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Theory of Boundary Conditions for the Boltzmann Equation

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In preceding papers, Refs. [1, 2], boundary conditions were developed for transport-relaxation equations by aid of a general reciprocity postulate for the interface. The same method is now used for the linearized Boltzmann equation. A new scheme emerges: the kinetic boundary conditions consist in a linear functional relation between interfacial "forces and fluxes" — in the sense of non-equilibrium thermodynamics — which are, broadly speaking, given by the sum and the difference of the molecular distribution function and its time-reversed, at the wall. The general properties of the kernels occurring in this atomistic boundary law are studied. The phenomenological surface coefficients of (generalized) linear thermo-hydrodynamics, as e. g. temperature jump, slip coefficients etc., can in a simple way be expressed by the kernel of the atomistic boundary law. This kernel is explicitly worked out for completely thermalizing wall collisions.

The reciprocity concept provides a natural access to the boundary conditions appropriate with the coupled differential equations of a generalized linear hydrodynamics [1, 2]. These transport-relaxation equations, with their first order time and space derivatives, originated by the moment method from the Boltzmann equation for dilute gases, though afterwards their range of phenomenological applicability may go beyond this gas regime. As a reminiscence of the said origin the reciprocity theorem for the linearized Boltzmann equation itself was marginally contained in References [1, 2].

In reversing the direction of the route, the question is now asked: what can one learn about boundary conditions for the linearized Boltzmann equation from what is known about those for the transport-relaxation equations? This desire is quite old. Already the very first paper, from 1967, on non-equilibrium thermodynamics of boundary conditions [3] contained a remark that this method may prove to be a hint for kinetic theory; again in [5] recourse to the surface scattering operator was felt highly desirable. Such a program now seems to be realized, with gain in understanding and in handling boundary conditions for the Boltzmann equation. Those hitherto in use exclusively, stated a linear functional relation between the distribution functions of the molecules approaching the wall and of those leaving it. By the new method, boundary conditions arise which state a linear functional relation between surface "forces and fluxes", Equations (4.15). The "forces and fluxes" in essence are given by the sum and the difference of the distribution function at the wall and its time-reversed counterpart, for molecular velocities directed to the wall, Equations (4.9) and (4.7). Such a scheme seamlessly connects the kinetic theory of dilute gases with non-equilibrium thermodynamics and also promises advantages for the applications. A few of them are developed at the end of this paper. At the beginning some necessary expositions of entropy etc. are given.

1. Linearized Boltzmann Equation and Non-Equilibrium Entropy of Gas

The one-particle distribution $f(t, \boldsymbol{x}, \boldsymbol{p})$ of the gas depends on time, space coordinates and particle momentum. Its normalization is such that the integral over the whole spaces

$$\iint f \, \mathrm{d}^3x \, \mathrm{d}^3p = N \tag{1.1}$$

gives the total number of particles. The distribution shall be close to an absolute equilibrium

$$f = f_0 (1 + \Phi) , \quad \text{“}|\Phi| \ll 1\text{”} , \tag{1.2}$$

where

$$f_0 = n_0 (2 \pi m k T_0)^{-3/2} \exp\{-p^2/2 m k T_0\} , \tag{1.3}$$

with

$$\iint f_0 \, \mathrm{d}^3x \, \mathrm{d}^3p = N_0 , \tag{1.4}$$

is a resting Maxwellian with number density n_0, temperature T_0, particle mass m and Boltzmann's k.

The relative deviation $\Phi(t, \boldsymbol{x}, \boldsymbol{p})$ is governed by the linearized Boltzmann equation

$$\frac{\partial \Phi}{\partial t} + c_\nu \frac{\partial \Phi}{\partial x_\nu} + \omega(\Phi) = 0 \quad \text{with} \quad c_\nu = \frac{p_\nu}{m} . \tag{1.5}$$

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Here, $\nu = 1, 2, 3$ numbers the Cartesian coordinates, to be summed; $\omega(\ldots)$ is the linearized collision operator. From (1.5) the "entropy" balance

$$\frac{\partial}{\partial t}\left(-\frac{P_0}{T_0}\int \frac{1}{2}\,\Phi^2\,\mathrm{d}\gamma\right) + \frac{\partial}{\partial x_\nu}\left(-\frac{P_0}{T_0}\int \frac{1}{2}\,\Phi\,c_\nu\,\Phi\,\mathrm{d}\gamma\right) = \frac{P_0}{T_0}\int \Phi\,\omega(\Phi)\,\mathrm{d}\gamma \geqq 0 \tag{1.6}$$

follows directly. The dimensionless integration element

$$\mathrm{d}\gamma \equiv (f_0/n_0)\,\mathrm{d}^3p\,, \quad \text{hence} \quad \int \mathrm{d}\gamma = 1\,, \tag{1.7}$$

has been employed. With it, the non-negativeness of the right side of (1.6) holds. The common constant factor P_0/T_0, absolute equilibrium pressure/temperature, gives the dimension of entropy density. It has been inserted in foresight of Equation (1.25).

Let us expand the distribution with respect to a complete basis $\{\varphi\}$

$$\Phi = \sum_1^\infty \varphi_{i'}(\boldsymbol{p})\,a_{i'}(t, \boldsymbol{x})\,. \tag{1.8}$$

The basis is chosen to be orthonormalized in the sense

$$\int \varphi_i\,\varphi_{i'}\,\mathrm{d}\gamma = \delta_{ii'}\,. \tag{1.9}$$

As an equivalent to (1.5) one obtains the transport-relaxation equations for the dimensionless a's

$$\frac{\partial a_i}{\partial t} + \sum c_{\nu ii'}\,\frac{\partial a_{i'}}{\partial x_\nu} + \sum \omega_{ii'}\,a_{i'} = 0\,. \tag{1.10}$$

The coefficients are

$$c_{\nu ii'} = \int \varphi_i\,c_\nu\,\varphi_{i'}\,\mathrm{d}\gamma\,, \quad \omega_{ii'} = \int \varphi_i\,\omega(\varphi_{i'})\,\mathrm{d}\gamma\,. \tag{1.11}$$

The φ's are numbered in such a way that the first few of them correspond to the conserved quantities. Hence, with a monatomic gas, one has

$$\omega(\varphi_i) = 0 \quad \text{for} \quad i = 1, \ldots, 5\,. \tag{1.12}$$

The pertinent a's shall be

$$a_{1,2,3\ldots5} \propto n - n_0\,,\; u - u_0\,,\; v_1\,,\; v_2\,,\; v_3\,, \tag{1.13}$$

namely the deviations from absolute equilibrium of the densities of number, internal energy and momentum (gas velocity). The "entropy" balance to be inferred from (1.10), equivalent to (1.6), is

$$\frac{\partial}{\partial t}\left(-\frac{P_0}{T_0}\sum_1^\infty \frac{1}{2}\,a_i^2\right) + \frac{\partial}{\partial x_\nu}\left(-\frac{P_0}{T_0}\sum_1^\infty \sum_1^\infty \frac{1}{2}\,a_i\,c_{\nu ii'}\,a_{i'}\right) = \frac{P_0}{T_0}\sum_6^\infty \sum_6^\infty a_i\,\omega_{ii'}\,a_{i'} > 0\,. \tag{1.14}$$

With minor changes these formulae are also valid for polyatomic gases.

From the H-theorem of the quadratic Boltzmann equation, the expression for a local kinetic non-equilibrium entropy density is well known:

$$s = -k \int f\,[\ln(f\,h^3) - 1]\,\mathrm{d}^3p\,. \tag{1.15}$$

Planck's constant h renders the argument of the logarithm dimensionless as it must be. In equilibrium the correct high temperature limit of quantum statistics is attained (correct chemical constant). But this is not essential in the following. More important is it to mention that the integral (1.15) is independent of the choice of the zero-point in momentum space; in other words: s is Galilean-invariant.

The decomposition (1.2) is inserted into (1.15). Up to terms quadratic in Φ one has

$$f[\ln(f\,h^3) - 1] \approx f_0\,[\ln(f_0\,h^3) - 1] + f_0 \ln(f_0\,h^3)\,\Phi + \tfrac{1}{2}\,f_0\,\Phi^2\,.$$

Introduction of the thermal de Broglie wavelength

$$l_0 = h/\sqrt{2\,\pi\,m\,k\,T_0} \tag{1.16}$$

gives

$$\ln(f_0\,h^3) = \ln(n_0\,l_0^3) - p^2/2\,m\,k\,T_0\,.$$

Hence, up to quadratic terms, the entropy density (1.15) is

$$s = s_0 - P_0/T_0 \int \{[\ln(n_0\,l_0^3) - p^2/2\,m\,k\,T_0]\,\Phi + \tfrac{1}{2}\,\Phi^2\}\,\mathrm{d}\gamma\,. \tag{1.17}$$

Use has been made of the ideal gas law

$$k\,n_0 = P_0/T_0\,. \tag{1.18}$$

Furthermore,

$$u_0 = \frac{3}{2}\,P_0\,, \quad s_0 = \frac{P_0}{T_0}\left[\frac{5}{2} - \ln(n_0\,l_0^3)\right] \equiv s_{\mathrm{eq}}(n_0, u_0) \tag{1.19}$$

are the equilibrium (internal) energy and entropy densities. The terms linear in Φ of (1.17) can be re-expressed:

$$\int \Phi\,\mathrm{d}\gamma = (n - n_0)/n_0 \tag{1.20}$$

$$\int \frac{p^2}{2\,m}\,\Phi\,\mathrm{d}\gamma = \frac{e - u_0}{n_0} \approx \frac{u - u_0}{n_0} + \frac{1}{2}\,m\,v^2\,, \tag{1.21}$$

where n and e are the number and total energy densities, $\boldsymbol{v}$ the gas velocity. With the equilibrium chemical potential per particle

$$\mu_0 = k\,T_0 \ln (n_0\, l_0{}^3)\ , \tag{1.22}$$

the entropy density (1.17) takes the form

$$s = s_0 - \frac{\mu_0}{T_0}(n - n_0) + \frac{1}{T_0}(e - u_0) - \frac{P_0}{T_0}\int \frac{1}{2}\,\Phi^2\,\mathrm{d}\gamma\,. \tag{1.23}$$

The integral can be expressed by the expansion coefficients from (1.8) which casts (1.23) into the equivalent form

$$s = s_0 - \frac{\mu_0}{T_0}(n - n_0) + \frac{1}{T_0}(e - u_0) - \frac{P_0}{T_0}\sum_1^\infty \frac{1}{2}\,a_i^2\,. \tag{1.24}$$

In the simple "entropy" balance (1.6) or (1.14) only the last purely quadratic term of (1.23) or (1.24) featured as "entropy density". This suffices to express the positivity of entropy production, right side of (1.6) or (1.14). The merit of the more cumbersome expressions (1.23) or (1.24) for the complete entropy density is that they fix the correct normalization of the quadratic terms. Recourse to that is necessary when two media in contact are considered and the transport-relaxation equations for both of them have to be properly fitted together ("same footing"). Details on this are in § 2.

The time derivative of the entropy density (1.23) or (1.24) is

$$\frac{\partial s}{\partial t} = -\frac{\mu_0}{T_0}\frac{\partial n}{\partial t} + \frac{1}{T_0}\frac{\partial e}{\partial t} + \dots$$

where the dots allude to the integral or sum term. The particle and energy conservation laws are

$$\frac{\partial n}{\partial t} + \frac{\partial n\, v_\nu}{\partial x_\nu} = 0\,,$$

$$\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_\nu}(e\, v_\nu + p_{\nu\mu}\, v_\mu + q_\nu) = 0\,,$$

with $p_{\nu\mu}$ and q_ν the pressure tensor and the heat flux. In quadratic approximation one has to put $e\, v_\nu = u\, v_\nu$. Hence

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial x_\nu}\frac{1}{T_0}[(-\mu_0\, n + u)\, v_\nu + p_{\nu\mu}\, v_\mu + q_\nu] + \dots$$

Re-use of (1.24) gives in quadratic approximation

$$\begin{aligned}(-\mu_0\, n + u)\, v_\nu &= [-\mu_0\, n_0 + u_0 + T_0(s - s_0)]\, v_\nu \\ &= (T_0\, s - P_0)\, v_\nu\,.\end{aligned}$$

With that and with (1.14) the complete entropy balance becomes

$$\begin{aligned}\frac{\partial s}{\partial t} + \frac{\partial}{\partial x_\nu}\Big[s\, v_\nu + \frac{1}{T_0}(p_{\nu\mu} - P_0\,\delta_{\nu\mu})\, v_\mu + \frac{1}{T_0}\, q_\mu \\ - \frac{P_0}{T_0}\sum_1^\infty\sum_1^\infty \frac{1}{2}\, a_i\, c_{\nu ii'}\, a_{i'}\Big] = \frac{P_0}{T_0}\sum_6^\infty\sum_6^\infty a_i\,\omega_{ii'}\, a_{i'} > 0\,.\end{aligned} \tag{1.25}$$

The expression in the square bracket of (1.25) is the complete entropy flux. Its normal component at an interface gives the contribution of the gas to the interfacial entropy production. A similar contribution comes from the medium on the other side, the solid wall, to be considered in § 2. However, one notices that the first three fluxes in the square bracket of (1.25) refer to quantities which have a meaning for any medium, gas or solid, because they originate from the universal conservation laws [they can be traced back to the $\ln(f_0\, h^3)$-term of the equilibrium canonical distribution in (1.17)]. The normal components of these three fluxes, added for both sides and integrated over the interface, give zero if there is – by assumption – no net transfer of mass, momentum and energy to the interface.

So, thanks to the conservation laws, it is allowed to forget about the first three terms of the complete entropy flux and focus on the fourth, purely quadratic one, whenever the interfacial entropy production $\dot{S}_\sigma$ is envisaged. In this sense, we may state that the contribution to it of the gas (medium I) is

$$\dot{S}_{\sigma\mathrm{I}} \triangleq \int \mathrm{d}\sigma\, \frac{P_0}{T_0}\Big[\sum_1^\infty\sum_1^\infty \frac{1}{2}\, a_i\, c_{ii'}\, a_{i'}\Big]_{\mathrm{I}} \tag{1.26}$$

$$= \int \mathrm{d}\sigma\, \frac{P_0}{T_0}\int \frac{1}{2}\, c\,\Phi^2\,\mathrm{d}\gamma\,. \tag{1.27}$$

The abbreviations

$$[c_{ii'} = c_{\nu ii'}\, n_\nu]_{\mathrm{I}} \tag{1.28}$$

and

$$c = c_\nu\, n_{\nu\mathrm{I}} \tag{1.29}$$

have been used; $n_{\nu\mathrm{I}}$ is the outer unit normal of the gas. Expression (1.26) has been obtained directly from the transport-relaxation equations first in [4], again in [5]. To call it "the surface entropy production" as it has been done, may be a little bit loose, but cannot cause misunderstanding.

One last remark shall be made about (1.24). Let us combine the first five terms of $\Sigma\, a_i^2$ with the first three terms of s. Together, they form a Taylor expansion of the equilibrium entropy about absolute equilibrium, up to quadratic terms. Hence, in the quadratic approximation — and nothing else is considered here — the non-equilibrium entropy density (1.24) can also be written as

$$s = s_{\mathrm{eq}}(n, u) - \frac{P_0}{T_0} \sum_{6}^{\infty} \frac{1}{2} a_i^2 . \qquad (1.30)$$

The reduced sum contains non-equilibrium quantities (heat flux, etc, etc) only. Both terms on the right side are now manifestly Galilean-invariant. To ignore the sum in (1.30) amounts to the "Gibbs assumption" of non-equilibrium thermodynamics in the narrow sense, based on ordinary (linear) hydrodynamics. The full expression (1.30) is typical for the non-equilibrium thermodynamics in the broad sense, based on the general (linear) transport-relaxation equations.

2. Transport-Relaxation Equations for Solid and Interfacial Entropy Production

The walls enclosing the gas are assumed to be at rest and to consist of an incompressible solid (medium II) completely described by the fields of temperature $T(t, \boldsymbol{x})$ and heat flux $\boldsymbol{q}(t, \boldsymbol{x})$. The linear differential equations for these are

$$\begin{aligned} \gamma_0 \frac{\partial (T - T_0)}{\partial t} + \nabla \cdot \boldsymbol{q} &= 0 , \\ \frac{\partial \boldsymbol{q}}{\partial t} + \lambda\, \omega \nabla (T - T_0) + \omega\, \boldsymbol{q} &= 0 . \end{aligned} \qquad (2.1)$$

T_0 is the same temperature of absolute equilibrium as in § 1. To emphasize the smallness of the deviations from equilibrium, the temperature variable has been taken as $T - T_0$ instead of simply T. The specific heat per unit volume is called $\gamma(T)$ and it is abbreviated

$$\gamma_0 = \gamma(T_0) . \qquad (2.2)$$

The heat conductivity is denoted by λ, the relaxation constant of the heat flux by ω.

The question is how to introduce, instead of $T - T_0$ and $\boldsymbol{q}$, new variables $a_{(\mathrm{II})}$ and $\boldsymbol{a}_{(\mathrm{II})}$ which obey transport-relaxation equations of type (1.10) and which are "on the same footing" with the variables $a_{i(\mathrm{I})}$, $i = 1, \ldots, \infty$, pertinent to the gas. The key to answer this question lies in Eq. (1.24). We use it to write down the entropy density of the solid in an equilibrium state different from the O-state, up to quadratic terms which (1.24) is good for,

$$s = s_{\mathrm{eq}} = s_0 + \frac{1}{T_0} (u - u_0) - \frac{P_0}{T_0} \frac{1}{2} a^2 . \qquad (2.3)$$

The second term of the right side of (1.24) does not appear because of incompressibility and one has $e = u$ because the solid is at rest. By means of the thermodynamical definitions

$$\mathrm{d}u = \gamma(T)\, \mathrm{d}T , \quad \mathrm{d}s_{\mathrm{eq}} = [\gamma(T)/T]\, \mathrm{d}T$$

one can on the other hand directly note the quadratic Taylor expansions

$$u = u_0 + \gamma_0 (T - T_0) + \tfrac{1}{2}\, \mathrm{d}\gamma_0/\mathrm{d}T_0 \ (T - T_0)^2 , \qquad (2.4)$$

$$s_{\mathrm{eq}} = s_0 + \frac{\gamma_0}{T_0} (T - T_0) + \frac{1}{2} \left(\frac{1}{T_0} \frac{\mathrm{d}\gamma_0}{\mathrm{d}T_0} - \frac{\gamma_0}{T_0^2} \right) (T - T_0)^2 . \qquad (2.5)$$

Dividing (2.4) by T_0 and subtracting it from (2.5) yields

$$s_{\mathrm{eq}} = s_0 + \frac{1}{T_0} (u - u_0) - \frac{1}{2} \gamma_0 \left(\frac{T - T_0}{T_0} \right)^2 . \qquad (2.6)$$

This has the form of (2.3) and shows how one has to identify:

$$a = \sqrt{\frac{\gamma_0 T_0}{P_0}}\, \frac{T - T_0}{T_0} . \qquad (2.7)$$

Herewith, the new dimensionless variable a is determined. Now it is compulsory to take

$$\boldsymbol{a} = \sqrt{\frac{\gamma_0 T_0}{P_0}}\, \frac{\boldsymbol{q}}{T_0 \sqrt{\gamma_0 \lambda\, \omega}} \qquad (2.8)$$

as the vectorial variable $\boldsymbol{a}$ in order to obtain transport-relaxation equations of the symmetrical form

$$\begin{aligned} \partial a/\partial t + c\, \nabla \cdot \boldsymbol{a} &= 0 , \\ \partial \boldsymbol{a}/\partial t + c\, \nabla a + \omega\, \boldsymbol{a} &= 0 , \end{aligned} \qquad (2.9)$$

instead of the original unsymmetrical Equations (2.1). The velocity constant c is given by

$$c_{(\mathrm{II})} = \sqrt{\lambda\, \omega / \gamma_0} . \qquad (2.10)$$

The "entropy" balance for the solid [special case of Eq. (1.14), again the purely quadratic balance, to be directly gathered from (2.9)] is

$$\frac{\partial}{\partial t} \left(- \frac{P_0}{T_0} \frac{1}{2} (a^2 + \boldsymbol{a} \cdot \boldsymbol{a}) \right) + \nabla \cdot \left(- \frac{P_0}{T_0} a\, c\, \boldsymbol{a} \right) = \frac{P_0}{T_0} \omega\, \boldsymbol{a} \cdot \boldsymbol{a} > 0 . \qquad (2.11)$$

From this one infers immediately the solid's (medium II) contribution to the interfacial entropy production rate

$$\dot{S}_{\sigma \mathrm{II}} = \int \mathrm{d}\sigma \, \frac{P_0}{T_0} \, [a\, c\, \boldsymbol{a} \cdot \boldsymbol{n}]_{\mathrm{II}} \,, \qquad (2.12)$$

where

$$\boldsymbol{n}_{\mathrm{II}} = -\boldsymbol{n}_{\mathrm{I}}$$

is the outer unit normal of the solid. It is gratifying (and necessary) that the dimensional factor P_0/T_0 in (2.12) and (1.26) consists of intensive absolute equilibrium qualities common to both media, gas and solid. This is inherent in "same footing". Replacing the a-variables according to (2.7) and (2.8) by the original ones, gives the alternative expression

$$\dot{S}_{\sigma \mathrm{II}} = \int \mathrm{d}\sigma \left[\frac{T - T_0}{T_0^2} \, \boldsymbol{q} \cdot \boldsymbol{n} \right]_{\mathrm{II}} \qquad (2.13)$$

which is no surprise.

Finally, adding the contributions of the gas [(1.26) or (1.27)] and of the solid [(2.12) or (2.13)] gives the total rate of interfacial entropy production

$$\begin{aligned} \dot{S}_{\sigma} &= \int_{\sigma_{\mathrm{I\,II}}} \mathrm{d}\sigma \, \frac{P_0}{T_0} \left\{ \left[\sum_1^{\infty} \sum_1^{\infty} \frac{1}{2} \, a_i \, c_{ii'} \, a_{i'} \right]_{\mathrm{I}} + [a\, c\, \boldsymbol{a} \cdot \boldsymbol{n}]_{\mathrm{II}} \right\} \\ &= \int_{\sigma_{\mathrm{I\,II}}} \mathrm{d}\sigma \, \frac{P_0}{T_0} \left\{ \int \frac{1}{2} \, c \, \Phi^2 \, \mathrm{d}\gamma + \left[\frac{T - T_0}{T_0} \, \frac{q}{P_0} \right]_{\mathrm{II}} \right\} > 0 \,, \end{aligned} \qquad (2.14)$$

where

$$q_{\mathrm{II}} = \boldsymbol{q}_{\mathrm{II}} . \boldsymbol{n}_{\mathrm{II}}$$

is the component of the solid's heat flux in the direction of the outer unit normal $\boldsymbol{n}_{\mathrm{II}}$ of the solid. To comply with the second law, positiveness of the interfacial entropy production has to be required. However, if there are no surface currents, as we assume, even positiveness of the integrand,

$$\int \frac{1}{2} \, c \, \Phi^2 \, \mathrm{d}\gamma + \left[\frac{T - T_0}{T_0} \, \frac{q}{P_0} \right]_{\mathrm{II}} > 0 \quad \text{at } \sigma_{\mathrm{I\,II}} \qquad (2.15)$$

must hold.

The procedure of this section to obtain the correctly defined variables a – namely by comparing equilibrium entropy expressions – always has to be applied when two media are combined to form one composite system. E. g. the postulate of universal reciprocity enunciated by Eq. (5.4) of Ref. [2] presupposes variables a_{I}, a_{II} which have been brought on the "same footing" by the said procedure. The linear homogeneous transport-relaxation equations themselves, different for two separate domains, are unable to fix their mutual normalization.

3. Reciprocity Postulate for Interface Gas/Solid

As the last preparation before establishing boundary conditions of the Boltzmann equation, we have to write down the local reciprocity postulate for an interface, Eq. (5.6) of Ref. [2], for our special case of a gas (I)/solid (II) system.

In matrix notation the reciprocity theorem for two stationary solutions, discerned by superscripts (1), (2), of the transport-relaxation equations (1.10) is [see Eq. (21 b) of Ref. [1]]

$$\int_{\sigma} \mathrm{d}\sigma \, \tilde{a}_{\mathrm{T}}^{(2)} \cdot c \cdot a^{(1)} = 0 \,. \qquad (3.1)$$

The time-reversed state is denoted by

$$a_{\mathrm{T}} = \Theta \cdot a \,; \qquad (3.2)$$

c is the "normal component" of the coefficient matrices c_{ν} of (1.10),

$$c = c_{\nu} \, n_{\nu} \,, \qquad (3.3)$$

where n_{ν} is chosen as the outer unit normal of the closed surface σ. For later convenience let us introduce the abbreviation

$$\tilde{a}_{\mathrm{T}}^{(2)} \cdot c \cdot a^{(1)} \equiv R^{(12)} = -R^{(21)} \qquad (3.4)$$

for the "reciprocity scalar" which has the dimension of a velocity. (According to § 1 and 2 the a's are dimensionless.)

The local reciprocity postulate for the interface between medium I (gas) and medium II (solid) in elaborate form (no interfacial currents admitted) is [see Eq. (5.6) of Ref. [2]]

$$R_{\mathrm{I}}^{(12)} + R_{\mathrm{II}}^{(12)} = 0 \quad \text{at } \sigma_{\mathrm{I\,II}} \,. \qquad (3.5)$$

Prerequisite is that the a_{I}, a_{II} are "on the same footing" as explained in § 2.

In components the R's are

$$R_{\mathbf{I}}^{(12)} = \left[\sum \sum a_{\mathrm{T}i}^{(2)} \, c_{ii'} \, a_{i'}^{(1)} \right]_{\mathrm{I}} \,, \qquad (3.6)$$

$$R_{\mathrm{II}}^{(12)} = \left[c \left(a_{\mathrm{T}}^{(2)} \, \boldsymbol{a}^{(1)} + \boldsymbol{a}_{\mathrm{T}}^{(2)} \, a^{(1)} \right) \cdot \boldsymbol{n} \right]_{\mathrm{II}} \,. \qquad (3.7)$$

The expression for R_{II}, with the underlying "four vector" $\{a, \boldsymbol{a}\}_{\mathrm{II}}$ from (2.7) and (2.8), is either taken directly from (2.9) and its time-reversed counterpart, or from the general form (R_{I}!) by aid of the special c-matrix

$$c_{\mathrm{II}} \begin{pmatrix} 0 & \tilde{\boldsymbol{n}} \\ \boldsymbol{n} & \mathbf{0} \end{pmatrix}_{\mathrm{II}}$$

for the heat conduction case (see § 7 of Ref. [2]; c_{II} had then been put $= 1$).

Again, the reciprocity scalar for the gas shall be expressed by the distribution Φ. For this purpose let us write Eq. (3.2) in components

$$a_{\mathrm{T}i} = \sum \Theta_{ii'}\, a_{i'} \,. \tag{3.8}$$

By introducing the time-(motion-) reversed basis functions, cf. (1.8),

$$\varphi_{\mathrm{T}i}(\boldsymbol{p}) \equiv \varphi_i(-\boldsymbol{p}) = \sum \Theta_{ii'}\, \varphi_{i'}(\boldsymbol{p}) \tag{3.9}$$

one gets the time reversal matrix in component form

$$\Theta_{ii'} = \int \varphi_{\mathrm{T}i}\, \varphi_{i'}\, \mathrm{d}\gamma = \Theta_{i'i} \,. \tag{3.10}$$

The distribution described by a_{T} therefore is

$$\sum \varphi_i\, a_{\mathrm{T}i} = \sum \sum \varphi_i\, \Theta_{ii'}\, a_{i'} = \sum \varphi_{\mathrm{T}i'}\, a_{i'} = \Phi_{\mathrm{T}} \,,$$

where

$$\Phi_{\mathrm{T}}(\boldsymbol{x}, \boldsymbol{p}) \equiv \Phi(\boldsymbol{x}, -\boldsymbol{p}) \,. \tag{3.11}$$

Hence, a_{T} describes the time-(motion) reversed distribution Φ_{T} corresponding to Φ.

Using (1.11), (1.28) and (1.29) one has therefore

$$R_{\mathrm{I}}^{(12)} = \int \sum \sum \,[a_{\mathrm{T}i}^{(2)}\, \varphi_i\, c\, \varphi_{i'}\, a_{i'}^{(1)}]_{\mathrm{I}}\, \mathrm{d}\gamma = \int \Phi_{\mathrm{T}}^{(2)}\, c\, \Phi^{(1)}\, \mathrm{d}\gamma \,. \tag{3.12}$$

This also comes from the monatomic gas case of Eq. (7.14) of Reference [2].

For the solid one has

$$[a_{\mathrm{T}} = a,\ \boldsymbol{a}_{\mathrm{T}} = -\boldsymbol{a}]_{\mathrm{II}} \,, \tag{3.13}$$

to be utilized in (3.7).

The local reciprocity postulate (3.5) now takes the equivalent shape

$$\int \Phi_{\mathrm{T}}^{(2)}\, c\, \Phi^{(1)}\, \mathrm{d}\gamma + [c\,(a^{(2)}\, \boldsymbol{a}^{(1)} \cdot \boldsymbol{n} - \boldsymbol{a}^{(2)} \cdot \boldsymbol{n}\, a^{(1)})\,]_{\mathrm{II}} = 0 \ \text{ at } \sigma_{\mathrm{I\,II}} \,. \tag{3.14}$$

The meaning of c in the integral is repeated: it is the component of the particle velocity in the direction of the outer unit normal $\boldsymbol{n}_{\mathrm{I}}$ of the gas

$$c = \boldsymbol{c} \cdot \boldsymbol{n}_{\mathrm{I}} \gtreqless 0 \,. \tag{3.15}$$

The constant c_{II} has been introduced by Equation (2.10). Now, it is a short way to the boundary conditions.

4. Boundary Conditions for Linearized Boltzmann Equation

In § 6 of Ref. [2], form and symmetries of interfacial boundary (matching) conditions for two sets of transport-relaxation equations, tacitly "on same footing", have been developed from the "postulate of universal reciprocity". The decisive step was to introduce, instead of the full "state vector" a (for each medium) at the interface, two linearly independent vectors, a surface force f and a surface flux j, belonging to a subspace, according to *

$$\begin{aligned} f &= \frac{1}{\sqrt{2}} P_{+} \cdot \quad (1 + \Theta) \cdot a \equiv \frac{1}{\sqrt{2}} P_{+} \cdot \quad (a + a_{\mathrm{T}}) \,, \\ j &= \frac{1}{\sqrt{2}} P_{+} \cdot c \cdot (1 - \Theta) \cdot a \equiv \frac{1}{\sqrt{2}} P_{+} \cdot c \cdot (a - a_{\mathrm{T}}) \,. \end{aligned} \tag{4.1}$$

This allows to rewrite the bilinear reciprocity scalar (3.4) as the difference of two "scalar products"

$$R^{(12)} \equiv \tilde{a}_{\mathrm{T}}^{(2)} \cdot c \cdot a^{(1)} = \tilde{f}^{(2)} \cdot j^{(1)} - \tilde{j}^{(2)} \cdot f^{(1)} \,. \tag{4.2}$$

It is recalled that the matrix P_{+}, defined in § 2 of Ref. [2], projects into the subspace of positive eigenvalues of the c-matrix. – With this at hand the formulation of boundary conditions is straightforward: linear relations between f's and j's for the gas and the solid. We begin with the solid.

As an illustration of (4.1), the force/flux pair belonging to the "state vector"

$$a_{\mathrm{II}} \equiv \begin{pmatrix} \mathrm{a}_{\mathrm{II}} \\ \boldsymbol{a}_{\mathrm{II}} \end{pmatrix} \tag{4.3}$$

of a heat conducting medium, has been established in § 7 of Ref. [2]:

$$f_{\mathrm{II}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \boldsymbol{n}_{\mathrm{II}} \end{pmatrix} \mathrm{a}_{\mathrm{II}} \,, \quad j_{\mathrm{II}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \boldsymbol{n}_{\mathrm{II}} \end{pmatrix} c_{\mathrm{II}} (\boldsymbol{a} \cdot \boldsymbol{n})_{\mathrm{II}} \,. \tag{4.4}$$

(In Ref. [2] the first component a of the state vector a was called a_0 and there was no $1/\sqrt{2}$.) The reciprocity scalar for the solid then is

$$R_{\mathrm{II}}^{(12)} = \tfrac{1}{2} (1\ \tilde{\boldsymbol{n}}_{\mathrm{II}}) \cdot \begin{pmatrix} 1 \\ \boldsymbol{n}_{\mathrm{II}} \end{pmatrix} [a^{(2)}\, c\, \boldsymbol{a}^{(1)} \cdot \boldsymbol{n} - c\, \boldsymbol{a}^{(2)} \cdot \boldsymbol{n}\, a^{(1)}]_{\mathrm{II}} \,.$$

The factor in front, half of the "scalar product" of the "four vector" $(1, n_1, n_2, n_3)$ with itself, is one. The square bracket on insertion of (2.7), (2.8), and (2.10) gives

$$R_{\mathrm{II}}^{(12)} = \frac{1}{T_0 P_0} [\,(T^{(2)} - T_0)\, q^{(1)} - q^{(2)}\, (T^{(1)} - T_0)\,]_{\mathrm{II}} \,. \tag{4.5}$$

---

* Incorporation of the factors $1/\sqrt{2}$ in definitions (4.1) leads to an entropy production $\dot{s} = f\, j$ without numerical factor, cf. Equation (4.19). In Ref. [2, 4, 5] the f, j were defined without the $1/\sqrt{2}$. So, Eq. (3.6) of Ref. [2], was $\dot{s} = \tfrac{1}{2} f\, j$, against the custom in non-equilibrium thermodynamics.

By q_{II} the normal component of the heat flux in the solid,

$$q_{\mathrm{II}} = \boldsymbol{q}_{\mathrm{II}} \cdot \boldsymbol{n}_{\mathrm{II}} \gtreqless 0 \,, \tag{4.6}$$

is understood. Form (4.5) seduces one, secondarily so to say, to define a new interfacial force/flux pair for the solid

$$F_{\mathrm{II}} = \frac{T_{\mathrm{II}} - T_0}{T_0} \,, \quad J_{\mathrm{II}} = \frac{q_{\mathrm{II}}}{P_0} \quad \text{at } \sigma_{\mathrm{I\,II}} \,, \tag{4.7}$$

dimensionless and a velocity, respectively. The reciprocity scalar of the solid then appears in the reduced shape

$$R_{\mathrm{II}}^{(12)} = [F^{(2)} J^{(1)} - J^{(2)} F^{(1)}]_{\mathrm{II}} \,. \tag{4.8}$$

The gas described by the distribution $\Phi(\boldsymbol{x}, \boldsymbol{p})$, will have a *surface force/flux pair* which also is a function of $\boldsymbol{p}$ (and of $\boldsymbol{x} \in \sigma_{\mathrm{I\,II}}$). The view of (4.1) suggests the ansatz

$$\begin{aligned} F_{\mathrm{I}} &= \frac{1}{\sqrt{2}} P_+ \; (\Phi + \Phi_{\mathrm{T}}) \,, \\ J_{\mathrm{I}} &= \frac{1}{\sqrt{2}} P_+ c \, (\Phi - \Phi_{\mathrm{T}}) \,. \end{aligned} \tag{4.9}$$

The P_+, and likewise P_-, are the Heaviside functions

$$\begin{aligned} P_+(c) &= 0 \text{ for } c < 0 \,, \quad = 1 \text{ for } c > 0 \\ P_-(c) &= 1 \text{ for } c < 0 \,, \quad = 0 \text{ for } c > 0 \,. \end{aligned} \tag{4.10}$$

They have the projector properties

$$P_+^2 = P_+ \,, \; P_-^2 = P_- \,, \; P_+ P_- = 0 \,, \tag{4.11}$$

are conjugate by time reversal and are "complete":

$$P_- = P_{+\mathrm{T}} \,, \quad P_+ + P_- = 1 \,, \tag{4.12}$$

as long as nothing singular happens at $c = 0$, i. e. for grazing velocities. (Whether an analogon of the projector P_0 of Ref. [2] should also be embodied, cannot be decided presently.) Now it is verified that the ansatz (4.9), plotted into the proper form of (4.2), indeed reproduces the reciprocity scalar (3.12) of the gas:

$$\begin{aligned} &\int [F^{(2)} J^{(1)} - J^{(2)} F^{(1)}]_{\mathrm{I}} \, \mathrm{d}\gamma \\ &= \tfrac{1}{2} \int P_+ c \, [\, (\Phi + \Phi_{\mathrm{T}})^{(2)} (\Phi - \Phi_{\mathrm{T}})^{(1)} \\ &\qquad - (\Phi - \Phi_{\mathrm{T}})^{(2)} (\Phi + \Phi_{\mathrm{T}})^{(1)}] \, \mathrm{d}\gamma \\ &= \int P_+ (\Phi_{\mathrm{T}}^{(2)} c \, \Phi^{(1)} - \Phi^{(2)} c \, \Phi_{\mathrm{T}}^{(1)}) \, \mathrm{d}\gamma \\ &= \int (P_+ + P_-) \, \Phi_{\mathrm{T}}^{(2)} c \, \Phi^{(1)} \, \mathrm{d}\gamma = \int \Phi_{\mathrm{T}}^{(2)} c \, \Phi^{(1)} \, \mathrm{d}\gamma = R_{\mathrm{I}}^{(12)} \,. \end{aligned} \tag{4.13}$$

Hence, we have made the correct ansatz.

With (4.8) and (4.13) the reciprocity postulate is

$$\begin{aligned} \int [F^{(2)} J^{(1)} - J^{(2)} F^{(1)}]_{\mathrm{I}} \, \mathrm{d}\gamma + [F^{(2)} J^{(1)} - J^{(2)} F^{(1)}]_{\mathrm{II}} \\ = 0 \quad \text{at } \sigma_{\mathrm{I\,II}} \,. \end{aligned} \tag{4.14}$$

This is the canonical form apt for investigating boundary conditions.

Following Eq. (6.1) of Ref. [2], we now propose the linear *boundary conditions at the gas/solid interface* (or the interfacial atomistic law), for any $\boldsymbol{x} \in \sigma_{\mathrm{I\,II}}$, in the form

$$\begin{aligned} &J_{\mathrm{I}}(\boldsymbol{x}, \boldsymbol{p}) = \\ &\int L_{\mathrm{I\,I}} (\boldsymbol{n}_{\mathrm{I}}, \boldsymbol{p}, \boldsymbol{p}') \, F_{\mathrm{I}} (\boldsymbol{x}, \boldsymbol{p}') \, \mathrm{d}\gamma' + L_{\mathrm{I\,II}} (\boldsymbol{n}_{\mathrm{I}}, \boldsymbol{p}) \, F_{\mathrm{II}}(\boldsymbol{x}) \\ &J_{\mathrm{II}}(\boldsymbol{x}) = \\ &\int L_{\mathrm{II\,I}} (\boldsymbol{n}_{\mathrm{I}}, \boldsymbol{p}') \quad F_{\mathrm{I}} (\boldsymbol{x}, \boldsymbol{p}') \, \mathrm{d}\gamma' + L_{\mathrm{II\,II}} \qquad F_{\mathrm{II}}(\boldsymbol{x}) \,. \end{aligned} \tag{4.15}$$

The interfacial coefficients (kernels) L, dimension of a velocity, will depend on the local unit normal $\boldsymbol{n}_{\mathrm{I}} = \boldsymbol{n}_{\mathrm{I}}(\boldsymbol{x})$ of the interface (as also P_+ does via $c = \boldsymbol{c} \cdot \boldsymbol{n}_{\mathrm{I}}$). This dependence will no more be explicitly indicated in the following. The dependence of the L's on T_0 is un-indicated in (4.15). If the wall consists of different materials, an extra $\boldsymbol{x}$-dependence of the L's will hold. The reciprocity (4.14) is fulfilled with arbitrary $F_{\mathrm{I}}(\boldsymbol{x}, \boldsymbol{p})$, $F_{\mathrm{II}}(\boldsymbol{x})$ iff the Onsager relations are fulfilled, see Eq. (6.5) of Ref. [2],

$$\begin{aligned} L_{\mathrm{I\,I}} (\boldsymbol{p}, \boldsymbol{p}') &= L_{\mathrm{I\,I}} (\boldsymbol{p}', \boldsymbol{p}) \,, \\ L_{\mathrm{I\,II}} (\boldsymbol{p}) &= L_{\mathrm{II\,I}} (\boldsymbol{p}) \,. \end{aligned} \tag{4.16}$$

In order to comply with the projection (or subspace or half range) properties of the force/flux pair F_{I}, J_{I} prescribed by (4.9), the L's themselves must have the projection properties, see Eq. (6.2) of Ref. [2],

$$\begin{aligned} P_+(c) \, L_{\mathrm{I\,I}} (\boldsymbol{p}, \boldsymbol{p}') \, P_+(c') \; &= L_{\mathrm{I\,I}} (\boldsymbol{p}, \boldsymbol{p}') \,, \\ P_+(c) \, L_{\mathrm{I\,II}} (\boldsymbol{p}) \; &= L_{\mathrm{I\,II}} (\boldsymbol{p}) \,, \\ L_{\mathrm{II\,I}} (\boldsymbol{p}') \, P_+(c') \; &= L_{\mathrm{II\,I}} (\boldsymbol{p}') \,. \end{aligned} \tag{4.17}$$

These are compatible with (4.16).

The boundary conditions (4.15) are characterized by the feature that they offer a linear connection between forces and fluxes (4.9) which are combinations of Φ and Φ_{T}, even and odd under exchange of both. This scheme has advantages, at least as far as general questions are concerned, in comparison with the boundary condition exclusively in use up to now, which offers a linear connection between the distribution functions of gas particles approaching ($c > 0$) and leaving ($c < 0$) the wall.

The positivity requirement of the L's must be inferred from the pertinent expression for the interfacial entropy production. As in (4.13) one verifies

$$\begin{aligned} \int F_{\mathrm{I}} J_{\mathrm{I}} \, \mathrm{d}\gamma &= \tfrac{1}{2} \int P_+ c \, (\Phi^2 - \Phi_{\mathrm{T}}^2) \, \mathrm{d}\gamma \\ &= \tfrac{1}{2} \int (P_+ + P_-) \, c \, \Phi^2 \, \mathrm{d}\gamma = \int \tfrac{1}{2} c \, \Phi^2 \, \mathrm{d}\gamma \,. \end{aligned} \tag{4.18}$$

With this, and by definitions (4.7), the interfacial entropy production rate (2.14) becomes

$$\dot{S}_\sigma = \int_{\sigma_{\mathrm{I\,II}}} \mathrm{d}\sigma \, \frac{P_0}{T_0} \{ \int F_{\mathrm{I}} J_{\mathrm{I}} \, \mathrm{d}\gamma + F_{\mathrm{II}} J_{\mathrm{II}} \} > 0 \, . \tag{4.19}$$

Absence of interfacial currents provided, the positivity requirement (2.15) holds:

$$\int F_{\mathrm{I}} J_{\mathrm{I}} \, \mathrm{d}\gamma + F_{\mathrm{II}} J_{\mathrm{II}} > 0 \, . \tag{4.20}$$

This entails the positivity properties of the L's. In § 5 we shall come back to this.

The forces and fluxes F, J have been defined in Eq. (4.9) by means of the Heaviside function P_+. In a fully detailed notation one would have to write F_+, J_+ for them and L_+ for the kernels of the interfacial law. The Heaviside function P_- has equal rights. Its use in (4.9) and (4.15) would lead to F_-, J_- and L_-. But because of

$$P_- = P_{+\mathrm{T}}$$

the "minus" force/flux simply is the time reversed "plus" force/flux

$$F_-(\boldsymbol{p}) = F_+(-\boldsymbol{p}) \, , \quad J_-(\boldsymbol{p}) = J_+(-\boldsymbol{p}) \, ,$$

and the kernels of the interfacial law are also linked with each other in a simple way:

$$L_-(\boldsymbol{p}, \boldsymbol{p}') = L_+(-\boldsymbol{p}, -\boldsymbol{p}') \, .$$

Thus, the "minus" boundary conditions are identical with the "plus" boundary conditions, just variables $-\boldsymbol{p}$, $-\boldsymbol{p}'$ instead of $+\boldsymbol{p}$, $+\boldsymbol{p}'$ being inserted. It is therefore legitimate to restrict oneself to the "plus" quantities and to omit the corresponding index, as it has already been done.

A formal remark is added on the relation between discrete forces and fluxes f_i, j_i and the continuous ones $F(\boldsymbol{p})$, $J(\boldsymbol{p})$. An entropy production rate represented by an integral over momentum space

$$\int \mathrm{d}\gamma \, F \, J = \frac{1}{n_0} \int \mathrm{d}^3 p \, f_0(p) \, F(\boldsymbol{p}) \, J(\boldsymbol{p})$$

can be considered as the limes of a sum

$$\dot{S} = \sum_i \gamma_i f_i j_i \tag{4.21}$$

with positive weights (metric) in it. Rewriting as

$$\dot{S} = \sum_i \sqrt{\gamma_i} f_i \sqrt{\gamma_i} j_i$$

produces the standard (scalar product) form, without weights, for forces and fluxes $\sqrt{\gamma_i} f_i$ and $\sqrt{\gamma_i} j_i$. These shall be primarily connected by a symmetrical matrix

$$\sqrt{\gamma_i} \, j_i = \sum \mathfrak{L}_{ik} \sqrt{\gamma_k} \, f_k \quad \text{with} \quad \mathfrak{L}_{ik} = \mathfrak{L}_{ki} \, .$$

Introducing

$$L_{ik} = \frac{1}{\sqrt{\gamma_i}} \mathfrak{L}_{ik} \frac{1}{\sqrt{\gamma_k}} = L_{ki}$$

yields the equivalent connection

$$j_i = \sum_k \gamma_k \, L_{ik} \, f_k \tag{4.22}$$

with a matrix L_{ik} which then is symmetrical too. The point is that the sum in (4.22) is and has to be the same weighted sum as in (4.21). Thus, if by "sum" the same weighted sum is understood throughout, all statements about Onsager relations etc. are unaltered. Our integration element $\mathrm{d}\gamma$ plays the role of the γ's in (4.21) and (4.22), not disturbing symmetries.

5. Subsidiary Conditions for Interfacial Kernels

The L's of the interfacial laws (4.15) are not only restricted by the symmetries (4.16). They also have to comply with the general requirements of particle and energy conservation. Momentum conservation plays no role here, because the solid wall is assumed to be fixed.

"Conservation of particles" shall mean that the interface is assumed not to absorb nor evaporate gas molecules. (The case of an interface with mass transfer across it has been treated in Reference [6].) Then, the particle flux normal to the wall vanishes

$$\int \boldsymbol{c} \, f_0 \, (1 + \Phi) \, \mathrm{d}^3 p \cdot \boldsymbol{n}_{\mathrm{I}} = n_0 \int c \, \Phi \, \mathrm{d}\gamma$$
$$= n_0 \int P_+ \, c \, (\Phi - \Phi_{\mathrm{T}}) \, \mathrm{d}\gamma = 0 \, ,$$

or after (4.9),

$$\int \mathrm{d}\gamma \, J_{\mathrm{I}} = 0 \tag{5.1}$$

for any point $\boldsymbol{x} \in \sigma_{\mathrm{I\,II}}$.

"Conservation of energy" means that no net energy transfer from bulk to the unit area of $\sigma_{\mathrm{I\,II}}$ is assumed to take place (no surface heat flux). This is expressed by

$$\int \frac{p^2}{2\,m} \boldsymbol{c} \, f_0 \, (1 + \Phi) \, \mathrm{d}^3 p \cdot \boldsymbol{n}_{\mathrm{I}} + \boldsymbol{q}_{\mathrm{II}} \cdot \boldsymbol{n}_{\mathrm{II}}$$
$$= P_0 \int \varepsilon \, c \, \Phi \, \mathrm{d}\gamma + q_{\mathrm{II}}$$
$$= P_0 \int P_+ \, \varepsilon \, c \, (\Phi - \Phi_{\mathrm{T}}) \, \mathrm{d}\gamma + q_{\mathrm{II}} = 0 \, .$$

The dimensionless energy

$$\varepsilon = \frac{p^2}{2\,m\,k\,T_0} \tag{5.2}$$

has been introduced. By use of (4.9) and (4.7) one has therefore

$$\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, J_{\mathrm{I}} + J_{\mathrm{II}} = 0 \tag{5.3}$$

for any $\boldsymbol{x} \in \sigma_{\mathrm{I\,II}}$.

Inserting the boundary laws (4.15) into particle conservation (5.1) yields

$$\int \mathrm{d}\gamma \, J_{\mathrm{I}} = \int \left[\int \mathrm{d}\gamma \, L_{\mathrm{I\,I}} \right] F_{\mathrm{I}}' \, \mathrm{d}\gamma' + \left[\int \mathrm{d}\gamma \, L_{\mathrm{I\,II}} \right] F_{\mathrm{II}} = 0$$

for arbitrary $F_{\mathrm{I}}, F_{\mathrm{II}}$. (The prime on F_{I} refers to its argument $\boldsymbol{p}'$.) Therefore $L_{\mathrm{I\,I}}$ has to obey the *subsidiary condition*

$$\int \mathrm{d}\gamma \, L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}') = 0 \quad \text{for any } \boldsymbol{p}' , \tag{5.4}$$

and due to (4.16) also

$$\int L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}') \, \mathrm{d}\gamma' = 0 \quad \text{for any } \boldsymbol{p} . \tag{5.4 a}$$

$L_{\mathrm{I\,II}}$ must obey

$$\int \mathrm{d}\gamma \, L_{\mathrm{I\,II}}(\boldsymbol{p}) = 0 . \tag{5.4 b}$$

Energy conservation (5.3) yields in the same way

$$\begin{aligned} \sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, J_{\mathrm{I}} + J_{\mathrm{II}} &= \int \left[\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,I}} + L_{\mathrm{II\,I}} \right] F_{\mathrm{I}}' \, \mathrm{d}\gamma' \\ &\quad + \left[\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,II}} + L_{\mathrm{II\,II}} \right] F_{\mathrm{II}} = 0 \end{aligned}$$

for arbitrary $F_{\mathrm{I}}, F_{\mathrm{II}}$. Hence

$$\begin{aligned} &\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,I}} + L_{\mathrm{II\,I}} = 0 , \\ &\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,II}} + L_{\mathrm{II\,II}} = 0 . \end{aligned} \tag{5.5}$$

This means that $L_{\mathrm{II\,I}}$ $(= L_{\mathrm{I\,II}})$ *and* $L_{\mathrm{II\,II}}$ are *determined by* $L_{\mathrm{I\,I}}$ *alone:*

$$L_{\mathrm{II\,I}}(\boldsymbol{p}') = -\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}') , \tag{5.6}$$

therefore

$$L_{\mathrm{I\,II}}(\boldsymbol{p}) = -\sqrt{2} \int L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}') \, \varepsilon' \, \mathrm{d}\gamma' , \tag{5.7}$$

and

$$L_{\mathrm{II\,II}} = 2 \iint \mathrm{d}\gamma \, \varepsilon \, L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}') \, \varepsilon' \, \mathrm{d}\gamma' . \tag{5.8}$$

Utilizing this in (4.15) gives the following *elaborate form of the boundary law*

$$\begin{aligned} J_{\mathrm{I}}(\boldsymbol{x}, \boldsymbol{p}) &= \int L_{\mathrm{I\,I}}(\boldsymbol{n}_{\mathrm{I}}, \boldsymbol{p}, \boldsymbol{p}') \, F_{\mathrm{I\,II}}(\boldsymbol{x}, \boldsymbol{p}') \, \mathrm{d}\gamma' , \\ J_{\mathrm{II}}(\boldsymbol{x}) &= -\sqrt{2} \int \mathrm{d}\gamma \, \varepsilon \, J_{\mathrm{I}}(\boldsymbol{x}, \boldsymbol{p}) , \end{aligned} \tag{5.9}$$

with the one "mixed" force

$$F_{\mathrm{I\,II}}(\boldsymbol{x}, \boldsymbol{p}) \equiv F_{\mathrm{I}}(\boldsymbol{x}, \boldsymbol{p}) - \sqrt{2} \, P_{+}(c) \, \varepsilon \, F_{\mathrm{II}}(\boldsymbol{x}) . \tag{5.10}$$

The kernel $L_{\mathrm{I\,I}}$ is restricted by (4.16) and (5.4).

Now, the second law's requirements can be neatly formulated in terms of $L_{\mathrm{I\,I}}$ only. After (5.9) and (5.10) the inequality (4.20) is

$$\begin{aligned} \int \mathrm{d}\gamma \, F_{\mathrm{I}} J_{\mathrm{I}} + F_{\mathrm{II}} J_{\mathrm{II}} &= \int \mathrm{d}\gamma \, F_{\mathrm{I\,II}} \, J_{\mathrm{I}} \\ &= \iint \mathrm{d}\gamma \, F_{\mathrm{I\,II}} \, L_{\mathrm{I\,I}} \, F'_{\mathrm{I\,II}} \, \mathrm{d}\gamma' > 0 \end{aligned} \tag{5.11}$$

for arbitrary $F_{\mathrm{I\,II}}$. The second law is satisfied by requiring the kernel $L_{\mathrm{I\,I}}(\boldsymbol{p}, \boldsymbol{p}')$ to be positive-definite in the sense of (5.11).

Herewith, all the general properties of the coefficient kernels occurring in the interfacial atomistic law have been listed.

The kernel $L_{\mathrm{I\,I}}$ replaces the kernel which hitherto has been in exclusive use for describing the molecular collisions with the wall and which constitutes a linear functional relation between the distributions of the molecules approaching the wall and those leaving it. The connection between both kernels not simple, going through an operator inversion:

$$\begin{aligned} \mathcal{H} &= (P_{+} + \hat{L})^{-1} (P_{+} - \hat{L}) \\ \text{or} \quad \hat{L} &= (P_{+} + \mathcal{H})^{-1} (P_{+} - \mathcal{H}) , \end{aligned} \tag{5.12}$$

with

$$\hat{L} = c^{-1/2} \, L \, c^{-1/2}, \quad P_{+} \hat{L} = \hat{L} P_{+} = \hat{L} .$$

The symmetries $L = \tilde{L}$ and $\mathcal{H} = \tilde{\mathcal{H}}$ are equivalent.

6. First Applications

Three of them are considered i) thermal equilibrium different from O-state ii) connection between interfacial kernels and interfacial coefficient matrices iii) kernel $L_{\mathrm{I\,I}}$ for completely thermalizing wall collisions.

i) The temperature of wall and gas, in thermal equilibrium with each other, be $T_1 \neq T_0$; the number density of the gas be $n_1 \neq n_0$.

The fluxes defined in (4.9) and (4.7) vanish in equilibrium

$$J_{\mathrm{I}} = 0 , \quad J_{\mathrm{II}} = 0 \tag{6.1}$$

and again after (4.7) one has

$$F_{\mathrm{II}} = (T_1 - T_0)/T_0 .$$

From (5.9) and (5.4 a) one concludes that

$$F_{\mathrm{I\,II}}(\boldsymbol{p}) = P_{+} \, \text{const} \tag{6.2}$$

or with definition (5.10)

$$F_{\mathrm{I}}(\boldsymbol{p}) = \sqrt{2} \, P_{+} (\varepsilon \, F_{\mathrm{II}} + \text{const}) . \tag{6.3}$$

What is the distribution Φ in this state? Definition (4.9) shows that J_{I} vanishes if $\Phi = \Phi_{\mathrm{T}}$ (for $c > 0$). Then one has, again after (4.9),

$$\sqrt{2} \, P_{+} \Phi = F_{\mathrm{I}} \quad \text{and} \quad \Phi = \varepsilon \frac{T_1 - T_0}{T_0} + \text{const} . \tag{6.4}$$

The constant has to be chosen in such a way that the prescribed number density n_1 is attained in the bulk gas (the boundary conditions are not concerned with that). One has to put

$$\text{const} = \frac{n_1 - n_0}{n_0} - \frac{3}{2} \frac{T_1 - T_0}{T_0} .$$

According to

$$f_1 \approx f_0\,(1+\Phi)$$

the above Φ then indeed describes the relative deviation of the Maxwellian f_1 from that in state 0. Thus, our boundary conditions give the correct "displaced" equilibrium.

ii) A rarefied gas may approximately be described by a finite set of transport-relaxation equations somewhere between ordinary hydrodynamics and the linear Boltzmann equation. Quite intricate situations can be treated in this way [7]. In such a description the simple boundary conditions of hydrodynamics no more suffice. One has to introduce several phenomenological jump and slip coefficients determining the behaviour of the proper hydrodynamical quantities at the surface and several new phenomenological surface coefficients for newly introduced "moments". *All these surface coefficients can be expressed in terms of the basic kernel* $L_{\mathrm{II}}(\mathbf{p},\mathbf{p}')$ *from (4.15) which completely describes the interaction between gas and wall.*

To find this connection, we plot the expansion (1.8)

$$\Phi = \sum \varphi_{i'}\, a_{\mathrm{I}i'}$$

into the J_{I}, F_{I} of boundary conditions (4.15), obtaining

$$\begin{aligned}\sqrt{2}\,J_{\mathrm{I}} &= \sum P_+\, c\, \varphi_{i'}\,(a-a_{\mathrm{T}})_{\mathrm{I}i'}\\ &= \sum \int L_{\mathrm{II}}\,\varphi'_{i'}\,\mathrm{d}\gamma'\;(a+a_{\mathrm{T}})_{\mathrm{I}i'}+\dots\end{aligned} \quad (6.5)$$

The definition (4.9) is recalled. The projector P_+ of F_{I} does not appear; it is absorbed by L_{II}, after (4.17). By multiplying (6.5) with φ_i and integrating, one gets

$$\sum (P_+\,c)_{ii'}\,(a-a_{\mathrm{T}})_{\mathrm{I}i'} = \sum L_{\mathrm{II}ii'}\,(a+a_{\mathrm{T}})_{\mathrm{I}i'}+\dots \quad (6.6)$$

with the matrix elements

$$(P_+\,c)_{ii'} = \int \mathrm{d}\gamma\,\varphi_i\,P_+\,c\,\varphi_{i'}\,, \quad (6.7)$$

$$L_{\mathrm{II}ii'} = \iint \mathrm{d}\gamma\,\varphi_i\,L_{\mathrm{II}}\,\varphi'_{i'}\,\mathrm{d}\gamma'\,. \quad (6.8)$$

The φ's shall be complete:

$$\sum_k \varphi_k(\mathbf{p})\,\varphi_k(\mathbf{p}')\,\mathrm{d}\gamma' = \delta(\mathbf{p},\mathbf{p}')\,\mathrm{d}^3p'\,. \quad (6.9)$$

Then one can decompose

$$(P_+\,c)_{ii'} = \sum_k P_{+ik}\,c_{ki'} \quad (6.10)$$

with

$$P_{+ik} = \int \mathrm{d}\gamma\,\varphi_i\,P_+\,\varphi_k\,, \quad (6.11)$$

$$c_{ki'} = \int \varphi_k{}'\,c'\,\varphi_{i'}{}'\,\mathrm{d}\gamma'\,. \quad (6.12)$$

With the force/flux matrices (the shorthand notation without indices is now used)

$$f = \frac{1}{\sqrt{2}}\,P_+(a+a_{\mathrm{T}})\,,\quad j = \frac{1}{\sqrt{2}}\,P_+\,c\,(a-a_{\mathrm{T}})\,, \quad (6.13)$$

Eq. (6.6) becomes

$$j_{\mathrm{I}} = L_{\mathrm{II}}\,f_{\mathrm{I}}+\dots \quad (6.14)$$

This has the same form as the boundary conditions (6.1) of Ref. [2], for the transport-relaxation equations. This is not astonishing, we went from one representation to another, everything is equivalent.

In practice the moment expansion of the distribution function is truncated, the basis no more complete as it was in (6.9). But it is hopefully still a good approximation if the *boundary coefficients* (temperature jump, slip, etc) *of the generalized hydrodynamics*, i. e. the $L_{\mathrm{II}ii'}$ of Ref. [2], are again *connected with the atomistic kernel* $L_{\mathrm{II}}(\mathbf{p},\mathbf{p}')$ in the manner

$$L_{\mathrm{II}ii'} = \iint \mathrm{d}\gamma\,\varphi_i(\mathbf{p})\,L_{\mathrm{II}}(\mathbf{p},\mathbf{p}')\,\varphi_{i'}(\mathbf{p}')\,\mathrm{d}\gamma'\,. \quad (6.15)$$

The φ's now are a finite number of functions suitably chosen. Equation (6.8) was exact; Eq. (6.15) is perhaps the best available in its context. Inserting the energy ε for φ_i and $\varphi_{i'}$ gives the temperature jump coefficient; etc.

That the connection is now so simple is a consequence of the new form (4.15) of the atomistic boundary conditions.

iii) *"Completely thermalizing wall"* signifies that the particles receding from it have a Maxwellian distribution with the wall temperature. Without restricting generality, we can take

$$F_{\mathrm{II}} = 0\,,$$

i. e. the wall has, at the point considered, the temperature T_0. Then the distribution of the receding particles simply is

$$\Phi = \mathrm{const} \equiv \frac{\delta n}{n_0}\ \text{for}\ c<0\,,$$

or equivalently

$$P_+\,\Phi_{\mathrm{T}} = P_+\,\frac{\delta n}{n_0}\,. \quad (6.16)$$

The constant δn of course is determined by the arbitrary distribution of the particles approaching the wall. Indeed,

$$\begin{aligned}0 = \int c\,\Phi\,\mathrm{d}\gamma &= \int P_+\,c\,(\Phi-\Phi_{\mathrm{T}})\,\mathrm{d}\gamma\\ &= \int P_+\,c\,\Phi\,\mathrm{d}\gamma - \frac{\delta n}{n_0}\int P_+\,c\,\mathrm{d}\gamma\end{aligned}$$

or

$$\frac{\delta n}{n_0} = \frac{1}{\hat{c}_0} \int P_+ c\, \Phi\, \mathrm{d}\gamma\,, \qquad (6.17)$$

with the abbreviation

$$\hat{c}_0 = \int P_+{}' c'\, \mathrm{d}\gamma' = \sqrt{k T_0 / 2 \pi m}\,. \qquad (6.18)$$

In order to find the kernel $L_{\mathrm{I\,I}}$ for the completely thermalizing wall, let us write down the boundary condition (4.15), utilizing $F_{\mathrm{II}} = 0$ and the subsidiary property (5.4 a) of any $L_{\mathrm{I\,I}}$,

$$J_{\mathrm{I}} \equiv \frac{1}{\sqrt{2}} P_+ c \left(\Phi - \frac{\delta n}{n_0} \right) = \int L_{\mathrm{I\,I}} F_{\mathrm{I}}{}'\, \mathrm{d}\gamma' \equiv \int L_{\mathrm{I\,I}} \frac{1}{\sqrt{2}} P_+{}'\, \Phi'\, \mathrm{d}\gamma'$$

or

$$P_+(c)\, c [\Phi(\mathbf{p}) - \frac{1}{\hat{c}_0} \int c' P_+(c')\, \Phi(\mathbf{p}')\, \mathrm{d}\gamma'] = \int L_{\mathrm{I\,I}}(\mathbf{p}, \mathbf{p}')\, \Phi(\mathbf{p}')\, \mathrm{d}\gamma'\,. \qquad (6.19)$$

The left side is rewritten

$$\int P_+(c) \left[c\, \delta(\mathbf{p}, \mathbf{p}') \frac{\mathrm{d}^3 p'}{\mathrm{d}\gamma'} - \frac{1}{\hat{c}_0} c\, c' \right] P_+(c')\, \Phi(\mathbf{p}')\, \mathrm{d}\gamma' = \dots\,.$$

Comparison with the right side of (6.19) shows that

$$L_{\mathrm{I\,I}}(T_0, \mathbf{n}_{\mathrm{I}}, \mathbf{p}, \mathbf{p}') = P_+(c) \left[c\, \delta(\mathbf{p}, \mathbf{p}') \frac{\mathrm{d}^3 p'}{\mathrm{d}\gamma'} - \frac{1}{\hat{c}_0} c\, c' \right] P_+(c') \qquad (6.20)$$

is the *interfacial kernel for the completely thermalizing wall.* The kernel (6.20) has the symmetry (4.16) and the properties (4.17) and (5.4). It is positive-definite:

$$\begin{aligned}
\iint \mathrm{d}\gamma\, F_{\mathrm{I}}\, L_{\mathrm{I\,I}}\, F_{\mathrm{I}}{}'\, \mathrm{d}\gamma'
&= \iint \mathrm{d}\gamma\, F_{\mathrm{I}} \left[c\, \delta(\mathbf{p}, \mathbf{p}')\, \mathrm{d}^3 p' - \frac{1}{\hat{c}_0} c\, c'\, \mathrm{d}\gamma' \right] F_{\mathrm{I}}{}' \\
&= \frac{1}{\hat{c}_0} \iint \mathrm{d}\gamma\, (F_{\mathrm{I}}\, c\, F_{\mathrm{I}}\, P_+{}' c' - F_{\mathrm{I}}\, c\, c'\, F_{\mathrm{I}}{}')\, \mathrm{d}\gamma' \\
&= \frac{1}{2 \hat{c}_0} \iint \mathrm{d}\gamma\, P_+ P_+{}'\, c\, c' (F_{\mathrm{I}} - F_{\mathrm{I}}{}')^2\, \mathrm{d}\gamma' > 0\,.
\end{aligned}$$

The identity $P_+ F_{\mathrm{I}} = F_{\mathrm{I}}$ has been used. Hence, the kernel (6.20) has all the necessary properties. The other coefficients $L_{\mathrm{I\,II}}$ and $L_{\mathrm{II\,II}}$ of the boundary law (4.15), expressible by $L_{\mathrm{I\,I}}$ according to (5.7) and (5.8), can be written down explicitly by means of the auxiliary formula

$$\int P_+ c\, \varepsilon^n\, \mathrm{d}\gamma = (n+1)!\, \hat{c}_0\,. \qquad (6.21)$$

The immediate result is

$$\begin{aligned}
L_{\mathrm{I\,II}}(T_0, \mathbf{n}_{\mathrm{I}}, \mathbf{p}) &= -\sqrt{2}\, P_+(c)\, c\, (\varepsilon - 2)\,, \\
L_{\mathrm{II\,II}}(T_0) &= 4\, \hat{c}_0\,.
\end{aligned} \qquad (6.22)$$

According to Eq. (6.15) and analogous formulae for $L_{\mathrm{I\,II}}$ and $L_{\mathrm{II\,II}}$, one can at once calculate any desired surface coefficient for the completely thermalizing wall.

More applications are possible. E. g. a formula can now be given, exact in principle, for the heat transferred between two parallel plates through a gas of arbitrary pressure, in terms of certain eigenfunctions. But this is a little too lengthy to be added here.

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