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QUASI-HARMONIC FINITE STRAIN EQUATIONS OF STATE OF SOLIDS*

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Abstract—Thomsen's 'fourth-order anharmonic' theory, which explicitly evaluates thermal effects in finite strain equations of elasticity according to the fourth-order approximation in lattice dynamics, is reconsidered for the special case of isotropic stresses and strains. It is shown that the approximations made in the finite strain theory are independent from those made in the lattice dynamics theory, with the result that strain dependence may be described in terms of any frame-indifferent strain tensor, not just the 'Lagrangian' strain tensor, η, and that the finite strain expansions may be taken to any order, not just the fourth. This result is valid for general stresses and strains. Illustrative pressure-volume equations are derived in terms of three strain measures, including η and the frame-indifferent analogue, E, of the 'Eulerian' strain tensor, ϵ. The reference state is here left arbitrary, rather than identifying it with the 'rest' state. This results in greater convenience in applying the equations. Not being restricted to fourth order, the present equations do not depend for their application on knowing the second pressure derivatives of the bulk modulus. Expressions are obtained for isentropes and Hugoniots in terms of the same parameters as enter the original equations, which have the form of isotherms. Ultrasonic, thermal expansion and calorimetric data for MgO are used to evaluate the parameters of third-order equations of state of MgO. The equations of state are tested and refined with Hugoniot data. The third-order 'E' Hugoniot is much closer to the data than the third-order 'η' Hugoniot. Inclusion of fourth-order terms allows both 'E' and 'η' Hugoniots to fit the data within their scatter. The separation of Hugoniots corresponding to different initial densities is predicted within the accuracy of the data by the thermal part of this theory.

1. INTRODUCTION

IN AN important pair of papers, Thomsen [1, 2] has given a theory extending lattice dynamics into the domain of finite strain. Such a theory allows thermal effects to be explicitly accounted for at large stresses and in terms of a small number of parameters. However, Thomsen claims that such a theory can be written only in terms of a particular 'Lagrangian' strain tensor, η, with the following reasoning. The 'fourth-order' theory of lattice dynamics of Leibfried and Ludwig[3] is based on a Taylor expansion of the lattice potential energy, ϕ, in terms of atomic displacements which is truncated after the fourth-order terms. Finite strain equations of elasticity are based on a truncated expansion of the Helmholtz free energy, A, in terms of a strain measure (of which there are an infinity of possibilities). Since both microscopic thermal motions and a macroscopic homogeneous strain involve displacements of atoms, it follows, Thomsen argued, that in a theory which purports to describe both thermal and large strain effects, the lattice dynamics and finite strain parts of the theory should both be based on expansions to the same order in terms of the same displacement measure, so that the same approximation is involved in each part of the theory. Thomsen[1, 2] conclude that η was the appropriate measure.

This argument ignores the fact, that, macroscopically, strain and temperature are independent state variables. Microscopically, the *mean relative* displacements of atoms due to a macroscopic straining of the lattice can be varied independently of the *instantaneous relative* displacements due to thermal vibrations. Thus for the isothermal description of

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properties through large strains, thermal effects need not be considered at all, macroscopically, while the isobaric description of properties to high temperatures, for instance, requires only small strains to be accounted for. The independence of strain and temperature means that the usual arbitrariness in the definition of finite strain measures[1, 4] applies (within the restrictions imposed by the 'frame-indifference' requirement[4–6]). Thus 'finite strain' equations may be written as Taylor expansions in terms of any frame-indifferent strain parameter, and truncated at any order. The role of the lattice dynamics theory is to give (approximately) the explicit temperature dependence of such equations.

In this paper, expressions for the Helmholtz free energy and the pressure resulting from the fourth-order anharmonic theory of lattice dynamics[3] are expanded in terms of three different strain parameters to obtain 'finite strain' equations with explicit temperature dependence. Since only the 'quasi-harmonic' contributions to anharmonic thermal effects enter these equations[1, 3], they are referred to here as 'quasi-harmonic equations of state.' Brief illustrative applications are given.

So that the essential points at issue will not be obscured, the treatment in this paper will be limited to the case of isotropic stresses and strains. It will thus be applicable to either isotropic materials or materials of cubic symmetry under hydrostatic stress. The strain parameters considered here, as examples of the infinity of possible strain measures, are the 'Lagrangian' strain tensor, $\boldsymbol{\eta}$, the frame-indifferent analogue, **E**, of the 'Eulerian' strain tensor, $\boldsymbol{\epsilon}$[2, 6], and the displacement gradient, **e**, defined by Thomsen[1] (see below).

An incidental point made here is fourth-order finite strain expansions in terms of $\boldsymbol{\eta}$ do not, in fact, involve the same approximation as that in the fourth-order lattice dynamics theory, as claimed by Thomsen[1], since $\boldsymbol{\eta}$ does not depend linearly on atomic displacements. The appropriate strain measure would be **e**.

A further difference from Thomsen's approach is that the reference state is here left arbitrary, rather than identifying it with the 'rest' state as Thomsen[1] did. The parameters of the equations are then related to measured quantities, such as the bulk modulus and its pressure and temperature derivatives, in the reference state. An inconvenient aspect of Thomsen's[1] equations is thereby avoided. Thomsen's procedure requires the solution of six simultaneous non-linear algebraic equations (his equations (40)) in order to determine the rest-state parameters from room temperature data. In the present procedure, the reference state can be identified with that of the data, and the parameters evaluated with simple independent equations.

Since expressions are obtained here for the Helmholtz free energy and the pressure as functions of both specific volume and temperature it is possible to derive expressions for any other (P, V, T) locus from these. No new parameters or approximations need be introduced in this procedure. Expressions will be derived here for isentropes and Hugoniots.

Available ultrasonic, thermal expansion and calorimetric data for MgO are sufficient to evaluate the equation of state parameters of MgO. The equations of state thus determined are sufficient to predict Hugoniots of MgO. Shock-wave data can then be used to test and refine these equations of state. Comparisons will be given of the thermal and finite strain parts of the equations of state resulting from the use of different strain measures, and of the present equations with those of Thomsen[1].

2. FREE ENERGY AND THE MIE–GRÜNEISEN EQUATION

Leibfried and Ludwig[3] and Ludwig[7] have reviewed the 'fourth-order' theory of anharmonic lattice dynamics, i.e. the case where the lattice potential energy, ϕ, is expanded to fourth-order in atomic displacements. Let the initial and final position coordinates of an atom in a lattice be $X_{i\overset{\mathbf{m}}{\mu}}$ and $x_{i\overset{\mathbf{m}}{\mu}}$ respectively, where $\mathbf{m}$ 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

$$u_{i\overset{\mathbf{m}}{\mu}} = e_{i\overset{\mathbf{m}}{\mu}j\overset{\mathbf{m}}{\mu}} X_{j\overset{\mathbf{m}}{\mu}}, \tag{2}$$

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

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

(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

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

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

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

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-centrosymmetric 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].

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

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:

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

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

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

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

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

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

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

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:

$$U = A + TS, \tag{14}$$

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

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

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

$$\gamma_j = -\frac{\mathrm{d}\ln\omega_j}{\mathrm{d}\ln V} \tag{16}$$

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

$$P = -\frac{\mathrm{d}\bar{\phi}}{\mathrm{d}V} + \gamma U_q/V, \tag{17}$$

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

$$\gamma_e = \frac{1}{U_q}\sum_j \gamma_j\epsilon_j. \tag{18}$$

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.

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, $\boldsymbol{\eta}$[5], is an example of a material tensor, and the 'Eulerian' strain tensor, $\boldsymbol{\epsilon}$[5], is an example of a spatial tensor. Thus $\boldsymbol{\epsilon}$ should not be used without explicit consideration of the frame-indifference requirement. The frequent use of $\boldsymbol{\epsilon}$ 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 $\boldsymbol{\eta}$ and a frame-indifferent analogue, $\boldsymbol{E}$[2], of $\boldsymbol{\epsilon}$. $\boldsymbol{E}$ has the property that it is identical to $\boldsymbol{\epsilon}$ for isotropic strains, and its frame-indifference follows from its relationship with $\boldsymbol{\eta}$: $(1-2\boldsymbol{E}) = (1+2\boldsymbol{\eta})^{-1}$. 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, $\mathbf{e}$, 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,

$$\omega_j^2 = (\omega_j^2)_0(1+g_je+\tfrac{1}{2}h_je^2+\cdots), \quad (22)$$

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 ω_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:

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

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

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

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

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

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

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

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

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,

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

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 $\bar{\phi}$, yields an equation of state of the form

$$P(e,T) = -\frac{(1+e)}{3V}\left(\frac{\partial A}{\partial e}\right)_T = \frac{(1+e)^{-2}}{3V_0}(a_0+a_1e+a_2e^2+a_3e^3+\cdots), \quad (31)$$

where

$$a_0 = \left(\frac{\mathrm{d}\bar{\phi}}{\mathrm{d}e}\right)_0+\frac{1}{2}gU_q{}^0, \quad (31a)$$

$$a_1 = \left(\frac{\mathrm{d}^2\bar{\phi}}{\mathrm{d}e^2}\right)_0+\frac{1}{4}(2h-g^2)U_q{}^0-\frac{1}{4}g^2TC_q{}^0, \quad (31b)$$

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

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

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 $(\mathrm{d}^2\bar{\phi}/\mathrm{d}e^2)$—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 truncated two terms earlier than the static contribution.

The analogous equations in terms of η and E are

$$P(\eta, T) = -\frac{(1+2\eta)^{-1/2}}{3V_0}(b_0 + b_1\eta + b_2\eta^2 + b_3\eta^3 + \cdots), \tag{32}$$

$$b_0 = \left(\frac{\mathrm{d}\bar{\phi}}{\mathrm{d}\eta}\right)_0 + \frac{1}{2}gU_q{}^0, \tag{32a}$$

$$b_1 = \left(\frac{\mathrm{d}^2\bar{\phi}}{\mathrm{d}\eta^2}\right)_0 + \frac{1}{4}(2h' - g^2)U_q{}^0 - \frac{1}{4}g^2TC_q{}^0, \tag{32b}$$

$$b_2 = \frac{1}{2}\left(\frac{\mathrm{d}\bar{\phi}}{\mathrm{d}\eta^3}\right)_0 + \cdots, \tag{32c}$$

$$b_3 = \frac{1}{6}\left(\frac{\mathrm{d}^4\bar{\phi}}{d\eta^4}\right)_0 + \cdots, \tag{32d}$$

and

$$P(E, T) = -\frac{(1-2E)^{5/2}}{3V_0}(c_0 + c_1E + c_eE^2 + c_3E^3 + \cdots), \tag{33}$$

where c_0, c_1, etc. are defined analogously. Again, the thermal contributions are truncated two terms earlier than the static contributions.

Before some further remarks about these equations are made, in the next section, the parameters entering these equations will be related to quantities which are commonly (or potentially) determined experimentally. By successive differentiation of equation (31), the isothermal bulk modulus $K_T = -V(\partial P/\partial V)_T$, and its isothermal pressure derivatives, $K_T' = (\partial K_T/\partial P)_T$, etc., can be obtained in terms of the a's. Evaluating these and equation (31) at $e = 0$, we can solve for the a's in terms of P_0, K_0, etc., where the subscript '0' denotes evaluation at $e = 0$ and the subscript 'T' is dropped for now, obtaining

$$a_0 = -3V_0P_0, \tag{34a}$$

$$a_1 = -3V_0(-3K_0 + 2P_0), \tag{34b}$$

$$a_2 = -3V_0\left(\frac{9}{2}K_0K_0' - \frac{9}{2}K_0 + P_0\right), \tag{34c}$$

$$a_3 = -3V_0\left[-\frac{9}{2}K_0{}^2K_0'' - \frac{9}{2}K_0K_0'(K_0' - 1) - K_0\right]. \tag{34d}$$

Similarly, from equations (32) and (33),

$$b_0 = -3V_0P_0, \tag{35a}$$

$$b_1 = -3V_0(-3K_0 + 3P_0), \tag{35b}$$

$$b_2 = -3V_0\left(\frac{9}{2}K_0K' - \frac{7}{2}P_0\right), \tag{35c}$$

$$b_3 = -3V_0\left[-\frac{9}{2}K_0{}^2K_0'' - \frac{9}{2}K_0K_0'(K_0' + 1) + \frac{1}{2}K_0 + \frac{19}{2}P_0\right], \tag{35d}$$

$$c_0 = -3V_0P_0, \tag{36a}$$

$$c_1 = -3V_0(-3K_0 + 5P_0), \tag{36b}$$

$$c_2 = -3V_0\left(\frac{9}{2}K_0K_0' - 18K_0 + \frac{35}{2}P_0\right), \tag{36c}$$

$$c_3 = -3V_0\left[-\frac{9}{2}K_0{}^2K_0'' - \frac{9}{2}K_0K_0'(K_0' - 7) - \frac{143}{2}K_0 + \frac{105}{2}P_0\right]. \tag{36d}$$

To obtain g and h, we first differentiate equation (24) for γ and solve for g and h, obtaining

$$g = -6\gamma_0, \tag{37}$$

$$h = g\left[3\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_{0T} + g - 1\right]. \tag{38}$$

γ_0 can be obtained from the thermodynamic identity

$$\gamma = \frac{V\alpha K_T}{C_V}, \tag{39}$$

and the volume derivative of γ is given by the identity[12]

$$\left(\frac{\partial \ln \gamma}{\partial \ln V}\right)_T = 1+\delta_T - K'_T - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T, \quad (40)$$

where

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right). \quad (41)$$

In these equations, C_V is the specific heat at constant volume and $\alpha = (\partial V/\partial T)_P/V$ is the volume coefficient of thermal expansion.

Equations (34) to (41) determine the six equation of state parameters V_0, a_1, a_2, a_3, g and h in terms of the six laboratory quantities V_0, K_0, K'_0, K''_0, and $(\partial K/\partial T)_P$. P_0 and a_0 are determined by V_0 and g through (31a) and (34a).

The procedure for determining the parameters is as follows. Assuming that V_0, K_0, K'_0, K''_0, α and $(\partial K/\partial T)_P$ are known at some temperature T_0 and zero pressure, then g and h (which are temperature independent) and a_1, a_2 and a_3 can be evaluated, using (34–41), at T_0. This serves to define the reference state as $P = 0$, $T = T_0$, $V = V_0$. Then $P_0(T_0) = 0 = a_0(T_0)$. Finally, a_0 and a_1, which include the temperature dependence of the equation of state (31), can be evaluated at any temperature T using (31a) and (31b):

$$a_0(T) = a_0(T_0) + \tfrac{1}{2}g[U_q{}^0(T) - U_q{}^0(T_0)], \quad (42a)$$

$$\begin{aligned} a_1(T) = a_1(T_0) &+ \tfrac{1}{4}(2h-g^2) \\ &\times [U_q{}^0(T) - U_q{}^0(T_0)] \\ &-\tfrac{1}{4}g^2[TC_q{}^0(T) - T_0C_q{}^0(T_0)]. \end{aligned} \quad (42b)$$

Of course, in this procedure, $U_q{}^0$ and $C_q{}^0$ must be known or estimated as functions of temperature. For many applications, the Debye or Einstein models can be used to estimate these. These require the empirical input of the characteristic temperature of the solid. If more extensive empirical input of $U_q{}^0$ and $C_q{}^0$ is desired, the specifically anharmonic contribution to the U and C_v must be subtracted before such data are used[3, Part VII].

Illustrative numerical applications of the equations derived in this section are given in a later section and in another paper[13].

4. FURTHER DISCUSSION OF THE THEORY

Firstly, some further comments on the approximations used in the derivation of these equations will be made.

Equations (31), (32) and (33) are all derived from fourth-order expansions (in terms of the appropriate strain) of the free energy. According to the discussion of the previous section, however, these expansions can, in general, be taken to any order. For example if the 'Eulerian' equation is truncated after the third-order term, and P_0 is assumed to be zero, the well known 'Birch–Murnaghan' equation [5, 11] results. The contribution of the present theory is to give, approximately, the explicit temperature dependence of such finite strain equations.

The 'Mie–Grüneisen approximation' was invoked at several points in this derivation. Strictly, such a strong assumption is not necessary. If we were to follow the procedure used in deriving the Mie–Grüneisen form (17) of the equation of state, then we would define, in (30), another mean of the derivatives of the ω_j, and the corresponding summations could thus be replaced. In general, however, these means bear no simple relation to each other. In the Mie–Grüneisen approximation, all of the quantities being averaged are identical and this difficulty is removed. An alternative, weaker assumption, discussed by Leibfried and Ludwig[3] is to replace the means of these derivatives with the derivatives of the mean of the $\omega_j{}^2$, which can be fairly easily calculated from lattice models. Evidently, this approximation may be reasonable at very low or very high temperatures (relative to the Debye temperature), but will be poorer at intermediate temperatures. We see, for instance, that this approximation leaves γ independent of temperature. At high temperatures, γ is observed to be fairly constant, but below the Debye temperature it usually becomes temperature dependent.

The relationship of Thompsen's[1] equations to those derived here should be clarified. Thomsen's equation (40) is analogous to the present equation (32), in terms of η, truncated after the fourth order term. The only substantial difference is that the reference state has not been specified here, whereas Thomsen identified it with the stress-free rest configuration of the lattice. From the point of view of lattice dynamics, the latter is the natural reference state, but if the present equations are viewed as finite strain equations, in which thermal effects are (approximately) explicitly included, then the reference state is arbitrary (with the qualification that the approximation is poorer further from the rest state). Considerable convenience accrues in some applications from identifying the reference state as that at which experimental data are available, since Thomsen's[1] set of six simultaneous non-linear equations, relating his parameters to experimental quantities, is thereby avoided.

The expressions (24), (27) and (28) for γ given here have a certain arbitrariness. It would be possible, for instance, to expand them to the appropriate order in strain, or to do as Thomsen[1] did, i.e. by analogy to the pressure equation, to retain the factor arising from the volume differentiation and expand the remaining quotient. Thomsen's expression (43) for γ, apart from the reference state, is

$$\gamma = (V/V_0)^{2/3}(\gamma_0 + 3\lambda\eta), \tag{43}$$

where $\lambda = -(h' - g^2)/18$, which could be obtained from (27). In principle, there is no reason to prefer any of these forms over the others, but some trial calculations indicate that equations (24), (27) or (28) are less likely to give negative values of γ at large compressions than (43) or its analogues. This may not be a sufficient criterion in some cases, however, since γ may approach zero near a phase change[14].

Thomsen's assertion[1], that the use of a fourth-order expansion in terms of η assures consistency with the expansion (3) of ϕ upon which the lattice dynamics is based can be seen to be incorrect. In fact, from (19) and (21), $\eta = e + \frac{1}{2}e^2$. Substitution of this relation into a fourth-order η expansion would yield up to eighth-order terms in e. Thus truncation of an e expansion at the fourth order would involve a different truncation error, and hence a different approximation.

Finally, some comments on the capabilities of the present theory. Thomsen[2, p. 367] pointed out that although this theory predicts that the elastic moduli (in the present case, K) are linear in T at high temperature and at constant *volume*, this does not imply linearity at constant *pressure*. Thus, measured nonlinearity of elastic moduli with T, taken at zero pressure, does not imply that a higher-order thermal theory is required. However, Thomsen[1, p. 2009, 2010; 2, p. 370] goes on to claim that non-zero values of $(\partial^2 c_{\alpha\beta}/\partial P \partial T)$, where $c_{\alpha\beta}$ is an elastic modulus, *do* require a higher-order theory for their description. It has been argued here that the Mie–Grüneisen equation is valid at arbitrary volumes; therefore an arbitrary number of derivatives may be taken and the thermal contribution will be concluded, though it will still be $0(\delta^2)$. Thus, thermal contributions to all pressure derivatives of elastic moduli will result from this theory. Of course, the predicted *value* of the temperature coefficient may not agree with measured values, but the mere existence of a non-zero temperature coefficient is not sufficient grounds for requiring a higher order *thermal* theory.

5. ISENTROPES

The Mie–Grüneisen equation (17) can be regarded as giving the pressure either as a function of strain and temperature, or as a function of strain and entropy. Thus an expression for the pressure along an isentrope can be obtained by expanding (17) in terms of strain at constant entropy. The temperature, or entropy, dependence of (17) is through U_q. From the result[3, p. 356] that

$$\left(\frac{\partial U_q}{\partial V}\right)_s = -\frac{\gamma}{V}U_q, \tag{44}$$

one can obtain the expansion of U_q in terms of e, for instance, at constant entropy:

$$U_q(e, S) = U_q{}^0 + \tfrac{1}{2}gU_q{}^0 e + \tfrac{1}{8}(2h - g^2)U_q{}^0 e^2 + \cdots. \tag{45}$$

The result of substituting (45) into (17) is an equation of exactly the same form as (31):

$$P(e, S) = -\frac{(1+e)^{-2}}{3V_0}(a_{0s} + a_{1s}e + a_{2s}e^2 + a_{3s}e^3 + \cdots) \tag{46}$$

where the new coefficients are

$$a_{0s} = \phi_0{}^{\mathrm{I}} + \tfrac{1}{2}gU_q{}^0, \tag{46a}$$

$$a_{1s} = \phi_0{}^{\mathrm{II}} + \tfrac{1}{4}(2h - g^2)U_q{}^0, \tag{46b}$$

$$a_{2s} = \tfrac{1}{2}\phi_0{}^{\mathrm{III}} + \cdots, \tag{46c}$$

$$a_{3s} = \tfrac{1}{6}\phi_0{}^{\mathrm{IV}} + \cdots. \tag{46d}$$

Analogous results are obtained for the equations in terms of η and E. Equations (46) thus give the pressure along an isentrope in terms of the same parameters (namely g, h, and the derivatives of ϕ) as (31) for an isotherm.

6. HUGONIOTS

In principle, it is possible to relate derivatives along a Hugoniot to isothermal derivatives in a manner similar to that of the previous section, but since these relations are more complicated, it is easier to obtain the Hugoniot pressure from the energy difference between it and some reference curve. Expressions for Hugoniots have been given, for instance, by Thomsen[1] who related the Hugoniot to the static pressure $-(\mathrm{d}\phi/\mathrm{d}V)$, and, for example, Ahrens *et al.* [15] and McQueen *et al.*[16] who relate the Hugoniot to an isentrope. Since the latter method does not require the intermediate calculation of the derivatives of ϕ, and since the results of the last section can be used, it will be used here.

The Hugoniot equation derived here will be generalized to take account of possible initial porosity of the material or a phase change during the shock process. The term 'high pressure phase' will be taken here to include the compacted, non-porous material in the case of initial porosity.

Take the initial state of the material to be $P = 0$, $V = V_0'$, $T = T_0$, the $(P = 0, T = T_0)$ volume of the high pressure phase to be V_0, and the final shocked state to be (P_h, V, T_h). The Rankine–Hugoniot equations give, in this case,

$$U(V, T) - U(V_0', T_0) = \tfrac{1}{2}P(V_0' - V), \tag{47}$$

where U is the total internal energy, which, in the quasi-harmonic approximation, is $U = \bar{\phi} + U_q$. Define the transition energy E_t as

$$E_t = U(V_0, T_0) - U(V_0', T_0). \tag{48}$$

E_t can be obtained from the enthalpy of phase change, if it is known. If there is no phase transition, i.e. if there is only a reduction of porosity, then this can be taken as zero (the surface energy of the pores can be neglected [17]).

If the pressure and temperature on the isentrope centered at $P = 0$, $V = V_0$ are P_s and T_s, respectively, at V, then, from (17)

$$P_h - P_s = \frac{\gamma}{V}[U_q(V, T_h) - U_q(V, T_s)]. \tag{49}$$

P_s can be calculated according to the previous section. From the identity

$$P = -\left(\frac{\partial U}{\partial V}\right)_s, \tag{50}$$

we see that

$$\Delta U \equiv U(V, T_s) - U(V_0, T_0)$$
$$= -\int_{V_0}^{V} P_s \, \mathrm{d}V. \quad (51)$$

Thus for instance, if P_s is given in terms of e,

$$\Delta U = a_{0s}e + \tfrac{1}{2}a_{1s}e^2 + \tfrac{1}{3}a_{2s}e^3 + \tfrac{1}{4}a_{3s}e^4. \quad (52)$$

Eliminating $U_q(V, T_h)$ between (47) and (49), using (48) and noting that $\phi(V_0) = 0$, the final expression for the Hugoniot is

$$P_h\left[1 - \frac{\gamma}{2}\left(\frac{V_0'}{V} - 1\right)\right] = P_s - \frac{\gamma}{V}(\Delta U + E_t). \quad (53)$$

7. EQUATION OF STATE OF MgO

The elastic moduli of single-crystal MgO have been measured as a function of pressure and temperature by Spetzler[18]. The bulk modulus and its first pressure and temperature derivatives can be determined from such measurements. The parameters determined by Spetzler[18] are listed in Table 1, along with the density, thermal expansion coefficient and specific heat of MgO, from the indicated sources.

Table 1. *Zero pressure elastic and thermodynamic data of magnesium oxide at* 300°K

ρ_0(g/cm^3) [20]	3·584
K_{0T} (Mb) [18]	1·605
K'_{0T} [18]	3·89
$(\partial K_{0T}/\partial T)_P$ (Kb/°K) [18]	$-0{\cdot}272$
α_0 (°K)$^{-1}$ [20]	$3{\cdot}15 \times 10^{-5}$
C_V (erg/g°K) [21]	$9{\cdot}25 \times 10^{6}$

These parameters were used in (34–41) to determine the parameters of the equations of state (32) and (33), in terms of η and E, respectively. Since the second pressure derivative of the bulk modulus, K'', is not given, only the third-order versions of these equations are determined in this way.

Using the 300°K isotherms given by (32) and (33) the corresponding isentropes and Hugoniots were calculated according to the previous sections.

The fact that both the finite strain and the thermal parts of the equation of state are determined, so that Hugoniots can be calculated with reasonable accuracy, means, in effect, that extrapolations of the lower pressure data (specifically, the ultrasonic data) can be tested against Hugoniot data.

Carter *et al.*[19] have given data for a series of MgO Hugoniots, corresponding to different initial densities of the MgO samples. The lower initial density Hugoniots obtained by them are offset to higher pressures, and hence higher temperatures, than the single-crystal Hugoniot at the same density. These data thus provide a test of both the finite strain and the thermal parts of the present theory.

First, consider the finite strain part of the theory. In Fig. 1 are shown the single-crystal

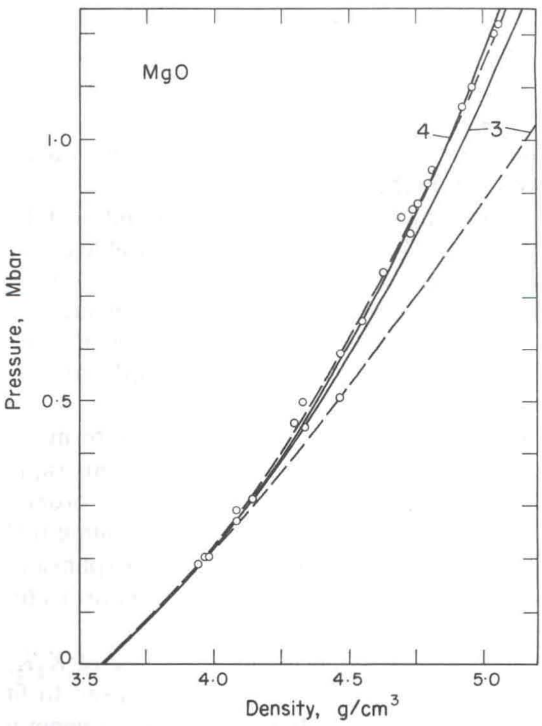

Fig. 1. Third- and fourth-order single-crystal MgO Hugoniots calculated in terms of E (solid) and η (dashed), compared with Hugoniot data of Carter *et al.*[19].

Hugoniot data of Carter *et al.*[19], along with the corresponding third-order Hugoniots calculated in terms of both the η and E strain measures. It can be seen that the 'E' Hugoniot is considerably closer to the data than the 'η' Hugoniot. This is an example of the empirical superiority of the 'E' equations which was, of course, pointed out by Birch [9, 10], and is the reason for the subsequent popularity of the 'Birch–Murnaghan' equation [11].

Also shown in Fig. 1 are fourth-order η and E Hugoniots in which K_0'' was determined by requiring a least-squares fit of the calculated curve to the data. The resulting values of (K_0K_0'') are given in Table 2. Clearly, the fourth-order η and E Hugoniots fit equally well within the scatter of the data.

Table 2. Values of K_0K_0'' of MgO determined from Hugoniot data

Strain measure	K_0K_0''
η	10·5
E	−1·1

Comments on two important points can be made here. Firstly, it is clearly desirable to use an equation of state which involves the least number of disposable parameters, while still giving an acceptable representation of data. The greater success of the third-order E equation indicates faster convergence of the expansion in terms of E than that in terms of η. While there is no guarantee that this rapid convergence will continue to higher orders, it is certainly more reasonable to assume this about the E expansion than the η expansion, and E therefore appears to be a more useful strain measure than η.

The second point is that the value of K_0K_0'' obtained depends on the equation used to fit the data (Table 2). It is, of course, a general property of truncated series expansions that the higher-order coefficients are less well determined empirically, but it is one that seems to have received little notice in the context of finite strain expansions.

The thermal part of the equation of state will now be discussed. The volume dependence of γ resulting from equations (24, 27, 28, 43) is shown in Fig. 2. For the range of compressions, shown, the differences are not large. At larger compressions, γ given by (43) will be the first to become negative.

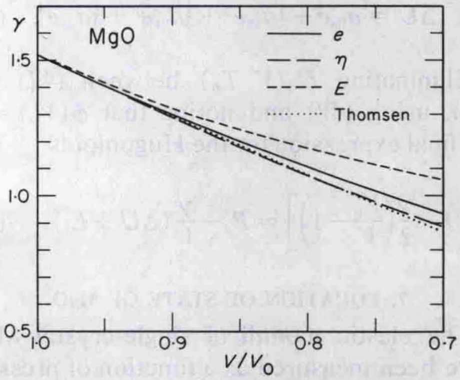

Fig. 2. Grüneisen parameter, γ, of MgO calculated from equations (24), (27) and (28), in terms of e, η and E, respectively, and from (43) given by Thomsen[1].

As mentioned previously, the Hugoniot data for different initial densities provide a test of the thermal part of the theory. The fourth-order E equations, with K_0'' evaluated from the single-crystal Hugoniot data (Table 2), were used to calculate the corresponding family of Hugoniots. These are compared with the data in Fig. 3. There is considerable scatter in the data but the separation of the various Hugoniots is quite apparent. The calculated Hugoniots reproduce this separation to within the scatter of the data. The fourth-order η equations would have yielded slightly smaller separations, as shown by the extrapolations of γ in Fig. 2, and would thus appear to be slightly less successful in explaining the data, but the evidence is marginal.

In conclusion, the finite strain extrapolations of the Mie–Grüneisen equation devel-

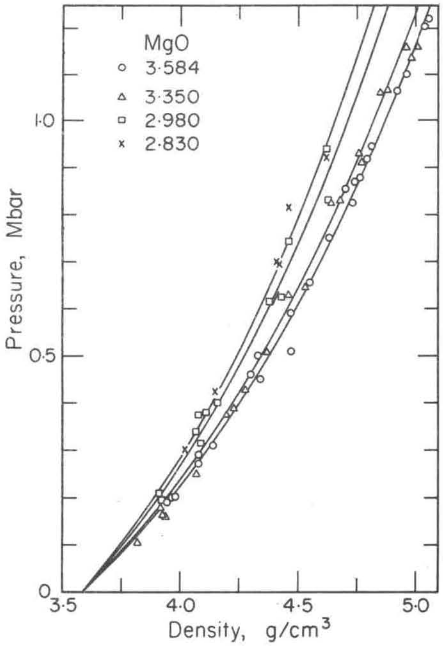

Fig. 3. Calculated MgO Hugoniots of different initial densities compared with Hugoniot data of Carter *et al.* [19]. Symbols are labelled with initial density of samples.

oped here appear to explain the available MgO Hugoniot data quite successfully. The strain parameter E appears to be more empirically successful than η.

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