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Thermodynamics for Elastic Solids. General Formulation

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A condensed collection of all the thermodynamic formulas involving first derivatives for elastic solids under the outside variations of only temperature and stress is presented. The application is illustrated with some examples.

INTRODUCTION

LITTLE attention has been concentrated on the thermodynamic treatment of elastic solids.[1–4] One of the possible difficulties arises from the fact that most of the discussions concerning the relations between stress and strain are confined at constant temperature. To be able to apply thermodynamic principles to elastic solids, the definition of strain has to be generalized to use only one configuration as reference state for the calculation of all strain at different temperatures and stress. Let the thermodynamic system for strained solids be a very small volume element in the body. If one regards temperature and stress as the only outside variables, this system of constant composition has seven degrees of freedom. On applying the principle of Jacobians,[5] it is possible to prepare tables which will help to obtain all first derivatives in terms of measurable quantities and consequently all possible relations among the first derivatives. It is the purpose of this communication to present these tables and to illustrate the application with some examples.

DEFINITION OF SYMBOLS

The six components of strain, $\epsilon_1, \epsilon_2, \cdots, \epsilon_6$, at any point of any configuration are defined as relative to a particular configuration chosen as the reference state.[3,6–8] The strain will therefore vary with the temperature T as well as with the six components of stress, $\tau_1, \tau_2, \cdots, \tau_6$, at this point. There are six coefficients of thermal expansion, $\alpha_i=(\partial\epsilon_i/\partial T)_\tau$, and thermal stress, $\beta_i=(\partial\tau_i/\partial T)_\epsilon$; and 36 isothermal elastic coefficients, $c_{ij}=(\partial\tau_i/\partial\epsilon_j)_{T,\epsilon'}$ and the coefficients of isothermal compliance $k_{ij}=(\partial\epsilon_i/\partial\tau_j)_{T,\tau'}$, where both i and $j=1, 2, \cdots, 6$, τ and ϵ represent the stress and strain respectively, and ϵ' and τ' represent all the components of strain and stress respectively except the jth component. Through simple mathematical manipulation, it can be shown that these coefficients are connected by the following relations:

$$\alpha_i=-\textstyle\sum_j k_{ij}\beta_j, \tag{1}$$

$$\beta_i=-\textstyle\sum_j c_{ij}\alpha_j, \tag{2}$$

$$(c_{ij})=(k_{ij})^{-1}, \tag{3}$$

where ( ) represents the 6×6 square matrix with the inside coefficients as elements. It is also easy to prove that these matrices are symmetric.

In view of the fact that small deformation of short duration happens usually at constant entropy instead of constant temperature, another two sets of the adiabatic elastic coefficients and the coefficients of adiabatic compliance are defined: $a_{ij}=(\partial\tau_i/\partial\epsilon_j)_{S,\epsilon'}$, $q_{ij}=(\partial\epsilon_i/\partial\tau_j)_{S,\tau'}$. They are again connected by $(a_{ij})=(q_{ij})^{-1}$, where the matrices are also symmetric. By the use of simple relations of partial derivatives, these coefficients are related to the isothermal coefficients through the following equations:

$$a_{ij}=c_{ij}+TV_0\beta_i\beta_j/C_\epsilon, \tag{4}$$

$$q_{ij}=k_{ij}-TV_0\alpha_i\alpha_j/C_\tau, \tag{5}$$

where C_ϵ is the heat capacity at constant strain and C_τ that at constant stress for the small material element at the point of consideration. This small material element has volume V_0 at the reference state.

For simplicity of later presentation, the following symbols are defined:

Isothermal Hooke's law stress: $\sigma_i=\sum_j c_{ij}\epsilon_j$,
Isothermal Hooke's law strain: $e_i=\sum_j k_{ij}\tau_j$,
Adiabatic Hooke's law stress: $\mu_i=\sum_j a_{ij}\epsilon_j$,
Adiabatic Hooke's law strain: $\xi_i=\sum_j q_{ij}\tau_j$,

Temperature coefficient of strain energy at constant stress: $\omega_\tau=V_0\sum_i\alpha_i\tau_i=-V_0\sum_j\beta_j e_j$,

Temperature coefficient of strain energy at constant strain: $\omega_\epsilon=-V_0\sum_i\alpha_i\sigma_i=V_0\sum_j\beta_j\epsilon_j$.

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[2] *Mathematical and Physical Papers by Sir William Thomson* (Cambridge University Press, Cambridge, 1882), Vol. I, p. 291.

[3] *The Collected Works of J. Willard Gibbs* edited by W. R. Langley and R. G. Van Name (Longmans Green and Company, New York, 1928), Vol. I, p. 184.

[4] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, p. 108.

[5] F. H. Crawford, Am. J. Phys. **17**, 1 (1949); see also J. C. M. Li, J. Chem. Phys. **26**, 909 (1957).

[6] Reference 4, Chap. I.

[7] C. Zener, *Elasticity and Anelasticity* (The University of Chicago Press, Chicago, Illinois, 1948), p. 7.

[8] I. S. Sokolnikoff, *Mathematical Theory of Elasticity* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. I.

TABLE I. First derivatives with temperature and strain as independent variables.

	$\partial/\partial T$	$\partial/\partial\epsilon_j$
T	1	0
ϵ_i	0	δ_{ij}
τ_i	β_i	c_{ij}
U	C_ϵ	$V_0(\tau_j-T\beta_j)$
H	$C_\epsilon-\omega_\epsilon$	$V_0(-T\beta_j-\sigma_j)$
S	C_ϵ/T	$-V_0\beta_j$
F	$-S-\omega_\epsilon$	$V_0\sigma_j$
A	$-S$	$V_0\tau_j$

TABLE II. First derivatives with entropy and strain as independent variables.

	$\partial/\partial S$	$\partial/\partial\epsilon_j$
T	T/C_ϵ	$TV_0\beta_j/C_\epsilon$
ϵ_i	0	δ_{ij}
τ_i	$T\beta_i/C_\epsilon$	a_{ij}
U	T	$V_0\tau_j$
H	$T(C_\epsilon-\omega_\epsilon)/C_\epsilon$	$-V_0\mu_j$
S	1	0
F	$-T(S+\omega_\epsilon)/C_\epsilon$	$V_0(-\mu_j-TS\beta_j/C_\epsilon)$
A	$-TS/C_\epsilon$	$V_0(\tau_j-TS\beta_j/C_\epsilon)$

TABLES OF FIRST DERIVATIVES

Tables I, II, III, and IV give the first derivatives of the functions T, ϵ_1, ϵ_2, $\cdots$, ϵ_6, τ_1, τ_2, $\cdots$, τ_6, U, H, S, F, and A with respect to the following independent variables:

Table I, temperature and the six components of strain;
Table II, entropy and the six components of strain;
Table III, temperature and the six components of stress;
Table IV, entropy and the six components of stress.

In these tables, $i=1, 2, \cdots, 6$, and $\delta_{ij}=0$ for $i\neq j$ and $\delta_{ii}=1$. The thermodynamic functions have the usual definitions except that between H and U, the following relation is defined:

$$H=U-V_0\textstyle\sum_i\tau_i\epsilon_i.$$

The Jacobians of any set of seven variables or functions can be calculated from each table with respect to the same independent variables as used by the table. Any first derivative such as $(\partial H/\partial F)_\epsilon$ can be obtained from the ratio of two Jacobians as explained by Crawford.[5] However, different expressions representing the same quantity may result from different tables. Also the complexity of the Jacobian determinants is different for different tables. Therefore in order to take full advantage of these tables, first derivatives with most of the independent variables indicated in the title of the table can probably be obtained most easily from the very table.

To illustrate the application of these tables, let us evaluate $(\partial H/\partial F)_\epsilon$ from each table: It is equal to the ratio of the two Jacobians: $J(H,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)$ and $J(F,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)$. Thus from Table I:

$$J(H,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=\begin{vmatrix} C_\epsilon-\omega_\epsilon & V_0(-\beta_1T-\sigma_1) & V_0(-\beta_2T-\sigma_2) & \cdots & V_0(-\beta_6T-\sigma_6) \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ 0 & 0 & 0 & \cdots & 1 \end{vmatrix}$$

$$=C_\epsilon-\omega_\epsilon,$$

$$J(F,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=\begin{vmatrix} -\omega_\epsilon-S & -V_0\sigma_1 & -V_0\sigma_2 & \cdots & -V_0\sigma_6 \\ 0 & 1 & 0 & \cdots & 1 \\ 0 & 0 & 1 & \cdots & 0 \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ 0 & 0 & 0 & \cdots & 1 \end{vmatrix}$$

$$=-\omega_\epsilon-S.$$

TABLE III. First derivatives with temperature and stress as independent variables.

	$\partial/\partial T$	$\partial/\partial\tau_j$
T	1	0
ϵ_i	α_i	k_{ij}
τ_i	0	δ_{ij}
U	$C_\tau+\omega_\tau$	$V_0(T\alpha_j+e_j)$
H	C_τ	$V_0(T\alpha_j-\epsilon_j)$
S	C_τ/T	$V_0\alpha_j$
F	$-S$	$-V_0\epsilon_j$
A	$-S+\omega_\tau$	V_0e_j

TABLE IV. First derivatives with entropy and stress as independent variables.

	$\partial/\partial S$	$\partial/\partial\tau_j$
T	T/C_τ	$-TV_0\alpha_j/C_\tau$
ϵ_i	$T\alpha_i/C_\tau$	q_{ij}
τ_i	0	δ_{ij}
U	$T(C_\tau+\omega_\tau)/C_\tau$	$V_0\xi_j$
H	T	$-V_0\epsilon_j$
S	1	0
F	$-TS/C_\tau$	$V_0(-\epsilon_j+TS\alpha_j/C_\tau)$
A	$T(-S+\omega_\tau)/C_\tau$	$V_0(\xi_j+TS\alpha_j/C_\tau)$

Therefore $(\partial H/\partial F)_\epsilon=(\omega_\epsilon-C_\epsilon)/(\omega_\epsilon+S)$. Similarly, from Table II, $J(H,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=T(1-\omega_\epsilon/C_\epsilon)$ and $J(F,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=-T(\omega_\epsilon+S)/C_\epsilon$, which gives the same result for $(\partial H/\partial F)_\epsilon$. Now if Table III is used, $J(H,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=(C_\tau+TV_0\sum_i\alpha_i\beta_i-\omega_\epsilon)|(k_{ij})|$ and $J(F,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=-(\omega_\epsilon+S)|(k_{ij})|$, where $|(k_{ij})|$ is the determinant of the (k_{ij}) matrix. It is seen that $(\partial H/\partial F)_\epsilon=(\omega_\epsilon-C_\tau-TV_0\sum_i\alpha_i\beta_i)/(\omega_\epsilon+S)$ which is identical with the result from Tables I or II since it will be seen later that $C_\tau=C_\epsilon-TV_0\sum_i\alpha_i\beta_i$. To complete the illustration, let us calculate also from Table IV: $J(H,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=T(C_\tau+TV_0\sum_i\alpha_i\beta_i-\omega_\epsilon)|(k_{ij})|/C_\tau$ and $J(F,\epsilon_1,\epsilon_2,\cdots,\epsilon_6)=-T(S+\omega_\epsilon)|(k_{ij})|/C_\tau$. This gives again the identical result for $(\partial H/\partial F)_\epsilon$ but with more complicated Jacobian determinants. In evaluating these determinants, the relation between q_{ij} and k_{ij} as shown by Eq. (5) has been used.

HEAT CAPACITIES AT CONSTANT STRESS AND STRAIN

As an example of the application of these tables, the most important first derivatives, namely the heat capacities, will be discussed here. When $C_\tau=(\partial H/\partial T)_\tau$ is evaluated from Table I or $C_\epsilon=(\partial U/\partial T)_\epsilon$ is evaluated from Table III, one obtains

$$\begin{aligned} C_\tau &= C_\epsilon-TV_0\textstyle\sum_i\alpha_i\beta_i \\ &= C_\epsilon+TV_0\textstyle\sum_i\sum_j c_{ij}\alpha_i\alpha_j. \end{aligned} \tag{6}$$

This may be compared with the equation for fluid which is equivalent to an isotropic elastic solid under uniform pressure. Let the configuration in question be the reference state for the calculation of strain, that is $V_0=V$. Since the pressure is uniform, $\epsilon_1=\epsilon_2=\epsilon_3$ and $\epsilon_4=\epsilon_5=\epsilon_6=0$ will hold at any temperature and therefore $\alpha_1=\alpha_2=\alpha_3$ and $\alpha_4=\alpha_5=\alpha_6=0$. If α is the coefficient of volumetric thermal expansion, $\alpha=3\alpha_1$; and if k is the coefficient of isothermal volumetric compressibility, $k=\sum_{i=1}{}^3\sum_{j=1}{}^3k_{ij}$, where k_{ij} are the elements of the isotropic (k_{ij}) matrix. Since $(k_{ij})=(c_{ij})^{-1}$, $k_{11}=(c_{11}+c_{12})/[(c_{11}-c_{12})(c_{11}+2c_{12})]$ and $k_{12}=c_{12}/[(c_{11}-c_{12})\times(c_{11}+2c_{12})]$. With all the above relations, Eq. (6) is reduced to

$$C_P=C_V+TV\alpha^2/k, \tag{7}$$

which is identical with that usually found for fluids.[9,10]

Now if C_τ is evaluated from Table II or C_ϵ is evaluated from Table IV, one obtains

$$\frac{C_\tau}{C_\epsilon}=\frac{|(a_{ij})|}{|(c_{ij})|}=\frac{|(k_{ij})|}{|(q_{ij})|}. \tag{8}$$

Again this equation can be compared with that for a fluid. In addition to the above relations concerning isotropic solids under uniform pressure, the relation between k_{ij} and q_{ij} as shown by Eq. (5) is useful, and if q is the coefficient of adiabatic volumetric compressibility, then $q=\sum_{i=1}{}^3\sum_{j=1}{}^3q_{ij}$. Equation (8) is reduced to

$$C_P/C_V=k/q, \tag{9}$$

which is identical with that usually found for fluids.[11,12]

Equations (6) and (8) are believed to be new. This illustrates the numerous possible applications of the tables which will prove useful in deriving exact thermodynamic relations for elastic solids. More discussion will be published elsewhere.

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[9] F. D. Rossini, *Chemical Thermodynamics* (John Wiley and Sons, Inc., New York, 1950), p. 107.

[10] E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1949), p. 87.

[11] Reference 10, p. 102.

[12] M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company Inc., New York, 1951), p. 255.