Chapter 3
3.1 THERMO-ACOUSTIC PARAMETERS

The Gruneisen parameter is an important quantity of current interest. This parameter, which relates the thermal and mechanical properties of solids [40], determines its pressure response to energy deposition. It has been found to be a useful tool in describing inter-chain interactions, molecular structure and other properties of solids and solid polymers [50-54]. Warfield [50] showed that in polymers there are two distinct modes of lattice vibrations viz., inter-change (low frequency, long wavelength) and intra-chain (high frequency, short wavelength) vibrations. Anharmonicity of postulated lattice vibrations, treating polymers as quasi-solids has been shown to be exhibited [51, 53] only by the inter-chain vibrations which can be expressed in terms of the lattice Gruneisen parameter $b$. However, the temperature dependence of bulk modulus has been found to be an important parameter for the Gruneisen equation of state solids [55]. Also, the Rao’s empirical relation [32] is of importance in describing physico-chemical properties.

The Gruneisen parameter $\Gamma$ is also useful as a measure of anharmonicity of molecular vibrations in studying internal structure, molecular order and thermo-acoustic properties of solids and solid polymers [57-62]. Recently, Sharma [61] has shown that the three (dimensionless) anharmonic parameters, the isochoric $\Gamma''$, isothermal $\Gamma'$ and isoboric $\Gamma$, microscopic (lattice) Gruneisen parameters are related to each other. It has been shown that the contribution of the isochoric temperature derivative of bulk modulus, $C_1$, is of significance. Following a model-dependent approximation by Dedugdale and MacDonald [63], which is valid at all pressures, $\Gamma''$ and $\Gamma$ can be determined as temperature dependent functions of bulk modulus [35, 64, 65].

Many workers have studied the thermo-acoustic properties of liquified gases [56], liquids [35, 64, 65], polymers [61, 66], molten metals [67] and metals including rare earth metals and reference materials [88].

The Gruneisen parameter, widely used in equation of serves as an important parameter in determining the frequency dependence of ultrasonic absorption. It is useful in establishing the contribution of absorption due to phonon-phonon interaction. The model cited by Sharma [40, 69] has been used in the present work for calculating the Gruneisen parameter of pure metals and copper-zinc and aluminium-zinc alloys. In the present work, it is aimed at examining and analysing the various possible relationships between microscopic Gruneisen
parameter $\Gamma$, the Moelwyn-Hughes parameter $C_1$, Rao's acoustical parameter $& Beyer's nonlinearity parameter $(B/A)$. Other thermo-acoustic parameters are interrelated through the microscopic Gruneisen parameter, in turn the Moelwyn-Hughes parameter. This type of analysis is rarely found in literature. Present study demonstrates the importance of the Moelwyn-Hughes parameter (in turn lattice Gruneisen parameter) in evaluating thermo-acoustic parameters of metals and alloys. The so called thermodynamic Gruneisen parameter $\Gamma$ is related to the lattice Gruneisen parameter.

3.2 THEORETICAL EVALUATIONS OF THE PARAMETERS

3.2.1 GRUNEISEN PARAMETERS

The microscopic isoboric $\Gamma$, isothermal $\Gamma'$ and isochoric $\Gamma''$ Gruneisen parameters as a measure of anharmonicity of normal mode frequency of molecular vibrations, may be related \[58,69,70\] to the corresponding acoustical parameters $K$, $K'$ and $K''$ and expressed in terms of volume expansivity as \[70\]

$$
\Gamma = -(d \ln v / d \ln V)_T \\
= -1/2 \left[ 1 + (d \ln B_T / d \ln T)_T / \alpha T \right] \quad \text{(3.2.1)} \\
= - (d \ln U / d T)_T / \alpha + 0.33 \\
= K + 0.33 \quad \ldots (3.2.1a) \\
= 5/3 + (2\alpha T)^{-1} + 2\alpha T/3 \quad \ldots (3.2.1b)
$$

where $V$ is the molar volume, $B_T$, isothermal bulk modulus and $U$, ultrasonic velocity.

$$
\Gamma' = -(d \ln v / d \ln V)_T \\
= 1/2 \left[ (d B_T / d P)_T - 1 \right] \\
= K' + 0.33 \\
= B_T (d \ln U / d P)_T \quad \ldots (3.2.2)
$$

and

$$
\Gamma'' = (d \ln v / d \ln T)_T / \alpha T \\
= \Gamma' - \Gamma \\
= K' - K = K'' \\
= (d \ln B_T / d \ln T)_T / 2\alpha T \\
= \left[ 1 - \beta_T^* \left( 1 - 2 \alpha T / \beta_T^* \right) / P_i \beta_T^* \right] \quad \ldots (3.2.3)
$$

where $\beta_T^*$ is the isothermal compressibility at absolute zero temperature and zero pressure and $P_i$ is the internal pressure. It may be noted that $\beta_T^*$ can only be extrapolated.
γ'' can be expressed in terms of ultrasonic velocity U through the relation

\[ \gamma'' = \frac{(d \ln U/dT)_v}{\alpha} \] ...(3.2.3a).

Following Slater's presentation [64] based on the Debye theory of specific heats, the maximum normal mode frequency is proportional to \( U/V^{1/3} \). It can be shown [72-74] that \( \Gamma = K + 0.33 \) and \( \Gamma' = K' + 0.33 \).

3.2.2 MOELWYN-HUGHES PARAMETER

Moelwyn Hughes [38] defined the pressure coefficient of bulk modulus, \( C_i \), which serves as a severe test of equation of state

\[ C_i = \left[ \frac{d(1/\beta_T)}{dP} \right] \]
\[ = \left[ \frac{d \ln B_T/d \ln V}{\tau} \right] \]
\[ = 13/3 + (\alpha T)^{-1} + 4\alpha T/3 \] ...(3.2.4)

Hartmann [72] showed that the anharmonicity of intermolecular potential is responsible for thermal expansion. Anharmonicity gives rise to volume dependence of normal modes of lattice. The interrelationship between \( \alpha \) and \( T \) is, therefore, expected in accordance with Eqn. (3.2.4).

3.2.3 FIRST ORDER ISOCHORIC TEMPERATURE COEFFICIENT OF INTERNAL PRESSURE

The first order isochoric temperature coefficient of internal pressure \( P_i \) in the zero pressure limit can be expressed [38-41] in terms of the volume expansivity \( \alpha \) and temperature \( T \) as

\[ X = \left[ \frac{\ln P_i/d \ln T}{\gamma} \right] \]
\[ = -2 \left( 2\alpha T + 1 \right)/V^* \] ...(3.2.5)

where \( V = V/V^* \) ...(3.2.6)
\[ V^* = \left[ 1 + \alpha T/3(1+\alpha T) \right]^3 \] ...(3.2.7)

\( V^* \), is the characteristic (hard core) specific volume at absolute zero temperature and pressure.

3.2.4 THERMODYNAMIC GRUNEISEN PARAMETER

The thermodynamic Gruneisen parameter \( \Gamma \), which expresses the relationship between thermal and mechanical properties, is defined in terms of the internal energy derivative of the
pressure or temperature [38-41] as

\[ r = \frac{p}{V/T_c} \]

\[ = V \left( \frac{dP}{dE} \right)_v \]

\[ = (d \ln T/d \ln E)_v / \left( 1 + (r)^{-1} \right) \]

\[ = \alpha V/\beta C_v \]

\[ = \alpha V/\beta C_p \]

\[ = \alpha \mu U^2/C_p \]

\[ = (\gamma - 1)/\alpha T \]

\[ \ldots (3.2.8) \]

3.2.5 BEYER'S NONLINEARITY PARAMETER

Beyer's nonlinearity parameter \((B/A)\), which is a particular combination of the temperature and pressure derivatives of the sound velocity \(U\) [38-43, 73-75] may be expressed as

\[ B/A = (B/A)' + (B/A)'' \]

\[ \ldots (3.2.9) \]

in which \((B/A)'\) and \((B/A)''\) are expressed as

\[ (B/A)' = (2 M U^2/V) (dln U/dP)_T = 2\gamma K' \]

\[ \ldots (3.2.10) \]

\[ (B/A)'' = (2 M \alpha T U^2/C_p) (dln U/dT)_p = -2(\gamma - 1)K \]

\[ = -2\Gamma \alpha T \]

\[ \ldots (3.2.11) \]

Then \((B/A) = 2\Gamma + 0.66 - 2\Gamma''\)

\[ = 2\gamma \Gamma' - 2\Gamma \Gamma' \alpha T \]

\[ = 2\Gamma + 2\gamma \Gamma'' \]

\[ = C_1 - 1 + 2\gamma \Gamma'' \]

\[ = 2(\Gamma + \gamma) \]

\[ \ldots (3.2.12) \]

Sharma [68] proposed a relation as

\[ (B/A)_o = C_1 - 1 \]

\[ \ldots (3.2.13) \]

where \((B/A)_o = (m + n + 3)/3\)

\[ = 2\Gamma \]

\[ = 2(K + 0.33) \]

\[ \ldots (3.2.14) \]

Here \(m\) & \(n\) are respectively the exponents describing the magnitude of attractive and repulsive forces of molecules. \((B/A)_o\) is the value of \((B/A)\) corresponding to the volume \(V\).

If \(m = 6\)

\[ n = 3[(B/A)_o - 3] \]

\[ = 2(C_1 - 4) \]

\[ \ldots (3.2.15) \]

The above relation signifies the intermolecular force through the repulsive exponent \(n\), which plays a vital role in establishing a close relationship between the anharmonic and nonlinear properties.
3.2.6 FRACTIONAL FREE VOLUME (V_o/V)

The fractional free volume, as a measure of disorder due to the increased mobility of molecules, can be expressed in terms of \( \Gamma \) [75] as
\[
K = \Gamma - 0.33 \\
= [(V/V_o) - 1] - 0.33 \\
= [(C_i - 1)/2] - 0.33 \quad \ldots(3.2.18)
\]
in which the available molar volume of a solid molecule is given by
\[
V_o = V - V_o \quad \ldots(3.2.17)
\]
where \( V_o \) is the molar volume at absolute zero temperature.
\[
V_o/V = [2/(C_i + 1)] \quad \ldots(3.2.18)
\]

3.2.7 ISOCHORIC ACOUSTICAL PARAMETER AND MOLECULAR CONSTANT

Sharma [38-41, 76-81] has introduced two (dimensionless) parameters \( S_o \) and \( S^\ast \). They may be expressed as
\[
S_o = - (X/2) (3 + 4 \alpha T) \\
= \delta (3 + 4 \alpha T) \\
= 3 \delta S^\ast \quad \ldots(3.2.19)
\]
and
\[
S^\ast = [1 + \{(4/3) \alpha T\}] \quad \ldots(3.2.20)
\]
where \( \delta \) is the isochoric acoustical parameter and it can be computed as
\[
\delta = (2 \alpha T + 1)/(V)^{\alpha_i} \\
= -(X/2) \quad \ldots(3.2.21)
\]

Isochoric Gruneisen parameter can be expressed in terms of
\( S_o \), \( X \), or \( \delta \) as follows
\[
\Gamma'' = 1 - S_o [\alpha T (3+4 \alpha T)]^{-1} \quad \ldots(3.2.22)
\]
\[
\Gamma'' = 1 + (X/2 \alpha T) \quad \ldots(3.2.23)
\]
\[
\Gamma'' = 1 - (\delta / \alpha T) \quad \ldots(3.2.24)
\]
The molecular constant \( \Gamma \), can be calculated using the value of \( \delta \) as
\[
\Gamma = P_i/e \\
= (1 + X/2)^{-1} \\
= (1 - \delta)^{-1} \\
= [1 - ((2 \alpha T + 1)/(V)^{\alpha_i})]^{-1} \quad \ldots(3.2.25)
\]
where \( P_i \) and \( e \) are the internal pressure and cohesive energy density.

The above equations demonstrate the importance of the Gruneisen or Moelwyn-Hughes parameter in evaluating various thermoacoustic parameters. As shown earlier, the Gruneisen parameter \( \Gamma \)
and the Moelwyn-Hughes parameter $C_i$, can be expressed in many ways which demonstrate how simply $\Gamma$ or $C_i$ is related to other thermo-acoustic parameters.

Hence $K, (B/A)_0, (V_a/V), n, \Gamma, \Gamma'$ and $\Gamma''$ are directly related to the Gruneisen parameter $\Gamma$ or the Moelwyn-Hughes parameter $C_i$ only.