

On the Second Law of Thermodynamics for a Singular Surface*

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1. Introduction

In the recent years considerable attention has been given to thermodynamic properties of singular surfaces in continuous medium. Green and Naghdy [1] developed a rather general thermodynamic theory in which surface sources were involved. Recently Wilmanski [3, 4] presented a new form of Kottchine's condition in which the surface sources were taken into account. This form of Kottchine's condition was used to obtain Clausius-Duhem inequality for a singular surface.

In the present paper a somewhat more different point of view is adopted, although the approach taken is similar to that of the earlier papers [3, 4]. Using the formulation on Meixner's theory wherein the local Clausius-Duhem inequality is replaced by the so-called fundamental inequality a new local thermodynamic inequality for a singular surface is obtained.

The definition of singular surface, the generalized balance equation for a continuous medium and Kottchine's condition are given in the second section. In the third section we derive a new local thermodynamic inequality for a singular surface. The fourth section is devoted to the particular case of the material at rest before being reched by a singular surface.

2. Preliminaries

In [4] the following generalized form of balance equation is given

$$(2.1) \quad \frac{d}{dt} \int_v \varphi \, d v = \oint_{\partial v} (\mu + \mu^*) \, ds + \int_v (\gamma + \lambda^*) \, d v,$$

where the surface sources are denoted with star.

The eq. (2.1) is assumed to hold for any subvolume v and for any field quantity φ .

Definition of Singular Surface. Let a surface σ , oriented by a unit vector \mathbf{n} , be a part of the region $\partial v^- \cap \partial v^+$, Fig. 1. Let the field φ , described by the balance equation (2.1), is smooth in v^- and v^+ , i. e. it is continuously di-

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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 $\text{grad } \varphi$ approaches limits $(\text{grad } \varphi)^-$, $(\text{grad } \varphi)^+$ 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 (2.1), 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 [4].

We consider a medium, in which a singular surface σ is moving with a velocity $\mathbf{u}(\mathbf{x})$, $\mathbf{x} \in \sigma$, and the balance eq. (2.1) is fulfilled v .

It is deduced in [4]

$$(2.2) \quad [\varphi(\dot{\mathbf{x}}_n - u_n)] - [\mu] = [\mu^*],$$

which is called the generalized Kottchine's condition for a singular surface.

The following form of Clausius-Duhem inequality for a singular surface is obtained [4]

$$(2.3) \quad [\varrho \eta(\dot{\mathbf{x}}_n - u_n)] - [h] \geq 0 \quad \text{almost everywhere } s \text{ on } \sigma,$$

where: ϱ — mass density, η — entropy density and h — entropy flux.

It is interesting to note that the surface sources of entropy h^* vanish in eq. (2.3). The standard notation of Christoffel is used

$$[\varrho \eta(\dot{\mathbf{x}}_n - u_n)] := \varrho^+ \eta^+(\dot{\mathbf{x}}_n^+ - u_n) - \varrho^- \eta^-(\dot{\mathbf{x}}_n^- - u_n)$$

$$[h] := h^+ - h^-.$$

3. A Local Thermodynamic Inequality for a Singular Surface

The base of our investigation is the fundamental inequality given by Meixner [2]. Starting from equilibrium state at $t = -\infty$, we have

$$(3.1) \quad \int_{-\infty}^{\tau} \{ \varrho(A_{st}(\varepsilon) - \mathcal{V}) \dot{\varepsilon} + \nabla \cdot \mathbf{A} \cdot \mathbf{q} \} dt \geq 0 \quad \text{for all } \tau \text{ and } v.$$

The following assumptions are introduced:

A 1. There exists a thermodynamic temperature function $A = A(\varepsilon, \dot{\varepsilon})$ [6] with the properties

$$(3.2) \quad A|_E = \frac{1}{\theta_{st}}$$

and an energy flux $\mathbf{q} = -\mathbf{k}(\varepsilon, \dot{\varepsilon})$, where θ_{st} is the Kelvin temperature and ε — an independent variable (energy density),

A 2. There exists only energy function in equilibrium state

$$(3.3) \quad \eta_{st}(\varepsilon) := \eta(\varepsilon, 0) \geq \eta(\varepsilon, \dot{\varepsilon}),$$

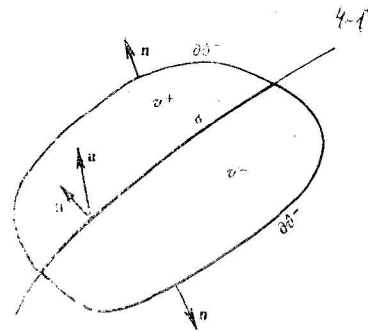


Fig. 1

where the relation between $A_{st}(\varepsilon)$ and $\eta_{st}(\varepsilon)$ is given by

$$(3.4) \quad A_{st}(\varepsilon) = \frac{d \eta_{st}(\varepsilon)}{d \varepsilon}.$$

Bearing in mind the relation (3.4) and the first law of thermodynamics [2].

$$\dot{\varepsilon} + \nabla \cdot \mathbf{q} = 0$$

we can rewrite the inequality (3.1) in the form

$$(3.1)_1 \quad \int_{-\infty}^{\tau} \{ \varrho \dot{\eta}_{st}(\varepsilon) + \nabla \cdot (A\mathbf{q}) \} dt \geq 0 \quad \text{for all } \tau \text{ and } v,$$

or

$$(3.1)_2 \quad \int_v \{ \varrho \dot{\eta}_{st}(\varepsilon) + \nabla \cdot (A\mathbf{q}) \} d v \geq 0,$$

since the process is fast.

The local formula of inequality (3.1)₂ yields

$$(3.5) \quad \varrho \dot{\eta}_{st}(\varepsilon) + \nabla \cdot (A\mathbf{q}) \geq 0.$$

Comparing eq. (3.1)₂ with eq. (2.1) we conclude that

$$(3.6) \quad \varphi \equiv \varrho \eta_{st}(\varepsilon) \quad \text{and} \quad -(\mu + \mu^*) \equiv A\mathbf{q} \cdot \mathbf{n},$$

since the vector \mathbf{q} is pointed inwards.

There are two possibilities to obtain the local thermodynamic inequality for a singular surface.

P 1. We use the generalized Katchine's condition (2.2), relations (3.6) and the second law of thermodynamics (3.1).

P 2. We apply directly the definition of singular surface to the inequality (3.1)₂ and afterwards we take a limit $s(\sigma) \rightarrow 0$.

We choose the second possibility. At first we rewrite the inequality (3.1)₂ in the form

$$(3.1)_3 \quad \int_v \varrho \dot{\eta}_{st}(\varepsilon) d v + \oint_{\delta v} (A\mathbf{q}) \cdot \mathbf{n} d s \geq 0.$$

The first term of eq. (3.1)₃ can be written as

$$(3.7) \quad \begin{aligned} \frac{d}{d t} \int_v \varrho \eta_{st}(\varepsilon) d v &= \int_{v^-} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d v + \int_{v^+} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d v \\ &+ \oint_{\partial v^-} \varrho \eta_{st}(\varepsilon) V_n d s + \oint_{\partial v^+} \varrho \eta_{st}(\varepsilon) V_n d s, \end{aligned}$$

where V_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 $\mathbf{V}_n = \dot{\mathbf{x}} \cdot \mathbf{n}$, while for σ we have $\mathbf{V} = \mathbf{u}$. Separating the common part of ∂v^- and ∂v^+ , we obtain from (3.7)

$$(3.8) \quad \frac{d}{dt} \int_{\mathcal{V}} \varrho \eta_{st}(\varepsilon) d\mathcal{V} = \int_{\mathcal{V}^-} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d\mathcal{V} + \int_{\mathcal{V}^+} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d\mathcal{V} \\ - \int_{\widehat{\partial \mathcal{V}}^-} \varrho \eta_{st}(\varepsilon) \dot{x}_n d\varepsilon + \int_{\widehat{\partial \mathcal{V}}^+} \varrho \eta_{st}(\varepsilon) \dot{x}_n d\varepsilon + \int_{\sigma} \varrho \eta_{st}^-(\varepsilon) u_n d\varepsilon - \int_{\sigma} \varrho \eta_{st}^+(\varepsilon) u_n d\varepsilon,$$

where we have taken into account the change of orientation of the surface $\mathcal{V}^+ \cap \sigma$.

The second term of eq. (3.1)₃ can be written in the form

$$(3.9) \quad \oint_{\partial \mathcal{V}} (\Delta \mathbf{q}) \cdot \mathbf{n} d\varepsilon = - \int_{\widehat{\partial \mathcal{V}}^-} (\Delta \mathbf{q}) \cdot \mathbf{n} d\varepsilon + \int_{\widehat{\partial \mathcal{V}}^+} (\Delta \mathbf{q}) \cdot \mathbf{n} d\varepsilon \\ + \int_{\sigma} (\Delta \mathbf{q})^- \cdot \mathbf{n} d\varepsilon - \int_{\sigma} (\Delta \mathbf{q})^+ \cdot \mathbf{n} d\varepsilon,$$

where we have taken into account the change of orientation of surface $\mathcal{V}^+ \cap \sigma$. However, the third and fourth terms are zero in relation (3.9) since \mathbf{q} is the energy flux vector through the surface $\partial \mathcal{V} = \widehat{\partial \mathcal{V}}^+ \cup \widehat{\partial \mathcal{V}}^-$.

Substitution of eqs. (3.8) and (3.9) into eq. (3.1)₃ yields

$$(3.10) \quad \int_{\mathcal{V}^-} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d\mathcal{V} + \int_{\mathcal{V}^+} \varrho \frac{\partial \eta_{st}(\varepsilon)}{\partial t} d\mathcal{V} - \int_{\widehat{\partial \mathcal{V}}^-} \varrho \eta_{st}(\varepsilon) \dot{x}_n d\varepsilon \\ + \int_{\widehat{\partial \mathcal{V}}^+} \varrho \eta_{st}(\varepsilon) \dot{x}_n d\varepsilon + \int_{\sigma} \varrho \eta_{st}^-(\varepsilon) u_n d\varepsilon - \int_{\sigma} \varrho \eta_{st}^+(\varepsilon) u_n d\varepsilon \\ - \int_{\widehat{\partial \mathcal{V}}^-} (\Delta \mathbf{q}) \cdot \mathbf{n} d\varepsilon + \int_{\widehat{\partial \mathcal{V}}^+} (\Delta \mathbf{q}) \cdot \mathbf{n} d\varepsilon \geq 0.$$

Under our assumptions the inequality (3.10) must hold for any \mathcal{V} . Then we are allowed to take a limit $\mathcal{V} \rightarrow 0$ in eq. (3.10) and we shrink down $\widehat{\partial \mathcal{V}}^-$ and $\widehat{\partial \mathcal{V}}^+$ to σ . Hence $\mathcal{V}^- \rightarrow 0$, $\mathcal{V}^+ \rightarrow 0$, preserving σ . Bearing in mind the definition of the singular surface, we obtain

$$(3.11) \quad - \int_{\sigma} \varrho \eta_{st}^-(\varepsilon) \dot{x}_n^- d\varepsilon + \int_{\sigma} \varrho \eta_{st}^+(\varepsilon) \dot{x}_n^+ d\varepsilon + \int_{\sigma} \varrho \eta_{st}^-(\varepsilon) u_n d\varepsilon \\ - \int_{\sigma} \varrho \eta_{st}^+(\varepsilon) u_n d\varepsilon - \int_{\sigma} (\Delta \mathbf{q})^- \cdot \mathbf{n} d\varepsilon + \int_{\sigma} (\Delta \mathbf{q})^+ \cdot \mathbf{n} d\varepsilon \geq 0,$$

where $(\Delta \mathbf{q})^-$ is the limit of $(\Delta \mathbf{q})$ from \mathcal{V}^- and $(\Delta \mathbf{q})^+$ — from \mathcal{V}^+ .

Using the standard notation of Christoffel

$$[\varrho \eta_{st}(\varepsilon) (\dot{x}_n - u_n)] := \varrho \eta_{st}^+(\varepsilon) (\dot{x}_n^+ - u_n) - \varrho \eta_{st}^-(\varepsilon) (\dot{x}_n^- - u_n),$$

$$[\Delta \mathbf{q}] \cdot \mathbf{n} := \{(\Delta \mathbf{q})^+ - (\Delta \mathbf{q})^-\} \cdot \mathbf{n},$$

then the inequality (3.11) can be written in the form

$$(3.12) \quad \int_{\sigma} \{[\varrho\eta_{st}(\varepsilon)(\dot{x}_n - u_n)] + [A\mathbf{q} \cdot \mathbf{n}]\} d s \geq 0.$$

The function A may be accepted as a continuous scalar function for all values of ε , $\dot{\varepsilon}$, i. e. $[A]=0$. Then the inequality (3.12) yields

$$(3.13) \quad \int_{\sigma} \{[\varrho\eta_{st}(\varepsilon)(\dot{x}_n - u_n)] + A[\mathbf{q} \cdot \mathbf{n}]\} d s \geq 0.$$

Assuming the continuity of the integrand on σ , we can take a limit from the relation (3.13)

$$\lim_{S(\sigma) \rightarrow 0} \frac{1}{S(\sigma)} \int_{\sigma} \{[\varrho\eta_{st}(\varepsilon)(\dot{x}_n - u_n)] + A[\mathbf{q} \cdot \mathbf{n}]\} d s \geq 0,$$

where $S(\sigma)$ is the area of surface σ . Hence the relation (3.13) is equivalent to the following local formula

$$(3.14) \quad [\varrho\eta_{st}(\varepsilon)(\dot{x}_n - u_n)] + A[\mathbf{q} \cdot \mathbf{n}] \geq 0 \text{ almost everywhere } S \text{ on } \sigma.$$

The inequality (3.14) is the main result of our investigation. In comparison with inequality (2.3) it has some distincts:

- i. The inequality (3.14) does not contain the entropy function η and entropy flux h ,
- ii. The inequality (3.14) contains the entropy function in equilibrium state η_{st} and thermodynamic temperature function A . Also it contains the energy flux vector \mathbf{q} .

4. Material at rest

We consider as [4] a material which has been at rest before being reached by the surface σ , i. e. $\dot{\mathbf{x}} \equiv 0$ at any point of σ^+ . In this particular case the inequality (3.14) takes the following form

$$(4.1) \quad [\varrho\eta_{st}(\varepsilon)]u_n + \varrho^-\eta_{st}^-(\varepsilon)\dot{x}_n^- - A[\mathbf{q} \cdot \mathbf{n}] \leq 0.$$

If we assume that $[\mathbf{q}]=0$ then the following inequality yields

$$(4.2) \quad [\varrho\eta_{st}(\varepsilon)]u_n + \varrho^-\eta_{st}^-(\varepsilon)\dot{x}_n^- \leq 0.$$

Bearing in mind the balance of mass — (6.4) from [4]

$$u_n = \frac{\varrho^-}{[\varrho]}\dot{x}_n^-$$

we can write the inequality (4.2) in the form

$$(4.3) \quad \varrho^-[\eta_{st}(\varepsilon)]\dot{x}_n^- \geq 0.$$

But in equilibrium state $[\eta_{st}(\varepsilon)] > 0$ and therefore the inequality (4.3) takes the form

$$(4.4) \quad [\varrho]\dot{x}_n^- \geq 0.$$

The result (4.4) has been obtained previously by Wilmanski on other basis.

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