

Slip Effects in Mixtures of Monatomic Gases for General Surface Accommodation

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Macroscopic slip velocity, macroscopic temperature jump, thermal creep velocity and diffusion slip velocity for a mixture of monatomic gases are calculated by using a method developed recently (modified Maxwell-method) for a general gas-gas and gas-surface interaction law, and for a possibly anisotropic surface. The results are expressed in terms of accommodation coefficients of first and second order. Specialization is made for a binary gas mixture. For a comparison the results obtained by Maxwell's original method and general surface accommodation are given. In the case of surface-anisotropy several new slip effects occur.

I. Introduction

Since 1967 variational methods are used^{1–3} in the treatment of slip problems by solving the linearized Boltzmann equation within the Knudsen layer. Without special assumptions on the gas-gas intermolecular force law or the gas-surface interaction law Loyalka derived simple and accurate expressions for the velocity slip coefficient, the slip velocity in the thermal creep and the temperature jump coefficient for a simple gas⁴, and for the velocity slip⁵ and the temperature jump coefficient⁶ for a multicomponent gas mixture, as well as for the diffusion slip velocity in a gas mixture⁵. In a further paper⁷ Loyalka rederived his results for the velocity slip and for the temperature jump coefficient of a simple gas with an approximation method, namely by a simple modification of Maxwell's assumption on the velocity distribution of the gas molecules impinging on the wall. This method, shortly denoted by "modified Maxwell-method", is also used by Lang and Loyalka⁸ rederiving the expression for the diffusion slip velocity of a binary gas mixture. The final results of Loyalka are presented in terms of scalar products involving the pertinent Chapman-Enskog⁹ solution and an operator \mathbf{A} containing the effects of gas-wall interactions.

Klinc and Kuščer^{10, 17} also derived equations for the velocity and the temperature slip coefficients for a simple monatomic gas and a general gas-surface scattering law by a variational method.

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Moreover, they have solved the equations for the Chapman-Enskog solutions with a variational approximation and represented the results for the slip coefficients in terms of a set of accommodation coefficients. As recently¹¹ was shown, these results are in agreement with those gained by introducing the accommodation coefficients into the corresponding final expressions of Loyalka, and taking into account the first order terms in the development of the Chapman-Enskog solutions with respect to Sonine's polynomials.

In the present paper at first the results of Loyalka^{5, 6} and an expression for the thermal creep velocity for multicomponent gas mixtures are derived with the modified Maxwell-method. Generalization is given for anisotropy of the surface. The particular slip effects are not treated separately, but it is assumed that far from the surface there exists a mass flow (in y -direction parallel to the surface) as well as a temperature gradient (with x -, y - and z -components). If the surface is anisotropic a number of new slip effects occurs, for instance a change of the slip velocity caused by a temperature jump, and conversely ("crossing"-slip-effects). Even if the surface is invariant with respect to rotations through 180° about the surface normal, but not completely isotropic, there appears a change of the thermal creep velocity and the diffusion slip velocity due to the z -component of the temperature gradient (whereas the mass flow has y -direction). Furtheron, the accommodation coefficients are introduced, which are certain moments of the scattering



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operator \mathbf{A} and characterize certain aspects of the gas-surface interaction in a compressed form. All expressions are compared with those obtained by applying Maxwell's original assumption concerning the velocity distribution of the incident gas particles. Finally, the results are specialized to the case of a binary gas mixture.

In this connection it should also be referred to the papers of Cipolla, Lang and Loyalka, who calculated the temperature and pressure jumps during evaporation and condensation of a simple gas assuming a special gas-liquid surface scattering law (with a variational method)¹² and for general gas-liquid surface interaction¹³, as well as for a multi-component gas mixture (with the modified Maxwell-method)¹⁴.

II. Formulation of Equations

A multicomponent mixture of monatomic gases is considered, occupying the half space $x > 0$ and bounded by a flat plate located at $x = 0$. The starting point of the analysis is the steady Boltzmann-equation for the i -th constituent distribution function $f_i (i = 1, \dots, N)$ of an N -component gas mixture. For small deviations from equilibrium this equation may be linearized by introducing the relative perturbation $\Phi_i(\mathbf{r}, \mathbf{c})$ of the distribution function f_i with respect to an absolute Maxwellian f_{i0} through the definitions

$$f_i = f_{i0}(1 + \Phi_i), \quad (1)$$

$$f_{i0} = n_{i0} \left(\frac{m_i}{2\pi k T_0} \right)^{3/2} \exp \left\{ -\frac{m_i}{2k T_0} c^2 \right\}, \quad (2)$$

where \mathbf{r} is the position vector, \mathbf{c} the velocity, m_i the mass of an i -molecule, n_{i0} the density n_i of the i -th component at $\mathbf{r} = 0$, k Boltzmann's constant, and T_0 the surface temperature at $\mathbf{r} = 0$.

Introducing (1), (2) into Boltzmann's equation and neglecting terms of higher than linear order leads to the linearized Boltzmann-equation

$$\mathbf{c} \cdot \partial \Phi_i / \partial \mathbf{r} = L(\Phi_i), \quad (3)$$

where¹⁵

$$L[\Phi_i(\mathbf{c})] = \sum_{j=1, \dots, N} \iiint f_{j0}(\bar{\mathbf{c}}) [\Phi_i(\mathbf{c}') + \Phi_j(\bar{\mathbf{c}}') - \Phi_i(\mathbf{c}) - \Phi_j(\bar{\mathbf{c}})] |\bar{\mathbf{c}} - \mathbf{c}| b \, d\mathbf{b} \, d\mathbf{c} \, d\bar{\mathbf{c}}.$$

The linear collision operator L is Hermitian,

$$[f_i, L(g_i)] = [L(f_i), g_i]$$

with respect to the inner product

$$[f_i, g_i] = \sum_i \int f_{i0} f_i g_i \, d\mathbf{c},$$

where f_i and g_i are arbitrary (square-integrable) functions of \mathbf{c} .

As a consequence of properties of L the macroscopic conservation relations take (correct to first order terms) the form, that the divergence of the following quantities vanishes.

$$n_{i0} \mathbf{u}_i = \int f_{i0} \Phi_i(\mathbf{r}, \mathbf{c}) \mathbf{c} \, d\mathbf{c}, \quad (4)$$

$$n_0 \mathbf{u} = \sum_i n_{i0} \mathbf{u}_i = [\mathbf{c}, \Phi_i(\mathbf{r}, \mathbf{c})], \quad (5)$$

$$\rho_0 \mathbf{q} = \sum_i m_i n_{i0} \mathbf{u}_i = [m_i \mathbf{c}, \Phi_i(\mathbf{r}, \mathbf{c})], \quad (6)$$

$$\mathbf{P} = p_0 \mathbf{1} + [m_i \mathbf{c} \mathbf{c}, \Phi_i(\mathbf{r}, \mathbf{c})], \quad (7)$$

$$\mathbf{Q}_T = \frac{m_i}{2} [c^2 \mathbf{c}, \Phi_i(\mathbf{r}, \mathbf{c})]. \quad (8)$$

In these equations \mathbf{u}_i is the mean particle velocity of component i , \mathbf{u} is the mean particle velocity of the mixture, \mathbf{q} is the mass velocity of the mixture, \mathbf{P} is the pressure tensor, and \mathbf{Q}_T the total flux of kinetic energy in the mixture. Total particle density, mass density of the i -th component, and mass density of the mixture are

$$n_0 = \sum_i n_{i0},$$

$$\rho_0 = m_i n_{i0},$$

$$\rho_0 = \sum_i \rho_{i0},$$

the hydrostatic pressure is

$$p_0 = \sum_i p_{i0} + n_0 k T_0.$$

$\mathbf{1}$ denotes the second-order unit tensor.

The conductive heat transfer \mathbf{Q}_c' measured with respect to the velocity \mathbf{u} is given by

$$\begin{aligned} \frac{\mathbf{Q}_c'}{k T_0} &= \frac{\mathbf{Q}_T}{k T_0} - \frac{5}{2} n_0 \mathbf{u} \\ &= \left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \mathbf{c}, \Phi_i(\mathbf{r}, \mathbf{c}) \right]. \end{aligned} \quad (9)$$

Thus, it is seen that in this steady, linear problem all mass and energy flows have vanishing divergence.

III. Boundary Condition

The boundary condition for Φ_i is formulated with the gas-surface scattering kernel $P_i(\mathbf{c}' \rightarrow \mathbf{c})$ and the scattering operator A_i . $P_i(\mathbf{c}' \rightarrow \mathbf{c})$ is the probability density that, if a gas particle of the i -th kind hits the surface at a certain point with the

velocity \mathbf{c}' , this or another gas particle of the i -th kind leaves the surface at nearly the same time and point with the velocity \mathbf{c} within the velocity space element $d\mathbf{c}$ ^{16, 17}. Therefore, P_i fulfills the equation

$$c_x f_i(\mathbf{c}) = \int |c_x'| f_i(\mathbf{c}') P_i(\mathbf{c}' \rightarrow \mathbf{c}) d\mathbf{c}' \quad (c_x > 0) \quad (10)$$

A subscript $-$ (or $+$) with the integral sign indicates that the integration is taken over the half-space $c_x < 0$ (or > 0). Equation (10) represents the boundary condition for the distribution function f_i . P_i depends on the properties of the gas

and the wall (especially of the local temperature of the wall). As a probability density P_i is non-negative, and normalized

$$\int_+ P_i(\mathbf{c}' \rightarrow \mathbf{c}) d\mathbf{c} = 1 \quad (c_x' < 0), \quad (11)$$

since adsorption, evaporation and condensation phenomena are not considered here. All gas-surface scattering kernels satisfy the reciprocity relation¹⁶⁻¹⁸. Written with dimensionless velocities

$$\mathbf{v}^{(n)} = \sqrt{m_i/2kT_0} \mathbf{c}^{(n)}$$

the reciprocity relation at $\mathbf{r} = 0$ runs

$$|v_x'| e^{-v'^2} P_i(\mathbf{v}' \rightarrow \mathbf{v}) = v_x e^{-v^2} P_i(-\mathbf{v} \rightarrow -\mathbf{v}') \quad (v_x > 0, v_x' < 0). \quad (12)$$

Substituting (1), (2) into the boundary condition (10) at $\mathbf{r} = 0$ and applying Eqs. (11, 12) it results

$$\Phi_i(\mathbf{r} = 0, \mathbf{c}) = A_i \Phi_i(\mathbf{r} = 0, \mathbf{c}) \quad (c_x > 0), \quad (13)$$

where A_i is the scattering operator given by

$$A_i \Phi_i(0, \mathbf{c}) = \int \frac{f_{i0}(\mathbf{c}') |c_x'|}{f_{i0}(\mathbf{c}) c_x} P_i(\mathbf{c}' \rightarrow \mathbf{c}) \Phi_i(0, \mathbf{c}') d\mathbf{c}' \quad (c_x > 0). \quad (14)$$

IV. The Asymptotic Distribution

To complete the formulation of the problem it is necessary to specify the form of the distribution f_i in the region far from the surface. In that region ($x \rightarrow \infty$) f_i is given by the Chapman-Enskog solutions as

$$f_{i,\text{asy}} = f_i^{(0)} (1 + \Phi_i^{(1)}), \quad (15)$$

where $f_i^{(0)}$ is the local Maxwellian

$$f_i^{(0)} = n_{i,\text{asy}}(\mathbf{r}) \left(\frac{m_i}{2\pi k T_{\text{asy}}(\mathbf{r})} \right)^{\frac{3}{2}} \exp \left\{ - \frac{m_i [\mathbf{c} - \mathbf{q}_{\text{asy}}(\mathbf{r})]^2}{2 k T_{\text{asy}}(\mathbf{r})} \right\} \quad (16)$$

and $\Phi_i^{(1)}$ is given in¹⁵. In (16) $T(\mathbf{r})$ is the temperature, $\mathbf{q}(\mathbf{r})$ the mass velocity of the gas mixture, and the subscript "asy" refers to the asymptotic continuum region.

For small deviations from equilibrium linearizing is justified and leads [with Eqs. (1) and (15)] to

$$f_{i,\text{asy}}(\mathbf{r}, \mathbf{c}) = f_{i0} [1 + \Phi_{i,\text{asy}}(\mathbf{r}, \mathbf{c})],$$

where

$$\Phi_{i,\text{asy}}(\mathbf{r}, \mathbf{c}) = g_i(\mathbf{r}, \mathbf{c}) + \Phi_i^{(1)}(\mathbf{r}, \mathbf{c}), \quad (17)$$

and

$$g_i(\mathbf{r}, \mathbf{c}) = \frac{p_{i,\text{asy}}(\mathbf{r}) - p_{i0}}{p_{i0}} + \left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \frac{T_{\text{asy}}(\mathbf{r}) - T_0}{T_0} + \frac{m_i}{k T_0} \mathbf{q}_{\text{asy}}(\mathbf{r}) \cdot \mathbf{c}, \quad (18)$$

$$\Phi_i^{(1)}(\mathbf{r}, \mathbf{c}) = - \frac{1}{n_0} \sum_j D_i^j(c) \mathbf{c} \cdot \mathbf{d}_j - \frac{1}{n_0} A_i(c) \mathbf{c} \cdot \boldsymbol{\kappa} - \frac{1}{n_0} B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \cdot \nabla \mathbf{q}_{\text{asy}}(\mathbf{r}). \quad (19)$$

$p_i(\mathbf{r})$ is the partial pressure of component i , $p_{i0} = p_i(0)$. In (19)

$$\boldsymbol{\kappa} = (1/T_0) \nabla T_{\text{asy}}(\mathbf{r}).$$

Substituting Eq. (19) into Eq. (7) it follows

$$\mathbf{P}_{\text{asy}} = p_{\text{asy}} \mathbf{1} - 2 \mu \mathbf{S}_{\text{asy}},$$

where μ is the coefficient of viscosity

$$\mu = \frac{1}{10 n_0} [B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}), m_i (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1})], \quad (20)$$

an \mathbf{S} denotes the rate-of-shear tensor¹⁵. An in¹⁵, if the factors of the inner products are tensors of the same order, the integrands of the bracket integrals contain the appropriate scalar products so that the bracket integrals are scalar quantities.

The spatial dependence of \mathbf{q}_{asy} is assumed to be nearly linearly. Then the vanishing divergence of \mathbf{P} (7) leads to

$$\nabla p_{\text{asy}} = 0.$$

Therefore, \mathbf{d}_j does not contain ∇p_{asy} :

$$\mathbf{d}_j = \nabla [p_{j,\text{asy}}(\mathbf{r})/p_{\text{asy}}],$$

where

$$\sum_j \mathbf{d}_j = 0.$$

The functions $D_i^j(c)$, $A_i(c)$ and $B_i(c)$ are the Chapman-Enskog diffusion, thermal conductivity and viscosity solutions defined in¹⁵. For instance

$$L[B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1})] = -n_0 (m_i/k T_0) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}). \quad (21)$$

For calculating the slip coefficients and slip velocities it is considerably more convenient to introduce the modified Chapman-Enskog functions¹⁴

$$\begin{aligned} \tilde{D}_i^j(c) &= D_i^j(c) - (n_0 k/\lambda') D_{Tj} A_i(c) \quad (j=1, \dots, N), \\ \tilde{A}_i(c) &= A_i(c) - \sum_j k_{Tj} D_i^j(c), \end{aligned}$$

where diffusion coefficients D_{ij} , thermal diffusion coefficients D_{Ti} , partial or theoretical coefficient of thermal conductivity λ' , and thermal diffusion ratios k_{Tj} are defined in¹⁵.

These modified functions satisfy the relations

$$\tilde{D}_{ij} = \frac{1}{3 n_0 n_{i0}} \int f_{i0} \tilde{D}_i^j(c) c^2 d\mathbf{c}, \quad (22)$$

$$0 = \int f_{i0} \tilde{A}_i(c) c^2 d\mathbf{c} = \frac{n_{i0}}{n_0} \left[\tilde{D}_i^j(c) \mathbf{c}, \left(\frac{m_j c^2}{2 k T_0} - \frac{5}{2} \right) \mathbf{c} \right], \quad (23)$$

$$\lambda = \frac{k}{3 n_0} \left[\tilde{A}_i(c) \mathbf{c}, \left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \mathbf{c} \right], \quad (24)$$

where

$$\tilde{D}_{ij} = D_{ij} - (n_0 k/\lambda') D_{Ti} D_{Tj}, \quad (25)$$

$$\lambda = \lambda' - n_0 k \sum_i k_{Ti} D_{Ti}, \quad (26)$$

and

$$\tilde{D}_{ij} = \tilde{D}_{ji}, \quad \sum_i \varrho_{i0} \tilde{D}_{ij} = 0.$$

λ is seen to be the coefficient of thermal conductivity of the gas mixture¹⁵.

Written with the modified functions the perturbation $\Phi_i^{(1)}$ (19) takes the form

$$\Phi_i^{(1)}(\mathbf{r}, \mathbf{c}) = -\frac{1}{n_0} \sum_j \tilde{D}_i^j(c) \mathbf{c} \cdot \mathbf{d}_j - \frac{1}{n_0} \tilde{A}_i(c) \mathbf{c} \cdot \tilde{\boldsymbol{\kappa}} - \frac{1}{n_0} B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \cdot \nabla \mathbf{q}_{\text{asy}}(\mathbf{r}), \quad (27)$$

where the modified gradients have been used as

$$\tilde{\mathbf{d}}_j = \mathbf{d}_j + \frac{\lambda'}{\lambda} k_{Tj} \left(\boldsymbol{\kappa} + \frac{n_0 k}{\lambda'} \sum_l D_{Tl} \mathbf{d}_l \right), \quad (28)$$

$$\tilde{\boldsymbol{\kappa}} = \frac{\lambda'}{\lambda} \boldsymbol{\kappa} + \frac{n_0 k}{\lambda} \sum_l D_{Tl} \mathbf{d}_l. \quad (29)$$

With the modified quantities the diffusion velocities and heat flux take the simple forms

$$\mathbf{u}_i - \mathbf{q}_{\text{asy}}(\mathbf{r}) = - \sum_j \tilde{D}_{ij} \tilde{\mathbf{a}}_j, \quad \mathbf{Q}_c'/kT_0 = - (\lambda/k) \tilde{\boldsymbol{\kappa}}.$$

Furtheron the following relation results

$$L[\tilde{A}_i(c) \mathbf{c}] = -n_0 \left(\frac{m_i c^2}{2kT_0} - \frac{5}{2} - \frac{n_0}{n_{i0}} kT_i \right) \mathbf{c}. \quad (30)$$

V. Calculation of Inner Products

To find an approximate solution for the extrapolation $\mathbf{q}_{\text{asy}}(0)$ of the mass velocity to the wall and for the macroscopic temperature jump

$$\varepsilon_t = [T_{\text{asy}}(0) - T_0]/T_0 \quad (31)$$

in the vicinity of the surface, the inner products of the perturbation Φ_i [Eq. (1)] and of the asymptotic distribution $\Phi_{i,\text{asy}}$ [Eqs. (17, 18, 27)] with some special functions are considered. Multiplication of $m_i \mathbf{c} \mathbf{c}$ and of $((m_i c^2)/(2kT_0) - 5/2) \mathbf{c}$ by $\Phi_{i,\text{asy}}$ leads to

$$[m_i \mathbf{c} \mathbf{c}, \Phi_{i,\text{asy}}(\mathbf{r}, \mathbf{c})] = (p_{\text{asy}} - p_0) \mathbf{1} - 2\mu \mathbf{S}_{\text{asy}}, \quad (32)$$

and

$$\left[\left(\frac{m_i c^2}{2kT_0} - \frac{5}{2} \right) \mathbf{c}, \Phi_{i,\text{asy}}(\mathbf{r}, \mathbf{c}) \right] = - \frac{\lambda}{k} \tilde{\boldsymbol{\kappa}}, \quad (33)$$

whereby the identities (23), (24) have been used.

Next the gradients of the inner products of $\tilde{A}_i(c) \mathbf{c} \mathbf{c}$ and $B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \mathbf{c}$ with Φ_i are calculated. With (3), the hermiticity of L, and the Eqs. (30) and (21) it follows

$$\nabla \cdot [\tilde{A}_i(c) \mathbf{c} \mathbf{c}, \Phi_i] = -n_0 \left[\left(\frac{m_i c^2}{2kT_0} - \frac{5}{2} - \frac{n_0}{n_{i0}} kT_i \right) \mathbf{c}, \Phi_i \right], \quad (34)$$

$$\nabla \cdot [B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \mathbf{c}, \Phi_i] = -n_0 \left[\frac{m_i}{kT_0} (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}), \Phi_i \right]. \quad (35)$$

Evaluation of (34) with the asymptotic distribution $\Phi_{i,\text{asy}}$ instead of Φ_i using the Eqs. (22) to (24), (26) and (29) leads to

$$\nabla \cdot [\tilde{A}_i(c) \mathbf{c} \mathbf{c}, \Phi_{i,\text{asy}}] = n_0 (\lambda/k) \boldsymbol{\kappa}. \quad (36)$$

With $\Phi_{i,\text{asy}}$ instead of Φ_i (35) turns to

$$\nabla \cdot [B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \mathbf{c}, \Phi_{i,\text{asy}}] = (2n_0/kT_0) \mu \mathbf{S}_{\text{asy}}. \quad (37)$$

Lastly it holds

$$\left[\left(- \frac{n_0}{n_{i0}} kT_i \right) \mathbf{c}, \Phi_{i,\text{asy}} \right] = \frac{\lambda}{k} (\tilde{\boldsymbol{\kappa}} - \boldsymbol{\kappa}), \quad (38)$$

and

$$[B_i(c) \mathbf{c} \mathbf{c} \mathbf{c}, \Phi_{i,\text{asy}}] = \mu \frac{n_0}{kT_0} 3 \overline{\overline{\mathbf{1} \mathbf{q}_{\text{asy}}(\mathbf{r})}} - \frac{1}{5n_0} [B_i(c) c^4, \sum_j \tilde{D}_i^j(c) \overline{\overline{\mathbf{1} \tilde{\mathbf{a}}_j}} + \tilde{A}_i(c) \overline{\overline{\mathbf{1} \tilde{\boldsymbol{\kappa}}}}], \quad (39)$$

where $\overline{\overline{w}}$ denotes the symmetric part of the third-order tensor w , and

$$[\tilde{A}_i(c) \mathbf{c} \mathbf{c}, \Phi_{i,\text{asy}}] = n_0 \frac{\lambda}{k} \frac{T_{\text{asy}}(\mathbf{r}) - T_0}{T_0} \mathbf{1} - \frac{2}{15n_0} [\tilde{A}_i(c) c^4, B_i(c)] \mathbf{S}_{\text{asy}}. \quad (40)$$

The relations (38) and (39) have been derived with the useful general integral theorem

$$\int F(C) \mathbf{C} \mathbf{C} \mathbf{C} \mathbf{C} d\mathbf{C} = \frac{1}{5} \int F(C) C^4 d\mathbf{C} \overline{\overline{\mathbf{1} \mathbf{1}}},$$

where $F(C)$ is any function of C , and $\overline{\overline{\mathbf{1} \mathbf{1}}}$ is the symmetric part of the fourth-order tensor $\mathbf{1} \mathbf{1}$, and with the relations

$$\overline{\overline{\mathbf{1} \mathbf{1}}} \cdot \mathbf{a} = \overline{\overline{\mathbf{1} \mathbf{a}}}, \quad \overline{\overline{\mathbf{1} \mathbf{1}}} \cdot \mathbf{w} = \frac{2}{3} \overline{\overline{\mathbf{w}}} + \frac{1}{3} \mathbf{1} \text{tr}(\mathbf{w}),$$

where \mathbf{a} is any vector, \mathbf{w} any second-order tensor, and $\text{tr}(\mathbf{w})$ the trace (or divergence) of \mathbf{w} .

VI. Determination Equations

As in the Kramers problem the gas mixture far from the surface is maintained at a mass velocity $\mathbf{q}_{\text{asy}}(\mathbf{r})$ with constant direction parallel to the surface and constant gradient of q_{asy} normal to the plate. This direction of \mathbf{q}_{asy} is chosen as the y -direction, so that

$$\mathbf{S}_{\text{asy}} = \begin{pmatrix} 0 & \frac{1}{2} \frac{\partial q_{\text{asy}}}{\partial x} & 0 \\ \frac{1}{2} \frac{\partial q_{\text{asy}}}{\partial x} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Moreover, the temperature gradient of the gas mixture far from the plate is maintained constant, so that $\partial T_{\text{asy}}(\mathbf{r})/\partial x$ is independent of x . $\nabla T_{\text{asy}}(\mathbf{r})$ may have any direction with normal (x -) and parallel (y - and z -) components.

Furtheron, in the whole gas, including the Knudsen-layer, the dependences of the perturbation Φ_i ($i = 1, \dots, N$) upon the coordinates y and z parallel to the surface are assumed to be small enough, so that the five expressions $\nabla_t \cdot \mathbf{P}$, $\nabla_t \cdot \mathbf{Q}'_c$, $\nabla_t \cdot \mathbf{u}_i$, $\nabla_t \cdot [\tilde{A}_i(c) \mathbf{c} c_x, \Phi_i]$,

and

$$\nabla_t \cdot [B_i(c) (\mathbf{c} c_y - \frac{1}{3} c^2 \mathbf{i}_y) c_x, \Phi_i]$$

can be neglected, or are at least independent of x (analogous to Welander's¹⁹ original assumption for the temperature jump calculation). Hereby ∇_t denotes the part of the divergence arising from differentiations with respect to coordinates parallel to the surface,

$$\nabla_t = \mathbf{i}_y \partial/\partial y + \mathbf{i}_z \partial/\partial z,$$

and \mathbf{i}_x , \mathbf{i}_y , \mathbf{i}_z denote the unit vectors in x -, y -, z -direction.

In this case the divergences of the pressure tensor \mathbf{P} , the heat flux vector \mathbf{Q}'_c , the mean particle velocity \mathbf{u}_i , and the vectors $[\tilde{A}_i(c) \mathbf{c} c_x, \Phi_i]$ and $[B_i(c) (\mathbf{c} c_y - \frac{1}{3} c^2 \mathbf{i}_y) c_x, \Phi_i]$ can be replaced by the sum of their parts $\mathbf{i}_x(\partial/\partial x)$ and quantities independent of x , for example

$$\nabla \cdot \mathbf{u}_i = \frac{\partial}{\partial x} u_{ix} + \text{const.}$$

Then from the discussions at Eqs. (7) and (9) it follows at first that the derivation

$$\partial/\partial x [m_i \mathbf{c} c_x, \Phi_i(\mathbf{r}, \mathbf{c})]$$

of the pressure tensor normal component $\mathbf{i}_x \cdot \mathbf{P}^{(1)}$, and that one

$$\frac{\partial}{\partial x} \left[\left(\frac{m_i c^2}{2} - \frac{5}{2} k T_0 \right) c_x, \Phi_i(\mathbf{r}, \mathbf{c}) \right]$$

of the heat flux vector normal coordinate Q'_{cx} are independent of x and can be evaluated by $\Phi_{i, \text{asy}}$.

The Eqs. (32), (33) lead to

$$[m_i \mathbf{c} c_x, \Phi_i(\mathbf{r}, \mathbf{c})] = (p_{\text{asy}} - p_0) \mathbf{i}_x - 2 \mu \mathbf{S}_{\text{asy}} \cdot \mathbf{i}_x, \quad (41)$$

$$\left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \Phi_i(\mathbf{r}, \mathbf{c}) \right] = - \frac{\lambda}{k} \tilde{\alpha}_x, \quad (42)$$

and to

$$[m_i (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}), \Phi_i(\mathbf{r}, \mathbf{c})] \cdot \mathbf{i}_x = -2 \mu \mathbf{S}_{\text{asy}} \cdot \mathbf{i}_x. \quad (43)$$

The shear stress y -coordinate from (43) is

$$\mathbf{i}_y \cdot [m_i (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}), \Phi_i(\mathbf{r}, \mathbf{c})] \cdot \mathbf{i}_x = -\mu \frac{\partial}{\partial x} q_{\text{asy}}. \quad (44)$$

It follows from (44) and (35) that $\mathbf{i}_y \cdot [\nabla \cdot (B_i(c) (\mathbf{c} \mathbf{c} - \frac{1}{3} c^2 \mathbf{1}) \mathbf{c}, \Phi_i)] \cdot \mathbf{i}_x$ is independent of x . Hence $\partial/\partial x [B_i(c) c_x^2 c_y, \Phi_i]$ is independent of x and $[B_i(c) c_x^2 c_y, \Phi_i]$ can be evaluated by the use of the asym-

ptotic solution. With Eqs. (37), (39) the result is

$$[B_i(c) c_x^2 c_y, \Phi_i(\mathbf{r}, \mathbf{c})] = \frac{n_0}{k T_0} \mu \frac{\partial q_{\text{asy}}}{\partial x} x + \frac{n_0}{k T_0} \mu q_{\text{asy}}(0) - \frac{1}{15 n_0} [B_i(c) c^4, \sum_j \tilde{D}_i^j \tilde{d}_{jy} + \tilde{A}_i(c) \tilde{z}_y]. \quad (45)$$

It follows from before Eq. (4) and the discussions at the beginning of Section VI. that the normal component u_{ix} of the mean particle velocity \mathbf{u}_i of sort i can be evaluated by the use of $\Phi_{i, \text{asy}}$. The same is valid for the expression $[(-n_0/n_{i0}) k_{Ti} c_x, \Phi_i(\mathbf{r}, \mathbf{c})]$. Therefore, the Eqs. (42), (38) lead to

$$\left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} - \frac{n_0}{n_{i0}} k_{Ti} \right) c_x, \Phi_i(\mathbf{r}, \mathbf{c}) \right] = - \frac{\lambda}{k} \kappa_x. \quad (46)$$

It follows from (46) and (34) that $\nabla \cdot [\tilde{A}_i(c) \mathbf{c} c_x, \Phi_i]$ is independent of x . Hence, $\partial/\partial x [\tilde{A}_i(c) c_x^2, \Phi_i]$ is independent of x so that $[A_i(c) c_x^2, \Phi_i]$ is linear in x and can also be calculated by the use of $\Phi_{i, \text{asy}}$. The result is, using Eqs. (36), (40)

$$[\tilde{A}_i(c) c_x^2, \Phi_i(\mathbf{r}, \mathbf{c})] = n_0 \frac{\lambda}{k} \kappa_x x + n_0 \frac{\lambda}{k} \frac{T_{\text{asy}}(\mathbf{r}) - T_0}{T_0}. \quad (47)$$

According to the assumptions at the beginning of Section VI. $\partial q_{\text{asy}}(x)/\partial x$, κ , d_{jy} and κ_y are constant. From (44), (45), (42), (47) and (31) the following four Eqs. at the wall at $\mathbf{r}=0$ arise

$$[m_i c_y c_x, \Phi_i(0, \mathbf{c})] = - \mu \frac{\partial}{\partial x} q_{\text{asy}}(x), \quad (48)$$

$$[B_i(c) c_x^2 c_y, \Phi_i(0, \mathbf{c})] = \frac{n_0}{k T_0} \mu q_{\text{asy}}(0) - \frac{1}{15 n_0} [B_i(c) c^4, \sum_j \tilde{D}_i^j(c) \tilde{d}_{jy} + \tilde{A}_i(c) \tilde{z}_y], \quad (49)$$

$$\left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \Phi_i(0, \mathbf{c}) \right] = - \frac{\lambda}{k} \tilde{\kappa}_{x0}, \quad (50)$$

$$[\tilde{A}_i(c) c_x^2, \Phi_i(0, \mathbf{c})] = n_0 (\lambda/k) \varepsilon_t, \quad (51)$$

where $\tilde{\kappa}_{x0}$ is the value of $\tilde{\kappa}_x$ at $x=0$.

VII. Maxwell's Assumption and Modified Maxwell-Method

Maxwell's arguments amount to assuming

$$\Phi_i(\mathbf{r}=0, \mathbf{c}) = \Phi_{i, \text{asy}}(\mathbf{r}=0, \mathbf{c}) \quad (c_x < 0)$$

for the (first order correction of the) velocity distribution function of the molecules approaching the wall. Therefore, with the function

$$\eta(c_x) = \begin{cases} 1, & \text{for } c_x > 0, \\ 0, & \text{for } c_x < 0, \end{cases}$$

and the boundary condition (13) the whole distribution near the wall at $\mathbf{r}=0$ can be written

$$\Phi_i(0, \mathbf{c}) = [\eta(-c_x) + \eta(c_x) A_i] \Phi_{i, \text{asy}}(0, \mathbf{c}). \quad (52)$$

Inserting the ansatz (52) into Eq. (48) gives the macroscopic slip velocity, into Eq. (50) the macroscopic temperature jump.

The modified Maxwell-method, first used by Loyalka⁷, and analogously applied for the cases treated here, consists in using another distribution function instead of (52). For the calculation of slip velocity it differs from (52) only by containing an unknown constant a_p instead of $q_{\text{asy}}(0)$, for the calculation of temperature jump it differs from (52) only by containing the unknown constant a_T instead of ε_t in g_i (18). The two unknowns $q_{\text{asy}}(0)$ and a_p are calculated solving the system of Eqs. (48), (49); correspondingly ε_t and a_T are calculated with the Eqs. (50), (51).

The results are of the form

$$q_{\text{asy}}(0) = \zeta_\varepsilon \varepsilon_t + \sum_j \tilde{\zeta}_j \cdot \tilde{\mathbf{d}}_{j0} + \tilde{\zeta}_\kappa \cdot \tilde{\mathbf{x}}_0 + \zeta \frac{\partial q_{\text{asy}}(x)}{\partial x}, \quad (53)$$

$$\varepsilon_t = \zeta_{\lambda q} q_{\text{asy}}(0) + \sum_j \tilde{\zeta}_{\lambda j} \cdot \tilde{\mathbf{d}}_{j0} + \tilde{\zeta}_\lambda \cdot \tilde{\mathbf{x}}_0 + \zeta_{\lambda \mu} \frac{\partial q_{\text{asy}}(x)}{\partial x}. \quad (54)$$

In (53) ζ is the usual velocity-slip coefficient, the sum of the second and third summand is the sum of diffusion slip and thermal creep velocity, and the first summand is a certain slip velocity caused by a macroscopic temperature jump and vanishing for isotropic surfaces, as will be seen later.

$\tilde{\zeta}_\lambda$ in (54) is the (modified) temperature-slip coefficient, the other slip coefficients $\zeta_{\lambda q}$, $\tilde{\zeta}_{\lambda j}$, $\zeta_{\lambda \mu}$ again vanish for isotropic surfaces, as shall be discussed in the following.

Inserting (54) into (53), the macroscopic slip velocity $q_{\text{asy}}(0)$ can be represented, as usually, depending only on the forces $\tilde{\mathbf{d}}_{j0}$, $\tilde{\mathbf{x}}_0$ and $\partial q_{\text{asy}}(x)/\partial x$; conversely the macroscopic temperature jump ε_t by inserting (53) into (54).

According to Maxwell's assumption (index M) the equations for the slip velocity and temperature jump are

$$\begin{aligned} q_{\text{asy},M}(0) &= \frac{k T_0}{[m_i c_y c_x, \eta(c_x) (1 - A_i) m_i c_y]} \left\{ \left[m_i c_y c_x, \eta(c_x) A_i \left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \right] \varepsilon_t \right. \\ &\quad + \frac{1}{n_0} [m_i c_y c_x, \eta(c_x) (c_y \mathbf{i}_y - A_i \mathbf{c}) \cdot (\sum_j \tilde{D}_i^j(c) \tilde{\mathbf{d}}_{j0} + \tilde{A}_i(c) \tilde{\mathbf{x}}_0)] \\ &\quad \left. + \frac{1}{n_0} [m_i c_y c_x, \eta(c_x) (1 - A_i) B_i(c) c_y c_x] \frac{\partial q_{\text{asy}}}{\partial x} \right\}, \\ \varepsilon_{t,M} &= \frac{1}{\left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \eta(c_x) (1 - A_i) \left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \right]} \\ &\quad \cdot \left\{ \left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \eta(c_x) A_i c_y \left(\frac{m_i}{k T_0} q_{\text{asy}}(0) - \frac{1}{n_0} B_i(c) c_x \frac{\partial q_{\text{asy}}}{\partial x} \right) \right] \right. \\ &\quad - \frac{1}{n_0} \sum_j \left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \eta(c_x) (c_x \mathbf{i}_x + A_i \mathbf{c}) \tilde{D}_i^j(c) \right] \cdot \tilde{\mathbf{d}}_{j0} \\ &\quad \left. + \frac{1}{n_0} \left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \eta(c_x) (c_x \mathbf{i}_x - A_i \mathbf{c}) \tilde{A}_i(c) \right] \cdot \tilde{\mathbf{x}}_0 \right\}. \end{aligned} \quad (55)$$

The modified Maxwell-method leads to

$$\begin{aligned} q_{\text{asy}}(0) &= \frac{k T_0}{\mu n_0} \left\{ \left[B_i(c) c_x^2 c_y, \eta(c_x) A_i \left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) \right] \varepsilon_t \right. \\ &\quad + \frac{1}{n_0} [B_i(c) c_x^2 c_y, \eta(c_x) (c_y \mathbf{i}_y - A_i \mathbf{c}) \cdot (\sum_j \tilde{D}_i^j(c) \tilde{\mathbf{d}}_{j0} + \tilde{A}_i(c) \tilde{\mathbf{x}}_0)] \\ &\quad + \frac{1}{n_0} [B_i(c) c_x^2 c_y, \eta(c_x) (1 - A_i) B_i(c) c_y c_x] \frac{\partial q_{\text{asy}}}{\partial x} \\ &\quad \left. + [m_i c_y c_x, \eta(c_x) (1 - A_i) B_i(c) c_y c_x] \frac{q_{\text{asy},M}(0)}{k T_0} \right\}, \end{aligned} \quad (57)$$

$$\begin{aligned} \varepsilon_t &= \frac{k}{\lambda n_0} \left\{ \left[\left(\frac{m_i c^2}{2 k T_0} - \frac{5}{2} \right) c_x, \eta(c_x) (1 - A_i) \tilde{A}_i(c) c_x \right] \varepsilon_{t,M} \right. \\ &\quad + \left[\tilde{A}_i(c) c_x^2, \eta(c_x) A_i c_y \left(\frac{m_i}{k T_0} q_{\text{asy}}(0) - \frac{1}{n_0} B_i(c) c_x \frac{\partial q_{\text{asy}}}{\partial x} \right) \right] \\ &\quad \left. + \frac{1}{n_0} \left[\tilde{A}_i(c) c_x^2, \eta(c_x) (c_x \mathbf{i}_x - A_i \mathbf{c}) \cdot (\sum_j \tilde{D}_i^j(c) \tilde{\mathbf{d}}_{j0} + \tilde{A}_i(c) \tilde{\mathbf{x}}_0) \right] \right\}. \end{aligned} \quad (58)$$

For the derivation of these four equations the reciprocity relation (12) the definitions (20) and (24), and the first equation (23) were used. The slip coefficients in (53), (54) follow directly from the expressions in (55) to (58).

VIII. Introduction of Accommodation Coefficients

Corresponding to ^{14, 15} for the modified Chapman-Enskog functions the ansatz is made

$$\begin{aligned}\tilde{D}_i^j(c) &= \frac{m_i}{2kT_0} \sum_{p=0}^{n-1} \tilde{d}_{i,p}^{j(n)} S_{\frac{1}{2}}^{(p)} \left(\frac{m_i c^2}{2kT_0} \right), \\ \tilde{A}_i(c) &= -\frac{m_i}{2kT_0} \sum_{p=0}^n \tilde{a}_{i,p}^{(n)} S_{\frac{1}{2}}^{(p)} \left(\frac{m_i c^2}{2kT_0} \right), \\ B_i(c) &= \frac{m_i}{2kT_0} \sum_{p=0}^{n-1} b_{i,p}^{(n)} S_{\frac{1}{2}}^{(p)} \left(\frac{m_i c^2}{2kT_0} \right),\end{aligned}$$

where $S_\nu^{(p)}$ denotes the Sonine polynomial of order n and index ν . In a first order approximation it follows

$$\tilde{D}_i^j(c) = 2n_0 \frac{m_i}{2kT_0} \tilde{D}_{ij}, \quad (59)$$

$$\tilde{A}_i(c) = -\frac{4}{5} n_0 \frac{m_i}{2kT_0} \frac{\lambda_i}{k n_{i0}} \left(\frac{5}{2} - \frac{m_i c^2}{2kT_0} \right), \quad (60)$$

$$B_i(c) = n_0 \frac{m_i}{(kT_0)^2} \frac{\mu_i}{n_{i0}}, \quad (61)$$

where \tilde{D}_{ij} , λ_i and μ_i are the first order approximations of the diffusion coefficients, the thermal conductivity, and the viscosity of the species i , with $\lambda = \sum_i \lambda_i$, $\mu = \sum_i \mu_i$.

The functions (59) to (61) are inserted into the inner products of Eqs. (55) to (58). The results are represented in terms of the so-called Knudsen accommodation coefficients, defined by Kuščer¹⁷. The generalization of that definition for the case of possibly anisotropic surfaces is performed with the R-operator:

$$\text{Rh}(\mathbf{v}) = \begin{cases} h(-\mathbf{v}) & \text{for anisotropy of the surface,} \\ h(\mathbf{v}_R) & \text{for isotropy of the surface,} \end{cases}$$

where h is an arbitrary function of the dimensionless velocity \mathbf{v} , and \mathbf{v}_R is the velocity reflected on the surface:

$$\mathbf{v}_R = (-v_x, v_y, v_z).$$

The operator \hat{P}_i is defined by

$$\hat{P}_i h(\mathbf{v}) = \int_{\pm} R P_i(\mathbf{v} \rightarrow \mathbf{v}') h(\mathbf{v}') d\mathbf{v}' \quad (v_x > 0).$$

\hat{P}_i is connected with the scattering operator A_i (14) by the equation

$$\hat{P}_i \Phi(0, \mathbf{v}) = A_i R \Phi(0, \mathbf{v}) \quad (v_x > 0),$$

following from the reciprocity relation. The application of the operator \hat{P}_p for perfect accommodation is denoted by a triangular bracket.

$$\hat{P}_p h = \frac{2}{\pi} \int_{\pm} v_x' \exp(-v'^2) h(\mathbf{v}') d\mathbf{v}' = \langle h \rangle. \quad (62)$$

In consequence of the reciprocity \hat{P}_i is Hermitian with respect to the inner product defined by the average (62):

$$\langle h_1 \hat{P}_i h_2 \rangle = \langle (\hat{P}_i h_1) h_2 \rangle,$$

where h_1, h_2 are arbitrary functions.

The definition of the general accommodation coefficient for the species i and the dynamic quantity $Q_j(\mathbf{v})$ runs

$$a_{j,i} = \frac{\Phi_{j,i}^- - \Phi_{j,i}^+}{\Phi_{j,i}^- - \Phi_{j,i}^*},$$

where

$$\Phi_{j,i}^- = - \int v_x Q_j(\mathbf{v}_R) f_i^-(\mathbf{v}) d\mathbf{v}$$

is the normal coordinate of the $Q_j(\mathbf{v}_R)$ -flux of the incident i -particles with the velocity distribution $f_i^-(\mathbf{v})$,

$$\Phi_{j,i}^+ = \int_{\pm} v_x Q_j(\mathbf{v}) f_i^+(\mathbf{v}) d\mathbf{v}$$

the corresponding normal coordinate of the $Q_j(\mathbf{v})$ -flux of the reflected i -particles with the velocity distribution $f_i^+(\mathbf{v})$, and $\Phi_{j,i}^*$ the value of $\Phi_{j,i}^+$ for perfect accommodation.

Multiplication of Q_j by a constant does not affect $a_{j,i}$, and because of particle conservation (11) addition of a constant is irrelevant too.

Therefore, all Q_j can be modified in such a way as to make $\langle Q_i \rangle = 0$.

Then, if the incident distribution is written

$$R f_i^-(\mathbf{v}) = \frac{2 C_i}{\pi} e^{-v^2} [1 + g_i(\mathbf{v})] \quad (v_x > 0) \quad (63)$$

(C_i : constant), the general accommodation coefficient turns to

$$a_{j,i}(g_i) = 1 - \frac{\langle g_i \hat{P}_i Q_j \rangle}{\langle (R g_{iR}) Q_j \rangle}, \quad (64)$$

where the reflected function g_{iR} is defined by

$$g_{iR}(\mathbf{v}) = g_i(\mathbf{v}_R) .$$

The Knudsen accommodation coefficient $\alpha_{jk,i}$ is the special case of (64) for

$$g_i(\mathbf{v}) = \varepsilon Q_k(\mathbf{v})$$

(ε : constant), so that

$$\alpha_{jk,i} = \alpha_{ji}(Q_k) = 1 - \frac{\langle Q_k \hat{P}_i Q_j \rangle}{\langle (R Q_{kR}) Q_j \rangle} .$$

As quantities Q_k all the polynomials from the 13-moments method of Grad¹⁶ are used, supplemented by v^4 :

$$\begin{aligned} Q_1 &= v_x - \sqrt{\pi}/2, & Q_5 &= v_x v_y, & Q_{10} &= v_x v^2 - \frac{5}{4} \sqrt{\pi}, \\ Q_2 &= v_y, & Q_6 &= v_x v_z, & Q_{11} &= v_y v^2, \\ Q_3 &= v_z, & Q_7 &= v_y v_z, & Q_{12} &= v_z v^2, \\ Q_4 &= v^2 - 2, & Q_8 &= v_y^2 - \frac{1}{2}, & Q_{13} &= v^4 - 6, \\ & & Q_9 &= v_z^2 - \frac{1}{2}, \end{aligned}$$

IX. Results

With Maxwell's assumption the results for the slip coefficients are, with the abbreviations

$$I_i = n_{i0} \sqrt{\frac{k T_0}{2 \pi m_i}}$$

for the flux of i -particles impinging the surface,

$$A_{22} = \sum_i m_i I_i \alpha_{22,i},$$

$$A_{44} = \sum_i I_i \alpha_{44,i},$$

and

$$Z_{jk,i} = \langle Q_j \hat{P}_i Q_k \rangle ,$$

$$\zeta_{\varepsilon,M} = \frac{1}{A_{22}} \sum_i \sqrt{2 k T_0} \sqrt{m_i} I_i Z_{24,i}, \quad (65)$$

$$\tilde{\zeta}_{j,x,M} = 0, \quad (66)$$

$$\tilde{\zeta}_{j,y,M} = \frac{1}{A_{22}} \sum_i m_i I_i \alpha_{22,i} \tilde{D}_{ij}, \quad (67)$$

$$\tilde{\zeta}_{j,z,M} = \frac{2}{A_{22}} \sum_i m_i I_i Z_{23,i} \tilde{D}_{ij}, \quad (68)$$

$$\tilde{\zeta}_{\kappa,x,M} = \frac{2}{A_{22}} \sum_i m_i \frac{\lambda_i}{k} \frac{I_i}{n_{i0}} \left(\frac{2}{5} Z_{2,10,i} - Z_{12,i} \right), \quad (69)$$

$$\tilde{\zeta}_{\kappa,y,M} = \frac{1}{A_{22}} \sum_i m_i \frac{\lambda_i}{k} \frac{I_i}{n_{i0}} \left(\frac{6}{5} \alpha_{2,11,i} - \alpha_{22,i} \right), \quad (70)$$

$$\tilde{\zeta}_{\kappa,z,M} = \frac{2}{A_{22}} \sum_i m_i \frac{\lambda_i}{k} \frac{I_i}{n_{i0}} \left(\frac{2}{5} Z_{2,12,i} - Z_{23,i} \right), \quad (71)$$

$$\zeta_M = \frac{1}{2 A_{22}} \sum_i \mu_i (2 - \alpha_{25,i}), \quad (72)$$

$$\zeta_{\lambda,q,M} = - \frac{1}{2 \sqrt{\pi} A_{44}} \sum_i n_{i0} Z_{24,i}, \quad (73)$$

$$\tilde{\zeta}_{\lambda,j,M} = 0, \quad (74)$$

$$\tilde{\zeta}_{\lambda,x,M} = \frac{1}{4 A_{44}} \sum_i \frac{\lambda_i}{k} \left[2 - \frac{1}{2} (3 \alpha_{4,10,i} - \alpha_{14,i}) \right], \quad (75)$$

$$\tilde{\zeta}_{\lambda,y,M} = \frac{1}{2 \sqrt{\pi} A_{44}} \sum_i \frac{\lambda_i}{k} \left(\frac{2}{5} Z_{4,11,i} - Z_{24,i} \right), \quad (76)$$

$$\tilde{\zeta}_{\lambda,z,M} = \frac{1}{2 \sqrt{\pi} A_{44}} \sum_i \frac{\lambda_i}{k} \left(\frac{2}{5} Z_{4,12,i} - Z_{34,i} \right), \quad (77)$$

$$\zeta_{\lambda,\mu,M} = - \frac{1}{A_{44}} \sum_i \frac{\mu_i}{p_{i0}} I_i Z_{45,i}. \quad (78)$$

The results gained with the modified Maxwell-method are, with the abbreviations

$$A_{25} = \frac{1}{2} \sum_i \frac{\mu_i}{\mu} (2 - \alpha_{25,i}),$$

$$\begin{aligned} A_{14} &= \frac{1}{4} \sum_i \frac{\lambda_i}{\lambda} (4 + \alpha_{14,i} - 3 \alpha_{4,10,i}) \\ &= 2 \frac{k}{\lambda} A_{44} \tilde{\zeta}_{\lambda,x,M}, \end{aligned}$$

$$\zeta_{\varepsilon} = A_{25} \zeta_{\varepsilon,M} + 2 \sum_i \frac{\mu_i}{\mu} \frac{I_i}{n_{i0}} Z_{45,i}, \quad (79)$$

$$\tilde{\zeta}_{jx} = 0, \quad (80)$$

$$\tilde{\zeta}_{jy} = A_{25} \tilde{\zeta}_{jyM} + \frac{1}{2} \sum_i \frac{\mu_i}{\mu} \alpha_{25,i} \tilde{D}_{ij}, \quad (81)$$

$$\tilde{\zeta}_{jz} = A_{25} \tilde{\zeta}_{jzM} + \frac{2}{\sqrt{\pi}} \sum_i \frac{\mu_i}{\mu} Z_{35,i} \tilde{D}_{ij}, \quad (82)$$

$$\begin{aligned} \tilde{\zeta}_{\kappa x} &= A_{25} \tilde{\zeta}_{\kappa xM} + \frac{2}{\sqrt{\pi}} \sum_i \frac{\mu_i}{\mu} \frac{\lambda_i}{k} \frac{1}{n_{i0}} \left(\frac{2}{5} Z_{5,10,i} - Z_{15,i} \right), \\ & \quad (83) \end{aligned}$$

$$\begin{aligned} \tilde{\zeta}_{\kappa y} &= A_{25} \tilde{\zeta}_{\kappa yM} + \frac{1}{10} \sum_i \frac{\mu_i}{\mu} \frac{\lambda_i}{k} \frac{1}{n_{i0}} (7 \alpha_{11,5,i} - 5 \alpha_{25,i}), \\ & \quad (84) \end{aligned}$$

$$\begin{aligned} \tilde{\zeta}_{\kappa z} &= A_{25} \tilde{\zeta}_{\kappa zM} + \frac{2}{\sqrt{\pi}} \sum_i \frac{\mu_i}{\mu} \frac{\lambda_i}{k} \frac{1}{n_{i0}} \left(\frac{2}{5} Z_{5,12,i} - Z_{35,i} \right), \\ & \quad (85) \end{aligned}$$

$$\zeta = A_{25} \zeta_M + \frac{1}{\pi} \sum_i \frac{\mu_i^2}{\mu m_i I_i} (2 - \alpha_{55,i}), \quad (86)$$

$$\begin{aligned} \zeta_{\lambda q} &= A_{14} \zeta_{\lambda qM} + 2 \sum_i \frac{\lambda_i}{\lambda} \frac{m_i I_i}{p_{i0}} (Z_{12,i} - \frac{2}{5} Z_{2,10,i}), \\ & \quad (87) \end{aligned}$$

$$\tilde{\zeta}_{ijx} = 0, \quad (88)$$

$$\tilde{\zeta}_{lij} = \frac{\sqrt{2}}{\sqrt{\pi} k T_0} \sum_i \sqrt{m_i} \frac{\lambda_i}{\lambda} \left(\frac{2}{5} Z_{2,10,i} - Z_{12,i} \right) \tilde{D}_{ij}, \quad (89)$$

$$\tilde{\zeta}_{lij} = \frac{\sqrt{2}}{\sqrt{\pi} k T_0} \sum_i \sqrt{m_i} \frac{\lambda_i}{\lambda} \left(\frac{2}{5} Z_{3,10,i} - Z_{13,i} \right) \tilde{D}_{ij}, \quad (90)$$

$$\tilde{\zeta}_{lx} = A_{14} \tilde{\zeta}_{lxM} + \frac{1}{\pi} \sum_i \frac{\lambda_i^2}{k \lambda} \frac{1}{I_i} \left(\frac{26}{25} - \left(1 - \frac{\pi}{4} \right) a_{11,i} \right. \\ \left. + \frac{4}{5} \left(3 - \frac{5}{8} \pi \right) a_{1,10,i} - \left(\frac{48}{25} - \frac{\pi}{4} \right) a_{10,10,i} \right), \quad (91)$$

$$\tilde{\zeta}_{ly} = A_{14} \tilde{\zeta}_{lyM} + \frac{1}{\pi} \sum_i \frac{\lambda_i^2}{k \lambda} \frac{1}{I_i} \left(Z_{12,i} - \frac{2}{5} Z_{1,11,i} \right. \\ \left. - \frac{2}{5} Z_{2,10,i} + \frac{4}{25} Z_{10,11,i} \right), \quad (92)$$

$$\tilde{\zeta}_{lz} = A_{14} \tilde{\zeta}_{lzM} + \frac{1}{\pi} \sum_i \frac{\lambda_i^2}{k \lambda} \frac{1}{I_i} \left(Z_{13,i} - \frac{2}{5} Z_{1,12,i} \right. \\ \left. - \frac{2}{5} Z_{3,10,i} + \frac{4}{25} Z_{10,12,i} \right), \quad (93)$$

$$\tilde{\zeta}_{l\mu} = A_{14} \tilde{\zeta}_{l\mu M} + \frac{\sqrt{2}}{\pi} \sum_i \frac{\lambda_i}{\lambda} \frac{\mu_i}{\sqrt{m_i} k T_0 I_i} \\ \cdot \left(Z_{15,i} - \frac{2}{5} Z_{5,10,i} \right). \quad (94)$$

The slip coefficients $\tilde{\zeta}_{jxM}$, $\tilde{\zeta}_{lijxM}$, $\tilde{\zeta}_{jx}$, $\tilde{\zeta}_{lijx}$ vanish since there is no i -particle flux through the surface, i. e. $u_{ix} - q_{asy,x}(0) = 0$.

The expression $Z_{jk,i}$ is proportional to the x -coordinate $\Phi_{k,i}^+$ of the Q_k -flux of the reflected i -particles, if the perturbation g_i of the incident distribution (63) is proportional to Q_j . All the $Z_{jk,i}$ in the equations (65) to (94) vanish, if the surface is isotropic, i. e., if the scattering kernel P_i is invariant under rotations about the x -axis. But already invariance of P_i with respect to rotations through 180° about the x -axis is sufficient for the vanishing of almost all $Z_{jk,i}$ in these equations, with the only exception of the four terms $Z_{23,i}$, $Z_{2,12,i}$, $Z_{35,i}$, and $Z_{5,12,i}$. These four terms cause non-vanishing slip coefficients $\tilde{\zeta}_{jz}$ and $\tilde{\zeta}_{xz}$, and a change of the slip velocity $q_{asy}(0)$ due to the z -component of the temperature gradient $\nabla T_{asy}(\mathbf{r})$ (together with the mass flow in y -direction). The change of the thermal creep velocity occurs also in the special case of a simple gas. $Z_{23,i}$ vanishes if P_i is invariant under rotations through 90° about the x -axis.

The four most important slip coefficients can be written in the following form.

Velocity-slip coefficient.

$$\zeta = \frac{\sum_i \mu_i (2 - a_{25,i})}{2 \mu \sum_i m_i I_i a_{22,i}} \left[\sum_i \mu_i \left(1 - \frac{a_{25,i}}{2} \right) \right. \\ \left. + \frac{2}{\pi} \sum_i m_i I_i a_{22,i} \frac{\sum_i \frac{\mu_i^2}{m_i I_i} (2 - a_{55,i})}{\sum_i \mu_i (2 - a_{25,i})} \right]. \quad (95)$$

Modified temperature-slip coefficient.

$$\tilde{\zeta}_{lx} = \frac{1}{4 k \lambda} \frac{\sum_i \lambda_i (2 - a_{14,i})}{\sum_i I_i a_{44,i}} \\ \cdot \left[\frac{9}{4} \left(\frac{\sum_i \lambda_i [2 - a_{4,10,i} - \frac{1}{8} (2 - a_{14,i})]}{\sum_i \lambda_i (2 - a_{14,i})} \right)^2 \right. \\ \cdot \sum_i \lambda_i \left(1 - \frac{a_{14,i}}{2} \right) \\ \left. + \frac{8}{25 \pi} \frac{\sum_i I_i a_{44,i}}{\sum_i \lambda_i (2 - a_{14,i})} \sum_i \frac{\lambda_i^2}{I_i} \left(13 - \frac{25}{2} \left(1 - \frac{\pi}{4} \right) a_{11,i} \right. \right. \\ \left. \left. + 10 \left(3 - \frac{5}{8} \pi \right) a_{1,10,i} - \left(24 - \frac{25}{8} \pi \right) a_{10,10,i} \right) \right]. \quad (96)$$

Modified thermal creep coefficient.

$$\tilde{\zeta}_{xy} = \frac{1}{2 \mu} \sum_i \frac{\lambda_i}{5 k n_{i0}} \left[\mu_i (7 a_{5,11,i} - 5 a_{25,i}) \right. \\ \left. + m_i I_i (6 a_{2,11,i} - 5 a_{22,i}) \frac{\sum_k \mu_k (2 - a_{25,k})}{\sum_k m_k I_k a_{22,k}} \right]. \quad (97)$$

Modified diffusion-slip coefficient.

$$\tilde{\zeta}_{jy} = \frac{1}{2 \mu} \sum_i \left[\mu_i a_{25,i} \right. \\ \left. + m_i I_i a_{22,i} \frac{\sum_k \mu_k (2 - a_{25,k})}{\sum_k m_k I_k a_{22,k}} \right] \tilde{D}_{ij}. \quad (98)$$

For the special case of a simple gas the expressions (95), (96) turn to those given by Klinc and Kuščer^{10, 17}, as directly can be seen.

The velocity slip coefficient ζ mainly depend on the Knudsen accommodation coefficients $a_{22,i}$ of tangential momentum, the modified temperature-slip coefficient $\tilde{\zeta}_{lx}$ mainly on the a.c.s. $a_{44,i}$ of

energy. These a.c.s., and the radiometric a.c.s $\alpha_{14,i}$ have been measured under free molecular flow conditions by several authors, as is discussed in ¹⁷. Also ideas for measuring the a.c.s. $\alpha_{11,i}$ of normal momentum, and the higher order a.c.s $\alpha_{25,i}$, $\alpha_{4,10,i}$, $\alpha_{1,10,i}$, and $\alpha_{2,11,i}$ can be given, suggested by their definitions ¹⁷. Methods of measurement can also be constructed for all those fluxes $Z_{jk,i}$ with $j \leq 4$ or $k \leq 4$ (or j and k not greater than four).

The higher order a.c.s $\alpha_{55,i}$, $\alpha_{10,10,i}$, $\alpha_{5,11,i}$, and the higher order fluxes $Z_{jk,i}$ with $j > 4$ and $k > 4$ can be evaluated only indirectly. Under free molecular flow conditions all these coefficients can be gained measuring the gas-surface scattering kernel $P_i(\mathbf{c}' \rightarrow \mathbf{c})$ in molecular beam experiments, and calculating the corresponding moments of P_i . Less expensive is the introduction of models for P_i having the general physical properties [non-negativity, normalization (11) and reciprocity (12)] and containing parameters that are intended for fitting experimental data ²⁰.

But the results obtained in such a way cannot be used in all cases for the slip flow regime since the state of the surface, especially adsorption, depends on gas density. During the re-entry of a space vehicle, however, there exist slip flow conditions within the pressure region of 10^{-4} mm Hg $\lesssim p \lesssim 10^{-2}$ mm Hg ²¹. Furtheron, investigations carried out recently by Seidl and Scherber ²² seem to indicate that the adsorption state for some technical surfaces does not change within the above mentioned pressure region. Therefore, the values of the Knudsen a.c.s measured in this pressure region, and the results of molecular beam experiments (performed at 10^{-5} mm Hg $\lesssim p \lesssim 10^{-4}$ mm Hg) can be used for the calculation of the coefficients (79) to (94) for the slip flow phase of the re-entry process.

X. Binary Gas-Mixture

In a binary gas mixture only one independent diffusion coefficient \tilde{D}_{11} appears. Therefore, in the case of a binary gas-mixture some of the expressions in Sect. IX take a special form, because of

$$\begin{aligned}\tilde{D}_{12} &= -\frac{Q_{10}}{Q_{20}} \tilde{D}_{11} = \tilde{D}_{21}, \\ \tilde{D}_{22} &= \left(\frac{Q_{10}}{Q_{20}}\right)^2 \tilde{D}_{11}.\end{aligned}$$

So, for a binary gas mixture the Eqs. (67), (68) turn to

$$\begin{aligned}\tilde{\zeta}_{1yM} &= \frac{1}{A_{22}} m_1 I_1 \left(\alpha_{22,1} - \alpha_{22,2} \sqrt{\frac{m_1}{m_2}} \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{2yM} &= -\frac{Q_{10}}{Q_{20}} \tilde{\zeta}_{1yM}, \\ \tilde{\zeta}_{1zM} &= \frac{2}{A_{22}} m_1 I_1 \left(Z_{23,1} - Z_{23,2} \sqrt{\frac{m_1}{m_2}} \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{2zM} &= -\frac{Q_{10}}{Q_{20}} \tilde{\zeta}_{1zM}.\end{aligned}$$

The Eqs. (81), (98) are for that case

$$\begin{aligned}\tilde{\zeta}_{1y} &= \frac{1}{2\mu} \left(\mu_1 \alpha_{25,1} - \frac{Q_{10}}{Q_{20}} \mu_2 \alpha_{25,2} \right. \\ &\quad \left. + m_1 I_1 \left(\alpha_{22,1} - \alpha_{22,2} \sqrt{\frac{m_1}{m_2}} \right) \frac{\sum_k \mu_k (2 - \alpha_{25,k})}{\sum_k m_k I_k \alpha_{22,k}} \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{2y} &= -\left(Q_{10}/Q_{20} \right) \tilde{\zeta}_{1y},\end{aligned}$$

and the Eqs. (82), (89) and (90)

$$\begin{aligned}\tilde{\zeta}_{1z} &= \frac{2}{\sqrt{\pi} \mu} \left(\mu_1 Z_{35,1} - \frac{Q_{10}}{Q_{20}} \mu_2 Z_{35,2} \right. \\ &\quad \left. + m_1 I_1 \left(Z_{23,1} - Z_{23,2} \sqrt{\frac{m_1}{m_2}} \right) \frac{\sqrt{\pi} \sum_k \mu_k (2 - \alpha_{25,k})}{2 \sum_k m_k I_k \alpha_{22,k}} \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{2z} &= -\left(Q_{10}/Q_{20} \right) \tilde{\zeta}_{1z}, \\ \tilde{\zeta}_{\lambda 1y} &= \frac{\sqrt{2}}{\sqrt{\pi} k T_0} \left(\sqrt{m_1} \frac{\lambda_1}{\lambda} \left(\frac{2}{3} Z_{2,10,1} - Z_{12,1} \right) \right. \\ &\quad \left. - \frac{Q_{10}}{Q_{20}} \sqrt{m_2} \frac{\lambda_2}{\lambda} \left(\frac{2}{3} Z_{2,10,2} - Z_{12,2} \right) \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{\lambda 2y} &= -\left(Q_{10}/Q_{20} \right) \tilde{\zeta}_{\lambda 1y}, \\ \tilde{\zeta}_{\lambda 1z} &= \frac{\sqrt{2}}{\sqrt{\pi} k T_0} \left(\sqrt{m_1} \frac{\lambda_1}{\lambda} \left(\frac{2}{3} Z_{3,10,1} - Z_{13,1} \right) \right. \\ &\quad \left. - \frac{Q_{10}}{Q_{20}} \sqrt{m_2} \frac{\lambda_2}{\lambda} \left(\frac{2}{3} Z_{3,10,2} - Z_{13,2} \right) \right) \tilde{D}_{11}, \\ \tilde{\zeta}_{\lambda 2z} &= -\left(Q_{10}/Q_{20} \right) \tilde{\zeta}_{\lambda 1z}.\end{aligned}$$

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