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The Entropy Principle and its Mathematical Impact

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Contains:

- The history of the Second Law of Thermodynamics
- The distributional Entropy Principle $\partial_t H + \operatorname{div}\Psi \geq 0$
- Example: Collision of two masses
- Example: Hyperbolic shock waves
- Example: Surface tension

§ 1. *The Second Law of Thermodynamics*

According to the principles of thermodynamics one can introduce for any macroscopic system a state function S, the entropy of the system, which has the following properties.

The variation of the entropy dS may be written as the sum of two terms

$$dS = d_eS + d_iS , \qquad (1)$$

where d_eS is the entropy supplied to the system by its surroundings, and d_iS the entropy produced inside the system. The second law of thermodynamics states that d_iS must be zero for reversible (or equilibrium) transformations and positive for irreversible transformations of the system:

$$d_iS \geqslant 0 . \qquad (2)$$

The entropy supplied, d_eS, on the other hand may be positive, zero or negative, depending on the interaction of the system with its surroundings. Thus for an adiabatically insulated system (*i.e.* a system which can exchange neither heat nor matter with its surroundings) d_eS is equal to zero, and it follows from (1) and (2) that

$$dS \geqslant 0 \text{ for an adiabatically insulated system.} \qquad (3)$$

This is a well-known form of the second law of thermodynamics.

For a so-called closed system, which may only exchange heat with its surroundings, we have according to the theorem of Carnot–Clausius:

$$d_eS = \frac{dQ}{T} , \qquad (4)$$

where dQ is the heat supplied to the system by its surroundings and T

the absolute temperature at which heat is received by the system. From (1) and (2) it follows for this case that

$$dS \geqslant \frac{dQ}{T} \quad \text{for a closed system ,} \qquad (5)$$

which is also a well-known form of the second law of thermodynamics.

For open systems, *i.e.* systems which may exchange heat as well as matter with their surroundings d_eS contains also a term connected with the transfer of matter (*cf.* also § 2 of this chapter). The theorem of Carnot–Clausius, which is contained in formulae (1), (2) and (4), does not apply to such systems. However the very general statements contained in (1) and (2) alone remain valid.

We may remark at this point that thermodynamics in the customary sense is concerned with the study of the reversible transformations for which the equality in (2) holds. In thermodynamics of irreversible processes, however, one of the important objectives is to relate the quantity d_iS, the entropy production, to the various irreversible phenomena which may occur inside the system. Before calculating the entropy production in terms of the quantities which characterize the irreversible phenomena, we shall rewrite (1) and (2) in a form which is more suitable for the description of systems in which the densities of the extensive properties (such as mass and energy, considered in the previous chapter) are continuous functions of space coordinates. Let us write

$$S = \int^V \rho s dV , \qquad (6)$$

$$\frac{d_eS}{dt} = - \int^\Omega \boldsymbol{J}_{s,\text{tot}} \cdot d\boldsymbol{\Omega} , \qquad (7)$$

$$\frac{d_iS}{dt} = \int^V \sigma \, dV , \qquad (8)$$

where s is the entropy per unit mass, $\boldsymbol{J}_{s,\text{tot}}$ the total entropy flow per unit area and unit time, and σ the entropy source strength or entropy production per unit volume and unit time.

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[S.R. de Groot & P. Mazur. *Non-equilibrium Thermodynamics*
North Holland 1962]

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$$S = \int^V \rho s \, dV , \tag{6}$$

$$\frac{d_eS}{dt} = - \int^\Omega \boldsymbol{J}_{s,\,tot} \cdot d\boldsymbol{\Omega} , \tag{7}$$

$$\frac{d_iS}{dt} = \int^V \sigma \, dV , \tag{8}$$

where s is the entropy per unit mass, $\boldsymbol{J}_{s,\,tot}$ the total entropy flow per unit area and unit time, and σ the entropy source strength or entropy production per unit volume and unit time.

With (6), (7) and (8), formula (1) may be rewritten, using also Gauss'

theorem, in the form

$$\int^V \left(\frac{\partial \rho s}{\partial t} + \text{div} \, \boldsymbol{J}_{s,\,tot} - \sigma \right) dV = 0 . \tag{9}$$

From this relation it follows, since (1) and (2) must hold for an arbitrary volume V, that

$$\frac{\partial \rho s}{\partial t} = - \text{div} \, \boldsymbol{J}_{s,\,tot} + \sigma , \tag{10}$$

$$\sigma \geqslant 0 . \tag{11}$$

These two formulae are the local forms of (1) and (2), *i.e.* the local mathematical expression for the second law of thermodynamics. Equation (10) is formally a balance equation for the entropy density ρs, with a source term σ which satisfies the important inequality (11). With the help of relation (II.16), equation (10) can be rewritten in a slightly different form,

$$\rho \frac{ds}{dt} = - \text{div} \, \boldsymbol{J}_s + \sigma , \tag{12}$$

where the entropy flux $\boldsymbol{J}_s$ is the difference between the total entropy flux $\boldsymbol{J}_{s,\,tot}$ and a convective term $\rho s \boldsymbol{v}$

$$\boldsymbol{J}_s = \boldsymbol{J}_{s,\,tot} - \rho s \boldsymbol{v} . \tag{13}$$

In obtaining (10) and (11) we have assumed that the statements (1) and (2) also hold for infinitesimally small parts of the system, or in other words, that the laws which are valid for macroscopic systems remain valid for infinitesimally small parts of it. This is in agreement with the point of view currently adopted in a macroscopic description of a continuous system. It implies, on a microscopic model, that the local macroscopic measurements performed on the system, are really measurements of the properties of small parts of the system, which still contain a large number of the constituting particles. Such small parts of the system one might call physically infinitesimal. With this in mind it still makes sense to speak about the local values of such fundamentally macroscopic concepts as entropy and entropy production.

[S.R. de Groot & P. Mazur. *Non-equilibrium Thermodynamics* North Holland 1962]

(a) (Entropy balance)

The entropy is an additive quantity whose equation of balance in regular points of the body we write as

$$\frac{\partial \rho\eta}{\partial t} + \frac{\partial}{\partial x_j}(\rho\eta v_j + \Phi_j) = \sigma. \tag{6.20}$$

(b) (Constitutive property)

The specific entropy η and its flux Φ_i are an objective scalar and vector respectively and both are given by constitutive relations that obey the principle of material frame indifference. In particular in a mixture of inviscid fluids we have

$$\eta = \eta(\rho_\beta, T)$$

$$\Phi_i = \sum_{\beta=1}^{\nu} \varphi_\rho^\beta \rho_{\beta,i} + \sum_{\beta=1}^{\nu-1} \varphi_V^\beta V_i^\beta + \varphi_T T_{,i}, \tag{6.21}$$

where φ_ρ^β, φ_V^β and φ_T may be functions of ρ_β, T.

(c) (Entropy inequality)

The entropy production σ is non-negative for all thermodynamic processes, so that the inequality

$$\frac{\partial \rho\eta}{\partial t} + \frac{\partial}{\partial x_j}(\rho\eta v_j + \Phi_j) \geqslant 0 \tag{6.22}$$

holds.

[I. Müller. *Thermodynamics.* Pitman 1985]

Therefore the local forms of the balance equations, viz.

$$\frac{\partial \mathbf{F}^0}{\partial t} + \frac{\partial \mathbf{F}^i}{\partial x^i} = \mathbf{\Pi} \quad \text{with} \quad \mathbf{F}^i = \mathbf{F}^i(\mathbf{F}^0) \quad \text{and} \quad \mathbf{\Pi} = \mathbf{\Pi}(\mathbf{F}^0) \tag{1}$$

provide a system of first-order, quasi-linear differential equations for the densities $\mathbf{F}^0$. The form of the constitutive functions is restricted in its generality by just two universal principles

- the entropy principle, and
- the principle of relativity.

In this respect rational extended thermodynamics reflects the procedure of rational mechanics by Truesdell & Noll [1] and rational thermodynamics by Truesdell [2].

The entropy principle requires that the entropy inequality

$$\frac{\partial h^0}{\partial t} + \frac{\partial h^i}{\partial x^i} = \Sigma \geq 0 \quad \text{with} \quad h^0 = h^0(\mathbf{F}^0), \quad h^i = h^i(\mathbf{F}^0), \quad \Sigma = \Sigma(\mathbf{F}^0) \tag{2}$$

hold for all solutions of the field equations (1) and that $h^0(\mathbf{F}^0)$ be a concave function. The principle of relativity states that the field equations (1) have the same form in all Galilean frames. The two principles together go a long way to make the constitutive functions explicit. And they ensure that the system (1) has symmetric hyperbolic structure.

[I. Müller & T. Ruggeri. *Rational Extended Thermodynamics*
Springer Tracts in Natural Philosophy 37, 1998]

$$\rho^s \frac{d^s}{dt} e^s + \boldsymbol{\nabla} \cdot \mathbf{J}_e^s + \mathbf{n} \cdot [(\mathbf{v} - \mathbf{v}^s)\rho(e - e^s) + \mathbf{J}_e]_- = 0 \qquad (2.5.4)$$

The excess energy flow is along the dividing surface [cf. Eq. (2.3.7)]:

$$\mathbf{n} \cdot \mathbf{J}_e^s = 0 \qquad (2.5.5)$$

Using the balance equations (2.4.10) and (2.4.13) for the kinetic- and potential-energy densities as well as the balance equation (2.5.4) for the total energy, one finds as the balance equation for the excess internal energy

$$\begin{aligned}
\rho^s \frac{d^s}{dt} u^s = & -\boldsymbol{\nabla} \cdot \mathbf{J}_q^s - \mathsf{P}^s : \boldsymbol{\nabla}\mathbf{v}^s + \sum_{k=1}^n \mathbf{F}_k \cdot \mathbf{J}_k^s \\
& -\mathbf{n} \cdot \{(\mathbf{v} - \mathbf{v}^s)\rho[u - u^s - \tfrac{1}{2}|\mathbf{v} - \mathbf{v}^s|^2] + \mathbf{J}_q \\
& +[(\mathbf{v} - \mathbf{v}^s)\rho(\mathbf{v} - \mathbf{v}^s) + \mathsf{P}] \cdot (\mathbf{v} - \mathbf{v}^s)\}_-
\end{aligned} \qquad (2.5.6)$$

It follows from Eqs. (2.2.15), (2.4.4), and (2.5.3) that the excess heat flow is also along the dividing surface:

$$\mathbf{n} \cdot \mathbf{J}_q^s = 0 \qquad (2.5.7)$$

The internal energy of the system is not conserved, because of conversion of kinetic and potential energy into internal energy. The balance equation (2.5.6) for the excess internal energy gives the first law of thermodynamics for the interface.

III. ENTROPY BALANCE

A. The Second Law of Thermodynamics

The balance equation for the entropy density is given by

$$\frac{\partial}{\partial t}\rho s + \operatorname{div}(\rho s \mathbf{v} + \mathbf{J}) = \sigma \qquad (3.1.1)$$

where s is the entropy density per unit of mass, $\mathbf{J}$ is the entropy current,*

* The subscript s used in de Groot and Mazur[3] has been dropped because it would in this case clearly be confusing.

One may now conclude[3] from the second law of thermodynamics that

$$\sigma^{\pm} \geq 0 \qquad (3.1.3)$$

For the interface, one finds the following balance equation [cf. Eq. (2.3.6)]:

$$\rho^s \frac{d^s}{dt} s^s = -\boldsymbol{\nabla} \cdot \mathbf{J}^s - \mathbf{n} \cdot [(\mathbf{v} - \mathbf{v}^s)\rho(s - s^s) + \mathbf{J}]_- + \sigma^s \qquad (3.1.4)$$

From the second law of thermodyanics, it now follows that

$$\sigma^s \geq 0 \qquad (3.1.5)$$

As is to be expected, not only is entropy produced in the bulk regions, but there is also an excess of this production in the interfacial region, which according to the second law is also positive.

B. The Entropy Production

From thermodynamics we know that the entropy for a system in equilibrium is a well-defined function of the various parameters necessary to define the macroscopic state of the system. As discussed already by Gibbs,[5] this is also the case for a system with two phases separated by a surface of discontinuity. For the system under consideration, we use as parameters the internal energy, the specific volume $v^{\pm} \equiv 1/\rho^{\pm}$ or specific surface area $v^s \equiv 1/\rho^s$, and the mass fractions. We may then write

$$s^- = s^-(u^-, v^-, c_k^-), \qquad s^+ = s^+(u^+, v^+, c_k^+), \qquad \text{and} \qquad s^s = s^s(u^s, v^s, c_k^s) \qquad (3.2.1)$$

Three different functions are needed to give the entropies for the two bulk phases and for the interface. At equilibrium the total differential of the entropy is given by the Gibbs relation. In the bulk regions, this

[D. Bedeaux. *Nonequilibrium Thermodynamics and Statistical Physics of Surfaces.* Advance in Chemical Physics, Vol. LXIV, Wiley 1986]

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Standard definition for a set $\mathcal{P}$ of processes

For each solution in $\mathcal{P}$ there exists an entropy pair (H, Ψ) with

$$\partial_t H + \operatorname{div} \Psi \geq 0 \quad \text{in } \mathcal{D}'(\Omega), \quad \Omega \subset \mathbb{R} \times \mathbb{R}^n$$

Equation transforms as a scalar equation (i.e. $\zeta \circ Y = \zeta^*$)
($\Rightarrow H$ objective scalar, Ψ objective vector)

Entropy principle means for test funcions ζ:

$$\langle -\partial_t \zeta, H \rangle + \langle -\nabla \zeta, \Psi \rangle \geq 0 \quad \text{for } \zeta \geq 0, \, \zeta \in C_0^\infty(\Omega; \mathbb{R})$$

Goes back to entropy principle for funcions in (t, x):

$$\langle \xi, H \rangle = \int_\Omega \xi \eta \, \mathrm{d}(t, x) \text{ for } \xi \in C_0^\infty(\Omega) \qquad (\eta \text{ entropy})$$

similar $\Psi = \psi \mathsf{L}_{n+1} \llcorner \Omega$ (ψ entropy flux), such that

$$\sigma := \partial_t \eta + \operatorname{div} \psi \geq 0 \quad \text{pointwise in } \Omega \subset \mathbb{R} \times \mathbb{R}^n$$

Of course, there are constitutive relations for (η, ψ) depending on $\mathcal{P}$

Example 1 : **System of hyperbolic conservation laws**

$$\partial_t u_k + \operatorname{div} q_k(u) = f_k(u) \quad (k = 1, \ldots, N)$$

Constitutive ansatz : $\eta = \widehat{\eta}(u)$, $\psi = \widehat{\psi}(u)$, $u = (u_1, \ldots, u_N)$

$$\partial_t \eta = \sum_k \eta'_k \partial_t u_k = -\sum_k \eta'_k \operatorname{div} q_k + \sum_k \eta'_k f_k$$

$$0 \leq \sigma := \partial_t \eta + \operatorname{div} \psi = \operatorname{div} \psi - \sum_k \eta'_k \operatorname{div} q_k + \sum_k \eta'_k f_k$$

$$= \sum_l \left(\psi'_l - \sum_k \eta'_k q_{k'l} \right) \bullet \nabla u_l + \sum_k \eta'_k f_k$$

Requirement: This holds for all solutions of the system

Result : Entropy principle is satisfied, if

$$\psi'_l(u) = \sum_k \eta'_k(u) q_{k'l}(u) \text{ for all } l \qquad \left(\Rightarrow \mathsf{D}^2\eta \mathsf{D}q = (\mathsf{D}q)^\mathsf{T} \mathsf{D}^2\eta \right)$$

$$\sum_k \eta'_k(u) f_k(u) \geq 0 \qquad\qquad\qquad \left(\Rightarrow \nabla\eta \bullet f \geq 0 \right)$$

Entropy principle has consequence for $u \mapsto f_k(u)$ and $u \mapsto q_{k'l}(u)$ of the system

Example 2 : **Compressible fluid**

$$\partial_t \varrho + \mathrm{div}(\varrho v) = 0$$

$$\partial_t(\varrho v) + \mathrm{div}(\varrho v v^\mathsf{T} + \Pi) = \mathbf{f} \qquad (\Pi \text{ pressure tensor})$$

$$\partial_t e + \mathrm{div}(ev + \Pi^\mathsf{T} v + q) = v \bullet \mathbf{f} \qquad (e \text{ total energy})$$

$$e = \varepsilon + \frac{\varrho}{2} |v|^2 \qquad (\varepsilon \text{ inner energy})$$

Constitutive ansatz : $\eta = \widehat{\eta}(\varrho, \varepsilon)$ \qquad (η is objective scalar)

$$\dot{\varrho} + \varrho \mathrm{div} v = 0 \qquad (\dot{} = \partial_t + v \bullet \nabla)$$

$$\dot{\varepsilon} + \varepsilon \mathrm{div} v = -\mathrm{div} q - \mathrm{D}v \bullet \Pi \qquad (\text{here no force } \mathbf{f})$$

$$0 \le \sigma := \partial_t \eta + \mathrm{div}\psi = \dot{\eta} + \eta \mathrm{div} v + \mathrm{div}(\psi - \eta v)$$

$$= \eta'_\varrho \dot{\varrho} + \eta'_\varepsilon \dot{\varepsilon} + \eta \mathrm{div} v + \mathrm{div}(\psi - \eta v)$$

$$= -\eta'_\varepsilon \mathrm{div} q + \mathrm{D}v \bullet \big((\eta - \varrho \eta'_\varrho - \varepsilon \eta'_\varepsilon)\mathrm{Id} - \eta'_\varepsilon \Pi \big) + \mathrm{div}(\psi - \eta v)$$

$$= \nabla \eta'_\varepsilon \bullet q + \mathrm{D}v \bullet \big((\eta - \varrho \eta'_\varrho - \varepsilon \eta'_\varepsilon)\mathrm{Id} - \eta'_\varepsilon \Pi \big)$$

$$+ \mathrm{div}(\psi - \eta v - \eta'_\varepsilon q)$$

Temperature : θ with $\frac{1}{\theta} = \eta'_\varepsilon(\varrho, \varepsilon) > 0$

Use temperature and obtain

$$\frac{1}{\theta} = \eta'_\varepsilon$$

$$0 \leq \sigma := \partial_t \eta + \mathrm{div}\psi$$
$$= \nabla\eta'_\varepsilon \bullet q + \mathrm{D}v \bullet \big((\eta - \varrho\eta'_\varrho - \varepsilon\eta'_\varepsilon)\mathrm{Id} - \eta'_\varepsilon \Pi\big)$$
$$\qquad + \mathrm{div}(\psi - \eta v - \eta'_\varepsilon q)$$
$$= \nabla\Big(\frac{1}{\theta}\Big) \bullet q + \mathrm{D}v \bullet \Big(\frac{1}{\theta}\big(p\mathrm{Id} - \Pi\big)\Big) + \mathrm{div}(\psi - \eta v - \frac{1}{\theta}q)$$

where $\quad p = \frac{1}{\eta'_\varepsilon}(\eta - \varrho\eta'_\varrho - \varepsilon\eta'_\varepsilon) = -\varepsilon + \frac{\eta - \varrho\eta'_\varrho}{\eta'_\varepsilon}$

Requirement : $\sigma \geq 0$ for all solutions of the system

Result : Entropy principle is satisfied, if

$$\Pi = p\mathrm{Id} - S \qquad\qquad \text{(Momentum tensor)}$$
$$\psi = \eta v + \frac{1}{\theta}q \qquad\qquad \text{(Clausius-Duhem flux)}$$
$$\eta = \varrho\eta'_\varrho + (\varepsilon + p)\eta'_\varepsilon \qquad \text{(Gibbs relation)}$$
$$\sigma = \frac{1}{\theta}\mathrm{D}v \bullet S + \nabla\Big(\frac{1}{\theta}\Big) \bullet q \geq 0 \quad \text{(Dissipative terms)}$$

Entropy principle has consequences for the system

Let $(\varrho, \varepsilon) \mapsto \eta(\varrho, \varepsilon)$ be the entropy and define

$$\theta = \frac{1}{\eta'_\varepsilon} > 0 \text{ temperature} \qquad p \text{ pressure}$$

$$f = \varepsilon - \theta\eta \text{ internal free energy} \qquad v_\mathsf{s} = \frac{1}{\varrho} \text{ specific volume}$$

$$\eta_\mathsf{s} = \frac{\eta}{\varrho} \text{ etc. specific quantities}$$

The following is equivalent :

- $\eta = \varrho\eta'_\varrho + (\varepsilon + p)\eta'_\varepsilon$ (Gibbs Relation)
- $\eta_{\mathsf{s}'_\varrho} + (\varepsilon_\mathsf{s} + p_\mathsf{s})\eta_{\mathsf{s}'_\varepsilon} = 0$
- $\mathrm{d}\eta_\mathsf{s} = \dfrac{1}{\theta}\,\mathrm{d}\varepsilon_\mathsf{s} + \dfrac{p}{\theta}\,\mathrm{d}v_\mathsf{s}$ (Second Law: "$dS = \frac{1}{T}dQ$")
- $\mathrm{d}f_\mathsf{s} = -\eta_\mathsf{s}\,\mathrm{d}\theta - p\,\mathrm{d}v_\mathsf{s}$
- $\mathrm{d}(\varepsilon_\mathsf{s} + p_\mathsf{s}) = \theta\,\mathrm{d}\eta_\mathsf{s} + v_\mathsf{s}\,\mathrm{d}p$ ($\varepsilon_\mathsf{s} + p_\mathsf{s}$ is the enthalpy)

This follows by computing differential forms with (ϱ, ε) as unknowns

Hence the classical formulas hold e.g. for homogeneous systems

Classical Thermodynamics

Zeroth Law   There exists for every thermodynamic system in equilibrium a property called temperature. Equality of temperature is a necessary and sufficient condition for thermal equilibrium.

First Law   There exists for every thermodynamic system a property called the energy. The change of energy of a system is equal to the mechanical work done on the system in an adiabatic process. In a non-adiabatic process, the change in energy is equal to the heat added to the system minus the mechanical work done by the system.

Second Law   There exists for every thermodynamic system in equilibrium an extensive scalar property called the entropy, S, such that in an infinitesimal reversible change of state of the system, $dS = dQ/T$, where T is the absolute temperature and dQ is the amount of heat received by the system. The entropy of a thermally insulated system cannot decrease and is constant if and only if all processes are reversible.

[MIT, Lecture on Thermodynamics (Spakovszky, Fall 2008)]
(This is the so-called "axiomatic formulation")

Classical Thermodynamics

Zeroth Law   There exists for every thermodynamic system in equilibrium a property called temperature. Equality of temperature is a necessary and sufficient condition for thermal equilibrium.

$$\theta \text{ absolute temperature}$$

First Law   There exists for every thermodynamic system a property called the energy

$$e \text{ (total) energy}$$

$$\partial_t e + \mathrm{div}\,\varphi = \ldots$$

Second Law   There exists for every thermodynamic system in equilibrium an extensive scalar property called the entropy, S, such that in an infinitesimal ... change ... of the system, $dS = dQ/T$

$$\eta \text{ entropy}, \qquad \eta'_\varepsilon = \frac{1}{\theta}, \qquad \varepsilon \text{ internal energy}$$

The entropy of a thermally insulated system cannot decrease

$$\partial_t \eta + \mathrm{div}\,\psi \geq 0$$

Example 3 : Collision of particles

Two particles with mass m^α which move with speed v^α at space points $\overline{x}^\alpha$

Collision : At (t_*, x_*), i.e. $x_* = \overline{x}^1(t_*) = \overline{x}^2(t_*)$. Let

$$\langle \zeta, \boldsymbol{\mu}_{\overline{x}^\alpha} \rangle = \int_{\mathbb{R}} \zeta(t, \overline{x}^\alpha(t)) \, \mathrm{d}t \text{ for } \zeta \in C_0^\infty(\mathbb{R} \times \mathbb{R}^n; \mathbb{R})$$

Distributional mass-momentum-energy balance

$$\partial_t \Big(\sum_\alpha m^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) + \mathrm{div} \Big(\sum_\alpha m^\alpha v^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) = 0$$

$$\partial_t \Big(\sum_\alpha m^\alpha v^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) + \mathrm{div} \Big(\sum_\alpha m^\alpha v^\alpha v^{\alpha\mathsf{T}} \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) = \sum_\alpha \mathbf{f}^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha}$$

$$\partial_t \Big(\sum_\alpha e^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) + \mathrm{div} \Big(\sum_\alpha e^\alpha v^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha} \Big) = \sum_\alpha v^\alpha \bullet \mathbf{f}^\alpha \boldsymbol{\mu}_{\overline{x}^\alpha}, \quad e^\alpha = \varepsilon^\alpha + \frac{m^\alpha}{2}|v^\alpha|^2$$

is equivalent to $v^\alpha(t, \overline{x}(t)) = \dot{\overline{x}}^\alpha(t)$ and m^α, ε^α locally constant in $t \neq t_*$ and

$$m^\alpha \ddot{\overline{x}}^\alpha = \mathbf{f}^\alpha \qquad\qquad\qquad \text{for } \alpha = 1, 2 \text{ and } t \neq t_*$$

$$
\begin{aligned}
m_-^1 + m_-^2 &= m_+^1 + m_+^2 && \text{(mass conservation in } t_*) \\
m_-^1 v_-^1 + m_-^2 v_-^2 &= m_+^1 v_+^1 + m_+^2 v_+^2 && \text{(momentum conservation in } t_*) \\
\sum_\alpha \Big(\varepsilon_-^\alpha + \frac{m_-^\alpha}{2}|v_-^\alpha|^2 \Big) &= \sum_\alpha \Big(\varepsilon_+^\alpha + \frac{m_+^\alpha}{2}|v_+^\alpha|^2 \Big) && \text{(energy conservation in } t_*)
\end{aligned}
$$

What is the entropy principle?

Use an entropy η^α and the claim is: With an entropy production h

$$h\,\boldsymbol{\delta}_{(t_*,x_*)} = \partial_t\Big(\sum_\alpha \eta^\alpha\boldsymbol{\mu}_{\overline{x}^\alpha}\Big) + \operatorname{div}\Big(\sum_\alpha \eta^\alpha v^\alpha\boldsymbol{\mu}_{\overline{x}^\alpha}\Big) \geq 0$$

This identity is equivalent to

$$-(\zeta h)(t_*,x_*) = -\big\langle\, \zeta\,,\, h\,\boldsymbol{\delta}_{(t_*,x_*)}\,\big\rangle = \Big\langle\, \partial_t\zeta\,,\, \sum_\alpha \eta^\alpha\boldsymbol{\mu}_{\overline{x}^\alpha}\,\Big\rangle + \Big\langle\, \nabla\zeta\,,\, \sum_\alpha \eta^\alpha v^\alpha\boldsymbol{\mu}_{\overline{x}^\alpha}\,\Big\rangle$$

$$= \sum_\alpha\Big(\int_{\mathbb{R}}(\partial_t\zeta)(t,\overline{x}^\alpha(t))\eta^\alpha(t,\overline{x}(t))\,\mathrm{d}t + \int_{\mathbb{R}}(\nabla\zeta)(t,\overline{x}^\alpha(t))\bullet \underbrace{(\eta^\alpha v^\alpha)(t,\overline{x}^\alpha(t))}_{\eta^\alpha(t,\overline{x}^\alpha(t))\dot{\overline{x}}^\alpha(t)}\,\mathrm{d}t$$

$$= \sum_\alpha\int_{\mathbb{R}\backslash\{t_*\}}\frac{\mathrm{d}}{\mathrm{d}t}\Big(\zeta(t,\overline{x}^\alpha(t))\Big)\eta^\alpha(t,\overline{x}^\alpha(t))\,\mathrm{d}t = \sum_\alpha\int_{\mathbb{R}\backslash\{t_*\}}\frac{\mathrm{d}}{\mathrm{d}t}\Big(\zeta(t,\overline{x}^\alpha(t))\eta^\alpha(t,\overline{x}^\alpha(t))\Big)\,\mathrm{d}t$$

$$\text{(if } \eta^\alpha = \widehat{\eta}^\alpha(m^\alpha,\varepsilon^\alpha) \text{ and since } (m^\alpha,\varepsilon^\alpha) \text{ is locally constant for } t\neq t_*)$$

$$= \sum_\alpha \zeta(t_*,\overline{x}^\alpha(t_*))(\eta_-^\alpha - \eta_+^\alpha) = \zeta(t_*,x_*)\sum_\alpha(\eta_-^\alpha - \eta_+^\alpha)$$

that is, if $\eta^\alpha = \widehat{\eta}^\alpha(m^\alpha,\varepsilon^\alpha)$ for $t\neq t_*$,
then the entropy principle is equivalent to

$$h(t_*,x_*) + \sum_\alpha \eta_-^\alpha = \sum_\alpha \eta_+^\alpha$$

$$h(t_*,x_*) \geq 0$$

$$\sum_\alpha m_-^\alpha = \sum_\alpha m_+^\alpha$$

$$\sum_\alpha m_-^\alpha v_-^\alpha = \sum_\alpha m_+^\alpha v_+^\alpha$$

$$\sum_\alpha\Big(\varepsilon_-^\alpha + \frac{m_-^\alpha}{2}|v_-^\alpha|^2\Big) = \sum_\alpha\Big(\varepsilon_+^\alpha + \frac{m_+^\alpha}{2}|v_+^\alpha|^2\Big)$$

Example 4 : Shock solution of gas equations

The equations for a fluid are

$$\partial_t \varrho + \text{div}(\varrho v) = 0$$
$$\partial_t(\varrho v) + \text{div}(\varrho v v^\top + \Pi) = \mathbf{f}, \qquad\qquad \Pi = p\text{Id} - S$$
$$\partial_t e + \text{div}(ev + \Pi^\top v + q) = v \bullet \mathbf{f}, \qquad\qquad e = \varepsilon + \frac{\varrho}{2}|v|^2$$
$$\partial_t \eta + \text{div}\left(\eta v + \frac{1}{\theta}q\right) = \frac{1}{\theta}\text{D}v \bullet S + \nabla\left(\frac{1}{\theta}\right)\bullet q \geq 0, \quad \eta = \widehat{\eta}(\varrho, \varepsilon) = \varrho\eta'_\varrho + (\varepsilon + p)\eta'_\varepsilon$$

Neglecting $S \approx 0$ and $q \approx 0$ one considers
weak solutions (that is, L^∞-solutions) of the gas equations

$$\partial_t \varrho + \text{div}(\varrho v) = 0$$
$$\partial_t(\varrho v) + \text{div}(\varrho v v^\top + p\text{Id}) = \mathbf{f}, \qquad \eta = \varrho\eta_\varrho + (\varepsilon + p)\eta_\varepsilon$$
$$\partial_t e + \text{div}((e + p)v) = v \bullet \mathbf{f}, \qquad e = \varepsilon + \frac{\varrho}{2}|v|^2$$

These are distributional solutions. One considers only solutions satisfying

$$\partial_t \eta + \text{div}(\eta v) \geq 0, \quad \eta = \widehat{\eta}(\varrho, \varepsilon)$$

Remark: For smooth solutions $(\varrho, v, \varepsilon)$ one has $\partial_t \eta + \text{div}(\eta v) = 0$.
What is the meaning of this inequality? It defines the correct shocks!

Case: An interface Γ with $\Omega = \Omega^1 \cup \Gamma \cup \Omega^2 \subset \mathbb{R} \times \mathbb{R}^n$

If the L^∞-solution has the form

$$\varrho \mathsf{L}_{n+1} = \sum_m \varrho^m \boldsymbol{\mu}_{\Omega^m}, \text{ similar } v^m, \, p^m, \, \varepsilon^m, \, \mathbf{f}^m, \qquad \langle \xi, \boldsymbol{\mu}_{\Omega^m} \rangle = \int_{\mathbb{R}} \int_{\Omega_t^m} \xi(t,x) \, \mathrm{d}x \, \mathrm{d}t$$

the above distributional differential equations can be written as

$$\partial_t \Big(\sum_m \varrho^m \boldsymbol{\mu}_{\Omega^m} \Big) + \mathrm{div} \Big(\sum_m \varrho^m v^m \boldsymbol{\mu}_{\Omega^m} \Big) = 0$$

$$\partial_t \Big(\sum_m \varrho^m v^m \boldsymbol{\mu}_{\Omega^m} \Big) + \mathrm{div} \Big(\sum_m (\varrho^m v^m v^{m\mathsf{T}} + p^m \mathrm{Id}) \boldsymbol{\mu}_{\Omega^m} \Big) = \sum_m \mathbf{f}^m \boldsymbol{\mu}_{\Omega^m}$$

$$\partial_t \Big(\sum_m e^m \boldsymbol{\mu}_{\Omega^m} \Big) + \mathrm{div} \Big(\sum_m (e^m + p^m) v^m \boldsymbol{\mu}_{\Omega^m} \Big) = \sum_m v^m \bullet \mathbf{f}^m \boldsymbol{\mu}_{\Omega^m}$$

where $p^m = \widehat{p}(\varrho^m, \varepsilon^m)$ and $e^m = \varepsilon^m + \frac{\varrho^m}{2} |v^m|^2$.

This is equivalent to the differential equations for $(\varrho^m, v^m, \varepsilon^m)$ in Ω^m, and on Γ

$$\left. \begin{array}{l} \sum_m \varrho^m (v^m - v_\Gamma) \bullet \nu_{\Omega^m} = 0 \\[1em] \sum_m (\varrho^m (v^m - v_\Gamma) \bullet \nu_{\Omega^m} v^m + p^m \nu_{\Omega^m}) = 0 \\[1em] \sum_m (e^m (v^m - v_\Gamma) \bullet \nu_{\Omega^m} + p^m v^m \bullet \nu_{\Omega^m}) = 0 \end{array} \right\} \left\{ \begin{array}{l} \mathbf{M} \text{ is defined} \\ \mathbf{M} \cdot v_{tan}^1 = \mathbf{M} \cdot v_{tan}^2 \\ p^1 + \mathbf{M} \cdot \lambda^1 = p^2 + \mathbf{M} \cdot \lambda^2 \\ \mathbf{M} \cdot \big(\varepsilon_\mathsf{s}^1 + p_\mathsf{s}^1 + \frac{|\lambda^1|^2}{2} \big) \\ \qquad = \mathbf{M} \cdot \big(\varepsilon_\mathsf{s}^2 + p_\mathsf{s}^2 + \frac{|\lambda^2|^2}{2} \big) \end{array} \right.$$

Definition: This is called a "shock", if in the mass conservation

$$\mathbf{M} := \varrho^1 \lambda^1 = \varrho^2 \lambda^2 \neq 0, \qquad \lambda^m := (v^m - v_\Gamma) \bullet \nu_{\Omega^1}$$

For shocks, that is $M \neq 0$, the momentum and energy balance on Γ say:

$$v_{tan}^1 = v_{tan}^2$$

$$p^1 + \varrho^1 |\lambda^1|^2 = p^2 + \varrho^2 |\lambda^2|^2$$

$$\varepsilon_s^1 + p_s^1 + \frac{|\lambda^1|^2}{2}$$

$$= \varepsilon_s^2 + p_s^2 + \frac{|\lambda^2|^2}{2}$$

Here $\lambda^m := (v^m - v_\Gamma) \bullet \nu_{\Omega^1}$

Im zweiten Falle ist der Massenstrom und damit auch v_{1x} und v_{2x} von Null verschieden. Dann erhalten wir aus (81,1) und (81,4)

$$[v_y] = 0 , \qquad [v_z] = 0 , \tag{81,6}$$

d. h., die tangentiale Geschwindigkeit ist auf der Unstetigkeitsfläche stetig. Die Dichte, der Druck (und daher auch die anderen thermodynamischen Größen) sowie die Normalkomponente der Geschwindigkeit erleiden einen Sprung. Die Sprünge dieser Größen werden durch die Beziehungen (81,1)—(81,3) miteinander verknüpft. In der Bedingung (81,2) können wir auf Grund von (81,1) ϱv_x kürzen, und statt v^2 kann man v_x^2 schreiben wegen der Stetigkeit von v_y und v_z. Auf der Unstetigkeitsfläche müssen also im betrachteten Falle die Bedingungen

$$\begin{aligned} [\varrho v_x] &= 0 , \\ \left[\frac{v_x^2}{2} + w\right] &= 0 , \\ [p + \varrho v_x^2] &= 0 \end{aligned} \right\} \tag{81,7}$$

erfüllt sein. Unstetigkeiten dieses Typs nennt man *Stoßwellen*.

§ 82. Die Stoßadiabate

Wir kommen jetzt zur ausführlichen Untersuchung von Stoßwellen. Wie wir gesehen haben, ist bei diesen Unstetigkeiten die Tangentialkomponente der Strömungsgeschwindigkeit stetig. Man kann daher ein Koordinatensystem wählen, in dem ein betrachtetes Element der Unstetigkeitsfläche ruht und die Tangentialkomponente der Strömungsgeschwindigkeit auf beiden Seiten der Fläche gleich Null ist.[1]) Dann kann man statt der Normalkomponente v_x einfach v schreiben, und die Bedingungen (81,7) lauten

$$\varrho_1 v_1 = \varrho_2 v_2 \equiv j , \tag{82,1}$$

$$p_1 + \varrho_1 v_1^2 = p_2 + \varrho_2 v_2^2 , \tag{82,2}$$

$$w_1 + \frac{v_1^2}{2} = w_2 + \frac{v_2^2}{2} . \tag{82,3}$$

[L.D. Landau, E.M. Lifschitz. *Lehrbuch der Theoretischen Physik VI. Hydrodynamik* 3. Auflage Akademie-Verlag 1974]

The entropy principle is

$$\partial_t H + \mathrm{div}\, \Psi \geq 0 \,, \quad H = \sum_m \eta^m \boldsymbol{\mu}_{\Omega^m} \,, \quad \Psi = \sum_m \eta^m v^m \boldsymbol{\mu}_{\Omega^m} \,, \quad \eta^m = \widehat{\eta}(\varrho^m, \varepsilon^m)$$

That is, the entropy inequality is satisfied in distributional sense.
It is equivalent to

$$\partial_t \eta^m + \mathrm{div}(\eta^m v^m) = 0 \text{ in } \Omega^m \quad (\text{since } \eta^m = \widehat{\eta}(\varrho^m, \varepsilon^m))$$

$$\sum_m \eta^m (v^m - v_\Gamma) \bullet \nu_{\Omega^m} \geq 0 \text{ on } \Gamma$$

and this is (in the shock case) equivalent to $\qquad\qquad\qquad \left(\eta_{\mathsf{s}}^m = \frac{\eta^m}{\varrho^m} \right)$

$$\mathbf{M} \cdot (\eta_{\mathsf{s}}^1 - \eta_{\mathsf{s}}^2) \geq 0 \quad \text{or} \quad \begin{cases} \eta_{\mathsf{s}}^1 \geq \eta_{\mathsf{s}}^2 \text{ if } \mathbf{M} > 0 \\ \eta_{\mathsf{s}}^1 \leq \eta_{\mathsf{s}}^2 \text{ if } \mathbf{M} < 0 \end{cases}$$

Neben anderen thermodynamischen Größen erfährt auch die Entropie in der Stoßwelle einen Sprung. Auf Grund des Gesetzes vom Anwachsen der Entropie muß die Entropie des Gases bei dessen Bewegung zunehmen. Daher muß die Entropie s_2 des Gases nach dem Durchgang der Stoßwelle größer sein als der Anfangswert s_1 der Entropie:

$$s_2 > s_1 \,. \tag{82,11}$$

Wie wir später sehen werden, schränkt diese Bedingung die Art der Änderung aller Größen in einer Stoßwelle wesentlich ein.

[L.D. Landau, E.M. Lifschitz. *Lehrbuch der Theoretischen Physik VI. Hydrodynamik* 3. Auflage Akademie-Verlag 1974]

A single balance law is an equality (resp. inequality) of the form

$$\partial_t E + \mathrm{div} Q = \ (\text{resp. } \leq) \ F \quad \text{in } \mathcal{D}'(\Omega)$$

Theorem It is equivalent

$$\partial_t \Big(\underbrace{\sum_{m=1}^{2} e^m \boldsymbol{\mu}_{\Omega^m} + e^s \boldsymbol{\mu}_\Gamma}_{= E} \Big) + \mathrm{div} \Big(\underbrace{\sum_{m=1}^{2} q^m \boldsymbol{\mu}_{\Omega^m} + q^s \boldsymbol{\mu}_\Gamma}_{= Q} \Big) = (\text{resp. } \leq) \underbrace{\sum_{m=1}^{2} f^m \boldsymbol{\mu}_{\Omega^m} + f^s \boldsymbol{\mu}_\Gamma}_{= F}$$

and

1. $\partial_t e^m + \mathrm{div} q^m = \ (\text{resp. } \leq) \ f^m$ for $m = 1, 2$ in Ω^m

2. $(q^s - e^s v_\Gamma)(t, x) \in T_x(\Gamma_t)$ for all $(t, x) \in \Gamma$

3. $\partial_t^\Gamma e^s + \mathrm{div}^\Gamma q^s = \ (\text{resp. } \leq) \ f^s + \sum_{m=1}^{2} (q^m - e^m v_\Gamma) \bullet \nu_{\Omega^m}$ on Γ

This includes "Rankine-Hugoniot" conditions and "Kotchine" conditions
We have that $\partial_t^\Gamma e^s + \mathrm{div}^\Gamma q^s = \partial_t^\Gamma e^s - e^s \kappa \bullet v_\Gamma + \mathrm{div}^\Gamma (q^s - e^s v_\Gamma)$

[H.W. Alt. *The Entropy Principle for Interfaces. Fluids and Solids.* AMSA 19, pp. 585-663, 2009]

3. Balance laws on phase boundaries

The phase boundary between ice and water is represented by a moving non-material singular orientable surface. This is essentially Gibbs's [25] idea. The general form of a balance law on such a surface is (Fig. 2)

$$\frac{d}{dt} \int_{\sigma(t)} \psi_\sigma(\xi^\alpha, t)\, da = - \oint_{\mathscr{C}(s)} \phi^\alpha_\sigma h_\alpha\, ds$$

$$- \int_{\sigma(t)} [\![\phi^k + \psi_v(v^k - w^k)]\!] e_k\, da \qquad (3.1)$$

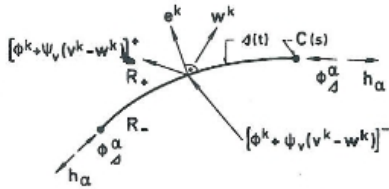$$+ \int_{\sigma(t)} (\pi_\sigma + \sigma_\sigma)\, da .$$

Fig. 2: Flux contributions at a non-material singular surface.

Here s denotes the arc length along $\mathscr{C}(s)$; its orientation is counterclockwise around the surface normal e_k. This curve is chosen to be material in the sense that it possesses the same tangential velocity w^α as do material particles sitting instantaneously on the surface. The singular surface is a whole, however, is non-material; because matter may cross it when it represents a phase boundary. Moreover, da is the area element on $\sigma(t)$, and d/dt denotes total time derivative following the advective velocity w^k. The field quantities have the meaning:

$\psi_\sigma(\xi^\beta, t)$ = surface density of an additive quantity Ψ per unit area on $\sigma(t)$.

$\phi^\alpha_\sigma(\xi^\beta, t)$ = influx of Ψ along the tangent planes of $\sigma(t)$ per unit time and unit length through the bounding curve $\mathscr{C}(s)$ moving with velocity w^α.

$\pi_\sigma, \sigma_\sigma$ = surface production and supply densities of Ψ per unit time and unit area of $\sigma(t)$, respectively.

$\phi^k(x, t)$ = bulk influx of Ψ per unit time and unit area through a material surface in the bulk moving with material velocity v^k.

$\psi_v(x, t)$ = bulk density of Ψ per unit volume of the bulk material.

$[\![\phi^k + \psi_v(v^k - w^k)]\!] e_k := [\phi^k_+ + \psi_v^+ (v^k_+ - w^k)] e_k - [\phi^k_- + \psi_v^- (v^k_- - w^k)] e_k =$
= normal jump contribution of the bulk flux of Ψ per unit time and unit area through $\sigma(t)$. It represents the influx to $\sigma(t)$ from the adjacent bulk materials. $\phi^k_\pm, \psi_v^\pm, v^k_\pm$ are the limiting values of the bulk fields as the singular surface $\sigma(t)$ is approached from R_+ and R_-, respectively.

The jump contribution in (3.1) is derivable from the general balance equation for the bulk material. Our aim is the deduction of a local version of (3.1) when sufficient differentiability assumptions are satisfied. To this end, we first interchange in (3.1) the time derivative and the integration. This is done with the aid of the transport theorem (2.19). Second the divergence theorem is invoked on the surface integral term. This process yields

$$\int_{\sigma(t)} \left[\frac{\partial \psi_\sigma}{\partial t} - 2\psi_\sigma K_M w_n + (\phi^\alpha_\sigma + \psi_\sigma w^\alpha)_{;\alpha} + \right.$$

$$\left. + [\![\phi^k + \psi_v(v^k - w^k)]\!] e_k - (\pi_\sigma + \sigma_\sigma) \right] da = 0 , \qquad (3.2)$$

a relation that must hold for every non-material singular surface. Consequently,

$$\frac{\partial \psi_\sigma}{\partial t} - 2\psi_\sigma K_M w_n + (\phi^\alpha_\sigma + \psi_\sigma w^\alpha)_{;\alpha} = - [\![\phi^m + \psi_v(v^m - w^m)]\!] e_m + \pi_\sigma + \sigma_\sigma . \quad (3.3)$$

This is the local form of a balance equation for any additive quantity ψ defined on a moving non-material singular surface.

wave theory," contributions due to for example, interfacial temperature and velocity fluctuations. These expressions are given in the general case of a nonplanar equilibrium shape of the interface. Some recent work by Bedeaux and Weeks[13] on the behavior of the density–density correlation function and the direct correlation function in the neighborhood of the interface is discussed. For the density–density correlation function, their expressions are generalized to the case of finite bulk compressibilities.

In Section VI the description is extended by the inclusion of random fluxes. Fluctuation–dissipation theorems for these random fluxes are given.[11]

The general method of nonequilibrium thermodynamics is, as we shall discuss in more detail, inherently limited to the description of time-dependent phenomena over distances large compared with the bulk correlation length. We shall therefore not discuss the behavior near and in the surface of discontinuity on a molecular level. The reader is instead referred to the extensive literature on this subject.[14]

B. On the Mathematical Description of Interfaces

We consider here dynamical processes of a system in which two phases coexist. The phases are separated by a moving surface of discontinuity, or interface as we shall often call it, with a time-dependent curvature. The term "surface of discontinuity" does not imply that the discontinuity is sharp, nor that it distinguishes any surface with mathematical precision.[5] It is taken to denote the nonhomogeneous film that separates the two bulk phases. The width of this film is on the order of the bulk correlation length.

In the mathematical description of the dynamical properties of the system, we want to choose a method such that details of the description on length scales smaller than the bulk correlation length do not play a role. In the bulk phases, this implies that one replaces, for example, the molecular density by a continuous field that is obtained after averaging over cells with a diameter of the order of the bulk correlation length. Such a procedure gives an adequate description of the behavior of a bulk phase on a distance scale large compared with the bulk correlation length if the variation of the fields over a bulk correlation length is small. The surface of discontinuity is, in this context, a two-dimensional layer of cells in which the variables change rapidly in one direction over a distance of the order of a bulk correlation length from the value in one phase to the value in the other phase, but change slowly in the other two directions. One now chooses a time-dependent dividing surface in this two-dimensional layer of cells such that the radii of curvature are large compared with the bulk correlation length. Surfaces of discontinuity for

we shall return to it below.

To describe the time-dependent location of the dividing surface, it is convenient to use a set of time-dependent orthogonal curvilinear coordinates:[15] $\xi_i(\mathbf{r}, t)$, $i = 1, 2, 3$, where $\mathbf{r} = (x, y, z)$ are the Cartesian coordinates and t the time. These curvilinear coordinates are choosen in such a way that the location of the dividing surface at time t is given by

$$\xi_1(\mathbf{r}, t) = 0 \qquad (1.2.1)$$

The dynamical properties of the system are described using balance equations. Consider as an example the balance equation for a variable $d(\mathbf{r}, t)$:

$$\frac{\partial}{\partial t} d(\mathbf{r}, t) + \operatorname{div} \mathbf{J}_d(\mathbf{r}, t) = \sigma_d(\mathbf{r}, t) \qquad (1.2.2)$$

where $\mathbf{J}_d$ is the current of d and σ_d the production of d in the system. In our description d, $\mathbf{J}_d$ and σ_d vary continuously in the bulk regions while the total excess (to be defined precisely below) of d, $\mathbf{J}_d$, and σ_d near the surface of discontinuity is located as a singularity at the dividing surface. We thus write d, $\mathbf{J}_d$, and σ_d in the following form:

$$d(\mathbf{r}, t) = d^-(\mathbf{r}, t)\Theta^-(\mathbf{r}, t) + d^s(\mathbf{r}, t)\delta^s(\mathbf{r}, t) + d^+(\mathbf{r}, t)\Theta^+(\mathbf{r}, t) \qquad (1.2.3)$$

$$\begin{aligned} \mathbf{J}_d(\mathbf{r}, t) = \mathbf{J}_d^-(\mathbf{r}, t)\Theta^-(\mathbf{r}, t) + \mathbf{J}_d^s(\mathbf{r}, t)\delta^s(\mathbf{r}, t) \\ + \mathbf{J}_d^-(\mathbf{r}, t)\Theta^+(\mathbf{r}, t) \end{aligned} \qquad (1.2.4)$$

$$\begin{aligned} \sigma_d(\mathbf{r}, t) = \sigma_d^-(\mathbf{r}, t)\Theta^-(\mathbf{r}, t) + \sigma_d^s(\mathbf{r}, t)\delta^s(\mathbf{r}, t) \\ + \sigma_d^+(\mathbf{r}, t)\Theta^+(\mathbf{r}, t) \end{aligned} \qquad (1.2.5)$$

Here Θ^- and Θ^+ are the time-dependent characteristic functions of the two bulk phases, which are 1 in one phase and zero in the other. Using the time-dependent curvilinear coordinates, one may write these characteristic functions as

$$\Theta^\pm(\mathbf{r}, t) \equiv \Theta(\pm\xi_1(\mathbf{r}, t)) \qquad (1.2.6)$$

[D. Bedeaux. *Nonequilibrium Thermodynamics and Statistical Physics of Surfaces.* Advance in Chemical Physics Vol. LXIV, Wiley 1986]

Using this velocity field, one may show[6] that the time derivative of the characteristic functions for the bulk phases is given by

$$\frac{\partial}{\partial t} \Theta^{\pm}(\mathbf{r}, t) = \mp w_n^s \delta^s(\mathbf{r}, t) \qquad (1.2.15)$$

where the subscript n indicates the normal component. Similarly, one may show[6] that the time derivative of the characteristic function for the surface of discontinuity is given by

$$\frac{\partial}{\partial t} \delta^s(\mathbf{r}, t) = -w_n^s \mathbf{n} \cdot \nabla \delta^s(\mathbf{r}, t) \qquad (1.2.16)$$

where $\nabla \equiv (\partial/\partial x, \partial/\partial y, \partial/\partial z)$ is the Cartesian gradient. One may also show that the gradient of δ^s is normal to the dividing surface:[6]

$$\nabla \delta^s(\mathbf{r}, t) = \mathbf{nn} \cdot \nabla \delta^s(\mathbf{r}, t) \qquad (1.2.17)$$

These formulas make it possible to analyze the balance equation for d in more detail. In particular, we are interested in the precise form of the balance equation for the excess density d^s. Substitution of the expressions (1.2.3)–(1.2.5) for d, $\mathbf{J}_d$, and σ_d into the general balance equation (1.2.2) and use of the definitions and identities (1.2.6)–(1.2.17) leads to the following more detailed formula for the balance of d:

$$\left[\frac{\partial}{\partial t} d^-(\mathbf{r}, t) + \operatorname{div} \mathbf{J}_d^-(\mathbf{r}, t) - \sigma_d^-(\mathbf{r}, t)\right]\Theta^-(\mathbf{r}, t)$$
$$+ \left[\frac{\partial}{\partial t} d^+(\mathbf{r}, t) + \operatorname{div} \mathbf{J}_d^+(\mathbf{r}, t) - \sigma_d^+(\mathbf{r}, t)\right]\Theta^+(\mathbf{r}, t)$$
$$+ \left[\frac{\partial}{\partial t} d^s(\mathbf{r}, t) + \operatorname{div} \mathbf{J}_d^s(\mathbf{r}, t) - \sigma_d^s(\mathbf{r}, t)\right.$$
$$+ J_{d,n}^+(\mathbf{r}, t) - J_{d,n}^-(\mathbf{r}, t) - w_n^s(\mathbf{r}, t)(d^+(\mathbf{r}, t) - d^-(\mathbf{r}, t))\right]\delta^s(\mathbf{r}, t)$$
$$+ [J_{d,n}^s(\mathbf{r}, t) - w_n^s(\mathbf{r}, t)d^s(\mathbf{r}, t)]\mathbf{n}(\mathbf{r}, t) \cdot \nabla \delta^s(\mathbf{r}, t) = 0 \qquad (1.2.18)$$

The first two terms in this formula describe the balance in the bulk

phases:

$$\frac{\partial}{\partial t} d^{\pm} + \operatorname{div} \mathbf{J}_d^{\pm} = \sigma_d^{\pm} \qquad \text{for} \quad \pm \xi_1(\mathbf{r}, t) > 0 \qquad (1.2.19)$$

The third term in formula (1.2.18) describes the balance of the excess density:

$$\frac{\partial}{\partial t} d^s + \operatorname{div} \mathbf{J}_d^s + J_{d,n,-} - w_n^s d_- = \sigma_d^s \qquad \text{for} \quad \xi_1(\mathbf{r}, t) = 0 \qquad (1.2.20)$$

where the subscript $-$ indicates the difference of the corresponding quantity in the bulk phases from one side of the surface of discontinuity to the other; thus

$$d_-(\mathbf{r}, t) \equiv d^+(\xi_1 = 0, \xi_2(\mathbf{r}, t), \xi_3(\mathbf{r}, t), t) - d^-(\xi_1 = 0, \xi_2(\mathbf{r}, t), \xi_3(\mathbf{r}, t), t) \qquad (1.2.21)$$

and similarly for $J_{d,n,-}$. We do not follow the more conventional notation, which uses square brackets to indicate this difference.[16,17] The balance equation (1.2.20) for the excess density shows that in addition to the usual contribution occurring also in the balance equation (1.2.19) for the bulk phases, one has a contribution $J_{d,n,-}$, due to flow from the bulk regions into or away from the surface of discontinuity and a contribution $-w_n^s d_-$ due to the fact that the moving surface of discontinuity "scoops up" material on one side and leaves material behind on the other side. The last term in formula (1.2.18) gives

$$J_{d,n}^s - w_n^s d^s = 0 \qquad (1.2.22)$$

This condition expresses the fact that the excess current in a reference frame moving with the surface of discontinuity flows along the dividing surface. Although the validity of this condition is intuitively clear, the above derivation shows that it is also a necessary condition in the context of the above description.

We will now briefly discuss how one may obtain the excess densities and currents from a more detailed description. Crucial to this procedure is the fact that, as we have already elaborated, we are interested only in the temporal behavior of spatial variations over distances long compared with the bulk correlation length. Spatial variations over distances smaller than or comparable to the bulk correlation length are assumed to be in local equilibrium. The description given in the context of non-equilibrium

[D. Bedeaux. *Nonequilibrium Thermodynamics and Statistical Physics of Surfaces.* Advance in Chemical Physics Vol. LXIV, Wiley 1986]

Example 5 : **Surface tension**

We consider two fluids (e.g. water and oil) with surface tension

$$\partial_t\big(\varrho^m\boldsymbol{\mu}_{\Omega^m}\big) + \mathsf{div}\big(\varrho^m v\boldsymbol{\mu}_{\Omega^m}\big) = 0 \text{ for } m = 1,2$$

$$v \text{ continuous at } \Gamma$$

$$\partial_t\big(\sum_m \varrho^m v\boldsymbol{\mu}_{\Omega^m}\big) + \mathsf{div}\big(\sum_m(\varrho^m v\otimes v + \Pi^m)\boldsymbol{\mu}_{\Omega^m} + \Pi^s\boldsymbol{\mu}_\Gamma\big) = \sum_m \mathbf{f}^m\boldsymbol{\mu}_{\Omega^m}$$

$$\partial_t\big(\sum_m e^m\boldsymbol{\mu}_{\Omega^m} + \varepsilon^s\boldsymbol{\mu}_\Gamma\big) + \mathsf{div}\big(\sum_m(e^m v + (\Pi^m)^\mathsf{T} v + q^m)\boldsymbol{\mu}_{\Omega^m} + (\Pi^s)^\mathsf{T} v\boldsymbol{\mu}_\Gamma\big) = \sum_m v\bullet\mathbf{f}^m\boldsymbol{\mu}_{\Omega^m}$$

$$\theta \text{ continuous at } \Gamma, \text{ i.e. } \eta^1_{,\varepsilon}(\varrho^1,\varepsilon^1) = \eta^2_{,\varepsilon}(\varrho^2,\varepsilon^2)$$

It is the purpose to determine ε^s and Π^s. Here we assume for the two fluids that the standard entropy principle holds for $m = 1,2$

$$\sigma^m := \partial_t\eta^m + \mathsf{div}\big(\eta^m v + \frac{1}{\theta}q^m\big) = \frac{1}{\theta}\mathsf{D}v\bullet S^m + \nabla\big(\frac{1}{\theta}\big)\bullet q^m \geq 0 \text{ in } \Omega^m$$

and quantities for the two fluids are given as above.

The more general entropy principle for the system is

$$\Sigma := \partial_t\big(\sum_m \eta^m\boldsymbol{\mu}_{\Omega^m} + \eta^s\boldsymbol{\mu}_\Gamma\big) + \mathsf{div}\big(\sum_m\big(\eta^m v + \frac{1}{\theta}q^m\big)\boldsymbol{\mu}_{\Omega^m} + (\eta^s v + q^s)\boldsymbol{\mu}_\Gamma\big) \geq 0$$

Exploitation of the entropy principle:

For the distributional entropy principle

$$\Sigma := \partial_t\Big(\sum_m \eta^m\boldsymbol{\mu}_{\Omega^m} + \eta^s\boldsymbol{\mu}_\Gamma\Big) + \mathrm{div}\Big(\sum_m \big(\eta^m v + \frac{1}{\theta}q^m\big)\boldsymbol{\mu}_{\Omega^m} + (\eta^s v + q^s)\boldsymbol{\mu}_\Gamma\Big) \geq 0$$

we compute

$$\Sigma = \sum_m \sigma^m\boldsymbol{\mu}_{\Omega^m} + \sigma^s\boldsymbol{\mu}_\Gamma \geq 0 \qquad\qquad (\sigma^m \text{ as above})$$

which is equivalent to $\sigma^m \geq 0$ in Ω^m and $\sigma^s \geq 0$ in Γ. It is (since $(v - v_\Gamma)\bullet\nu = 0$)

$$\sigma^s = \partial_t^\Gamma \eta^s + \mathrm{div}^\Gamma(\eta^s v + q^s) - \sum_m \frac{1}{\theta}q^m\bullet\nu_{\Omega^m}, \qquad \sum_m \frac{1}{\theta}q^m\bullet\nu_{\Omega^m} = \frac{1}{\theta}\sum_m q^m\bullet\nu_{\Omega^m}$$

$$\sum_m q^m\bullet\nu_{\Omega^m} = \partial_t^\Gamma \varepsilon^s + \mathrm{div}^\Gamma(\varepsilon^s v + \Pi^s v) - v\bullet\sum_m \Pi^m\nu_{\Omega^m} \text{ (energy)}$$

$$\sum_m \Pi^m\nu_{\Omega^m} = \mathrm{div}^\Gamma\Pi^s \text{ (momentum)}$$

$$\sum_m q^m\bullet\nu_{\Omega^m} = \partial_t^\Gamma \varepsilon^s + \mathrm{div}^\Gamma(\varepsilon^s v) + \mathrm{D}^\Gamma v\bullet\Pi^s$$

and therefore

$$\sigma^s = \partial_t^\Gamma \eta^s + \mathrm{div}^\Gamma(\eta^s v + q^s) - \frac{1}{\theta}\big(\partial_t^\Gamma \varepsilon^s + \mathrm{div}^\Gamma(\varepsilon^s v)\big) - \frac{1}{\theta}\mathrm{D}^\Gamma v\bullet\Pi^s \quad \big(v = v_\Gamma + v_{tan}\big)$$

$$= \dot\eta^s - \frac{1}{\theta}\dot\varepsilon^s + \mathrm{div}^\Gamma q^s \quad \big(\dot{} = \partial_t^\Gamma + v\bullet\nabla^\Gamma = \partial_t + v_\Gamma\bullet\nabla + v\bullet\nabla^\Gamma = \partial_t + v\bullet\nabla\big)$$

$$+\mathrm{D}^\Gamma v\bullet\big((\eta^s - \frac{1}{\theta}\varepsilon^s)(\mathrm{Id} - \nu\otimes\nu) - \frac{1}{\theta}\Pi^s\big)$$

For the entropy principle $\Sigma \geq 0$ it remains $\sigma^s \geq 0$ with

$$\sigma^s = \dot{\eta}^s - \frac{1}{\theta}\dot{\varepsilon}^s + \mathsf{div}^{\ulcorner} q^s + \mathsf{D}^{\ulcorner} v \bullet \left((\eta^s - \frac{1}{\theta}\varepsilon^s)(\mathsf{Id} - \nu \otimes \nu) - \frac{1}{\theta}\Pi^s \right)$$

Result : The entropy principle is satisfied, if $q^s = 0$ and

$$\Pi^s = -\gamma(\mathsf{Id} - \nu \otimes \nu) - S^s \,, \quad \gamma = \varepsilon^s - \theta\eta^s$$

$$\eta^s = \hat{\eta}^s(\varepsilon^s) \,, \quad \eta^s_{,\varepsilon^s} = \frac{1}{\theta} \,, \quad \varepsilon^s = \hat{\varepsilon}^s(\theta)$$

and if the above properties for the fluids are satisfied.

The remaining inequality on the surface is

$$\sigma^s = \frac{1}{\theta}\mathsf{D}^{\ulcorner} v \bullet S^s \geq 0 \qquad \text{(for example, if } S^s = 0)$$

Mathematical literature for the isothermal case:

[I.V. Denisova. *Solvability in weighted Hölder spaces for a problem governing the evolution of two compressible fluids.* Zap. Nauchn. Sem. 295, pp. 57-89 (2003)]