On the Exact Relation Between the Specific Heats of an Elastic Solid

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1. Introduction. The relation between the specific heats at constant volume and at constant pressure is usually claimed to hold not only for fluids but also for solids¹. The meaning of this generalisation, however, is not very clear, and its proof cannot be considered satisfactory, when, as is the case, nothing is said about the state of the solid body which is chosen as a reference or about the value of the pressure at which the specific heat is computed. In fact, the exact character of such a generalisation and its validity have even been questioned², and there are some who consider it nothing more than a good approximation, valid when the thermal expansion is constant and the specific heat is independent of volume or pressure.

Obviously the correct relation between the specific heats of solids can be obtained only from the general theory of finite thermoelastic deformations. As is shown in the present paper, the relation can be derived without introducing any hypothesis on the type of strain energy, by considering only a certain invariance requirement which characterizes the dependence of the thermoelastic potential upon temperature. A new proof of this requirement, making very evident its physical meaning, is given; the difference of the specific heats is then computed, and it is found that the well known relation for fluids holds exactly also for homogeneous isotropic elastic bodies, when they are in a natural equilibrium state, entirely free from stress.

2. An invariance requirement for the thermoelastic potential. The thermoelastic potential (or free energy) F of an elastic solid in its actual state C , at the uni-

¹ See for example: M. PLANCK: *Treatise on Thermodynamics*, Dover, 1945, pp. 59, 126; E. A. GUGGENHEIM: *Thermodynamics*, North Holland Publishing Co., 1950, p. 87.

² See J. C. SLATER: *Introduction to Chemical Physics*, McGraw Hill, 1939, p. 205.

form temperature T , is a function of the components of strain (computed with respect to some reference state), of T , and, for dimensional reasons, of a second temperature. If the body is homogenous and isotropic when no external forces act on it and its temperature has a uniform value τ , the most convenient reference is the natural equilibrium state C_τ of the solid in the above conditions. It has been proved that for every value of τ , all the C_τ 's are similar to one another³ and free from internal stress.⁴

When a natural state is chosen as reference, F cannot depend directly either upon the coordinates (owing to homogeneity) or upon the several components of strain (owing to isotropy) but is necessarily a function of three independent strain invariants and of the temperatures T and τ . The strain invariants chosen in the following will be the Jacobian $\bar{D}$, the linear invariant $\bar{I}_1$, and the quadratic invariant $\bar{I}_2$, of the strain components $\bar{\epsilon}_{rs}$ of the *inverse displacement* $C \rightarrow C_\tau$. The reason for this choice is that later in computing the compressibility we shall need to use the functional dependence of the stress components upon the $\bar{\epsilon}_{rs}$ only, whilst a similar dependence does not hold in general for the strain components of the *direct displacement*⁵ $C_\tau \rightarrow C$. It is therefore simpler to consider just one displacement, which is necessarily $C \rightarrow C_\tau$, and to compute with respect to it both the strain coefficients and their invariants.

In general the temperatures τ and T have different values. It will be convenient to consider $C \rightarrow C_\tau$ as the operational product of two deformations: the first is an isothermal strain from C to the natural equilibrium state C_τ having the same uniform temperature as the final state; the second is a thermal expansion under no external forces from C_τ to C_τ . During the last process the internal stress remains zero, the temperature being uniform.

The value of the free energy in C may therefore be obtained (to within a linear function of T) by adding to the value of F in C_τ its change for the $C \rightarrow C_\tau$ deformation. Let $s(\tau)$ be the entropy per unit mass in C_τ ; the free energy in C_τ is necessarily

$$(1) \quad -\mathfrak{E} \int_{T_0}^T s(\tau) d\tau = -\mathfrak{E} \int_{T_0}^T d\tau \int_{\tau_0}^{\tau} c_{p_0}(\tau') \frac{d\tau'}{\tau'},$$

where $\mathfrak{E}$ is the mechanical equivalent of a calorie; T_0 is the arbitrary temperature, taken as zero level for entropy; τ_0 is another arbitrary temperature; c_{p_0} is the specific heat (in calories per unit mass) at constant (zero) pressure.

For the isothermal deformation $C \rightarrow C_\tau$ the change in free energy is due only to the difference W_τ between the isothermal strain energy in C and in C_τ . As the elastic body is homogeneous and isotropic in C_τ , W_τ depends only upon

³ See A. SIGNORINI: *Trasformazioni termoelastiche finite* (Memoria I) "Annali di Matematica", **22**, (1943), p. 143.

⁴ See A. SIGNORINI: *Trasformazioni termoelastiche finite* (Memoria II) "Annali di Matematica", **30**, (1949), p. 3.

⁵ See *loc. cit.* footnote (3), p. 139.

the *isothermal invariants* $\bar{I}_1^{(T)}$, $\bar{I}_2^{(T)}$, $\bar{D}^{(T)}$ of the inverse deformation $C \rightarrow C_T$ and upon the temperature T . Owing to the properties of perfect elasticity⁶, W_T must also satisfy the inequality,

$$W_T(\bar{I}_1^{(T)}, \bar{I}_2^{(T)}, \bar{D}^{(T)}) \geq 0,$$

where equality holds only for $C \equiv C_T$.

The value of F in the final state C is then obtained by adding W_T to (1). Since W_T is usually referred to unit volume in the unstressed state, it must be divided by the uniform density k_T of C_T in order to get the free energy per unit mass by the formula

$$(2) \quad F = \frac{1}{k_T} W_T(\bar{I}_1^{(T)}, \bar{I}_2^{(T)}, \bar{D}^{(T)}) - \mathfrak{E} \int_{T_0}^T d\tau \int_{\tau_0}^{\tau} c_{p0}(\tau') \frac{d\tau'}{\tau'}.$$

Every trace of the auxiliary reference state C_T is cancelled in (2) if k_T and the isothermal invariants are expressed by means of the density k_τ in C_τ , of the invariants $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$ for the total deformation $C \rightarrow C_\tau$, and of the similitude ratio $\rho = l_T/l_\tau$ between C_T and C_τ . This is easily done by means of the formulae which give the values of invariants when the reference state is changed⁷. In addition to the obvious relation $k_T = \rho^{-3} k_\tau$, one gets

$$(3) \quad \begin{aligned} \bar{I}_1^{(T)} &= \frac{3}{2}(\rho^2 - 1) + \rho^2 \bar{I}_1, \\ \bar{I}_2^{(T)} &= \frac{3}{4}(\rho^2 - 1)^2 + \rho^2 (\rho^2 - 1) \bar{I}_1 + \rho^4 \bar{I}_2, \\ \bar{D}^{(T)} &= \rho^3 \bar{D}. \end{aligned}$$

The physical meaning of the isothermal invariants makes it clear that the left members of (3) remain constant when C_τ is changed into $C_{\tau'}$, while in the right members ρ is replaced by $\rho' = l_T/l_{\tau'}$, and the three invariants $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$ of $C \rightarrow C_\tau$ are replaced by the corresponding ones $\bar{I}'_1$, $\bar{I}'_2$, $\bar{D}'$ of $C \rightarrow C_{\tau'}$. Hence the isothermal invariants, considered as functions of τ , T and $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$, satisfy the invariance requirement, the necessary character of which was first pointed out by A. SIGNORINI⁸. Moreover, being independent of each other, they are the only functions which satisfy that requirement and, for $\tau = T$, coincide with $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$. It follows that the expression (2) for the free energy also satisfies the above requirement and is the most general one which enjoys this property.

In this way, the invariant character of (2) has been established from purely physical remarks on the isothermal invariants, without solving the partial differential equation obtained by C. TOLOTTI for any expression of the free energy satisfying the invariance requirement.⁹

⁶ See *loc. cit.* footnote (4), p. 7.

⁷ See *loc. cit.* footnote (3), p. 64.

⁸ See *loc. cit.* footnote (4), p. 38.

⁹ C. TOLOTTI: *Sul potenziale termodinamico dei solidi elastici omogenei ed isotropi per*

It may be added that the inequalities for the strain invariants derived in a previous paper¹⁰ must be also satisfied for any value of $\rho > 0$ by the functions of $\bar{I}_1, \bar{I}_2, \bar{D}$ given by the right members of (3). In fact the inequalities, being of a purely geometrical character, are necessarily independent of the temperature of the solid, and therefore must hold also for the isothermal invariants.

As a general consequence of the invariance requirement, the free energy per unit mass of a homogeneous isotropic elastic solid may always be considered as the sum of two terms with a very different physical meaning. The first term, W_τ/k_τ , is non-negative and depends on the final state of the solid but not on the reference state. Since W_τ vanishes with the stress, at any given value of the final temperature T , the free energy takes its minimum value in the natural equilibrium state C_τ . Nothing can be said in general about the sign of the second term of F , since it is defined to within a linear function of temperature. However, it is entirely independent of strain, being a function only of the temperatures in the actual and reference states.

3. Specific heat at constant configuration. When the specific heat at constant configuration c_v for the final state C is wanted, the free energy given by (2) must first be differentiated twice with respect to temperature, while the strain invariants of the total deformation $C \rightarrow C_\tau$, that is, $\bar{I}_1, \bar{I}_2, \bar{D}$, are kept constant; then the derivative must be multiplied by $-T/\mathfrak{E}$. The special value c_{v_0} assumed by c_v in the reference state C_τ is then obtained putting $T = \tau$ in the general expression for the specific heat and making the strain vanish.

If primes denote partial derivatives with respect to T when $\bar{I}_1, \bar{I}_2, \bar{D}$ are kept constant, the value of c_{v_0} is given by

$$(6) \quad c_{v_0} = -\frac{\tau}{\mathfrak{E}} (F'')_{\substack{i=0 \\ T=\tau}} = c_{p_0} - \frac{\tau}{\mathfrak{E}k_\tau} [(6\rho\rho'^2 + 3\rho^2\rho'')W_\tau + 6\rho^2\rho'W'_\tau + \rho^3W''_\tau]_{\substack{i=0 \\ T=\tau}},$$

where $\rho^{-3}k_\tau$ has been substituted for k_τ , according to a previous remark.

In every natural state C_τ the isothermal strain energy vanishes, according to its definition; hence the first term in brackets of (6) gives no contribution to c_{v_0} . To obtain W'_τ the strain energy may be considered as a function of the isothermal invariants and of T

$$(7) \quad W'_\tau = \frac{\partial W_\tau}{\partial \bar{I}_1^{(T)}} \frac{\partial \bar{I}_1^{(T)}}{\partial T} + \frac{\partial W_\tau}{\partial \bar{I}_2^{(T)}} \frac{\partial \bar{I}_2^{(T)}}{\partial T} + \frac{\partial W_\tau}{\partial \bar{D}^{(T)}} \frac{\partial \bar{D}^{(T)}}{\partial T} + \frac{\partial W_\tau}{\partial T},$$

where $\partial W_\tau/\partial T$ denotes the partial derivative of the strain energy computed when the isothermal invariants $\bar{I}_1^{(T)}, \bar{I}_2^{(T)}, \bar{D}^{(T)}$ are kept constant¹¹.

trasformazioni finite. "Mem. R. Accad. d'Italia", **14**, (1943), 529. See also C. TRUESDELL: *The mechanical foundations of elasticity and fluid dynamics*. "Journ. Rat. Mech. and Analysis", **1**, (1952), p. 196.

¹⁰ *Limitazioni per gli invarianti di deformazione*. "Rend. di Matematica", **14**, (1955), p. 269.

¹¹ In W'_τ the general invariants $\bar{I}_1, \bar{I}_2, \bar{D}$ are kept constant.

The partial derivatives of the isothermal invariants are immediately obtained from (3). Putting $\rho = 1$ and $[d\rho/dT]_{T=\rho} = \rho'_\tau$, for the values of the isothermal invariants in C_τ we get

$$(8) \quad \left(\frac{\partial \bar{I}_1^{(T)}}{\partial T} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = \left(\frac{\partial \bar{D}^{(T)}}{\partial T} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = 3\rho'_\tau, \quad \left(\frac{\partial \bar{I}_2^{(T)}}{\partial T} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = 0.$$

It must be observed that in C_τ the partial derivatives of W_τ with respect to $\bar{I}_1^{(T)}$ and $\bar{D}^{(T)}$ have opposite values, as the natural state is free from stress¹². The first three terms of W_τ then vanish in C_τ , and the same happens with $\partial W_\tau / \partial T$; otherwise W_τ could not be zero in *every* natural state.

The only contribution of the isothermal strain energy to c_{v_0} is that given by its second derivative. To compute W_τ'' from (7), the four partial derivatives of W_τ must be considered as functions of the four variables $\bar{I}_1^{(T)}$, $\bar{I}_2^{(T)}$, $\bar{D}^{(T)}$, and T . In this way ten independent derivatives of the second order are obtained for W_τ , to which must be added the three terms containing the second order derivatives of the isothermal invariants computed in C_τ :

$$(9) \quad \left(\frac{\partial^2 \bar{I}_1^{(T)}}{\partial T^2} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = 3(\rho_\tau'^2 + \rho_\tau''); \quad \left(\frac{\partial^2 \bar{I}_2^{(T)}}{\partial T^2} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = 6\rho_\tau'^2, \\ \left(\frac{\partial^2 \bar{D}^{(T)}}{\partial T^2} \right)_{\substack{\bar{\epsilon}=0 \\ T=\tau}} = 3(2\rho_\tau'^2 + \rho_\tau'').$$

The final expression for c_{v_0} can be made considerably simpler by observing that in C_τ the four terms containing $\partial \bar{I}_2^{(T)} / \partial T$ as a factor vanish, according to the second of (8). The same must happen with $\partial^2 W_\tau / \partial T^2$, since otherwise the isothermal energy could not be zero in *every* natural state. The first of (8) shows also that the derivatives

$$\frac{\partial^2 W_\tau}{\partial T \partial \bar{I}_1^{(T)}}, \quad \frac{\partial^2 W_\tau}{\partial T \partial \bar{D}^{(T)}}$$

have the same coefficient, $3\rho_\tau'$, when W_τ'' is computed in C_τ . Moreover their sum must necessarily be zero for $\bar{\epsilon} = 0$ and $T = \tau$, since otherwise not *every* natural state would be free from stress. Finally the terms containing $\partial W_\tau / \partial \bar{I}_1^{(T)}$ and $\partial W_\tau / \partial \bar{D}^{(T)}$ can be collected, as in C_τ the above derivatives have opposite values. The expression of W_τ'' reduces then to the sum of five terms only, and c_{v_0} is given by

$$(10) \quad c_{v_0}(\tau) = c_{p_0}(\tau) - \frac{\tau}{\mathfrak{E}} \frac{9\rho_\tau'^2}{k_\tau} \left[\frac{\partial^2 W_\tau}{\partial \bar{I}_1^{(T)2}} + \frac{\partial^2 W_\tau}{\partial \bar{D}^{(T)2}} + 2 \frac{\partial^2 W_\tau}{\partial \bar{I}_1^{(T)} \partial \bar{D}^{(T)}} - \frac{1}{3} \frac{\partial W_\tau}{\partial \bar{I}_1^{(T)}} + \frac{2}{3} \frac{\partial W_\tau}{\partial \bar{I}_2^{(T)}} \right]_{\substack{\bar{\epsilon}=0 \\ T=\tau}}.$$

¹² See for example *loc. cit.* note (9), p. 535.

It may be observed that the factor $9\rho_\tau'^2$ is nothing else than the square of the thermal expansion coefficient α_c . In fact, according to the definition of ρ , its derivative is given by

$$(11) \quad \rho'_\tau = \frac{1}{l_\tau} \left(\frac{dl_\tau}{dT} \right)_{T=\tau} = \frac{1}{3} \frac{1}{V_\tau} \left(\frac{dV_\tau}{dT} \right)_{T=\tau} = \frac{\alpha_c}{3}$$

where V_τ and V_T are the volumes of the body in C_τ and C_T , which, owing to similitude between the natural states, must be necessarily proportional to l_τ^3 and to l_T^3 .

4. Isothermal compressibility and exact relation between the specific heats. To find the relation between the term in brackets of (10) and the isothermal compressibility, an exact expression must be obtained for the latter by applying the general stress-strain equations to an isothermal strain under uniform pressure.

When $T = \tau$ the partial derivatives of F with respect to $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$ coincide, according to (2), with the partial derivatives of W_τ/k_τ with respect to the isothermal invariants $\bar{I}_1^{(\tau)}$, $\bar{I}_2^{(\tau)}$, $\bar{D}^{(\tau)}$. When the state of stress reduces to a uniform pressure, the principal stresses have a common value B , while the principal strains have a common value $\bar{E}$.

In the case considered the stress-strain equations are as follows:

$$(12) \quad B = \bar{D}^{(\tau)} \left\{ \bar{D}^{(\tau)} \frac{\partial W_\tau}{\partial \bar{D}^{(\tau)}} + \frac{\partial W_\tau}{\partial \bar{I}_1^{(\tau)}} + \bar{I}_1^{(\tau)} \frac{\partial W_\tau}{\partial \bar{I}_2^{(\tau)}} \right. \\ \left. + 2\bar{E} \left[\frac{\partial W_\tau}{\partial \bar{I}_1^{(\tau)}} + \bar{I}_1^{(\tau)} \frac{\partial W_\tau}{\partial \bar{I}_2^{(\tau)}} - \frac{1}{2} \frac{\partial W_\tau}{\partial \bar{I}_2^{(\tau)}} \right] - 2\bar{E}^2 \frac{\partial W_\tau}{\partial \bar{I}_2^{(\tau)}} \right\}_{T=\tau}.$$

When $T = \tau$, by (3) the isothermal invariants do not differ from $\bar{I}_1$, $\bar{I}_2$, $\bar{D}$. Their values and that of the principal strain $\bar{E}$ are related to the volume V_τ in C_τ and to its value V in C by the formulae¹³

$$(13) \quad \bar{D} = \frac{V_\tau}{V}, \quad \bar{E} = \frac{\bar{I}_1}{3}, \quad \bar{I}_1 = \frac{2}{3}(\bar{D}^3 - 1), \quad \bar{I}_2 = \frac{\bar{I}_1^2}{3}.$$

To obtain the inverse of the isothermal compressibility in C_τ , that is, χ_{τ_0} , the derivative of B with respect to V must be multiplied by $-V$ and then $\bar{\epsilon}$ set equal to 0. When the common factor $\bar{D}^{(\tau)}$ in the right member of (12) is differentiated, the term in brackets vanishes with $\bar{\epsilon}$, since C_τ is free from stress. The same happens with the derivatives of the terms having $\bar{E}$ or $\bar{I}_1^{(\tau)}$ as factors. From (13)

¹³ See for example *loc. cit.* footnote (10) p. 275.

the derivatives of $\bar{E}$, $\bar{I}_1^{(T)}$, $\bar{I}_2^{(T)}$ $\bar{D}^{(T)}$ with respect to V have the values

$$(14) \quad \begin{aligned} - \left(V \frac{\partial D^{(T)}}{\partial V} \right)_{\substack{\bar{e}=0 \\ T=\tau}} &= - \left(V \frac{\partial \bar{I}_1^{(T)}}{\partial V} \right)_{\substack{\bar{e}=0 \\ T=\tau}} = 1, \\ - \left(V \frac{\partial \bar{E}}{\partial V} \right)_{\substack{\bar{e}=0 \\ T=\tau}} &= \frac{1}{3}, \quad - \left(V \frac{\partial \bar{I}_2^{(T)}}{\partial V} \right)_{\substack{\bar{e}=0 \\ T=\tau}} = 0. \end{aligned}$$

Substituting (14) into the derivative of (12), one gets¹⁵

$$(15) \quad \begin{aligned} \frac{1}{\chi \tau_0} &= - \left(V \frac{\partial B}{\partial V} \right)_{\substack{\bar{e}=0 \\ T=\tau}} \\ &= \left(\frac{\partial^2 W_T}{\partial \bar{I}_1^{(T)2}} + \frac{\partial^2 W_T}{\partial \bar{D}^{(T)2}} + 2 \frac{\partial^2 W_T}{\partial \bar{I}_1^{(T)} \partial \bar{D}^{(T)}} - \frac{1}{3} \frac{\partial W_T}{\partial \bar{I}_1^{(T)}} + \frac{2}{3} \frac{\partial W_T}{\partial \bar{I}_2^{(T)}} \right)_{\substack{\bar{e}=0 \\ T=\tau}}. \end{aligned}$$

By comparison with (10) and (11) we then get the very simple formula,

$$(16) \quad c_{v_0}(\tau) = c_{p_0}(\tau) - \frac{\tau}{\mathcal{E}} \frac{\alpha_c^2}{k_\tau \chi \tau_0}.$$

The relation (16) has been obtained as a direct consequence of the invariance requirement, without introducing any hypothesis on the form of the thermodynamic potential. It must therefore hold for any homogeneous isotropic elastic body. It shows that in every natural equilibrium state the relation between the specific heats at constant configuration and at constant (zero) pressure is *exactly* the same as for non-viscous fluids.

¹⁵ The derivatives of W_T with respect to $\bar{I}^{(T)}$ and $D^{(T)}$ have opposite values in C .