

EFFECTIVE ELASTIC MODULI UNDER HYDROSTATIC STRESS—I. QUASI-HARMONIC THEORY*

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Abstract—Fourth-order finite strain expressions for the effective elastic moduli of a solid under hydrostatic stress are derived from a general expression for effective elastic moduli. Expressions in terms of the strain tensors \mathbf{E} and $\boldsymbol{\eta}$ are given. The expressions are then written in terms of the moduli and their pressure derivatives evaluated at an arbitrary reference state. The temperature dependence of these expressions is derived from the fourth-order quasi-harmonic expression for the lattice vibrational energy. Some general thermodynamic relations are derived between the parameters which specify the thermal effects and the pressure and temperature derivatives of the elastic moduli at the reference state. General relations between isothermal and isentropic elastic moduli and their pressure and temperature derivatives are also given. Much of the development is valid for materials of arbitrary symmetry, but the complete development is given only for materials of cubic symmetry.

1. INTRODUCTION

In a previous paper [1], henceforth referred to as Paper I, finite strain equations were derived giving pressure in solids as a function of volume and temperature, the thermal contribution being evaluated in the quasi-harmonic approximation, which results from the fourth-order anharmonic theory of lattice dynamics [2]. Paper I was a reconsideration of the theory given by Thomsen [3]. As Thomsen [4] generalized his theory, so this paper generalizes Paper I to give the effective elastic moduli of a solid as functions of volume and temperature.

A number of points which were made in Paper I carry directly over to the present treatment, and so these points will not be discussed in detail here. In particular, it may be noted that general finite strain relations may be written in an implicitly frame-indifferent form in terms of a whole class of frame-indifferent strain tensors, and not just in terms of the “Lagrangian” strain tensor, $\boldsymbol{\eta}$ (defined later) [5]. Also, that the finite strain expansion of quasi-harmonic thermal contributions may be terminated two orders earlier than the expansion of the static lattice contributions, and that the reference state will again be left arbitrary. The equa-

tions will again be developed in terms of the particular strain tensors $\boldsymbol{\eta}$ and \mathbf{E} . It should again be emphasized that the frame-indifferent analogue, \mathbf{E} , of the “Eulerian” strain tensor, $\boldsymbol{\epsilon}$, should be used rather than $\boldsymbol{\epsilon}$, in general. Equations in terms of the displacement gradient, \mathbf{e} (defined later), will not be developed here. They were useful to the discussion in Paper I, but are not essential to the development.

The equations developed in Paper I can be generalized in two ways—by including the effects of non-hydrostatic stress, and by considering anisotropic materials. A number of authors have discussed the various ways in which second- and higher-order elastic constants (which arise when arbitrary large stresses are considered) may be defined, and their relationship with the “effective” elastic moduli (which arise when infinitesimal stresses are added to prevailing large stresses) [e.g. 3, 6–13]. In general, materials cannot sustain very large non-hydrostatic stresses, and, especially in geophysics, the case of most interest is that of an infinitesimal non-hydrostatic stress superimposed on an arbitrarily large hydrostatic stress. Accordingly, equations will be developed directly for this special case, without reference to the more general treatments. Although much of this paper is valid for materials of arbitrary symmetry, parts of the treatment are greatly simplified by considering only isotropic materials or materials of cubic symmetry, for which the response to a hydrostatic stress is an isotropic

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strain, which can be specified with a single scalar strain parameter.

The treatment separates into three parts. First, the appropriate finite strain expressions for the effective elastic moduli are derived and written in terms of the moduli and their pressure derivatives at zero pressure. Second, the temperature dependence of these moduli is derived from lattice dynamics. Third, some general thermodynamic relations are derived between the equation of state parameters and the elastic moduli and their pressure and temperature derivatives, and between isothermal and isentropic elastic moduli and their pressure and temperature derivatives.

2. EFFECTIVE ELASTIC MODULI UNDER HYDROSTATIC STRESS

In this section, exact general expressions for effective elastic moduli under arbitrary prestress [e.g. 7, 10] are specialized to the case of hydrostatic prestress and, further, to the case of a material of cubic symmetry. The general expressions can be derived by considering either the response of a prestressed material to a further infinitesimal stress, or the equations governing small amplitude waves. The expressions, after specialization, will also be written explicitly in terms of the particular finite strain measures to be used here, and the parameters in these expressions will be related to the pressure derivatives of the effective moduli.

The treatment requires measures of the finite strain induced by the large prestress and of the additional superposed infinitesimal strain. Consider a point in the material which, in the "natural", i.e. unstressed, state has position vector (referred to Cartesian axes) $\mathbf{a} = (a_1, a_2, a_3)$. Denote its position vector after the material is subjected to the prestress as \mathbf{X} , and its position vector after the additional infinitesimal stress as \mathbf{x} . Then the displacement gradients \mathbf{e} , \mathbf{f} and \mathbf{u} may be defined by

$$x_i - a_i = e_{ij}a_j = f_{ij}x_j, \quad (1)$$

$$x_i - X_i = u_{ij}X_j, \quad (2)$$

where u_{ij} is infinitesimal, all quantities are referred to the same Cartesian axes, and the summation convention for repeated indices is assumed.

The Cauchy stress tensor, \mathbf{T} , is related, in general, to the Helmholtz free energy, A , and the density, ρ , of a material by [14, Section 82]

$$T_{ij} = \rho \left(\frac{\partial A}{\partial u_{ij}} \right)_T, \quad (3)$$

and the effective elastic moduli are [7]

$$C_{ijkl} = \frac{\partial T_{ij}}{\partial u_{kl}} \quad (4a)$$

$$= \rho \frac{\partial^2 A}{\partial u_{ij} \partial u_{kl}} - T_{ij} \delta_{kl}. \quad (4b)$$

In deriving (4b), the following relation [4] was used:

$$\frac{\partial \rho}{\partial u_{kl}} = -\rho \delta_{kl}. \quad (5)$$

The moduli defined by (4a) are isothermal or isentropic according to whether the derivative is taken isothermally or isentropically.

Thurston [7] showed that in the special case of hydrostatic prestress the effective moduli are identically given by either \mathbf{C} or \mathbf{c} :

$$c_{ijkl} \equiv \frac{\partial T_{ij}}{\partial s_{kl}} = C_{ijkl} \quad (6)$$

where s is the symmetric component of \mathbf{u} :

$$s_{ij} = \frac{1}{2}(u_{ij} + u_{ji}), \quad \omega_{ij} = \frac{1}{2}(u_{ij} - u_{ji}), \quad (7)$$

and ω is the antisymmetric component. Rewriting \mathbf{u} as

$$\begin{aligned} u_{ij} &= s_{ij} + \omega_{ij} \\ &= \frac{1}{2}(s_{ij} + s_{ji} + \omega_{ij} - \omega_{ji}), \end{aligned} \quad (8)$$

and differentiating, one obtains that

$$\frac{\partial}{\partial s_{kl}} = \frac{1}{2} \left(\frac{\partial}{\partial u_{kl}} + \frac{\partial}{\partial u_{lk}} \right). \quad (9)$$

Thus, in the special case of hydrostatic prestress, $T_{ij} = -P\delta_{ij}$, the effective elastic moduli can be written

$$c_{ijkl} = \frac{1}{2} \left(\frac{\partial T_{ij}}{\partial u_{kl}} + \frac{\partial T_{ij}}{\partial u_{lk}} \right) \quad (10a)$$

$$= \frac{1}{2} \rho \left(\frac{\partial^2 A}{\partial u_{ij} \partial u_{kl}} + \frac{\partial^2 A}{\partial u_{ij} \partial u_{lk}} \right) + P\delta_{ij}\delta_{kl}. \quad (10b)$$

Note that the form (10b) is symmetric under the interchange of subscript pairs $(ij)-(kl)$, as well as under the interchange of k and l . This guarantees symmetry under the interchange of i and j . Thus the form (10) has the full Voigt symmetry of moduli associated with infinitesimal deformations.

The expressions (3) and (10) are referred, through \mathbf{u} , to the prestressed state described through the coordinates \mathbf{X} . They can be referred to the natural state, described by \mathbf{a} , through \mathbf{e} or \mathbf{f} , defined by (1). The tensors \mathbf{e} and \mathbf{f} are not themselves frame-indifferent [5, 14], and so will not lead to constitu-

tive relations which are implicitly frame-indifferent [5]. For this purpose, the tensors \mathbf{E} and $\boldsymbol{\eta}$ (below) will be used as examples of the infinity of possible frame-indifferent strain tensors;

$$E_{ij} = \frac{1}{2}(f_{ij} + f_{ji} - f_{ik}f_{jk}), \quad (11)$$

$$\eta_{ij} = \frac{1}{2}(e_{ij} + e_{ji} + e_{ki}e_{kj}). \quad (12)$$

\mathbf{E} is the invariant analogue of the conventional "Eulerian" strain tensor, $\boldsymbol{\epsilon}$, and $\boldsymbol{\eta}$ is the conventional "Lagrangian" strain tensor [4, 5]. It is convenient to define the deformation gradients \mathbf{G} and \mathbf{F} as

$$G_{ij} = \frac{\partial a_i}{\partial X_j} = \delta_{ij} - f_{ij}, \quad (13)$$

$$F_{ij} = \frac{\partial X_i}{\partial a_j} = \delta_{ij} + e_{ij} = (G^{-1})_{ij}, \quad (14)$$

and to note the relations

$$\frac{\partial}{\partial u_{kl}} = G_{pk} \frac{\partial}{\partial f_{pl}} = F_{lp} \frac{\partial}{\partial e_{kp}}. \quad (15)$$

Expressions for \mathbf{T} and \mathbf{c} in terms of \mathbf{E} and $\boldsymbol{\eta}$ can now be derived using (11)–(15):

$$T_{ij} = \rho G_{mi} \frac{\partial A}{\partial E_{mn}} G_{nj}, \quad (16)$$

$$c_{ijkl} = \rho G_{mi} G_{pk} \frac{\partial^2 A}{\partial E_{mn} \partial E_{pq}} G_{nj} G_{ql} - P \Delta_{ij}^{kl}, \quad (17)$$

where

$$\Delta_{ij}^{kl} = -\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{ij} \delta_{kl}, \quad (18)$$

and

$$T_{ij} = \rho F_{im} \frac{\partial A}{\partial \eta_{mn}} F_{jn}, \quad (19)$$

$$c_{ijkl} = \rho F_{im} F_{kp} \frac{\partial^2 A}{\partial \eta_{mn} \partial \eta_{pq}} F_{jn} F_{lq} - P \delta_{ij}^{kl} \quad (20)$$

where

$$\delta_{ij}^{kl} = \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - \delta_{ij} \delta_{kl}. \quad (21)$$

The application of these expressions requires that the free energy, A , be specified as a function of strain, the usual approach in finite strain theory being to expand A as a Taylor series in some suitable strain measure, such as \mathbf{E} or $\boldsymbol{\eta}$. In practice, these expansions will be truncated, and different truncation errors will be associated with expansions in terms of different strain measures. Thus the descriptions in terms of different strain tensors, equivalent up to this point, will no longer yield

identical results. The development is simplified at this stage by specializing to the case where the material has cubic symmetry. In this case the response to hydrostatic stress is isotropic strain, so that the strain tensors reduce to scalar multiples of the unit tensor. These scalar strains are [1, 3, 4]

$$E = \frac{1}{2}[1 - (\rho/\rho_0)^{2/3}], \quad (22)$$

$$\eta = \frac{1}{2}[(\rho/\rho_0)^{-2/3} - 1]. \quad (23)$$

Thus, expanding A in terms of E , (16) and (17) take the form

$$P = -\frac{1}{3}\rho_0(1-2E)^{5/2}(c_0 + c_1E + c_2E^2 + c_3E^3 + \dots), \quad (24)$$

$$c_{ijkl} = \rho_0(1-2E)^{7/2}(r_{ijkl}^0 + r_{ijkl}^1E + \frac{1}{2}r_{ijkl}^2E^2 + \dots) - P\Delta_{ij}^{kl}. \quad (25)$$

The expression (24) for P has been given previously [1]. The parameters r_{ijkl}^n can be related to the c_{ijkl} and their pressure derivatives, evaluated in the natural state (where $E = 0$), by differentiating (25) and evaluating at $E = 0$:

$$r_{ijkl}^0 = V_0(c_{ijkl} + P_0\Delta_{ij}^{kl}), \quad (26)$$

$$r_{ijkl}^1 = -3V_0K_0(c'_{ijkl} + \Delta_{ij}^{kl}) + 7r_{ijkl}^0, \quad (27)$$

$$r_{ijkl}^2 = 9V_0K_0^2c''_{ijkl} - 3K_0'(r_{ijkl}^1 - 7r_{ijkl}^0) + 16r_{ijkl}^1 - 49r_{ijkl}^0, \quad (28)$$

where a prime denotes a pressure derivative, $V = 1/\rho$ is the specific volume, $K = -V(\partial P/\partial V)$ is the bulk modulus and subscript "0" denotes evaluation at $E = 0$ (implicit in c'_{ijkl} and c''_{ijkl}). The analogous expressions derived from (19) and (20) are:

$$P = -\frac{1}{3}\rho_0(1+2\eta)^{-1/2}(b_0 + b_1\eta + b_2\eta^2 + b_3\eta^3 + \dots), \quad (29)$$

$$c_{ijkl} = \rho_0(1+2\eta)^{1/2}\left(t_{ijkl}^0 + t_{ijkl}^1\eta + \frac{1}{2}t_{ijkl}^2\eta^2 + \dots\right) - P\delta_{ij}^{kl}, \quad (30)$$

$$t_{ijkl}^0 = V_0(c_{ijkl} + P_0\delta_{ij}^{kl}), \quad (31)$$

$$t_{ijkl}^1 = -3V_0K_0(c'_{ijkl} + \delta_{ij}^{kl}) - t_{ijkl}^0, \quad (32)$$

$$t_{ijkl}^2 = 9V_0K_0^2c''_{ijkl} - 3K_0'(t_{ijkl}^1 + t_{ijkl}^0) - 4t_{ijkl}^1 - t_{ijkl}^0. \quad (33)$$

Equations equivalent to (32) and (33) have been given by Birch [15] and Barsch and Chang [13]. It may be noted that the r_{ijkl}^n and t_{ijkl}^n can also be

related to partial contractions of the third and fourth order elastic constants [13]. For the case of cubic symmetry considered here, the parameters c_n of (24) are related to the parameters r_{ijkl}^n of (25) by

$$c_1 = 3(r_{1111}^0 + 2r_{1122}^0), \quad (34)$$

$$c_2 = \frac{3}{2}(r_{1111}^1 + 2r_{1122}^1), \quad (35)$$

$$c_3 = \frac{1}{2}(r_{1111}^2 + 2r_{1122}^2). \quad (36)$$

Analogous relations hold between the b_n of (29) and the t_{ijkl}^n of (30). Again, for cubic symmetry,

$$\Delta_{11}^{11} = -3, \quad \Delta_{11}^{22} = -1, \quad \Delta_{23}^{33} = -1, \quad (37)$$

$$\delta_{11}^{11} = 1, \quad \delta_{11}^{22} = -1, \quad \delta_{23}^{33} = 1. \quad (38)$$

Note that the pressure terms in (25) and (30) need not be taken to the same order as the expressions (24) and (29). For instance, if the original expansion of A in terms of E was to the fourth order, terms up to the third order in E would be kept in (24), but only terms up to second order in E need be kept in (25), since the c_{ijkl} involve second derivatives of A , whereas the pressure involves the first derivative. This truncation procedure differs from that of Thomsen [4], who retained the cubic term in the pressure term in his fourth-order expression for c_{ijkl} . This cubic term is incomplete.

3. THERMAL EFFECTS IN THE QUASI-HARMONIC APPROXIMATION

An approximate description of thermal effects can be included in the preceding finite strain equations by expanding the theory of lattice dynamics, in the quasi-harmonic approximation, into the domain of finite strain. This extension in the present case is a straightforward generalization of the treatment given in Paper I. The Helmholtz free energy of a lattice, A , is the sum of the static lattice potential, $\bar{\phi}$, and the vibrational energy, A_v . In the quasi-harmonic approximation, $A_s = A_q$, where A_q , the quasi-harmonic vibrational energy, depends on strain only through the lattice eigenfrequencies, ω_i [1, 2]. The strain dependence of A_q can thus be made explicit by expanding the (squared) eigenfrequencies in terms of strain. For instance, in terms of \mathbf{E} , the generalization of equation (26) of Paper I is

$$\omega_i^2 = (\omega_i^2)_0 \left(1 + g_{ij}^v E_{ij} + \frac{1}{2} h_{ijkl}^v E_{ij} E_{kl} + \dots \right), \quad (39)$$

where g_{ij}^v and h_{ijkl}^v , etc. are parameters. With the parameters thus defined, the corresponding expansion of A_q is

$$A_q(\mathbf{E}, T) = A_q^0(T) + \frac{1}{2} g_{ij}^v U_q^0 E_{ij} + \frac{1}{8} [(2h_{ijkl}^v - g_{ij}^v g_{kl}^v) U_q^0 - g_{ij}^v g_{kl}^v T C_q^0] E_{ij} E_{kl} + \dots, \quad (40)$$

where

$$U_q = A_q - T \left(\frac{\partial A_q}{\partial T} \right)_{\mathbf{E}} \quad (41)$$

is the vibrational contribution to the internal energy in the quasi-harmonic approximation, and

$$C_q = \left(\frac{\partial U_q}{\partial T} \right)_{\mathbf{E}} \quad (42)$$

is the specific heat at constant strain in the quasi-harmonic approximation. As in Paper I, the extended Grüneisen approximation has been invoked by assuming that the g_{ij}^v and h_{ijkl}^v are independent of ν (or can be replaced by averages over ν [1]), so that the index ν has been dropped in (40). Comparing the expansion (40) with (17) and its expanded form, (25), and recalling that $A = \bar{\phi} + A_q$, the temperature dependence of the parameters r_{ijkl}^n can be derived. Thus,

$$r_{ijkl}^0 = \bar{\phi}_{ijkl}^0 + \frac{1}{4} (2h_{ijkl}^v - g_{ij}^v g_{kl}^v) U_q^0 - \frac{1}{4} g_{ij}^v g_{kl}^v T C_q^0, \quad (43)$$

where the $\bar{\phi}_{ijkl}^0$ are second derivatives of $\bar{\phi}$ with respect to \mathbf{E} . By the argument given at length in Paper I, the expansion of A_q need be carried only to two orders less than the expansion of $\bar{\phi}$. Thus, for a fourth-order expansion of $\bar{\phi}$, for instance, it is sufficient to include the thermal terms only up to c_1 and r_{ijkl}^0 in (24) and (25).

Equations analogous to these in terms of $\boldsymbol{\eta}$ can be derived in a similar manner. Thus, writing

$$\omega_i^2 = (\omega_i^2)_0 \left(1 + g_{ij}^v \eta_{ij} + \frac{1}{2} h_{ijkl}^v \eta_{ij} \eta_{kl} + \dots \right), \quad (44)$$

one obtains

$$t_{ijkl}^0 = \bar{\phi}_{ijkl}^0 + \frac{1}{4} (2h_{ijkl}^v - g_{ij}^v g_{kl}^v) U_q^0 - \frac{1}{4} g_{ij}^v g_{kl}^v T C_q^0. \quad (45)$$

The parameters g_{ij}^v and h_{ijkl}^v can be related to a generalized Grüneisen parameter and its strain derivatives. A generalized Grüneisen parameter can be defined thermodynamically as

$$\gamma_{ij} \equiv -V \left(\frac{\partial T_{ij}}{\partial U} \right)_u, \quad (46)$$

where U is the internal energy. The correct microscopic definition must be found so as to be consistent with this definition. Equation (3) may be written

$$T_{ij} = \rho \frac{d\bar{\phi}}{du_{ij}} + \rho \sum_{\nu} \frac{d \ln \omega_{\nu}}{du_{ij}} \left(\frac{\partial A_{\nu}}{\partial \ln \omega_{\nu}} \right)_T. \quad (47)$$

By defining

$$\gamma_{ij}^{\nu} \equiv -\frac{1}{2} \frac{d \ln \omega_{\nu}^2}{du_{ij}}, \quad (48)$$

and substituting into (47), we can get, using the Grüneisen approximation (i.e. assuming γ_{ij}^{ν} to be independent of ν),

$$\left(\frac{\partial T_{ij}}{\partial U} \right)_u = -\rho \gamma_{ij}, \quad (49)$$

to which (46) reduces in the present approximation.

Now, substituting the expansion (39) into the definition (48), suppressing the index ν , and using (5), (13) and (15), one obtains

$$\gamma_{ij} = -\frac{\omega_0^2}{4\omega^2} (G_{ki}G_{lj} + G_{li}G_{kj})(g_{kl} + h_{klmn}E_{mn} + \dots). \quad (50)$$

Evaluating this and its derivative at $\mathbf{E} = 0$, one can derive that

$$g_{ij} = -2\gamma_{ij}^0, \quad (51)$$

$$h_{ijkl} = -2 \left(\frac{\partial \gamma_{ij}^0}{\partial S_{kl}} \right)_0 + g_{ij}g_{kl} + g_{ik}\delta_{jl} + g_{jk}\delta_{il}. \quad (52)$$

From the definitions, in (39), of g_{ij} and h_{ijkl} and the symmetry of E_{ij} , it may be seen that g_{ij} , and hence γ_{ij} , is symmetric in i and j , and that h_{ijkl} has the full Voigt symmetry, in analogy with the effective elastic moduli, c_{ijkl} .

Again, similar development in terms of η yields

$$g'_{ij} = -2\gamma'_{ij} = g_{ij}, \quad (53)$$

$$h'_{ijkl} = -2 \left(\frac{\partial \gamma'_{ij}}{\partial S_{kl}} \right)_0 + g_{ij}g_{kl} - g_{ik}\delta_{jl} - g_{jk}\delta_{il}. \quad (54)$$

If the material has cubic symmetry, the number of independent parameters g_{ij} and h_{ijkl} is reduced. Thus γ_{ij} , and hence g_{ij} , reduces to a scalar multiple of the unit tensor[2]:

$$\gamma_{ij} = \gamma \delta_{ij}. \quad (55)$$

Also, h_{ijkl} , in analogy with the elastic moduli, reduce to three independent components, h_{1111} , h_{1122} and h_{1212} , or, in the Voigt abbreviated notation, h_{11} , h_{12} and h_{44} . The bulk parameters g and h defined in

Paper I (the actual notation was h'') can be related to g_{ij} and h_{ijkl} by comparing (39) with the corresponding scalar expansion in Paper I:

$$g = g_{ii}, \quad h = h_{iikk}. \quad (56)$$

Thus, for cubic symmetry,

$$g_{ij} = \frac{1}{3}g\delta_{ij}, \quad h = 3(h_{11} + 2h_{12}). \quad (57)$$

Then the general expression (52) reduces to

$$h_{1111} = -2 \left(\frac{\partial \gamma_{11}}{\partial S_{11}} \right)_0 + \frac{g^2}{9} + \frac{2g}{3}, \quad (58)$$

$$h_{1122} = -2 \left(\frac{\partial \gamma_{11}}{\partial S_{22}} \right)_0 + \frac{g^2}{9}, \quad (59)$$

$$h_{1212} = -2 \left(\frac{\partial \gamma_{12}}{\partial S_{12}} \right)_0 + \frac{g}{3}. \quad (60)$$

Similarly, (43) gives

$$r_{11}^0 = \bar{\phi}_{11}^0 + \frac{1}{4}(2h_{11} - g^2/9)U_q^0 - g^2TC_q^0/36, \quad (61)$$

$$r_{12}^0 = \bar{\phi}_{12}^0 + \frac{1}{4}(2h_{12} - g^2/9)U_q^0 - g^2TC_q^0/36, \quad (62)$$

$$r_{44}^0 = \bar{\phi}_{44}^0 + \frac{1}{2}h_{44}U_q^0, \quad (63)$$

where $\bar{\phi}_{\alpha\beta}$ is the appropriate combination of derivatives of $\bar{\phi}$.

The analogues of (58–60) are, from (54),

$$h'_{1111} = -2 \left(\frac{\partial \gamma_{11}}{\partial S_{11}} \right)_0 + \frac{g^2}{9} - \frac{2g}{3}, \quad (64)$$

$$h'_{1122} = -2 \left(\frac{\partial \gamma_{11}}{\partial S_{22}} \right)_0 + \frac{g^2}{9}, \quad (65)$$

$$h'_{1212} = -2 \left(\frac{\partial \gamma_{12}}{\partial S_{12}} \right)_0 - \frac{g}{3}. \quad (66)$$

The analogues of (61–63), derived from (45), have exactly the same form, but with h'_{ijkl} replacing h_{ijkl} .

The above expressions for the temperature dependence of the r_{ijkl}^n and t_{ijkl}^n are for the isothermal parameters, i.e. for the parameters entering the finite strain expansions of the isothermal elastic moduli. The modifications to the derivation necessary to derive the isentropic parameters are simple generalizations of those made in Paper I. The resulting isentropic analogue of (43), for instance, is

$$r_{ijkl}^{0s} = \bar{\phi}_{ijkl}^0 + \frac{1}{4}(2h_{ij} - g_{ij}g_{kl})U_q^0. \quad (67)$$

Note, in particular, that

$$r_{44}^{0s} = \bar{\phi}_{44}^0 + \frac{1}{2} h_{44} U_q^0 \quad (68)$$

which is identical to its isothermal analogue. Thus there is no difference between c_{44}^s and c_{44}^T . This is a well known result.

4. THERMODYNAMIC RELATIONS

In the "isotropic strain" theory of Paper I, the Grüneisen parameter and its volume derivative were related to the bulk modulus and its pressure and temperature derivatives through thermodynamic identities. These identities must be generalized for the present case. The initial part of the treatment given here is similar to that given by Mason [16]. The infinitesimal symmetric strain s defined by (7) will be used in this section. The temperature and entropy will be denoted by θ and σ , respectively, to avoid confusion with the stress, T , and the strain, s .

It is convenient to consider first the relation between isothermal and isentropic elastic moduli. From the first and second laws of thermodynamics, the change of internal energy per unit volume of a system in a reversible process is given by

$$dU = T_i ds_i + \theta d\sigma, \quad (69)$$

where the stress and strain are written in the Voigt notation, as will be all relations henceforth, unless otherwise noted. The Helmholtz free energy, A , is defined by

$$A = U - \theta\sigma, \quad (70)$$

whence

$$dA = T_i ds_i - \sigma d\theta, \quad (71)$$

and

$$T_i = \left(\frac{\partial A}{\partial s_i} \right)_\theta, \quad \sigma = - \left(\frac{\partial A}{\partial \theta} \right)_s. \quad (72)$$

With s_i and θ as independent variables, we may write

$$d\sigma = \lambda_i ds_i + \left(\frac{\partial \sigma}{\partial \theta} \right)_s d\theta, \quad (73)$$

where

$$\lambda_i = \left(\frac{\partial \sigma}{\partial s_i} \right)_\theta = - \left(\frac{\partial T_i}{\partial \theta} \right)_s, \quad (74)$$

using equation (72). In a reversible process, the quantity of heat absorbed by the system is

$$dQ = \theta d\sigma = \theta \lambda_i ds_i + \theta \left(\frac{\partial \sigma}{\partial \theta} \right)_s d\theta, \quad (75)$$

from which we can make the identification

$$\left(\frac{\partial \sigma}{\partial \theta} \right)_s = \frac{\rho C_s}{\theta}, \quad (76)$$

where ρ is density and C_s is the specific heat at constant strain. In an isentropic process, i.e. $d\sigma = 0$, the change in temperature is, from (73),

$$d\theta = - \frac{\theta \lambda_i}{\rho C_s} ds_i. \quad (77)$$

Now, again in terms of s_i and θ , the change in stress is

$$dT_i = c_{ij}^\theta ds_j - \lambda_i d\theta \quad (78)$$

where

$$c_{ij}^\theta = \left(\frac{\partial T_i}{\partial s_j} \right)_\theta \quad (79)$$

is the isothermal elastic modulus. Thus, using (77), the isentropic change in stress is

$$dT_i = \left(c_{ij}^\theta + \frac{\theta \lambda_i \lambda_j}{\rho C_s} \right) ds_j, \quad (80)$$

from which the isentropic elastic modulus is

$$c_{ij}^\sigma = c_{ij}^\theta + \frac{\theta \lambda_i \lambda_j}{\rho C_s}. \quad (81)$$

Using the chain rule of differentiation, we see that

$$\lambda_i = \left(\frac{\partial s_j}{\partial \theta} \right)_T \left(\frac{\partial T_i}{\partial s_j} \right)_\theta = \alpha_i c_{ij}^\theta, \quad (82)$$

where α_i is the thermal expansion tensor.

Next, consider the Grüneisen parameter and its strain derivatives. From the thermodynamic definition (46) of the generalized Grüneisen parameter (using the Voigt notation, and recalling that U is now energy per unit volume),

$$\begin{aligned} \gamma_i &= - \left(\frac{\partial T_i}{\partial \theta} \right)_s \left(\frac{\partial \theta}{\partial U} \right)_s \\ &= V \lambda_i / C_s = V \alpha_i c_{ij}^\theta / C_s, \end{aligned} \quad (83)$$

which generalizes the usual Grüneisen relation.

Equation (83) can be differentiated with respect to s_k , and, using the relations

$$\left(\frac{\partial V}{\partial s_k} \right)_\theta = V \delta_k, \quad (84)$$

where

$$\delta_k = 1 \quad \text{if } k = 1, 2, 3, \quad (85)$$

$$\delta_k = 0 \quad \text{if } k = 4, 5, 6,$$

and

$$\left(\frac{\partial \lambda_i}{\partial s_k} \right)_\theta = - \left(\frac{\partial c_{ik}^\theta}{\partial \theta} \right)_s, \quad (86)$$

(using equation 74), the result is

$$\left(\frac{\partial \gamma_i}{\partial s_k}\right)_\theta = \gamma_i Q_k + D_{ik}^\theta + \gamma_i \left(\frac{\partial c_{ik}^\theta}{\partial T_i}\right)_\theta, \quad (87)$$

where

$$Q_k = \delta_k - \left(\frac{\partial \ln C_s}{\partial s_k}\right)_\theta, \quad (88)$$

$$D_{ik}^\theta = -\frac{V}{C_s} \left(\frac{\partial c_{ik}^\theta}{\partial \theta}\right)_T. \quad (89)$$

The following identity was also used in deriving (87):

$$\left(\frac{\partial}{\partial \theta}\right)_s = \left(\frac{\partial}{\partial \theta}\right)_T - \lambda_i \left(\frac{\partial}{\partial T_i}\right)_\theta. \quad (90)$$

Relations between the derivatives of the isothermal and isentropic elastic moduli can be derived as follows. Define

$$\mu_{ij} = c_{ij}^\sigma - c_{ij}^\theta = \theta \lambda_i \lambda_j / \rho C_s = \theta \rho C_s \gamma_i \gamma_j. \quad (91)$$

Differentiating (91) and using (87),

$$\left(\frac{\partial \mu_{ij}}{\partial T_k}\right)_\theta = S_{nk}^\theta (R_{ijn} - \mu_{ij} Q_n), \quad (92)$$

where

$$S_{ij}^\theta = \left(\frac{\partial s_i}{\partial T_j}\right)_\theta = (c^\theta)_{ij}^{-1}, \quad (93)$$

i.e. S_{ij}^θ are the isothermal elastic compliances, and

$$R_{ijk} = \theta \rho C_s \left[\frac{\partial (\gamma_i \gamma_j)}{\partial s_k}\right]_\theta \quad (94)$$

$$= 2\mu_{ij} Q_k + \theta \rho \lambda_i D_{jk}^\theta + \theta \rho \lambda_j D_{ik}^\theta + \mu_{ij} c_{jk,i}^\theta + \mu_{ij} c_{ik,j}^\theta, \quad (95)$$

where a comma preceding a subscript denotes differentiation with respect to the corresponding stress component.

Similarly, differentiating (91) with respect to θ , and using (90),

$$\left(\frac{\partial \mu_{ij}}{\partial \ln \theta}\right)_T = \mu_{ij} \left[1 + \left(\frac{\partial \ln C_s}{\partial \ln \theta}\right)_s\right] + \theta \rho C_s \left[\frac{\partial (\gamma_i \gamma_j)}{\partial \ln \theta}\right]_s + \theta \lambda_k \left(\frac{\partial \mu_{ij}}{\partial T_k}\right)_\theta. \quad (96)$$

The relations developed so far in this section, i.e. equations (81), (83), (87), (92) and (96), are completely general in that they refer to a material of arbitrary symmetry under an arbitrary stress. They will now be specialized to the case of a material of cubic symmetry under a hydrostatic stress. As was pointed out in Section 2, only one strain parameter is required in this case, so that the application of these relations is simplified. Of

course, the resulting relations can also be further specialized to the case of an isotropic material.

Under cubic symmetry, the thermal expansion tensor becomes

$$\alpha_i = \frac{1}{3} \alpha \delta_i, \quad \alpha = \alpha_i \delta_i = \left(\frac{\partial \ln V}{\partial \theta}\right)_T. \quad (97)$$

Thus,

$$\lambda_i = \frac{\alpha}{3} c_{ij}^\theta \delta_j = \frac{\alpha}{3} (c_{11}^\theta + 2c_{12}^\theta) \delta_i = \alpha K_\theta \delta_i = \lambda \delta_i, \quad (98)$$

where K_θ is the isothermal bulk modulus, and

$$\gamma_i = \frac{\alpha K_\theta}{\rho C_s} \delta_i = \gamma \delta_i, \quad (99)$$

$$\mu_{ij} = \alpha \gamma \theta K_\theta \delta_i \delta_j = \mu \delta_i \delta_j. \quad (100)$$

Note, in particular, that $\mu_{11} = \mu_{12}$ and $\mu_{44} = 0$.

Under hydrostatic stress, $T_i = -P \delta_i$, where P is the pressure, and the strain of a material of cubic symmetry can be specified by the specific volume V . Thus

$$Q_i = \left[1 - \left(\frac{\partial \ln C_v}{\partial \ln V}\right)_\theta\right] \delta_i = Q \delta_i, \quad (101)$$

$$D_{ij}^\theta = -\frac{\gamma}{\alpha K_\theta} \left(\frac{\partial c_{ij}^\theta}{\partial \theta}\right)_P = \gamma \delta_{ij}^\theta, \quad (102)$$

where δ_{ij}^θ is the generalized isothermal analogue of the Anderson-Grüneisen parameter [17, 18]. With these results, equation (87) becomes

$$\left(\frac{\partial \gamma_i}{\partial s_j}\right)_\theta = \gamma \left[Q \delta_i \delta_j + \delta_{ij}^\theta - \left(\frac{\partial c_{ij}^\theta}{\partial P}\right)_\theta\right]. \quad (103)$$

There are three independent derivatives of γ_i in this case, just as there are three independent components each of c_{ij}^θ and δ_{ij}^θ . Note that Q does not contribute to $(\partial \gamma_i / \partial s_i)$. It may also be noted that this derivative is non-zero, even though under cubic symmetry γ_4 is zero. This is because the strain s_4 destroys cubic symmetry, thus allowing γ_4 to vary from zero as s_4 varies from zero. From (103)

$$\left(\frac{\partial \gamma}{\partial \ln V}\right)_\theta = \gamma \left[Q + \delta^\theta - \left(\frac{\partial K_\theta}{\partial P}\right)_\theta\right], \quad (104)$$

where $\delta^\theta = (\delta_{11}^\theta + 2\delta_{12}^\theta)/3$; (104) was given by Basset *et al.* [19].

To specialize equations (92) and (96), note first that

$$\left(\frac{\partial \mu_{ij}}{\partial P}\right)_\theta = -\left(\frac{\partial \mu_{ij}}{\partial T_k}\right)_\theta \delta_k$$

and that $S_{nk} \delta_k = \delta_n / 3K_\theta$. Then

$$R_{ijk}\delta_k = R\delta_i\delta_j = 6\mu\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_\theta \delta_i\delta_j, \quad (105)$$

and

$$\begin{aligned} \left(\frac{\partial \mu_{ij}}{\partial P}\right)_\theta &= \left(\frac{\partial \mu}{\partial P}\right)_\theta \delta_i\delta_j \\ &= -(R - 3\mu Q)/3K_\theta \delta_i\delta_j \\ &= -\frac{\mu}{K_\theta} \left[2\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_\theta - Q \right] \delta_i\delta_j. \end{aligned} \quad (106)$$

The specialization of equation (96) is

$$\left(\frac{\partial \mu}{\partial \theta}\right)_P = \frac{\mu}{\theta} \left[1 + \left(\frac{\partial \ln C_V}{\partial \ln \theta}\right)_V + 2\left(\frac{\partial \ln \gamma}{\partial \ln \theta}\right)_V \right] - \lambda \left(\frac{\partial \mu}{\partial P}\right). \quad (107)$$

Relations equivalent to (106), (107) were given by Barsch [20].

Finally, note that equation (104) involves the derivatives of the isothermal elastic modulus, whereas it is usually the derivatives of the isentropic modulus which are measured experimentally. The conversion from the temperature derivative of one to the other involves $(\partial \mu / \partial \theta)_P$, which involves $(\partial \mu / \partial P)_\theta$, which in turn involves δ^{θ} . Equations (102), (104), (106) and (107) can be solved for $(\partial \mu / \partial P)_\theta$ in terms of just derivatives of isentropic quantities:

$$\begin{aligned} \left(\frac{\partial \mu}{\partial P}\right)_\theta &= \frac{\mu}{K_\theta} \left\{ 2\left(\frac{\partial K_\sigma}{\partial P}\right)_\theta - Q + \frac{2}{\lambda} \left(\frac{\partial K_\sigma}{\partial \theta}\right)_P \right. \\ &\quad \left. - 2\gamma \left[1 + \left(\frac{\partial \ln C_V}{\partial \ln \theta}\right)_V + 2\left(\frac{\partial \ln \gamma}{\partial \ln \theta}\right)_V \right] \right\}. \end{aligned} \quad (108)$$

5. DISCUSSION

The comments made in Paper I, Section 4, concerning the independence of the approximations made in the thermal and finite strain parts of the theory, the Grüneisen approximation, the expansion of γ as a function of volume, the relationship of this work to that of Thomsen [3, 4] and the capabilities of this theory all apply here in the more general case. In particular, note that this theory predicts that the $c_{\alpha\beta}$ are non-linear in temperature at high temperature and constant pressure [4], and that the $(\partial^2 c_{\alpha\beta} / \partial P \partial T)$ are non-zero, in general. Thus, a non-zero value of one of these mixed derivatives does not necessarily mean that a higher order thermal theory is required. Tests of the adequacy of the quasi-harmonic theory will be discussed in a subsequent paper.

The more general theory given here contains the

special theory of Paper I, which can be obtained through the relations (34–36), (56) and (57). It is thus a theory of great utility which is capable of describing the effects of shock-compression and isothermal compression as well as the elastic moduli and elastic velocities as functions of pressure and temperature. Applications demonstrating this utility will be given in a subsequent paper.

The primary parameters which enter these equations are the $r_{\alpha\beta}^n$ or $t_{\alpha\beta}^n$ of (25) and (30), the g_α and $h_{\alpha\beta}$ or $h'_{\alpha\beta}$ of (43) and (45), and the density in the reference state, ρ_0 . These are related to a similar number of secondary parameters: to $c_{\alpha\beta}$, $c'_{\alpha\beta}$, etc. through (26–28) or (31–33), to the thermal expansion tensor, α_β , through (51) and (83), and to the temperature derivatives of the elastic moduli through (52) and (87–89). In the case of cubic symmetry and hydrostatic prestress, the volume coefficient of thermal expansion, α , enters through (99), and the temperature derivatives of the $c_{\alpha\beta}$ through (58–60), (64–66) and (101–103). The evaluation of these parameters follows a scheme analogous to that outlined in Paper I.

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