3. FINITE STRAIN EQUATIONS OF STATE

The Mie–Grüneisen equation (17), with γ_e of (18) replacing γ, will now be expanded into the domain of finite strain.

There exists an arbitrariness in the definition of measures of finite strain[1, 4–6, 9]. The practical consequence of this is that when Taylor expansions in terms of different strain measures are truncated, different approximations result. The relative empirical merits of some different strains have been discussed previously[e.g. 9]. Of fundamental importance is the requirement that constitutive relations be invariant under changes of frame of reference, or 'frame-indifferent'[4]. In hyperelastic materials, i.e. those elastic materials for which a strain energy function, σ, can be defined, frame-indifference of the stress-strain relation is assured if σ itself is frame-indifferent, and this in turn is assured if σ depends only on a strain measure which is frame indifferent[4–6]. Strain tensors separate into two classes: *material* strain tensors, in which the deformation is referred to the *initial* state, and *spatial* strain tensors, in which the deformation is referred to the *final* state. Material strain tensors are frame-indifferent, while spatial strain tensors are not[4, 6]. The conventional 'Lagrangian' strain tensor, η [5], is an example of a material tensor, and the 'Eulerian' strain tensor, ϵ [5], is an example of a spatial tensor. Thus ϵ should not be used without explicit consideration of the frame-indifference requirement. The frequent use of ϵ in the geophysical literature, through the 'Birch–Murnaghan' and related equations[5, 9–11], has not raised any difficulties because only special situations, in which frame-indifference is trivially satisfied, have been considered[6].

In this paper, equations will be derived in terms of η and a frame-indifferent analogue, E [2], of ϵ. E has the property that it is identical to ϵ for isotropic strains, and its frame-indifference follows from its relationship with η: $(1 - 2E) = (1 + 2\eta)^{-1}$. In terms of specific volume, for isotropic strains, we have[1, 5]

$$\eta_{ij} = \eta \delta_{ij}; \quad \eta = \tfrac{1}{2}[(V/V_0)^{2/3} - 1], \quad (19)$$

$$E_{ij} = E \delta_{ij}; \quad E = \tfrac{1}{2}[1 - (V/V_0)^{-2/3}], \quad (20)$$

where V_0 is the specific volume in the reference (initial) configuration. Although $\epsilon_{ij} = \epsilon \delta_{ij}$, where $\epsilon = E$, in this case, the symbol E will be used henceforth to emphasize the restrictions imposed by the frame-indifference requirement. A displacement gradient, e, analogous to that defined in (2), can also be defined[1], and for isotropic strains,

$$e_{ij} = e \delta_{ij}; \quad e = (V/V_0)^{1/3} - 1. \quad (21)$$

The strain dependence of the vibrational terms A_q and U_q is through the ω_j, so it is made explicit by writing, for instance,

$$\omega_j{}^2 = (\omega_j{}^2)_0 (1 + g_j e + \tfrac{1}{2} h_j e^2 + \cdots), \quad (22)$$

where g_j and h_j are constants. The *square* of ω_j is expanded here because a simple interpretation of g_j and h_j follows in this case. The $\omega_j{}^2$ are linear combinations of the second derivatives of ϕ with respect to displacements, evaluated at the mean configuration[3, p. 304]. Since e is linear in displacements (see equation (2)), it follows from the definitions of g_j and h_j in (22) that they are, respectively, linear combinations of the third and fourth derivatives of ϕ with respect to displacement, evaluated at the mean configuration. Insertion of (22) into the definition (16) of γ_j; leads to an expression for the strain dependence of γ_j:

$$\gamma_j = -\frac{(1 + e)(g_j + h_j e + \cdots)}{6(1 + g_j e + \tfrac{1}{2} h_j e^2 + \cdots)}. \quad (23)$$

If the Mie–Grüneisen approximation is extended, and it is assumed that all of the g_j and h_j are the same, the volume dependence of γ is

$$\gamma = -\frac{(1 + e)(g + h e + \cdots)}{6(1 + g e + \tfrac{1}{2} h e^2 + \cdots)}. \quad (24)$$

If analogous expansions in terms of η and E are made, analogous expressions are obtained:

$$\omega_j^2 = (\omega_j^2)_0(1 + g'\eta + \tfrac{1}{2}h'\eta^2 + \cdots) \quad (25)$$

$$= (\omega_j^2)_0(1 + g''E + \tfrac{1}{2}h''E^2 + \cdots), \quad (26)$$

$$\gamma = -\frac{(1+2\eta)(g' + h'\eta + \cdots)}{6(1 + g'\eta + \tfrac{1}{2}h'\eta^2 + \cdots)} \quad (27)$$

$$= -\frac{(1-2E)(g'' + h''E + \cdots)}{6(1 + g''E + \tfrac{1}{2}h''E^2 + \cdots)}. \quad (28)$$

It is easy to show that

$$\begin{aligned} g' &= g'' = g, \\ h' &= h - g, \\ h'' &= h + 3g. \end{aligned} \quad (29)$$

By a procedure similar to the derivation of (15)[3, p. 356], expansions of A_q and U_q can be derived. For example,

$$A_q(e, T) = A_q^0(T) + \tfrac{1}{2}g U_q^0 e$$
$$+ \tfrac{1}{8}[(2h - g^2)U_q^0 - g^2 T C_q^0]e^2 + \cdots, \quad (30)$$

where $C_q = (\partial U_q/\partial T)_V$ is the quasi harmonic contribution to the specific heat at constant volume, and the extended Mie–Grüneisen approximation has been assumed. Substitution of (30) into (11), combined with a straight-forward expansion of $\overline{\phi}$, yields an equation of state of the form

$$P(e, T) = -\frac{(1+e)}{3V}\left(\frac{\partial A}{\partial e}\right)_T$$
$$= -\frac{(1+e)^{-2}}{3V_0}(a_0 + a_1 e + a_2 e^2 \quad (31)$$
$$+ a_3 e^3 + \cdots),$$

where

$$a_0 = \left(\frac{d\overline{\phi}}{de}\right)_0 + \frac{1}{2}g U_q^0, \quad (31a)$$

$$a_1 = \left(\frac{d^2\overline{\phi}}{de^2}\right)_0 + \frac{1}{4}(2h - g^2)U_q^0 - \frac{1}{4}g^2 T C_q^0, \quad (31b)$$

$$a_2 = \frac{1}{2}\left(\frac{d^3\overline{\phi}}{de^3}\right) + \cdots, \quad (31c)$$

$$a_3 = \frac{1}{6}\left(\frac{d^4\overline{\phi}}{de^4}\right) + \cdots. \quad (31d)$$

Before analogous expressions in terms of η and E are derived, the truncation of the expansion in (31) will be discussed.

It was emphasized in the last section that the quasi-harmonic equation (13) is valid at arbitrary specific volumes, and hence at arbitrary strains. Thus, in principle, an arbitrary number of terms can be retained in its finite strain expansion. The truncation of the expansion will limit its accuracy outside a specified range of strains.

The relative smallness of the thermal contributions means that they need not be carried for as many terms as the static contributions. Consider for instance, equation (31b).

At higher temperatures than the Debye temperature, U_q^0 is approximately linear in T, and C_q^0 is approximately constant. The temperature is the macroscopic expression of the mean thermal vibration amplitude (temperature is proportional to energy, which is proportional to amplitude squared, classically). The presence of h, involving fourth derivatives of ϕ, and g^2 (g involves third derivatives of ϕ) indicates that these thermal terms are $0(\delta^2)$ relative to $(d^2\overline{\phi}/de^2)$—recall that δ specifies the magnitude of Φ_3 and Φ_4 relative to Φ_2, in effect. Similar arguments establish that the thermal contributions to subsequent terms $(a_2, a_3, \ldots)$ are $0(\delta^2)$ relative to the static contribution (the presence of an arbitrary factor in a_0 depending on the choice of the reference state complicates consideration of a_0). Thus, for instance, terms to $0(e^3)$ are included in (31), so thermal terms to $0(e\delta^2)$ need only be retained—in general, the expansion of the thermal contribution can be