Non-Equilibrium Thermodynamics of Phase-Transitions

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The entropy production — (3.8.) — in the boundary between two phases of a one-component system contains two scalar force-flux pairs. The "forces" are the jumps of the temperature and of (essentially) the chemical potential at the interface; the "fluxes" are the heat and mass fluxes normal to the interface. So, four phenomenological coefficients appear in the pertaining local linear constitutive laws — (4.14 and 15) — for the boundary conditions. They can in principle be determined by a stationary heat conduction and phase transition experiment. Only measurements of temperature jumps — (5.14 and 15) — are involved. These jumps vanish if the four coefficients vanish.

The method previously used for the thermodynamical treatment of boundary conditions [1] can readily be applied to phase transitions. The only difference with the previous case of two immiscible fluids is that now also mass transfer between the two phases has to be considered. But in so far as no flows along the interface have to be dealt with, the present case is even simpler than the previous one. What is made, is merely a translation of the DE GROOT-MAZUR [2] treatment of discontinuous systems into the language of local boundary (interfacial) conditions. These contain a 2×2 matrix of interfacial transport coefficients. The merit of the whole procedure may be to reopen the question how these coefficients can be measured (§ 5).

§ 1. Preliminaries

Let us distinguish the phases by subscripts I, II. Their mass densities and velocities are denoted by $\varrho_{\mathrm{I(II)}}$ and $\boldsymbol{v}_{\mathrm{I(II)}}$. The phases, contained in volumes $\tau_{\mathrm{I(II)}}$, contact each other along the interface σ (marked by a jump of density) with velocity $\boldsymbol{v}^{(\sigma)}$. The normal in any point of σ, outward with respect to τ_{I} (τ_{II}), be $\boldsymbol{n}_{\mathrm{I}}$ ($\boldsymbol{n}_{\mathrm{II}}$). Obviously one has

$$\boldsymbol{n}_{\mathrm{I}}+\boldsymbol{n}_{\mathrm{II}}=0\,. \tag{1.1}$$

The mass fluxes (mass per unit area and time) leaving I and II respectively are

$$j_{\mathrm{I}}=\varrho_{\mathrm{I}}(\boldsymbol{v}_{\mathrm{I}}-\boldsymbol{v}^{(\sigma)})\cdot\boldsymbol{n}_{\mathrm{I}}\,,\quad j_{\mathrm{II}}=\ldots\,. \tag{1.2}$$

According to mass conservation one has per definition

$$j_{\mathrm{I}}+j_{\mathrm{II}}=0\,. \tag{1.3}$$

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Therefore it is appropriate to write

$$j_{\mathrm{I}}\equiv j_{\mathrm{I\,II}}=-j_{\mathrm{II\,I}}\equiv -j_{\mathrm{II}}\,, \tag{1.4}$$

where $j_{\mathrm{I\,II}}$ means the mass flux leaving I and entering II.

Now let us define a quantity a per unit mass in both phases. The total amount then is

$$A=\Big(\int_{\tau} a\,\varrho\,\mathrm{d}\tau\Big)_{\mathrm{I}}+(\ldots)_{\mathrm{II}}\,. \tag{1.5}$$

Here, the assumption is made that no surface density of A (amount per unit area) exists. The change with time is

$$\frac{\mathrm{d}A}{\mathrm{d}t}=\left(\int_{\tau}\frac{\mathrm{d}a}{\mathrm{d}t}\,\varrho\,\mathrm{d}\tau\right)_{\mathrm{I}}+\Big(\cdots\Big)_{\mathrm{II}}-\int_{\sigma}(a_{\mathrm{I}}\,j_{\mathrm{I}}+a_{\mathrm{II}}\,j_{\mathrm{II}})\,\mathrm{d}\sigma\,.$$

With the abbreviation

$$a_{\mathrm{I\,II}}=a_{\mathrm{I}}-a_{\mathrm{II}} \tag{1.6}$$

one also has according to (1.4)

$$\frac{\mathrm{d}A}{\mathrm{d}t}=\left(\int_{\tau}\frac{\mathrm{d}a}{\mathrm{d}t}\,\varrho\,\mathrm{d}\tau\right)_{\mathrm{I}}+\Big(\ldots\Big)_{\mathrm{II}}-\int_{\sigma}a_{\mathrm{I\,II}}\,j_{\mathrm{I\,II}}\,\mathrm{d}\sigma\,. \tag{1.7}$$

It should be noted that $(\mathrm{d}a/\mathrm{d}t)_{\mathrm{I}}$ means the substantial time derivative of quantity a in phase I.

§ 2. Conservation Laws

The total momentum is

$$\boldsymbol{P}=(\int_{\tau}\boldsymbol{v}\,\varrho\,\mathrm{d}\tau)_{\mathrm{I}}+(\ldots)_{\mathrm{II}}\,.$$

Its rate of change, given by (1.7) with $a=\boldsymbol{v}$, is rewritten by use of the equation of motion (for I and II)

$$\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t}\,\varrho=-\nabla\cdot\mathbf{p}\,,$$

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($\mathbf{p}$ the pressure tensor) and of Gauß' theorem. *Conservation of total momentum* is thus expressed by

$$\mathrm{d}\boldsymbol{P}/\mathrm{d}t = -\int_\sigma [\boldsymbol{k} + \boldsymbol{v}_{\mathrm{I\,II}}\, j_{\mathrm{I\,II}}]\, \mathrm{d}\sigma = 0\,, \qquad (2.1)$$

where

$$\boldsymbol{k} = \boldsymbol{k}_{\mathrm{I}} + \boldsymbol{k}_{\mathrm{II}} \quad \text{with} \quad \boldsymbol{k}_{\mathrm{I}} = (\boldsymbol{n}\cdot\mathbf{p})_{\mathrm{I}}\,, \boldsymbol{k}_{\mathrm{II}} = (\ldots)_{\mathrm{II}} \qquad (2.2)$$

is the force exerted by the pressure tensors in I, II on the unit area of the interface. Again, the abbreviation

$$\boldsymbol{v}_{\mathrm{I\,II}} = \boldsymbol{v}_{\mathrm{I}} - \boldsymbol{v}_{\mathrm{II}} \qquad (2.3)$$

has been introduced.

The total energy E is obtained by putting in (1.5)

$$a = e = \tfrac{1}{2}\,\boldsymbol{v}\cdot\boldsymbol{v} + u$$

where u is the internal energy per unit mass. The rate of change is rewritten by use of the energy equation (for I and II)

$$\frac{\mathrm{d}e}{\mathrm{d}t}\,\varrho = -\nabla\cdot\boldsymbol{e}\,,$$

where

$$\boldsymbol{e} = \mathbf{p}\cdot\boldsymbol{v} + \boldsymbol{q} \qquad (2.4)$$

and $\boldsymbol{q}$ are the energy and the heat fluxes respectively, and by use of Gauß' theorem. *Conservation of total energy* is thus expressed, after (1.6 and 7), by

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\int_\sigma [(\boldsymbol{n}\cdot\boldsymbol{e})_{\mathrm{I}} + (\boldsymbol{n}\cdot\boldsymbol{e})_{\mathrm{II}} + e_{\mathrm{I\,II}}\, j_{\mathrm{I\,II}}]\, \mathrm{d}\sigma = 0\,. \qquad (2.5)$$

Again, the difference $e_{\mathrm{I\,II}} = e_{\mathrm{I}} - e_{\mathrm{II}}$ enters.

If the interface itself does not carry flows of momentum and energy, which will be assumed from now on, the global conservation laws (2.1) and (2.5) have to be fulfilled by requiring that even the integrands vanish: *local conservation laws* of the interface.

With *momentum*, this means

$$\boldsymbol{k} + \boldsymbol{v}_{\mathrm{I\,II}}\, j_{\mathrm{I\,II}} = 0\,. \qquad (2.6)$$

The second term is the force exerted on the interface by mass transfer ("recoil" term); it is quadratic in the relative velocities and therefore negligible in slow phase transitions.

With *energy*, local conservation means according to (2.2, 4 and 5)

$$(\boldsymbol{k}\cdot\boldsymbol{v})_{\mathrm{I}} + (\boldsymbol{k}\cdot\boldsymbol{v})_{\mathrm{II}} + q + e_{\mathrm{I\,II}}\, j_{\mathrm{I\,II}} = 0$$

where

$$q = (\boldsymbol{n}\cdot\boldsymbol{q})_{\mathrm{I}} + (\boldsymbol{n}\cdot\boldsymbol{q})_{\mathrm{II}} = q_{\mathrm{I}} + q_{\mathrm{II}}\,. \qquad (2.7)$$

By use of

$$\boldsymbol{k}_{\mathrm{I\,II}} = \tfrac{1}{2}(\boldsymbol{k}_{\mathrm{I}} - \boldsymbol{k}_{\mathrm{II}}) \qquad (2.8)$$

and of (2.6) this is rewritten as

$$\boldsymbol{k}_{\mathrm{I\,II}}\cdot\boldsymbol{v}_{\mathrm{I\,II}} + q + u_{\mathrm{I\,II}}\, j_{\mathrm{I\,II}} = 0\,, \qquad (2.9)$$

where

$$u_{\mathrm{I\,II}} = u_{\mathrm{I}} - u_{\mathrm{II}} \qquad (2.10)$$

means the difference of internal energies per unit mass. Kinetic energy has thus been eliminated by aid of the momentum law.

Furthermore, force $\boldsymbol{k}_{\mathrm{I\,II}}$ and velocity $\boldsymbol{v}_{\mathrm{I\,II}}$ are decomposed into their components normal and tangential to the interface:

$$\boldsymbol{k}_{\mathrm{I\,II}}\cdot\boldsymbol{v}_{\mathrm{I\,II}} = k\,v + \boldsymbol{k}_{\mathrm{I\,II}}^{\tan}\cdot\boldsymbol{v}_{\mathrm{I\,II}}^{\tan}$$

with

$$k = \tfrac{1}{2}(\boldsymbol{k}_{\mathrm{I}}\cdot\boldsymbol{n}_{\mathrm{I}} + \boldsymbol{k}_{\mathrm{II}}\cdot\boldsymbol{n}_{\mathrm{II}})\,, v = \boldsymbol{v}_{\mathrm{I}}\cdot\boldsymbol{n}_{\mathrm{I}} + \boldsymbol{v}_{\mathrm{II}}\cdot\boldsymbol{n}_{\mathrm{II}}\,. \qquad (2.11)$$

But due to (1.1 – 4) one has also

$$v = \varrho_{\mathrm{I}}^{-1}\, j_{\mathrm{I}} + \varrho_{\mathrm{II}}^{-1}\, j_{\mathrm{II}} = \varrho_{\mathrm{I\,II}}^{-1}\, j_{\mathrm{I\,II}} \qquad (2.12)$$

with

$$\varrho_{\mathrm{I\,II}}^{-1} = \varrho_{\mathrm{I}}^{-1} - \varrho_{\mathrm{II}}^{-1}\,. \qquad (2.13)$$

So, Eq. (2.9) also is

$$-q = \boldsymbol{v}_{\mathrm{I\,II}}^{\tan}\cdot\boldsymbol{k}_{\mathrm{I\,II}}^{\tan} + (u_{\mathrm{I\,II}} + k\,\varrho_{\mathrm{I\,II}}^{-1})\, j_{\mathrm{I\,II}}\,. \qquad (2.14)$$

Again, this may be rewritten by splitting the pressure tensor in its isotropic static part and the friction tensor $\mathbf{p}'$ (which for a Newtonian fluid is linear in the space derivatives of velocity). This splitting is conveyed to the forces on the interface and gives

$$k = p + k'\,, \qquad (2.15)$$

where

$$p = \tfrac{1}{2}(p_{\mathrm{I}} + p_{\mathrm{II}}) \qquad (2.16)$$

is the mean scalar static pressure at any point of the interface. The tangential force is due only to friction, one has the identity

$$\boldsymbol{k}_{\mathrm{I\,II}}^{\tan} = \boldsymbol{k}_{\mathrm{I\,II}}^{\prime\tan}\,. \qquad (2.17)$$

Now one has exactly

$$u_{\mathrm{I\,II}} + p\,\varrho_{\mathrm{I\,II}}^{-1} = h_{\mathrm{I\,II}} - p_{\mathrm{I\,II}}\,\varrho^{-1}.$$

Here, the abbreviations

$$h_{\mathrm{I\,II}} = h_{\mathrm{I}} - h_{\mathrm{II}}\,, p_{\mathrm{I\,II}} = p_{\mathrm{I}} - p_{\mathrm{II}}\,, \varrho^{-1} = \tfrac{1}{2}(\varrho_{\mathrm{I}}^{-1} + \varrho_{\mathrm{II}}^{-1}) \qquad (2.18)$$

have been introduced and

$$h_{\mathrm{I}} = u_{\mathrm{I}} + p_{\mathrm{I}}\,\varrho_{\mathrm{I}}^{-1}, \qquad h_{\mathrm{II}} = \ldots \qquad (2.19)$$

denote the enthalpies per unit mass. Inserting into (2.14) yields the alternative form of local energy conservation

$$-q = \boldsymbol{v}_{\mathrm{I\,II}}^{\tan}\cdot\boldsymbol{k}_{\mathrm{I\,II}}^{\prime\tan} + (h_{\mathrm{I\,II}} - p_{\mathrm{I\,II}}\,\varrho^{-1} + k'\,\varrho_{\mathrm{I\,II}}^{-1})\, j_{\mathrm{I\,II}}\,. \qquad (2.20)$$

Both forms, (2.14) and (2.20), will be used in the following.

§ 3. Interfacial Entropy Production

Under the assumption – made before with momentum and energy – that the interface does not contain entropy per unit area, the total entropy is

$$S = (\int s\,\varrho\,\mathrm{d}\tau)_{\mathrm{I}} + (\ldots)_{\mathrm{II}}\,.$$

Its rate of change according to (1.7) is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \left(\int_\tau \frac{\mathrm{d}s}{\mathrm{d}t}\,\varrho\,\mathrm{d}\tau\right)_{\mathrm{I}} + \left(\cdots\right)_{\mathrm{II}} - \int_\sigma s_{\mathrm{I\,II}}\,j_{\mathrm{I\,II}}\,\mathrm{d}\sigma\,, \quad (3.1)$$

where

$$s_{\mathrm{I\,II}} = s_{\mathrm{I}} - s_{\mathrm{II}} \quad (3.2)$$

is the difference of entropies per unit mass on both sides at any point of the interface. By aid of the well-known local entropy balance (for I and II)

$$\frac{\mathrm{d}s}{\mathrm{d}t}\,\varrho = -T^{-1}(\nabla \boldsymbol{v}) : \mathbf{p}' + \nabla T^{-1}\cdot \boldsymbol{q} - \nabla\cdot(T^{-1}\boldsymbol{q})$$

and of Gauß' theorem, Eq. (3.1) can be transcribed into

$$\mathrm{d}S/\mathrm{d}t = \vartheta_{\mathrm{I}} + \vartheta_{\mathrm{II}} + \Theta\,.$$

Here $\vartheta_{\mathrm{I,II}}$ are the well-known expressions for the entropy productions within the bulk media I and II, not interesting here, whereas

$$\Theta = -\int_\sigma (T_{\mathrm{I}}^{-1} q_{\mathrm{I}} + T_{\mathrm{II}}^{-1} q_{\mathrm{II}} + s_{\mathrm{I\,II}}\,j_{\mathrm{I\,II}})\,\mathrm{d}\sigma \quad (3.3)$$

denotes the interfacial entropy production which presently is of special concern. It can also be written as

$$\Theta = -\int_\sigma (T^{-1} q + T_{\mathrm{I\,II}}^{-1}\,q_{\mathrm{I\,II}} + s_{\mathrm{I\,II}}\,j_{\mathrm{I\,II}})\,\mathrm{d}\sigma\,. \quad (3.4)$$

The meaning of the symbols is repeated for convenience:

$$T^{-1} = \tfrac{1}{2}(T_{\mathrm{I}}^{-1} + T_{\mathrm{II}}^{-1}), \quad T_{\mathrm{I\,II}}^{-1} = T_{\mathrm{I}}^{-1} - T_{\mathrm{II}}^{-1}, \quad (3.5)$$

$$q = q_{\mathrm{I}} + q_{\mathrm{II}}\,, \qquad q_{\mathrm{I\,II}} = \tfrac{1}{2}(q_{\mathrm{I}} - q_{\mathrm{II}}) \quad (3.6)$$

with

$$q_{\mathrm{I}} = (\boldsymbol{n}\cdot\boldsymbol{q})_{\mathrm{I}}\,, \quad q_{\mathrm{II}} = (\boldsymbol{n}\cdot\boldsymbol{q})_{\mathrm{II}}\,. \quad (3.7)$$

But still Eq. (3.4) has not the form ready for the derivation of linear boundary (interfacial) conditions.

To achieve this form one has to observe that, see (2.14), the heat q, entering the unit area of the interface per unit time, is itself bilinear in differences (I II) as the other parts of the integrand in (3.4) are. Hence, (2.14) must be substituted into (3.4) to give

$$\Theta = \int_\sigma \{T^{-1}\,\boldsymbol{v}_{\mathrm{I\,II}}^{\tan}\cdot \boldsymbol{k}_{\mathrm{I\,II}}^{\prime\tan} - T_{\mathrm{I\,II}}^{-1} q_{\mathrm{I\,II}} + [T^{-1}(u_{\mathrm{I\,II}} + k\,\varrho_{\mathrm{I\,II}}^{-1}) - s_{\mathrm{I\,II}}]\,j_{\mathrm{I\,II}}\}\,\mathrm{d}\sigma\,. \quad (3.8)$$

This expression for the interfacial entropy production is bilinear in the "thermodynamical fluxes" $\boldsymbol{k}_{\mathrm{I\,II}}^{\prime\tan}$, $q_{\mathrm{I\,II}}$, $j_{\mathrm{I\,II}}$ and their conjugate "forces" and is appropriate to formulate the phenomenological laws for the boundary conditions.

§ 4. Phenomenological Laws for the Boundary Conditions

From the entropy production (3.8) one takes the following constitutive laws for the scalar "fluxes" $q_{\mathrm{I\,II}}$, $j_{\mathrm{I\,II}}$ and their "forces":

$$-T_{\mathrm{I\,II}}^{-1} = \alpha\,q_{\mathrm{I\,II}} + \beta\,j_{\mathrm{I\,II}}\,, \quad (4.1)$$

$$(T^{-1})\,(u_{\mathrm{I\,II}} + k\,\varrho_{\mathrm{I\,II}}^{-1}) - s_{\mathrm{I\,II}} = \tilde{\beta}\,q_{\mathrm{I\,II}} + \gamma\,j_{\mathrm{I\,II}}\,. \quad (4.2)$$

The "forces and fluxes" vanish in thermal equilibrium. Indeed, one has in this case $T_{\mathrm{I}} = T_{\mathrm{II}}$, $p_{\mathrm{I}} = p_{\mathrm{II}}$ and, as the condition for phase equilibrium, equality of free enthalpies $g_{\mathrm{I}} = g_{\mathrm{II}}$, which means that the left sides of (4.1 and 2) are zero ($g = u + p\,\varrho^{-1} - T\,s$). And likewise, there are no fluxes of heat $q_{\mathrm{I\,II}}$ and of mass $j_{\mathrm{I\,II}}$ in equilibrium. In a non-equilibrium situation, Eq. (4.1) gives the temperature jump due to heat and mass fluxes across the interface, whereas Eq. (4.2) tells something about the deviations from phase equilibrium connected with the said fluxes. In order to have the entropy production (3.8) positive, one must postulate

$$\alpha > 0\,, \quad \gamma > 0\,, \quad \alpha\gamma - \beta\tilde{\beta} > 0\,. \quad (4.3)$$

The Onsager symmetry is

$$\beta = \tilde{\beta}\,. \quad (4.4)$$

The vector "fluxes and forces" $\boldsymbol{k}_{\mathrm{I\,II}}^{\prime\tan}$, etc. in (3.8) lead to mechanical slip. This presents nothing new in comparison with the previous paper[1] and is skipped. – Together with the interfacial conservation Eqs. (1.3), (2.6 and 14), the interfacial constitutive laws form a complete system of boundary conditions which necessarily and sufficiently connects all of the functions T, p, $\boldsymbol{v}$ and their gradients on both sides I, II with each other.

Hitherto the considerations have been rather exact and general. Now, a particular situation shall be

treated in a somewhat approximate way: *slow phase transitions*. In this case the "recoil" term in the momentum equation (2.6) is negligible:

$$\boldsymbol{k} \approx 0 .$$

Hence one has also

$$\boldsymbol{n}_{\mathrm{I}} \cdot \boldsymbol{k} = k_{\mathrm{I}} - k_{\mathrm{II}} = p_{\mathrm{I\,II}} + k'_{\mathrm{I\,II}} \approx 0 .$$

But in this case the frictional forces $k'_{\mathrm{I\,II}}$ too will play no important role and may be neglected. This leads to

$$p_{\mathrm{I\,II}} \approx 0 \quad \text{or} \quad p_{\mathrm{I}} \approx p_{\mathrm{II}} \approx p \approx k , \tag{4.5}$$

which means uniform pressure throughout the system. In consequence of this, the "force" on the left side of (4.2) can be cast into a new, physically more appealing form.

To this end, let us start from the condition of phase equilibrium at the mean temperature

$$\overline{T} = \tfrac{1}{2}(T_{\mathrm{I}} + T_{\mathrm{II}})$$

in any surface point:

$$g_{\mathrm{I}}(\overline{T}, p_{\mathrm{eq}}(\overline{T})) = g_{\mathrm{II}}(\overline{T}, p_{\mathrm{eq}}(\overline{T})) . \tag{4.6}$$

Here, g denotes the free enthalpy; $p_{\mathrm{eq}}(T)$ is the equilibrium pressure of the two coexisting phases at temperature T (vapour pressure etc.). From the differential

$$\mathrm{d}g = -s\,\mathrm{d}T + \varrho^{-1}\,\mathrm{d}p$$

one takes for small deviations $T_{\mathrm{I\,II}}$, $p - p_{\mathrm{eq}}$

$$\begin{aligned} g_{\mathrm{I}}(T_{\mathrm{I}}, p) &= g_{\mathrm{I}}(\overline{T} + \tfrac{1}{2} T_{\mathrm{I\,II}}, p_{\mathrm{eq}}(\overline{T}) + p - p_{\mathrm{eq}}(\overline{T})) \\ &\approx g_{\mathrm{I}}(\overline{T}, p_{\mathrm{eq}}(\overline{T})) - s_{\mathrm{I}} \cdot \tfrac{1}{2} T_{\mathrm{I\,II}} + \varrho_{\mathrm{I}}^{-1}(p - p_{\mathrm{eq}}(\overline{T})) \end{aligned} \tag{4.7}$$

and analogously

$$\begin{aligned} g_{\mathrm{II}}(T_{\mathrm{II}}, p) \approx\; & g_{\mathrm{II}}(\overline{T}, p_{\mathrm{eq}}(\overline{T})) \\ & + s_{\mathrm{II}} \cdot \tfrac{1}{2} T_{\mathrm{I\,II}} + \varrho_{\mathrm{II}}^{-1}(p - p_{\mathrm{eq}}(\overline{T})) . \end{aligned} \tag{4.8}$$

Substracting (4.8) from (4.7) and using (4.6) gives

$$g_{\mathrm{I\,II}} = -s\,T_{\mathrm{I\,II}} + \varrho_{\mathrm{I\,II}}^{-1}(p - p_{\mathrm{eq}}(\overline{T})) \tag{4.9}$$

with

$$s = \tfrac{1}{2}(s_{\mathrm{I}} + s_{\mathrm{II}}) . \tag{4.10}$$

But on the other hand one has, with $p_{\mathrm{I}} = p_{\mathrm{II}} = p$, the representation

$$\begin{aligned} g_{\mathrm{I\,II}} &\equiv (u + p\,\varrho^{-1} - T\,s)_{\mathrm{I\,II}} \\ &= u_{\mathrm{I\,II}} + p\,\varrho_{\mathrm{I\,II}}^{-1} - T_{\mathrm{I\,II}}\,s - \overline{T}\,s_{\mathrm{I\,II}} . \end{aligned} \tag{4.11}$$

Comparison of (4.9 and 11) shows that

$$u_{\mathrm{I\,II}} + p\,\varrho_{\mathrm{I\,II}}^{-1} - \overline{T}\,s_{\mathrm{I\,II}} = \varrho_{\mathrm{I\,II}}^{-1}(p - p_{\mathrm{eq}}(\overline{T})) . \tag{4.12}$$

In applying this to the "force" on the left side of (4.2), one has preliminarily to notice that the factor (T^{-1}) in front means $\frac{1}{2}(T_{\mathrm{I}}^{-1} + T_{\mathrm{II}}^{-1})$ rather than $1/\overline{T}$ with $\overline{T} = \frac{1}{2}(T_{\mathrm{I}} + T_{\mathrm{II}})$. Indeed one gets from (4.12)

$$\begin{aligned} &(T^{-1})(u_{\mathrm{I\,II}} + p\,\varrho_{\mathrm{I\,II}}^{-1}) - s_{\mathrm{I\,II}} \\ &\quad = (T^{-1})\,\varrho_{\mathrm{I\,II}}^{-1}(p - p_{\mathrm{eq}}(\overline{T})) + [(T^{-1})\,\overline{T} - 1]\,s_{\mathrm{I\,II}} . \end{aligned} \tag{4.13}$$

But it is exactly

$$(T^{-1})\,\overline{T} - 1 = T_{\mathrm{I\,II}}^2 / 4\,T_{\mathrm{I}}\,T_{\mathrm{II}} ,$$

which means that as long as linear relations between "forces and fluxes" are considered the difference between (T^{-1}) and $1/\overline{T}$ can be and has to be neglected. Then the constitutive laws (4.1 and 2) for the interface take the more simple form

$$T_{\mathrm{I\,II}} = T^2\,(\alpha\,q_{\mathrm{I\,II}} + \beta\,j_{\mathrm{I\,II}}) , \tag{4.14}$$

$$p - p_{\mathrm{eq}}(\overline{T}) = \frac{T}{\varrho_{\mathrm{I\,II}}^{-1}}\,(\tilde{\beta}\,q_{\mathrm{I\,II}} + \gamma\,j_{\mathrm{I\,II}}) . \tag{4.15}$$

As the driving thermodynamical "forces" on the left side now appear the temperature jump $T_{\mathrm{I\,II}}$ at any point of the interface and the difference $p - p_{\mathrm{eq}}(\overline{T})$ of the actual pressure, uniform in the whole system, and the equilibrium pressure belonging to the mean temperature $\overline{T} = \frac{1}{2}(T_{\mathrm{I}} + T_{\mathrm{II}})$ at any point of the interface.

The energy equation for the interface is in the case of slow phase transitions advantageously taken from (2.20). With due simplifications one obtains

$$q \approx -h_{\mathrm{I\,II}}\,j_{\mathrm{I\,II}} , \tag{4.16}$$

an equation which is of paramount importance in the applications.

§ 5. Measurability of the Coefficients $\alpha, \beta, \tilde{\beta}, \gamma$

Finally the question is treated how the phenomenological coefficients $\alpha, \ldots \gamma$ in (4.14 and 15) can be measured in a direct, hopefully practicable way [3]. To this end a special arrangement is considered in which stationary heat conduction and phase transition processes are going on.

Two flat vessels a, b of the same kind, see Fig. 1, are filled with liquid II and its vapour I. The walls of the vessels are kept at different uniform temperatures T_{a}, T_{b}. The vessels are connected by two channels $\mathrm{C_I}$, $\mathrm{C_{II}}$, wide enough so that no appreciable thermo-osmosis takes place. This means that the pressures in both vessels are equal

$$p_{\mathrm{a}} = p_{\mathrm{b}} = p \tag{5.1}$$

and that the interfaces I/II are at the same level on both sides. Let us take $T_a > T_b$ throughout. Then, stationary state being established, the temperatures in both vessels will roughly be as drawn in Figure 2. The interfaces in both vessels at $z = d_{II}$ adopt roughly the same temperatures $\overline{T}_a \approx \overline{T}_b \approx \frac{1}{2}(T_a + T_b)$. The interface in a is heated from the walls through I and II and produces vapour. This again condenses into the interface in b which is cooled through I and II from the walls. Through channel C_{II} the liquid flows back to vessel a. But the temperature in the vicinity of the interfaces has a "fine structure" qualitatively shown in Figure 3. This fine structure depends on the coefficients α, β, $\tilde{\beta}$, γ and will be our main concern in the following.

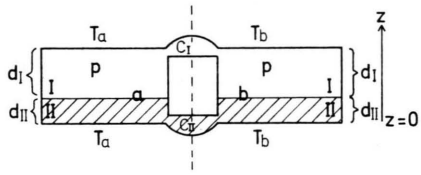

Fig. 1. Arrangement for stationary heat conduction and phase transition.

For a quantitative treatment let us first state the conservation laws for mass and energy. The stationary mass fluxes I → II in a and b are opposite

$$j_{\mathrm{I\,II\,a}} = -j_{\mathrm{I\,II\,b}}\,. \tag{5.2}$$

From this and from (4.16) one has for the heat fluxes

$$q_a = -h_{\mathrm{I\,II}}\, j_{\mathrm{I\,II\,a}} = h_{\mathrm{I\,II}}\, j_{\mathrm{I\,II\,b}} = -q_b\,. \tag{5.3}$$

The differences of the enthalpies h in vessels a, b are neglected; they would give rise to effects quadratic in the applied temperature difference $T_a - T_b$. Convection too will be disregarded in the following.

Now, in a *zeroth approximation*, the coefficients $\alpha, \ldots, \gamma$ are put equal to zero. Then, Eq. (4.14) tells that there is no temperature jump in both interfaces a and b. Equation (4.15) in connection with (5.1) tells that

$$p_{eq}(\overline{T}_a) \approx p_{eq}(\overline{T}_b)$$

or

$$\overline{T}_a \approx \overline{T}_b \approx \overline{T}\,, \tag{5.4}$$

a fact already mentioned above. The heat fluxes going from phases I and II into the interface a are respectively

$$\begin{aligned} q_{\mathrm{I\,a}} &= \left(\frac{\lambda}{d}\right)_{\mathrm{I}} (T_a - \overline{T}) \\ q_{\mathrm{II\,a}} &= \left(\frac{\lambda}{d}\right)_{\mathrm{II}} (T_a - \overline{T}), \end{aligned} \tag{5.5}$$

where $\lambda_{\mathrm{I,II}}$ denote the heat conductivities of the gas and the liquid. So, the total heat flux $q_a = q_{\mathrm{I\,a}} + q_{\mathrm{II\,a}}$, entering the interface a, is

$$q_a = (\lambda/d)\,(T_a - \overline{T}) \tag{5.6}$$

with the abbreviation

$$\lambda/d = (\lambda/d)_{\mathrm{I}} + (\lambda/d)_{\mathrm{II}}\,. \tag{5.7}$$

Analogously one has

$$q_b = (\lambda/d)\,(T_b - \overline{T})\,. \tag{5.8}$$

But in stationary state there is no total heat flux into both interfaces (and into the entire system)

$$q_a + q_b = 0\,,$$

which is already contained in (5.3). Inserting (5.6 and 8) immediately gives

$$\overline{T} = \tfrac{1}{2}(T_a + T_b)\,. \tag{5.9}$$

This is all which is needed to draw Figure 2. – But for later use let us also rewrite Eqs. (5.6 and 8) by (5.9):

$$q_a = \frac{1}{2}\frac{\lambda}{d}\,(T_a - T_b) = -q_b\,. \tag{5.10}$$

And lastly, let us write down the heat flux differences in zeroth approximation. After (5.5 and 9) one has

$$q_{\mathrm{I\,II\,a}} \equiv \tfrac{1}{2}(q_{\mathrm{I\,a}} - q_{\mathrm{II\,a}}) = \tfrac{1}{2}(\lambda/d)_{\mathrm{I\,II}}(T_a - T_b) \tag{5.11}$$

with the abbreviation

$$(\lambda/d)_{\mathrm{I\,II}} = \tfrac{1}{2}[(\lambda/d)_{\mathrm{I}} - (\lambda/d)_{\mathrm{II}}]\,. \tag{5.12}$$

For vessel b one has analogously

$$q_{\mathrm{I\,II\,b}} = \tfrac{1}{2}(\lambda/d)_{\mathrm{I\,II}}(T_b - T_a) = -q_{\mathrm{I\,II\,a}}\,. \tag{5.13}$$

So much about the zeroth approximation.

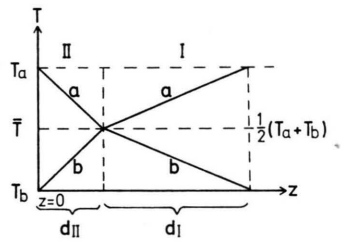

Fig. 2. Zeroth order picture of temperatures in vessels a, b as functions of height z.

The *first* (and final) *approximation* for the temperatures, as sketched in Fig. 3, is obtained by inserting the above fluxes into the constitutive laws (4.14 and 15). To begin with, the mass flux in the

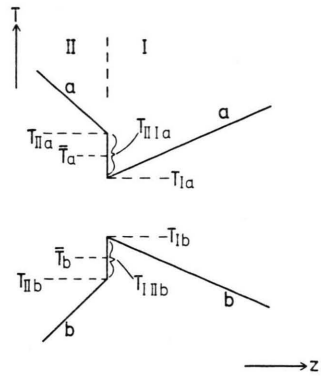

Fig. 3. "Fine Structure" of temperatures in vessels a, b near interfaces, enlarged in comparison with Figure 2.

laws is expressed by the heat flux according to (5.3):

$$T_{\mathrm{I\,II}} = T^2 \left(\alpha\, q_{\mathrm{I\,II}} - \frac{\beta}{h_{\mathrm{I\,II}}}\, q \right),$$

$$p - p_{\mathrm{eq}}(\bar{T}) = \frac{T}{\varrho_{\mathrm{I\,II}}^{-1}} \left(\tilde{\beta}\, q_{\mathrm{I\,II}} - \frac{\gamma}{h_{\mathrm{I\,II}}}\, q \right),$$

valid for a, b respectively. Inserting of (5.10, 11 and 13) gives for the temperature jumps at both interfaces a, b

$$T_{\mathrm{I\,II\,a}} = -T_{\mathrm{I\,II\,b}} = \tfrac{1}{2}\, T^2 \left[\alpha \left(\frac{\lambda}{d} \right)_{\mathrm{I\,II}} - \frac{\beta}{h_{\mathrm{I\,II}}} \frac{\lambda}{d} \right] (T_{\mathrm{a}} - T_{\mathrm{b}}). \quad (5.14)$$

Likewise, the differences $p - p_{\mathrm{eq}}(\bar{T})$ are of equal magnitude and opposite sign for vessels a and b. Substracting both values from each other in order to eliminate the common pressure p gives

$$p_{\mathrm{eq}}(\bar{T}_{\mathrm{b}}) - p_{\mathrm{eq}}(\bar{T}_{\mathrm{a}}) = 2 \frac{T}{\varrho_{\mathrm{I\,II}}^{-1}} \left(\tilde{\beta}\, q_{\mathrm{I\,II\,a}} - \frac{\gamma}{h_{\mathrm{I\,II}}}\, q_{\mathrm{a}} \right).$$

To the left side, the Clausius-Clapeyron relation

$$p_{\mathrm{eq}}(\bar{T}_{\mathrm{b}}) - p_{\mathrm{eq}}(\bar{T}_{\mathrm{a}}) = (h_{\mathrm{I\,II}}/T\, \varrho_{\mathrm{I\,II}}^{-1})\, (\bar{T}_{\mathrm{b}} - \bar{T}_{\mathrm{a}})$$

is applied. This yields for the mean temperatures $\bar{T}_{\mathrm{a}}, \bar{T}_{\mathrm{b}}$ of both interfaces

$$\bar{T}_{\mathrm{a}} - \bar{T}_{\mathrm{b}} = 2\, T^2 \left(-\frac{\tilde{\beta}}{h_{\mathrm{I\,II}}}\, q_{\mathrm{I\,II\,a}} + \frac{\gamma}{h_{\mathrm{I\,II}}^2}\, q_{\mathrm{a}} \right).$$

Again, inserting (5.10 and 11) gives

$$\bar{T}_{\mathrm{a}} - \bar{T}_{\mathrm{b}} = T^2 \left[-\frac{\tilde{\beta}}{h_{\mathrm{I\,II}}} \left(\frac{\lambda}{d} \right)_{\mathrm{I\,II}} + \frac{\gamma}{h_{\mathrm{I\,II}}^2} \frac{\lambda}{d} \right] (T_{\mathrm{a}} - T_{\mathrm{b}}) \quad (5.15)$$

for the difference between the mean temperatures of both interfaces. Equations (5.14 and 15) are the main results. They show that the differences $T_{\mathrm{I\,II\,a}}$ and $\bar{T}_{\mathrm{a}} - \bar{T}_{\mathrm{b}}$ are proportional to the applied temperature difference $T_{\mathrm{a}} - T_{\mathrm{b}}$ and are small of the order of $\alpha, \ldots, \gamma$. The quantities λ/d and $(\lambda/d)_{\mathrm{I\,II}}$ may be supposed to be known. Then, measuring $T_{\mathrm{I\,II\,a}}$ and $\bar{T}_{\mathrm{a}} - \bar{T}_{\mathrm{b}}$ for different values of $(\lambda/d)_{\mathrm{I\,II}}$ yields the coefficients $\alpha, \ldots, \gamma$.

Let us first take $(\lambda/d)_{\mathrm{I\,II}} = 0$. As $\lambda_{\mathrm{II}} > \lambda_{\mathrm{I}}$, one has to choose $d_{\mathrm{II}} > d_{\mathrm{I}}$, i. e. comparatively much liquid. In this case, Eqs. (5,14 and 15) give $\beta/h_{\mathrm{I\,II}}$ and $\gamma/h_{\mathrm{I\,II}}^2$. In another special case, viz. $d_{\mathrm{II}} \ll d_{\mathrm{I}}$, i. e. only a thin layer of liquid, one has

$$(\lambda/d)_{\mathrm{I\,II}} \approx -\tfrac{1}{2}\, \lambda/d\,.$$

In this case Eqs. (5.14 and 15) yield $\frac{1}{2}\, \alpha + (\beta/h_{\mathrm{I\,II}})$ and $\frac{1}{2}\, (\tilde{\beta}/h_{\mathrm{I\,II}}) + (\gamma/h_{\mathrm{I\,II}}^2)$. Of course other temperature differences can also be considered, as e. g. $T_{\mathrm{I\,a}} - T_{\mathrm{I\,b}}$ which in the example of Fig. 3 is distinguished by the fact that it is the very smallest temperature difference existing between vessels a and b.

Incidentally, the lines in Fig. 3 may even intersect (if $\alpha > 4\, \gamma/h_{\mathrm{I\,II}}^2$). At least this is not forbidden by thermodynamical reasons.

All the interesting temperature differences are of the type of temperature jumps. In order that these are observable, the pressure has to be low enough so that the free path of the vapour molecules is not too small in comparison with the thickness d_{I}. In the zeroth approximation discussed above, with comparatively high pressure and thick layers, the rate of evaporation, i. e. the mass current circulating between the two vessels, is solely determined by heat conduction within the bulk phases. The measurement of this rate would not be a good way to find the interfacial coefficients. However, the temperature differences studied in this section are homogeneous and linear in the interfacial transport coefficients. So, it is the measurement of these differences which should give the most direct and accurate information about the said coefficients.

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[2] S. R. DE GROOT and P. MAZUR, Non-Equilibrium Thermodynamics, North-Holland Publ. Co. 1962, Chap. XV.

[3] The previous proposal by W. J. BORNHORST and G. N. HATSOPOULOS, J. Appl. Mechanics, Dec. **1967**, p. 840, amounts to the indirect determination of $\alpha, \ldots, \gamma$ from small differences of much larger quantities, as e. g. the actual pressure p and the equilibrium pressure $p_{\mathrm{eq}}(\bar{T})$.