ordinates of an atom in a lattice be $X_i{}^m_\mu$ and $x_i{}^m_\mu$ respectively, where **m** defines the particular unit cell, μ 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 α, $(\mathbf{n}, \nu, j)$ by β, etc. The displacement μ_α is defined as

$$u_\alpha = x_\alpha - X_\alpha, \tag{1}$$

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

$$u_i{}^m_\mu = e_i{}^m_\mu{}_j{}^m_\mu X_j{}^m_\mu, \tag{2}$$

where the long notation is used because the summation is only over j, not over **m** and μ. The expansion of the lattice potential energy, ϕ, is then

$$\phi = \phi_0 + \phi_\alpha{}^0 u_\alpha + \tfrac{1}{2}\phi^0_{\alpha\beta} u_\alpha u_\beta + \cdots$$
$$= \phi^0 + \phi_\alpha{}^0 X_\beta e_{\alpha\beta} + \tfrac{1}{2}\phi^0_{\alpha\beta} X_\gamma X_\delta e_{\alpha\gamma} e_{\beta\delta} + \cdots \tag{3}$$
$$= \Phi_0 + \Phi_1 + \Phi_2 + \cdots.$$

(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

$$H = E_k + \Phi_0 + \Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 \tag{4}$$
$$= H_0 + H_a,$$

where

$$H_0 = E_k + \Phi_0 + \Phi_2, \tag{5}$$
$$H_a = \Phi_1 + \Phi_3 + \Phi_4, \tag{6}$$

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 Φ_3 and Φ_4. In order to relinearize it, Leibfried and Ludwig[3] use a perturbation technique based on the assumption that Φ_3 and Φ_4 are small. They assume, in effect, that

$$|\Phi_3| \sim \delta|H_0|,$$
$$|\Phi_4| \sim \delta^2|H_0|, \tag{7}$$

where δ is small compared to unity. The term Φ_1, can, in centro-systemetric lattices, be eliminated by the choice of the reference configuration of the lattice. In non-centro-symmetric lattices, a residual term Φ_1 remains, which is of the order of Φ_3 [3, p. 354]:

$$|\Phi_1| \sim \delta|H_0|. \tag{8}$$

Note also that since Φ_0 depends on the arbitrary energy reference level, the significant potential term in H_0 is Φ_2. Thus the effect of (7) is to assume Φ_3 and Φ_4 to be small relative to Φ_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 $0(\delta^2)$. The result has the form [3, p. 324].

$$A = \overline{\phi} + A_s$$
$$= \overline{\phi} + A_q + A_a, \tag{9}$$

where $\overline{\phi}$ 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:

$$A_q = kT \sum_j \ln \left[2 \sinh \left(\tfrac{1}{2}\hbar\omega_j/kT \right) \right], \tag{10}$$

where T is temperature, k is Boltzmann's constant, $\hbar$ is Planck's constant and ω_j is the frequency of the jth 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

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

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

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

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

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

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, ω_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 ϕ, the $\phi^0_{\alpha\beta}$, 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 Φ_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:

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

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

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

where ϵ_j is the energy of the jth mode of vibration and

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

is the jth 'mode Grüneisen parameter'. Invoking the 'Grüneisen approximation', that all of the γ_j are equal, (15) becomes

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

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

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

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