Chapter 5

Quasi-Harmonic Theory of Thermal Expansion

5.1 Introduction

The quasi-harmonic approximation is a computationally efficient method for evaluating thermal properties of materials. Planes and Manosa [1] reports the variation of mode Gruneisen parameter [GP] calculated for Cu based alloys. Anil et al. [2] and Jayachandran and Liu [3] have used the same procedure to calculate the GP for various crystals. The determination of GP, which measure the strain dependence of the lattice vibrational frequencies is a subject of much attention, due to their importance in understanding the macroscopic behaviour of solids. The anharmonicity of a crystal lattice can be studied using GPs which in turn can shed more light on the thermal properties. At low temperatures thermal expansion coefficient of any crystal is mainly determined by the acoustic modes of the elastic waves and their dependence on the strains of the lattice. For cubic materials it is enough to consider the dependence of the frequency on the volume strain. The behavior of thermal expansion coefficient $\alpha$ at low temperatures is governed by the generalised mode GP $\gamma(\theta, \phi)$. Manosa and Planes [1] and Anil et al. [2] reports that using the generalized GP, the low temperature limit of the GP can be calculated. In the harmonic approximation, the atom executes symmetric
vibrations about its mean position. At higher temperatures, the vibrations become more and more vigorous but the mean position of the atom remains unchanged. Thus in a harmonic solid, there can be no thermal expansion. Therefore, the Gruneisen’s constant is zero for a harmonic solid. Hence, deviations of $\gamma$ from zero can be interpreted as a direct measure of anharmonicity. The thermal expansion of a solid, therefore, is a property arising strictly due to the anharmonicity of the lattice. A simple method of taking the anharmonicity of the lattice vibrations into account is the quasi-harmonic approximation. Here, the vibrations are assumed to be harmonic even in a strained lattice but the interatomic forces and hence the lattice frequencies are assumed to be functions of the strain components in the lattice. The thermal energy of a simple lattice is treated as the energy of a spectrum of elastic waves, having at any temperature a certain maximum frequency of vibration.

The variation of mode GPs of Cu based SMA have been studied as a function of propagation direction at various temperatures. Planes and Manosa. [1] showed that complementary information on vibrational anharmonicity can be obtained by plotting the GPs as a function of direction of the applied uniaxial stress [1]. Variation of mode GP of Cu based alloys are plotted for different propagation directions at different temperatures by Comas et al. [4] and Jurado et al. [5]. Nagasawa et al. [6,7] have determined GPs for several shape memory alloys at room temperature. These are the results of experimental studies and theoretical investigations are yet to be reported. The present study aims at theoretical evaluation of mode GPs and hence the low temperature limits of the thermal
expansion of selected Cu based shape memory alloys – Cu-Al-Ni, Cu-Al-Zn, Cu-
Al-Be and Cu-Al-Pd.

5.2 Quasi-harmonic Theory of Thermal Expansion

In the harmonic approximation, the atoms in a solid are assumed to
oscillate symmetrically about their equilibrium positions, which remain unaltered
irrespective of the temperature. The thermal expansion of a solid, therefore, is a
property arising strictly due to the anharmonicity of the lattice. In the quasi-
harmonic approximation, the oscillations are still assumed to be harmonic in
nature but the frequencies are taken to be functions of the strain components in
the lattice. The strained state of the lattice is specified fully by the six strain
components $\eta_{rs}$ (r, s = 1, 2, 3; $\eta_{rs} = \eta_{sr}$).

A normal mode with frequency $\omega(q,j)$ makes a contribution $F(q,j)$ to the
total vibrational free energy $F_{vib}$, given by

$$ F(q,j) = K_B T [\frac{1}{2} X + \log(1 - e^{-X})] $$

where $X = \frac{\hbar \omega(q,j)}{K_B T}$ and $\hbar = \hbar/2\pi$,

$h$ being the Plank’s constant, $K_B$ is the Boltzmann’s constant, $T$ is the absolute
temperature and $q$ is the wave vector of the $j^{th}$ acoustic mode. The total
vibrational free energy is, therefore

$$ F_{vib} = \sum_{q,j} F(q,j) $$
\[= K_B T \sum_{q,j} \left[ \frac{1}{2}X + \log (1 - e^{-X}) \right] \] (5.2)

The thermal expansion coefficients \(\alpha_{lm}\) of a crystal of volume \(V\) are obtained as

\[V \alpha_{lm} = -\left[ \frac{\partial^2 F_{ab}}{\partial \sigma_{lm} \partial T} \right] \] (5.3)

\[= \sum_{q,j} \sum_{\sigma} S_{lm,rs} \gamma_{rs}(q,j) K_B \sigma[\omega(q,j), T] \]

Here, thermal expansion coefficient \(\alpha_{lm} = \left( \frac{\partial \eta_{lm}}{\partial T} \right) \) (5.4)

\(\sigma_{lm}\) are the components of the stress tensor

\(S_{lm,rs}\) are the compliance coefficients relating \(\eta_{rs}\) and \(\sigma_{lm}\) and

\[\gamma_{rs}(q,j) = \left[ \frac{\partial \log \omega(q,j)}{\partial \eta_{rs}} \right] \] (5.5)

where, \(\gamma_{rs}\) are the generalised GPs of the normal mode frequencies. In equation (5.3), the subscript \(\sigma'\) and \(T\) means that all other \(\sigma_{ik}\) and temperature are to be held constant while differentiating with respect to \(\sigma_{lm}\) and subscript \(\sigma\) means that all \(\sigma_{lm}\) are held constant.

\[\sigma[\omega(q,j), T] = X^2 e^{-X}/(1 - e^{-X})^2\] is the Einstein specific heat function. (5.6)

(i) In the quasi-harmonic approximation, the GPs are assumed to be constants independent of temperature. It is more advantageous to choose such strains that
do not alter the crystal symmetry, instead of choosing any arbitrary strain, while defining $\gamma_{j}(0,\phi)$.

For cubic symmetry as we know, there is only one principal thermal expansion coefficient namely $\alpha$, which can be along either of the three axial directions. Thus it is convenient to use a uniform longitudinal strain along one of the three principal axis for the determination of the thermal expansion.

Then $\eta_{11} = \eta_{22} = \eta_{33} = \varepsilon = d\log a$, where $a$ is the lattice parameter and all other $\eta_{rs}$ vanish.

$$\therefore \gamma_{11}(q_j) = \gamma_{22}(q_j) = \gamma_{33}(q_j) = \gamma(q_j) = -\frac{\partial \log \omega(q_j)}{\partial \log a}$$ (5.7)

From equation (1.25), we now obtain

$$V\alpha = \sum_{q_j} [S_{11} + 2S_{12}] \gamma(q_j) K_{B} \sigma(\omega(q_j),T)$$ (5.8)

The effective Gruneisen Parameters are defined as

$$\gamma(T) = \left[ \left( C_{11}^{s} + 2C_{12}^{s} \right) a \right] V / C_{p}$$ (5.9)

The $C_{ij}^{s}$ are the adiabatic elastic constants, $C_{p}$ is the specific heat at constant pressure and $V$ is the volume of the crystal.

Comparing equations (5.9) with (5.8), we get
\[ \gamma_j(T) = \frac{\sum_{q,j} \gamma(q, j) \sigma(\mathbf{q}, j, T)}{\sum_{q,j} \sigma(\mathbf{q}, j, T)} \]  

(5.10)

The expression (5.10) gives the temperature dependence of effective GP.

In the low temperature limit, only the low frequency acoustic modes make a contribution to the specific heat. The number of such normal modes in the \( j \)th acoustic branch is proportional to \( v_j^{-3}(\theta, \phi) \), where \( v_j(\theta, \phi) \) is the velocity of the \( j \)th acoustic mode travelling in the direction \((\theta, \phi)\). The GP \( \gamma(q,j) \) depends only on the branch index \( j \) and the direction \((\theta, \phi)\). It is independent of the magnitude of the wave vector \( q \). The effective lattice GPs \( \gamma_j \) thus approach the limits defined below, at low temperatures.

\[ \lim_{T \to 0} \gamma(T) = \gamma_L = \frac{\int \sum_{j=1}^{3} \gamma_j(\theta, \phi) v_j^{-3}(\theta, \phi) d\Omega}{\int \sum_{j=1}^{3} v_j^{-3}(\theta, \phi) d\Omega} \]  

(5.11)

where \( \gamma(\theta, \phi) \) are the GPs for the acoustic modes propagating in the direction \((\theta, \phi)\). Calculation of the low temperature limit \( \gamma_L \) is possible knowing the pressure derivatives of the second-order elastic constants (SOEC) or the third-order elastic constants (TOEC) of the crystal. The evaluation of the low temperature limits \( \gamma_L \) for the selected Cu based shape memory alloys is given in the following section.
5.3 Procedure to Obtain the Lattice Thermal Expansion

The low temperature limit of the GP $\gamma_L$ depends on the generalised GPs $\gamma_j(\theta, \phi)$ of the acoustic modes propagating in different directions in the crystal lattice along with its velocity. A method of calculation of the generalised GPs $\gamma_j(\theta, \phi)$ for selected Cu based shape memory alloys from their higher order elastic constants is presented here.

A medium is homogeneously strained when the components of the strain tensor $\eta_{ij}$ do not vary from point to point, in the medium [BnHng]. Let the co-ordinates of the lattice point in the strained state be $X_i$ ($i = 1, 2, 3$). When the lattice is given infinitesimal displacements $u_i$ from the strained state, the resulting state is referred by the co-ordinates $x_i = X_i + u_i$

the equation of motion is

$$\rho \ddot{x}_j = \frac{\partial}{\partial x_k} \tau_{kj}$$

(5.12)

where $\rho$ is the density in the strained state and $\tau_{kj}$ is the stress tensor. The condition of equilibrium requires that the stress tensor be symmetric, i.e.,

$$\tau_{jk} = \tau_{kj}$$

(5.13)

We have for the Jacobian $J$

$$\frac{\partial}{\partial x_k} \left( \frac{1}{J} \frac{\partial x_i}{\partial a_p} \right) = 0$$

(5.14)
Using equations (5.12) and (5.13), we can arrive at the following wave equation in a homogeneously strained lattice in terms of the displacements $u_j$.

$$\rho_0 \ddot{u}_j = A_{jk,pm}^s \frac{\partial^2 u_k}{\partial a_p \partial a_m}$$  \hspace{1cm} (5.15)

where $J$ in equation (5.14) is defined as

$$J = \text{Det} \left( \frac{\partial x_i}{\partial a_j} \right)$$  \hspace{1cm} (5.16)

with $a_i$ ($i = 1, 2, 3$) being the position co-ordinates of a lattice point in the unstrained state. In equation (5.15), $\rho_0$ is the density of the crystal before deformation and

$$A_{jk,pm}^s = \delta_{jk} \bar{t}_{pm} + \frac{\partial x_j}{\partial a_q} \frac{\partial x_k}{\partial a_i} \left( \frac{\partial \bar{t}_{pm}}{\partial \eta_{mi}} \right)$$  \hspace{1cm} (5.17)

where $\bar{t}_{pm} = \left( \frac{\partial U}{\partial \eta_{pm}} \right)_s$  \hspace{1cm} (5.18)

The ‘bar’ denotes that the quantities have to be evaluated in the homogeneously strained state of the lattice. $\delta_{jk}$ is the Kronecker delta symbol and $\eta$’s are the Lagrangian strains. $U$ is the internal energy of the lattice, which is a function of entropy $S$ and Lagrangian strain components $\eta_{ij}$. $U$ can be expanded in powers of the strain parameters about the unstrained state as

$$U = U_0 + \frac{1}{2} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{3} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn} + \ldots$$  \hspace{1cm} (5.19)
The linear term in strain is absent because the unstrained state is one where $U$ is minimum. $C_{ij,kl}$ and $C_{ij,kl,mm}$ are the second- and third-order elastic constants defined as

$$C_{ij,kl} = \left[ \frac{\partial^2 U}{\partial \eta_i \partial \eta_j \partial \eta_{kl}} \right]_{0, S} \tag{5.20}$$

$$C_{ij,kl,mm} = \left[ \frac{\partial^3 U}{\partial \eta_i \partial \eta_j \partial \eta_{kl} \partial \eta_{mn}} \right]_{0, S} \tag{5.21}$$

Here, the derivatives are to be evaluated at equilibrium configuration and at constant entropy. The elements of the position co-ordinates $dx_i$ are related to $da_i$ as

$$dx_i = \frac{\partial x_i}{\partial a_j} da_j$$

$$= \sum_{j=1}^{3} (\delta_{ij} + \varepsilon_{ij}) da_j \tag{5.22}$$

where $\varepsilon_{ij}$ are deformation parameters.

Using equations (5.19) and (5.22), we get $A_{jk,pm}^S$ in equation (5.17) to the first order in $\varepsilon_{jk}$ as

$$A_{jk,pm}^S = C_{pj,mk} + \sum_{rs} \left( C_{pj,mk,rs} + C_{pm,rs} \delta_{jk} \right) \varepsilon_{rs}$$

$$+ \sum_q C_{pq,mk} \varepsilon_{jq} \sum_q C_{pj,nq} \varepsilon_{kq} \tag{5.23}$$
The plane wave solution in strained co-ordinate is

\[ u_j = u_j^0 \exp \left( \omega t - \frac{n_i X_i}{W} \right) \]  \hspace{1cm} (5.24)

\[ \text{where } W \text{ is the actual velocity of the wave in the strained state and } \omega \text{ the frequency of the wave in the strained state. } n_i \text{ are the direction cosines of wave propagation and } t \text{ is the time. } u_j, \text{ the displacements in equation (5.24) can be expressed as} \]

\[ u_j = u_j^0 \exp \left( \omega t - \frac{N_i a_i}{v} \right) \]  \hspace{1cm} (5.25)

\[ \text{where } v \text{ is the natural velocity and } N_i \text{ are the direction cosines of the wave in the unstrained state. Let } \lambda_0 \text{ be the wavelength of a given wave in the unstrained state travelling along a direction having direction cosines } N_i. \text{ After deformation, the wavelength of the elastic wave changes to } \lambda \text{ and the wave propagation direction also is changed and the corresponding direction cosines are } n_i. \text{ The frequency of the wave changes from } \omega_0 \text{ to } \omega. \text{ In the unstrained state, the actual velocity } W_0 \text{ in the direction } N \text{ is} \]

\[ W_0 = \frac{\omega_0 \lambda_0}{2\pi} \]  \hspace{1cm} (5.26)

\[ \text{In the strained state, the actual velocity } W \text{ of the wave is} \]

\[ W = \frac{\omega \lambda}{2\pi} \]  \hspace{1cm} (5.27)
and the natural velocity of the wave is

\[ v = \frac{\omega \lambda_0}{2\pi} \]  

(5.28)

The ratio \( \frac{\omega}{\omega_0} \) directly gives \( \frac{v}{W_0} \) without involving the changes in the dimensions.

Substituting (5.25) in (5.15), we get

\[ \rho_0 v^2 \sum u_j^0 = \sum A_{jk,pm}^S N_p N_m u_k^j \]  

(5.29)

The three linear homogeneous equations (5.29) corresponding to \( j = 1, 2, 3 \) can be solved only if

\[ \left| \rho_0 v^2 \delta_{jk} - D_{jk} \right| = 0 \]  

(5.30)

where \( D_{jk} = \sum A_{jk,pm}^S N_p N_m \)  

(5.31)

giving the natural velocities for any direction of wave propagation. The generalised Gruneisen functions \( \gamma_j(\theta, \phi) \) for the \( j^{th} \) acoustic mode propagating in the direction \((\theta, \phi)\) can be defined as

\[ \gamma_j(\theta, \phi) = - \frac{\partial \log v_j(\theta, \phi)}{\partial \log V} \]  

(5.32)

where \( V \) is the molar volume of the crystal. \( v_j(\theta, \phi) \) is the natural velocity of the \( j^{th} \) acoustic mode propagating in the direction \((\theta, \phi)\) when the lattice is
homogeneously strained by a uniform volume strain $\varepsilon = d\log V$. When a cubic crystal subjected to a hydrostatic pressure, it will experience a uniform volume strain $\varepsilon$ and we have $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \left( \frac{\varepsilon}{3} \right)$. The other components of $\varepsilon_{ij}$ vanish. Expanding (5.31) using (5.23) for this class of crystals with the non-vanishing terms

$$D_{xx} = [C_{11}N_x^2 + \left( N_y^2 + N_z^2 \right) C_{44}] + \frac{\varepsilon}{3}\left[ (C_{111} + 2C_{112} + 3C_{11} + 2C_{12})N_x^2 + (2C_{155} + C_{144} + 2C_{112} + C_{11})N_y^2 + (2C_{155} + C_{144} + 2C_{12} + 2C_{12})N_z^2 \right]$$

$$D_{yy} = [C_{44}N_x^2 + C_{11}N_y^2 + C_{44}N_z^2] + \frac{\varepsilon}{3}\left[ (2C_{155} + C_{144} + 2C_{11} + 2C_{12} + C_{144})N_y^2 + (C_{144} + 2C_{155} + 2C_{112} + 2C_{12} + 2C_{44})N_z^2 \right]$$

$$D_{zz} = [C_{44}(N_x^2 + N_y^2) + C_{11}N_z^2] + \frac{\varepsilon}{3}\left[ (2C_{155} + C_{144} + C_{11} + 2C_{12} + 2C_{44})N_x^2 + (C_{144} + 2C_{155} + C_{112} + 2C_{12} + 2C_{44})N_y^2 + (2C_{112} + C_{12} + C_{111} + 3C_{11})N_z^2 \right]$$

$$D_{xy} = [(C_{12} + C_{44})N_xN_y]\left[ \frac{\varepsilon}{3} \left( 2C_{112} + 2C_{155} + 2C_{12} + 2C_{44} + C_{123} + C_{144} \right)N_xN_y \right]$$

$$D_{xz} = [(C_{12} + C_{44})N_xN_z]\left[ \frac{\varepsilon}{3} \left( 2C_{112} + 2C_{155} + 2C_{12} + 2C_{44} + C_{123} + C_{144} \right)N_xN_z \right]$$

(5.33)
Putting $\rho_0 v^2 = X$, the determinantal equation (5.30) can be expanded to give the cubic equation

$$X^3 - AX^2 + BX - C = 0$$

(5.34)

where $A = D_{xx} + D_{yy} + D_{zz}$

\[
B = \begin{vmatrix} D_{xx} & D_{xy} \\ D_{xy} & D_{yy} \end{vmatrix} + \begin{vmatrix} D_{yy} & D_{yz} \\ D_{yz} & D_{zz} \end{vmatrix} + \begin{vmatrix} D_{zz} & D_{xz} \\ D_{xz} & D_{xx} \end{vmatrix}
\]

\[
C = \begin{vmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{xy} & D_{yy} & D_{yz} \\ D_{xz} & D_{yz} & D_{zz} \end{vmatrix}
\]

(5.35)

The coefficients A, B and C are functions of $\varepsilon$. In the unstrained state, i.e. when $\varepsilon$ is zero, their values are $\overline{A}$, $\overline{B}$ and $\overline{C}$ and the roots of the equation are $\overline{X}_1$, $\overline{X}_2$ and $\overline{X}_3$. Differentiating equation (5.34) with respect to $\varepsilon$ and using the definition

$$\gamma_j(\theta, \phi) = -\frac{1}{2} \frac{\partial \log X_j}{\partial \varepsilon},$$

we have

$$\gamma_j(\theta, \phi) = -\frac{1}{2X_j} \left[ \frac{\overline{X}_j \frac{\partial}{\partial \varepsilon} (A + B) - \frac{\partial}{\partial \varepsilon} (AB - C^2)}{2\overline{X}_j - \overline{A}_0 + \overline{B}_0} \right]$$

(5.36)

The derivatives of A, B and C are to be evaluated at equilibrium configuration. The low temperature limits of the effective GP can be calculated.
using the individual generalised GP of the acoustic modes. In the present study we have considered the variation of the acoustic wave velocities and the generalised GPs as a function of $\theta$, which gives the direction of wave propagation. At very low temperatures where only acoustic modes of long wavelength are predominant the low temperature limit of the GP is calculated using

$$
\gamma_L = \frac{\int \sum_{j=1}^{3} \gamma_j(\theta) v_j^{-3}(\theta) \ d\Omega}{\int \sum_{j=1}^{3} v_j^{-3}(\theta) \ d\Omega}
$$

(5.37)

Here, $v_j(\theta)$ is the velocity of the long wavelength acoustic modes of polarisation index $j$ and $\Omega$ is the solid angle. The low temperature limits in equation (5.37) is evaluated using the generalised GPs of the acoustic modes by numerical integration. Since the solid angle of the cone of semi-vertical angle $\theta$ is proportional to $\sin \theta$, the value $\gamma_j X_j^{\gamma} \sin \theta$ and $X_j^{\gamma} \sin \theta$ at any angle $\theta$ is multiplied by $\sin \theta$ and the sum $\sum \gamma_j X_j^{\gamma} \sin \theta$ over all $\theta$ values is taken to be proportional to $\int \gamma_j X_j^{\gamma} \sin \theta \ d\Omega$. Thus the low temperature limit is obtained as

$$
\gamma_L = \frac{\sum_n \left( \sum_{j=1}^{3} \gamma_j X_j^{\gamma} \right) \sin \theta_n}{\sum_n \left( \sum_{j=1}^{3} X_j^{\gamma} \right) \sin \theta_n}
$$

(5.38)
Jayachandran and Menon [8] reports that the Anderson-Gruneisen Parameter, which accounts for the intrinsic variation of the GP with pressure is given by

$$\delta = \left( \frac{dK}{dp} \right) - 1, \quad (5.39)$$

where $K$ is the bulk modulus of the strained cubic crystal which is given by

$$K = \frac{C_{11} + 2C_{12}}{3} \quad (5.40)$$

Perin [9] reports that the Anderson–Gruneisen Parameter is an important physical quantity, which has been used to describe the adiabatic bulk modulous of a crystalline solid. We can calculate the Anderson–Gruneisen Parameter in terms of SOEC and TOEC as

$$\delta = -1 - \frac{(C_{111} + 6C_{112} + 2C_{123})}{3(C_{11} + 2C_{12})} \quad (5.41)$$

References


