J. Phys. Chem. Solids Pergamon Press 1970. Vol. 31, pp. 2003–2016. Printed in Great Britain.

ON THE FOURTH-ORDER ANHARMONIC EQUATION OF STATE OF SOLIDS*

LEON THOMSEN
Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y. 10964, U.S.A.

(*Received* 21 *April* 1969; *in revised form* 8 *September* 1969)

Abstract – The non-uniqueness of the definition of finite 'strain' is demonstrated to lead to significant ambiguities in the equation of state of elastic solids. The ambiguities are resolved by the rigorous derivation (due to Leibfried and Ludwig) of the Mie–Grüneisen equation. Closed expressions for $\phi_0(V)$ and $\gamma(V)$ are presented which contain *no* assumptions additional to those already present in the simple M–G equation. Numerical equations of state for NaCl and MgO are presented which satisfy all ultrasonic and shock-compression data. Comparison with previous tabulations for NaCl reveals small but significant discrepancies.

1. FINITE STRAIN

It is a well-known result[1, 2] of continuum mechanics that the theory of finite strain may be written equivalently in terms of any of an infinite number of different definitions of the 'strain'. For the case of an *elastic* solid (i.e. one possessing a free-energy function which is uniquely defined in terms of deformation and temperature), this result implies, specifically, that the *stress–strain relation* may be written equivalently in an infinite number of ways.

As examples, if the strain $\mathbf{e}$ is defined implicitly in terms of the deformation $\mathbf{R}-\mathbf{R}_0$ by

$$\mathbf{R}-\mathbf{R}_0 \equiv \mathbf{e}\mathbf{R}_0 \tag{1}$$

then the stress–strain relation is

$$\boldsymbol{\sigma} = (\mathbf{1}+\mathbf{e})\left(\frac{\partial F}{\partial \boldsymbol{\eta}}\right)_T(\mathbf{1}+\mathbf{e}^\dagger)\frac{1}{V}. \tag{2}$$

Here $\mathbf{R}$ is a vector to a point in the deformed lattice, $\mathbf{R}_0$ is the vector to the same point in the undeformed reference state, denoted in this section by a sub-zero. The components of both are referred to the same set of Cartesian axes. $\mathbf{e}$ is the finite strain tensor defined by (1). $\boldsymbol{\sigma}$ is the (homogeneous) stress at the point $\mathbf{R}$. $\mathbf{1}$ is the unit 3×3 tensor, $(\mathbf{1})_{ij} = \delta_{ij}$. F is the Helmholtz free energy, or 'elastic energy' function. $\boldsymbol{\eta}$ is the symmetric finite strain tensor defined in relation to $\mathbf{e}$ by

$$\eta_{ij} \equiv \tfrac{1}{2}(e_{ij}+e_{ji}+e_{mj}e_{mi}). \tag{3}$$

Equation (2) is exact, i.e. independent of the size of $\mathbf{e}$. It is derived by, e.g. Leibfried and Ludwig[3] and by Murnaghan[4].

Alternatively, the strain $\mathbf{f}$ can be defined implicitly by

$$\mathbf{R}-\mathbf{R}_0 \equiv \mathbf{f}\mathbf{R} \tag{4}$$

and then the stress–strain relation is

$$\boldsymbol{\sigma} = (\mathbf{1}-2\boldsymbol{\epsilon})\left(\frac{\partial F}{\partial \boldsymbol{\epsilon}}\right)_T\frac{1}{V} \tag{5}$$

with the symmetric tensor $\boldsymbol{\epsilon}$ defined in relation to $\mathbf{f}$ by

$$\epsilon_{ij} \equiv \tfrac{1}{2}(f_{ij}+f_{ji}-f_{mj}f_{mi}). \tag{6}$$

Equation (5) is also exact, though its generality is restricted to special situations, including the important cases of isotropic bodies, and of

---

*Lamont-Doherty Geological Observatory Contribution No. 1424.

pure strains unaccompanied by rotations. It is derived by, e.g. Murnaghan[5].

Not directly involved in the proofs of (2) and (5) are the relations between strain and volume change:

$$\left(\frac{V}{V_0}\right)^2 = |\det(\mathbf{1}+2\boldsymbol{\eta})| \tag{7}$$

$$\left(\frac{V_0}{V}\right)^2 = |\det(\mathbf{1}-2\boldsymbol{\epsilon})| \tag{8}$$

V is, of course, specific volume.

The difference between these two definitions of strain (1) and (4) is clearly in the choice of the characteristic lengths used as coefficients of the strain on the RHS of the two definitions. In the first case, the characteristic lengths are taken from the reference state; in the second, from the deformed state. Because of this essential difference, the strains **e** and $\boldsymbol{\eta}$ are called *Lagrangian* or *material* definitions of strain; the strains **f** and $\boldsymbol{\epsilon}$ are called *Eulerian* or *spatial*. These, and other definitions of strain can be, and have been, derived with more generality than is needed here. An elegant, and exhaustive, discussion of finite strain is given by Truesdell[1]; a more limited, pedagogic treatment is given by Thomsen[6].

Although (2) and (5) are exact, their usefulness is limited by the need for expressions for the free energy as a function of the strain. In general, the physical description of the free energy in terms of interatomic forces, etc. will impose requirements on the choice of a definition of strain[7]. Also, any approximations made in F will affect the results of the choice of a definition of strain. Hence, the *application* of (2) and (5) to real solids will *not* be exact, and further, will depend critically upon the choice of a definition of strain. Different choices lead to non-equivalent equations of state.

As an illustration of this, consider the special case of hydrostatic pressure P on an isotropic body. Both (2) and (5) reduce to

$$P = -\left(\frac{\partial F}{\partial V}\right). \tag{9}$$

Equations (7) and (8), however, do *not* reduce to the same form, but rather to

$$\eta = \frac{1}{2}\left[\left(\frac{V}{V_0}\right)^{2/3} - 1\right] \tag{7a}$$

$$\epsilon = -\frac{1}{2}\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right] \tag{8a}$$

$$= \left(\frac{V_0}{V}\right)^{2/3}\eta. \tag{8b}$$

The fact that V_0 appears in the denominator of (7a) and in the numerator of (8a) is an expression of the essential difference between the Lagrangian and the Eulerian definitions of strain.

If the free energy is assumed to be of the form

$$F = \sum_{i=1}^{i_m} A_i\eta^i \tag{10}$$

with $i_m = 3$, then (9) and (7a) give the *third-order Lagrangian isotherm*

$$P = \tfrac{3}{2}K_0(y^{1/3} - y^{-1/3})\left[1 - \tfrac{3}{4}K_0'(y^{-2/3} - 1)\right] \tag{11}$$

where y is the volume ratio

$$y = \frac{V_0}{V} = \frac{\rho}{\rho_0}. \tag{12}$$

Here the coefficients A_i have been evaluated in terms of the boundary value measurements at the reference state, taken here to be defined by $P = 0$, $T = T_0$ = room temperature. K is the isothermal incompressibility; K' is $(\partial K/\partial P)_T$; ρ is density. This equation appears in Murnaghan's 1951 monograph[4], p. 71.

As is clear from the symmetry apparent in (2) and (5), or in (9), (7a) and (8a), an assumption equally as plausible (at this point in the argument) as (10) is