# THERMODYNAMICS OF SOLIDS UNDER STRESS

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## ABSTRACT

This expository paper discusses how the equilibrium thermodynamics of an ideal elastic solid differs from that of a fluid. Because at least some species are immobile, there is no unique Gibbs energy. There are six independent finite strain parameters, $n_\lambda$, referred to a chosen reference state. Thermodynamic manipulations are straightforward if stresses $t_\lambda$ are defined conjugate to the $\eta_\lambda$, but these can be identified with the Cauchy stresses, $\sigma_\lambda$, only in the reference state. Typical experimental conditions are described directly by the $\sigma_\lambda$, which have to be related to the $t_\lambda$ before experimental quantities like $C_p$ can be related to formally derived quantities like $C_t$.

## 1. INTRODUCTION

This paper discusses the thermodynamics of ideal solids which can sustain a permanent shear stress. The theory is now well established, and is of increasing importance in solid state physics. However, rigorous discussions are available only in some specialized texts[1,2], which are not always easy to read. In addition to results given in such texts, this account presents some new results relating experimental quantities to ones of theoretical application.

A rigid solid must contain a framework of atoms in which neighbours remain neighbours throughout any deformation (although mobile species can also be present). Processes in which there is transport of the immobile atoms, including exchange with another phase, are forbidden. Consequently the solid need not be in a state of thermochemical equilibrium; in general a chemical potential can be defined only for mobile species. There is therefore no unique Gibbs energy $G$, although it may be convenient to define analogous functions (see §2). True thermochemical equilibrium is reached only under isotropic stress (hydrostatic pressure)†. Consequently, normal fluid thermodynamics can be applied to solids under isotropic stress (e.g. a solid immersed

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† McLellan[3] has derived a chemical potential by assuming thermochemical equilibrium. His result thus appears to be valid only under hydrostatic pressure.

in a fluid). However, care is needed, especially for non-cubic solids. For example, the relation $C_V = C_p - \beta^2 V T/\kappa_T$‡ gives not the heat capacity of a solid whose dimensions are kept constant, but that of a solid whose shape changes to keep the stress isotropic at constant volume[4].

When transport is negligible during the time of an experiment, a solid under shear stress is in a metastable state with a well defined entropy $S$ and Helmholtz energy $A$, which are functions of the strain and temperature. The thermodynamics of this state is our main topic. We deal only with thermo-elastic properties, omitting electric and magnetic effects.

## 2. THERMODYNAMIC THEORY FOR SOLIDS

### Description of strain

We treat the solid as a continuum, and consider only strains which are effectively uniform over distances of several atomic spacings. The strain can be specified by the displacement of each point in the solid from its position $(\overset{\circ}{x}_1, \overset{\circ}{x}_2, \overset{\circ}{x}_3)$ in some *reference configuration*. A superposed circle will denote properties of this configuration. For a uniform strain the new positions are given in tensor notation[5] by

$$x_i = (\delta_{ij} + u_{ij})\,\overset{\circ}{x}_j \tag{1}$$

where summation from 1 to 3 is implied over a repeated suffix. If the displacements $u_{ij}$ are small, their symmetric and antisymmetric parts give, to first order, pure strains and pure rotations

$$e_{ij} \equiv \tfrac{1}{2}(u_{ij} + u_{ji}), \qquad \omega_{ij} \equiv \tfrac{1}{2}(u_{ij} - u_{ji}) \tag{2}$$

Thus infinitesimal strains are specified by the six $e_{ij}$.

However, finite strains are not specified by the $e_{ij}$. An arbitrary vector $\overset{\circ}{\mathbf{r}}$ in the reference configuration which becomes the vector $\mathbf{r}$ in the strained configuration changes in length by[6]

$$r^2 - \overset{\circ}{r}^2 = (u_{ij} + u_{ji} + u_{ki}u_{kj})\,\overset{\circ}{r}_i\overset{\circ}{r}_j \tag{3}$$

where the second-order terms depend on the $\omega_{ij}$ as well as the $e_{ij}$. We can thus specify arbitrary strain by the symmetric *Lagrange finite strain tensor*

$$\eta_{ij} \equiv \tfrac{1}{2}(u_{ij} + u_{ji} + u_{ki}u_{kj}) \tag{4}$$

which can be reduced to $e_{ij}$ for infinitesimal strains. We shall use the *Voigt abbreviated notation*[7]

$$\eta_1 = \eta_{11}, \eta_2 = \eta_{22}, \eta_3 = \eta_{33}; \tag{5}$$

$$\eta_4 = 2\eta_{23}, \eta_5 = 2\eta_{31}, \eta_6 = 2\eta_{12} \tag{6}$$

the factors of two in equation 6 are introduced for later convenience. Voigt subscripts will be denoted by Greek letters $\lambda$, etc. $(\lambda = 1, \ldots 6)$. A similar scheme defines infinitesimal strains $e_\lambda$.

‡ $\beta$ is used for the volumetric expansion to avoid confusion with the Grüneisen function $\gamma$.

## Description of stress

The stress is most directly described by the well-known *Cauchy stress tensor*[8], which in the absence of couple stresses is symmetric[9]. However, the Cauchy stress has the disadvantage for thermodynamic purposes that it does not determine the strain unless the orientation is specified (or unless the stress is isotropic). We therefore define other stress parameters, $t_\lambda$, which are thermodynamically conjugate to the strain parameters $\eta_\lambda$, and so depend on this prior choice of strain parameter.

The energy $U$ and Helmholtz energy $A$ are functions of the strain and one other variable. The stresses $t_\lambda$ are defined by

$$\overset{\circ}{V} t_\lambda \equiv (\partial U / \partial \eta_\lambda)_{\eta', S} = (\partial A / \partial \eta_\lambda)_{\eta', T} \qquad (7)$$

where the subscript $\eta'$ denotes that all the $\eta_\mu$ except $\eta_\lambda$ are kept constant during differentiation. The $t_\lambda$ have the dimensions of (negative) pressure, and are sometimes called the *thermodynamic tensions*[1,2]. One may also retain tensor notation to define stresses $t_{ij}$ by equations like 7, with this convention[10] for differentiation with respect to the components of a symmetric tensor. Write the function to be differentiated symmetrically in $\eta_{ij}$ and $\eta_{ji}$ and then differentiate treating all nine $\eta_{ij}$ as independent. The resulting tensor is symmetric, and is related to the $t_\lambda$ by a scheme like equations 5 and 6 without the factors of two.

The relation of $t_{ij}$ to the Cauchy stress $\sigma_{ij}$ is discussed in §3.

## Energy functions and Maxwell relations

We define quantities analogous to the enthalpy and Gibbs energy

$$H' \equiv U - \overset{\circ}{V} t_\lambda \eta_\lambda, \qquad G' \equiv A - \overset{\circ}{V} t_\lambda \eta_\lambda \qquad (8)$$

where the primes remind us that these cannot be identified with the functions $H$ and $G$ defined under hydrostatic pressure. The repeated subscript $\lambda$ denotes summation from 1 to 6; by virtue of the factors of two in the abbreviated notation for strains but not for tensions, $t_\lambda \eta_\lambda$ is equal to $t_{ij}\eta_{ij}$.

The differentials of the functions $U$, $A$, $H'$ and $G'$ are given to first order by

$$dU - T\,dS = \overset{\circ}{V} t_\lambda\,d\eta_\lambda = dA + S\,dT \qquad (9)$$

$$dH' - T\,dS = -\overset{\circ}{V}\eta_\lambda\,dt_\lambda = dG' + S\,dT \qquad (10)$$

Maxwell relations follow as for fluids, e.g.

$$(\partial S/\partial \eta_\lambda)_{\eta', T} = -(\partial^2 A/\partial \eta_\lambda\,\partial T)_{\eta'} = -\overset{\circ}{V}(\partial t_\lambda/\partial T)_\eta \qquad (11)$$

$$(\partial T/\partial t_\lambda)_{t', S} = (\partial^2 H'/\partial t_\lambda\,\partial S)_{t'} = -\overset{\circ}{V}(\partial \eta_\lambda/\partial S)_t \qquad (12)$$

and two similar expressions derived from $dU$ and $dG'$. Relations of this type also establish the symmetry of the isothermal elastic stiffnesses, analogous to the bulk modulus $B$ for fluids:

$$C_{\lambda\mu}^T \equiv \left(\frac{\partial t_\lambda}{\partial \eta_\mu}\right)_{\eta', T} = \frac{1}{\overset{\circ}{V}}\left(\frac{\partial^2 A}{\partial \eta_\mu\,\partial \eta_\lambda}\right)_{\eta', T} = C_{\mu\lambda}^T \qquad (13)$$

and similarly for the adiabatic stiffnesses $C_{\lambda\mu}^S$ and the compliances $S_{\lambda\mu}$ $= (\partial\eta_\lambda/\partial t_\mu)_{t'}$. The same full symmetry is possessed by simple higher-order elastic constants, e.g.

$$C_{\lambda\mu\nu}^T \equiv (\partial C_{\lambda\mu}^T/\partial\eta_\nu)_{\eta',T} = (\partial^3 A/\partial\eta_\lambda\,\partial\eta_\mu\,\partial\eta_\nu)/\overset{\circ}{V} \tag{14}$$

but mixed constants like $(\partial C_{\lambda\mu}^S/\partial\eta_\nu)_{\eta'\,T}$ have lower symmetry[11].

From these generalized energy functions a selfconsistent thermodynamic theory can be developed[1,2] in much the same way as for fluids. The development again depends strongly on the elementary theory of partial differentiation, suitably extended to seven independent variables instead of two. For instance, just as $(\partial p/\partial T)_V$ is equal to $-(\partial p/\partial V)_T(\partial V/\partial T)_p$, so

$$(\partial t_\lambda/\partial T)_\eta = -(\partial t_\lambda/\partial\eta_\mu)_{\eta',T}(\partial\eta_\mu/\partial T)_t \tag{15}$$

where it should be recalled that by the summation convention the RHS is a sum of six terms. In the present brief account this example must suffice; it is used in obtaining equation 32.

## 3. USE OF THE CAUCHY STRESS TENSOR

### The problem

We come now to a major source of difficulty and confusion. Although the $t_\lambda$ are by their definition convenient for thermodynamic analysis, it is the Cauchy stresses $\sigma_\lambda$ which are most simply related to experimental conditions. We have therefore to relate properties defined in terms of the $\sigma_\lambda$ to the thermodynamic results obtained in terms of the $t_\lambda$, which can require rather complex expressions.

Elementary treatments[8] attempt to avoid this difficulty by always choosing the instantaneous (often unstressed) configuration for the reference configuration and considering only infinitesimal strains. Then

$$dU(e, \omega, S) = T\,dS + \overset{\circ}{V}\sigma_\lambda\,de_\lambda \tag{16}$$

Since to first order $de_\lambda = d\eta_\lambda$ we see from equation 7 that $\overset{\circ}{\sigma}_\lambda = \overset{\circ}{t}_\lambda$. We may then define coefficients of thermal expansion

$$\alpha_\lambda \equiv (\partial e_\lambda/\partial T)_{\sigma,\omega} \tag{17}$$

stiffnesses

$$c_{\lambda\mu}^T \equiv (\partial\sigma_\lambda/\partial e_\mu)_{e',\omega,T} \tag{18}$$

and other properties directly related to physical measurements. The difficulty is that since these relations hold only at the reference configuration, we cannot differentiate a second time with respect to strain or stress. So, for example, there is no Maxwell relation like equation 13.

### Relation of $\sigma_{ij}$ to $t_{ij}$

By treating the configuration reached by displacements $u_{ij}$ as a new reference configuration and then applying the result $\overset{\circ}{\sigma}_{ij} = \overset{\circ}{t}_{ij}$, we can show[2,10] that

$$\sigma_{ij} = (V/\overset{\circ}{V})(\delta_{ip} + u_{ip})(\delta_{jq} + u_{jq})\,t_{pq} \tag{19}$$

To first order in the displacements this gives

$$\sigma_{ij} = t_{ij} + P_{ijkl}e_{kl} + Q_{ijkl}\omega_{kl} \tag{20}$$

where

$$P_{ijkl} = \tfrac{1}{2}(\mathring{\sigma}_{jl}\delta_{ik} + \mathring{\sigma}_{il}\delta_{jk} + \mathring{\sigma}_{ik}\delta_{jl} + \mathring{\sigma}_{jk}\delta_{il}) - \mathring{\sigma}_{ij}\delta_{kl} \tag{21}$$

$$Q_{ijkl} = \tfrac{1}{2}(\mathring{\sigma}_{jl}\delta_{ik} + \mathring{\sigma}_{il}\delta_{jk} - \mathring{\sigma}_{ik}\delta_{lj} - \mathring{\sigma}_{jk}\delta_{il}) \tag{22}$$

This result, together with the observations that to first order

$$de_\lambda = d\eta_\lambda, \quad (dt)_\eta = (d\sigma)_{e,\omega} \tag{23}$$

can be used to derive thermodynamic relations for measured quantities.

A particularly simple example following directly from equation 20 by differentiation with respect to strain relates $c^T_{\lambda\mu}$ [equation 18] to $C^T_{\lambda\mu}$ [equation 13] by

$$c^T_{\lambda\mu} = C^T_{\lambda\mu} + P_{\lambda\mu} \tag{24}$$

where $P_{14} = P_{1123}$, etc. Hence $c^T_{\lambda\mu} = C^T_{\lambda\mu}$ only for a solid under zero stress[6]. Examination of equation 21 shows that $P_{\lambda\mu}$ is symmetric only when $\mathring{\sigma}_{ij}$ represents a hydrostatic pressure, so that for an anisotropic stress $c^T_{\lambda\mu} \neq c^T_{\mu\lambda}$. The compliance $s^T_{\lambda\mu} = (\partial e_\lambda/\partial\sigma_\mu)_{\sigma',\omega,T}$ is inverse to $c^T_{\lambda\mu}$ (i.e. $s^T_{\lambda\mu}c^T_{\mu\nu} = \delta_{\lambda\nu}$), so that $s_{\lambda\mu}$ too is symmetric only under isotropic stress.

## Maxwell relations

Because of equation 23, the analogues of equation 11 and the similar relation deduced from d$U$ remain valid:

$$(\partial S/\partial e_\lambda)_{e',\omega,T} = -\mathring{V}(\partial\sigma_\lambda/\partial T)_{e,\omega} \tag{25}$$

$$(\partial T/\partial e_\lambda)_{e',\omega,S} = \mathring{V}(\partial\sigma_\lambda/\partial S)_{e,\omega} \tag{26}$$

Let us now try to derive the analogue of equation 12. We have

$$(\partial T/\partial\sigma_\lambda)_{\sigma',\omega,S} = (\partial T/\partial e_\mu)_{e',\omega,S}(\partial e_\mu/\partial\sigma_\lambda)_{\sigma',\omega,S} \tag{27}$$

$$= \mathring{V}(\partial e_\mu/\partial\sigma_\lambda)_{\sigma',\omega,S}(\partial\sigma_\mu/\partial S)_{e,\omega} \tag{28}$$

by equation 26. The RHS of equation 28 will equal $-\mathring{V}(\partial e_\lambda/\partial S)_{e,\omega}$ if the compliance $s^S_{\lambda\mu}$ is symmetric, that is, if the stress $\mathring{\sigma}_{ij}$ is isotropic. So the analogue of equation 12 is valid only under hydrostatic pressure. It follows that expressions derived assuming the validity of this Maxwell relation under anisotropic stress involve errors of the order of the fractional difference between $s_{\lambda\mu}$ and $s_{\mu\lambda}$. Similarly, the analogue of the relation like equation 12 derived from d$G'$ is valid only under isotropic stress.

## Some further results

The heat capacity most readily measurable is that at constant stress, $C_\sigma \equiv T(\partial S/\partial T)_{\sigma,\omega}$. It differs from its analogue at constant tension, $C_t$, by a power series in the stress components. To first order in an isotropic pressure $\sigma_{ij} = -p\delta_{ij}$, when $C_\sigma \equiv C_p$, the result becomes

$$C_t - C_\sigma = pVT(\beta^2 - 2\alpha_\lambda\alpha_\lambda) \tag{29}$$

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for cubic solids $C_t \geqslant C_\sigma$, but for non-cubic solids $C_t$ may be less than $C_\sigma$.

Although in general analogous quantities defined in terms of the physical variables $e$ and $\sigma$ differ from those in terms of the thermodynamic variables $\eta$ and $t$, some quantities are the same in both systems, and so form an important link between them. One such quantity is the heat capacity at constant strain, $C_\eta \equiv T(\partial S/\partial T)_\eta = T(\partial S/\partial T)_e$, as follows from equation 23. $C_\eta$ is related to $C_\sigma$ and $C_t$ by[4]

$$C_\eta = C_\sigma - TV c^T_{\lambda\mu}\alpha_\lambda\alpha_\mu = C_t - T\mathring{V} C^T_{\lambda\mu}a_\lambda a_\mu \qquad (30)$$

where the $a_\lambda$ are thermal expansion coefficients $(\partial\eta_\lambda/\partial T)_t$. Another unique quantity is the Grüneisen function defined by[12]

$$\gamma_\lambda \equiv (\partial S/\partial\eta_\lambda)_{\eta', T}/C_\eta = (\partial S/\partial e_\lambda)_{e', \omega, T}/C_\eta \qquad (31)$$

Through the Maxwell relations 11 and 25 and equation 15 these equations can be transformed to

$$\gamma_\lambda = \mathring{V} C^T_{\lambda\mu}a_\mu/C_\eta = V c^T_{\lambda\mu}\alpha_\mu/C_\eta \qquad (32)$$

which can be shown to be equal to

$$\gamma_\lambda = \mathring{V} C^S_{\lambda\mu}a_\mu/C_t = V c^S_{\lambda\mu}\alpha_\mu/C_\sigma \qquad (33)$$

## 4. CONCLUSION

In general, an extended thermodynamic theory is required for solids. It is most naturally developed in terms of the conjugate variables $\eta_\lambda$ and $t_\lambda$, but experiments are often more readily described by $e_\lambda$ and $\sigma_\lambda$. Analogous quantities in the two systems differ by amounts depending on the magnitude and anisotropy of the stress. Consequently, care is needed in comparing theory and experiment at high pressures, particularly for highly compressible solids like helium.

## REFERENCES

[1]  C. Truesdell and R. A. Toupin, *Handb. der Phys.* **III**/1, 226 (1960).
[2]  R. N. Thurston, *Physical Acoustics*, **1A**, 1 (1964).
[3]  A. G. McLellan, *Proc. Roy. Soc. A*, **307**, 1 (1968).
[4]  T. H. K. Barron and R. W. Munn, *J. Phys. Chem.* **1**, 1 (1968).
[5]  H. Jeffreys, *Cartesian Tensors*, p 71. Cambridge University Press: London (1963).
[6]  T. H. K. Barron and M. L. Klein, *Proc. Phys. Soc.* **85**, 523 (1965).
[7]  K. Brugger, *Phys. Rev.* **133**, A1611 (1964).
[8]  H. B. Callen, *Thermodynamics*, p 213. Wiley: New York (1960).
[9]  M. Lax, *Lattice Dynamics*, p 583. Pergamon Press: London (1965).
[10]  F. D. Murnagham, *Finite Deformation of an Elastic Solid*, p 43. Dover Publications: New York (1967).
[11]  M. J. Skove and B. E. Powell, *J. Appl. Phys.* **38**, 404 (1967).
[12]  T. H. K. Barron and R. W. Munn, *Phil. Mag. VIII*, **15**, 85 (1967).