On the theory of nonequilibrium phenomena in the flow of a gas mixture in a capillary

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Based on the linearized kinetic equation, expressions for the heat and mass fluxes between two vessels linked by a cylindrical capillary are obtained. The cross-section averages of the diffusion fluxes, heat fluxes, and mass-averaged gas velocity are expressed in terms of pressure, temperature, and component concentration gradients, and the moments of the distribution function at the capillary wall. It is shown that the Burnett terms can be separated explicitly in the fluxes and that the expressions of interest can be written down in terms of the slip velocity and the moments of the Knudsen part of the distribution function. The kinetic expression for boundary entropy production is analyzed, by means of which a system of linear phenomenological equations for the slip velocity and the fluxes localized in the Knudsen layer is constructed.

1. INTRODUCTION

The general relations describing the transfer of mass and heat between two vessels linked by a narrow capillary are known to be established by the irreversible thermodynamics of discontinuous systems.[1] Of independent interest is the kinetic justification of the corresponding system of linear phenomenological transport equations—allowing, in particular, the determination of an explicit form of the kinetic coefficients of the Onsager matrix. For flows of a gas mixture in a capillary, this problem can be solved through the use of the linearized Boltzmann kinetic equation.[2,3] Attempts at calculating the kinetic coefficients for the case of a cylindrical channel and arbitrary Knudsen numbers have so far been usually specialized in character, mostly using a model collision integral in the Boltzmann equation.[3–8] On the other hand, fairly general relations for capillary heat and mass fluxes can be derived on the basis of the kinetic equation with an exact collision integral. For the flow of a pure monatomic gas in a plane channel, this has recently been demonstrated in Ref. 9.

The present paper analyzes heat and mass transfer taking place in a multicomponent gas mixture under the action of pressure, temperature, and partial concentration gradients, the mixture flowing in a circular cylindrical capillary. It proves possible to express the cross-section averaged diffusion and heat fluxes, as well as the mass-averaged velocity of the mixture, in terms of the corresponding gradients and the moments of the distribution function as determined directly at the wall. The moments themselves then appear as functionals of, first, the familiar diffusion, viscosity, and heat conductivity solutions obtained within the usual Chapman–Enskog approximation, and second, the Burnett solution arising in a higher-order approximation of the same method.[10,2] A formal representation of the obtained expressions based on the separation of the bulk and Knudsen contributions to the wall values of the moments makes it possible to separate the Burnett terms explicitly in the flux expressions and so to reduce the problem to that of calculating the slip velocity and the moments of the Knudsen distribution function. These latter turn out to be closely related to the Knudsen layer localized heat and mass fluxes. All the above quantities can be calculated using the methods (e.g., variational ones) developed for the solution of the boundary problems of kinetic theory.[3,11–13]

The paper also analyzes the kinetic expression for entropy production. Along with the known expressions, the so-called boundary entropy production is introduced,[14,15] on which basis the system of linear phenomenological equations for the slip velocity and for the fluxes localized in the Knudsen layer is constructed. The resulting equations add importantly to the conventional irreversible thermodynamics relations in that they form, in a sense, a system of boundary conditions for the flow of the gas mixture in a capillary.

2. AVERAGED DIFFUSION AND HEAT FLUXES

Consider an N-component gas mixture flowing in a circular cylindrical capillary of radius R under the action of a pressure gradient ($k=p^{-1}\nabla_z p$), temperature gradient ($\tau=T^{-1}\nabla_z T$), and partial concentration gradient [$s_\alpha=\nabla_z(n_\alpha/n)$]. It is assumed that p, T, and n_α vary slowly over the typical molecular mean free path l so that

$$|kl|\ll 1,\quad |\tau l|\ll 1,\quad |s_\alpha l|\ll 1. \tag{1}$$

If the mixture flows slowly in the channel (the flow velocity u is appreciably less than the typical thermal molecular velocity), the distribution function for the molecules of species α is sought in the form[16,17]

$$f_\alpha(\mathbf{v}_\alpha,\mathbf{r})=f_\alpha^{(0)}[1+\Phi_\alpha(\mathbf{v}_\alpha,\mathbf{x}_\perp)], \tag{2}$$

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$$f_\alpha^{(0)}=f_{\alpha0}[1+kz+(\beta_\alpha v_\alpha^2-5/2)\tau z].$$

Here $\mathbf{x}_\perp$ is the two-dimensional radius-vector in the transverse cross section of the channel; the z axis is directed along the capillary; $\beta_\alpha=m_\alpha/2k_BT_0$, k_B is the Boltzmann constant, and the index zero corresponds to the parameters of the absolute Maxwellian distribution $f_{\alpha0}$. The nonequilibrium correction to the distribution function, Φ_α, satisfies the system of linearized kinetic equations[16–18]

$$\mathbf{v}_{\alpha\perp}\frac{\partial\Phi_\alpha}{\partial\mathbf{x}_\perp}+v_{\alpha z}\left(\frac{m_\alpha n}{\rho}k+\frac{n}{n_\alpha}d_{\alpha z}\right)$$
$$+v_{\alpha z}(\beta_\alpha v_\alpha^2-\tfrac{5}{2})\tau$$
$$=\sum_\beta L_{\alpha\beta}(\Phi_\alpha,\Phi_\beta), \tag{3}$$

where $L_{\alpha\beta}$ is the linearized collision integral for molecular species α and β,

$$d_{\alpha z}=s_\alpha-\left(\frac{n_\alpha}{n}-\frac{\rho_\alpha}{\rho}\right)k, \tag{4}$$

where $\rho_\alpha=m_\alpha n_\alpha$ is the mass density of the molecular species α, $n=\Sigma_\alpha n_\alpha$, $\rho=\Sigma_\alpha\rho_\alpha$.

Equations (3) must be completed by the boundary conditions for Φ_α at the wall of the channel[11,16]

$$\Phi_\alpha(\mathbf{x}_\perp^F,\mathbf{v}_\alpha)=\hat{A}\Phi_\alpha(\mathbf{x}_\perp^F,\mathbf{v}_\alpha)$$
$$=\int d\mathbf{v}'_\alpha\theta(-\mathbf{v}'_{\alpha\perp}\mathbf{n}_\perp)f_{\alpha0}(\mathbf{v}'_\alpha)|\mathbf{v}_{\alpha\perp}\mathbf{n}_\perp|. \tag{5}$$
$$B_\alpha(\mathbf{v}_\alpha\to\mathbf{v}'_\alpha)\Phi_\alpha(\mathbf{x}_\perp^F,\mathbf{v}'_\alpha)\quad \mathbf{v}_{\alpha\perp}\mathbf{n}_\perp(x_\perp^F)>0,\quad \mathbf{x}_\perp^F\in dF.$$

Here $\hat{A}$ is the generalized boundary operator possessing the reciprocity property, i.e., $B_\alpha(\mathbf{v}_\alpha\to\mathbf{v}'_\alpha)=B_\alpha(-\mathbf{v}'_\alpha\to-\mathbf{v}_\alpha)$; $n_\perp(\mathbf{x}_\perp^F)$ is the unit normal at the point $x_\perp^F$ of the channel surface, directed inward; dF is the differential element of the surface, and θ is the Heaviside step function.

Let us define the diffusion velocity $\mathbf{w}_\alpha=\mathbf{u}_\alpha-\mathbf{u}$ and the reduced heat flux $\mathbf{h}_\alpha=\mathbf{q}_\alpha-\frac{5}{2}p_\alpha\mathbf{w}_\alpha$ of the molecular species α, both in the z direction, by

$$n_\alpha w_{\alpha z}=\int(v_{\alpha z}-u_z)f_{\alpha0}\Phi_\alpha d\mathbf{v}_\alpha, \tag{6}$$

$$h_{\alpha z}=k_BT\int(\beta_\alpha v_\alpha^2-\tfrac{5}{2})v_{\alpha z}f_{\alpha0}\Phi_\alpha d\mathbf{v}_\alpha, \tag{7}$$

where $\mathbf{u}=\Sigma_\alpha(\rho_\alpha/\rho)\mathbf{u}_\alpha$ is the mass-averaged flow velocity and $p_\alpha=n_\alpha k_BT$. In the following we will be interested in the cross section averages of the diffusion velocity, $\langle w_{\alpha z}\rangle$, and of the total heat flux, $\langle q_z\rangle=\Sigma_\alpha\langle h_{\alpha z}\rangle+\frac{5}{2}\Sigma_\alpha p_\alpha\langle w_{\alpha z}\rangle$. Let us show that these may be expressed, using (3), in terms of certain moments of the distribution function on the wall of the channel, to be determined independently.

To this end we employ the well-known integral relations of the Chapman–Enskog method which arise in the solution of diffusion and heat conductivity problems in infinite space,[2,10]

$$\frac{n}{n_\alpha}\left(\delta_{\alpha\gamma}-\frac{\rho_\alpha}{\rho}\right)v_{\alpha z}=\sum_\beta L_{\alpha\beta}(v_z\Phi_d^\gamma), \tag{8}$$

$$(\beta_\alpha v_\alpha^2-\tfrac{5}{2})v_{\alpha z}=\sum_\beta L_{\alpha\beta}(v_z\Phi_t), \tag{9}$$

where the functions $\Phi_{d\alpha}^\gamma$ and $\Phi_{t\alpha}$ satisfy the conditions

$$\sum_\alpha m_\alpha\int v_{\alpha z}^2 f_{\alpha0}\Phi_{d\alpha}^\gamma d\mathbf{v}_\alpha=0,$$

$$\sum_\alpha m_\alpha\int v_{\alpha z}^2 f_{\alpha0}\Phi_{t\alpha}d\mathbf{v}_\alpha=0. \tag{10}$$

Let us consider the diffusive transport of a given molecular species. The diffusion velocity $\langle w_{\gamma z}\rangle$ averaged over the channel cross section S may be written as

$$\langle w_{\gamma z}\rangle=\frac{1}{S}\int_S dS\left[\int\frac{1}{n_\gamma}v_{\gamma z}f_{\gamma0}\Phi_\gamma d\mathbf{v}_\gamma\right.$$
$$\left.-\frac{1}{\rho}\sum_\beta\int m_\beta v_{\beta z}f_{\beta0}\Phi_\beta d\mathbf{v}_\beta\right]$$
$$=\frac{1}{S}\int_S dS\int\frac{1}{n}\sum_\beta\frac{n}{n_\beta}\left(\delta_{\beta\gamma}-\frac{\rho_\beta}{\rho}\right)v_{\beta z}f_{\beta0}\Phi_\beta d\mathbf{v}_\beta. \tag{11}$$

Using (8) we rewrite (11) in the form

$$\langle w_{\gamma z}\rangle=\frac{1}{nS}\int_S[\Phi,L(v_z\Phi_d^\gamma)]dS, \tag{12}$$

where we have introduced the notation

$$[\Phi,\Psi]=\sum_\alpha\int f_{\alpha0}\Phi_\alpha\Psi_\alpha d\mathbf{v}_\alpha,$$
$$L(v_z\Phi_d^\gamma)=\sum_\beta L_{\alpha\beta}(v_z\Phi_d^\gamma). \tag{13}$$

Owing to the symmetry property of the linearized collision operator ($[\Phi,L]=[L,\Phi]$) we may put (12) in the form

$$\langle w_{\gamma z}\rangle=\frac{1}{nS}\int_S[v_z\Phi_d^\gamma,L(\Phi)]dS. \tag{14}$$

Replacing $L(\Phi)$ by the left-hand side of Eq. (3) and performing the velocity and cross section integrations, we find (index γ is replaced by α in the final expression)

$$\langle w_{\alpha z}\rangle=-\sum_\beta D_{\alpha\beta}d_{\beta z}-D_{T\alpha}\nabla_z\ln T+\frac{2}{nR}M_d^\alpha(R). \tag{15}$$

Here

$$D_{\alpha\beta}=-\frac{1}{n_\beta}\int v_{\beta z}^2 f_{\beta0}\Phi_{d\beta}^\alpha d\mathbf{v}_\beta, \tag{16}$$

$$D_{T\alpha}=-[v_z(\beta v^2-\tfrac{5}{2}),v_z\Phi_d^\alpha], \tag{17}$$

$$\frac{2}{R}M_d^\alpha=\frac{1}{S}\int_S\left[v_z\Phi_d^\alpha,\frac{\partial\mathbf{v}_\perp\Phi}{\partial\mathbf{x}_\perp}\right]dS. \tag{18}$$

The last term in (15) is easily transformed by the two-dimensional Gauss divergence theorem (after introducing $v_z\Phi_d^\alpha$ under the divergence sign). In particular, for a circular cylindrical capillary,

$$M_d^\alpha(R)=[v_z\Phi_d^\alpha,v_z\Phi(R)]\,. \tag{19}$$

The coefficients $D_{\alpha\beta}$ and $D_{T\alpha}$ in (15) correspond to the familiar diffusion and thermal-diffusion coefficients for a multicomponent mixture.[2,19] The total-pressure gradient term in (15) vanishes upon integration on account of the first of the conditions (10). Note, however, that the pressure gradient dependence (barodiffusion) is accounted for through the $d_{\beta z}$ contribution and is present in the $M_d^\alpha(R)$ term.

In a similar way, an expression for the averaged heat flux is found. Let us express $\langle h_z\rangle=\Sigma_\alpha\langle h_{\alpha z}\rangle$ in the form

$$\langle h_z\rangle=\frac{k_BT}{S}\int_S dS\sum_\alpha\int v_{\alpha z}(\beta_\alpha v_\alpha^2-\tfrac{5}{2})f_{\alpha 0}\Phi_\alpha d\mathbf{v}_\alpha$$

or, using (9),

$$\langle h_z\rangle=\frac{k_BT}{S}\int_S dS\sum_\alpha\sum_\beta\int f_{\alpha 0}\Phi_\alpha L(v_z\Phi_t)d\mathbf{v}_\alpha. \tag{20}$$

Using the symmetry property of the collision integral and replacing $L(\Phi)$ by the left-hand side of (3), after the appropriate integration we have

$$\langle q_z\rangle=-\lambda'\nabla_zT-k_BT\sum_\beta D_{T\beta}nd_{\beta z}+\tfrac{5}{2}\sum_\alpha p_\alpha\langle w_{\alpha z}\rangle$$
$$+\frac{2k_BT}{R}M_q(R)\,. \tag{21}$$

Here

$$\lambda'=-k_B[v_z\Phi_t,v_z(\beta v^2-5/2)], \tag{22}$$

$$D_{T\beta}=-\frac{1}{n_\beta}\int v_{\beta z}^2 f_{\beta 0}\Phi_{t\beta}d\mathbf{v}_\beta, \tag{23}$$

$$M_q(R)=[v_z\Phi_t,v_r\Phi(R)]. \tag{24}$$

The pressure gradient term in (21) vanishes in view of the second condition of (10).

Introducing the thermal diffusion relations[2]

$$\sum_\beta D_{\alpha\beta}K_{T\beta}=D_{T\alpha},\quad \sum_\alpha K_{T\alpha}=0$$

and the thermal conductivity of a multicomponent mixture

$$\lambda=\lambda'-nk_B\sum_\alpha K_{T\alpha}D_{T\alpha}, \tag{25}$$

it is convenient to write $\langle q_z\rangle$ in the form

$$\langle q_z\rangle=-\lambda\nabla_zT-p\sum_\alpha D_{T\alpha}(d_{\alpha z}+K_{T\alpha}\nabla_z\ln T)$$
$$+\frac{5}{2}\sum_\alpha p_\alpha\langle w_{\alpha z}\rangle+\frac{2k_BT}{R}M_q(R). \tag{26}$$

3. MASS-AVERAGED VELOCITY OF A GAS MIXTURE IN A CHANNEL

In order to determine the cross-section-averaged velocity of the mixture flow, $\langle u_z\rangle$, we use the integral relations

$$2\beta_\alpha v_{\alpha r}v_{\alpha z}=\sum_\beta L_{\alpha\beta}(v_rv_z\Phi_p), \tag{27}$$

$$v_{\alpha\perp}^2\,v_{\alpha z}\Phi_{p\alpha}+\frac{2m_\alpha}{\rho k_BT}\eta v_{\alpha z}=\sum_\beta L_{\alpha\beta}(v_z\Phi_B)\,. \tag{28}$$

The first of these arises in the solution of the mixture viscosity problem according to the usual Chapman–Enskog method[2,10] (the corresponding solution is denoted by Φ_p), the second is the extension to the case of a circular cylindrical capillary of the corresponding plane-flow relation of Ref. 20 for the Burnett correction (Φ_B) to the distribution function. Note that the viscosity of the mixture is defined in this context by the expression

$$\eta=-[mv_rv_z,v_rv_z\Phi_p]\,. \tag{29}$$

From Eq. (28) we express the combination

$$m_\alpha v_{\alpha z}=\frac{1}{2}\frac{\rho k_BT}{\eta}\left(\sum_\beta L_{\alpha\beta}(v_z\Phi_B)-v_{\alpha z}v_{\alpha\perp}^2\,\Phi_{p\alpha}\right).$$

For the cross-section-averaged velocity $\langle u_z\rangle$ we have

$$\langle u_z\rangle=\frac{1}{\rho S}\int_S dS\sum_\alpha\int m_\alpha v_{\alpha z}f_{\alpha 0}\Phi_\alpha dv_\alpha$$
$$=\frac{k_BT}{2\eta S}\int_S dS\{[\Phi,L(v_z\Phi_B)]-[v_\perp^2\,v_z\Phi_p,\Phi]\}.$$

Using again the symmetry property of the collision integral and replacing $L(\Phi)$ by the left-hand side of (3), in view of the condition[2]

$$\sum_\alpha\int m_\alpha v_{\alpha z}^2 f_{\alpha 0}\Phi_{B\alpha}d\mathbf{v}_\alpha=0 \tag{30}$$

we have

$$\langle u_z\rangle=-\frac{k_BT}{\eta}\left(a_B\nabla_z\ln T+\sum_\alpha b_\alpha d_{\alpha z}\right)$$
$$+\frac{k_BT}{2\eta}\left\{\frac{2}{R}M_B(R)-\langle M_p\rangle\right\}. \tag{31}$$

Here

$$a_B=-\tfrac{1}{2}[v_z\Phi_B,v_z(\beta v^2-\tfrac{5}{2})], \tag{32}$$

$$b_\alpha=-\frac{1}{2}\frac{n}{n_\alpha}\int v_{\alpha z}^2 f_{\alpha 0}\Phi_{B\alpha}d\mathbf{v}_\alpha, \tag{33}$$

$$M_B=[v_z\Phi_B,v_r\Phi(R)], \tag{34}$$

$$\langle M_p\rangle=\frac{1}{S}\int_S dS[v_\perp^2\,v_z\Phi_p,\Phi]\,. \tag{35}$$

Now let us try to relate $\langle M_p\rangle$ to certain wall moment values. For this it is convenient to write Eq. (3) in cylindrical coordinates, which corresponds to representing the first term on the left-hand side of (3) in the form[21]

$$\mathbf{v}_{\alpha\perp}\frac{\partial\Phi_\alpha}{\partial\mathbf{x}_\perp}=v_{\alpha r}\frac{\partial\Phi_\alpha}{\partial r}+\frac{v_{\alpha\varphi}^2}{r}\frac{\partial\Phi_\alpha}{\partial v_{\alpha r}}-\frac{v_{\alpha r}v_{\alpha\varphi}}{r}\frac{\partial\Phi_\alpha}{\partial v_{\alpha\varphi}}. \tag{36}$$

Multiplying (3), with (36), by $m_\alpha v_{\alpha z} f_{\alpha 0}$, integrating over the velocities and summing over α we find

$$\frac{1}{r}\frac{\partial}{\partial r}(r[mv_z,v_r\Phi])+\nabla_z p=0. \tag{37}$$

Integration of (37) gives

$$[mv_z,v_r\Phi]=-\frac{r}{2}\nabla_z p. \tag{38}$$

Now let us multiply (3) by $v_{\alpha r}v_{\alpha z}f_{\alpha 0}\Phi_{p\alpha}$. Integrating over the velocities and summing over α we obtain

$$\frac{\partial}{\partial r}[v_r v_z\Phi_p,\Phi]+\frac{1}{r}\left[v_z v_r v_\varphi^2\Phi_p,\frac{\partial\Phi}{\partial v_r}\right]-\frac{1}{r}\left[v_z v_r^2 v_\varphi\Phi_p,\frac{\partial\Phi}{\partial v_\varphi}\right]$$
$$=[v_r v_z\Phi_p,L(\Phi)]. \tag{39}$$

For a transformation of the right-hand side we use the symmetry of the collision integral as well as the relations (27) and (38), whereas on the left we integrate by part in the last two terms. The result is

$$\frac{1}{r}\frac{\partial}{\partial r}(r[v_z v_r^2\Phi_p,\Phi])-\frac{1}{r}[v_z v_\varphi^2\Phi_p,\Phi]=-\frac{1}{k_BT}\frac{r}{2}\nabla_z p.$$

Integration over r yields

$$[v_z v_r^2\Phi_p,\Phi]=\frac{1}{r}\int_0^r[v_z v_\varphi^2\Phi_p,\Phi]dr-\frac{r^2}{6k_BT}\nabla_z p. \tag{40}$$

Now substitute (40) into the expression for $\langle M_p\rangle$, Eq. (35), remembering that $v_{\perp\alpha}^2=v_{r\alpha}^2+v_{\varphi\alpha}^2$. For a circular cylindrical capillary we find

$$\langle M_p\rangle=\frac{2}{R^2}\left\{\int_0^R[v_z v_\varphi^2\Phi_p,\Phi]rdr+\int_0^R dr\int_0^r[v_z v_\varphi^2\Phi_p,\Phi]dr'\right\}-\frac{1}{12k_BT}R^2\nabla_z p.$$

After integrating by parts in the second term we obtain

$$\langle M_p\rangle=\frac{2}{R}\int_0^R[v_z v_\varphi^2\Phi_p,\Phi]dr-\frac{1}{12k_BT}R^2\nabla_z p. \tag{41}$$

Replacing the integral in (41) by using (40) for $r=R$ finally gives

$$\langle M_p\rangle=-\frac{1}{4k_BT}R^2\nabla_z p+2[v_z v_r^2\Phi_p,\Phi(R)]. \tag{42}$$

Substitution of (42) into (31) results in

$$\langle u_z\rangle=-\frac{R^2}{8\eta}\nabla_z p-\frac{k_BT}{\eta}\left(a_B\nabla_z\ln T+\sum_\alpha b_\alpha d_{\alpha z}\right)$$
$$+\frac{k_BT}{\eta}\left\{\frac{1}{R}M_B(R)-M_p(R)\right\}, \tag{43}$$

where

$$M_p(R)=[v_z v_r^2\Phi_p,\Phi(R)]. \tag{44}$$

4. SEPARATION OF THE BULK AND KNUDSEN CONTRIBUTIONS TO THE FLUXES

Note that the expressions for the diffusion velocity, Eq. (15), and for the heat flux, Eq. (26), are formally free of terms associated with the presence of the Burnett contributions. However, the existence of the bulk heat flux[1,19] and of the barodiffusion effect in a viscous gas flow,[10,22] which are due to precisely the Burnett terms, are well known. On the other hand, in the velocity of the gas mixture flow as a whole [formula (43)] there appear the bulk Burnett contributions (the terms proportional to $a_B\tau$ and $b_\alpha d_{\alpha z}$) absent from the usual hydrodynamic description.[23] As in the pure-gas case,[9] the problem is easily resolved by noting that the bulk contributions are contained in the moments of the distribution function as measured at the wall. We will show this by employing the real structure of the distribution function, with the bulk and Knudsen parts separated in it. Let us express Φ_α in the form $\Phi_{b\alpha}+\varphi_\alpha$, where[20,18]

$$\Phi_{b\alpha}=2\beta_\alpha v_{\alpha z}u_h(r)+v_{\alpha r}v_{\alpha z}\Phi_{p\alpha}u_h'(r)+v_{\alpha z}\Phi_{B\alpha}u_h''$$
$$+v_{\alpha z}\sum_\beta\Phi_{d\alpha}^\beta d_{\beta z}+v_{\alpha z}\Phi_{t\alpha}\tau. \tag{45}$$

Here $u_h(r)$ is the hydrodynamic velocity of the mixture. For a circular cylindrical capillary[23]

$$u_h(r)=u_h(R)-\frac{1}{4\eta}(R^2-r^2)p_0k, \tag{46}$$

where $u_h'(r)$ and $u_h''(r)$ are the first and second derivatives of the velocity with respect to r, with $u_h'(R)=(R/2\eta)\nabla_z p$. The gas velocity at the wall (or slip velocity) $u_h(R)$ must be found independent of the solution of the corresponding kinetic problem. Note that for small Knudsen numbers ($l/R\ll1$) the Knudsen part of the distribution function, φ_α, is localized in a thin boundary layer near the wall, but in the general case the division into $\Phi_{b\alpha}$ and φ_α is formal in character.

Substituting (45) into (19) we find

$$M_d^\alpha(R)=[v_z\Phi_d^\alpha,v_r^2v_z\Phi_p]\frac{R}{2\eta}\nabla_z p+[v_z\Phi_d^\alpha,v_r\varphi(R)]. \tag{47}$$

The remaining terms disappear on integration because of the unevenness with respect to v_r. Substitution of (47) into (15) gives

$$\langle w_{\alpha z}\rangle=-\sum_\beta D_{\alpha\beta}d_{\beta z}-D_{T\alpha}\nabla_z\ln T-b_\alpha\frac{1}{\eta}\nabla_z p$$
$$+\frac{2}{nR}[v_z\Phi_d^\alpha,v_r\varphi(R)], \tag{48}$$

where

$$b_\alpha=-[v_z\Phi_d^\alpha,v_r^2v_z\Phi_p]. \tag{49}$$

Similarly, for $M_q(R)$ we have

$$M_q(R)=[v_z\Phi_t,v_r^2v_z\Phi_p]\,\frac{R}{2\eta}\,\nabla_z p+[v_z\Phi_t,v_r\varphi(R)]$$

and

$$\langle q_z\rangle=-\lambda\nabla_z T-p\sum_\alpha D_{T\alpha}(d_{\alpha z}+K_{T\alpha}\nabla_z\ln T)$$
$$-a_B\frac{k_BT}{\eta}\nabla_z p+\frac{5}{2}\sum_\alpha p_\alpha\langle w_{\alpha z}\rangle$$
$$+\frac{2k_BT}{R}\,[v_z\Phi_t,v_r\varphi(R)],\qquad(50)$$

where

$$a_B=-[v_z\Phi_t,v_r^2v_z\Phi_p]\,.\qquad(51)$$

It is easy to show that the coefficients b_α and a_B do relate to the Burnett contributions to the diffusion and heat fluxes, and that the expressions (49) and (51) are in fact identical with (33) and (32). We demonstrate this by taking the coefficient b_α as an example. Note that instead of (49) we may write

$$b_\alpha=-\frac{1}{2}\left[v_z\Phi_d^\alpha,(v_r^2+v_\varphi^2)\Phi_p+\frac{m}{\rho k_BT}\,\eta v_z\right].$$

Here we have used (40) with Φ replaced by $v_z\Phi_d^\alpha$ (which is independent of r); and the conditions $[v_z\Phi_d^\alpha,1]=0$ (Ref. 2) and $[v_z^2\Phi_d^\alpha,m]=0$, the latter following from (10). Using (28) we have

$$b_\alpha=-\frac{1}{2}\,[v_z\Phi_d^\alpha,L(v_z\Phi_B)]=-\frac{1}{2}\,[v_z\Phi_B,L(v_z\Phi_d^\alpha)]$$
$$=-\frac{1}{2}\sum_\beta\int v_{\beta z}^2f_{\beta 0}\Phi_{B\beta}\left(\delta_{\alpha\beta}-\frac{\rho_\beta}{\rho}\right)\frac{n}{n_\beta}\,d\mathbf{v}_\beta\,.$$

The term proportional to ρ_β/ρ goes to zero on account of the condition (30) giving

$$b_\alpha=-\frac{1}{2}\frac{n}{n_\alpha}\int v_{\alpha z}^2f_{\alpha 0}\Phi_{B\alpha}d\mathbf{v}_\alpha,$$

which is identical with (33).

A similar argument shows the identity of (51) and (32).

Now let us transform the expression for $\langle u_z\rangle$. Using (45) we have

$$M_B=[v_z\Phi_B,v_r^2v_z\Phi_p]\,\frac{R}{2\eta}\,\nabla_z p+[v_z\Phi_B,v_r\varphi(R)],\qquad(52)$$

$$M_p=\frac{1}{k_BT}\,[mv_r^2v_z^2\Phi_p]u_h(R)+[v_r^2v_z\Phi_p,v_z\Phi_B]\,\frac{\nabla_z p}{2\eta}$$
$$+[v_rv_z\Phi_p,v_z\Phi_t]\nabla_z\ln T+\left[v_r^2v_z\Phi_p,v_z\sum_\beta\Phi_d^\beta d_\beta\right]$$
$$+[v_r^2v_z\Phi_p,\varphi(R)]\,.\qquad(53)$$

After (52) and (53) are substituted into (43) and the definitions (49) and (51), are used a considerable part of the terms cancel out and the final expression for $\langle u_z\rangle$ takes the form

$$\langle u_z\rangle=-\frac{R^2}{8\eta}\nabla_z p+u_h(R)+\frac{k_BT}{\eta}\left\{\frac{1}{R}\,[v_z\Phi_B,v_r\varphi(R)]\right.$$
$$\left.-[v_r^2v_z\Phi_p,\varphi(R)]\right\}.\qquad(54)$$

Let us show that the moments of the Knudsen distribution function at the wall of the channel can be expressed in terms of the Knudsen layer localized heat and mass fluxes. To this end we turn to consider the equation for φ_α

$$\mathbf{v}_{\perp\,\alpha}\frac{\partial\varphi_\alpha}{\partial\mathbf{x}_\perp}=\sum_\beta L_{\alpha\beta}(\varphi)\,.\qquad(55)$$

Multiplying this by $v_{\alpha z}f_{\alpha 0}\Phi_{d\alpha}^\gamma$, integrating over the velocities, summing over α, and averaging over the cross section of the channel, we can easily show by means of transformations similar to those given in Sec. 2 that (in the final expression γ is replaced by α)

$$\frac{2}{nR}\,[v_z\Phi_d^\alpha,v_r\varphi(R)]=\hat{j}_{w\alpha}/n_\alpha\,.\qquad(56)$$

Here $\hat{j}_{w\alpha}=\hat{j}_\alpha-(n_\alpha/\rho)\hat{j}_m$ is the Knudsen layer localized diffusion flux of particles of species α. Note that $\hat{j}_m=\Sigma_\alpha m_\alpha\hat{j}_\alpha$ and

$$\hat{j}_\alpha=\frac{1}{S}\int_S dS\int v_{\alpha z}f_{\alpha 0}\varphi_\alpha d\mathbf{v}_\alpha\,.\qquad(57)$$

In a similar way it is established that

$$\frac{2}{R}\,[v_z\Phi_t,v_r\varphi(R)]=\frac{\hat{j}_q}{k_BT},\qquad(58)$$

where

$$\frac{\hat{j}_q}{k_BT}=\sum_\alpha\frac{1}{S}\int_S dS\int v_{\alpha z}(\beta_\alpha v_\alpha^2-\tfrac{5}{2})f_{\alpha 0}\varphi_\alpha d\mathbf{v}_\alpha\,.\qquad(59)$$

Now let us consider the structure of φ_α terms which enter the expression for $\langle u_z\rangle$. Multiplying (55) by $m_\alpha v_{\alpha z}f_{\alpha 0}$ with the use of (36) and then integrating over the velocities and summing over α we find

$$\frac{1}{r}\frac{\partial}{\partial r}\,(r[mv_z,v_r\varphi])=0,$$

from which, in view of the symmetry of the channel, it follows that

$$[mv_z,v_r\varphi(R)]=0\,.\qquad(60)$$

Now repeating the procedure used in Sec. 3, using (60) we find

$$[v_zv_r^2\Phi_p,\varphi(R)]=0\,.$$

Finally, using (60) one can obtain

$$\frac{1}{R}\,[v_z\Phi_B,v_r\varphi(R)]=\frac{\eta}{\rho k_BT}\,\hat{j}_m\,.\qquad(61)$$

It should be emphasized that localization in the Knudsen layer has a direct physical meaning only in the case when this layer is clearly separable—for example, for Knudsen numbers $\mathrm{Kn}\ll 1$. In the general case, to the Knudsen fluxes actually corresponds the difference between the fluxes calculated from the total distribution function and the wall-extrapolated hydrodynamic (or bulk) fluxes.

Using (56), (57), (59), and (61), the final expressions for the cross section averages of the diffusion velocity, heat flux, and mass-averaged gas mixture velocity can be written in the form

$$\langle w_{\alpha z}\rangle=-\sum_{\beta} D_{\alpha\beta}d_{\beta z}-D_{T\alpha}\nabla_z \ln T-b_\alpha \frac{1}{\eta}\nabla_z p+\frac{\hat{j}_{w\alpha}}{n_\alpha}, \quad (62)$$

$$\langle q_z\rangle=-\lambda\nabla_z T-p\sum_{\alpha} D_{T\alpha}(d_{\alpha z}+K_{T\alpha}\nabla_z \ln T)$$
$$+\frac{5}{2}\sum_{\alpha} p_\alpha\langle w_{\alpha z}\rangle-a_B\frac{k_B T}{\eta}\nabla_z p+\hat{j}_q, \quad (63)$$

$$\langle u_z\rangle=-\frac{R^2}{8\eta}\nabla_z p+u_h(R)+\frac{\hat{j}_m}{\rho}. \quad (64)$$

Note that the Burnett coefficients a_B and b_a, as is seen from (51) and (49), can be calculated using the familiar expressions for Φ_d^α, Φ_p, and Φ_t (Refs. 2, 19). A complete calculation of the cross section averages of the velocities and heat fluxes makes it necessary to determine $u_h(R)$ and the moments of the Knudsen distribution function at the wall of the channel, which can be accomplished in the framework of the methods developed for the solution of the linearized kinetic equation for boundary problems.[3,21] We will not present the details of this kind of calculations (see, e.g., Refs. 11–13, 24, 18) but rather will focus on the derivation of general relations complementing the system of equations (62)–(64). These relations follow from the analysis of the kinetic expression for entropy production and extend the system of linear phenomenological equations commonly used in irreversible thermodynamics.[1]

5. PRODUCTION OF ENTROPY IN THE GAS MIXTURE CAPILLARY FLOW

Following Refs. 14 and 15, consider the individual components of the entropy production obtained from the system of kinetic equations (3). The production of entropy due to intermolecular collisions is given by the expression

$$\Delta S_m=-k_B\sum_{\alpha}\sum_{\beta}\int \Phi_\alpha L_{\alpha\beta}(\Phi_\alpha,\Phi_\beta)f_{\alpha 0}d\mathbf{v}_\alpha$$
$$=-k_B[\Phi,L(\Phi)]. \quad (65)$$

Substituting for $L(\Phi)$ from the left-hand side of the kinetic equations (3), integrating over the velocities and averaging over the channel cross section we obtain

$$\langle\Delta S_m\rangle=-\langle h_z\rangle\frac{\nabla_z T}{T_0^2}-\langle u_z\rangle\frac{\nabla_z p}{T_0}-\frac{p_0}{T_0}\sum_{\beta}\langle w_{\beta z}\rangle d_{\beta z}$$
$$-\frac{k_B}{R}[v_r,\Phi^2(R)]. \quad (66)$$

The production of entropy in molecule-wall collisions is equal, with opposite sign, to the entropy flux onto the wall,[14]

$$\langle\Delta S_\sigma\rangle=\frac{k_B}{R}[v_r,\Phi^2(R)].$$

As a result, for the total entropy production we arrive at the classical result[1,25]

$$\langle\Delta S\rangle=-\langle h_z\rangle\frac{\nabla_z T}{T_0^2}-\langle u_z\rangle\frac{\nabla_z p}{T_0}-\frac{p_0}{T_0}\sum_{\beta=1}^{N-1}(\langle w_{\beta z}\rangle$$
$$-\langle w_{Nz}\rangle)d_{\beta z}. \quad (67)$$

In writing the last term it is taken into account that $\Sigma_{\beta=1}^{N}d_{\beta z}=0$. To the $\langle\Delta S\rangle$ expression there corresponds the system of phenomenological equations[1,25]

$$\langle w_\beta\rangle-\langle w_N\rangle=-\frac{1}{T_0}\sum_{\alpha=1}^{N-1}\lambda_{\beta\alpha}pd_{\beta z}-\lambda_{\beta N}\frac{\nabla_z p}{T_0}-\lambda_{\beta,N+1}\frac{\nabla_z T}{T_0^2},$$
$$\langle u_z\rangle=-\frac{1}{T_0}\sum_{\beta=1}^{N-1}\lambda_{N\beta}pd_{\beta z}-\lambda_{NN}\frac{\nabla_z p}{T_0}-\lambda_{N,N+1}\frac{\nabla_z T}{T_0^2}, \quad (68)$$
$$\langle h_z\rangle=-\frac{1}{T_0}\sum_{\beta=1}^{N-1}\lambda_{N+1,\beta}pd_{\beta z}-\lambda_{N+1,N}\frac{\nabla_z p}{T_0}$$
$$-\lambda_{N+1,N+1}\frac{\nabla_z T}{T_0^2},$$

where the λ_{ij} are the kinetic coefficients satisfying Onsager's symmetry relations, and T_0 is the average temperature of the gas.

The entropy production as determined by the bulk distribution function is

$$\Delta S_b=-k_B[\Phi_b,L(\Phi_b)]. \quad (69)$$

The bulk distribution function satisfies equations (3) with Φ_α replaced by $\Phi_{b\alpha}$. With their help, for the cross-section average of ΔS_b we find

$$\langle\Delta S_b\rangle=-\langle h_{bz}\rangle\frac{\nabla_z T}{T_0^2}-\langle u_{bz}\rangle\frac{\nabla_z p}{T_0}-\frac{p_0}{T_0}\sum_{\beta=1}^{N-1}(\langle w_{\beta z}^b\rangle$$
$$-\langle w_{Nz}^b\rangle)d_{\beta z}-\frac{k_B}{R}[v_r,\Phi_b^2(R)]. \quad (70)$$

By subtracting from (67) the entropy production $\langle\Delta S_b\rangle$ we obtain the so-called boundary entropy production

$$\Delta S_\Sigma=-\left(\hat{j}_q-\frac{5}{2}k_B T_0\sum_{\alpha}\hat{j}_{w\alpha}\right)\frac{\nabla_z T}{T_0^2}-\hat{j}_m\frac{\nabla_z p}{\rho T_0}$$
$$-\frac{p_0}{T_0}\sum_{\beta=1}^{N-1}\left(\frac{j_{w\beta}}{n_\beta}-\frac{j_{wN}}{n_N}\right)d_{\beta z}+\frac{k_B}{R}[v_r,\Phi_b^2(R)]. \quad (71)$$

Here $\hat{j}_{w\alpha}$, $\hat{j}_q$, and $\hat{j}_m$ are defined by expressions (57), (58), and (61).

Physically, the entropy production (71) is the sum of the contributions due to molecular collisions with the wall; due to collisions among the molecules "having" the Knudsen distribution function; and due to collisions of the same molecules with those obeying the bulk distribution function.[15] The last term in (71) can be calculated using the bulk distribution function (45). The result is

$$\frac{k_B}{R}\,[v_r,\Phi_b^2(R)]=-\frac{2}{R}\,k_B u_h'(R)\left\{\frac{\eta}{k_B T_0}\,u_h(R)-a_B\frac{\nabla_z T}{T_0}\right.$$
$$\left.-c_B\frac{\nabla_z p}{\eta}-\sum_\alpha n b_\alpha d_{\alpha z}\right\},\qquad(72)$$

where

$$c_B=-[v_r^2 v_z^2\Phi_p,\Phi_B(R)]\,.\qquad(73)$$

The system of phenomenological equations corresponding to the entropy production ΔS_Σ with (72), can be written in the form

$$\frac{2}{R}\,k_B\left\{\frac{\eta}{k_B T_0}\,u_h(R)-a_B\frac{\nabla_z T}{T_0}-c_B\frac{\nabla_z p}{\eta}-\sum_\alpha n b_\alpha d_{\alpha z}\right\}$$
$$=\Lambda_{00}\,u_h'(R)-\sum_{\beta=1}^{N-1}\Lambda_{0\beta}d_{\beta z}+\Lambda_{0N}\frac{\nabla_z T}{T_0^2}+\Lambda_{0,N+1}\frac{\nabla_z p}{T_0},$$
$$nk_B\left(\frac{\hat{j}_{w\alpha}}{n_\alpha}-\frac{\hat{j}_{wN}}{n_N}\right)=\Lambda_{\alpha 0}u_h'(R)+\sum_{\beta=1}^{N-1}\Lambda_{\alpha\beta}d_{\beta z}+\Lambda_{\alpha N}\frac{\nabla_z T}{T_0^2}$$
$$+\Lambda_{\alpha,N+1}\frac{\nabla_z p}{T_0},\qquad(74)$$
$$\hat{j}_q-\frac{5}{2}\,k_B T_0\sum_\alpha\hat{j}_{w\alpha}=\Lambda_{N0}u_h'(R)+\sum_{\beta=1}^{N-1}\Lambda_{N\beta}d_{\beta z}+\Lambda_{N,N}\frac{\nabla_z T}{T_0^2}$$
$$+\Lambda_{N,N+1}\frac{\nabla_z p}{T_0},$$
$$\frac{\hat{j}_m}{\rho}=\Lambda_{N+1,0}u_h'(R)+\sum_{\beta=1}^{N-1}\Lambda_{N+1,\beta}d_{\beta z}+\Lambda_{N+1,N}\frac{\nabla_z T}{T_0^2}$$
$$+\Lambda_{N+1,N+1}\frac{\nabla_z p}{T_0}\,.$$

Equations (74) complement (62)–(64) representing, in a sense, a system of boundary conditions for the flow of a multicomponent mixture in a channel.

For small Knudsen numbers, the first equation describes the viscous, diffusion, and thermal slip effects as well as the baroslip effect.[11,12] The next three equations characterize the diffusion and the heat and mass transfer in the boundary layers. Onsager's symmetry relations $\Lambda_{ij}=\Lambda_{ji}$ interrelate heat and matter fluxes in the boundary layers, caused by various thermodynamic "forces." The equalities $\Lambda_{0k}=\Lambda_{k0}$ relate gas slip velocities of various types and, what results from changes in the hydrodynamic normal-to-surface velocity, the heat and matter fluxes in kinetic boundary layers.

For intermediate and large Knudsen numbers, the separation of the system (74) is formal and difficult to interpret. In these mixture flow regimes the system (74) just indicates that, first, we can separate from the total fluxes (68) certain parts expressible through the Knudsen distribution function and, second, that it is possible to derive symmetry relations for the coefficients characterizing these parts.

6. THE SYMMETRY OF THE KINETIC COEFFICIENTS

It is known that the kinetic coefficients $\lambda_{\alpha\beta}$ in the system of phenomenological equations (68) satisfy Onsager's reciprocity relations.[1] The proof of the corresponding symmetry relations is obtainable in the framework of the general statistical concepts of irreversible thermodynamics as well at the level of the purely kinetic approach. For the flow of a pure gas, the symmetry of the coefficients $\lambda_{\alpha\beta}$ has been proved in Refs. 16, 17, and 9. Since the system of phenomenological equations (74) depends on only a part of entropy production for its construction, the question may arise as to the validity of Onsager's relations for the kinetic coefficients $\Lambda_{\alpha\beta}$. Below we prove the symmetry of these coefficients based on the kinetic approach first used in Ref. 9.

We make use of a relation obtained in Ref. 17, which is easily extended to the flow of a multicomponent mixture in a capillary and can be written in the form

$$[\mathscr{L}\psi_1(\mathbf{v}_\perp\,\mathbf{n}_\perp)\psi_2]_{r=R}=0,\qquad(75)$$

where ψ_1 and ψ_2 are the solutions of the Boltzmann equation (3) with homogeneous boundary conditions, and $\mathscr{L}$ is the operator of inversion in velocity space, i.e., $\mathscr{L}\psi(\mathbf{v})=\psi(-\mathbf{v})$.

The relation (75) is easily proved by using the boundary conditions (5). Then (75) is rewritten in the form

$$[\mathscr{L}\psi_1(\mathbf{v}_\perp\,\mathbf{n}_\perp)\psi_2]=\Big[\mathscr{L}\psi_1(\mathbf{v}_\perp\,\mathbf{n}_\perp)\int d\mathbf{v}'\theta(-\mathbf{v}_\perp'\,\mathbf{n}_\perp)$$
$$f_0(\mathbf{v}')\,|\mathbf{v}_\perp'\,\mathbf{n}_\perp|\,B(\mathbf{v},\mathbf{v}')\psi_2(\mathbf{v}')\Big]_{\mathbf{v}_\perp\,\mathbf{n}_\perp>0}$$
$$-\Big[(\mathbf{v}_\perp\,\mathbf{n}_\perp)\int d\mathbf{v}'\theta(-\mathbf{v}_\perp'\,\mathbf{n}_\perp)f_0(\mathbf{v}')\Big|\mathbf{v}_\perp'\,\mathbf{n}_\perp\Big|.\qquad(76)$$
$$B(\mathbf{v},\mathbf{v}')\psi_1(\mathbf{v}'),\,\mathscr{L}\psi_2\Big]_{\mathbf{v}_\perp\,\mathbf{n}_\perp>0}=0.$$

The vanishing of this difference is ensured by the reciprocity relations for the kernel of the scattering operator, $B(\mathbf{v},\mathbf{v}')$.

We turn now to the general form of the distribution function (45). Note that the unknowns in this expansion are the slip velocity $u_h(R)$ and the Knudsen distribution functions φ_α, whereas the remaining parameters [$\nabla_z p$, $\nabla_z T$, $d_{\alpha z}$, and $u_h'(R)$] are considered specified. Because of the linearity of the original problem and of the boundary conditions themselves, one may consider $u_h(R)$ and φ_α to be linear combinations of the relevant quantities, so that

$$u_h(R)=u_h^u\frac{u_h'(R)}{v_t}+u_h^p\frac{\nabla_z p}{p_0}+u_h^T\frac{\nabla_z T}{T_0}+\sum_\alpha u_{h\alpha}^d d_{\alpha z},$$
$$\varphi_\alpha=\varphi_\alpha^u\frac{u_h'(R)}{v_T}+\varphi_\alpha^p\frac{\nabla_z p}{p_0}+\varphi_\alpha^T\frac{\nabla_z T}{T_0}+\sum_\beta\varphi_\beta^{d,\alpha}d_{\beta z}.\qquad(77)$$

Here $v_T=(2k_BT_0/\mu_{\alpha\beta})^{1/2}$ is the characteristic thermal velocity of the molecules and $\mu_{\alpha\beta}$ is the reduced mass of the molecules of species α and β.

As an example, we now prove the symmetry of the coefficients Λ_{0N} and Λ_{N0} by using the equality (75), in which ψ_1 stands for the solution proportional to u_h', and ψ_2 that proportional to ∇_zT/T_0. We can do that, because for either of these parts of the distribution function the boundary conditions (5) are homogeneous, which is exactly what is needed to justify (75). Substitution of φ_α^u and φ_α^T into (75) gives

$$[\mathscr{L}(2\beta v_zu_h^u+v_rv_z\Phi_p+\varphi^u)u_h',v_n \times(2\beta v_zu_h^T+v_z\Phi_t+\varphi^T)\nabla_z\ln T]=0, \qquad (78)$$

where $v_n=\mathbf{v}_\perp\,\mathbf{n}_\perp$.

Dropping the terms which vanish upon the velocity integration, after opening the brackets we obtain

$$\{-2[\beta v_r^2v_z^2\Phi_p]u_h^T+[\mathscr{L}\varphi^u,v_nv_z\Phi_t]+[\mathscr{L}v_nv_z\Phi_p,v_n\varphi^T] +[v_r^2v_z^2\Phi_p,\Phi_t]+[\mathscr{L}\varphi^u,v_n\varphi^T]\}u_h'\nabla_z\ln T=0. \qquad (79)$$

Now drop the common multiplier $u_h'\nabla_z\ln T$ and integrate (79) over the capillary perimeter. As a result, using (29) and (51) we find

$$2\pi R\left(\frac{\eta u_h^T}{k_BT_0}-a_B\right)+\oint[\varphi^u,v_nv_z\Phi_t]dl+\oint[v_nv_z\Phi_p,v_n\varphi^T]dl +\oint[\mathscr{L}\varphi^u,v_n\varphi^T]dl=0. \qquad (80)$$

The first of the integrals on the left-hand side of (80) is transformed as follows:

$$\begin{aligned}\oint[\varphi^u,v_nv_z\Phi_t]dl&=\int_S\left[\frac{\partial\mathbf{v}_\perp\,\varphi^u}{\partial\mathbf{x}_\perp},v_z\Phi_t\right]dS\\&=\int_S[L(\varphi^u),v_z\Phi_t]dS\\&=\int_S[\varphi^u,L(v_z\Phi_t)]dS\\&=\int[\varphi^u,v_z(\beta v^2-\tfrac{5}{2})]dS\\&=\frac{\pi R^2}{kT_0}\left(\hat{j}_q^u-\frac{5}{2}k_BT_0\sum_\alpha\hat{j}_{w\alpha}^u\right).\end{aligned} \qquad (81)$$

It is easily shown that the second integral in (80) vanishes. This is seen by applying the same transformations used in obtaining (81) to give

$$\oint[v_nv_z\Phi_p,v_n\varphi^T]dl=\frac{1}{k_BT}\int_S[mv_rv_z,\varphi^T]dS.$$

The vanishing of the last integral follows from the condition (60).

Now let us show that the third integral in (80) also goes to zero. To this end note that

$$[\mathscr{L}\varphi^u,v_n\varphi^T]=-[\mathscr{L}\varphi^T,v_n\varphi^u]. \qquad (82)$$

The quantities φ_α^u and φ_α^T each satisfy Eq. (55). Multiply the equation for φ_α^u by $\mathscr{L}\varphi_\alpha^T$ and that for φ_α^T, by $\mathscr{L}\varphi_\alpha^u$. Subtracting one from the other, integrating over the $f_{\alpha0}$-weighted velocities, and summing over α we have, using the evenness of the operator $\mathscr{L}$ in velocity space and condition (82),

$$\left[\mathscr{L}\varphi^T,\frac{\partial\mathbf{v}_\perp\,\varphi^u}{\partial\mathbf{x}_\perp}\right]-\left[\mathscr{L}\varphi^u,\frac{\partial\mathbf{v}_\perp\,\varphi^T}{\partial\mathbf{x}_\perp}\right] =\frac{\partial}{\partial\mathbf{x}_\perp}[\mathscr{L}\varphi^T,\mathbf{v}_\perp\,\varphi^u]=0.$$

Integrating this over the cross section and using Gauss' theorem yields

$$\oint[\mathscr{L}\varphi^T,v_n\varphi^u]dl=0.$$

As a result, instead of (80) we can write

$$-\frac{2}{R}\left(\frac{\eta u_h^T}{k_BT_0}-a_B\right)=\frac{1}{k_BT_0}\left(\hat{j}_q^u-\tfrac{5}{2}k_BT_0\sum_\alpha\hat{j}_{w\alpha}^u\cdot\right). \qquad (83)$$

By comparing the left- and right-hand sides of (83) with the system of equations (74), we readily see that the combination on the left-hand side of (83) represents the coefficient Λ_{0N}/k_BT_0, whereas that on the right-hand side is Λ_{N0}/k_BT_0, so that Eq. (83) is equivalent to the Onsager reciprocity relations being valid for the kinetic coefficients $\Lambda_{0N}=\Lambda_{N0}$. In a similar way one establishes the validity of the Onsager relations for any other symmetric kinetic coefficients in the system (74).

In conclusion we note that, on the face of it, the proof of the reciprocity relations does not require the symmetry properties of the linearized collision integral but rests entirely on the symmetry of the kernel of the wall scattering operator for the particles. In reality this is not true because there are certain relations involved in the course of the proof that follow from connections which exist between the fluxes and the wall-related moments of the distribution function and whose derivation is based, in turn, on the use of the symmetry of the collision integral.

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