# Heat Transfer Through a Gas Between Parallel Plates

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Within the framework of boundary conditions recently developed for the linearized Boltzmann equation <sup>1</sup>, the problem of heat transfer between parallel plates can be solved in terms of "transport-relaxation eigenfunctions". The particle distribution function and the total heat transfer in the Knudsen case are exactly expressed by integrals over the interfacial scattering kernel occurring in the new scheme. A detailed discussion of the general case gives an exact formula and sign statement for the temperature jump at parallel plates. An approximation, which encompasses v. Smoluchowski's approach, lies at hand. This approximation is also readily confirmed by a moment method.

As another application of the boundary conditions recently developed for the Boltzmann equation <sup>1</sup>, the heat transfer through a Boltzmann gas between two parallel plates of slightly different temperatures is studied in this paper. The new boundary conditions, of quite a general character, form a closer union with the linearized Boltzmann equation than those which have been in use up to now. As a consequence thereof, a lucid formal solution of the said heat transfer problem is now possible, for any pressure from the Knudsen to the hydrodynamical regime.

The boundary value problem in the kinetic theory of gases is old. It dates from Maxwell's times and is still fascinating. The general properties of surface scattering laws have been studied not so long ago <sup>2,3</sup>, but in a way different from the method developed in Reference <sup>1</sup>. An extended literature exists already on the heat transfer through a gas between parallel plates, see <sup>4</sup>. Because the present approach has a novel starting point, it may be permitted and convenient to give a rather coherent account of the theory. An excerpt has been published before <sup>5</sup>. The present paper also supplements related approximate considerations of the same problem <sup>6</sup>.

### 1. Formulation of the Problem

The gas, medium I, shall be confined between the two parallel plates resting at  $x=\pm d/2$ , of the same material, medium II. The temperatures of the plates  $T_{\rm II}(\pm d/2)$ , slightly different, are given. The stationary state of the gas has to be determined from

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the linearized Boltzmann equation and its boundary conditions.

The distribution function of the gas deviates slightly from an absolute resting Maxwellian with temperature  $T_0$ :

$$f = f_0 (1 + \Phi)$$
.

The relative deviation  $\Phi$ , in the following simply called "the distribution", depends, besides the momentum, on the x-coordinate only and obeys the linearized Boltzmann equation

$$c_x \, \partial \Phi / \partial x + \omega (\Phi) = 0 \,. \tag{1.1}$$

As to the dependence on the particle momentum, the distribution is rotationally invariant about the  $p_x$ -axis:

$$\Phi = \Phi(x, \mathbf{p}) = \Phi(x, p_x, p^2)$$
 (1.2) with  $p^2 = p_x^2 + p_y^2 + p_z^2$ .

The "thermodynamical force exerted by the solid at the interface" x=d/2 or -d/2 is

$$F_{\rm II} = (T_{\rm II} - T_{\rm 0})/T_{\rm 0},$$
 (1.3)

cf. § 4 of Reference <sup>1</sup>. The  $F_{\rm II}(\pm d/2)$  are the applied "driving forces". The resulting distribution will be linear in them.

Without loss of generality, let us from now on choose

$$-F_{\rm II}\left(-\frac{d}{2}\right) = F_{\rm II}\left(\frac{d}{2}\right). \tag{1.4}$$

This means that the "driving force" is unchanged if the plate arrangement is reflected at the point  $\mathbf{x}=0$ , with simultaneous sign reversal on the  $F_{\rm II}$ 's. So, because  $\Phi$  is proportional to, say,  $F_{\rm II}(d/2)$ , the distribution must have the corresponding (anti-) symmetry

$$-\Phi(-x,-\mathbf{p})=\Phi(x,\mathbf{p}). \qquad (1.5)$$



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Denoting the "time reversed" state by

$$\Phi_{\mathrm{T}}(x, \mathbf{p}) \equiv \Phi(x, -\mathbf{p}),$$
 (1.6)

one can express the symmetry (1.5) in an abbreviating manner as

$$-\Phi_{\mathrm{T}}(-x) = \Phi(x) . \qquad (1.7)$$

The boundary conditions have been formulated in Ref. <sup>1</sup> in terms of the *interfacial force-flux pair of the gas* 

$$\begin{split} F_{\rm I} &= \frac{1}{\sqrt{2}} P_+ (\Phi + \Phi_{\rm T})_{x = d/2}, \\ J_{\rm I} &= \frac{1}{\sqrt{2}} P_+ c (\Phi - \Phi_{\rm T})_{x = d/2} \end{split} \tag{1.8}$$

and of the interfacial force-flux pair of the solid

$$F_{\rm II} = \left(T_{\rm II} \left(\frac{d}{2}\right) - T_{\rm 0}\right) / T_{\rm 0},$$

$$J_{\rm II} = q_{\rm II} \left(\frac{d}{2}\right) / P_{\rm 0}. \tag{1.9}$$

Due to (1.4) and (1.5) it is only necessary to talk about the wall x = d/2. In (1.8)

$$P_{+}=P_{+}(c)$$

means the Heaviside step function,  $P_{+}=0$  for c<0,  $P_{+}=1$  for c>0, of the particle velocity component in the direction of the outer unit normal  $\boldsymbol{n}_{\rm I}$  of the gas

$$c = \boldsymbol{c} \cdot \boldsymbol{n}_{\mathrm{I}}$$
, hence  $c = c_x$  at  $x = d/2$ . (1.10)

The heat flux component  $q_{\rm II}$  in (1.9) has the meaning

$$q_{\rm II} = \boldsymbol{q}_{\rm II} \cdot \boldsymbol{n}_{\rm II}$$
, hence  $q_{\rm II} = -q_x$  at  $x = d/2$ , (1.11)

where  $\mathbf{n}_{\text{II}} = -\mathbf{n}_{\text{I}}$  is the outer unit normal of the solid.  $P_0 = n_0 k T_0$  is the absolute equilibrium pressure.

In terms of these quantities, the boundary conditions at the resting wall at x = d/2 are

$$J_{\mathrm{I}}(\boldsymbol{p}) = \int L_{\mathrm{II}}(\boldsymbol{p}, \boldsymbol{p}') F_{\mathrm{I}}(\boldsymbol{p}') \, \mathrm{d}\gamma' + L_{\mathrm{III}}(\boldsymbol{p}) F_{\mathrm{II}}$$

$$J_{\mathrm{II}} = \int L_{\mathrm{III}}(\boldsymbol{p}') F_{\mathrm{I}}(\boldsymbol{p}') \, \mathrm{d}\gamma' + L_{\mathrm{IIII}} F_{\mathrm{II}},$$
(1.13)

according to Eqs. (4.15) of Reference <sup>1</sup>. The integration element is

$$d\gamma = \frac{f_0}{n_0} d^3p$$
, hence  $\int d\gamma = 1$ . (1.14)

The kernel  $L_{II}$ , with the dimension of a velocity, Onsager-symmetrical in  $\boldsymbol{p}, \boldsymbol{p}'$ , has the projection properties

$$P_{+}(c) L_{\text{II}}(\boldsymbol{p}, \boldsymbol{p}') = L_{\text{II}}(\boldsymbol{p}, \boldsymbol{p}') P_{+}(c')$$
$$= L_{\text{II}}(\boldsymbol{p}, \boldsymbol{p}'). \qquad (1.15)$$

The impenetrability of the wall for the gas particles is expressed by

$$\int d\gamma L_{II}(\boldsymbol{p}, \boldsymbol{p}') = 0. \qquad (1.16)$$

Energy conservation in the interface entails the dependences

$$L_{\text{III}}(\boldsymbol{p}) = -\sqrt{2} \int L_{\text{II}}(\boldsymbol{p}, \boldsymbol{p}') \, \varepsilon' \, \mathrm{d}\gamma' \qquad (1.17)$$

$$L_{\rm II\,II} = -\sqrt{2} \int d\gamma \, \varepsilon \, L_{\rm I\,II}(\boldsymbol{p})$$
  
=  $2 \iint d\gamma \, \varepsilon \, L_{\rm I\,I}(\boldsymbol{p}, \boldsymbol{p}') \, \varepsilon' \, d\gamma'$ . (1.18)

The dimensionless energy

$$\varepsilon = p^2/2 \ m \ k \ T_0 \tag{1.19}$$

has been introduced. In view of (1.17) and (1.18) one may say that the kernel  $L_{\rm II}$  completely describes the scattering properties of the wall. The second boundary condition (1.13) is a linear consequence of the first condition (1.12).

### 2. Transport-Relaxation Eigenfunctions

The method to treat the plate problem starts from particular distributions with an exponential behaviour in space

$$\Phi \propto e^{-k \, \boldsymbol{e} \cdot \boldsymbol{x}} \, \psi(\boldsymbol{p}) \,, \qquad (2.1)$$

where e is an arbitrary unit vector, k an eigenvalue parameter. Insertion into the linearized Boltzmann equation gives

$$-k \mathbf{c} \cdot \mathbf{e} \psi + \omega(\psi) = 0$$
.

Eigenfunctions with cylindrical symmetry

$$\psi = \psi(p_x, p^2) \tag{2.2}$$

are needed only and considered in this paper. Identifying  $\mathbf{e} \cdot \mathbf{e} = c_x$  and assuming the eigenvalues  $k_i$  to be discrete, leads to the eigenvalue equation for the "transport-relaxation eigenfunctions"  $\psi_i$ 

$$-k_i c_x \psi_i + \omega(\psi_i) = 0. \qquad (2.3)$$

The linearized Boltzmann collision operator and therefore also the  $k_i$  are proportional to the absolute equilibrium pressure

$$\omega() \propto P_0, \quad k_i \propto P_0.$$
 (2.4)

The time-reversal operation,  $\boldsymbol{p} \rightarrow -\boldsymbol{p}$ , transforms (2.3) into

$$k_i c_x \psi_{iT} + \omega (\psi_{iT}) = 0, \qquad (2.5)$$

because the collision operator is invariant under time-reversal,  $[\omega(\psi)]_T = \omega(\psi_T)$ . Equation (2.5) says that  $\psi_{iT}$  is also eigenfunction, with the eigenvalue  $-k_i$ ; they are in pairs. It is convenient to number in the following way

$$\psi_{iT} = \psi_{-i}, \quad -\infty \leq i \leq +\infty, \quad (2.6)$$

which implies the correspondence

$$k_{-i} = -k_i$$
. (2.7)

For definiteness, the eigenvalues shall be ordered according to

$$k_{i+1} > k_i > 0 \text{ for } i \ge 1.$$
 (2.8)

Equation (2.3) contains two selfadjoint operators,  $c_x$  and  $\omega$ . In this form it is not yet an ordinary eigenvalue equation. However, the positive-semi-definite collision operator,

$$\int \psi \,\omega(\psi) \,\mathrm{d}\gamma \geqq 0\,,\tag{2.9}$$

can transiently be made positive-definite by replacing it by

$$\omega_+(\psi) \equiv \omega(\psi) + \Omega \psi$$
 where  $\Omega \rightarrow +0$ . (2.10)

Then, the square root operator  $\omega_{+}^{-1/2}$  exists and instead of (2.3) one can write

$$-k\,\omega_{+}^{-1/2}\,c_{x}\,\omega_{+}^{-1/2}\,\omega_{+}^{1/2}(\psi)\,+\omega_{+}^{1/2}(\psi)=0.$$
(2.11)

This is now an ordinary eigenvalue problem for the selfadjoint operator  $\omega_{+}^{-1/2} c_x \omega_{+}^{-1/2}$  with complete, orthonormalized eigenfunctions  $\omega_{+}^{1/2}(\psi)$ .

This orthonormalization can equivalently be inferred from Eq. (2.3) itself, written down for two different eigenvalues  $k_i$ ,  $k_{i'}$ . Multiplying by  $\psi_{i'}$  and  $-\psi_i$  respectively, integrating over  $\mathrm{d}\gamma$  and summing gives

$$(-k_i+k_{i'})\int \psi_i\,c_x\,\psi_{i'}\,\mathrm{d}\gamma=0$$
 .

Use has been made of the selfadjointness

$$\int \psi_i \,\omega(\psi_{i'}) \,\mathrm{d}\gamma = \int \psi_{i'} \,\omega(\psi_i) \,\mathrm{d}\gamma \,. \tag{2.12}$$

Under the non-degeneracy assumption

$$k_i = k_{i'}$$
 only for  $i = i'$ ,

one can "orthonormalize" in the sense

$$k_i \int \psi_i \, c_x \, \psi_{i'} \, \mathrm{d}\gamma = \delta_{ii'} \,. \tag{2.13}$$

For  $i \neq i'$  this is clear, and for i = i' one has

$$k_i \int \psi_i c_x \psi_i d\gamma = \int \psi_i \omega_+(\psi_i) d\gamma > 0$$
, (2.14)

which is positive indeed and can be put equal to one. From (2.4) and (2.13) follows

$$\psi_i \propto P_0^{-1/2} \tag{2.15}$$

as the dependence of the normalized eigenfunctions on the absolute pressure.

The two pairs of near-to-zero eigenvalues of (2.3), with  $\omega_+$  instead of  $\omega_*$  are

$$k_{+1} \propto \Omega$$
,  $k_{+2} \propto \sqrt{\Omega}$ . (2.16)

The eigenvalues for  $|i| \ge 3$  however have non-zero values for  $\Omega=0$ . This is discussed in the appendix. In § 3 we shall treat the eigenfunctions  $\psi_{\pm 1}$ ,  $\psi_{\pm 2}$  on the same footing with the others for  $|i| \ge 3$ . This implies that the limit  $\Omega \to +0$  is taken only afterwards. A most uniform description is thus attained, but the physical meaning will remain hidden to some extent. In § 5 we shall dismiss  $\psi_{\pm 1}$ ,  $\psi_{\pm 2}$  altogether and instead of them use new equivalent linear combinations. This amounts to putting  $\Omega=0$  from the very beginning. The description then is less uniform, but the physical meaning will be clearly visible.

A remark about the null-solutions of the linearized collision operator has to be added. Because of the restriction to cylindrical symmetry (2.2), three conserved quantities or collisional invariants occur

$$\omega(\varphi_a) = 0$$
,  $\alpha = 1, 2, 3$ , (2.17)

where

$$\varphi_1 = 1$$
,  $\varphi_2 = \sqrt{\frac{2}{3}} \left( \varepsilon - \frac{3}{2} \right)$ ,  $\varphi_3 = \frac{1}{\sqrt{m \, k \, T_0}} p_x$ . (2.18)

The normalization here is the usual one:

$$\int \varphi_{\alpha} \, \varphi_{\alpha'} \, \mathrm{d}\gamma = \delta_{\alpha\alpha'} \,. \tag{2.19}$$

All the eigenfunctions  $\psi_i$  from (2.3), for  $|i| \ge 3$ , are "orthogonal", in the sense of (2.13), to the collisional invariants:

$$k_{i} \int \varphi_{\alpha} c_{x} \psi_{i} d\gamma = \int \varphi_{\alpha} \omega(\psi_{i}) d\gamma$$

$$= \int \omega(\varphi_{\alpha}) \psi_{i} d\gamma = 0 \text{ for } \alpha = 1, 2, 3; |i| \geq 3.$$

This means that a distribution represented by a sum of  $\psi_i$ 's with  $|i| \ge 3$  does not carry a flux of the conserved quantities. Such fluxes are exclusively carried by the terms  $\psi_i$  with |i| = 1, 2.

For later use we also need the completeness relation of the transport-relaxation eigenfunctions. Let us expand a sufficiently decent function of the type of interest (1.2) in a series of the eigenfunctions (2.3)

$$\Phi(\boldsymbol{p}) = \Phi(p_x, p^2) = \sum_{n=-\infty}^{\infty} \psi_{i'}(\boldsymbol{p}) A_{i'}.$$
 (2.21)

To be precise:  $\omega_+$  instead of  $\omega$  should now be employed in (2.3) so that the eigenfunctions |i|=1, 2 don't play an extra-role. The "orthonormalization" (2.13) gives the necessary coefficients

$$A_i = \int k_i \, \psi_i \, c_x \, \Phi \, \mathrm{d} \gamma$$
.

Re-inserting this into (2.21) yields

$$\Phi(\mathbf{p}) = \int \sum_{-\infty}^{\infty} k_i \, \psi_i(\mathbf{p}) \, \psi_i(\mathbf{p}') \, c_x' \, \Phi(\mathbf{p}') \, \mathrm{d}\gamma'.$$

This shows that completeness means

$$\sum_{-\infty}^{\infty} k_i \, \psi_i(\boldsymbol{p}) \, \psi_i(\boldsymbol{p}') \, c_x' \, \mathrm{d}\gamma' = \delta(\boldsymbol{p}, \boldsymbol{p}') \, \mathrm{d}^3 p' \,. \quad (2.22)$$

Of course, the  $\delta(\boldsymbol{p}, \boldsymbol{p}')$ -function should be applied with functions of the type  $\Phi(p_x, p^2)$  only; to express this, one would have to write

$$\delta(p_x, p_x') \delta(p^2, p'^2) dp_x' dp'^2$$

instead, which however is unnecessarily cumbersome. — If the transport-relaxation eigenfunctions are not discrete, but continuous or mixed, one has to do with integrals, with the pertinent spectral measure in them, instead of the above summations over the subscript *i*. It is unnecessary to dwell on this.

# 3. Very Formal Solution of the Plate Problem. First Positivity Statement

The distribution of the gas is expanded with respect to the particular solutions (2.1) of the linearized Boltzmann equation

$$\Phi = \sum_{i=0}^{\infty} e^{-k_i x} \psi_i A_i. \tag{3.1}$$

The time-reversed distribution is

$$\Phi_{T} = \sum_{-\infty}^{\infty} e^{-k_{i}x} \psi_{-i} A_{i} = \sum_{-\infty}^{\infty} e^{k_{i}x} \psi_{i} A_{-i}. \quad (3.2)$$

Relations (2.6) and (2.7) were used. The symmetry (1.7) is fulfilled if

$$-A_{-i} = A_i$$
. (3.3)

Utilizing this, one can rewrite (3.1) and (3.2)

$$\Phi = \sum_{1}^{\infty} (e^{-k_{i}x} \psi_{i} - e^{k_{i}x} \psi_{iT}) A_{i},$$

$$\Phi_{T} = \sum_{1}^{\infty} (-e^{k_{i}x} \psi_{i} + e^{-k_{i}x} \psi_{iT}) A_{i}.$$
(3.4)

The force-flux pair (1.8) of the gas at the interface x = d/2 now assumes the form

$$F_{\rm I} = -P_{+} \sum_{1}^{\infty} (\psi_{i} + \psi_{iT}) B_{i},$$

$$J_{\rm I} = P_{+} c_{x} \sum_{1}^{\infty} (\psi_{i} - \psi_{iT}) \coth\left(k_{i} \frac{d}{2}\right) B_{i},$$

$$(3.5)$$

where

$$B_i = \sqrt{2} \sinh\left(k_i \frac{d}{2}\right) A_i \tag{3.6}$$

has been abbreviated.

We are ready to write down the first boundary condition (1.12)

$$P_{+} c_{x} \sum_{1}^{\infty} (\psi_{i'} - \psi_{i'T}) \coth\left(k_{i'} \frac{d}{2}\right) B_{i'}$$

$$= -\int L_{II} \sum_{1}^{\infty} (\psi'_{i'} + \psi'_{i'T}) d\gamma' B_{i'} + L_{III} F_{II}.$$
(3.7)

This is transformed into an algebraic system by taking moments, i.e. multiplying by  $\psi_i + \psi_{iT}$  and integrating over  $d\gamma$  on both sides. On the left side appears the integral

$$\int P_{+}(\psi_{i} + \psi_{iT}) c_{x}(\psi_{i'} - \psi_{i'T}) d\gamma 
= \int (P_{+} + P_{-}) \psi_{i} c_{x} (\psi_{i'} - \psi_{i'T}) d\gamma 
= \int \psi_{i} c_{x} (\psi_{i'} - \psi_{-i'}) d\gamma 
= \frac{1}{k_{i}} (\delta_{ii'} - \delta_{i-i'}) = \frac{1}{k_{i}} \delta_{ii'} \text{ for } i, i' \geq 1.$$
(3.8)

The "orthonormalization" (2.13) has been used. On the right side the matrix elements appear

$$L_{\text{II}\,ii'} = \int \int d\gamma \, (\psi_i + \psi_{iT}) \, L_{\text{II}} \, (\psi'_{i'} + \psi'_{i'T}) \, d\gamma', (3.9)$$

with the dimension of a length, and

$$L_{\text{III}\,i} = \int d\gamma \left(\psi_i + \psi_{iT}\right) L_{\text{III}}. \tag{3.10}$$

Herewith, the boundary condition (3.7) becomes

$$\sum_{1}^{\infty} \left[ \frac{1}{k_{i}} \coth\left(k_{i} \frac{d}{2}\right) \delta_{ii'} + L_{\text{II}\,ii'} \right] B_{i'}$$

$$= L_{\text{III}\,i} F_{\text{II}} \text{ for } i \geq 1. \quad (3.11)$$

This infinite linear system can in principle be inverted to yield the  $B_i$ 's which are proportional to the "applied force"  $F_{\rm II}$ . This is the "very formal solu-

tion of the plate problem." The diagonal first term in the []-bracket of (3.11) contains bulk quantities only and the plate distance d. The non-diagonal second term depends on the boundary and bulk properties, according to the  $L_{\rm II}$  and the  $\psi_i$ 's occurring in the integral (3.9).

The physical way to a positivity statement goes via the expression (4.20) of Ref. <sup>1</sup> for the interfacial entropy production rate per unit area

$$d\dot{S}_{\sigma}/d\sigma = (P_0/T_0) [\int F_{\rm I} J_{\rm I} d\gamma + F_{\rm II} J_{\rm II}] > 0.$$
 (3.12)

This positivity is guaranteed by the corresponding positivity property of the interfacial kernel  $L_{\rm II}$  and its associates  $L_{\rm III}$ ,  $L_{\rm IIII}$ . The rate (3.12) shall be rewritten in terms of the matrix elements (3.9) and (3.10), by use of the boundary conditions (1.12) and (1.13), together with the expansion (3.5) of  $F_{\rm I}$ :

$$\int F_{\rm I} J_{\rm I} \,\mathrm{d}\gamma + F_{\rm II} J_{\rm II} \tag{3.13}$$

$$= \sum\limits_{1}^{\infty} \sum\limits_{1}^{\infty} B_i \, L_{\text{II}\,ii'} \, B_{i'} - 2 \, \sum\limits_{1}^{\infty} B_i \, L_{\text{III}\,i} \, F_{\text{II}} \ + L_{\text{II}\,\text{II}} \, F_{\text{II}^2} \! > \! 0 \; .$$

The matrix  $L_{\text{II}\,ii'}$ , with its associates  $L_{\text{III}\,i}$ ,  $L_{\text{IIII}}$  again is positive-definite, in the sense of (3.13), for arbitrary  $B_i$ 's and  $F_{\text{II}}$ . But the contribution of the gas can also be directly expressed in terms of the  $B_i$ 's alone, by use of (3.5) and (3.8):

$$\int F_{\rm I} J_{\rm I} \, \mathrm{d}\gamma = -\sum_{1}^{\infty} \sum_{1}^{\infty} \int P_{+}(\psi_{i} + \psi_{iT})$$

$$\cdot c_{x}(\psi_{i'} - \psi_{i'T}) \, \mathrm{d}\gamma \, B_{i} \coth\left(k_{i'} \frac{d}{2}\right) B_{i'}$$

$$= -\sum_{1}^{\infty} \frac{1}{k_{i}} \coth\left(k_{i} \frac{d}{2}\right) B_{i^{2}} < 0. \tag{3.14}$$

This contribution is negative; it exactly counterbalances the positive entropy production rate in the bulk gas. Combining Eqs. (3.13) and (3.14) gives the positivity statement

$$F_{\rm II}J_{\rm II} = \sum_{1}^{\infty} \frac{1}{k_i} \coth\left(k_i \frac{d}{2}\right) B_i^2 \tag{3.15}$$

$$+ \sum\limits_{1}^{\infty} \sum\limits_{1}^{\infty} B_i \, L_{{\rm II}\,ii'} \, B_{i'} - 2 \, \sum\limits_{1}^{\infty} B_i \, L_{{\rm III}\,i} \, F_{{\rm II}} + L_{{\rm II}\,{\rm II}} \, F_{{\rm II}^2} > 0 \; .$$

The right side consists of two positive parts. The first sum represents the entropy production rate in the bulk, apart from the factor  $P_0/T_0$ . The other three terms together form the interfacial entropy production rate, cf. (3.12) and (3.13). Both parts combine to give the entropy which enters medium II, per unit time and area, and which on the other hand equals  $F_{\rm II} J_{\rm II}$ , the left side of (3.15). Now it is

clear that the heat transfer  $q_{\rm II} = P_0 J_{\rm II}$  always has the same sign as the applied temperature difference  $T_{\rm II} - T_0 = T_0 F_{\rm II}$ , as it is required by the second law. Thus, this positivity statement can easily be interpreted term by term. In § 6, an additional, even more detailed positivity statement will be derived.

The above positivity statement can also be obtained from the boundary conditions in a merely mathematical way. From (3.11), a descendent of the first boundary condition (1.12), one concludes

$$0 = \sum_{1}^{\infty} \frac{1}{k_{i}} \coth\left(k_{i} \frac{d}{2}\right) B_{i}^{2} + \sum_{1}^{\infty} \sum_{1}^{\infty} B_{i} L_{\text{II} ii'} B_{i'} - \sum_{1}^{\infty} B_{i} L_{\text{III} i} F_{\text{II}}.$$
(3.16)

The second boundary condition (1.13), by use of (3.5) and (3.10), is

$$egin{aligned} J_{\mathrm{II}} &= -\int L_{\mathrm{I\,II}} \sum_{1}^{\infty} (\psi_i + \psi_{iT}) \, B_i \, \mathrm{d}\gamma + L_{\mathrm{II\,II}} \, F_{\mathrm{II}} \ &= -\sum_{1}^{\infty} L_{\mathrm{I\,II\,}i} \, B_i \, + L_{\mathrm{II\,II}} \, F_{\mathrm{II}} \,, \end{aligned}$$

so that

$$F_{\rm II} J_{\rm II} = -\sum_{1}^{\infty} F_{\rm II} L_{\rm III} {}_{i} B_{i} + L_{\rm III} {}_{II} F_{\rm II}^{2} .$$
 (3.17)

Adding Eqs. (3.16) and (3.17) restores Equation (3.15).

#### 4. The Knudsen Case

The Knudsen case is obtained if the pressure  $P_0$  goes to zero, with constant distance d of the plates. After (2.4) this means that all the eigenvalues  $k_i$  go to zero too, so that in the []-bracket of (3.11) only the first term survives:

$$\frac{1}{k_i^2 d/2} B_i = \frac{\sqrt{2}}{k_i} A_i = L_{\text{III}\,i} F_{\text{II}}. \tag{4.1}$$

Definition (3.6) has been used. Insertion in (3.4) gives the Knudsen distribution

$$\Phi_{K} = \frac{1}{\sqrt{2}} \sum_{1}^{\infty} (\psi_{i} - \psi_{iT}) k_{i} L_{\text{III} i} F_{\text{II}}, \qquad (4.2)$$

which is independent of x and of the plate distance. By recalling the definition (3.10) and relations (2.6) and (2.7), one can rewrite this in the way

$$\begin{split} \boldsymbol{\varphi}_{K} &= \\ \frac{1}{\sqrt{2}} \int_{1}^{\infty} (k_{i} \, \boldsymbol{\psi}_{i} + k_{-i} \, \boldsymbol{\psi}_{-i}) \, \left( \boldsymbol{\psi}_{i}^{\, \prime} + \boldsymbol{\psi}_{\, iT}^{\prime} \right) \, L_{\mathrm{I\,II}}(\boldsymbol{p}^{\prime}) \, \mathrm{d}\boldsymbol{\gamma}^{\prime} \, \boldsymbol{F}_{\mathrm{II}} \\ &= \frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} k_{i} \, \boldsymbol{\psi}_{i}(\boldsymbol{\psi}_{i}^{\, \prime} + \boldsymbol{\psi}_{\, iT}^{\prime}) \, L_{\mathrm{I\,II}}(\boldsymbol{p}^{\prime}) \, \mathrm{d}\boldsymbol{\gamma}^{\prime} \, \boldsymbol{F}_{\mathrm{II}} \, . \end{split}$$

Now the completeness (2.22) is employed:

$$egin{aligned} \Phi_{K} &= rac{1}{V^2} \int rac{1}{c_x} \left[ \delta\left( oldsymbol{p}, oldsymbol{p}' 
ight) + \delta\left( oldsymbol{p}, -oldsymbol{p}' 
ight) 
ight] \ \cdot L_{ ext{III}}(oldsymbol{p}') \, \mathrm{d} \gamma' \, F_{ ext{II}} \, . \end{aligned}$$

This gives the Knudsen distribution in the form

$$\Phi_{K} = \frac{1}{\sqrt{2} c_{x}} \left[ L_{\text{III}}(\boldsymbol{p}) + L_{\text{III}}(-\boldsymbol{p}) \right] F_{\text{II}}. \quad (4.3)$$

Thus, the "associates"  $L_{\rm III}(\pm \boldsymbol{p})$  of the interfacial scattering law, with the projection properties

$$\begin{split} L_{\text{III}}(\boldsymbol{p}) &= L_{\text{III}}(\boldsymbol{p} \cdot \boldsymbol{n}_{\text{I}}, p^2) P_{+}(\boldsymbol{c} \cdot \boldsymbol{n}_{\text{I}}) , \\ L_{\text{III}}(-\boldsymbol{p}) &= L_{\text{III}}(-\boldsymbol{p} \cdot \boldsymbol{n}_{\text{I}}, p^2) P_{-}(\boldsymbol{c} \cdot \boldsymbol{n}_{\text{I}}) , \end{split}$$
(4.4)

have a direct physical meaning: they are the  $P_+$ -and  $P_-$ -parts of the Knudsen distribution between parallel plates.

The use of the expansion and its completeness relation can of course be avoided. From the Boltzmann equation, collisionless in the Knudsen case,

$$c_x \partial \Phi_{\rm K}/\partial x = 0$$
,

follows that

$$\Phi_{K} = \Phi_{K}(\boldsymbol{p})$$

is independent of x. The symmetry (1.7) then is

$$[-\Phi_T = \Phi]_K, \tag{4.5}$$

so that the "force exerted by the Knudsen gas at the interface" vanishes

$$[F_{\rm I} \propto \Phi + \Phi_T]_{\rm K} = 0. \tag{4.6}$$

As a consequence, one also has

$$\int F_{\rm I} J_{\rm I} \, \mathrm{d} \gamma = 0$$

which is equivalent to the statement that the entropy production in the bulk Knudsen gas vanishes. This had to be expected for the collisionless state. The first boundary condition (1.12), with (1.8) and (4.5), now immediately gives

$$\sqrt{2} P_{+} c_{x} \Phi_{K} = L_{III}(\boldsymbol{p}) F_{II}. \qquad (4.7)$$

This is again the  $P_+$ -part of (4.3). The  $P_-$ -part is obtained by use of the symmetry (4.5).

The heat transfer through the Knudsen gas can be directly inferred from the second boundary condition (1.13). With (4.6) it yields

$$J_{\rm II} = L_{\rm II II} F_{\rm II} , \qquad (4.8)$$

or, after (1.9)

$$q_{II} = (P_0/T_0) L_{IIII} (T_{II} - T_0)$$
. (4.9)

Again, the interfacial coefficient  $L_{\rm II\,II}$  (dimension of a velocity) has a direct physical meaning, as the heat transfer coefficient of the Knudsen gas between parallel plates.

For the completely thermalizing wall one has, after Eq. (6.22) of Ref. <sup>1</sup>, at x = d/2, the values

$$L_{\rm III}(\mathbf{p}) = -\sqrt{2} P_{+}(c_x) c_x(\varepsilon - 2) , \quad (4.10)$$

$$L_{\rm II II} = \bar{c}_0 = \sqrt{8 k T_0 / \pi m}$$
 (4.11)

Definition (1.19) is recalled. Thus, the Knudsen distribution (4.3) between completely thermalizing walls is

$$\Phi_{\rm K} = [-P_{+}(c_x) + P_{-}(c_x)] (\varepsilon - 2) F_{\rm II}.$$
 (4.12)

The heat flux is given by

$$q_x = -\frac{1}{2} \frac{P_0}{T_0} \overline{c}_0 \left[ T_{\text{II}} \left( \frac{d}{2} \right) - T_{\text{II}} \left( -\frac{d}{2} \right) \right].$$
 (4.13)

These results are of course well-known.

# 5. More Detailed Solution of the Plate Problem. The Temperature Jump

In § 2 it has been mentioned that the eigenvalues k of Eq. (2.3) vanish for |i|=1,2. Therefore, the first two terms of the expansion (3.4) necessitate a special discussion. We abbreviate them by

$$\hat{\Phi} = \sum_{1}^{2} (e^{-k_i x} \psi_i - e^{k_i x} \psi_{iT}) A_i, \qquad (5.1)$$

which for  $k_{1,2} \rightarrow 0$  will have the structure

$$\widehat{\Phi}(x, \mathbf{p}) = x \varphi(p_x, p^2) + \psi(p_x, p^2) . \qquad (5.2)$$

Form (1.2) is recalled. Thus, instead of looking in detail at the eigenfunctions  $\psi_{1,2}$ , which is done in the appendix, one can try to determine the functions  $\varphi$  and  $\psi$  in (5.2) directly. This is done here.

The expression (5.2) must fulfill the linearized Boltzmann equation, as every part of the sum (3.4) does,

$$c_x \varphi + x \omega(\varphi) + \omega(\psi) = 0. \tag{5.3}$$

The coordinate x occurs only in the middle term, hence

$$\omega(\varphi) = 0. \tag{5.4}$$

The function  $\varphi$  simply is a linear combination with coefficients  $d_{\beta}$  of the collisional invariants from (2.18)

$$\varphi = \sum_{1}^{3} \varphi_{\beta} \, \mathrm{d}_{\beta} \,. \tag{5.5}$$

One is left with

$$\omega(\psi) = -c_x \varphi. \tag{5.6}$$

This integral equation has a solution only if the right side is orthogonal to the collisional invariants  $\varphi_{1,2,3}$ . As is well-known, this requires  $\varphi$  to be of the form

$$\varphi = (\varepsilon - \frac{5}{2}) a, \qquad (5.7)$$

where a is a constant. We introduce the Chapman-Enskog "standard solution" for heat conduction  $\chi$  according to

$$\omega(\chi) = -c_x(\varepsilon - \frac{5}{2}). \tag{5.8}$$

The function  $\chi$ , for uniqueness, shall be orthogonal, in the usual sense, to the collisional invariants:

$$\int \varphi_{\alpha} \chi \, d\gamma = 0 \,, \quad \alpha = 1, 2, 3. \tag{5.9}$$

It has the symmetry and pressure dependence

$$\chi = -\chi_{\rm T} \propto P_0^{-1} \,. \tag{5.10}$$

Besides,  $\chi$  is eo ipso orthogonal, in the sense of (2.13), to the eigenfunctions  $\psi_i$  with  $i \geq 3$ :

$$k_i \int \chi \, c_x \, \psi_i \, \mathrm{d}\gamma = \int \chi \, \omega \, (\psi_i) \, \mathrm{d}\gamma$$

$$= \int \omega \, (\chi) \, \psi_i \, \mathrm{d}\gamma = -\int (\varepsilon - \frac{5}{2}) \, c_x \, \psi_i \, \mathrm{d}\gamma = 0 \,.$$
(5.11)

Equation (2.20) has been used. The general solution of (5.6) can now be written in the form

$$\psi = \sum_{1}^{3} \varphi_{\alpha} b_{\alpha} + \chi a. \qquad (5.12)$$

Insertion of expressions (5.7) and (5.12) in (5.2) gives a distribution  $\hat{\Phi}$  with four constants a,  $b_{1,2,3}$  which replace the original four constants  $A_{\pm 1}$ ,  $A_{\pm 2}$  from (3.1). However, because of the symmetry (1.7) and because the gas is at rest, the coefficients  $b_{1,2,3}$  vanish and we are left with the very simple form

$$\widehat{\Phi} = \left[x\left(\varepsilon - \frac{5}{2}\right) + \chi\right]a. \tag{5.13}$$

For comparison, the distribution in an unbounded heat conducting gas (or  $P_0 = \infty$ !)

$$\Phi_{\text{C.E.}} = \left[ x \left( \varepsilon - \frac{5}{2} \right) + \chi \right] \frac{\partial T}{T_0 \partial x}, \quad (5.14)$$

the well-known Chapman-Enskog solution, is noted. Its heat flux is

$$q_{x \text{C.E.}} = P_0 \int c_x \left( \varepsilon - \frac{5}{2} \right) \Phi_{\text{C.E.}} \, d\gamma$$

$$= \frac{P_0}{T_0} \int c_x \left( \varepsilon - \frac{5}{2} \right) \chi \, d\gamma \, \frac{\partial T}{\partial x} = -\lambda_{\text{I}} \frac{\partial T}{\partial x}.$$
(5.15)

The heat conductivity of the gas

$$\lambda_{\rm I} = (P_{\rm o}/T_{\rm o}) \int \chi \, \omega \left(\chi\right) \, \mathrm{d}\gamma \tag{5.16}$$

is independent of the pressure  $P_0$ .

The full solution, Eq. (3.4), of the plate problem now assumes the form

$$\Phi = [x(\varepsilon - \frac{5}{2}) + \chi] a + \sum_{3}^{\infty} (e^{-k_i x} \psi_i - e^{k_i x} \psi_{iT}) A_i.$$
(5.17)

According to (2.20), the sum term does not contribute to the heat flux which by comparison with (5.14) and (5.15) is exactly

$$q_x = -\lambda_{\rm I} T_0 a. \tag{5.18}$$

Hence, our coefficient a has a direct physical meaning: the heat flux. After (1.9) one has also, at the plate x = d/2,

$$a = \frac{P_0}{T_0 \lambda_{\rm I}} J_{\rm II}. \tag{5.19}$$

Besides that, it is practical to introduce an "effective temperature gradient"  $(\partial T/\partial x)^*$  or an effective applied force  $F_{II}^*$  according to

$$a = \frac{1}{T_0} \left( \frac{\partial T}{\partial x} \right)^* = \frac{F_{II}^*}{d/2}.$$
 (5.20)

 $F_{\rm II}^*$  is that "thermodynamical force" in the sense of (1.9) which would have to be applied with ordinary heat conduction  $(P_0=\infty\,!)$  in order to yield the actual heat flux  $q_x$ .

The force-flux pair from (1.8) at x = d/2 now becomes, by use of Eqs. (5.17), (5.10) and (5.20),

$$\begin{split} F_{\mathrm{I}} &= P_{+} \left[ \sqrt{2} \left( \varepsilon - \frac{5}{2} \right) F_{\mathrm{II}}^{*} - \sum_{3}^{\infty} \left( \psi_{i} + \psi_{iT} \right) \right. \\ J_{\mathrm{I}} &= P_{+} c_{x} \left[ \sqrt{2} \chi \right] \quad a + \sum_{3}^{\infty} \left( \psi_{i} - \psi_{iT} \right) \coth \left( k_{i} \frac{d}{2} \right) B_{i} \right]. \end{split}$$

$$(5.21)$$

The first boundary condition (1.12), under use of (1.17), reads

$$P_{+} c_{x} \left[ V \overline{2} \chi a + \sum_{3}^{\infty} (\psi_{i'} - \psi_{i'T}) \coth \left( k_{i'} \frac{d}{2} \right) B_{i'} \right]$$

$$= -\sum_{3}^{\infty} \int L_{\text{II}} (\boldsymbol{p}, \boldsymbol{p}') (\psi'_{i'} + \psi'_{i'T}) d\gamma' B_{i'} + L_{\text{III}} \delta F,$$
(5.22)

with the abbreviation

$$\delta F = F_{II} - F_{II}^* \equiv \delta T / T_0. \tag{5.23}$$

Equation (5.23) gives an exact definition for the temperature jump  $\delta T$  at the parallel plates, in terms of quantities which are already exactly defined. The second boundary condition (1.13) is

$$J_{\rm II} = -\sum_{3}^{\infty} L_{{\rm III}\,i}\,B_i + L_{{\rm IIII}}\,\delta F\,.$$
 (5.24)

Use has been made of definition (3.10).

Now let us again take moments as it has been done with Equation (3.7).

Firstly, we multiply (5.22) by  $\sqrt{2} (\varepsilon - \frac{5}{2})$  and integrate. The left side gives, with (5.16) and (5.19),

$$\begin{split} 2\int \mathrm{d}\gamma\, P_+(\varepsilon - \tfrac{5}{2})\, c_x\, \chi\, a = & \int \mathrm{d}\gamma\, (\varepsilon - \tfrac{5}{2})\, c_x\, \chi\, a \\ = & -\frac{T_0}{P_0}\, \lambda_\mathrm{I}\, a = -J_\mathrm{II}\,. \end{split}$$

For the right side, Eqs. (1.17) and (3.10) are recalled. This first moment of Eq. (5.22) thus is

$$-J_{\rm II} = \sum_{3}^{\infty} L_{\rm I \, II \, i} \, B_i - L_{\rm II \, II} \, \delta F \,. \tag{5.25}$$

It coincides with the second boundary condition (5.24). This is no surprise. The second boundary condition follows from the first one via energy conservation.

Secondly, we multiply (5.22) by  $\psi_i + \psi_{iT}$ , with  $i \ge 3$ , and integrate. By aid of the "orthonormality" (3.8) and of the definition (3.9), we obtain

$$\sum_{3}^{\infty} \left[ \frac{1}{k_{i}} \coth\left(k_{i} \frac{d}{2}\right) \delta_{ii'} + L_{\text{II}\,ii'} \right] B_{i'}$$

$$= L_{\text{III}\,i} \, \delta F \text{ for } i \geq 3.$$
(5.26)

This is to be compared with the system (3.11). The difference lies in the range of i, i' and in the right side, with  $\delta F$  instead of  $F_{II}$ .

By inversion of the system (5.26), the B's for  $i \geq 3$  are obtained in terms of the temperature jump  $\delta F$ . Insertion into (5.25) gives the heat flux, in terms of  $\delta F$  again. Then, by (5.20) and (5.23), also the connection between heat flux and applied temperature difference,  $F_{\rm II}$  or  $T_{\rm II}-T_0$ , is known. This will be further discussed in the following section.

# 6. Second Positivity Statement. Sign of Temperature Jump. v. Smoluchowski Approximation

Due to the differences between the systems (3.11) and (5.26), a second relevant positivity statement can be made which involves the temperature jump

whereas (3.15) deals with the applied temperature difference. We multiply (5.25) by  $F_{\rm II}^*$  and (5.26) by  $-B_i$ , sum and obtain

$$0 = F_{II} * J_{II} + \sum_{3}^{\infty} \frac{1}{k_{i}} \coth\left(k_{i} \frac{d}{2}\right) B_{i}^{2}$$

$$+ \sum_{3}^{\infty} \sum_{3}^{\infty} B_{i} L_{II\,ii'} B_{i'} + F_{II} * \sum_{3}^{\infty} L_{III\,i} B_{i}$$

$$- \left(F_{II} * L_{II\,II} + \sum_{3}^{\infty} B_{i} L_{I\,II\,i}\right) \delta F. \qquad (6.1)$$

From the second boundary condition (5.24) follows

$$F_{\rm II} J_{\rm II} = -F_{\rm II} \sum_{3}^{\infty} L_{{
m I\,II}\,i} B_i + F_{{
m II}} L_{{
m II\,II}} \delta F$$
. (6.2)

Equations (6.1) and (6.2) correspond to Eqs. (3.16) and (3.17). Addition of (6.1) and (6.2) yields, by use of definition (5.23),

$$F_{II} J_{II} = F_{II} * J_{II} + \sum_{3}^{\infty} \frac{1}{k_{i}} \coth \left( k_{i} \frac{d}{2} \right) B_{i}^{2}$$

$$+ \sum_{3}^{\infty} \sum_{2}^{\infty} B_{i} L_{II\,ii'} B_{i'} - 2 \sum_{3}^{\infty} B_{i} L_{II\,i\,i} \delta F + L_{II\,II} (\delta F)^{2}.$$
(6.3)

The first term on the right side

$$F_{\rm II}^* J_{\rm II} = \frac{T_0 \lambda_{\rm I}}{P_0 d/2} F_{\rm II}^{*2} > 0$$
 (6.4)

is obviously positive; it is a part of the entropy production in the bulk gas. Together with the second positive term on the right side, namely the sum over  $B_i^2$ , it forms the entire bulk entropy production rate. The last three terms on the right side, positive together, give the entropy production rate in the interface. From (6.3) one concludes

$$\begin{split} & \delta F \, J_{\rm II} = (F_{\rm II} - F_{\rm II}^*) \, J_{\rm II} = \sum_{3}^{\infty} \frac{1}{k_i} \, \coth \left( k_i \, \frac{d}{2} \right) \, B_i^2 \\ & + \sum_{3}^{\infty} \sum_{3}^{\infty} B_i \, L_{{\rm II}\, ii'} \, B_{i'} - 2 \sum_{3}^{\infty} B_i \, L_{{\rm III}\, i} \, \delta F + L_{{\rm II}\, {\rm II}} (\delta F)^2 \, . \end{split}$$

$$(6.5)$$

This is another positive combination. Thus, besides the very general result (3.15) which was

$$F_{\rm II}J_{\rm II} > 0, \qquad (6.6)$$

it is, more specially, also true that the products

$$F_{\rm II}^* J_{\rm II} > 0$$
,  $\delta F J_{\rm II} > 0$  (6.7)

are positive. This is our second positivity statement. It means that the inequality holds

$$|F_{\rm II}| > |F_{\rm II}^*|, \tag{6.8}$$

in words: the temperature jump at the parallel plates is such that the "effective" temperature difference is always smaller in absolute value than the applied temperature difference.

We return to the linear equations of § 5 and write down Eqs. (5.25) and (5.26) in the way

$$L_{\text{II II}} \delta F - \sum_{3}^{\infty} L_{\text{I II } i} B_{i} = J_{\text{II}}$$
 $-L_{\text{I II } i} \delta F + \sum_{3}^{\infty} K_{ii'} B_{i'} = 0, \quad i \ge 3, \quad (6.9)$ 

with the abbreviation

$$K_{ii'}(d) = \frac{1}{k_i} \coth\left(k_i \frac{d}{2}\right) \delta_{ii'} + L_{\text{II}ii'}.$$
 (6.10)

The flux  $J_{\rm II}$  now figures as the given inhomogeneity,  $\delta F$  and the B's are the unknowns. The matrix of the system (6.9) is positive-definite. The L's are positive-definite anyhow, and adding positive terms in the diagonal, as it is prescribed in (6.10), even strengthens positive-definiteness. We solve the second line of Eq. (6.9) for  $B_i$ 

$$B_i = \sum_{3}^{\infty} K_{ii'}^{-1} L_{\mathrm{III}\,i'} \, \delta F$$

and insert into the first line

$$\delta F = J_{\text{II}} / \left( L_{\text{II II}} - \sum_{3}^{\infty} \sum_{3}^{\infty} L_{\text{III } i} K_{ii'}^{-1} L_{\text{III } i'} \right). \quad (6.11)$$

In terms of the physical quantities themselves, this is

$$\delta T = T_{\text{II}} - T_{\text{II}}^{*} 
= \frac{T_{0}}{P_{0}} q_{\text{II}} / \left( L_{\text{II II}} - \sum_{3}^{\infty} \sum_{3}^{\infty} L_{\text{III } i} K_{ii'}^{-1} L_{\text{III } i'} \right).$$
(6.12)

The double sum in the ()-parenthesis, with the inverse positive matrix  $K^{-1}$  in it, is positive, but in any case smaller than  $L_{\rm H\,II}$  according to (6.7).

Neglect of the double sum in (6.12) gives the approximation for the temperature jump of the parallel plates

$$\delta T_{\rm appr} = \frac{T_0}{P_0 L_{\rm II\,II}} q_{\rm II}, \qquad (6.13)$$

which sets a lower bound to the absolute value of the exact temperature jump of the plates:

$$|\delta T| > |\delta T_{\text{appr}}|$$
 (6.14)

A next approximation is not easily obtained. In the hydrodynamical case,  $d = \infty$ , one has

$$K_{ii'}(d=\infty) = \frac{1}{k_i} \delta_{ii'} + L_{\text{II}\,ii'}.$$
 (6.15)

To evaluate the double sum of (6.11) in the hydrodynamical case is not easier than doing this in the most general case.

With thermalizing wall collisions one has, after the last equation of Ref. <sup>1</sup>,

$$L_{\text{II II}} = 4 \, \hat{c}_0 = \overline{c}_0 = \sqrt{8 \, k \, T_0 / \pi \, m} \,.$$
 (6.16)

The temperature jump then is approximately

$$\delta T_{\rm appr} = \frac{T_0}{P_0 \overline{c}_0} q_{\rm II}. \qquad (6.17)$$

This is v. Smoluchowski's value for complete accommodation 7.

## 7. The Moment Method for Comparison

It has been emphasized in Ref. <sup>1</sup> that the new boundary conditions form a seamless union with the linearized Boltzmann equation, so that one and the same truncated moment expansion of the distribution can be used for both, the integro-differential equation and its boundary conditions. This scheme, generally indicated in § 6 of Ref. <sup>1</sup>, shall now be exemplified by the application to the heat transport case. It may be compared with the exact solution of the preceding sections.

The distribution is approximated by the polynomial

$$\Phi = \varphi_1 a_1 + \varphi_2 a_2 + \varphi_1 \cdot a_1 + \varphi_2 \cdot a_2. \quad (7.1)$$

The orthonormalized functions of  $\boldsymbol{p}$  are chosen as

$$\begin{array}{ll} \varphi_{1} = 1 \; , & \varphi_{2} = \sqrt{\frac{2}{3}} \left( \varepsilon - \frac{3}{2} \right) \; , \\ \boldsymbol{\varphi}_{1} = \boldsymbol{p} / m \; c_{0} \; , & \boldsymbol{\varphi}_{2} = \sqrt{\frac{2}{5}} \left( \varepsilon - \frac{5}{2} \right) \boldsymbol{p} / m \; c_{0} \; , \end{array}$$
 (7.2)

with the abbreviation

$$c_0 = \sqrt{k T_0/m} \ . \tag{7.3}$$

The coefficients, dependent on t and x, have the physical meaning

$$\begin{array}{ll} a_1 = (n_{\rm I} - n_0)/n_0 \,, & a_2 = \sqrt{\frac{3}{2}} \left( T_{\rm I} - T_0 \right)/T_0 \,, \\ a_1 = v_{\rm I}/c_0 \,, & a_2 = \sqrt{\frac{2}{5}} \, q_{\rm I}/P_0 \, c_0 \,. \end{array} \right\} \eqno(7.4)$$

The number density, temperature, velocity and heat flux, n, T, v and q, bear the subscript I, to stress that they belong to the gas. The interfacial force-flux pair of the gas is given by

$$F_{\rm I} = \frac{1}{\sqrt{2}} P_+ (\Phi + \Phi_{\rm T}) = \sqrt{2} P_+ (\varphi_1 a_1 + \varphi_2 a_2) , (7.5)$$

$$J_{\mathrm{I}} = \frac{1}{\sqrt{2}} P_{+} c \left( \boldsymbol{\Phi} - \boldsymbol{\Phi}_{\mathrm{T}} \right) = \sqrt{2} P_{+} c \left( \boldsymbol{\varphi}_{1} \cdot \boldsymbol{a}_{1} + \boldsymbol{\varphi}_{2} \cdot \boldsymbol{a}_{2} \right).$$

$$(7.6)$$

Definition (1.10) is recalled. The boundary conditions (1.12) and (1.13) are

$$V\overline{2} P_{+} c (\boldsymbol{\varphi}_{1} \cdot \boldsymbol{a}_{1} + \boldsymbol{\varphi}_{2} \cdot \boldsymbol{a}_{2})$$

$$= \int L_{\text{II}} (\boldsymbol{p}, \boldsymbol{p}') V\overline{2} \varphi_{2}' a_{2} d\gamma' + L_{\text{III}} (\boldsymbol{p}) F_{\text{II}} \qquad (7.7)$$

$$J_{\text{II}} = \int L_{\text{III}} (\boldsymbol{p}') V\overline{2} \qquad \varphi_{2}' a_{2} d\gamma' + L_{\text{IIII}} \qquad F_{\text{II}}. \qquad (7.8)$$

The  $\varphi_1$ -term of  $F_I$  has been omitted; because of the subsidiary condition (1.16) it does not contribute to the integral. Of course, these functional relations, especially (7.7), can be fulfilled only approximately, not exactly for every value of  $\boldsymbol{p}$ . The same happens with the linearized Boltzmann equation, in the same stage of polynomial approximation.

The condition (7.8), which contains no  $\boldsymbol{p}$ -variable, is nothing but the approximate temperature jump condition (6.13). Indeed, the meaning (7.2) and (7.4) of  $\varphi_2$ ,  $a_2$  and the use of (1.18) allow to rewrite the integral term as

$$\int L_{\rm I\,II}({m p}')\,\sqrt{2}\,\varphi_2{}'\,{\rm d}\gamma'\,a_2 = -L_{\rm II\,II}\,(T_{\rm I}-T_{\rm 0})/T_{\rm 0}$$
.

Thus, by use also of the definitions (1.9), condition (7.8) assumes the form

$$\frac{q_{\rm II}}{P_0} = L_{\rm II\,II} \, \frac{T_{\rm II} - T_{\rm I}}{T_0} \,. \tag{7.9}$$

This coincides with the approximation (6.13) of the temperature jump found for the parallel plates, if the effective applied temperature  $T_{\rm II}^*$ , introduced by Eq. (5.20) and occurring in the exact formula (6.12), is, approximately again, identified with the temperature  $T_{\rm I}$  of the gas at the plate x=d/2. This approximation does not sound unreasonable.

There is still the first boundary condition (7.7) to be discussed. To get rid of its  $\boldsymbol{p}$ -dependence which cannot hold exactly, one will take moments by multiplying with  $\varphi_1$ ,  $\varphi_2$  and integrating. After a little algebra and with the abbreviation  $\int \mathrm{d}\gamma \dots = \langle \dots \rangle$ , one obtains the matrix elements on the left side

$$\begin{split} \langle \varphi_1 P_+ \, c \; \boldsymbol{\varphi}_1 \rangle &= \tfrac{1}{2} \, c_0 \, \boldsymbol{n}_{\mathrm{I}} \,, \quad \langle \varphi_1 P_+ \, c \; \boldsymbol{\varphi}_2 \rangle = 0 \;, \\ \langle \varphi_2 P_+ \, c \; \boldsymbol{\varphi}_1 \rangle &= \frac{1}{\sqrt{6}} \, c_0 \, \boldsymbol{n}_{\mathrm{I}} \,, \; \langle \varphi_2 P_+ \, c \; \boldsymbol{\varphi}_2 \rangle = \sqrt{\tfrac{5}{12}} \, c_0 \, \boldsymbol{n}_{\mathrm{I}} \,. \end{split}$$

On the right side only two non-zero matrix elements appear

$$\langle \varphi_2 \int L_{\text{II}} \sqrt{2} \, \varphi_2' \, d\gamma' \rangle = \frac{\sqrt{2}}{3} \, L_{\text{III}},$$

$$\langle \varphi_2 L_{\text{III}} \rangle = -\frac{1}{\sqrt{3}} \, L_{\text{III}}. \quad (7.11)$$

Thus, the two moment equations naturally belonging to the condition (7.7) are

$$\frac{\boldsymbol{n}_{\mathrm{I}} \cdot \boldsymbol{a}_{1} = 0, \qquad (7.12)}{\sqrt{\frac{2 k T_{0}}{m}} \boldsymbol{n}_{\mathrm{I}} \cdot \left(\frac{1}{\sqrt{6}} \boldsymbol{a}_{1} + \sqrt{\frac{5}{12}} \boldsymbol{a}_{2}\right) 
= L_{\mathrm{II} \mathrm{II}} \left(\frac{\sqrt{2}}{3} \boldsymbol{a}_{2} - \frac{1}{\sqrt{3}} F_{\mathrm{II}}\right). \quad (7.13)$$

Replacing  $a_2$ ,  $\mathbf{a}_2$  according to (7.4), one recovers the temperature jump formula (7.9).

The polynomial approximation (7.1) can be improved by adding terms in  $\varphi_3$ ,  $\varphi_3$ , etc., containing the next higher powers in the energy, as it was done in Reference <sup>6</sup>. The pertinent enlarged boundary conditions involving  $a_3$ ,  $a_3$ , etc. will be found in close analogy with the presentation here.

### Appendix

# The Transport-Relaxation Eigenfunctions

$$\boldsymbol{\psi}_{\pm 1}, \, \boldsymbol{\psi}_{\pm 2}$$

In this appendix, the artificial positive parameter  $\Omega$  from (2.12) is assumed to be small, but nonzero. Then, there are two pairs of eigenfunctions  $\psi_{\pm 1}$ ,  $\psi_{\pm 2}$  with eigenvalues  $k_{\pm 1}$ ,  $k_{\pm 2}$  which also are small, but non-zero.

With the selfadjoint operator

$$l_x = \omega_+^{-1/2} c_x \omega_+^{-1/2},$$
 (A1)

the eigenvalue problem (2.11) for the function

$$\hat{\psi} = \omega_{\perp}^{1/2} \, \psi \tag{A 2}$$

has the simple form

$$l_x \, \widehat{\psi} = (1/k) \, \widehat{\psi} \,. \tag{A 3}$$

Now, let us switch over to a representation based on the eigenfunctions  $\varphi_a$  of the collision operator  $\omega$ 

$$\omega \varphi_a = \omega_a \varphi_a \,, \tag{A 4}$$

with eigenvalues  $\omega_a$ . One has  $\omega_{1,2,3}=0$ , and  $\omega_a>0$  for  $a\geq 4$ . For  $\varphi_{1,2,3}$  see (2.18). Again, if the  $\omega$ -spectrum is otherwise continuous, integrals instead of sums should be imagined in the following. We expand

$$\psi = \sum_{1}^{\infty} \varphi_a a_a, \quad \hat{\psi} = \sum_{1}^{\infty} \varphi_a \hat{a}_a, \quad (A 5)$$

with

$$\hat{a}_a = \sqrt{\omega_a + \Omega} a_a. \tag{A 6}$$

Equation (A3) then is

$$\sum_{1}^{\infty} l_{\alpha a'} \, \hat{a}_{a'} = (1/k) \, \hat{a}_a \,. \tag{A 7}$$

It has been abbreviated

$$l_{aa'} = l_{a'a} = \frac{c_{aa'}}{V(\omega_a + \Omega) (\omega_{a'} + \Omega)}, \quad (A 8)$$

with

$$c_{aa'} = c_{a'a} = \int \varphi_a c_x \varphi_{a'} d\gamma$$
. (A9)

The diagonal elements of the c-matrix vanish and some more special values which will be needed, are listed too:

$$c_{aa} = 0$$
;  $c_{1a} = \delta_{3a} c_0$  for all  $\alpha$ ;  $c_{23} = \sqrt{\frac{2}{3}} c_0$  (A 10) with

$$c_0 = \sqrt{k T_0/m}$$
.

The eigenvalue system (A 7), for small  ${\mathcal Q}$  now is in detail

a = 1, 2, 3:

$$\frac{1}{\Omega} \sum_{1}^{3} c_{aa'} \hat{a}_{a'} + \frac{1}{\sqrt{\Omega}} \sum_{4}^{\infty} \frac{c_{aa'}}{\sqrt{\omega_{a'}}} \hat{a}_{a'} \approx \frac{1}{k} \hat{a}_{a} \quad (A11)$$

 $\alpha \geq 4$ 

$$\frac{1}{\sqrt{\Omega}} \sum_{1}^{3} \frac{c_{aa'}}{\sqrt{\omega_a}} \hat{a}_{a'} + \sum_{4}^{\infty} \frac{c_{aa'}}{\sqrt{\omega_a \omega_{a'}}} \hat{a}_{a'} \approx \frac{1}{k} \hat{a}_a. \quad (A 12)$$

With eigenvalues which go to zero if  $\Omega$  goes to zero, one can neglect the second sum in (A 12). This yields

$$a \ge 4$$
:  $\hat{a}_a \approx \frac{k}{\sqrt{Q} \, \omega_a} \sum_{1}^{3} \, c_{aa'} \, \hat{a}_{a'}$ . (A 13)

Insertion of these  $\hat{a}_{\alpha}$ 's into (A 11) leads to the following simple  $3 \times 3$  eigenvalue problem

$$rac{1}{arOmega} \sum_{3}^{1} \left( c_{lphalpha'} + k \, d_{lphalpha'} 
ight) \hat{a}_{lpha'} pprox rac{1}{k} \, \hat{a}_{lpha} \qquad ext{(A 14)}$$

with  $\alpha = 1, 2, 3$  and the abbreviation

$$d_{aa'} = d_{a'a} = \sum_{a}^{\infty} c_{aa''} c_{a''a'} / \omega_{a''}$$
. (A 15)

From (A 10) and from later considerations, see (A 32), follows

$$d_{1a} = 0$$
 for  $a = 1, 2, 3$ ;  $d_{22} = 0$ . (A 16)

Again according to (A 10) and after multiplying by k, the Eqs. (A 14) are explicitly

$$\begin{split} \hat{a}_1 & -\frac{k\,c_0}{\varOmega}\,\hat{a}_3 = 0 \\ & \left(1 - \frac{k^2\,d_{22}}{\varOmega}\right)\hat{a}_2 & -\sqrt{\frac{2}{3}}\,\frac{k\,c_0}{\varOmega}\,\hat{a}_3 = 0 \\ & -\frac{k\,c_0}{\varOmega}\,\hat{a}_1 - \sqrt{\frac{2}{3}}\,\frac{k\,c_0}{\varOmega}\,\hat{a}_2 + \left(1 - \frac{k^2\,d_{33}}{\varOmega}\right)\hat{a}_3 = 0 \;. \end{split} \tag{A 17}$$

The condition for vanishing determinant is

$$\bigg(1-\frac{k^2\,d_{22}}{\varOmega}\bigg)\bigg(1-\frac{k^2\,d_{33}}{\varOmega}\bigg)-\bigg(\frac{5}{3}-\frac{k^2\,d_{22}}{\varOmega}\bigg)\frac{k^2\,c_0^2}{\varOmega^2}=0\;, \eqno(A\;18)$$

a quadratic equation for  $k^2$ . The first approximation for the roots is readily obtained by assuming:

i)  $k \propto \Omega$ , which implies  $k^2/\Omega \rightarrow 0$ , so that after (A 18)

$$1 - \frac{5}{3} \frac{k^2 c_0^2}{\Omega^2} = 0$$
 or  $k_{\pm 1} = \pm \sqrt{\frac{3}{5}} \frac{\Omega}{c_0}$ , (A 19)

ii)  $k \propto V\Omega$ , which implies  $k^2/\Omega^2 \to \infty$ , so that after (A 18)

$$\frac{5}{3} - \frac{k^2 d_{22}}{\Omega} = 0$$
 or  $k_{\pm 2} = \pm \sqrt{\frac{5 \Omega}{3 d_{22}}}$ . (A 20)

Herewith, the eigenvalues are already known accurately enough. The eigenfunctions are, after (A 5) and (A 13)

$$\psi = \frac{1}{V\Omega} \sum_{1}^{3} (\varphi_a + k \chi_a) \hat{a}_a \qquad (A 21)$$

where three new functions

$$\chi_{a} = \sum_{4}^{\infty} \varphi_{a'} \left( c_{a'a} / \omega_{a'} \right) \tag{A 22}$$

automatically appear. The k-values are to be taken from (A 19) and (A 20), the corresponding  $\hat{a}$ 's from (A 17).

Before writing down the eigenfunctions, let us discuss the  $\chi$ 's. They contain only  $\varphi$ 's with  $\alpha \ge 4$  so that they are orthogonal to the collisional invariants:

$$\int \varphi_{\alpha} \chi \, d\gamma = 0$$
 for  $\alpha = 1, 2, 3$ . (A 23)

After (A 10) one has

$$\chi_1 = 0. \tag{A 24}$$

Application of the collision operator gives

$$\omega \chi_a = \sum_{1}^{\infty} \varphi_{a'} c_{a'a} - \sum_{1}^{3} \varphi_{a'} c_{a'a}.$$

The first sum can be rewritten by aid of the completeness relation [cf. the remark after Eq. (2.22)]

$$\sum\limits_{1}^{\infty}arphi_{a^{'}}(oldsymbol{p})\;arphi_{a^{'}}(oldsymbol{p}')=\delta\left(oldsymbol{p},oldsymbol{p}'
ight)\mathrm{d}^{3}p'/\mathrm{d}\gamma'\,.$$

This gives

$$\omega \chi_a = c_x \varphi_a - \sum_{1}^{3} \varphi_{a'} c_{a'a}.$$
 (A 25)

The meaning of the  $\chi$ 's therefore is: solution of the (collision) integral equation with  $c_x \varphi_a$ , ortho-

gonalized to  $\varphi_{1,2,3}$ , as the inhomogeneity. Calling

$$\varphi_1 - V_{\frac{3}{2}} \varphi_2 \equiv \varphi = \frac{5}{2} - \varepsilon,$$
 (A 26)

one has for

$$\chi_1 - V^{\frac{3}{2}} \chi_2 = -V^{\frac{3}{2}} \chi_2 \equiv \chi$$
 (A 27)

the equation

$$\omega \chi = c_x \varphi . \tag{A 28}$$

Thus,  $\chi$  is indeed the Chapman-Enskog "standard solution" for heat conduction from (5.8).

The "diffusivities"  $d_{\alpha\alpha'}$ , introduced in (A 15), are linked with the  $\chi$ 's. Let us consider

$$\begin{split} \int \chi_a \, \omega \, \chi_\beta \, \mathrm{d}\gamma &= \sum_4^\infty \int \varphi_{a'} \, \frac{c_{a'a}}{\omega_{a'}} \, (c_x \, \varphi_\beta - \ldots) \, \mathrm{d}\gamma \\ &= \sum_4^\infty c_{a'\beta} \, c_{a'a} / \omega_{a'} = d_{a\beta} \, . \end{split}$$

The dotted orthogonality term drops out on integration. Thus we have

$$d_{\alpha\beta} = \int \chi_{\alpha} \, \omega \, \chi_{\beta} \, \mathrm{d}\gamma \,. \tag{A 29}$$

Use of (A 27) and (5.16) now shows that

$$d_{22} = 2 T_0 \lambda / 3 P_0$$
. (A 30)

This says that  $d_{22}$  is the thermal diffusivity of the monatomic gas. The discussion of a unidirectional (non-stationary) compression flow, somewhat similar to the discussion in Eqs. (5.14) - (5.16), shows that

$$d_{33} = 4 \eta/3 \varrho_0$$
, (A 31)

where  $\eta/\varrho_0$  is the kinematic viscosity. Furthermore, because  $\chi_2$  is odd,  $\omega \chi_3$  even in  $\boldsymbol{p}$ , the cross element vanishes

$$d_{23} = 0$$
. (A 32)

This had been anticipated in (A 16).

Now, the eigenfunctions  $\psi_{\pm 1}$ ,  $\psi_{\pm 2}$  are composed according to (A 21), with the coefficients  $\hat{a}_{1,2,3}$  to be obtained from system (A 17) where  $k_{\pm 1}$ ,  $k_{\pm 2}$  have to be inserted respectively. A normalization factor is still open. In accordance with Eq. (2.13) we require

$$\begin{split} \mathbf{1} &= \int \psi \,\, \omega_{+} \, \psi \,\, \mathrm{d}\gamma \\ &= \frac{1}{\Omega} \, \sum_{1=1}^{3} \sum_{1=1}^{3} \int \left( \varphi_{a} + k \, \chi_{a} \right) \, \omega_{+} \left( \varphi_{\beta} + k \, \chi_{\beta} \right) \, \mathrm{d}\gamma \,\, \hat{a}_{a} \,\hat{a}_{\beta} \,. \end{split}$$

By use of  $\omega_+ \varphi_\beta = \Omega \varphi_\beta$  and of (A 23) and (A 29) this is equivalent to the requirement

$$\sum_{1}^{3}\sum_{1}^{3}\left(\delta_{\alpha\beta}+\frac{k^{2}}{\varOmega}\ d_{\alpha\beta}\right)\hat{a}_{a}\,\hat{a}_{\beta}=1\ . \tag{A 34}$$

In the matrix thereof, the strongly vanishing term  $k^2 \int \chi_{\alpha} \chi_{\beta} d\gamma$  has been neglected. One obtains in this way the normalized eigenfunctions

$$\psi_{\pm 1} = \frac{1}{V\Omega} \left( \varphi_1 \sqrt{\frac{3}{10}} + \varphi_2 \sqrt{\frac{2}{10}} \pm \varphi_3 \sqrt{\frac{5}{10}} + \left[ \pm \chi_2 \sqrt{\frac{3}{25}} \frac{\Omega}{c_0} + \chi_3 \sqrt{\frac{3}{10}} \frac{\Omega}{c_0} \right] \right) \quad (A35)$$

$$\psi_{\pm 2} = \frac{1}{V\Omega} \left( \varphi_1 \sqrt{\frac{2}{10}} - \varphi_2 \sqrt{\frac{3}{10}} \pm \varphi_3 \frac{\sqrt{3} d_{22} \Omega}{5 c_0} \right) \mp \chi_2 \sqrt{\frac{5 \Omega}{10 d_{22}}} + \left[ \chi_3 \frac{\Omega}{\sqrt{5} c_0} \right]. \tag{A 36}$$

The smallest terms, in the parentheses, of power  $\Omega$ , have been set between []-brackets. They are not needed in the applications, e. g. to regain the results of § 5, especially Eq. (5.17), and they should not be taken too seriously, because of the early approximation underlying (A 13). The normalization factors in (A 35) and (A 36) have been calculated without the []-terms. — As a general remark, it shall be pointed out that putting  $\Omega$  equal to zero destroys the existence of  $\psi_{1,2}$ . This of course had to be expected. — The sign property  $\psi_{-1} = \psi_{+1T}$ ,  $\psi_{-2} = \psi_{+2T}$  is fulfilled, in recognition of  $\varphi_{1,2T} = \varphi_{1,2}$ ;  $\varphi_{3T} = -\varphi_3$ ;  $\chi_{2T} = -\chi_2$ ;  $\chi_{3T} = \chi_3$ .

The "orthogonality" of  $\psi_1$ ,  $\psi_2$ , in the sense of (2.13), shall be checked. It can be handled in the same manner as the normalization in (A 33) and (A 34). This leads to

$$\int \psi_1 \, \omega_+ \, \psi_2 \, \mathrm{d}\gamma \approx \sum_{1}^{3} \sum_{1}^{3} \left( \delta_{\alpha\beta} + \, \frac{k_1 \, k_2}{\Omega} \, d_{\alpha\beta} \right) \hat{a}_{1\alpha} \, \hat{a}_{2\beta} \,. \tag{A 37}$$

With

$$\frac{k_1\,k_2}{\varOmega} = \frac{1}{c_0}\,\sqrt{\frac{\varOmega}{d_{22}}}$$

and with the coefficients  $\hat{a}_{1}...$ ,  $\hat{a}_{2}...$  from (A 35) and (A 36), one finds

$$\int \psi_1 \, \omega_+ \, \psi_2 \, \mathrm{d}\gamma = \frac{\sqrt{6}}{10} \, \frac{d_{33}}{c_0^2} \, \Omega \approx 0 \,. \quad \text{(A 38)}$$

The terms independent of  $\Omega$  and those in  $\sqrt{\Omega}$  have cancelled. So far, "orthogonality" is fulfilled, which is a check of the calculation. The small non-orthogonality of order  $\Omega$ , indicated by (A 38), is not serious. By the way, orthogonality defined by

$$\int \psi_1 \, c_x \, \psi_2 \, \mathrm{d}\gamma = 0 \tag{A 39}$$

is exactly fulfilled if one uses (A 35) and (A 36) without the []-terms.

Finally, the fluxes  $j_a$  of conserved quantities  $\varphi_a$ , a = 1, 2, 3, borne by the eigenfunctions  $\psi_{\pm 1}, \psi_{\pm 2}$ shall be considered. After (A5) and (A6) one has

$$\begin{split} & j_a = n_0 \int \varphi_a \, c_x \, \psi \, \mathrm{d}\gamma \\ & = n_0 \int \varphi_a \, c_x \left( \sum_{1}^3 \varphi_{a'} \, \frac{\hat{a}_{a'}}{\sqrt{\Omega}} + \sum_{4}^{\infty} \, \varphi_{a''} \, \frac{\hat{a}_{a''}}{\sqrt{\omega_{a''}}} \right) \, \mathrm{d}\gamma \, . \end{split}$$

Using (A13) and (A15) one obtains

$$j_a = n_0 \sum_{1}^{3} (c_{aa'} + k d_{aa'}) a_{a'}.$$
 (A 41)

<sup>2</sup> I. Kuščer, Surface Sci. 25, 225 [1971].

Apart from dimensional factors, the three cases are:

$$\begin{split} & \text{particle flux} \qquad j_1 = n_0 \, c_0 \, a_3 \,, \\ & \text{energy flux} \qquad j_2 = n_0 \, c_0 \left( \sqrt{\frac{2}{3}} \, a_3 + \, \frac{1}{c_0} \, k \, d_{22} \, a_2 \, \right), \\ & \text{momentum flux } j_3 = n_0 \, c_0 \left( a_1 + \sqrt{\frac{2}{3}} \, a_2 + \, \frac{1}{c_0} \, k \, d_{33} \, a_3 \right). \end{split}$$

In  $j_2$ , one recognizes the convection part and the proper heat flux, proportional to  $d_{22}$ . In  $j_3$ , the static pressure and the friction pressure, proportional to  $d_{33}$ , appear. The respective a's have to be gathered from (A 35) and (A 36). It is unnecessary to pursue this in further detail.

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<sup>7</sup> M. v. Smoluchowski, S. Akad. Wiss. Wien 108, 5 [1899].

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<sup>&</sup>lt;sup>3</sup> C. Cercignani, Transp. Theory and Statist. Phys. 2, 27

<sup>&</sup>lt;sup>4</sup> C. Cercignani, Theory and Application of the Boltzmann Equation, Scottish Academic Press, Edinburgh 1975.