

ordinates of an atom in a lattice be  $X_{i\mu}^m$  and  $x_{i\mu}^m$  respectively, where  $\mathbf{m}$  defines the particular unit cell,  $\mu$  defines the particular atom in that cell and  $i$  defines the co-ordinate direction [1, 3]. For convenience, this notation will be contracted here by replacing  $(\mathbf{m}, \mu, i)$  by  $\alpha$ ,  $(\mathbf{n}, \nu, j)$  by  $\beta$ , etc. The displacement  $\mu_\alpha$  is defined as

$$u_\alpha = x_\alpha - X_\alpha, \quad (1)$$

and the displacement gradient,  $e_{\alpha\beta}$ , as

$$u_{i\mu}^m = e_{i\mu j}^m X_{j\mu}^m, \quad (2)$$

where the long notation is used because the summation is only over  $j$ , not over  $\mathbf{m}$  and  $\mu$ . The expansion of the lattice potential energy,  $\phi$ , is then

$$\begin{aligned} \phi &= \phi_0 + \phi_\alpha^0 u_\alpha + \frac{1}{2} \phi_{\alpha\beta}^0 u_\alpha u_\beta + \dots \\ &= \phi^0 + \phi_\alpha^0 X_\beta e_{\alpha\beta} + \frac{1}{2} \phi_{\alpha\beta}^0 X_\gamma X_\delta e_{\alpha\gamma} e_{\beta\delta} + \dots \quad (3) \\ &= \Phi_0 + \Phi_1 + \Phi_2 + \dots \end{aligned}$$

(Note that this contracted notation involves some ambiguity—the reader is referred to the sources [1, 3, 7] for the full expressions.)

If up to fourth-order terms are retained in (3), the Hamiltonian of the lattice is

$$\begin{aligned} H &= E_k + \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 \quad (4) \\ &= H_0 + H_a, \end{aligned}$$

where

$$H_0 = E_k + \Phi_0 + \Phi_2, \quad (5)$$

$$H_a = \Phi_1 + \Phi_3 + \Phi_4, \quad (6)$$

and  $E_k$  is the kinetic energy of the lattice.  $H_0$  is the 'harmonic' Hamiltonian, and  $H_a$  the anharmonic contribution. The equation of motion derived from (4) is non-linear because of the terms  $\Phi_3$  and  $\Phi_4$ . In order to relinearize it, Leibfried and Ludwig [3] use a perturbation technique based on the assumption that  $\Phi_3$  and  $\Phi_4$  are small. They assume, in effect,

that

$$\begin{aligned} |\Phi_3| &\sim \delta |H_0|, \\ |\Phi_4| &\sim \delta^2 |H_0|, \end{aligned} \quad (7)$$

where  $\delta$  is small compared to unity. The term  $\Phi_1$ , can, in centro-symmetric lattices, be eliminated by the choice of the reference configuration of the lattice. In non-centro-symmetric lattices, a residual term  $\Phi_1$  remains, which is of the order of  $\Phi_3$  [3, p. 354]:

$$|\Phi_1| \sim \delta |H_0|. \quad (8)$$

Note also that since  $\Phi_0$  depends on the arbitrary energy reference level, the significant potential term in  $H_0$  is  $\Phi_2$ . Thus the effect of (7) is to assume  $\Phi_3$  and  $\Phi_4$  to be small relative to  $\Phi_2$ .

The Helmholtz free energy,  $A$ , arising from the Hamiltonian given by (4) is calculated through statistical mechanics using a perturbation method [3, Section 5], retaining terms to  $O(\delta^2)$ . The result has the form [3, p. 324].

$$\begin{aligned} A &= \bar{\phi} + A_s \\ &= \bar{\phi} + A_q + A_a, \end{aligned} \quad (9)$$

where  $\bar{\phi}$  is the static potential energy with every atom in its mean position,  $A_s$  is the vibrational energy consisting of the 'quasi-harmonic' vibrational energy,  $A_q$ , and the 'anharmonic' vibrational energy,  $A_a$ .  $A_q$  has the form of the vibrational energy in the harmonic approximation, but with the eigenfrequencies dependent on the mean configuration:

$$A_q = kT \sum_j \ln [2 \sinh (\frac{1}{2} \hbar \omega_j / kT)], \quad (10)$$

where  $T$  is temperature,  $k$  is Boltzmann's constant,  $\hbar$  is Planck's constant and  $\omega_j$  is the frequency of the  $j$ th mode of vibration of the lattice. The summation is over all modes of vibration, of which there are  $3N$ , where  $N$  is the number of atoms in the lattice.  $A_a$  is a sum of several terms, the forms of which are not important here.

The pressure,  $P$ , is calculated from the identity

$$P = -\left(\frac{\partial A}{\partial V}\right)_T, \quad (11)$$

where  $V$  is specific volume. It is shown by Leibfried and Ludwig[3, Sections 7, 10] that

$$\left(\frac{\partial A_q}{\partial V}\right)_T \sim 0(\delta^3), \quad (12)$$

so that, in the present approximation, this term can be neglected in (11). Thus, from (9),

$$P = -\frac{d\bar{\phi}}{dV} - \left(\frac{\partial A_q}{\partial V}\right)_T + 0(\delta^3), \quad (13)$$

i.e. only the quasi-harmonic vibrational effects enter the pressure.

Equation (13) is thus a *quasi-harmonic* equation of state in which thermal effects enter explicitly through  $A_q$ , and which is implicitly strain (volume) dependent, the second term through the strain dependence of the eigenfrequencies,  $\omega_j$ . The thermal effects are given approximately according to the approximation made in (7), to  $0(\delta^2)$ . For a given material, and thus a given  $\phi$ , the  $\phi_{\alpha\beta}^0$ , etc. are fixed, and the effect of the approximation (7) is to limit the amplitudes of the thermally induced vibrations of the lattice. Macroscopically, the effect is to limit the range of temperatures over which (13) is accurate. Apart from the choice of the mean configuration such that  $\Phi_1$  is eliminated, no other assumption has been made about the mean configuration. This one assumption can be avoided simply by including a constant pressure term in (13). Thus (13) is valid for *arbitrary* specific volumes and confining pressures. The derivation of finite strain expansions of (13) is the subject of the next section. The explicit statements (7, 12, 13) of the approximations in the thermal contribution to (13) will be referred to when the truncation of the expansions of the two terms in (13) is considered.

Finally, the 'Mie-Grüneisen equation' [1, 2, 8] follows from (13) in one additional step. From the form (10) of  $A_q$  and the thermodynamic relation between  $A$ , the internal energy,  $U$ , and the entropy,  $S$ :

$$U = A + TS, \quad (14)$$

it can be shown that[3, p. 355]

$$\begin{aligned} P &= -\frac{d\bar{\phi}}{dV} - \sum_j \frac{d \ln \omega_j}{dV} \left(\frac{\partial A_q}{\partial \ln \omega_j}\right)_T \\ &= -\frac{d\bar{\phi}}{dV} + \frac{1}{V} \sum_j \gamma_j \epsilon_j, \end{aligned} \quad (15)$$

where  $\epsilon_j$  is the energy of the  $j$ th mode of vibration and

$$\gamma_j = -\frac{d \ln \omega_j}{d \ln V} \quad (16)$$

is the  $j$ th 'mode Grüneisen parameter'. Invoking the 'Grüneisen approximation', that all of the  $\gamma_j$  are equal, (15) becomes

$$P = -\frac{d\bar{\phi}}{dV} + \gamma U_q/V, \quad (17)$$

where  $U_q = \sum_j \epsilon_j$  is the quasi-harmonic internal energy, and the  $j$  can be dropped from  $\gamma$ . Equation (17) is the Mie-Grüneisen equation, and the Grüneisen parameter,  $\gamma$ , defined in this way, depends only on  $V$ . A less restrictive procedure is to define a mean Grüneisen parameter,  $\gamma_e$ , as

$$\gamma_e = \frac{1}{U_q} \sum_j \gamma_j \epsilon_j. \quad (18)$$

Using (18) in (15) yields the same form as (17), with  $\gamma_e$  replacing  $\gamma$ . At higher temperatures, when all modes of vibration are excited,  $\gamma_e$  approaches  $\gamma$ , but at lower temperatures  $\gamma_e$  may deviate from  $\gamma$  since the average in (18) is only over the excited modes.