

THERMODYNAMICS OF SOLIDS WITH A STATE EQUATION

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The thermodynamic relations describing equilibrium of a multi-phase thermoelastic solid are obtained in a way similar to that used in the multiphase fluid theory. The phase transitions of the first order are defined and equilibrium equations of the Clapeyron-Clausius type are derived. Also, the phase transitions of the second order are introduced and equilibrium equations of the Ehrenfest type are obtained. A general theory is illustrated by examples.

Key words: thermodynamics, thermoelasticity, phase transitions

1. Introduction

The paper aims at giving description of a solid within the frame of classical thermodynamics based on the assumption that a state equation describing behaviour of the solid exists; in particular, a thermoelastic solid may be described in this way.

It is well known that the laws of thermodynamics based on such concepts as the temperature, internal energy and entropy are generally accepted. Albert Einstein in his scientific autobiography in 1949 wrote *A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown (for the special attention of those who are skeptics on principle).*

In the present paper we discuss an analogy between classical thermodynamics of fluids and solids, and derive

- Relations of Maxwell type

- Constitutive consequences of these relations for a thermoelastic body
- Relations of the Clapeyron-Clausius type for the phase transitions of the first order
- Ehrenfest relations for the phase transitions of the second order
- Formulae for the stress-temperature tensor of a nonlinear solid.

These results have not been included in previously published works; e.g.,

- Landau and Lifszic (1959) discussed phase transitions of the second order for a body subject to the hydrostatic pressure only, cf also Lubarski (1961)
- Born and Huang (1956), and Khachatryan (1974) dealt with the phase transitions on an atomic level only; see also works by Likhachev and Malinin (1993), Roytburd (1974), Roytburd and Slutsker (1995), Raniecki and Tanaka (1994), and Raniecki (1996), in which the phase transformations of solids on a macroscopic level are discussed. The author (Wojnar, 1995) obtained only the Maxwell relations and thermodynamic functions describing the phase transitions in a solid with a state equation.

A multi-phase one-component thermoelastic solid discussed in the present paper can be considered as a generalization of a one-phase thermoelastic solid proposed by Landau and Lifszic (1958). For such a solid equilibrium equations of the Clapeyron-Clausius type for the phase transitions of the first order (when the temperature is constant) and equilibrium equations of the Ehrenfest type for the phase transitions of the second order (when the temperature changes) are obtained in a way similar to the multi-phase fluid theory by Landau and Lifszic (1959), and Werle (1957).

2. Constitutive equations

Let ε_{ij} and σ_{ij} denote the strain and stress tensor fields. If \mathbf{x} and t denote the space variable and time, respectively, we have e.g. $\varepsilon_{ij} = \varepsilon_{ij}(\mathbf{x}, t)$. Let T be the absolute temperature of a thermoelastic solid. The strain ε_{ij} is related to the displacement u_i by a relation which is to be specified later. Let the fields ε_{ij} , σ_{ij} and T be related by a constitutive law

$$\sigma_{ij} = \sigma_{ij}(\varepsilon_{ij}, T) \tag{2.1}$$

Thus, ε_{ij} and T are independent state variables i.e. $\partial\varepsilon_{ij}/\partial T = 0$. By taking the total derivative of Eq (2.1) we get

$$d\sigma_{ij} = \left. \frac{\partial\sigma_{ij}}{\partial T} \right|_{\varepsilon} dT + \left. \frac{\partial\sigma_{ij}}{\partial\varepsilon_{mn}} \right|_T d\varepsilon_{mn} \quad (2.2)$$

and if $\sigma_{ij} = \text{const}$

$$0 = \left. \frac{\partial\sigma_{ij}}{\partial T} \right|_{\varepsilon} dT + \left. \frac{\partial\sigma_{ij}}{\partial\varepsilon_{mn}} \right|_T d\varepsilon_{mn} \quad (2.3)$$

Therefore

$$\left. \frac{\partial\sigma_{ij}}{\partial T} \right|_{\varepsilon} = - \left. \frac{\partial\sigma_{ij}}{\partial\varepsilon_{mn}} \right|_T \left. \frac{\partial\varepsilon_{mn}}{\partial T} \right|_{\sigma} \quad (2.4)$$

Now, let us define the tensor fields

$$c_{ijmn} = \left. \frac{\partial\sigma_{ij}}{\partial\varepsilon_{mn}} \right|_T \quad \alpha_{ij} = \left. \frac{\partial\varepsilon_{ij}}{\partial T} \right|_{\sigma} \quad \gamma_{ij} = - \left. \frac{\partial\sigma_{ij}}{\partial T} \right|_{\varepsilon} \quad (2.5)$$

For a linear body c_{ijmn} , α_{ij} and γ_{ij} are known as the elasticity, thermal expansion and stress-temperature tensor fields, respectively.

The inverse relation of Eq (2.5)₁ reads

$$a_{ijmn} = \left. \frac{\partial\varepsilon_{ij}}{\partial\sigma_{mn}} \right|_T \quad (2.6)$$

where a_{ijmn} are compliances.

Using the above notation we rewrite Eq (2.4) in the form

$$\gamma_{ij} = c_{ijmn} \alpha_{mn} \quad (2.7)$$

3. Specific heats

Let u be the *internal energy per unit volume* of a thermoelastic body. The first law of thermodynamics reads, Landau and Lifszic (1958), cf also Werle (1957)

$$\delta Q = du - \sigma_{ij} d\varepsilon_{ij} \quad (3.1)$$

where δQ is the heat increment *per unit volume* of the body and δ denotes a differential (not *total* in general). Taking u as a function of T and ε_{ij} we have

$$du = \left. \frac{\partial u}{\partial T} \right|_{\varepsilon} dT + \left. \frac{\partial u}{\partial\varepsilon_{ij}} \right|_T d\varepsilon_{ij} \quad (3.2)$$

So, by virtue of Eq (3.1)

$$\delta Q = \left. \frac{\partial u}{\partial T} \right|_{\epsilon} dT + \left(\left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T - \sigma_{ij} \right) d\epsilon_{ij} \quad (3.3)$$

Hence the specific heat for a process characterized by an index r is given by

$$C_r = \left. \frac{\delta Q}{dT} \right|_r = \left. \frac{\partial u}{\partial T} \right|_{\epsilon} + \left(\left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T - \sigma_{ij} \right) \left. \frac{\partial \epsilon_{ij}}{\partial T} \right|_r \quad (3.4)$$

The specific heat at a constant deformation reads

$$C_{\epsilon} = \left. \frac{\partial u}{\partial T} \right|_{\epsilon} \quad (3.5)$$

while the specific heat at a constant stress is given by

$$C_{\sigma} = \left. \frac{\delta Q}{dT} \right|_{\sigma} = \left. \frac{\partial u}{\partial T} \right|_{\epsilon} + \left(\left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T - \sigma_{ij} \right) \left. \frac{\partial \epsilon_{ij}}{\partial T} \right|_{\sigma} \quad (3.6)$$

To simplify the last expression, the first law of thermodynamics is written in terms of the *enthalpy* or *heat function* (per unit volume)

$$h = u - \sigma_{ij} \epsilon_{ij} \quad (3.7)$$

and we obtain

$$\delta Q = dh + \epsilon_{ij} d\sigma_{ij} \quad (3.8)$$

and

$$C_{\sigma} = \left. \frac{\partial h}{\partial T} \right|_{\sigma} \quad (3.9)$$

From Eqs (3.5), (3.6) and (2.5)₂ it follows that

$$C_{\sigma} - C_{\epsilon} = \left(\left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T - \sigma_{ij} \right) \alpha_{ij} \quad (3.10)$$

Thus, to obtain C_{σ} , C_{ϵ} and $(C_{\sigma} - C_{\epsilon})$ it is necessary to know both the internal energy and state equation. It will be shown in Section 4 that to obtain the difference $(C_{\sigma} - C_{\epsilon})$ a state equation can be used only, cf Eq (4.20).

4. Entropy and Maxwell relations for a thermoelastic solid

The differential δQ , in general not *the total* differential, can be expressed by *the total* differential of *entropy* s as

$$\delta Q = T ds \quad (4.1)$$

and by Eq (3.1) we get

$$du = T ds + \sigma_{ij} d\varepsilon_{ij} \quad (4.2)$$

or

$$ds = \frac{1}{T} \left\{ \frac{\partial u}{\partial T} \Big|_{\varepsilon} dT + \left(\frac{\partial u}{\partial \varepsilon_{ij}} \Big|_T - \sigma_{ij} \right) d\varepsilon_{ij} \right\}$$

where T and ε_{ij} are assumed to be the independent variables.

On the other hand

$$ds = \frac{\partial s}{\partial T} \Big|_{\varepsilon} dT + \frac{\partial s}{\partial \varepsilon_{ij}} \Big|_T d\varepsilon_{ij}$$

Hence

$$\frac{\partial s}{\partial T} \Big|_{\varepsilon} = \frac{1}{T} \frac{\partial u}{\partial T} \Big|_{\varepsilon} = \frac{C_{\varepsilon}}{T} \quad \frac{\partial s}{\partial \varepsilon_{ij}} \Big|_T = \frac{1}{T} \left(\frac{\partial u}{\partial \varepsilon_{ij}} \Big|_T - \sigma_{ij} \right) \quad (4.3)$$

Comparing the mixed derivatives we get

$$\frac{\partial u}{\partial \varepsilon_{ij}} \Big|_T - \sigma_{ij} = -T \frac{\partial \sigma_{ij}}{\partial T} \Big|_{\varepsilon} \quad (4.4)$$

The first law of thermodynamics can be also written as, cf (3.8)

$$ds = \frac{1}{T} (dh + \varepsilon_{ij} d\sigma_{ij}) \quad (4.5)$$

or

$$ds = \frac{1}{T} \left\{ \frac{\partial h}{\partial T} \Big|_{\sigma} dT + \left(\frac{\partial h}{\partial \sigma_{ij}} \Big|_T + \varepsilon_{ij} \right) d\sigma_{ij} \right\}$$

Since

$$ds = \frac{\partial s}{\partial T} \Big|_{\sigma} dT + \frac{\partial s}{\partial \sigma_{ij}} \Big|_T d\sigma_{ij} \quad (4.6)$$

(T and σ_{ij} are considered as independent variables) we get

$$\frac{\partial s}{\partial T} \Big|_{\sigma} = \frac{1}{T} \frac{\partial h}{\partial T} \Big|_{\sigma} = \frac{C_{\sigma}}{T} \quad \frac{\partial s}{\partial \sigma_{ij}} \Big|_T = \frac{1}{T} \left(\frac{\partial h}{\partial \sigma_{ij}} \Big|_T + \varepsilon_{ij} \right) \quad (4.7)$$

Comparing the mixed derivatives we get

$$\left. \frac{\partial h}{\partial \sigma_{ij}} \right|_T + \varepsilon_{ij} = T \left. \frac{\partial \varepsilon_{ij}}{\partial T} \right|_\sigma \quad (4.8)$$

Now, introduce the *Helmholtz potential* (or *free energy*) by

$$f = u - Ts \quad (4.9)$$

Then the first law of thermodynamics takes the form

$$df = \sigma_{ij} d\varepsilon_{ij} - s dT \quad (4.10)$$

and we obtain

$$\left. \frac{\partial f}{\partial \varepsilon_{ij}} \right|_T = \sigma_{ij} \quad \left. \frac{\partial f}{\partial T} \right|_\varepsilon = -s \quad (4.11)$$

Comparing the mixed derivatives we receive the first set of *Maxwell equations*

$$\left. \frac{\partial \sigma_{ij}}{\partial T} \right|_\varepsilon = - \left. \frac{\partial s}{\partial \varepsilon_{ij}} \right|_T$$

or

$$\left. \frac{\partial s}{\partial \varepsilon_{ij}} \right|_T = - \left. \frac{\partial \sigma_{ij}}{\partial T} \right|_\varepsilon = \gamma_{ij} \quad (4.12)$$

Finally, if the first law of thermodynamics is written in terms of the *free enthalpy* or *Gibbs function* in the form

$$g = u - Ts - \sigma_{ij} \varepsilon_{ij} \quad (4.13)$$

then the first law reads

$$dg = -\varepsilon_{ij} d\sigma_{ij} - s dT \quad (4.14)$$

and we obtain

$$\left. \frac{\partial g}{\partial \sigma_{ij}} \right|_T = -\varepsilon_{ij} \quad \left. \frac{\partial g}{\partial T} \right|_\sigma = -s \quad (4.15)$$

Comparing the mixed derivatives we receive the second set of *Maxwell equations*

$$\left. \frac{\partial \varepsilon_{ij}}{\partial T} \right|_\sigma = \left. \frac{\partial s}{\partial \sigma_{ij}} \right|_T$$

or

$$\left. \frac{\partial s}{\partial \sigma_{ij}} \right|_T = \left. \frac{\partial \varepsilon_{ij}}{\partial T} \right|_\sigma = \alpha_{ij} \quad (4.16)$$

Eqs (4.4) and (4.8) imply the relations

$$\left. \frac{\partial C_\epsilon}{\partial \epsilon_{ij}} \right|_T = -T \left. \frac{\partial^2 \sigma_{ij}}{\partial T^2} \right|_\epsilon \qquad \left. \frac{\partial C_\sigma}{\partial \sigma_{ij}} \right|_T = T \left. \frac{\partial^2 \epsilon_{ij}}{\partial T^2} \right|_\sigma \qquad (4.17)$$

in which the derivatives of the specific heats are expressed by a state equation only. Using the definitions (2.5)₃ and (2.5)₂ we simplify Eqs (4.4), (4.8), and (4.17) to the form

$$\left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T - \sigma_{ij} = T \gamma_{ij} \qquad \left. \frac{\partial h}{\partial \sigma_{ij}} \right|_T + \epsilon_{ij} = T \alpha_{ij} \qquad (4.18)$$

$$\left. \frac{\partial C_\epsilon}{\partial \epsilon_{ij}} \right|_T = T \left. \frac{\partial \gamma_{ij}}{\partial T} \right|_\epsilon \qquad \left. \frac{\partial C_\sigma}{\partial \sigma_{ij}} \right|_T = T \left. \frac{\partial \alpha_{ij}}{\partial T} \right|_\sigma \qquad (4.19)$$

Also, using Eq (4.18)₁ we reduce Eq (3.10) to the form

$$C_\sigma - C_\epsilon = T \gamma_{ij} \alpha_{ij} \qquad (4.20)$$

or by Eq (2.7)

$$C_\sigma - C_\epsilon = T c_{ijmn} \alpha_{ij} \alpha_{mn} \qquad (4.21)$$

Thus to compute the difference $(C_\sigma - C_\epsilon)$ only a state equation is needed.

If c_{ijmn} is positive definite, the difference $(C_\sigma - C_\epsilon)$ is positive; i.e.

$$C_\sigma > C_\epsilon \qquad (4.22)$$

A similar relation was obtained for fluids (cf Werle, 1957).

Finally, note that from Eqs (4.9) and (4.11)₂ we get

$$f = u + T \left. \frac{\partial f}{\partial T} \right|_\epsilon \qquad (4.23)$$

and by virtue of Eqs (4.13), (3.7) and (4.15)₂ we receive

$$g = h + T \left. \frac{\partial g}{\partial T} \right|_\sigma \qquad (4.24)$$

Eqs (4.23) and (4.24) are known as the Helmholtz-Gibbs equations.

5. Differentials of entropy, internal energy and enthalpy

The differentials

$$ds = \left. \frac{\partial s}{\partial \epsilon_{ij}} \right|_T d\epsilon_{ij} + \left. \frac{\partial s}{\partial T} \right|_\epsilon dT \qquad \text{and} \qquad du = \left. \frac{\partial u}{\partial \epsilon_{ij}} \right|_T d\epsilon_{ij} + \left. \frac{\partial u}{\partial T} \right|_\epsilon dT$$

according to Eqs (4.12), (4.3)₁ and (4.18)₁ can be rewritten as

$$ds = \gamma_{ij}d\varepsilon_{ij} + \frac{C_\varepsilon}{T}dT \quad du = (\sigma_{ij} + T\gamma_{ij})d\varepsilon_{ij} + C_\varepsilon dT \quad (5.1)$$

Eqs (5.1) comply with the first law (4.2) and they are valid for every solid for which the state equation (2.1) is postulated. For a homogeneous thermoelastic body the constants C_ε and γ_{ij} appear e.g. in a monograph by Witold Nowacki (1966).

If σ_{ij} and T are considered to be independent variables; by virtue of Eqs (3.7) and (4.2) we have

$$dh = -\varepsilon_{ij}d\sigma_{ij} + Tds$$

or

$$dh = \left(-\varepsilon_{ij} + T \frac{\partial s}{\partial \sigma_{ij}} \Big|_T \right) d\sigma_{ij} + T \frac{\partial s}{\partial T} \Big|_\sigma dT$$

By comparing the mixed derivatives we get the Maxwell-type results, Eq (4.16). Next, by comparing the last equation with

$$dh = \frac{\partial h}{\partial \sigma_{ij}} \Big|_T d\sigma_{ij} + \frac{\partial h}{\partial T} \Big|_\sigma dT$$

we find that

$$\frac{\partial h}{\partial T} \Big|_\sigma = T \frac{\partial s}{\partial T} \Big|_\sigma$$

and by virtue of Eq (3.9) we arrive at the result (4.7)₁. On the other hand, the total differential of entropy s given by Eqs (4.6), (4.16) and (4.18)₂ reads

$$ds = \alpha_{ij}d\sigma_{ij} + \frac{C_\sigma}{T}dT \quad dh = (-\varepsilon_{ij} + \alpha_{ij}T)d\sigma_{ij} + C_\sigma dT \quad (5.2)$$

6. Joule Thomson type processes

Joule Thomson process is understood as a process in which the enthalpy (heat function) is kept constant at every point of the solid. Thus for such a process

$$dh = \frac{\partial h}{\partial T} \Big|_\sigma dT + \frac{\partial h}{\partial \sigma_{ij}} \Big|_T d\sigma_{ij} \quad \text{and} \quad dh = 0$$

and by Eq (3.9)

$$0 = C_\sigma \frac{\partial T}{\partial \sigma_{ij}} \Big|_h + \frac{\partial h}{\partial \sigma_{ij}} \Big|_T$$

Hence

$$\left. \frac{\partial T}{\partial \sigma_{ij}} \right|_h = -\frac{1}{C_\sigma} \left. \frac{\partial h}{\partial \sigma_{ij}} \right|_T$$

and by Eq (4.18)₂

$$\left. \frac{\partial T}{\partial \sigma_{ij}} \right|_h = \frac{1}{C_\sigma} (\varepsilon_{ij} - T\alpha_{ij}) \quad (6.1)$$

On the other hand, cf (4.5) with $dh = 0$, we get

$$\left. \frac{\partial s}{\partial \sigma_{ij}} \right|_h = \frac{\varepsilon_{ij}}{T} \quad (6.2)$$

In a similar way we obtain the relations describing a processes in which internal energy is kept constant at every point of the solid. From Eq (3.2) for $du = 0$, by virtue of Eq (3.5) we get

$$0 = C_\varepsilon \left. \frac{\partial T}{\partial \varepsilon_{ij}} \right|_u + \left. \frac{\partial u}{\partial \varepsilon_{ij}} \right|_T$$

Hence, and by Eq (4.18)₁, we obtain

$$\left. \frac{\partial T}{\partial \varepsilon_{ij}} \right|_u = -\frac{1}{C_\varepsilon} (\sigma_{ij} + T\gamma_{ij}) \quad (6.3)$$

In addition from Eq (4.2) for $u = \text{const}$, we get

$$\left. \frac{\partial s}{\partial \varepsilon_{ij}} \right|_u = -\frac{\sigma_{ij}}{T} \quad (6.4)$$

Eqs (6.1) and (6.3), and Eqs (6.2) and (6.4) are valid for a process in which the enthalpy and internal energy are kept constant at every point of the solid, respectively.

Let us discuss the entropy in a Joule-Thomson process in which an arbitrary reversible path is closed. Taking h and σ_{ij} as the independent variables we obtain

$$ds = \frac{1}{T} (dh + \varepsilon_{ij} d\sigma_{ij})$$

Integrating this along a curve of constant enthalpy on which $dh = 0$ we get

$$s(b) - s(a) = \int_a^b \frac{1}{T} \varepsilon_{ij} d\sigma_{ij}$$

and by an average value theorem we obtain

$$s(b) - s(a) = \left(\frac{1}{T} \varepsilon_{ij} \right)_{av} (\sigma_{ij}(b) - \sigma_{ij}(a))$$

The extension of a thermoelastic sample under adiabatic conditions is discussed in Section 13.

7. Necessary equilibrium conditions

The conditions of a minimum of the Gibbs function in a state of equilibrium at $T = \text{const}$ and $\sigma_{ij} = \text{const}$ read

$$du - T ds - \sigma_{ij} d\varepsilon_{ij} > 0 \quad (7.1)$$

and

$$\left. \frac{\partial u}{\partial s} \right|_{\varepsilon} = T \quad \left. \frac{\partial u}{\partial \varepsilon_{ij}} \right|_T = \sigma_{ij}$$

The inequality (7.1) may be also written in the quadratic form

$$\frac{\partial^2 u}{\partial s^2} ds^2 + \frac{\partial^2 u}{\partial s \partial \varepsilon_{ij}} ds d\varepsilon_{ij} + \frac{\partial^2 u}{\partial \varepsilon_{ij} \partial \varepsilon_{mn}} d\varepsilon_{ij} d\varepsilon_{mn} > 0$$

Adopting the notation in which $\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12}, \varepsilon_{32}, \varepsilon_{31}$ and ε_{21} are denoted by $\varepsilon_1, \varepsilon_2, \varepsilon_3, \varepsilon_4, \varepsilon_5, \varepsilon_6, \varepsilon_7, \varepsilon_8$ and ε_9 , respectively, (and similarly for σ_{ij}) the above condition may be rewritten in terms of ten positive Jacobians of the order k from 1 to 10.

The positiveness of the first order Jacobian means that

$$\left. \frac{\partial T}{\partial s} \right|_{\varepsilon} = \frac{T}{C_{\varepsilon}} > 0$$

and the positiveness of the second order Jacobian reads

$$\frac{\partial(T, \sigma_{11})}{\partial(s, \varepsilon_{11})} > 0$$

or

$$\frac{\frac{\partial(T, \sigma_{11})}{\partial(T, \varepsilon_{11})}}{\frac{\partial(s, \varepsilon_{11})}{\partial(T, \varepsilon_{11})}} = c_{1111} \frac{T}{C_{\varepsilon}} > 0$$

For the higher orders Jacobians, $r = 1, 2, \dots, 9$, we obtain

$$\frac{T}{C_{\varepsilon}} \frac{\partial(\sigma_1, \sigma_2, \dots, \sigma_r)}{\partial(\varepsilon_1, \varepsilon_2, \dots, \varepsilon_r)} > 0$$

These are the necessary stability conditions of a body.

8. Clapeyron-Clausius equations of phase transitions of the first order

An equilibrium condition between the phases I and K of the same body takes the form

$$g^I(\sigma_{ij}, T) = g^K(\sigma_{ij}, T) \quad (8.1)$$

where g^I and g^K denote the Gibbs potentials for the phases I and K , respectively. It means that passing from the phase I to the phase K the Gibbs function changes in a continuous manner. Its partial derivatives however, cf (4.15)

$$\left. \frac{\partial g}{\partial T} \right|_{\sigma} = -s \quad \left. \frac{\partial g}{\partial \sigma_{ij}} \right|_T = -\varepsilon_{ij} \quad (8.2)$$

do not have to be continuous. In the case of phase transitions of the first order, the jumps of entropy and strains are observed at a temperature of transition, i.e.

$$s^I \neq s^K \quad \varepsilon_{ij}^I \neq \varepsilon_{ij}^K \quad (8.3)$$

Because the quantity $T(s^I - s^K) = q^{IK}$ is equal to a heat released during the transition from phase I to phase K therefore the phase transitions of the first order are associated with a heat absorption or emission.

At a point of equilibrium, Eq (8.1) holds true. At an adjacent point to the point of equilibrium we have

$$g^I(\sigma_{ij} + d\sigma_{ij}, T + dT) = g^K(\sigma_{ij} + d\sigma_{ij}, T + dT) \quad (8.4)$$

or

$$g^I(\sigma_{ij}, T) + dg^I = g^K(\sigma_{ij}, T) + dg^K \quad (8.5)$$

and subtracting Eq (8.1) from Eq (8.4) we get

$$dg^I = -s^I dT - \varepsilon_{ij}^I d\sigma_{ij} = dg^K = -s^K dT - \varepsilon_{ij}^K d\sigma_{ij} \quad (8.6)$$

or

$$\left(\varepsilon_{ij}^I \frac{d\sigma_{ij}^I}{dT} - \varepsilon_{ij}^K \frac{d\sigma_{ij}^K}{dT} \right) = (s^K - s^I) \quad (8.7)$$

Hence

$$\left(\varepsilon_{ij}^I \frac{d\sigma_{ij}^I}{dT} - \varepsilon_{ij}^K \frac{d\sigma_{ij}^K}{dT} \right) = \frac{q^{IK}}{T} \quad (8.8)$$

and this is the Clapeyron-Clausius equation for a solid with two phases: the heat of a transition and the difference of deformations are related to the slopes of an equilibrium curve at both sides of the phase boundary.

9. Ehrenfest equations for the second order phase transition

The second order phase transitions are far more rare than the first order ones. For example, the second order phase transitions occur in ferromagnetics at the Curie point when a ferromagnetic becomes a paramagnetic, and in some metals when a superconductive metal transforms to a normal one.

Let us derive the equilibrium differential equation describing the second order phase transition. According to the definition of these transitions the first partial derivative of the Gibbs function must be continuous and only the second derivatives can suffer a jump at a phase change surface. Let us examine the physical meaning of the three partial second order derivatives of the function g . We find that

$$\begin{aligned} \frac{\partial^2 g}{\partial T^2} &= \frac{\partial}{\partial T} \left. \frac{\partial g}{\partial T} \right|_{\sigma} = - \left. \frac{\partial s}{\partial T} \right|_{\sigma} = - \frac{C_{\sigma}}{T} \\ \frac{\partial^2 g}{\partial \sigma_{mn} \partial \sigma_{ij}} &= \frac{\partial}{\partial \sigma_{mn}} \left. \frac{\partial g}{\partial \sigma_{ij}} \right|_T = \left. \frac{\partial \varepsilon_{ij}}{\partial \sigma_{mn}} \right|_T = a_{ijmn} \\ \frac{\partial^2 g}{\partial \sigma_{ij} \partial T} &= - \left. \frac{\partial s}{\partial \sigma_{ij}} \right|_T = - \left. \frac{\partial \varepsilon_{ij}}{\partial T} \right|_{\sigma} = -\alpha_{ij} \end{aligned} \quad (9.1)$$

cf Eq (4.15) and Eqs (4.7)₁, (2.5)₁, (4.16), respectively.

If we take as a starting point the entropy continuity condition

$$ds^I = ds^K \quad (9.2)$$

or

$$\left. \frac{\partial s^I}{\partial T} \right|_{\sigma} dT + \left. \frac{\partial s^I}{\partial \sigma_{ij}} \right|_T d\sigma_{ij}^I = \left. \frac{\partial s^K}{\partial T} \right|_{\sigma} dT + \left. \frac{\partial s^K}{\partial \sigma_{ij}} \right|_T d\sigma_{ij}^K \quad (9.3)$$

then multiplying both sides of Eq (9.3) by T and substituting for the values of partial derivatives from Eqs (9.1)_{1,3}; we get

$$C_{\sigma}^I dT + T \alpha_{ij}^I d\sigma_{ij}^I = C_{\sigma}^K dT + T \alpha_{ij}^K d\sigma_{ij}^K \quad (9.4)$$

Hence

$$-(\alpha_{ij}^K d\sigma_{ij}^K - \alpha_{ij}^I d\sigma_{ij}^I) T = (C_{\sigma}^K - C_{\sigma}^I) dT \quad (9.5)$$

or

$$\left(\alpha_{ij}^K \frac{d\sigma_{ij}^K}{dT} - \alpha_{ij}^I \frac{d\sigma_{ij}^I}{dT} \right) = - \frac{1}{T} (C_{\sigma}^K - C_{\sigma}^I) \quad (9.6)$$

However, if we take as a starting point the equality of deformations of both phases we obtain another expression for $d\sigma_{ij}/dT$. To this end we postulate that

$$d\varepsilon_{ij}^I = d\varepsilon_{ij}^K \quad (9.7)$$

or

$$\left. \frac{\partial \varepsilon_{ij}^I}{\partial T} \right|_{\sigma} dT + \left. \frac{\partial \varepsilon_{ij}^I}{\partial \sigma_{mn}} \right|_T d\sigma_{mn} = \left. \frac{\partial \varepsilon_{ij}^K}{\partial T} \right|_{\sigma} dT + \left. \frac{\partial \varepsilon_{ij}^K}{\partial \sigma_{mn}} \right|_T d\sigma_{mn}$$

and from Eqs (9.1)_{2,3} we receive

$$\alpha_{ij}^I dT + a_{ijmn}^I d\sigma_{mn}^I = \alpha_{ij}^K dT + a_{ijmn}^K d\sigma_{mn}^K \quad (9.8)$$

or

$$\left(a_{ijmn}^K \frac{d\sigma_{mn}^K}{dT} - a_{ijmn}^I \frac{d\sigma_{mn}^I}{dT} \right) = \alpha_{ij}^K - \alpha_{ij}^I \quad (9.9)$$

Eqs (9.6) and (9.9) form a set of equations of the Ehrenfest type for the second order phase transition for a solid. If the compliances and thermal expansions of both phases, treated as functions of the temperature, are known, Eq (9.9) may be integrated to obtain a curve of equilibrium. If the right-hand-sides of the Ehrenfest equations for a temperature are known, the stress in a small neighborhood of the temperature may be obtained.

10. Example 1 – linear homogeneous thermoelastic body

For a linear homogeneous body the functions a_{ijmn} , c_{ijmn} , α_{ij} , γ_{ij} and C_{ε} (cf Eqs (2.5) and (2.6)) are constant and Eqs (5.1) can be integrated.

Since in a natural state $u = 0$ and $s = 0$, for $\varepsilon_{ij} = 0$ and $T = T_0$, after integration we get

$$\begin{aligned} u &= \frac{1}{2} c_{ijmn} \varepsilon_{mn} \varepsilon_{ij} + \gamma_{ij} T_0 \varepsilon_{ij} + C_{\varepsilon} (T - T_0) \\ s &= \gamma_{ij} \varepsilon_{ij} + C_{\varepsilon} \ln \frac{T}{T_0} \end{aligned} \quad (10.1)$$

For the enthalpy we obtain

$$h = -\frac{1}{2} a_{ijmn} \sigma_{mn} \sigma_{ij} + \alpha_{ij} T_0 \sigma_{ij} + \int_{T_0}^T C_{\sigma} dT \quad (10.2)$$

We can also write

$$h = h_0 + \int_{T_0}^T C_\sigma dT \quad h_0 = -\frac{1}{2} a_{ijmn} \sigma_{ij} \sigma_{mn} + \alpha_{ij} T_0 \sigma_{ij} \quad (10.3)$$

and expressing the entropy by stresses we get

$$s = s_0 + \int_{T_0}^T \frac{1}{T} C_\sigma dT \quad s_0 = \alpha_{ij} \sigma_{ij} \quad (10.4)$$

The equilibrium condition

$$h^K - h^I = T(s^K - s^I) \quad (10.5)$$

can be expressed with use of (10.3) and (10.4) written for the phases I and K .

11. Example 2 – nonlinear thermoelastic body of the Kovalenko type

Kovalenko (1970) considered a thermoelastic body described by the free energy density

$$f = \frac{1}{2} c_{ijmn} \varepsilon_{ij} \varepsilon_{mn} - g_{ij} \varepsilon_{ij} (T - T_0) - \int_{T_0}^T dX \int_{T_0}^X \frac{C_{\varepsilon=0}}{T} dT \quad (11.1)$$

where

$$c_{ijmn} = \lambda \delta_{ij} \delta_{mn} + \mu (\delta_{im} \delta_{jn} + \delta_{jm} \delta_{in})$$

$$g_{ij} = g \delta_{ij} \quad g = (3\lambda + 2\mu) \alpha_T$$

and λ and μ are the Lamé temperature dependent moduli, α_T is the mean thermal coefficient of linear expansion, while $C_{\varepsilon=0}$ denotes the specific heat at a zero strain. All these coefficients are assumed to depend on the temperature T but not on the strain ε_{ij} . For a discussion of nonlinear thermoelasticity in which the material properties of a solid are temperature-dependent, see also Nowacki (1986), Noda (1986).

The stress σ_{ij} is derived from the relation $\sigma_{ij} = \partial f / \partial \varepsilon_{ij}$, cf Eq (4.11)₁ and the entropy density of the body is found from the relation $s = -\partial f / \partial T$, cf Eq (4.11)₂. Hence

$$\sigma_{ij} = c_{ijmn} \varepsilon_{mn} - g_{ij}(T - T_0) \quad (11.2)$$

$$s = -\frac{1}{2} \frac{\partial c_{ijmn}}{\partial T} \varepsilon_{ij} \varepsilon_{mn} + \frac{\partial}{\partial T} [g_{ij}(T - T_0)] \varepsilon_{ij} + \int_{T_0}^T \frac{C_{\varepsilon=0}}{T} dT$$

From Eqs (4.3)₁ and (4.12)₂ we find

$$\frac{C_\varepsilon}{T} = \frac{\partial s}{\partial T} = -\frac{1}{2} \frac{\partial^2 c_{ijmn}}{\partial T^2} \varepsilon_{ij} \varepsilon_{mn} + \frac{\partial^2}{\partial T^2} [g_{ij}(T - T_0)] \varepsilon_{ij} + \frac{1}{T} C_{(\varepsilon=0)} \quad (11.3)$$

$$\gamma_{ij} = \frac{\partial s}{\partial \varepsilon_{ij}} = -\frac{\partial c_{ijmn}}{\partial T} \varepsilon_{mn} + \frac{\partial}{\partial T} [g_{ij}(T - T_0)]$$

and

$$\gamma_{ij} (\varepsilon=0) = g_{ij} + \frac{\partial g_{ij}}{\partial T} (T - T_0)$$

The result (11.3)₂ may be also obtained by using Eqs (2.5)₃ and (11.2)₁.

Therefore, in this nonlinear body two different stress-temperature tensors occur: the first is to be identified with g_{ij} that appears in the material law (11.2)₁, while the second, derived *via* the entropy relation (11.3)₂, is equal to γ_{ij} . Clearly, γ_{ij} is consistent with the thermodynamical restrictions, so it complies with the Maxwell type equation (4.19)₁. Note that a complete system of nonlinear field equations of thermoelasticity include both tensors g_{ij} and γ_{ij} . It follows from Eq (11.3)₂ that a linearization of the model in which g_{ij} is independent of temperature leads to the identity $\gamma_{ij} = g_{ij}$.

12. Example 3 – special case of a nonlinear thermoelastic body

We assume the following form of free energy

$$f = \frac{1}{2} c_{ijmn} \varepsilon_{ij} \varepsilon_{mn} - g_{ij} \varepsilon_{ij} (T - T_0) - \int_{T_0}^T dX \int_{T_0}^X \frac{C}{T} dT - \frac{1}{2} A_{ij} \varepsilon_{ij} (T - T_0)^2 \quad (12.1)$$

where $c_{ijmn} = c_{ijmn}(T)$, while g_{ij} , C and A_{ij} are constants.

The entropy of the body is found from the relation $s = -\partial f/\partial T$, cf (4.11)₂ and we have

$$s = -\frac{1}{2} \frac{\partial c_{ijmn}}{\partial T} \varepsilon_{ij} \varepsilon_{mn} + g_{ij} \varepsilon_{ij} + \int_{T_0}^T \frac{C}{T} dT + A_{ij} \varepsilon_{ij} (T - T_0) \quad (12.2)$$

The thermoelastic coefficient γ_{ij} and the reduced specific heat C_ε/T are given by

$$\gamma_{ij} = \left. \frac{\partial s}{\partial \varepsilon_{ij}} \right|_T = -\frac{\partial c_{ijmn}}{\partial T} \varepsilon_{mn} + g_{ij} + A_{ij} (T - T_0) \quad (12.3)$$

$$\frac{C_\varepsilon}{T} = \left. \frac{\partial s}{\partial T} \right|_\varepsilon = -\frac{1}{2} \frac{\partial^2 c_{ijmn}}{\partial T^2} \varepsilon_{ij} \varepsilon_{mn} + \frac{C}{T} + A_{ij} \varepsilon_{ij}$$

and a relation between the stress σ_{ij} , the strain ε_{ij} and the absolute temperature T , cf (4.11)₁, takes the form

$$\sigma_{ij} = \left. \frac{\partial f}{\partial \varepsilon_{ij}} \right|_T = c_{ijmn} \varepsilon_{mn} - \left[g_{ij} + \frac{1}{2} A_{ij} (T - T_0) \right] (T - T_0) \quad (12.4)$$

Applying the definition (2.5)₃ to this equation we arrive at the relation (12.3)₁.

13. Example 4 – adiabatic extension

Let a thermoelastic body be subject to an adiabatic process. Consider the relation

$$\left. \frac{\partial T}{\partial \varepsilon_{ij}} \right|_s \equiv \left(\frac{\partial T}{\partial \varepsilon_{ij}} \right)_s \equiv \frac{\partial(T, s)}{\partial(\varepsilon_{ij}, s)} = \frac{\frac{\partial(T, s)}{\partial(\varepsilon_{ij}, T)}}{\frac{\partial(\varepsilon_{ij}, s)}{\partial(\varepsilon_{ij}, T)}} = -\frac{\left(\frac{\partial s}{\partial \varepsilon_{ij}} \right)_T}{\left(\frac{\partial s}{\partial T} \right)_\varepsilon} = -\frac{T}{C_\varepsilon} \left(\frac{\partial s}{\partial \varepsilon_{ij}} \right)_T \quad (13.1)$$

where the properties of a Jacobian and relation (4.3)₁ were used. From Eq (4.12) we get

$$\left. \frac{\partial s}{\partial \varepsilon_{ij}} \right|_T = -\left. \frac{\partial \sigma_{ij}}{\partial T} \right|_\varepsilon = \gamma_{ij} \quad (13.2)$$

Hence

$$\left. \frac{\partial T}{\partial \varepsilon_{ij}} \right|_s = -\frac{T}{C_\varepsilon} \gamma_{ij} \quad (13.3)$$

Next, using (4.7)₁ we obtain

$$\frac{\partial T}{\partial \sigma_{ij}} \Big|_s \equiv \left(\frac{\partial T}{\partial \sigma_{ij}} \right)_s \equiv \frac{\partial(T, s)}{\partial(\sigma_{ij}, s)} = \frac{\frac{\partial(T, s)}{\partial(\sigma_{ij}, T)}}{\frac{\partial(\sigma_{ij}, s)}{\partial(\sigma_{ij}, T)}} = - \frac{\left(\frac{\partial s}{\partial \sigma_{ij}} \right)_T}{\left(\frac{\partial T}{\partial T} \right)_\sigma} = - \frac{T}{C_\sigma} \left(\frac{\partial s}{\partial \sigma_{ij}} \right)_T$$
(13.4)

Since, by Eq (4.16)

$$\frac{\partial s}{\partial \sigma_{ij}} \Big|_T = - \frac{\partial \varepsilon_{ij}}{\partial T} \Big|_\sigma = \alpha_{ij}$$
(13.5)

hence

$$\frac{\partial T}{\partial \sigma_{ij}} \Big|_s = - \frac{T}{C_\sigma} \alpha_{ij}$$
(13.6)

As a result we arrive to the following conclusion: if component α_{11} is positive, and σ_{ij} has only one component $\sigma_{11} > 0$, then the temperature of a body subject to an adiabatic extension decreases.

14. Example 5 – adiabatic and isothermal elastic coefficients

Consider the adiabatic elastic coefficients defined by

$$b_{ijmn} \equiv \frac{\partial \sigma_{ij}}{\partial \varepsilon_{mn}} \Big|_s$$
(14.1)

or

$$\frac{\partial \sigma_{ij}}{\partial \varepsilon_{mn}} \Big|_s \equiv \frac{\partial(\sigma_{ij}, s)}{\partial(\varepsilon_{mn}, s)} = \frac{\frac{\partial(\sigma_{ij}, s)}{\partial(\sigma_{ab}, T)}}{\frac{\partial(\varepsilon_{mn}, s)}{\partial(\varepsilon_{pq}, T)}} \frac{\partial(\sigma_{ab}, T)}{\partial(\varepsilon_{pq}, T)} =$$
(14.2)

$$= \frac{(\delta_{ia} \delta_{jb} + \delta_{ib} \delta_{ja}) \left(\frac{\partial s}{\partial T} \right)_\sigma}{(\delta_{mp} \delta_{nq} + \delta_{mq} \delta_{ns}) \left(\frac{\partial s}{\partial T} \right)_\varepsilon} \frac{\partial \sigma_{ab}}{\partial \varepsilon_{pq}} \Big|_T$$

Hence, by virtue of Eq (2.5)₁

$$b_{ijmn} = \frac{C_\sigma}{C_\varepsilon} c_{ijmn}$$
(14.3)

Eq (14.3) provides a relation between the adiabatic and isothermal elastic moduli for a thermoelastic solid.

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Termodynamika ciała stałego z równaniem stanu

Streszczenie

Analizujemy związki termodynamiczne opisujące równowagę ciała termosprężystego złożonego z wielu faz. Czynimy to w sposób podobny do stosowanego w teorii płynów wielofazowych. Po określeniu przejść fazowych pierwszego i drugiego rodzaju wyprowadzamy związki typu Clapeyrona-Clausiusza i Ehrenfesta. Ogólną teorię uzupełniamy przykładami.

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