts $\eta_0, \eta_1, \eta_2$ are calculated for $s, p$ and $d$ components.

### 3.28 Resistivity ($t$-Matrix)

In case of the noble or transition metals, the (NEF) approach is not appropriate due to the presence of a $d$ band high in the conduction band which complicates the picture. We use $t$-matrix of the pseudopotential to calculate the relevant scattering cross sections rather than the usual screened ion model potentials. The single scatter $t$-matrix form factors for energy conserving transition is given by [Evans (1971) and Evans et al. (1971, 1973)]

$$
t(\vec{k}, \vec{k}') = -\frac{2\pi\hbar^3}{m(2mE)^{1/2}\Omega_o} \sum_l (2l + 1) \sin \eta_l(E_F) \exp [i\eta_l(E_F)] P_l(\cos \theta) \quad (3.163)
$$

The $t$-matrix has the dimensions of energy and is normalized to the atomic volume $\Omega_o$. The resistivity takes the form with $y = \frac{q}{2K_F}$

$$
\rho = \frac{3\pi\Omega_o}{e^2\hbar^2\nu_f^2} \int_0^1 dy y^3 S(q) |t(\vec{k}, \vec{k}')|^2 dy
$$

(3.164)

The resistivity is calculated using this formula, the technique for calculating resistivity by (3.164) is outlined by Dreirach et al. [1972]. Their results
show that the \(d\)-components dominate in the transition metals. The approximate value of resistivity can be written [Evans et al. (1971)]

\[
\rho \cong \frac{30\pi^3 \hbar^3}{m e^2 \Omega \kappa F^2 E_F} \cdot \sin^2 \eta \langle E_F \rangle S (2K_F)
\]

(3.165)

### 3.29 Asphericity in the Fermi Surface

The Fermi surface is a surface of Fermi-energy \(E_F\) in the wave number space. The Fermi surface (FS) concept enables to visualise the relative fullness or occupation of the allowed empty lattice band geometrically in \(K\)-space. Such concept of FS helps in the theoretical determination of the electronic properties of a solid - it may be a metal, semiconductor or an insulator. In fact, the purpose of the FS construction is to know about the details of the motion of an itinerant electron in three dimensions.

The Fermi energy is determined by requiring that the total number of conduction electrons is equal to the number of electron states with energy equal to or less than the Fermi energy. Using this fact, Wallace [1972] has obtained an expression for Fermi vector \(K_F\) in second order in pseudopotential,

\[
|K_F| = K_F^0 + \frac{m}{\hbar^2 K_F^0} \sum Q |V(Q)|^2 \left[ \frac{1}{(E_{K_F} - E_{K_F+Q})} + \frac{m}{2\hbar^2 Q K_F^0} \ln \left| \frac{Q + 2K_F^0}{Q - 2K_F^0} \right| \right]
\]

(3.166)

where \(K_F^0\) is zeroth-order value of Fermi-vector. Here the dependence of \(|K_F|\) on the direction of \(K_F\) is contained in the dependence of the right-hand side on the direction of \(K_F\), through the energy denominators \(\left[ E_{K_F} - E_{K_F+Q} \right]^{-1}\). The Fermi vectors \(K_F\) and \(K_F^0\) lie in the same direction.

Schneider and Stoll [1967] have also studied the distortion in spherical (free electron) Fermi surface. These authors define the wave vector \(K_F\) as
follows

\[ K_F = K_F^0 [1 + \Delta(\theta)] \]  \hspace{1cm} (3.167)

where \( \theta \) is the angle between \( K_F \) and \( Q \) and \( K_F^0 \) is the free electron Fermi wave number.

Using second order perturbation theory and expanding \( K_F \) in the powers of \( \Delta(\theta) \), these authors have obtained the following expressions for the change in \( K_F \),

\[ \frac{\Delta K_F}{K_F^0} = \sum_Q \left\{ \frac{|V(Q)|^2}{E_F^0} \left[ \frac{1}{\hbar^2 Q^2/2m - 4E_F^0 \cos^2 \theta_K Q} - C(Q) \right] \right\} \]  \hspace{1cm} (3.168)

where

\[ C(Q) = \frac{m}{2\hbar^2 k_F^0 Q} \ln \left| \frac{Q + 2k_F^0}{Q - 2k_F^0} \right| \]  \hspace{1cm} (3.169)

Since both these approaches are equivalent, the numerical results obtained from them are identical. We have verified this fact in the present study.