

## Irreversible thermodynamics of flow in solids

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Dynamic deformation of solid materials is described in terms of nonuniform material motion and simultaneous thermoelastic strain and plastic flow. For deformations of arbitrary form and magnitude in an initially isotropic solid, an approximate expression for the entropy production is given, and the interrelations among the thermodynamic variables of stresses, elastic and plastic strains, and temperature and entropy are derived. The theory is specialized to plane-wave geometry, appropriate for describing a weak planar shock, and is compared with the relaxing solid model which has previously been used to analyze plane shocks in solids. A qualitative examination of the mechanics of elastic strain and plastic flow indicates that a thermodynamic description is accurate for many fast deformation processes in solids.

### I. INTRODUCTION

The dynamic flow processes of solids have come under careful study in recent years with the development and use of high-speed, high-stress diagnostic capabilities [for a recent review see Ref. 1(a)]. The resulting data have in turn provided the main basis for new developments in both microscopic and macroscopic theories for the equation-of-state, transport, and flow properties of solids at high stresses. Dislocation theory for example has been extensively used in modeling the flow properties of crystalline and polycrystalline materials. However, it is first of all necessary to obtain a clear macroscopic characterization of material flow properties exhibited in the experimental data. This necessitates an extended continuum mechanic flow formalism for solids, whose general formulation and thermodynamic validity is studied in this paper.

The purpose of this paper is to present a physical description of fast deformation processes in solids. The description is mechanic and thermodynamic; it is embodied in a coupled set of equations which governs the motion of the material and the simultaneous thermoelastic and flow processes. Before going into the formal theory, some discussion of the nature of these processes is useful.

In a thermoelastic process, the material passes through a sequence of equilibrium states, i.e., states characterized by zero entropy production, and the process is reversible. The variables are the anisotropic stresses and elastic strains, the energy, temperature, entropy, and so on; these variables are related in differential form by the standard equations of thermoelasticity.<sup>1(b),2</sup> The question arises: What are the limitations on the space and time rates at which system variables may change and still be treated by reversible thermodynamics? An answer in the spirit of statistical mechanics is that in space the system variables

must change by a small amount over a region large enough to contain many atoms, and in time the variables must change slowly in comparison with the characteristic rate (or rates) at which the system approaches equilibrium. Such restrictions do not rule out some rather fast thermoelastic processes; in transmitting an adiabatic sound disturbance with wavelength of order  $10^{-3}$  cm and period of order  $10^{-8}$  s, a solid can be described as a large number of material elements, each passing through a sequence of near-equilibrium states under the influence of slowly varying stresses imposed by neighboring material elements.

For the second type of process, a general and for the moment not complete definition is as follows: Flow is any dissipative rearrangement of the atoms within a material. When thinking of solids, we usually call this plastic flow. Such a process is by definition irreversible. It can still be described in thermodynamic terms, however, if the rate-of-change limitations mentioned above are satisfied. Then the material passes through a sequence of states which are close to thermodynamic equilibrium states and, hence, the state of the material is always described to a sufficient approximation by thermodynamic variables. To complete the description of the process, it is required to devise an explicit expression for the entropy production. These two requirements are at the base of the theory of irreversible thermodynamics.<sup>3,4</sup> For example, imagine a polycrystalline material with a shear stress  $\tau$  applied and slowly increased from zero. At first the material deforms elastically, and when  $\tau$  reaches the appropriate static yield value the flow, as measured by a plastic shear strain  $\psi$ , begins. The flow is irreversible and entropy production is positive. A phenomenological relation<sup>3</sup> of the form  $\tau \propto \psi$  does not hold because  $\tau$  reaches a finite value while  $\psi$  is still zero. This essential nonlinearity cannot be treated by standard irreversible thermodynamics; nevertheless there

is a driving force and there is a reciprocal flow, and it is possible in principle to relate these quantities to the entropy production. Further, such a relation can be determined, or verified, by experiment.

It is interesting to compare time-rate effects for the two types of process discussed. A thermoelastic process is rate independent (up to some limit), which means for example the stresses change "instantly" in response to changes in the elastic strains and the entropy. Flow, however, is intrinsically rate dependent. In the plastic shear experiment mentioned above, there is a functional relation, generally called the plastic constitutive relation, among the variables  $\tau$ ,  $\psi$ , and  $\dot{\psi}$ , where  $\dot{\psi}$  is the time derivative of  $\psi$  at a fixed material point. Formally it is  $f(\tau, \psi, \dot{\psi}) = 0$ , which means the driving stress  $\tau$  depends explicitly on how fast the flow is being driven. We note in passing that the indicated dependence on  $\psi$  is to account for strain hardening, and that the plastic constitutive relation depends also on the thermoelastic state variables.

Now with regard to time-rate effects, a point of some significance is as follows. A thermoelastic process can be very fast and still be, to a good approximation, reversible. On the other hand, again with reference to the plastic shear experiment, it is possible to control  $\tau$  so that  $\dot{\psi}$  is arbitrarily small, but the flow is still irreversible. Entropy production accompanies the process no matter how slowly it proceeds. Hence the thermodynamic reversibility of a process is not determined by its rate.

In the following section the general theory of dynamic deformation processes in an initially isotropic solid is presented. The theory is specialized in Sec. III to plane-wave geometry, appropriate for describing a planar shock, and the theory is compared in Sec. IV with the relaxing solid model. In Sec. V we discuss in qualitative terms the question of local thermodynamic equilibrium. In applying the present theory to shocks in solids, we limit consideration to weak shocks, i.e., ones in which the shock velocity is not greater than the elastic precursor velocity, which means shock stresses up to one hundred kbar or so.

## II. GENERAL THEORY

### A. Equations of motion

We consider a spatially continuous isotropic solid. The definition of isotropic solid is given in Sec. IV, but it should be noted in advance that such a material can support anisotropic elastic strain and in such a configuration the material is physically anisotropic. At any time  $t$  the location of a given infinitesimal mass element of the material is  $\vec{x}(t)$

in laboratory coordinates; at some initial (reference) time  $t_a$  it is  $\vec{x}(t_a) = \vec{X}$ , so that  $\vec{X}$  is the Lagrangian coordinate of the mass element. The field variable which denotes the whole material configuration is  $\vec{x}(\vec{X}, t)$  for all  $\vec{X}, t$ . The velocity field  $\vec{v}(\vec{X}, t)$  is the velocity in laboratory coordinates of each mass element:

$$\vec{v} = \left( \frac{\partial \vec{x}}{\partial t} \right)_{\vec{X}}. \quad (1)$$

We also use  $\vec{x}$  as an independent variable denoting location in laboratory coordinates; for example,  $\text{div} \vec{v}$  in the laboratory system is  $(\partial v_i / \partial x_i)_t$ , where  $i = 1, 2, 3$  are Cartesian indices and repeated indices are summed.

The material density is  $\rho$ , the stress tensor components are  $\tau_{ij}$ , and both are functions of  $\vec{X}, t$ , or equivalently of  $\vec{x}, t$ . The equations of motion are conveniently expressed in mixed Lagrangian-Eulerian form as follows<sup>5</sup>:

*Conservation of mass:*

$$\left( \frac{\partial \rho}{\partial t} \right)_{\vec{x}} = -\rho \left( \frac{\partial v_i}{\partial x_i} \right)_t. \quad (2)$$

*Conservation of linear momentum:*

$$\rho \left( \frac{\partial v_i}{\partial t} \right)_{\vec{x}} = \left( \frac{\partial \tau_{ij}}{\partial x_j} \right)_t. \quad (3)$$

*Conservation of angular momentum:*

$$\tau_{ij} = \tau_{ji}. \quad (4)$$

There is also an equation for conservation of energy. We can write the total energy of each mass element as a sum of two parts, the translational kinetic energy and the center-of-mass energy. It is easy to show that the translational kinetic energy is equal to the translational work done by the stresses, because of Newton's law which is Eq. (3); the energy balance for each mass element is then reduced to center-of-mass contributions, which are discussed below.

### B. Thermoelasticity<sup>1(b),2</sup>

Consider an incremental process, in which the material goes from the current state to the next state in an incremental time  $dt$ . The incremental displacement (motion) of each mass element is given by the field variable  $d\vec{u}(\vec{X}, t)$ ; the incremental displacement gradients are

$$du_{ij} = \left( \frac{\partial du_i}{\partial x_j} \right)_t, \quad (5a)$$

related to the velocity gradients by

$$du_{ij} = v_{ij} dt, \quad (5b)$$

where  $v_{ij} = (\partial v_i / \partial x_j)_t$ . The  $du_{ij}$  are precisely the

same as the displacement gradients  $u_{ij}$  of Refs. 1(b) and 2, when those  $u_{ij}$  are limited to infinitesimal magnitude and are always measured from the (continually changing) current configuration, instead of from a fixed Lagrangian configuration. In the incremental process, the work done by stresses in a local center-of-mass system is  $dW = \rho^{-1} \tau_{ij} du_{ij}$  per unit mass of material, and by conservation of energy this equals the increase  $dU$  of thermodynamic internal energy per unit mass (we are neglecting heat transport):

$$dU = dW = \rho^{-1} \tau_{ij} du_{ij}. \quad (6)$$

This equation, as with all thermodynamic equations, is Lagrangian in the sense that it holds for a given mass element, no matter how the mass element moves; hence (6) is equivalent to

$$\dot{U} = \rho^{-1} \tau_{ij} \dot{u}_{ij} = \rho^{-1} \tau_{ij} v_{ij},$$

where the dot signifies a Lagrangian time derivative:  $\dot{U} = (\partial U / \partial t)_{\bar{x}}$ .

The strains may be expressed as symmetric plus antisymmetric parts, where the symmetric part

$$d\epsilon_{ij} = \frac{1}{2} (du_{ij} + du_{ji}) \quad (7)$$

measures the pure strain and the antisymmetric part

$$d\omega_{ij} = \frac{1}{2} (du_{ij} - du_{ji}) \quad (8)$$

measures the pure (rigid) rotation. Further, the pure strain is presumed to result from a combination of elastic strain  $d\epsilon_{ij}^e$ , and some "flow" or "plastic" strain  $d\epsilon_{ij}^p$ , which is due to an internal rearrangement of the atoms of the material. As long as the process is infinitesimal, the two strain contributions are additive:

$$d\epsilon_{ij} = d\epsilon_{ij}^e + d\epsilon_{ij}^p. \quad (9)$$

The meaning of the  $d\epsilon_{ij}^p$  will be made precise a little later. We first set out the thermodynamic theory which is coupled to the elastic strains  $d\epsilon_{ij}^e$ , ignoring the explicit presence of the plastic strains.

In the theory of thermoelasticity, a complete set of variables which specify the thermodynamic state of a material (the state variables) are the elastic configuration and the entropy. In differential form these variables are  $d\epsilon_{ij}^e$  and  $dS$ , where  $S$  is the entropy per unit mass. Then the differential of any thermodynamic function, e.g.,  $U$ , can be written as

$$dU = \frac{\partial U}{\partial \epsilon_{ij}^e} d\epsilon_{ij}^e + \frac{\partial U}{\partial S} dS. \quad (10a)$$

Repeated indices are summed; in each partial derivative with respect to a given variable, all other independent variables are held fixed. Thermoelastic definitions of the stresses and the temperature

$T$  are<sup>1(b),2</sup>

$$\tau_{ij} = \rho \frac{\partial U}{\partial \epsilon_{ij}^e} \quad (10b)$$

at constant  $S$ , and

$$T = \left( \frac{\partial U}{\partial S} \right) \quad (10c)$$

at constant  $\epsilon_{ij}^e$ . Hence Eq. (10a) is

$$dU = \rho^{-1} \tau_{ij} d\epsilon_{ij}^e + T dS. \quad (11)$$

In a similar way the variations  $d\tau_{ij}$  and  $dT$  may be calculated and expressed as

$$d\tau_{ij} = B_{ijkl} d\epsilon_{kl}^e + \frac{\partial \tau_{ij}}{\partial \omega_{kl}} d\omega_{kl} - \rho \gamma_{ij} T dS, \quad (12)$$

$$dT = -T \gamma_{ij} d\epsilon_{ij}^e + (T/C_\eta) dS, \quad (13)$$

where  $C_\eta$  is the heat capacity at constant elastic configuration,  $B_{ijkl}$  are the adiabatic stress-strain coefficients, which can be measured in stress-strain experiments or in adiabatic sound-wave experiments, and  $\gamma_{ij}$  are the anisotropic Grüneisen parameters defined by<sup>2</sup>

$$\rho \gamma_{ij} = -T^{-1} \frac{\partial \tau_{ij}}{\partial S}. \quad (14a)$$

Derivatives at constant elastic configuration equivalent to (14a) are

$$\rho \gamma_{ij} = -C_\eta^{-1} \frac{\partial \tau_{ij}}{\partial T} = -\frac{\partial \tau_{ij}}{\partial U}. \quad (14b)$$

The rotation coefficient  $(\partial \tau_{ij} / \partial \omega_{kl})$  in (12) is given in Ref. 1(b); this term in  $d\tau_{ij}$  accounts for simultaneous incremental rigid rotation of a mass element and the stress tensor.

The thermoelastic equations (11)–(13) are not all independent. In fact, they form a hierarchy of coupled equations: The coefficients in  $dU$ , namely,  $\tau_{ij}$  and  $T$ , are first derivatives of  $U$  with respect to independent variables; the coefficients in  $d\tau_{ij}$  and  $dT$ , namely,  $B_{ijkl}$ ,  $\gamma_{ij}$ , and  $C_\eta$ , are second derivatives of  $U$  with respect to independent variables; and so on. In order to break the hierarchy at this point, we regard the second-order coefficients as known functions of the state variables.

A comment is in order concerning the convenient choice of thermodynamic state variables. In a theory which includes both elastic and plastic strains, the elastic configuration is a complicated nonlinear integral function of the total and the plastic-strain increments,  $d\epsilon_{ij}$  and  $d\epsilon_{ij}^p$ . While it is easy to use  $d\epsilon_{ij}^e$  and  $dS$  for differential state variables, as above, if integrated state variables are desired, it is most convenient to use the equivalent complete set  $\tau_{ij}$  and  $S$  (equivalent because stresses are elastically supported). The stresses are easily

calculated by integrating  $d\tau_{ij}$ , and with  $\tau_{ij}$  and  $S$  specified, all other thermodynamic functions, including the elastic configuration, are uniquely determined. To complete the thermodynamics, we need an equation for  $dS$ ; this is obtained below.

### C. Thermoplasticity

The mechanical theory of plastic flow is well described in textbooks.<sup>6-8</sup> It is based on two conditions on the plastic-strain increments; the first is the experimental observation that plastic strain is volume conserving. To express this, note that Eq. (2) for conservation of mass is precisely equivalent to

$$d \ln V = du_{ii} = d\epsilon_{ii}, \quad (15)$$

where  $V = \rho^{-1}$  is the volume per unit mass.  $d \ln V$  is then a sum of elastic and plastic contributions, and the plastic contribution is set to zero:

$$d\epsilon_{ii}^p = 0. \quad (16)$$

The second condition is the Prandtl-Reuss flow rule,<sup>9</sup> which requires some definitions. The average compressive stress is  $\bar{P}$ , and the stress deviators are  $s_{ij}$ :

$$\begin{aligned} \bar{P} &= -\frac{1}{3} \tau_{ii}, \\ s_{ij} &= \tau_{ij} + \bar{P} \delta_{ij}. \end{aligned} \quad (17)$$

An effective shear stress  $\tau$ , which is a measure of the stress which drives the plastic flow, is defined by

$$\tau^2 = \frac{3}{2} s_{ij} s_{ij}, \quad \tau \geq 0. \quad (18)$$

The Prandtl-Reuss flow rule then allows the several variables  $d\epsilon_{ij}^p$  to be expressed in terms of a single measure  $d\psi$  of the plastic strain:

$$d\epsilon_{ij}^p = \frac{3}{4} (s_{ij}/\tau) d\psi. \quad (19)$$

Since the definitions (17) imply  $s_{ii} = 0$ , then (17) and (19) together contain (16). Equation (19) represents the intuitively reasonable idea that the plastic-strain increments ought to be isotropically proportional to the stress deviators; it has some experimental verification for cases of complex flow.<sup>7,8</sup> Finally, the effective plastic-strain increment  $d\psi$  is determined by the von Mises criterion<sup>10</sup> in terms of a generalized flow function  $K$ :

$$\tau \leq K(\psi, \dot{\psi}, \tau_{ij}, S). \quad (20)$$

This equation has the following meaning: If  $\tau < K$ , the process is elastic and  $d\psi = 0$ ; if  $\tau$  is on the flow surface,  $d\psi > 0$  and is determined by the condition  $\tau = K$ .  $\psi = \int d\psi$  is the integrated plastic strain, and the dependences of  $K$  on  $\psi$  and  $\dot{\psi}$  represent, respectively, strain-hardening and strain-rate effects.  $K$  also depends on the thermoelastic state

variables  $\tau_{ij}$  and  $S$ , as indicated.

The thermodynamic theory of plastic flow requires, in addition to the above equations, a thermodynamic description of the energy associated with the process. This energy can be identified as part of the total center-of-mass energy. In Eq. (6) for the conservation of total energy, because  $\tau_{ij} = \tau_{ji}$ , the antisymmetric parts of  $du_{ij}$  sum to zero, giving

$$dW = \rho^{-1} \tau_{ij} d\epsilon_{ij} = dW^e + dW^p, \quad (21)$$

where  $dW^e$  and  $dW^p$  are work increments done against elastic and plastic strains, respectively:

$$dW^e = \rho^{-1} \tau_{ij} d\epsilon_{ij}^e, \quad (22a)$$

$$dW^p = \rho^{-1} \tau_{ij} d\epsilon_{ij}^p = 2V\tau d\psi. \quad (22b)$$

The last form in (22b) follows by using (17)–(19). In a classic experiment on metals, Farren and Taylor<sup>11</sup> observed that 87–95% of the plastic work was dissipated; we expect this same qualitative behavior for deformations involving dislocation motion, twinning, or viscous rearrangement of atoms in amorphous solids. Because it is a good approximation, and because it simplifies the theory conceptually, we assume that the plastic work  $dW^p$  is entirely dissipated:

$$TdS = 2V\tau d\psi. \quad (23)$$

The plastic flow is now completely defined. It follows the flow rule (19) and is totally dissipative. It includes any process which approximates these conditions. Further, the combined thermoelastic and thermoplastic theory is internally consistent, since the energy partition given by (21)–(23) makes the thermoelastic equation (11) for  $dU$  identical with (6).

As a matter of fact, in a real flow process in a real solid, a small part of the plastic work may go into creating a change in the defect structure of the material; for example, energy may be stored in the elastic strain field of an increased number of dislocations. Such stored energy is presumably responsible for work hardening (strain hardening). This energy is not included in ordinary thermoelastic theory, hence an explicit accounting of it will require a redefinition of the thermoelastic coefficients. Suppose, for example, that 90% of  $dW^p$  is dissipated in a given process, while the rest is stored; the entropy-production and energy-conservation equations then read

$$TdS = 0.9dW^p,$$

$$dU = \rho^{-1} \tau_{ij} (d\epsilon_{ij}^e + 0.1d\epsilon_{ij}^p) + TdS.$$

Comparison with (11) shows that the first-order coefficients  $\tau_{ij}$  and  $T$  are no longer given by the thermoelastic definitions (10b) and (10c). The effect carries

on to Eqs. (12) and (13), changing the definitions of the second-order coefficients  $B_{ijkl}$ ,  $\gamma_{ij}$ ,  $C_\eta$ , and so on. Thus in making the total dissipation approximation (23), we obtain a significant simplification of the theory, in exchange for introducing small errors into our thermodynamic computations. On the other hand, the major effect of hardening is properly contained in the theory, through the dependence of the flow function  $K$  on the total plastic strain  $\psi$ . It may also be noted that when a solid melts, the defect structure anneals, and the energy stored there is recovered as equivalent heat.

### III. PLANE-WAVE GEOMETRY

The theory is much simplified when it is specialized to the geometry appropriate for describing a plane compressive wave, such as a weak shock. This is an example of "principal axis flow": The principal axes coincide at all  $\vec{X}, t$  with a single invariant orthogonal (not necessarily Cartesian) coordinate system. Since the stress tensor is diagonal in this coordinate system, then for an isotropic solid both the elastic and plastic strains are diagonal; it is then convenient to express strains in terms of the transformation matrix  $\alpha$  which transforms the initial configuration  $\vec{X}$  to the current configuration  $\vec{x}$  at any time  $t$  (Refs. 1(b), 2):

$$\alpha_{ij} = \left( \frac{\partial x_i}{\partial X_j} \right)_t. \quad (24)$$

Because all strain measures are diagonal, we can use the Voigt indices  $\beta = 1, 2, 3$  to replace  $ij = 11, 22, 33$ , respectively, and write

$$\begin{aligned} \alpha_{ij} &= \alpha_\beta \delta_{ij}, \\ d\epsilon_{ij} &= d\epsilon_\beta \delta_{ij}. \end{aligned} \quad (25)$$

We now have  $du_\beta = d\epsilon_\beta$ , and the relation

$$d\epsilon_\beta = d \ln \alpha_\beta. \quad (26)$$

The logarithm appears in (26) because the  $\alpha_\beta$  are measured from a fixed (initial) configuration, while the  $\epsilon_\beta$  are measured from a continually varying (current) configuration. Again because the strain measures are diagonal, the total transformation  $\alpha$  is a matrix product of the elastic trans-

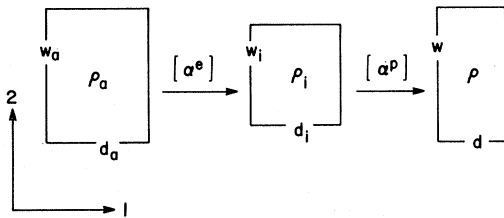


FIG. 1. Two-step transformation of a mass element in plane-wave geometry.

formation  $\alpha^e$  and the plastic transformation  $\alpha^p$ , as the following calculation shows:

$$\begin{aligned} \ln \alpha_\beta &= \int d\epsilon_\beta = \int d\epsilon_\beta^e + \int d\epsilon_\beta^p \\ &= \ln \alpha_\beta^e + \ln \alpha_\beta^p, \end{aligned} \quad (27)$$

or in matrix form

$$\begin{aligned} \alpha &= \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix} \\ &= \begin{pmatrix} \alpha_1^e & 0 & 0 \\ 0 & \alpha_2^e & 0 \\ 0 & 0 & \alpha_3^e \end{pmatrix} \begin{pmatrix} \alpha_1^p & 0 & 0 \\ 0 & \alpha_2^p & 0 \\ 0 & 0 & \alpha_3^p \end{pmatrix}. \end{aligned} \quad (28)$$

In plane-wave geometry, the wave propagates along Cartesian coordinate 1, and coordinates 2, 3 are equivalent transverse directions. Hence,  $\alpha_2 = \alpha_3$  and so on. The transformation of a mass element is shown in Fig. 1, from the initial configuration of density  $\rho_a$ , to an intermediate configuration of density  $\rho_i$ , to the current configuration of density  $\rho$ . No physical meaning is to be attached to the intermediate configuration; it is not reached in the physical process unless it coincides with the current configuration. The mass element has thickness  $d$  in direction 1 and width  $w$  in the two transverse directions. The initial dimensions  $d_a, w_a$  are presumed known, so there are four independent strain variables in the transformation, namely  $d_i, w_i, d, w$ . In terms of these we can write

$$\begin{aligned} \alpha_1 &= d/d_a, & \alpha_1^e &= d_i/d_a, & \alpha_1^p &= d/d_i, \\ \alpha_2 &= w/w_a, & \alpha_2^e &= w_i/w_a, & \alpha_2^p &= w/w_i. \end{aligned} \quad (29)$$

Plane-wave geometry requires the boundary condition that the total transverse strain of each mass element is zero:

$$w = w_a. \quad (30)$$

The volume conservation of plastic flow, Eq. (16), can be written

$$\rho = \rho_i. \quad (31)$$

With these conditions we are left only two independent strain variables, and for these we introduce the conventional plane-wave variables  $\epsilon, \psi$ , both positive in compression and defined by

$$\epsilon = 1 - \rho_a/\rho = 1 - V/V_a, \quad (32)$$

$$\psi = -\ln \alpha_1^p. \quad (33)$$

The flow strain  $\psi$  is the same as the natural or logarithmic plastic strain in simple tension or compression experiments. The transformation coefficients now become

$$\begin{aligned} \alpha_1 &= (1 - \epsilon), \quad \alpha_1^e = (1 - \epsilon)e^\psi, \quad \alpha_1^p = e^{-\psi}, \\ \alpha_2 &= 1, \quad \alpha_2^e = e^{-\psi/2}, \quad \alpha_2^p = e^{\psi/2}. \end{aligned} \quad (34)$$

The stress system is also simple in plane-wave geometry. The conventional variables are the normal stress  $\sigma$  and the shear stress  $\tau$ , both positive in compression and defined by

$$\begin{aligned} \sigma &= -\tau_1, \\ \tau &= -\frac{1}{2}(\tau_1 - \tau_2). \end{aligned} \quad (35)$$

These stresses are shown in Fig. 2. Note that the above definitions are completely consistent with the general thermoplastic theory of Sec. II: We have incorporated the volume-conserving condition (16), the shear stress  $\tau$  of (35) satisfies the definition (18), and the plastic strains  $d\epsilon_\beta^p = d \ln \alpha_\beta^p$  satisfy the flow rule (19). In fact the Prandtl-Reuss rule is superfluous in the case of plane-wave geometry because here we have only one independent plastic-strain variable.

Under the stress system (35), an originally isotropic solid has tetragonal symmetry, and the stress-strain coefficients  $B_{\alpha\beta}$  (Voigt indices) have the symmetry

$$\begin{pmatrix} B_{11} & B_{12} & B_{12} & & & \\ B_{21} & B_{22} & B_{23} & & 0 & \\ B_{21} & B_{23} & B_{22} & & & \\ & & & B_{44} & 0 & 0 \\ & 0 & & 0 & B_{66} & 0 \\ & & & 0 & 0 & B_{66} \end{pmatrix}. \quad (36)$$

The Grüneisen parameters, Eqs. (14), have the symmetry  $\gamma_{ij} = \gamma_\beta \delta_{ij}$ , and the thermoelastic equations for stresses and temperature reduce to

$$d\sigma = \rho \gamma_1 T dS - B_{11} d \ln(1 - \epsilon) - (B_{11} - B_{12}) d\psi, \quad (37)$$

$$d\tau = \frac{1}{2} \rho (\gamma_1 - \gamma_2) T dS - \frac{1}{2} (B_{11} - B_{21}) d \ln(1 - \epsilon) - \frac{1}{2} (B_{11} + \frac{1}{2} B_{22} + \frac{1}{2} B_{23} - B_{12} - B_{21}) d\psi, \quad (38)$$

$$dT = C_\eta^{-1} T dS - T \gamma_1 d \ln(1 - \epsilon) - T (\gamma_1 - \gamma_2) d\psi. \quad (39)$$

The equations of motion (2) and (3) for conservation of mass and linear momentum, respectively,

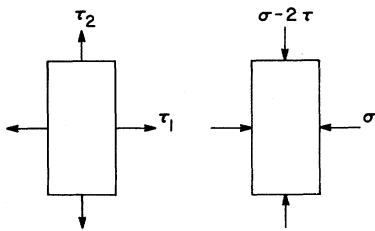


FIG. 2. Stresses in plane-wave geometry.

are

$$\left( \frac{\partial \rho}{\partial t} \right)_x = -\rho \left( \frac{\partial v}{\partial x} \right)_t, \quad (40)$$

$$\rho \left( \frac{\partial v}{\partial t} \right)_x = - \left( \frac{\partial \sigma}{\partial x} \right)_t, \quad (41)$$

where  $x$  is the laboratory coordinate and  $v$  the material velocity, both in the propagation direction. The Eqs. (37)–(41), together with the entropy production equation (23) and the flow criterion (20), are sufficient to calculate any dynamic flow process in plane-wave geometry, provided the coefficients  $C_\eta, \gamma_\beta, B_{\alpha\beta}$  and the flow function  $K(\psi, \dot{\psi}, \sigma, \tau, S)$  are known. The conservation of energy equation, which is uncoupled from the above system unless  $U$  is taken as a state variable, reduces to

$$dU = -\sigma dV = \sigma V_a d\epsilon. \quad (42)$$

#### IV. COMPARISON WITH RELAXING SOLID MODEL

##### A. Expansions for small anisotropy

In order to make a comparison with other models, we need to approximate the thermoelastic coefficients in the present theory. A systematic approximation can be based on the condition that the stress system is always close to isotropic, or equivalently that the anisotropic part of the elastic strain is small. We first construct a working definition of isotropic solid.

Consider an isotropic solid under arbitrary isotropic pressure  $P$ ; take  $V, S$  for state variables, so  $P, T, U$ , and so on are functions of  $V, S$ . Throughout this thermodynamic space, the solid is physically isotropic. Now from any state, say state 1, in the isotropic thermodynamic space, change the stress system to an anisotropic  $\tau_{ij}$  at constant  $S$ ; this brings the solid to a state of anisotropic elastic strains  $\eta_{ij}^e$ , where  $\eta_{ij}^e = \frac{1}{2} (\alpha_{ki}^e \alpha_{kj}^e - \delta_{ij})$  and all strains are measured from state 1. The dependence of any thermodynamic function on the strain matrix  $\eta^e$  can be expressed in terms of the three rotation invariants of  $\eta^e$ , which are

$$\begin{aligned} I_1 &= \eta_{ii}^e, \\ I_2 &= \sum_j \text{cof} \eta_{jj}^e, \\ I_3 &= \det \eta^e, \end{aligned} \quad (43)$$

where  $\text{cof} \eta_{jj}^e$  stands for the cofactor of  $\eta_{jj}^e$ . The above observations constitute a definition of isotropic solid. A strain expansion of the internal energy is given in Ref. 1(b), and this serves to define the second-order adiabatic Lamé coefficients  $\lambda, \mu$ , and the third-order adiabatic Murnaghan coefficients  $\zeta, \xi, \nu$ :

$$\rho_1 U(V, \eta_{ij}^e, S) = \rho_1 U(V, 0, S) - P I_1 + \left[ \frac{1}{2} (\lambda + 2\mu) I_1^2 - 2\mu I_2 \right] \\ + \left[ \frac{1}{3} (\zeta + 2\xi) I_1^3 - 2\xi I_1 I_2 + \nu I_3 \right] + \dots, \quad (44)$$

where  $\rho_1$  is the density at state 1, and the coefficients (of the strain functions) are all evaluated at state 1. The adiabatic bulk and shear moduli,  $B$  and  $G$ , respectively, at state 1 are<sup>1(b)</sup>

$$B = -V(\partial P / \partial V)_S = \lambda + \frac{2}{3}\mu + \frac{1}{3}P, \quad (45)$$

$$G = B_{44} = \frac{1}{2}(B_{11} - B_{12}) = \mu - P. \quad (46)$$

For application to the present theory of dynamic flow processes, it is convenient to restrict expansions such as (44) to the condition of fixed  $V$ ; then  $V, S$  are the same in the elastically anisotropic state (the current state), as in state 1 where all coefficients are evaluated. Hence  $V, S$  evaluated in the current state serve as state variables for the coefficients. For the case of plane-wave geometry, we have expanded the second-order thermoelastic coefficients at constant  $V, S$ , and expressed the results in powers of  $\tau/G$ , which should always be small. Results for the stress-strain coefficients are

$$B_{11} = (B + \frac{4}{3}G) - \frac{4}{3}(2\lambda + 5\mu + 2\xi - P)(\tau/G) + \dots, \\ \frac{1}{2}(B_{11} - B_{12}) = G - (\lambda + 4\mu + \xi + \frac{1}{6}\nu - \frac{4}{3}P)(\tau/G) + \dots, \\ \frac{1}{2}(B_{12} - B_{21}) = \tau, \quad (47) \\ \frac{1}{3}(B_{11} + \frac{1}{2}B_{22} + \frac{1}{2}B_{23} - B_{12} - B_{21}) \\ = G - (\mu + \frac{1}{6}\nu - \frac{1}{3}P)(\tau/G) + \dots,$$

where  $\dots$  means terms of relative order  $\tau^2/G^2$  and higher. For the remaining coefficients, with terms of order  $\tau/G$  represented by  $O(\tau/G)$ ,

$$C_\eta = C_V [1 + O(\tau/G)], \\ \gamma_1 - \gamma_2 = O(\tau/G), \quad (48) \\ \gamma_1 = \gamma [1 + O(\tau/G)],$$

where  $C_V$  is the heat capacity at constant volume, and  $\gamma$  is the ordinary Grüneisen parameter,

$$\rho\gamma = \left( \frac{\partial P}{\partial U} \right)_V. \quad (49)$$

We now gather up the thermoelastic and thermo-plastic equations of the preceding section for plane-wave geometry, put in the above expansions, and write each equation explicitly to leading order only as follows:

$$d\sigma = -(B + \frac{4}{3}G)d\ln(1 - \epsilon) - 2Gd\psi + O(\tau d\ln(1 - \epsilon), \tau d\psi), \quad (50)$$

$$d\tau = -G[d\ln(1 - \epsilon) + \frac{3}{2}d\psi] + O(\tau d\ln(1 - \epsilon), \tau d\psi), \quad (51)$$

$$\tau \leq K(\psi, \dot{\psi}, V, S), \quad (52)$$

$$TdS = 2V\tau d\psi, \quad (53)$$

$$dT = [C_V^{-1}TdS - \gamma T d\ln(1 - \epsilon)][1 + O(\tau/G)]. \quad (54)$$

Note  $\rho T dS = O(\tau d\psi)$ ; the terms  $O(\tau d\ln(1 - \epsilon))$  and  $O(\tau d\psi)$  in (50) and (51) are the  $TdS$  terms from Eqs. (37) and (38), and the terms of first order in  $\tau$  from Eqs. (47).

#### B. Relaxing solid model

In 1867, Maxwell<sup>12</sup> wrote a constitutive equation for a material which shows instantaneous elastic response plus stress relaxation according to a relaxation time. Malvern,<sup>13</sup> in studying plane-wave propagation in infinitesimal strain theory, generalized the Maxwell model by introducing a stress relaxation function. Taylor<sup>14</sup> investigated the shape of weak plane shocks with a constitutive equation which is a special case of Malvern's. Herrmann<sup>15</sup> has used the relaxing solid model extensively in analyzing plane shocks; his equations are the most general since they allow for finite strain and include the shear stress  $\tau$ . Equations (6) or (7) and (9) or (10) of Ref. 15, transcribed to the present notation,<sup>16</sup> are

$$d\sigma = -(B + \frac{4}{3}G)d\ln(1 - \epsilon) - 2Gd\psi, \quad (55)$$

$$d\tau = -G[d\ln(1 - \epsilon) + \frac{3}{2}d\psi], \quad (56)$$

$$\dot{\psi} = g^\pm(\sigma, \epsilon), \quad (57)$$

where  $g^\pm(\sigma, \epsilon)$  is the stress relaxation function, with  $g^+$  for compressive loading and  $g^-$  for unloading.

By comparison with Eqs. (50)–(54), it is seen that the system (55)–(57) neglects all effects due to entropy, and neglects all terms  $O(\tau d\ln(1 - \epsilon))$  and  $O(\tau d\psi)$  in  $d\sigma, d\tau$ . In plane shocks we generally have  $\tau \ll \sigma$ ; this means the terms of order  $\tau$  neglected in (55) are formally small, and (55) should integrate to give a reasonably accurate value of  $\sigma$  throughout the process. Terms of the same order are not negligible in (56), however, and the integral of that equation will give a value of  $\tau$  with an error formally of order  $\tau$ . With regard to the plastic-flow constitutive equations, it is interesting to note there is a formal equivalence between the von Mises condition and the relaxation function. Equation (52) can be inverted to  $\dot{\psi} = f(\tau, \psi, V, S)$ , and since  $\tau, \psi, V$  are coupled by one equation, they can be replaced by two variables, say  $\sigma, \epsilon$ , giving  $\dot{\psi} = f(\sigma, \epsilon, S)$ ; finally, if  $S$  is neglected as an independent variable, a relation of the form (57) is obtained.

#### V. THE QUESTION OF EQUILIBRIUM

A macroscopic treatment of a material process without thermodynamics is conceptually difficult.

Theory has to be founded in mechanical variables, which are specified in terms of atomic motions and interactions. For a given mass element containing a fixed assembly of atoms, or at least a fixed number in the case where mass transfer is allowed, the mechanical energy is always defined, and so are mechanical stresses in the form of forces acting across surfaces. Mechanical work is defined, but temperature and entropy are not. In order to examine the question of thermodynamic equilibrium, we have to imagine that we are first able to find a complete mechanical solution to the problem of motion; then we can study the space and time variations of the solution.

We begin by constructing a picture of continuum mechanics. The material is divided into mass elements which are macroscopically small but which still contain many atoms. The mass elements are considered as interacting mechanical systems, and the entire flow problem is expressed in terms of variables which give total mechanical properties of each mass element, for example, the position of the center of mass, the configuration, the energy, momentum, and stresses. These are macroscopic variables because they average the atomic properties over all the atoms in a mass element; they are functions of the time. To help bridge the gap between mechanics and thermodynamics it is useful to divide the deformation into two separate parts, defined as follows at any instant of time. The homogeneous deformation is that part of the deformation which is essentially constant over a mass element; this means the measure of strain varies by only a small amount over a region large enough to contain many atoms (at a fixed time), and hence it applies to the strain in any reversible thermoelastic process such as an adiabatic one, or a nonadiabatic one where the heat flux is spatially slowly varying. The other part of the deformation, that due to plastic flow, is heterogeneous on an atomic scale; this heterogeneity does not appear in detail in the macroscopic mechanical variables, only the average appears, but it is nevertheless important in the question of thermodynamic equilibrium. Incremental contributions to stresses, strains, and energies from the two types of deformation are additive.

The next step is to construct a physical model of an individual mass element as a mechanical system. A solid material is composed of ions and band electrons; the choice of which electrons are to be put in the ion cores and which in the bands is somewhat arbitrary and does not affect the present discussion. The mechanical states are quantum states. The ground state is a function only of the configuration, which is specified by the positions of the ions, and it is the  $T=0$  thermodynamic

state. For a given configuration, we may think of a distribution of quantum states with a unique ground state, such that the system's mechanical properties are represented by some average over the distribution. The mechanical variables are then written as a ground-state contribution plus an excitation contribution. For a thermodynamic equilibrium distribution of states, the excitation contribution becomes a thermodynamic quantity, generally called the thermal contribution, and is characterized by the temperature and the configuration. Thermodynamic variables are then written as a ground-state ( $T=0$ ) contribution plus a thermal contribution.

We now ask the following question: If the configuration is suddenly changed, at what strain rate can the ground state still be considered a thermodynamic state? Or, how fast do the ground-state electrons respond to a sudden motion of the ions? If the ion motion is a homogeneous strain, i.e., it is characterized by a wavelength long compared to the interionic distance. The band electrons respond collectively in a time of the order of an inverse plasma frequency,<sup>17,18</sup> say in about  $10^{-16}$  s. The polarization response of the ion cores should in principle be faster, but it will in practice be limited to the same rate as the collective response. Finally, for a short-wavelength (localized) motion of the ions, we expect the ground-state electron response to be equally fast, so for all practical purposes thermodynamic equilibrium can be assumed for the ground-state contributions to system variables.

The response of the excited states can also be estimated for near-equilibrium conditions. In the customary approximations of solid-state physics, the excitation modes of the ion-electron system are the phonons and the one-electron Fermi-Dirac excitations. Among the phonons, in a distribution which is anywhere near thermodynamic equilibrium at room temperature and above, practically all of the excitation energy is carried by short-wavelength motions, i.e., wavelengths of the order of one or two interionic spacings. We may assume that at room temperature and above, the lifetime of such phonons is limited by phonon-phonon collisions; experimental measurements for metals<sup>19</sup> give  $\tau_{pp} \lesssim 10^{-12}$  s, and Peierls<sup>20</sup> has estimated  $\tau_{pp} \lesssim 10^{-13}$  s for nonmetals at room temperature. These lifetimes should decrease as temperature increases. Long-wavelength phonons have much longer lifetimes, but we should be able to neglect their influence as long as we avoid low-temperature problems. For metals there are also electronic excitations. From the theory of thermal conduction at temperatures of the order and above the Debye temperature,<sup>20-22</sup> and from the measured



thermal-conductivity values, the relaxation time which describes the approach to equilibrium of the electrons due to collisions with phonons in equilibrium is estimated as  $\tau_{ep} \sim 10^{-14} - 10^{-13}$  s. This should decrease with increasing temperature. The electron-electron relaxation time is rather long at room temperature,<sup>18,20,21</sup>  $\tau_{ee} \sim 10^{-12}$  s, but it is expected to decrease with temperature as  $T^{-2}$ .

We can now draw the following conclusion: For a homogeneous deformation process, the electron-phonon system ought to be able to maintain itself near equilibrium as long as the deformation at any material point changes little in a time of order  $10^{-12}$  s; this means strain rates of order  $10^{10}$  s<sup>-1</sup> are easily allowed. Such strain rates are well beyond those induced by weak shocks. This result is helpful because in many fast deformation processes the homogeneous part gives the major contribution to thermal functions, and together with the ground state it represents the dominant contribution to thermodynamic functions. For the example of a 100-kbar shock in Al, the ground-state deformation and the thermal adiabatic homogeneous deformation account for 90% of the increase in internal energy and 99% of the increase in the stresses.

The last barrier to a complete thermodynamic description of dynamic deformation processes is the heterogeneous nature of plastic flow. On the finest scale, the flow is localized to atomic-sized regions, as in dislocations, which act as dispersed moving sources of mechanical excitations. The problem is to determine how long it takes this mechanical energy to become thermalized. We might imagine that the higher the rate at which plastic flow is driven, the finer the scale of this heterogeneity, and that near thermal equilibrium could be maintained for plastic strain rates up to the same order as those which limit homogeneous deformation processes. This argument then implies approximately local equilibrium in the presence of heterogeneities on a larger scale. Evidence for large scale thermal and mechanical inhomogeneities in the fast deformations of very brittle solids has been discussed.<sup>23</sup>

If the assumption of thermodynamic equilibrium fails, it is possible to identify the errors which can result. To illustrate, consider the passage of a plane compressive shock through a polycrystalline material; assume the material remains in lo-

cal thermodynamic equilibrium except for those mechanical excitations generated by plastic flow. The initial and final states are equilibrium states, and we will use the thermodynamic theory of Sec. III to calculate thermodynamic variables in the final state. The first step is to integrate the conservation equations (40) and (41), to find the normal stress  $\sigma$  as a function of the normal strain  $\epsilon$  through the process. The result for  $\sigma(\epsilon)$  is the proper thermodynamic value in the final state. The same is true for  $U(\epsilon)$  in the final state, computed by integrating Eq. (42). Through the process, however,  $\sigma(\epsilon)$  is a mechanical variable; its value is given correctly by the conservation equations, but it does not represent material in thermodynamic equilibrium. We thus make an error when we use thermodynamics to calculate  $\tau$  and  $\psi$  from  $\sigma(\epsilon)$ . But the error should be small, at most of the same order as the contribution of the entropy to the stresses. For a 100-kbar shock in Al, this is not greater than 1%. This now becomes the measure of the error in all thermodynamic quantities we calculate. As for the increase in the temperature from the initial to the final state, most is due to homogeneous adiabatic compression. The calculation of the entropy in the final state, and of the temperature increase due to dissipative heating, is based on integrating the inexact differential  $\tau d\psi$  [see Eqs. (22b) and (23)] along a path defined by  $\tau$  and  $\psi$ , so the error in the integral is at most of the same order as that in  $\tau$  and  $\psi$  along the path. From this point of view the assumption of thermodynamic equilibrium is seen as an approximation of very good accuracy.

## VI. CONCLUSION

In this work we have shown that within the conventional assumptions of plasticity theory, the complete thermoelastic-plastic equations of flow can be expected to have a wide range of applicability. Evaluation of these equations for general flow problems would require a large computer.<sup>24</sup> However, for one-dimensional strain problems a relatively simple system of equations results. These equations will be applied in the following two papers to experimental data on an extensively studied Al alloy in order to obtain model-independent information concerning its flow function and equation of state.

<sup>1</sup>(a) L. Davison and R. A. Graham, Phys. Rep. **55**, 255 (1979); (b) D. C. Wallace, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 25, p. 301.

<sup>2</sup>D. C. Wallace, *Thermodynamics of Crystals* (Wiley,

New York, 1972).

<sup>3</sup>I. Prigogine, *Thermodynamics of Irreversible Processes*, 2nd ed. (Interscience, New York, 1961).

<sup>4</sup>S. R. deGroot, *Thermodynamics of Irreversible Processes* (North-Holland, Amsterdam, 1958).

- <sup>5</sup>For a derivation of the equations of motion see, e.g., W. Prager, *Introduction to Mechanics of Continua* (Ginn, Boston, 1961).
- <sup>6</sup>R. Hill, *The Mathematical Theory of Plasticity* (Clarendon, Oxford, 1950).
- <sup>7</sup>A. Mendelson, *Plasticity: Theory and Application* (Macmillan, New York, 1968).
- <sup>8</sup>L. M. Kachanov, *Foundations of the Theory of Plasticity* (North-Holland, Amsterdam, 1971).
- <sup>9</sup>L. Prandtl, in *Proceedings of the First International Congress for Applied Mechanics*, edited by C. Biezeno and J. Burgers (Waltman, Delft, 1925), p. 43; A. Reuss, *Z. Angew. Math. Mech.* 10, 266 (1930).
- <sup>10</sup>R. von Mises, *Gött. Nachrichten, Math-Phys.* 1913, 582.
- <sup>11</sup>W. S. Farren and G. I. Taylor, *Proc. R. Soc. London* 107, 422 (1925).
- <sup>12</sup>J. C. Maxwell, *Philos. Trans. R. Soc. London* 157, 49 (1867).
- <sup>13</sup>L. E. Malvern, *Q. Appl. Math.* 8, 405 (1951).
- <sup>14</sup>J. W. Taylor, in *Dislocation Dynamics*, edited by A. R. Rosenfield *et al.* (McGraw-Hill, New York, 1968), p. 573.
- <sup>15</sup>W. Herrmann, in *Propagation of Shock Waves in Solids*, edited by E. Varley (ASME, New York, 1976), p. 1.
- <sup>16</sup>Herrmann uses a different definition of the Lamé coefficients; I have transcribed his  $\lambda + 2\mu$  and  $\mu$ , respectively, as  $B + \frac{4}{3}G$  and  $G$ .
- <sup>17</sup>C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
- <sup>18</sup>D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963).
- <sup>19</sup>B. N. Brockhouse *et al.*, in *Inelastic Scattering of Neutrons in Solids and Liquids*, (IAEA, Vienna, 1961), p. 531; R. Stedman and G. Nilsson, *Phys. Rev.* 145, 492 (1966); R. Stedman *et al.*, *ibid.* 162, 545 (1967).
- <sup>20</sup>R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955).
- <sup>21</sup>J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960).
- <sup>22</sup>J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974), part B.
- <sup>23</sup>D. E. Grady, in *High-Pressure Research*, edited by M. H. Manghnani and S. Akimoto (Academic, New York, 1977), p. 389.
- <sup>24</sup>A similar system of equations, in which plastic-strain-rate effects are modeled with artificial viscosity, has been studied numerically by M. L. Wilkins, in *Methods in Computational Physics*, edited by B. Alder *et al.* (Academic, New York, 1964), Vol. 3, p. 211; also Y. M. Chen and M. L. Wilkins, in *Mechanics of Fracture*, edited by G. C. Sih (Noordhoff, Leyden, 1977), Vol. 4, p. 295.