die üblichen Radienverhältnisse nur geringfügig ändern. Sofern die Werte für die optimale Trennung bei Rohren mit kleinem Durchmesser ($r_R/r_D < 20$) nicht zu stark von den theoretischen Werten für größere Radienverhältnisse abweichen, werden sich also Trennkurven für gleiche Temperaturverhältnisse und verschiedene Rohrradien stets schneiden. Diese

Folgerung stimmt gleichfalls gut mit den Messungen am Krypton überein [7].

Meinem Lehrer, Herrn Prof. Dr. Dr. h. c. KLAUS CLUSIUS, danke ich für die Anregung zu dieser Arbeit und für viele wertvolle Ratschläge bei ihrer Ausführung. Hern Prof. Dr. H. LABHART und Herrn Dr. H. RICHTERING möchte ich für freundliche Diskussionen bei der Niederschrift danken.

Non-Equilibrium Thermodynamics of Boundary Conditions

L. WALDMANN

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

In part I a well-known pair of cross phenomena, thermo-osmosis and mechano-caloric effect, in a dense gas is treated by a "thermo-hydrodynamical" method: the FOURIER and NAVIER–STOKES equations are adopted for heat conduction and viscous motion whereas in the boundary conditions MAXWELL's thermal slip (3.1) and a mechanical surface heat flow (3.7) appear. Both of them are connected by an ONSAGER relation (3.9). So far, the underlying geometry was a special one (circular cylindrical capillary). In part II the boundary conditions problem at the interface between two immiscible fluids is considered in the general case, by the method of continuum non-equilibrium thermodynamics. The fluids are in viscous motion and conducting heat, such that total mass, momentum, angular momentum and energy are conserved. It is assumed that none of these quantities is concentrated in the interface (vanishing densities per unit area). This leads to the global conditions (6.3) for the forces and (6.8) for the normal energy flows at the interface. After the general expression (7.8) for interfacial entropy production is at hand, the global conditions are replaced by stronger local ones in the vein of thermo-hydrodynamics. Two possibilities are considered in this context: the interface a) does not and b) does carry two-dimensional flows of momentum and energy. In case a) the ensuing local boundary conditions are merely mechanical slip for the velocity fields and temperature jump for the temperature fields. In addition to these, in case b) a pair of cross effects naturally comes out, namely thermal slip and mechanical surface heat flow, and a thermal surface heat flow as well. This reassures the results of part I which had been obtained in a somewhat indirect way.

Non-equilibrium thermodynamics imposes important restrictions on the coefficients which occur in the linear constitutive laws of continuum transport phenomena. The second law of thermodyanmics requires certain coefficients or matrices to be positive, microreversibility leads to the well-known ONSAGER symmetry relations between cross effects.

The constitutive laws, in the usual three-dimensional sense, are not everything. Inserted into the conservation equations they give e. g. the NAVIER–STOKES equation for frictional fluid motion or the FOURIER heat conduction equation. But these equations have to be supplemented by boundary conditions in order to be conclusive. In the boundary conditions, more phenomenological coefficients may

appear. The purpose of this article is to look at such coefficients from the thermodynamical point of view and especially to look for possible ONSAGER relations. To my perhaps incomplete knowledge this has not been done in the literature so far.

A variety of surface phenomena is imaginable. We shall confine ourselves to a special case and consider what might happen in the interface of two immiscible fluids in which friction and heat conduction occur. This forms the second (main) part of this paper. The first part, as a physical introduction, gives a brief account of the well-known thermo-osmotic and mechano-caloric effects in a capillary and an interpretation thereof from the present point of view.

Part I. Thermo-Osmosis [1] and Mechano-Caloric Effect in a Capillary

This case offers one of the simplest applications of ONSAGER's idea [2] and is treated in the monographs by DE GROOT [3] and DE GROOT–MAZUR [4]. For convenience the basic theory is recalled here.

Fig. 1 shows the arrangement: a pure gas is in two vessels which are connected by a capillary. The pressures and the temperatures of the gas are p, T and $p + \Delta p, T + \Delta T$ respectively in the two vessels. Within each vessel, pressure and temperature are supposed to be fairly uniform. The system is thus idealized as a discontinuous system, with only the two variables $\Delta p, \Delta T$.
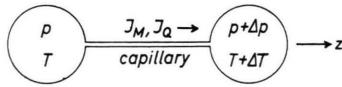

Fig. 1. Scheme of thermo-osmotic and mechano-caloric apparatus.

§ 1. Kinetic Theory for a Knudsen Gas

In this section we assume the mean free path of the gas to be large in comparison with the diameter of the capillary. The walls of the capillary are supposed to reflect the gas atoms specularly [5]. Then, the length of the capillary is immaterial for the mass flux J_M and the energy flux J_E through the capillary. Indeed, denoting the mass density of the gas by ϱ, the mean thermal velocity of its atoms of mass m by

$$\bar{c} = \sqrt{8\, k\, T / \pi\, m}$$

($k = $ BOLTZMANN's constant) and the cross section of the capillary by q, one has

$$J_M = -q\, \Delta\left(\tfrac{1}{4}\varrho\, \bar{c}\right) = -\tfrac{1}{4}\, q\, \varrho\, \bar{c}\left(\frac{\Delta p}{p} - \frac{1}{2}\frac{\Delta T}{T}\right), \quad (1.1)$$

$$J_E = -q\, \Delta\left(\tfrac{1}{2}p\, \bar{c}\right) = -\tfrac{1}{4}\, q\, p\, \bar{c}\left(2\,\frac{\Delta p}{p} + \frac{\Delta T}{T}\right). \quad (1.2)$$

For both fluxes, the sign is chosen positive if they are directed to the right in Fig. 1. Instead of the energy flux it is more convenient to consider the

heat flux defined by

$$J_Q = J_E - h\, J_M = -\tfrac{1}{4}\, q\, p\, \bar{c}\left(-\frac{1}{2}\frac{\Delta p}{p} + \frac{9}{4}\frac{\Delta T}{T}\right). \quad (1.3)$$

Here,

$$h = \tfrac{5}{2}\, p\, \varrho^{-1}$$

means the enthalpy per unit mass of the monatomic gas.

Eq. (1.1) says that in stationary state, $J_M = 0$, there is a pressure difference

$$\Delta p = \frac{1}{2}\, p\, \frac{\Delta T}{T} \qquad (1.4)$$

linked with a given temperature difference: thermo-osmotic pressure effect. On the other hand, in the isothermal case, a heat flux

$$J_Q = \tfrac{1}{8}\, q\, \bar{c}\, \Delta p$$

is linked with a given pressure difference (which at the same time causes a mass flux): mechano-caloric effect.

§ 2. Non-Equilibrium Thermodynamics of Discontinuous System

Now, we consider the same arrangement as before, but with an arbitrary mean free path of the gas, from the point of view of non-equilibrium thermodynamics. The entropy production is

$$\frac{dS}{dt} = \Delta(-T^{-1}\mu)\, J_M + \Delta(T^{-1})\, J_E. \quad (2.1)$$

Here,

$$\mu = h - T\, s$$

means the chemical potential per unit mass of the gas; s is its entropy per unit mass. Replacing the energy flux by the heat flux according to

$$J_E = h\, J_M + J_Q$$

and using

$$\Delta(-T^{-1}\mu) + h\, \Delta T^{-1} = (-\mu + h)\, \Delta T^{-1} - T^{-1}\, \Delta\mu$$
$$= T\, s\, \Delta T^{-1} - T^{-1}\, (-s\, \Delta T + \varrho^{-1}\, \Delta p)$$
$$= -T^{-1}\, \varrho^{-1}\, \Delta p,$$

one obtains, equivalent with (2.1),

$$\frac{dS}{dt} = (-T^{-1}\, \varrho^{-1}\, \Delta p)\, J_M + (-T^{-2}\, \Delta T)\, J_Q. \quad (2.2)$$

[1] We prefer this term, in use for an arrangement with a membrane instead of just one capillary, to the longer term "thermo-molecular pressure effect".
[2] L. ONSAGER, Phys. Rev. 37, 405 [1931].
[3] S. R. DE GROOT, Thermodynamics of Irreversible Processes, North-Holland Publ. Co. 1951, Chap. III.
[4] S. R. DE GROOT and P. MAZUR, Non-Equilibrium Thermodynamics, North-Holland Publ. Co. 1962, Chap. XV.
[5] Incidentally one might ask how in a KNUDSEN gas within such walls an irreversible process should happen. The right answer probably is the following. Taking averages like p and $p + \Delta p$ for each vessel means a coarse graining procedure. Apart from exceptional cases, such a procedure causes macroscopic irreversibility.

Therefore, the expressions in the parenthesises are the driving forces F_M, F_Q conjugate to the fluxes J_M, J_Q.

According to the principles of non-equilibrium thermodynamics the linear constitutive laws are

$$J_M = -L_{MM} T^{-1} \varrho^{-1} \Delta p - L_{MQ} T^{-2} \Delta T, \quad (2.3)$$

$$J_Q = -L_{QM} T^{-1} \varrho^{-1} \Delta p - L_{QQ} T^{-2} \Delta T. \quad (2.4)$$

The phenomenological coefficients L form a positive matrix and have the ONSAGER symmetry $L_{QM} = L_{MQ}$, both forces being even under time reversal.

By comparison of (2.3 and 4) with (1.1 and 3) one has for the KNUDSEN gas

$$\mathcal{L} = \tfrac{1}{4} q \varrho \bar{c} T \cdot \begin{pmatrix} \varrho \, p^{-1} & -\tfrac{1}{2} \\ -\tfrac{1}{2} & \tfrac{9}{4} \varrho^{-1} p \end{pmatrix}.$$

This matrix indeed has the said properties of positiveness and symmetry.

So far, everything is well known.

§ 3. Thermo-Hydrodynamical Treatment for Dense Gas

The considerations of § 1 are detailed, but restricted to the KNUDSEN gas. The theory of § 2 is general, but does not give insight into a detailed mechanism. Now, we want to set up a detailed continuum theory for the transport in a dense gas within a capillary, the walls of which bear a uniform temperature gradient dT/dz (z-coordinate directed to the right in Fig. 1).

Inside the capillary, radius R, the NAVIER–STOKES equation shall be valid. At the wall of the capillary the gas is supposed to slip with the velocity [6]

$$v_z(R) = \sigma \left(\frac{\lambda}{p} \frac{dT}{dz} \right)_{r=R}. \quad (3.1)$$

Here, λ is the heat conductivity of the gas (inserted for convenience only) and σ, the thermal slip number (of order 0.2 in many cases), is a new phenomenological coefficient characterizing the interaction gas/surface. The boundary condition (3.1) is due to MAXWELL [7]. Compressibility neglected, the NAVIER–STOKES equation together with the boundary condition (3.1) yields the velocity profile

$$v_z(r) = \frac{1}{4 \eta} \frac{dp}{dz} (r^2 - R^2) + \sigma \frac{\lambda}{p} \frac{dT}{dz}. \quad (3.2)$$

The first term on the right is the familiar POISEUILLE profile (r distance from capillary axis, η viscosity), the second term comes from thermal slip. Integration of (3.2) over the entire capillary cross section q gives the total mass flux

$$J_M = -\frac{q \varrho R^2}{8 \eta L} \Delta p + \sigma \frac{q \varrho \lambda}{p L} \Delta T, \quad (3.3)$$

where L means the length of the capillary.

In the stationary state, $J_M = 0$, a thermo-osmotic pressure difference

$$\Delta p = 8 \sigma \frac{\eta \lambda}{p R^2} \Delta T \quad (3.4)$$

is set up. For a monatomic gas, one has

$$\lambda = \frac{15}{4} \frac{k}{m} \eta .$$

With the mean free path

$$l = \eta / \varrho \bar{c} ,$$

Eq. (3.4), for the monatomic gas, may then be rewritten as

$$\Delta p = \frac{240}{\pi} \sigma \left(\frac{l}{R} \right)^2 p \frac{\Delta T}{T}. \quad (3.5)$$

This holds for a wide capillary, $R \gg l$, and is the counterpart of Eq. (1.4), valid for a narrow capillary.

What about heat flux? According to the thermodynamical theory of § 2 there must exist a mechanical heat flux if the mass flux, as is shown by (3.3), contains a thermal contribution. Comparison of (2.3) and (3.3) gives

$$-L_{MQ} T^{-2} = \sigma \frac{q \varrho \lambda}{p L}.$$

Therefore, after (2.4), the heat flux through a wide capillary must be, as $L_{QM} = L_{MQ}$,

$$J_Q = \sigma \frac{q \lambda T}{p L} \Delta p - L_{QQ} T^{-2} \Delta T. \quad (3.6)$$

The mechanical heat flux is again governed by the thermal slip number σ.

But now the question arises where this heat flux is located. Within the gas, acording to FOURIER's law, there exists only the thermal heat flow density $-\lambda \, dT/dz$. Properly evaluated, this will give the second term on the right side of (3.6) or rather the main part of it, but no mechanical heat flux at

---

[6] For simplicity we neglect mechanical slip. In (3.5) it would cause a correction of order l/R. But it should be stressed that in principle the second law requires a non-vanishing

mechanical slip if there is a non-vanishing thermal slip at all, see § 10.

[7] J. C. MAXWELL, Scient. Papers **2**, 709 [1879].

all. From this argument the latter can only be concentrated at the surface. For the geometry presently considered, one has to introduce a mechanical surface heat flow density (energy/length-time)

$$Q_{z,\,\text{mech}} = \varkappa \left(\frac{dv_z}{dr} \right)_{r=R}, \qquad (3.7)$$

where $\varkappa$ is a phenomenological constant again characterizing the interaction gas/surface. Besides this mechanical surface heat flow there will exist a thermal part too which contributes to the second term on the right side of (3.6). Indeed, in § 10 it is shown that such a contribution is required by the second law whenever a mechanical heat flux exists. For the moment the thermal part does not interest.

The coefficient $\varkappa$ can be expressed by the thermal slip number σ due to the ONSAGER relation. After (3.7 and 2) the mechanical surface heat flow density is also

$$Q_{z,\,\text{mech}} = \frac{\varkappa}{2\,\eta} \frac{dp}{dz} R. \qquad (3.8)$$

By multiplying this with the circumference $2\,\pi\,R$ of the capillary one obtains the total mechanical heat flux

$$J_{Q,\,\text{mech}} = \varkappa \frac{q}{\eta\,L} \Delta p.$$

Identification with the first term on the right side of (3.6) yields

$$\varkappa = \sigma \frac{\eta\,\lambda\,T}{p}, \qquad (3.9)$$

the desired relation between the phenomenological surface coefficients $\varkappa$ and σ.

What has here been depicted as surface phenomena, viz. thermal slip and related mechanical surface heat flow, will in reality take place in a layer of a thickness of some mean free path. Our picture consists in neglecting the thickness of this layer, by so to say projecting it unto the surface. This will be valid as a first step beyond a thermo-hydrodynamics which ignores these effects altogether, by assuming that the gas sticks to the surface and that there is no surface heat flow.

DERYAGUIN and BAKANOV [8] have looked at this problem from a different point of view. They have amplified FOURIER's continuum heat conduction law by a term which contains the pressure gradient (in the bulk material). Such a term indeed appears in the third approximation of the CHAPMAN–ENSKOG kinetic theory. DERYAGUIN and BAKANOV then work backward to thermo-osmosis by the thermodynamical method of § 2. Hence, in their theory no specific gas/surface interaction is taken into account which seems physically unsatisfactory, as expressed elsewhere [9].

That much about the special case of transport through a capillary. We now start to formulate the theory in a general way, valid for arbitrary geometry.

Part II. Thermodynamics of Interface Conditions for Two Adjacent Immiscible Fluids

We assume that in the bulk material of the two fluids I, II usual thermo-hydrodynamics is valid, i. e. the FOURIER and NAVIER–STOKES equations for heat conduction and frictional motion shall hold. The two fluids are supposed not to mix (no diffusion) and always to be in contact with each other along a two-dimensional curved interface. In order to obtain the boundary conditions at this changing interface, one has to look at the system as a whole and to set up the integral conservation laws and the integral entropy production.

Throughout we shall assume that the interface does not contain any mass, momentum, angular momentum, energy nor entropy per unit area. But the interface shall be penetrable for flows of these quantities with the exception of mass. In the following discussion of boundary conditions we shall first assume that within the interface there is no transport of momentum and energy (§ 8) and second we will assume that such transports do exist (§ 10). It will turn out that only by this second richer alternative thermo-osmosis and its cross effect can be described.

§ 4. Continuity and Discontinuity at Interface

The state variables in thermo-hydrodynamics are the mass density ϱ, the velocity v and the energy e per unit mass or the temperature T. All these variables depend on time t and space coordinates x. The outward unit normal of fluid I at any point of

[8] B. V. DERYAGUIN and S. P. BAKANOV, Dokl. Akad. Nauk, SSSR (Phys. Chem.) 147, 139 [1962].

[9] L. WALDMANN and K. H. SCHMITT, Thermophoresis and Diffusiophoresis of Aerosols; in Aerosol Science, ed. C. N. DAVIES, Academic Press, New York—London 1966, p. 149.

the interface shall be denoted by $\boldsymbol{n}_I$ (Fig. 2). For sake of symmetry we correspondingly introduce the unit vector $\boldsymbol{n}_{II}$ which at the same point of the interface is opposite to $\boldsymbol{n}_I$:
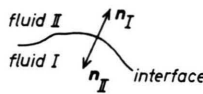
$$\boldsymbol{n}_I = -\boldsymbol{n}_{II} . \tag{4.1}$$

fluid II $\boldsymbol{n}_I$
fluid I $\boldsymbol{n}_I$ *interface*

Fig. 2. Outward normals of the fluids.

At any point of the time-dependent interface the fluids always have to stay in contact with each other. This means that the normal components

$$v_I = \boldsymbol{n}_I \cdot \boldsymbol{v}_I , \quad v_{II} = \boldsymbol{n}_{II} \cdot \boldsymbol{v}_{II} \tag{4.2}$$

have to obey the continuity condition

$$v_I + v_{II} = 0 . \tag{4.3}$$

All the other state variables mentioned before, including the tangential velocities, may be discontinuous at the interface.

§ 5. A Formula for a Time-Dependent Volume

Let the interface $\sigma(t)$ be closed and consider any quantity $a(t, \boldsymbol{x})$ per unit mass of the fluid inside. The fluid outside may extend to infinity or be bounded by a second closed interface beyond which there might be a third fluid. Surface integrals at infinity will never be mentioned explicitly in this article. Now we consider the total amount A of the quantity a contained within the time-dependent volume $\tau(t)$ enclosed by $\sigma(t)$:

$$A(t) = \int_{\tau(t)} d\tau \, \varrho \, a . \tag{5.1}$$

The mass density ϱ obeys the continuity equation

$$\frac{\partial \varrho}{\partial t} + \frac{\partial v_\nu \varrho}{\partial x_\nu} = 0 \quad (\nu = 1, 2, 3). \tag{5.2}$$

The CARTESIAN components of any vector or tensor are in this paper denoted by Greek subscripts for which the summation rule is adopted. For the change with time of A one has

$$\frac{dA}{dt} = \int_{\tau(t)} d\tau \, \frac{\partial \varrho a}{\partial t} + \int_{\sigma(t)} d\sigma \, n_\nu \, v_\nu \, \varrho \, a ,$$

because according to (4.3) the interface in its normal direction moves with the normal velocity of the fluid. The surface integral can be rewritten by GAUSS' theorem

$$\int_\sigma d\sigma \, n_\nu \ldots = \int_\tau d\tau \, \frac{\partial \ldots}{\partial x_\nu}$$

as

$$\frac{dA}{dt} = \int_{\tau(t)} d\tau \left(\frac{\partial \varrho \, a}{\partial t} + \frac{\partial v_\nu \, \varrho \, a}{\partial x_\nu} \right) .$$

With the substantial time derivative

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_\nu \frac{\partial}{\partial x_\nu} ,$$

which of course is different for fluids I and II, and by (5.2) one obtains the desired well-known formula

$$\frac{d}{dt} \int_{\tau(t)} d\tau \, \varrho \, a = \int_{\tau(t)} d\tau \, \varrho \, \frac{da}{dt} . \tag{5.3}$$

§ 6. The Conservation Laws for the Two Fluids System

Mass Conservation Restated

The mass of fluid I is

$$M_I = \int_{\tau_I} d\tau \, \varrho_I .$$

This means that in (5.1) one has to choose $a_I = 1$. Eq. (5.3) then gives immediately

$$dM_I/dt = 0 \quad \text{and likewise} \quad dM_{II}/dt = 0 .$$

Mass conservation for each fluid is refound. Indeed, it has, by (5.2), already been built into (5.3). The masses are conserved separately because the interface was supposed to be inpenetrable for mass (immiscible fluids).

Momentum Conservation

For the a_I in (5.1) we now take $v_{I\mu}$, the CARTESIAN μ-component of momentum per unit mass of fluid I; fluid II is treated correspondingly. The total μ-momentum of the two fluids system then is

$$P_\mu = \int_{\tau_I} d\tau \, \varrho_I \, v_{I\mu} + \int_{\tau_{II}} d\tau \, \varrho_{II} \, v_{II\mu} .$$

The assumption that there is no momentum per unit area in the interface has been used. From the equation of motion in the bulk fluids

$$\varrho_I \left(\frac{dv_{I\mu}}{dt} \right)_I = -\frac{\partial p_{I\nu\mu}}{\partial x_\nu} , \ldots , \tag{6.1}$$

where $p_{I\nu\mu}$ meas the pressure tensor of fluid I, from (5.3) and from conservation of total momentum one has

$$\frac{dP_\mu}{dt} = -\int_{\tau_I} d\tau \, \frac{\partial p_{I\nu\mu}}{\partial x_\nu} - \int_{\tau_{II}} d\tau \, \frac{\partial p_{II\nu\mu}}{\partial x_\nu} = 0 .$$

By GAUSS' theorem this can be rewritten as

$$-\int_\sigma d\sigma (n_{I\nu} \, p_{I\nu\mu} + n_{II\nu} \, p_{II\nu\mu}) = 0 .$$

Let us abbreviate

$$k_{I\mu} = n_{I\nu}\, p_{I\nu\mu}\,, \quad k_{II\mu} = n_{II\nu}\, p_{II\nu\mu}\,. \quad (6.2)$$

The k_μ's denote μ-components of forces per unit area exerted by the fluids on the interface. Momentum conservation therefore requires

$$\int_\sigma d\sigma\,(\boldsymbol{k}_I + \boldsymbol{k}_{II}) = 0\,. \quad (6.3)$$

This is a global condition by which the pressure tensors on both sides of the interface are linked.

Angular Momentum Conservation

Now we identify the a_I in (5.1) with $x_\mu\, v_{I\nu} - x_\nu\, v_{I\mu}$, the $\mu\nu$-component of angular momentum per unit mass, written as a CARTESIAN antisymmetric second rank tensor. The total $\mu\nu$-angular momentum of the two fluids system then is

$$L_{\mu\nu} = \int_{\tau_I} d\tau\, \varrho_I (x_\mu\, v_{I\nu} - x_\nu\, v_{I\mu})$$
$$+ \int_{\tau_{II}} d\tau\, \varrho_{II} (x_\mu\, v_{II\nu} - x_\nu\, v_{II\mu})\,.$$

Again, there shall be no angular momentum concentrated in the interface. Because of

$$\left(\frac{dx_\mu}{dt}\right)_I = v_{I\mu}$$

one has

$$\left[\frac{d}{dt}\,(x_\mu\, v_{I\nu} - x_\nu\, v_{I\mu})\right]_I = x_\mu\left(\frac{dv_{I\nu}}{dt}\right)_I - x_\nu\left(\frac{dv_{I\mu}}{dt}\right)_I.$$

Use of (5.3) and of the equation of motion (6.1) yields

$$\frac{dL_{\mu\nu}}{dt} = -\int_{\tau_I} d\tau \left(x_\mu\, \frac{\partial p_{I\lambda\nu}}{\partial x_\lambda} - x_\nu\, \frac{\partial p_{I\lambda\mu}}{\partial x_\lambda}\right) - $$
$$-\int_{\tau_{II}} d\tau \left(x_\mu\, \frac{\partial p_{II\lambda\nu}}{\partial x_\lambda} - x_\nu\, \frac{\partial p_{II\lambda\mu}}{\partial x_\lambda}\right).$$

The first integrand can be rewritten as

$$\frac{\partial}{\partial x_\lambda}(x_\mu\, p_{I\lambda\nu} - x_\nu\, p_{I\lambda\mu}) - p_{I\mu\nu} + p_{I\nu\mu}\,,$$

the second one correspondingly. On integration the divergence terms can be transformed into surface integrals by GAUSS' theorem, so that angular momentum conservation is also expressed by

$$\frac{dL_{\mu\nu}}{dt} = \int_{\tau_I} d\tau\,(p_{I\mu\nu} - p_{I\nu\mu}) + \int_{\tau_{II}} d\tau\,(p_{II\mu\nu} - p_{II\nu\mu})$$
$$-\int_\sigma d\sigma\,[x_\mu(k_{I\nu} + k_{II\nu}) - x_\nu(k_{I\mu} + k_{II\mu})]$$
$$= 0\,.$$

The surface integral has nothing to do with the volume integrals, so these have to vanish separately. This is guaranteed by

$$p_{I\mu\nu} = p_{I\nu\mu}\,, \ldots\,, \quad (6.4)$$

the familiar symmetry of the pressure tensors within the fluids (if, as has tacitly been assumed, there is no internal (spin) angular momentum present in the fluids). So, angular momentum conservation leaves us with the global condition

$$\int_\sigma d\sigma\,[x_\mu(k_{I\nu} + k_{II\nu}) - x_\nu(k_{I\mu} + k_{II\mu})] = 0\,. \quad (6.5)$$

Energy Conservation

For the a_I in (5.1) we now take

$$e_I = \tfrac{1}{2}\, \boldsymbol{v}_I \cdot \boldsymbol{v}_I + u_I\,,$$

the energy per unit mass of fluid I. As indicated this is the sum of the kinetic and the internal energy u_I per unit mass. The total energy of the two fluids system — again no energy concentrated in the interface — then is

$$E = \int_{\tau_I} d\tau\, \varrho_I\, e_I + \int_{\tau_{II}} d\tau\, \varrho_{II}\, e_{II}\,.$$

The local continuity equation for energy within the fluids is

$$\varrho_I\left(\frac{de_I}{dt}\right)_I = -\frac{\partial e_{I\nu}}{\partial x_\nu}\,, \ldots\,, \quad (6.6)$$

where the energy flow $\boldsymbol{e}_I$ is composed of two terms, a mechanical one and the heat flow $\boldsymbol{q}_I$:

$$e_{I\nu} = p_{I\nu\mu}\, v_{I\mu} + q_{I\nu}\,.$$

Hence, after (5.3), conservation of total energy is expressed by

$$\frac{dE}{dt} = -\int_{\tau_I} d\tau\, \frac{\partial e_{I\nu}}{\partial x_\nu} - \int_{\tau_{II}} d\tau\, \frac{\partial e_{II\nu}}{\partial x_\nu}$$
$$= -\int_\sigma d\sigma\,[n_{I\nu}(p_{I\nu\mu}\, v_{I\mu} + q_{I\nu}) + n_{II\nu}(p_{II\nu\mu}\, v_{II\mu} + q_{II\nu})]$$
$$= 0\,.$$

Abbreviating the normal heat flows at the interface by

$$q_I = n_{I\nu}\, q_{I\nu}\,, \quad q_{II} = n_{II\nu}\, q_{II\nu} \quad (6.7)$$

and using the notation (6.2) for the forces per unit area, we obtain as the global condition for energy conservation

$$\int_\sigma d\sigma\,(\boldsymbol{v}_I \cdot \boldsymbol{k}_I + q_I + \boldsymbol{v}_{II} \cdot \boldsymbol{k}_{II} + q_{II}) = 0\,. \quad (6.8)$$

This is a condition by which the heat flows on both sides of the interface are linked.

§ 7. Entropy Production

In accordance with the usual, simplest version of non-equilibrium thermodynamics we adopt for the local entropy s per unit mass within a fluid the "thermostatic" property

$$\mathrm{d}s = T^{-1}(\mathrm{d}u + p\,\mathrm{d}\varrho^{-1}). \qquad (7.1)$$

Here, T, u, p mean the local temperature, local internal energy per unit mass and local static pressure. Again there shall be no entropy per unit area in the interface.

From (7.1), one obtains the substantial time derivative of s by inserting

$$\varrho\,\frac{\mathrm{d}\varrho^{-1}}{\mathrm{d}t} = \frac{\partial v_\nu}{\partial x_\nu},$$

which is the same as (5.2), and by inserting

$$\varrho\,\frac{\mathrm{d}u}{\mathrm{d}t} = -\frac{\partial v_\mu}{\partial x_\nu}\,p_{\nu\mu} - \frac{\partial q_\nu}{\partial x_\nu},$$

which by virtue of (6.1) is equivalent to the energy equation (6.6). This gives immediately

$$\varrho\,\frac{\mathrm{d}s}{\mathrm{d}t} = -T^{-1}\left(\frac{\partial v_\mu}{\partial x_\nu}\,p'_{\nu\mu} + \frac{\partial q_\nu}{\partial x_\nu}\right) \qquad (7.2)$$

where $$p'_{\nu\mu} = p_{\nu\mu} - p\,\delta_{\nu\mu}$$

is the frictional pressure tensor. By replacing

$$T^{-1}\frac{\partial q_\nu}{\partial x_\nu} = -\frac{\partial T^{-1}}{\partial x_\nu}\,q_\nu + \frac{\partial T^{-1} q_\nu}{\partial x_\nu}$$

and applying Gauss' theorem to the divergence term, we obtain for the entropy S_I of fluid I

$$\frac{\mathrm{d}S_\mathrm{I}}{\mathrm{d}t} = \int_{\tau_\mathrm{I}}\mathrm{d}\tau\,\varrho_\mathrm{I}\left(\frac{\mathrm{d}s_\mathrm{I}}{\mathrm{d}t}\right)_\mathrm{I} = \vartheta_\mathrm{I} - \int_\sigma \mathrm{d}\sigma\,T_\mathrm{I}^{-1}\,q_\mathrm{I}.$$

Here,

$$\vartheta_\mathrm{I} = \int_{\tau_\mathrm{I}}\mathrm{d}\tau\left(-T_\mathrm{I}^{-1}\frac{\partial v_{\mathrm{I}\mu}}{\partial x_\nu}\,p'_{\mathrm{I}\nu\mu} + \frac{\partial T_\mathrm{I}^{-1}}{\partial x_\nu}\,q_{\mathrm{I}\nu}\right) \quad (7.3)$$

is the entropy production within fluid I. The total entropy production is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \vartheta_\mathrm{I} + \vartheta_\mathrm{II} + \Theta \qquad (7.4)$$

with

$$\Theta = -\int_\sigma \mathrm{d}\sigma(T_\mathrm{I}^{-1}\,q_\mathrm{I} + T_\mathrm{II}^{-1}\,q_\mathrm{II}), \qquad (7.5)$$

the entropy production concentrated in the interface. The meaning (6.7) of $q_{\mathrm{I,II}}$ is recalled.

The entropy productions ϑ_I, ϑ_II in the bulk materials lead in the usual way to the continuum constitutive laws. They must not be considered here. For us, the interfacial entropy production Θ is the important thing. By introducing

$$T^{-1} = \tfrac{1}{2}(T_\mathrm{I}^{-1} + T_\mathrm{II}^{-1}), \quad T^{-1}{}_\mathrm{I\,II} = T_\mathrm{I}^{-1} - T_\mathrm{II}^{-1} \quad (7.6)$$

and $$q = q_\mathrm{I} + q_\mathrm{II}, \quad q_\mathrm{I\,II} = \tfrac{1}{2}(q_\mathrm{I} - q_\mathrm{II}) \qquad (7.7)$$

it can be rewritten as

$$\Theta = -\int_\sigma \mathrm{d}\sigma(T^{-1}q + T^{-1}{}_\mathrm{I\,II}\,q_\mathrm{I\,II}). \qquad (7.8)$$

For further exploitation we shall distinguish between interfaces which don't carry and which do carry surface flows of momentum and energy.

§ 8. Boundary Conditions at an Interface without Surface Flows

Eqs. (6.3, 5 and 8) are necessary, global boundary conditions for any interface. In context with thermo-hydrodynamics which is based on local constitutive laws, we want to set up boundary conditions which are local too. If there are no two-dimensional flows of momentum and energy concentrated in the interface, then, by virtue of locality, we simply satisfy (6.3 and 8) by requiring

$$\boldsymbol{k}_\mathrm{I} + \boldsymbol{k}_\mathrm{II} = 0, \qquad (8.1)$$

$$\boldsymbol{v}_\mathrm{I}\cdot\boldsymbol{k}_\mathrm{I} + q_\mathrm{I} + \boldsymbol{v}_\mathrm{II}\cdot\boldsymbol{k}_\mathrm{II} + q_\mathrm{II} = 0 \qquad (8.2)$$

at every point of the interface. Physically, this means that no net momentum and energy enter any unit area of the interface. Obviously, the angular momentum condition (6.5) is then fulfilled automatically. But there is still the continuity condition (4.3) of the normal velocities to be kept in mind.

Now we use these conditions in order to rewrite Θ, the interfacial entropy production defined in (7.8). In analogy with (7.6 and 7) we abbreviate

$$\boldsymbol{v} = \tfrac{1}{2}(\boldsymbol{v}_\mathrm{I} + \boldsymbol{v}_\mathrm{II}), \quad \boldsymbol{v}_\mathrm{I\,II} = \boldsymbol{v}_\mathrm{I} - \boldsymbol{v}_\mathrm{II}, \quad (8.3)$$

$$\boldsymbol{k} = \boldsymbol{k}_\mathrm{I} + \boldsymbol{k}_\mathrm{II}, \quad \boldsymbol{k}_\mathrm{I\,II} = \tfrac{1}{2}(\boldsymbol{k}_\mathrm{I} - \boldsymbol{k}_\mathrm{II}). \quad (8.4)$$

After (4.3), the difference vector $\boldsymbol{v}_\mathrm{I\,II}$ has no component normal to the interface everywhere on the interface:

$$\boldsymbol{v}_\mathrm{I\,II} = \boldsymbol{v}_\mathrm{I\,II}{}^{\mathrm{tang}}. \qquad (8.5)$$

The superscript "tang" for any vector $\boldsymbol{a}$ means

$$\boldsymbol{a}^{\mathrm{tang}} = \boldsymbol{a} - \boldsymbol{n}\,\boldsymbol{n}\cdot\boldsymbol{a} \qquad (8.6)$$

where $\boldsymbol{n}$ may be understood as $\boldsymbol{n}_\mathrm{I}$ or $\boldsymbol{n}_\mathrm{II}$. With this, (8.2) together with (8.1) gives

$$\begin{aligned}q &= -\boldsymbol{v}\cdot\boldsymbol{k} - \boldsymbol{v}_\mathrm{I\,II}\cdot\boldsymbol{k}_\mathrm{I\,II}\\ &= -\boldsymbol{v}_\mathrm{I\,II}{}^{\mathrm{tang}}\cdot\boldsymbol{k}_\mathrm{I\,II}{}^{\mathrm{tang}}.\end{aligned} \qquad (8.7)$$

Inserting into (7.8) yields the desired expression for interfacial entropy production

$$\Theta = \int_\sigma d\sigma (T^{-1} \boldsymbol{v}_{\text{I II}}{}^{\text{tang}} \cdot \boldsymbol{k}_{\text{I II}}{}^{\text{tang}} - T^{-1}{}_{\text{I II}} q_{\text{I II}}). \quad (8.8)$$

This entropy production contains a pair of a two-dimensional vector flux and force $\boldsymbol{k}_{\text{I II}}{}^{\text{tang}}$ and $T^{-1} \boldsymbol{v}_{\text{I II}}{}^{\text{tang}}$ and a pair of a scalar flux and force $q_{\text{I II}}$ and $-T^{-1}{}_{\text{I II}}$. From geometrical reasons (Curie's law) they don't combine with each other in a local linear constitutive law which therefore finally is

$$\boldsymbol{k}_{\text{I II}}{}^{\text{tang}} = a \, T^{-1} \boldsymbol{v}_{\text{I II}}{}^{\text{tang}} \quad (8.9)$$

$$q_{\text{I II}} = -C \, T^{-1}{}_{\text{I II}}. \quad (8.10)$$

The phenomenological coefficients a, C have to be positive, in order to guarantee positiveness of Θ. Eq. (8.9) is the well-known boundary condition of mechanical (frictional) slip. Eq. (8.10) is the well-known boundary condition of temperature jump. Under the circumstances considered, no cross effects between velocities and temperatures appear (no thermal slip and no mechano-caloric effect).

If properly linearized, the Navier–Stokes and Fourier equations, together with the boundary conditions (4.3), (8.1, 2, 9 and 10) determine a unique solution for the velocity and temperature fields, due to the positiveness of entropy production. — That no cross effects appear stems from the assumption that no (two-dimensional) flows of momentum and energy in (along) the interface exist. Before we try to get rid of this restriciton, a short reminder seems appropriate of the tensor analysis in a two-dimensional curved surface imbedded in three-dimensional Euclidean space.

§ 9. A Mathematical Digression on Vectors and Tensors in an Interface

The moving interface shall be discribed by two Gaussian parameters ξ^1, ξ^2. The Cartesian coordinates x_μ ($\mu = 1, 2, 3$) of any surface point are functions of time and of these parameters

$$x_\mu = X_\mu(t, \xi^1, \xi^2). \quad (9.1)$$

Let us introduce the tangential Cartesian vectors ($\boldsymbol{n}$ normal of surface)

$$X_{\mu i} = \frac{\partial X_\mu}{\partial \xi^i}, \quad \text{hence} \quad n_\mu X_{\mu i} = 0, \; i = 1, 2. \quad (9.2)$$

The metric in the interface is then given by

$$dx_\mu \, dx_\mu = G_{ik} \, d\xi^i \, d\xi^k \quad (9.3)$$

with the 2×2 covariant metric tensor in ξ-space

$$G_{ik} = X_{\mu i} X_{\mu k} = G_{ki}. \quad (9.4)$$

For Latin sub- and superscripts the summation rule is adopted too. After (9.2), $X_{\mu i}$, for fixed μ, is a covariant vector in ξ-space. The pertaining contravariant vector in ξ-space $X_\mu{}^k$ is uniquely introduced by

$$X_{\mu i} X_\mu{}^k = \delta_i{}^k, \quad n_\mu X_\mu{}^k = 0, \quad k = 1, 2. \quad (9.5)$$

Thus, looked at as a Cartesian vector (k fixed), $X_\mu{}^k$ is tangential to the surface too. Furthermore, one has

$$X_{\mu i} X_\nu{}^i = \delta_{\mu\nu} - n_\mu n_\nu, \quad (9.6)$$

because this Cartesian tensor applied to the tangential vectors $X_{\nu k}$ reproduces them, after (9.5), and annihilates any vector perpendicular to the surface. In analogy with (9.4) one has

$$G^{ik} = X_\mu{}^i X_\mu{}^k = G^{ki}, \quad G_{il} G^{lk} = \delta_i{}^k. \quad (9.7)$$

The tensor G^{ik} is the contravariant metric tensor in ξ-space.

The connection between covariant and contravariant components A_i and A^i of a vector in ξ-space is

$$A^i = G^{ik} A_k, \quad A_i = G_{ik} A^k \quad (9.8)$$

(raising and lowering of Latin indices at will). By the aid of the "hybrid" tensors $X_{\mu i}$, $X_\mu{}^i$ (Cartesian vectors for fixed i, vectors in ξ-space for fixed μ) one can assign a tangential Cartesian vector a_μ to any vector A^i, A_i in ξ-space and vice versa, cf. (9.6),

$$a_\mu = X_{\mu i} A^i = X_\mu{}^i A_i,$$
$$A_i = a_\mu X_{\mu i}, \quad A^i = a_\mu X_\mu{}^i. \quad (9.9)$$

The surface element $d\sigma$ (true area) is given by

$$d\sigma = \sqrt{G} \, d\xi^1 \, d\xi^2 = \sqrt{G} \, d^2\xi, \quad (9.10)$$

where G is the determinant of the covariant metric tensor in ξ-space:

$$G = \begin{vmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{vmatrix}. \quad (9.11)$$

To describe surface flows one has to consider vector densities in ξ-space. Following Weyl's [10] notation we denote them by Gothic letters. A scalar, vector, etc. density in ξ-space is obtained by multiplying a scalar, vector, etc. in ξ-space by $\sqrt{G}$. We consider two examples.

[10] H. Weyl, Raum, Zeit, Materie, 5. Aufl., Springer, Berlin 1923, § 14.

First, a (surface) heat flow density $\mathfrak{Q}_i$ in ξ-space can be set up in the way

$$\mathfrak{Q}_i = - \sqrt{G}\, \varLambda \frac{\partial T}{\partial \xi^i}, \qquad (9.12)$$

where $\varLambda$ is a scalar surface heat conductivity. In analogy with (9.9) one may assign a tangential CARTESIAN vector which, for distinction, we denote by a Latin letter

$$Q_\mu = X_\mu{}^i \mathfrak{Q}_i / \sqrt{G} = - \varLambda\, X_\mu{}^i \frac{\partial T}{\partial \xi^i}$$
$$\text{or}\quad \mathbf{Q} = - \varLambda (\nabla T)^{\text{tang}}. \quad (9.13)$$

The second form, with the nabla vector, is simply a short-hand writing for the surface gradient. In § 10 we shall use the nabla vector only in this sense. The quantity $\partial \mathfrak{Q}^i / \partial \xi^i$ is a scalar density in ξ-space. Dividing by $\sqrt{G}$ gives

$$\frac{1}{\sqrt{G}} \frac{\partial \mathfrak{Q}^i}{\partial \xi^i}, \text{ the } scalar\ divergence \text{ in } \xi\text{-space.} \quad (9.14)$$

"Scalar", as always, means that this quantity is invariant under any one-to-one mapping of the surface parameters ξ. The interface shall be closed and the pertaining ξ-domain fixed once for all. For instance, one may think of the ξ's as the two polar angles taken from a fixed center lying inside the interface. Then GAUSS' theorem, applied to ξ-space, says

$$\iint\limits_{\xi\text{-domain}} d^2\xi \frac{\partial \mathfrak{Q}^i}{\partial \xi^i} = \int\limits_\sigma d\sigma \frac{1}{\sqrt{G}} \frac{\partial \mathfrak{Q}^i}{\partial \xi^i} = 0,$$
$$(9.15)$$

due to periodicity at the border of the ξ-domain.

Second, we consider a (surface) μ-momentum flow density $\mathfrak{p}_{\mu i}$ in ξ-space. This is a "hybrid" tensor density, similar to $X_{\mu i}$, which is a "hybrid" tensor. Indeed, the two CARTESIAN vectors, contained in $\mathfrak{p}_{\mu i}$, shall be tangential to the surface:

$$n_\mu\, \mathfrak{p}_{\mu i} = 0. \qquad (9.16)$$

This subsidiary condition means that $\mathfrak{p}_{\mu i}$ has four independent components or even only three because of symmetry (see below). What would be a constitutive law, somehow corresponding to Eq. (9.12), in that case? To set it up, we switch over to a pure tensor density in ξ-space, cf. (9.9),

$$\mathfrak{P}_{ki} = X_{\mu k}\, \mathfrak{p}_{\mu i} = \mathfrak{P}_{ik} \quad \text{or} \quad \mathfrak{p}_{\mu i} = X_\mu{}^k \mathfrak{P}_{ki}. \quad (9.17)$$

The symmetry is required by angular momentum conservation, as will be shown in § 10. Now, let v_μ be a velocity field at the interface. Then, in accor-

dance with tensorial behaviour, one might put

$$\mathfrak{P}_{ik} = \sqrt{G}(P\, G_{ik} - 2\, H\, \overline{V}_{ik}) \qquad (9.18)$$

with

$$\overline{V}_{ik} = \overline{V}_{ki}$$
$$= \tfrac{1}{2}\Big(\frac{\partial v_\mu}{\partial \xi^i} X_{\mu k} + \frac{\partial v_\mu}{\partial \xi^k} X_{\mu i}\Big) - \tfrac{1}{2}\, G_{ik} \frac{\partial v_\mu}{\partial \xi^l} X_\mu{}^l. \quad (9.19)$$

Eq. (9.19) defines an irreducible deformation-rate tensor in ξ-space with the property

$$\overline{V}_i{}^i = 0.$$

The P in (9.18) means the thermo-static surface pressure, the negative of surface tension, and is a scalar in ξ-space. It will be disregarded in § 10. The H (capital eta) is a scalar surface shear viscosity. Eq. (9.18) is only the simplest constitutive law for a dynamical surface pressure tensor density in ξ-space. A simple term, analogous to the three-dimensional bulk viscosity term, has been omitted, and no use has been made of the possible existence of curvature of ξ-space (the fourth rank RIEMANNian tensor). In conclusion let us look at the divergence operation. The quantities

$$\frac{1}{\sqrt{G}} \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i}, \text{ three } scalar\ divergences \text{ in } \xi\text{-space}$$
$$(\mu = 1, 2, 3) \qquad (9.20)$$

are invariant under any one-to-one mapping of the ξ's. Looked at from three dimensional space, they are the CARTESIAN components of a vector. GAUSS' theorem in ξ-space again says

$$\iint\limits_{\xi\text{-domain}} d^2\xi \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i} = \int\limits_\sigma d\sigma \frac{1}{\sqrt{G}} \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i} = 0. \quad (9.21)$$

This is enough to formulate what we have in mind.

§ 10. Boundary Conditions at an Interface with Surface Flows

The global conditions (6.3 and 8) required by conservation of momentum and energy have in § 8 been satisfied by the strong postulates (8.1 and 2). Sight of (9.15 and 21) suggests the following weaker postulates

$$k_{\mathrm{I}\mu} + k_{\mathrm{II}\mu} - \frac{1}{\sqrt{G}} \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i} = 0, \qquad (10.1)$$

$$v_{\mathrm{I}\mu} k_{\mathrm{I}\mu} + q_{\mathrm{I}} + v_{\mathrm{II}\mu} k_{\mathrm{II}\mu} + q_{\mathrm{II}} - \frac{1}{\sqrt{G}} \frac{\partial v_\mu\, \mathfrak{p}_\mu{}^i + \mathfrak{Q}^i}{\partial \xi^i} = 0.$$
$$(10.2)$$

The new terms indeed give zero on integration over the closed interface. Physically, (10.1) means that we have introduced a contravariant flow density $\mathfrak{p}_\mu{}^i$ in ξ-space of CARTESIAN μ-momentum, the divergence of which appears in the local momentum balance of the interface. Correspondingly, (10.2) means that a contravariant flow density $v_\mu \mathfrak{p}_\mu{}^i + \mathfrak{Q}^i$ in ξ-space of energy has been introduced, the divergence of which appears in the local energy balance of the interface. By $\boldsymbol{v}$ the average velocity defined in (8.3) is meant. The splitting of the surface energy flow density into a mechanical (work) part and the surface heat flow density $\mathfrak{Q}^i$ is appropriate. Heat flow is something which ought to be GALILEAN invariant. Let us consider a new primed CARTESIAN system moving with constant velocity $\boldsymbol{u}$ with respect to the original one. Then

$$\boldsymbol{v}_{\mathrm{I(II)}} = \boldsymbol{v'}_{\mathrm{I(II)}} + \boldsymbol{u}, \quad \boldsymbol{v} = \boldsymbol{v'} + \boldsymbol{u}. \quad (10.3)$$

The $\boldsymbol{k}_{\mathrm{I,II}}$ are invariant and with them $\mathfrak{p}_\mu{}^i$, after (10.1). The $q_{\mathrm{I,II}}$ are invariant too. Replacing in (10.2) the original velocities by the primed velocities according to (10.3) gives a term linear in $\boldsymbol{u}$

$$u_\mu\left(k_{\mathrm{I}\mu} + k_{\mathrm{II}\mu} - \frac{1}{\sqrt{G}} \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i}\right),$$

which vanishes after (10.1). Hence, (10.2) is true with the primed velocities instead of the original ones, which means that $\mathfrak{Q}^i = \mathfrak{Q}'^i$. The surface heat flow density, as introduced, is GALILEAN invariant.

If the interface would even carry a momentum and an energy per unit area, then in (10.1 and 2) time-derivatives of these surface densities would appear. This would again lead into a more general theory which we don't enter here.

Before turning to entropy production, let us look at the global angular momentum condition (6.5). With (10.1) and (9.1 and 10) it reads

$$\iint\limits_{\xi\text{-domain}} \mathrm{d}^2\xi\left(X_\mu \frac{\partial \mathfrak{p}_\nu{}^l}{\partial \xi^l} - X_\nu \frac{\partial \mathfrak{p}_\mu{}^l}{\partial \xi^l}\right) = 0.$$

As, cf. (9.2),

$$X_\mu \frac{\partial \mathfrak{p}_\nu{}^l}{\partial \xi^l} = \frac{\partial X_\mu \mathfrak{p}_\nu{}^l}{\partial \xi^l} - X_{\mu l} \mathfrak{p}_\nu{}^l$$

and as the first term on the right vanishes on integration due to GAUSS' theorem in ξ-space, we are left with

$$\iint \mathrm{d}^2\xi\,(-X_{\mu l} \mathfrak{p}_\nu{}^l + X_{\nu l} \mathfrak{p}_\mu{}^l) = 0.$$

This is guaranteed by the subsidiary condition

$$X_{\mu l} \mathfrak{p}_\nu{}^l = X_{\nu l} \mathfrak{p}_\mu{}^l \quad (10.4)$$

for the "hybrid" tensor density $\mathfrak{p}$. What does it mean? First, from (9.2), one concludes

$$X_{\mu l} n_\nu \mathfrak{p}_\nu{}^l = n_\nu X_{\nu l} \mathfrak{p}_\mu{}^l = 0.$$

As $X_{\mu l} \neq 0$ in general, one also has, as anticipated in (9.16),

$$n_\nu \mathfrak{p}_\nu{}^l = 0 \quad \text{or} \quad n_\nu \mathfrak{p}_{\nu l} = 0. \quad (10.4a)$$

This means that this "hybrid" tensor density has no CARTESIAN component normal to the surface. This is physically clear; such a component would rotate a surface element at an infinite acceleration. Second, let us multiply (10.4) by $X_\mu{}^i X_\nu{}^k$. After (9.5) this gives

$$\delta_l{}^i X_\nu{}^k \mathfrak{p}_\nu{}^l = \delta_l{}^k X_\mu{}^i \mathfrak{p}_\mu{}^l.$$

The sum over l can be carried out. The rest can be rewritten in terms of the pure tensor density in ξ-space which has been defined in (9.17), giving

$$\mathfrak{P}^{ki} = \mathfrak{P}^{ik}. \quad (10.5)$$

This is the symmetry anticipated in (9.17). It is analogous to the familiar symmetry of the three-dimensional pressure tensor, cf. (6.4), which also stems from angular momentum conservation.

Now we are ready to discuss the entropy production (7.8). From (10.2) we take, recalling the abbreviations (7.7), (8.3 and 4)

$$q = \frac{1}{\sqrt{G}} \frac{\partial v_\mu \mathfrak{p}_\mu{}^i + \mathfrak{Q}^i}{\partial \xi^i} - \boldsymbol{v} \cdot \boldsymbol{k} - \boldsymbol{v}_{\mathrm{I\,II}} \cdot \boldsymbol{k}_{\mathrm{I\,II}}.$$

By aid of (10.1) we replace $\boldsymbol{k}$:

$$q = \frac{1}{\sqrt{G}} \frac{\partial v_\mu \mathfrak{p}_\mu{}^i + \mathfrak{Q}^i}{\partial \xi^i} - v_\mu \frac{1}{\sqrt{G}} \frac{\partial \mathfrak{p}_\mu{}^i}{\partial \xi^i} - \boldsymbol{v}_{\mathrm{I\,II}} \cdot \boldsymbol{k}_{\mathrm{I\,II}},$$

or simplifying and remembering (8.5)

$$q = \frac{\partial v_\mu}{\partial \xi^i} \mathfrak{p}_\mu{}^i/\sqrt{G} + \frac{\partial \mathfrak{Q}^i}{\partial \xi^i}\Big/\sqrt{G} - \boldsymbol{v}_{\mathrm{I\,II}}^{\mathrm{tang}} \cdot \boldsymbol{k}_{\mathrm{I\,II}}^{\mathrm{tang}}.$$

We slightly rewrite this. Instead of the "hybrid" tensor density $\mathfrak{p}$ we introduce the pure tensor density $\mathfrak{P}$ in ξ-space according to (9.17 and 2)

$$\frac{\partial v_\mu}{\partial \xi^i} \mathfrak{p}_\mu{}^i = \frac{\partial v_\mu}{\partial \xi^i} X_{\mu k} \mathfrak{P}^{ki} = \frac{\partial v_\mu}{\partial \xi^i} \frac{\partial X_\mu}{\partial \xi^k} \mathfrak{P}^{ki}.$$

And, after having multiplied q with T^{-1}, we rewrite the middle term

$$T^{-1} \frac{\partial \mathfrak{Q}^i}{\partial \xi^i}\Big/\sqrt{G} = \frac{\partial T^{-1} \mathfrak{Q}^i}{\partial \xi^i}\Big/\sqrt{G} - \frac{\partial T^{-1}}{\partial \xi^i} \mathfrak{Q}^i/\sqrt{G}.$$

Here, the first term on the right is a divergence in ξ-space and gives no contribution on integration. So, the surface entropy production (7.8) for the

present model is

$$\Theta = \int_\sigma d\sigma \left(-T^{-1} \frac{\partial v_\mu}{\partial \xi^i} \frac{\partial X_\mu}{\partial \xi^k} \, \mathfrak{P}^{ki}/\sqrt{G} + \frac{\partial T^{-1}}{\partial \xi^i} \, \mathfrak{Q}^i/\sqrt{G} \right.$$
$$\left. + T^{-1} \boldsymbol{v}_{\mathrm{I\,II}}{}^{\mathrm{tang}} \cdot \boldsymbol{k}_{\mathrm{I\,II}}{}^{\mathrm{tang}} - T^{-1}{}_{\mathrm{I\,II}} \, q_{\mathrm{I\,II}} \right).$$
(10.6)

This enables us to set up constitutive laws for the interface.

Compared with (8.8) there are two new terms in the integrand: a force-flux pair of tensorial character in ξ-space, namely

$$-T^{-1} \frac{\partial v_\mu}{\partial \xi^i} \frac{\partial X_\mu}{\partial \xi^k} \quad \text{and} \quad \mathfrak{P}^{ki}/\sqrt{G},$$

and a force-flux pair of vectorial character in ξ-space, namely

$$\frac{\partial T^{-1}}{\partial \xi^i} \quad \text{and} \quad \mathfrak{Q}^i/\sqrt{G}.$$

The third term has the same character. Indeed, due to (9.6), instead of a CARTESIAN scalar product of tangential vectors one can write

$$\boldsymbol{v}_{\mathrm{I\,II}}{}^{\mathrm{tang}} \cdot \boldsymbol{k}_{\mathrm{I\,II}}{}^{\mathrm{tang}} = v_{\mathrm{I\,II}\mu} X_{\mu i} X_{,}{}^i k_{\mathrm{I\,II}\nu}, \quad (10.7)$$

a scalar product of two vectors in ξ-space. The fourth term simply has a scalar force-flux pair.

From geometrical reasons (CURIE's law) only quantities of the same tensorial character combine with each other in the constitutive laws.

Hence, from Eq. (10.6) with (10.5) one immediately recovers the surface friction law, contained in (9.18 and 19), as the simplest possibility [11]. Surface friction has first been discussed by BOUSSINESQ [12], later on by KLEMM [13]. We are not concerned with it here. Nor are we concerned with the scalar force-flux pair which has already been discussed after Eq. (8.10) [14].

But we have anew to look at the vectors. As there are now two vector forces in ξ-space, viz. $T^{-1} v_{\mathrm{I\,II}\mu} X_{\mu i}$, see (10.7), and $\partial T^{-1} \partial \xi^i$, there will be cross effects:

$$k_{\mathrm{I\,II}\nu} X_{\nu i} = a \, T^{-1} v_{\mathrm{I\,II}\mu} X_{\mu i} - b \, \frac{\partial T^{-1}}{\partial \xi^i}, \quad (10.8)$$

$$\mathfrak{Q}_i/\sqrt{G} = b \, T^{-1} v_{\mathrm{I\,II}\mu} X_{\mu i} + c \, \frac{\partial T^{-1}}{\partial \xi^i}. \quad (10.9)$$

The ONSAGER relation, already incorporated in (10.8 and 9), is one with the negative sign (an ONSAGER–CASIMIR relation [15]) because $T^{-1} v_{\mathrm{I\,II}\mu} X_{\mu i}$ is an odd force and $\partial T^-/\partial \xi^i$ is an even force under time reversal. The necessary and sufficient conditions for positiveness of entropy production therefore are: $a > 0, \ c > 0$.

For convenience we rewrite (10.8 and 9) in a twofold way. First, we turn it into a CARTESIAN vector form by multiplying both lines with $X_\mu{}^i$, re-using (9.6) and applying the notation from (9.13):

$$\boldsymbol{k}_{\mathrm{I\,II}}{}^{\mathrm{tang}} = a \, T^{-1} \boldsymbol{v}_{\mathrm{I\,II}}{}^{\mathrm{tang}} - b \, (\nabla T^{-1})^{\mathrm{tang}}, \quad (10.10)$$

$$\boldsymbol{Q} = b \, T^{-1} \boldsymbol{v}_{\mathrm{I\,II}}{}^{\mathrm{tang}} + c \, (\nabla T^{-1})^{\mathrm{tang}}. \quad (10.11)$$

By the way, we recover the restricted theory of § 8, especially Eq. (8.9), if b and c are put equal to zero. As a second alternative form we solve for the tangential slip velocity:

$$\boldsymbol{v}_{\mathrm{I\,II}}{}^{\mathrm{tang}} = \alpha \, T^{-1} \boldsymbol{k}_{\mathrm{I\,II}}{}^{\mathrm{tang}} + \beta \, (\nabla T^{-1})^{\mathrm{tang}}, \quad (10.12)$$

$$\boldsymbol{Q} = \beta \, T^{-1} \boldsymbol{k}_{\mathrm{I\,II}}{}^{\mathrm{tang}} + \gamma \, (\nabla T^{-1})^{\mathrm{tang}}. \quad (10.13)$$

with

$$\alpha = T^2/a > 0, \quad \beta = b \, T/a, \quad \gamma = c + b^2/a > 0,$$
$$\alpha \gamma - \beta^2 = T^2 \, c/a > 0. \quad (10.14)$$

Of course, this simply amounts to an interchange of the one force-flux pair. Both "forces" are now even, the ONSAGER matrix is symmetrical.

The physical significance and the comparison with the discussion in § 3 are readily at hand. The first term on the right of Eq. (10.12) is the mechanical slip velocity. The second term is the thermal slip velocity, for a special case introduced in (3.1). Comparison shows that

$$\beta = -\sigma \lambda \, T^2/p,$$

where σ is the thermal slip number of (3.1). The second term on the right of Eq. (10.13) is the thermal surface heat flow, γ being essentially the surface heat conductivity, see (9.13). The first term is the mechanical surface heat flow, for a special case introduced in (3.7). Comparison shows that also

$$\beta = -\varkappa \, T/\eta,$$

from which the previous relation (3.9) is recovered.

---

[11] It is understood that now one puts P equal to zero in (9.18). The thermo-static surface pressure (neg-tension) P had been lost when we made the assumption of vanishing (free) energy (and entropy) per unit area of the interface. For the system "dilute gas/fluid" this is perfectly legitimate. — To stress the vanishing of P, i. e. the fact that $\mathfrak{P}$ is only a surface *friction* tensor density, one might write $\mathfrak{P}'$ instead of $\mathfrak{P}$ everywhere.

[12] J. BOUSSINESQ, Ann. d. Chim. et Phys. **29**, 349 [1913].

[13] A. KLEMM, Phys. Z. **39**, 783 [1938].

[14] Perhaps we should be concerned, because the surface bulk viscosity term has the same character and that might lead to cross effects. But we don't pursue it here. (However, see note added in proof.)

[15] H. B. G. CASIMIR, Rev. Mod. Phys. **17**, 343 [1945].

Positiveness of entropy production requires: if $\beta \neq 0$, then $\alpha \neq 0$, $\gamma \neq 0$, see (10.14). That means: if there is a thermal slip, then *a fortiori* a mechanical slip and a thermal surface heat flow exist. This has been anticipated in § 3.

It is interesting to look at the coefficients α, β, γ for the system "dilute gas/fluid (or solid)". They can be reduced to three *ad hoc* mean free paths $l_\alpha > 0$, $l_\beta \lessgtr 0$, $l_\gamma > 0$ by putting

$$\alpha = \frac{T}{\eta} l_\alpha , \quad \beta = \left(\frac{T^3 k}{m} \right)^{1/2} l_\beta , \quad \gamma = \frac{T^2 k \eta}{m} l_\gamma .$$

From the second law condition then follows

$$l_\alpha l_\gamma > l_\beta^2 .$$

By order of magnitude the thermal surface heat flow therefore is

$$\boldsymbol{Q} = - l_\gamma \frac{k\eta}{m} (\nabla T)^{\text{tang}} \approx - l_\gamma \lambda \nabla T = l_\gamma \boldsymbol{q} ,$$

$$|Q| > \frac{l_\beta^2}{l_\alpha} |q| ,$$

where $\boldsymbol{q}$ denotes the ordinary heat flow somewhere within the gas. This suggests that the surface heat flow takes place in an (anisotropic) layer of thickness l_γ, which could be comparable with the ordinary mean free path $l = \eta / \varrho \bar{c}$. This might be a hint for kinetic theory.

However obscure the kinetic theory problem is, it seems allowed to say in conclusion that the phenomenological problem of boundary conditions at least fits very well into the framework of non-equilibrium thermodynamics.

Note added in proof (10. 7. 1967):

To understand the thermophoretic force on particles with large heat conductivity, it seems promising to include the surface bulk-viscosity term which had been omitted in the discussion of § 10, cf. footnote [14]. For this purpose one has to decompose the frictional surface pressure, occurring in (10.6), into its irreducible parts

$$\mathfrak{P}^{ki} = \mathfrak{P}^{ik} = G^{ki} \mathfrak{P} + \overline{\mathfrak{P}}^{ki} .$$

The irreducible second rank tensor density $\overline{\mathfrak{P}}^{ki}$ is characterized by

$$\overline{\mathfrak{P}}^{ki} = \overline{\mathfrak{P}}^{ik} , \quad \overline{\mathfrak{P}}_i^{i} = 0 .$$

So, the scalar density $\mathfrak{P}$ is given by ($\delta_i^i = 2!$)

$$\mathfrak{P} = \tfrac{1}{2} \mathfrak{P}_i^{i} .$$

The deformation-rate tensor which is multiplied with the frictional surface pressure in (10.6), has to be symmetrized because of the symmetry of the pressure tensor. The analogous decomposition into irreducible parts is already contained in (9.19):

$$\frac{1}{2} \left(\frac{\partial v_\mu}{\partial \xi^i} \frac{\partial X_\mu}{\partial \xi^k} + \frac{\partial v_\mu}{\partial \xi^k} \frac{\partial X_\mu}{\partial \xi^i} \right) = \overline{V}_{ik} + \frac{1}{2} G_{ik} \frac{\partial v_\mu}{\partial \xi^l} X_\mu^{l} .$$

The entropy production (10.6) then takes the fully elaborate form

$$\Theta = \int_\sigma d\sigma \left(- T^{-1} \overline{V}_{ik} \overline{\mathfrak{P}}^{ik} / \sqrt{G} + T^{-1} \boldsymbol{v}_{\mathrm{I\,II}}^{\text{tang}} \cdot \boldsymbol{k}_{\mathrm{I\,II}}^{\text{tang}} \right.$$
$$\left. + \frac{\partial T^{-1}}{\partial \xi^i} \mathfrak{Q}^i / \sqrt{G} - T^{-1} \frac{\partial v_\mu}{\partial \xi^l} X_\mu^{l} \mathfrak{P} / \sqrt{G} - T^{-1}_{\mathrm{I\,II}} q_{\mathrm{I\,II}} \right) .$$

This explicitly shows the existence of two scalar force-flux pairs, the last two terms in the parenthesis, besides the two vectorial force-flux pairs discussed in § 10 and the irreducible tensor force-flux pair which gives rise to surface shear viscosity, cf. (9.18) with $\overline{\mathfrak{P}}_{ik}$ instead of $\mathfrak{P}_{ik}$ and $P = 0$. The constitutive law for the scalars now is

$$\mathfrak{P} / \sqrt{G} = - A T^{-1} \frac{\partial v_\mu}{\partial \xi^l} X_\mu^{l} + B T^{-1}_{\mathrm{I\,II}} , \quad (\text{N 2})$$

$$q_{\mathrm{I\,II}} = - B T^{-1} \frac{\partial v_\mu}{\partial \xi^l} X_\mu^{l} - C T^{-1}_{\mathrm{I\,II}} , \quad (\text{N 3})$$

which is formally very similar to (10.8 and 9). The ONSAGER–CASIMIR symmetry has already been incorporated, the second law requires $A > 0$, $C > 0$. The phenomenological coefficient $A T^{-1}$ is the surface bulk viscosity, the coefficient C already appeared in (8.10). The coefficient B again produces a coupling of mechanical forces with thermal properties. This time the heat flux normal to the surface, $q_{\mathrm{I\,II}}$, is involved. That heat flux does not vanish at the surface of highly heat-conducting aerosol particles where the tangential temperature gradient becomes small. So, this coupling might play a role in the strong thermophoretic force observed with such particles [15].

---

[15] C. F. SCHADT and R. D. CADLE, J. Phys. Chem. **65,** 1689 [1961].