Archives of Mechanics • Archiwum Mechaniki Stosowanej • 27, 3, pp. 517–529, Warszawa 1975

Thermodynamic properties of singular surfaces in continuous media

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THE PAPER contains main thermodynamic relations for a singular surface in continuum. After the definition of such a surface we derive a generalized KOTCHINE's condition, where surface sources are taken into account. It leads to startling consequences, which are presented in the following two sections. In particular, CLAUSIUS-DUHEM inequality for a singular surface seems to be of greatest importance in the theories of defects and propagation of waves. Finally, we show some examples of the application of the results obtained.

W pracy omówiono podstawowe związki termodynamiczne dla powierzchni osobliwej w ośrodku ciągłym. Po definicji takiej powierzchni wyprowadzono uogólniony warunek KOTCHINE'a, w którym uwzględniono źródła powierzchniowe. Prowadzi to do ciekawych rezultatów, które przedstawiono w dwu następnych punktach. W szczególności nierówność CLAUSIUSA-DUHEMA dla powierzchni osobliwej wydaje się mieć duże znaczenie w teorii defektów i propagacji fal. Wreszcie podano kilka przykładów zastosowań otrzymanych wyników.

Работа содержит основные термодинамические соотношения для особой поверхности в сплошной среде. После определения такой поверхности выводим обобщенное условие Кочина, в котором учтены поверхностные источники. Это приводит к удивительным результатам, которые представлены в двух следующих пунктах. В частности неравенство Клаузиуса-Дюгема для особой поверхности кажется иметь большое значение в теории дефектов и распространения волн. Наконец представляем несколько примеров применений полученных результатов.

1. Introduction

THIS PAPER is an extended form of my earlier work [1]. Following the discussion after the lecture, I have weakened some assumptions, concerning particularly the properties of surface sources; at the same time, the physical interpretation is discussed in a wider range.

In the second section of the paper we deliver the balance equation for a continuous medium and we repeat a definition of a continuous medium with a singular surface (for details, see [2, 3]).

In the third section we derive the modified KOTCHINE's condition for a singular surface.

The fourth section contains the discussion of balance equations, resulting from KOTCHINE's condition, for a singular surface.

In the next section, we derive the main result of the paper — CLAUSIUS-DUHEM inequality for a singular surface.

The sixth section is devoted to the particular case of the material at rest before being reached by a singular surface and is an illustration of the problems under consideration.

The seventh section is a resumé of other conditions for a singular surface — HADAMARD's lemma and MAXWELL's theorem.

Finally, in the eighth section, we furnish some examples of applications.

It can easily be seen from the above scope of the paper that we do not deliver many new results. The procedure is standard and the main theorems are known. However, a new thermodynamic condition, presented in the fifth section makes the repetition worth while. In addition, some minor changes in classical theorems extend the range of their applications; for instance, they can be applied in the presented form to the theory of mixtures. Some other applications are also mentioned.

2. Preliminaries

In this section, we show only the most important notions and properties of continuous media. Details, concerning algebraic properties may be found in many papers (see revue in [2]), while the theory of balance equation has been presented in [3]. It is sufficient for the purposes of this paper to assume that we investigate a chosen configuration of a single continuum. It means, we are dealing with a certain collection of subsets of Euclidean space, which form Boolean algebra. We use in the paper the same notation for a member of this algebra and its volume measure.

Now, let us shortly repeat the main notions, concerning a balance equation. We say, that a set function Φ, defined on the above algebra, satisfies a *local balance equation*, if

$$\dot{\Phi}(v) = M(v, v^e) + M^*(v, v^e) \text{ almost everywhere } t, \tag{2.1}$$

where dot means the time derivative, v is any member of the algebra mentioned above. M is said to be a *total flux* from v^e to v, while M^* is said to be a *total source* in v. We make the usual continuity assumptions

$$\begin{gathered} \bigvee_{\alpha \in R^+} \Phi(v) \leqslant \alpha v, \\ \bigvee_{\alpha, \beta \in R^+} M(v_1, v_2) \leqslant \alpha v_1 + \beta \partial v_1 \cap v_2, \\ \bigvee_{\alpha, \beta \in R^+} M^*(v_1, v_2) \leqslant \alpha v_1 + \beta \partial v_1 \cap v_2. \end{gathered} \tag{2.2}$$

In this way we obtain the following representation of the balance equation

$$\frac{d}{dt} \int_v \varphi dv = \oint_{\partial v} (\mu + \mu^*) ds + \int_v (\lambda + \lambda^*) dv. \tag{2.3}$$

The only term, in which this equation differs from others discussed in literature, is the second one, describing the influence of surface sources (μ^*). We deal with its interpretation a little later. This equation is assumed to hold for any subset v (from the above mentioned algebra). If there is no singular surface, we can make a transition from (2.3) to the local form [see: the formula (7.6)]. However, our main aim is to describe a continuum with such a surface. Therefore, as the next step, we define a singular surface.

Let a surface σ, oriented by a unit vector $\mathbf{n}$, be a part of the region $\partial v^- \cap v^+$. Both v^- and v^+ are members of the above algebra. The field φ, described by the balance equation (2.3), is smooth in v^- and v^+, i.e. it is continuously differentiable in v^- and v^+, it approaches limits φ^- and φ^+ for every point $\mathbf{x} \in \sigma$, both limits are differentiable on any path on σ, and $\operatorname{grad}\varphi$ approaches limits $(\operatorname{grad}\varphi)^-$, $(\operatorname{grad}\varphi)^+$ on σ. For the fields λ, λ^*, continuous in $v^- \cup v^+$ and μ, μ^*, $\dot{\mathbf{x}}$ approaching limits μ^-, μ^+, μ^{*-}, μ^{*+}, $\dot{\mathbf{x}}^-$, $\dot{\mathbf{x}}^+$ on σ we say, that the surface σ is *singular with respect to the balance equation* (2.3), if at least one of the listed quantities has a jump on σ, i.e. the limits of this quantity on σ are not equal (e.g. see [1]).

We consider a continuum, in which a singular surface σ is moving with a velocity $\mathbf{u}(\mathbf{x})$, $\mathbf{x} \in \sigma$, and the balance equation (2.3) is satisfied for any region v. In the next section, we check the consequences of the above assumption in the case of a singular surface, passing through the region v (see Fig. 1).

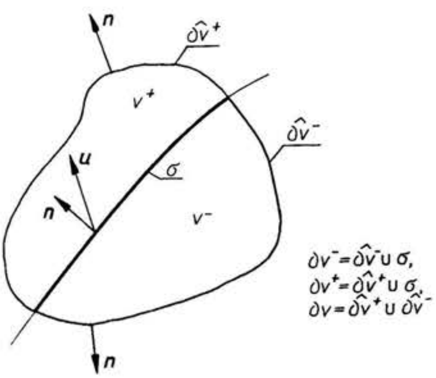

FIG. 1.

3. Kotchine's condition

In this section we repeat once again the derivation of the so-called *generalized* KOTCHINE's *condition* [1]. The procedure is standard and the only difference lies in the participation of surface sources in the balance equation (2.3). The left-hand side of the equation can be written in the form

$$(3.1) \qquad \frac{d}{dt}\int_v \varphi\, dv = \frac{d}{dt}\int_{v^-} \varphi\, dv + \frac{d}{dt}\int_{v^+} \varphi dv$$
$$= \int_{v^-} \frac{\partial\varphi}{\partial t} dv + \int_{v^+} \frac{\partial\varphi}{\partial t} dv + \oint_{\partial v^-} \varphi v_{\mathbf{n}} ds + \oint_{\partial v^+} \varphi v_{\mathbf{n}}\, ds,$$

where $v_{\mathbf{n}}$ is the normal component of a velocity of an arbitrary point on either ∂v^- or ∂v^+. If the point is lying on ∂v, then $\mathbf{v} = \dot{\mathbf{x}}$, and $v_{\mathbf{n}} = \dot{x}_{\mathbf{n}}$, while for σ we have $\mathbf{v} = \mathbf{u}$. Separating the common part of ∂v^- and v^+, we obtain from (3.1)

$$\frac{d}{dt}\int_v \varphi dv = \int_{v^-} \frac{\partial\varphi}{\partial t} dv + \int_{v^+} \frac{\partial\varphi}{\partial t} dv + \int_{\partial\hat{v}^-} \varphi \dot{x}_{\mathbf{n}} ds + \int_{\partial\hat{v}^+} \varphi \dot{x}_{\mathbf{n}} ds$$
$$+ \int_\sigma \varphi^- u_{\mathbf{n}} ds - \int_\sigma \varphi^+ u_{\mathbf{n}}\, ds,$$

where we have taken into account the change of orientation of the surface $v^+ \cap \sigma$.

Similar manipulations on the right-hand side of (2.3) lead to the following result:

$$(3.2)\qquad \int_{v^-} \frac{\partial\varphi}{\partial t}dv + \int_{v^+} \frac{\partial\varphi}{\partial t}dv + \int_{\partial\hat{v}^-} \varphi\dot{x}_n ds + \int_{\partial\hat{v}^+} \varphi\dot{x}_n ds$$

$$+ \int_{\sigma} \varphi^- u_n ds - \int_{\sigma} \varphi^+ u_n ds = \int_{\partial\hat{v}^-} (\mu+\mu^*) ds + \int_{\partial\hat{v}^+} (\mu+\mu^*) ds$$

$$+ \int_{v^-} (\lambda+\lambda^*) dv + \int_{v^+} (\lambda+\lambda^*) dv.$$

Under our assumptions, this relation must hold for any v. It means, we are allowed to take a limit $v \to 0$ in (3.2). Under this condition, we shrink down $\partial\hat{v}^-$ and $\partial\hat{v}^+$ to σ. Hence $v^- \to 0$, $v^+ \to 0$, preserving σ. Taking into account the definition of the singular surface, we obtain

$$-\int_{\sigma} \varphi^- \dot{x}_n^- ds + \int_{\sigma} \varphi^+ \dot{x}_n^+ ds + \int_{\sigma} \varphi^- u_n ds - \int_{\sigma} \varphi^+ u_n ds$$

$$= \int_{\sigma} (\mu^- + \mu^{*-}) ds + \int_{\sigma} (\mu^+ + \mu^{*+}) ds,$$

where, again, μ^- is the limit of μ from v^-, μ^+ — from v^+, and similarly for μ^*.

We use the standard notation of CHRISTOFFEL:

$$(3.3)\qquad \begin{aligned} [\varphi(\dot{x}_n - u_n)] &:= \varphi^+(\dot{x}_n^+ - u_n) - \varphi^-(\dot{x}_n^- - u_n), \\ [\mu+\mu^*] &:= \mu^+ + \mu^{*+} - \mu^- - \mu^{*-}. \end{aligned}$$

Then

$$(3.4)\qquad \int_{\sigma} \{[\varphi(\dot{x}_n - u_n)] - [\mu+\mu^*]\} ds = 0.$$

Assuming the continuity of the integrand on σ, we can take a limit from the above relation

$$\lim_{s(\sigma)\to 0} \frac{1}{s(\sigma)} \int_{\sigma} \{[\varphi(\dot{x}_n - u_n)] - [\mu+\mu^*]\} ds = 0,$$

where $s(\sigma)$ is the area of surface σ. Hence, the relation (3.4) is equivalent to the following local formula

$$(3.5)\qquad [\varphi(\dot{x}_n - u_n)] - [\mu] = [\mu^*] \text{ almost everywhere } s \text{ on } \sigma,$$

which is called a *generalized* KOTCHINE'*s condition.*

4. Surface balance equations

For completeness we repeat the particular relations for a continuum, following from (3.5);

i) Balance of mass; in this case

$$\varphi \equiv \varrho, \quad \mu^* = \varrho^* \quad \text{and} \quad \mu \equiv 0. \tag{4.1}$$

Then

$$[\varrho(\dot{x}_n - u_n)] = [\varrho^*] \quad \text{a.e. } s. \tag{4.2}$$

If the velocity field $\dot{x}_n$, density field ϱ, and mass sources field ϱ^* are known, the normal speed u_n of the singular surface σ can be found from this relation. Namely

$$u_n = \frac{[\varrho \dot{x}_n] - [\varrho^*]}{[\varrho]} \quad \text{for} \quad [\varrho] \neq 0, \quad \text{a.e. } s. \tag{4.3}$$

Hence the jump of the velocity field $[\dot{x}_n]$ is admissible if either $[\varrho] \neq 0$ (a classical condition for the propagation of shock waves), or $[\varrho^*] \neq 0$, or both. The latter may be of some importance in the case of a shock wave in mixture.

ii) Balance of momentum; here we have

$$\varphi \equiv \varrho \dot{\mathbf{x}}, \quad \mu \equiv \mathbf{t}, \quad \mu^* \equiv \mathbf{t}^*, \tag{4.4}$$

where $\mathbf{t}$ is a traction, and $\mathbf{t}^*$ is a vector of surface sources of momentum. As a matter of fact, the existence of vectors $\mathbf{t}$ and $\mathbf{t}^*$ cannot be proved. We are able to say only that $\mu + \mu^*$ is a vector, which is leading to the vector representation of either μ or μ^*, when the remaining field is vanishing. Therefore (4.4) must be treated rather as an assumption for an arbitrary continuum. In such a case, we obtain from (3.5) the following result

$$[\varrho \dot{\mathbf{x}}(\dot{x}_n - u_n)] - [\mathbf{t}] = [\mathbf{t}^*], \quad \text{a.e. } s. \tag{4.5}$$

It is interesting to check the consequences of (4.5) for a normal part of $\dot{\mathbf{x}}$. In this case, we have

$$[\varrho \dot{x}_n(\dot{x}_n - u_n)] - [t_n] = [t_n^*], \quad \text{a.e. } s, \tag{4.6}$$

where

$$t_n := \mathbf{t} \cdot \mathbf{n}, \quad t_n^* := \mathbf{t}^* \cdot \mathbf{n}. \tag{4.7}$$

Making use of (4.3), we get

$$[t_n] = [t_n^*] - [\varrho \dot{x}_n^2] + \frac{[\varrho \dot{x}_n]^2}{[\varrho]} - \frac{[\varrho^*]}{[\varrho]}, \quad \text{for } [\varrho] \neq 0, \quad \text{a.e. } s. \tag{4.8}$$

This relation means, that the non-zero jump of ϱ is creating the jump of tractions, if either the velocity field is not continuous ($[\dot{x}_n] \neq 0$), or the mass surface sources are not continuous ($[\varrho^*] \neq 0$). Even in the case of continuous fields $\dot{x}_n$ and ϱ and hence ϱ^*, the traction t_n can suffer a jump with respect to the discontinuity of t_n^*. The last two cases are important in the theory of mixtures.

iii) Balance of moment of momentum; in the case of simple interactions (without couple stresses) we have

$$\varphi \equiv \varrho \mathbf{p} \wedge \dot{\mathbf{x}}, \quad \mu \equiv \mathbf{p} \wedge \mathbf{t}, \quad \mu^* \equiv \mathbf{p} \wedge \mathbf{t}^*, \tag{4.9}$$

where $\mathbf{p}$ is a position vector of the arbitrary point with respect to some chosen origin. Using (3.5), we obtain

$$[\varrho \mathbf{p} \wedge \dot{\mathbf{x}}(\dot{x}_n - u_n)] - [\mathbf{p} \wedge \mathbf{t}] = [\mathbf{p} \wedge \mathbf{t}^*], \quad \text{a.e. } s. \tag{4.10}$$

If $[p] = 0$, we have

$$\mathbf{p}\wedge[\varrho\dot{\mathbf{x}}(\dot{x}_{\mathbf{n}}-u_{\mathbf{n}})]-\mathbf{p}\wedge[\mathbf{t}] = \mathbf{p}\wedge[\mathbf{t}^*], \quad \text{a.e. } s, \tag{4.11}$$

which is an identity with respect to (4.5). For $[p] \neq 0$, which may occur in the case of defects of materials, the full relation (4.10) must be used, independently of (4.5).

iv) Balance of energy; now we have

$$\varphi \equiv \varrho\left(e+\frac{1}{2}\dot{x}^2\right), \quad \mu \equiv \dot{\mathbf{x}}\cdot\mathbf{t}+q, \quad \mu^* \equiv \dot{\mathbf{x}}\cdot\mathbf{t}^*+q^*, \tag{4.12}$$

where e is the density of internal energy, q — heat flux, q^* — intensity of energy surface sources. Making use of the generalized KOTCHINE's condition (3.5), we obtain

$$\left[\varrho\left(e+\frac{1}{2}\dot{x}^2\right)(\dot{x}_{\mathbf{n}}-u_{\mathbf{n}})\right]-[\dot{\mathbf{x}}\cdot\mathbf{t}+q] = [\dot{\mathbf{x}}\cdot\mathbf{t}^*+q^*], \quad \text{a.e. } s. \tag{4.13}$$

We shall return to this relation a little later, discussing the implications of the second law of thermodynamics.

5. Clausius-Duhem inequality for a singular surface

The last balance equation, which should be considered for a continuum, is the entropy equation. In this case

$$\varphi \equiv \varrho\eta, \quad \mu \equiv h, \quad \mu^* \equiv h^*, \tag{5.1}$$

where η is the entropy density, h — entropy flux, h^* — surface sources of entropy. Then

$$[\varrho\eta(\dot{x}_{\mathbf{n}}-u_{\mathbf{n}})]-[h] = [h^*], \quad \text{a.e. } s. \tag{5.2}$$

We restrict this equation by the second law of thermodynamics. In general, it can be formulated, as in the following statement (e.g. see [2, 3]): "in any themrodynamic process the total entropy production in an arbitrary region v is non-negative".

The analytic form of this statement for a continuum

$$\int_v \varrho\eta^* dv + \oint_{\partial v} h^* ds \geqslant 0, \quad \text{a.e. } t, \tag{5.3}$$

is said to be a CLAUSIUS-DUHEM inequality. In this formula η^* is the density of volume sources of entropy.

R e m a r k. Almost all researchers in thermodynamics assume that the total entropy production is described by the first term of the inequality (5.3)(1). Besides the formal arguments for the second term, which we discuss somewhere else [3], many physical examples can be furnished to prove the necessity of its existence. Let us show the simplest. Let the thermally isolated container of surcharged steam be subjected to the impact, creating the shock wave. Due to the propagation of this wave, we can observe the condensation of steam beyond the front of the wave. In any region beyond the wave we may assume the thermodynamic process to be reversible. Simultaneously, the surcharged steam before

(1) Certain surface terms have been discussed in [4] for a different purpose.

being reached by the wave was in a thermally stable state, and, hence, the process there was reversible as well. At the same time, the thermodynamic process in the whole container is irreversible, and it means, that there is an entropy production due to the sources on the front of the shock wave. Many more complicated examples may be found in materials with defects, propagation of shock waves, etc.

For our purposes, the inequality (5.3) must be rewritten for the surface σ. Repeating the considerations, delivered at the beginning of the third section, we have

$$\lim_{v\to 0}\left\{\int_{v^-}\varrho\eta^* dv+\int_{v^+}\varrho\eta^* dv+\int_{\partial\hat{v}^-}h^* ds+\int_{\partial\hat{v}^+}h^* ds\right\}\geqslant 0. \tag{5.4}$$

Now, bearing in mind the definition of the singular surface, we obtain

$$-\int_{\sigma}h^{*-}ds+\int_{\sigma}h^{*+}ds\geqslant 0.$$

Assuming again the continuity of integrands on σ, we have

$$\lim_{s(\sigma)\to 0}\frac{1}{s(\sigma)}\int_{v}[h^*]ds\geqslant 0,$$

or, equivalently,

$$[h^*]\geqslant 0 \quad \text{almost everywhere } s \text{ on } \sigma. \tag{5.5}$$

Joining the relations (5.2) and (5.5), we finally have

$$[\varrho\eta(\dot{x}_n-u_n)]-[h]\geqslant 0, \quad \text{a.e. } s \text{ on } \sigma; \tag{5.6}$$

this formula is said to be the CLAUSIUS-DUHEM *inequality for a singular surface* [1].

The inequality (5.6) is the main result of this work. It seems to be of great importance in many applications, such as the theory of defects, the theory of propagation of waves, etc. Some examples we discuss further in this paper.

6. Material at rest

To summarize the results presented we consider the material which has been at rest before being reached by the surface σ, i.e. $\dot{\mathbf{x}}\equiv 0$ at any point of v^+. At the same time we assume the absence of all surface sources but the entropy sources h^*.

The generalized KOTCHINE's condition now takes the following form:

$$\varphi^-\dot{x}_n+[\varphi]u_n+[\mu]=\begin{cases}-[\mu^*] & \text{for the entropy,}\\ 0 & \text{for all remaining cases,}\end{cases} \tag{6.1}$$
$$\text{almost everywhere } s \text{ on } \sigma.$$

The balance of mass

$$\varrho^-\dot{x}_n^-+[\varrho]u_n=0, \quad \text{a.e. } s. \tag{6.2}$$

Let us introduce the notation

$$\varkappa:=\frac{\varrho^-}{[\varrho]}\equiv\frac{\varrho^-}{\varrho^+-\varrho^-}, \quad \text{for} \quad [\varrho]\neq 0. \tag{6.3}$$

Then

$$u_n = -\varkappa \dot{x}_n^- \quad \text{a.e. } s. \tag{6.4}$$

The balance of momentum

$$\varrho^- \dot{\mathbf{x}}^- (\dot{x}_n^- - u_n) - [\mathbf{t}] = 0,$$

or, making use of (6.4)

$$[\mathbf{t}] = \varrho^+ \varkappa \dot{x}_n^- \dot{\mathbf{x}}^-, \quad \text{a.e. } s. \tag{6.5}$$

This formula may be used in experimental verification of $[\mathbf{t}]$.

The balance of moment of momentum in this case

$$\mathbf{p}^- \wedge (\varrho^+ \varkappa \dot{x}_n^- \dot{\mathbf{x}}^-) + [\mathbf{p} \wedge \mathbf{t}] = 0, \quad \text{a.e. } s, \tag{6.6}$$

or, taking into account (6.5)

$$\mathbf{p}^- \wedge [\mathbf{t}] + [\mathbf{p} \wedge \mathbf{t}] = 0, \quad \text{a.e. } s, \tag{6.7}$$

which can be used to find $[\mathbf{p}]$.

Finally, the balance of energy

$$[\varrho e] u_n + \varrho^- e^- \dot{x}_n^- + \frac{1}{2} \varrho^- \dot{x}^{-2} (\dot{x}_n^- - u_n) - \dot{\mathbf{x}}^- \cdot \mathbf{t}^- + [q] = 0, \quad \text{a.e. } s. \tag{6.8}$$

For a given jump of energy, as for instance, in the theory of defects, the above relation can be used to find the discontinuity of heat flux $[q]$.

The CLAUSIUS-DUHEM inequality has, on the other hand, the following form:

$$\varrho^- \eta^- \dot{x}_n^- + [\varrho\eta] u_n + [h] \leqslant 0, \quad \text{a.e. } s. \tag{6.9}$$

In an even more particular case of a continuous entropy flux ($[h] = 0$), we have

$$\varrho^- \eta^- \dot{x}_n^- + [\varrho\eta] u \leqslant 0,$$

or, taking into account (6.4) and (6.3)

$$\varkappa \dot{x}_n^- [\eta] \geqslant 0, \quad \text{a.e. } s. \tag{6.10}$$

P. J. CHEN and M. E. GURTIN [5] have made an assumption

$$[\eta] \geqslant 0. \tag{6.11}$$

It is quite easy to see that such an inequality requires at the same time

$$\varkappa \dot{x}_n^- \geqslant 0, \tag{6.12}$$

which can be written as

$$\dot{x}_n^- [\varrho] \geqslant 0. \tag{6.13}$$

There is no reason to assume this inequality to hold in general.

7. Other conditions

In this section we present for completeness the classical theorems of MAXWELL and HADAMARD.

Let $\mathbf{x} = \mathbf{x}(\xi)$ be any path on the singular surface σ and φ be a smooth field in v. Then, HADAMARD's lemma asserts

$$\frac{d\varphi^-}{d\xi} = \frac{d\mathbf{x}}{d\xi} \cdot (\operatorname{grad}\varphi)^-, \qquad \frac{d\varphi^+}{d\xi} = \frac{d\mathbf{x}}{d\xi} \cdot (\operatorname{grad}\varphi)^+, \tag{7.1}$$

or, subtracting these equations

$$\frac{d}{d\xi}[\varphi] = \frac{d\mathbf{x}}{d\xi} \cdot [\operatorname{grad}\varphi]. \tag{7.2}$$

This relation is called HADAMARD's *compatibility condition.*

The following, particular case has many important applications, especially in the theory of the propagation of waves. Let us assume, that at any point $\mathbf{x}$ of the surface σ

$$[\varphi] = 0. \tag{7.3}$$

According to (7.2), we have

$$\frac{d\mathbf{x}}{d\xi} \cdot [\operatorname{grad}\varphi] = 0, \tag{7.4}$$

for all paths on σ. It means, that $[\operatorname{grad}\varphi]$ is perpendicular to the surface σ. Hence

$$[\operatorname{grad}\varphi] = a\mathbf{n}, \tag{7.5}$$

where a is called an *amplitude of discontinuity*. If φ is a scalar field, a is a scalar field, as well, on the surface σ. The relation (7.5) expresses MAXWELL's *theorem*.

Except for KOTCHINE's balance equation and the above compatibility conditions, we can derive some additional conditions directly from balance equations. It is quite easy to prove that if there is no singular surface but σ in v, then

$$\dot{\varphi} = \operatorname{div}(\boldsymbol{\mu} + \boldsymbol{\mu}^*) + \lambda + \lambda^*, \quad \text{a.e. } v, \tag{7.6}$$

where

$$\dot{\varphi} := \frac{\partial\varphi}{\partial t} + \dot{\mathbf{x}} \cdot \operatorname{grad}\varphi, \tag{7.7}$$

$$\operatorname{div}(\boldsymbol{\mu} + \boldsymbol{\mu}^*) := \lim_{v \to 0} \frac{1}{v} \oint_{\partial v} (\mu + \mu^*) ds. \tag{7.8}$$

Let us stress once again, that even if the limit in (7.8) exists, it does not mean, that there is a vector representation for both μ and μ^*. We can easily establish the existence of a common vector representation for $\mu + \mu^*$ (CAUCHY's theorem), and the separation, leading to representations $\boldsymbol{\mu}$ and $\boldsymbol{\mu}^*$ requires an additional assumption.

Applying (7.6) in both v^+ and v^- and taking limit from both sides of σ we finally obtain

$$[\dot{\varphi}] = [\operatorname{div}(\boldsymbol{\mu} + \boldsymbol{\mu}^*)]. \tag{7.9}$$

8. Some applications

This section contains only very simple examples of the application of the CLAUSIUS-DUHEM inequality for a singular surface to emphasize its importance. Many others require further research. Among these the theory of shock waves should be re-investigated from the point of view of thermodynamics.

Let us consider, for simplicity, a singular surface σ, moving through an isotropic material. According to the results of I. MÜLLER [6], entropy and heat fluxes are connected, in this case, by the relation

$$\mathbf{h} = \Lambda(\Theta, \dot{\Theta})\mathbf{q}, \tag{8.1}$$

where Λ is a coldness, which in the case of thermal equilibrium becomes the inverse of absolute temperature, Θ being an empirical temperature, and $\dot{\Theta}$—its time derivativative. If asume the continuity of coldness

$$[\Lambda] = 0, \tag{8.2}$$

from (6.9) it follows

$$\varrho^{-}\eta^{-}\dot{x}_{\mathbf{n}}^{-} + [\varrho\eta]u_{\mathbf{n}} + \Lambda[\mathbf{q}\cdot\mathbf{n}] \leqslant 0, \quad \text{a.e.}s. \tag{8.3}$$

Making use of the balance equation of energy (6.8), we can eliminate the heat flux from this inequality. Namely:

$$\left\{\varrho^{-}(\eta^{-} - \Lambda e^{-}) - \frac{1}{2}\varrho^{-}\dot{x}^{-2}\Lambda\right\}\dot{x}_{\mathbf{n}}^{-} + \left\{[\varrho(\eta - \Lambda e)] + \frac{1}{2}\varrho^{-}\dot{x}^{-2}\Lambda\right\}u_{\mathbf{n}} + \Lambda\dot{\mathbf{x}}^{-}\cdot\mathbf{t}^{-} \leqslant 0. \tag{8.4}$$

We can read some interesting limitations from this inequality in particular cases. For instance, if σ is a concentrated defect, moving through the material remaining at rest, then ($\dot{\mathbf{x}}^{-} \equiv 0$):

$$[\eta - \Lambda e]u_{\mathbf{n}} \leqslant 0, \quad \text{a.e. } s, \tag{8.5}$$

which means, that the defect is moving in the direction of the region with smaller value of $\eta - \Lambda e$, or, roughly speaking, in the direction of smaller dissipation.

More significant evaluation can be obtained from (8.3) by the use of the FOURIER-DUHAMEL relation

$$q = K\operatorname{grad}\Theta, \tag{8.6}$$

where K is the thermal conductivity of material. Taking into account MAXWELL's theorem we have

$$[\Theta] = 0 \;\&\; [K] = 0 \Rightarrow [\operatorname{grad}\Theta] = a_{\Theta}\mathbf{n}, \tag{8.7}$$

where a_{Θ} is a thermal amplitude on σ. Under the above assumptions, it follows from (8.3) that

$$[\varrho\eta]u_{\mathbf{n}} \leqslant -\varrho^{-}\eta^{-}\dot{x}_{\mathbf{n}}^{-} - \Lambda K a_{\Theta}, \quad \text{a.e. } s.$$

If, again, material remains at rest, we have

$$[\eta]u_{\mathbf{n}} \leqslant -\frac{\Lambda K a_{\Theta}}{\varrho}, \quad \text{a.e. } s. \tag{8.8}$$

Two important cases are to be distinguished; first — a defect increasing the entropy of medium ($\eta^- > \eta^+$); the second — a defect, changing the entropy continuously ($[\eta] = 0$). The former is described by the following relation:

$$u_n \geqslant \frac{\Lambda K a_\Theta}{\varrho(\eta^- - \eta^+)}, \tag{8.9}$$

which means, that such a process may occur only for sufficiently fast defects. The latter is limited by the inequality

$$a_\Theta \leqslant 0, \tag{8.10}$$

which means, that the medium is sharply cooled down by the defect of this type (Fig. 2; r is a distance from the singular surface σ).

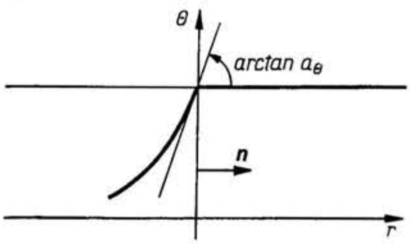

FIG. 2.

To emphasize the connection of the generalized CLAUSIUS-DUHEM inequality (5.6) and the theory of constitutive equations, we investigate one more example. The problem is, more or less, academic, because the relation assumed below has not been established experimentally. However, the required relation has never been sought and seems to be sufficiently reasonable to work on. Namely, let us investigate again an isotropic material with a singular surface. We have in this case

$$[\varrho\eta(\dot{x}_n - u_n)] - \Lambda K a_\Theta \geqslant 0, \quad \text{a.e. } s, \tag{8.11}$$

for $[\Lambda] = 0$, and $[K] = 0$. Let us assume that the velocity field is continuous ($[\dot{\mathbf{x}}] = 0$). According to (4.2), we obtain

$$[\varrho^*] = 0 \Rightarrow [\varrho] = 0. \tag{8.12}$$

Under these assumptions

$$\varrho(\dot{x}_n - u_n)[\eta] - \Lambda K a_\Theta \geqslant 0, \quad \text{a.e. } s. \tag{8.13}$$

The main constitutive assumption, we make now, is a linear relation between the entropy jump $[\eta]$, and the velocity of defect u_n:

$$[\eta] = -d u_n, \tag{8.14}$$

where d is a positive material constant. It is quite obvious that (8.14) does not satisfy the requirement of equipresence, but up to now no better relations are available. We shall return to this equation in another paper.

Let us enumerate, however, the properties of defects, described by (8.14).

i) If the normal velocity u_n of defect is vanishing, there is no jump of entropy $[\eta]$. It means, the distribution of entropy is continuous through a defect at rest.

ii) If the jump of entropy $[\eta]$ is vanishing, a defect is at rest. It means, we can treat the jump $[\eta]$ as a "thermodynamic force", moving singular surfaces.

The positive sign of d is assumed to obtain an extremum of dissipation being maximum.

Now, substituting (8.14) into (8.13), we obtain

$$u_n^2 - u_n \dot{x}_n - \frac{\Lambda K a_\Theta}{\varrho d} \geqslant 0. \tag{8.15}$$

Three cases can be distinguished:

i)

$$d = -\frac{4\Lambda K a_\Theta}{\varrho \dot{x}_n^2}. \tag{8.16}$$

In this case (8.13) is satisfied if, and only if,

$$u_n = \frac{1}{2}\dot{x}_n, \tag{8.17}$$

and, furthermore, processes, connected with the motion of a defect, are reversible — instead of inequality (8.15), we obtain an identity. This case may be used to verify experimentally the assumption (8.14). Namely, if (8.17) is satisfied for a sequence of $\dot{x}_n$, we should obtain the same value of d through (8.16). If it is not, d is not a material constant, and (8.14) is wrong as well.

Making use of the formula (8.14), the value of entropy jump can be calculated. Namely

$$[\eta] = -\frac{2\Lambda K a_\Theta}{\varrho \dot{x}_n}. \tag{8.18}$$

For the distribution of entropy of a system being homogeneous in the undeformed state, the plot of η against the distance r from the surface σ is shown in Fig. 3.

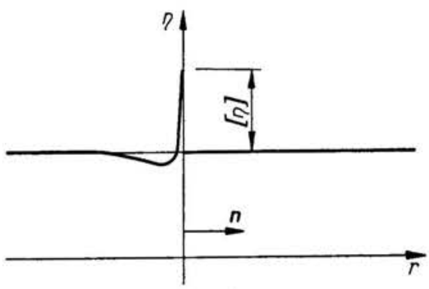

FIG. 3.

ii)

$$d > \frac{4\Lambda K a_\Theta}{\varrho \dot{x}_n^2}; \tag{8.19}$$

now, we obtain

$$\frac{1}{2}\left(\dot{x}_n - \sqrt{\dot{x}_n^2 - \frac{4\Lambda K a_\Theta}{\varrho d}}\right) \leqslant u_n \leqslant \frac{1}{2}\left(\dot{x}_n + \sqrt{\dot{x}_n - \frac{4\Lambda K a_\Theta}{\varrho d}}\right), \tag{8.20}$$

which means that thermodynamics delivers definite lower and upper bounds for a velocity of a defect.

On the other hand, if u_n is equal to its lower (upper) bound the process is again reversible, if it is so beyond the surface σ.

iii)

$$d < \frac{4\Lambda K a_{\Theta}}{\varrho \dot{x}_n^2}; \tag{8.21}$$

it is easy to check, that these values of d are thermodynamically forbidden. In other words, the CLAUSIUS-DUHEM inequality (8.15) cannot be satisfied, which means the linear relation (8.14) does not work in this case.

References

1. K. WILMAŃSKI, *Note on Clausius-Duhem inequality for a singular surface*, Bull. Acad. Polon. Sci., Série Sci. Techn., **22**, 10, 1974.
2. K. WILMAŃSKI, *Foundations of phenomenological thermodynamics* [in Polish], PWN, Warszawa 1974.
3. K. WILMAŃSKI, *Outline of neoclassical thermodynamics*, Arch. Rat. Mech. Anal. [to appear].
4. A. E. GREEN, P. M. NAGHDI, *On continuum thermodynamics*, Arch. Rat. Mech. Anal., **48**, 5, 1972.
5. P. J. CHEN, M. E. GURTIN, *Thermodynamic influences on the growth of one-dimensional shock waves in materials with memory*, ZAMP, **23**, 1972.
6. I. MÜLLER, *The coldness, a universal function in thermoelastic bodies*, Arch. Rat. Mech. Anal., **41**, 5, 1971.

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