BOUNDARY CONDITIONS FOR FLOWS OF MULTIATOMIC GASES

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We consider the problem of obtaining macroscopic boundary conditions for the equations of a strongly nonuniform, multitemperature boundary later in a gas with translational, rotational, and vibrational degrees of freedom and for arbitrary catalyticity of the solid surface with respect to various vibrational modes. The boundary conditions are analyzed on surfaces with properties favorable to flow modes with population inversion in the quantum equations.

It is well known that a rigorous derivation of macroscopic boundary conditions for gas flow at a solid surface is associated with a solution of the Boltzmann equation in a Knudsen layer.

A method has been proposed [1] for solution of this equation in asymptotically different flow regions with two-temperature vibrational relaxation present. An approximate solution was given [2] for the determination of boundary conditions in the flow of a monatomic gas at an equilibrium wall. The analogous problem for a nonequilibrium surface with two different temperatures has been discussed [3, 4]. The results of these papers are related to the flows of diatomic gases, since only a single internal degree of freedom was taken into consideration in them. The question of the possible existence of actual surfaces with vibrational nonequilibrium remained unanswered until recently. Nonetheless, it has already been shown [5] that in nonequilibrium flow of nitrogen in a boundary layer around a flat, thermally insulated surface, the translational—rotational temperature (T_w) and the vibrational temperature (T_{iw}) of the wall may be markedly different.

A study of vibrational relaxations of multiatomic gases on solid adsorbing surfaces showed [6] that the rate of damping of vibrational motion in various vibrational modes of linear molecules such as CO_2, NO_2, etc., depends on their orientation and residence time in the adsorbed state.

For the greater part of the time, the axes of a CO_2 molecule are parallel to the adsorbing surface; in this case, one of the vibrations of the deformation mode which is oriented perpendicularly to the surface is rapidly damped.

Because of Fermi resonance, this damping is propagated to all vibrations of the symmetric and deformation modes. Since antisymmetric vibrations are practically conserved in this case, a nonequilibrium distribution is created with respect to the vibrational energy in the various vibrational modes. From the macroscopic point of view, this means that there are flow modes with significantly different wall temperatures T_w and T_{iw} ($i=1, 2, 3, 3\ldots$), where the T_{iw} may also differ from one another. There is interest in the problem of obtaining boundary conditions for flows of multiatomic gases with several vibrational degress of freedom.

1. We consider this problem as applied to the equations of a boundary layer for arbitrary catalyticity of the surface over which the flow occurs. The asymptotic method for the solution of the generalized Boltzmann equation for a diatomic gas [1] can be extended to multiatomic gases such as CO_2 for example. We assume that there are various relaxation processes l_t, $l_{Vt} \sim l_I$ in the gas which in the scale of the mean free path $l \sim l_t$ correspond

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to resonance exchange of translational, translational-rotational, and vibrational energies. In addition, there is inelastic exchange of translational and vibrational energies (l_{tI}) and intermodal vibrational exchanges l_{II}. Of practical interest is the case where the inequality

$$l_t \sim l_{Vt} \sim l_I \ll l_{tI} \sim L \geqslant l_{II} \tag{1.1}$$

exists, where L is a typical hydrodynamic dimension. Then within the confines of the theory of multitemperature relaxation and assuming the satisfaction of the principle of detailed balance for all types of collision, we obtain the generalized Boltzmann equation in the following form [7]:

$$\mathrm{Kn}\left[\frac{\partial f}{\partial t} + \mathbf{c}\frac{\partial f}{\partial \mathbf{r}} - \sum_{(V,I)}{}' \int (f'f_1' - ff_1)\, dP'\right] = \sum_{(A)} \int (f'f_1' - ff_1)\, dP, \tag{1.2}$$

where Kn is the Knudsen number; c is the intrinsic velocity of the molecules; $\sum_{(V,I)}{}', \sum_{(A)}$ are the portions of the collision integrals connected with the elementary processes in the right and left portions of the inequality (1.1). Summation over V in Eq. (1.2) includes the contribution of rotational degrees of freedom and summation over I, the contribution of vibrational degrees of freedom; dp' and dP are abbreviated notation for multidimensional integration over the parameters of binary collisions.

The equilibrium distribution function has the form

$$\begin{aligned} f^{(0)} = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left(-\frac{mC^2}{2kT}\right)\left[\sum_{V=0}^{\infty}(2V+1)\exp\left(-\theta_R \times\right.\right. \\ \left.\left.\times \frac{V(V+1)}{kT}\right)\right]^{-1}(2V+1)\exp\left(-\theta_R\frac{V(V+1)}{kT}\right)\left[\sum_{M=0}^{\infty}\exp\times\right. \\ \left.\times\left(-\frac{E_M}{kT_1}\right)\right]^{-1}\exp\left(-\frac{E_M}{kT_1}\right)\left[\sum_{N=0}^{\infty}(N+1)\exp\left(-\frac{E_N}{kT_2}\right)\right]^{-1}\times \\ \times(N+1)\exp\left(-\frac{E_N}{kT_2}\right)\left[\sum_{P=0}^{\infty}\exp\left(-\frac{E_P}{kT_3}\right)\right]^{-1}\exp\left(-\frac{E_P}{kT_3}\right), \end{aligned} \tag{1.3}$$

where n is density, V is the rotational quantum number; $C = c - v$; $I = M, N, P$ are vibrational numbers for the symmetric, deformation, and antisymmetric modes of CO_2; E_M, E_N, and E_P are the vibrational energies and T_1, T_2, and T_3, the corresponding temperatures; $\theta_R = h^2/2I$ is the characteristic energy of a rotational quantum. Summing Eq. (1.3) over V, summing the denominator over M, N, and P, and integrating over velocity space, one can obtain the usual expression for the populations of the vibrational levels,

$$\frac{n_{MNP}}{n} = \left[1-\exp\left(-\frac{E_M}{kT_1}\right)\right]\left[1-\exp\left(-\frac{E_N}{kT_2}\right)\right]^2\left[1-\exp\left(-\frac{E_P}{kT_3}\right)\right]\exp\left(-\frac{E_M}{kT_1}\right)\left[N+1\right]\exp\left(-\frac{E_N}{kT_2}\right)\exp\left(-\frac{E_P}{kT_3}\right).$$

In the second approximation, through analogy with the case of two-temperature relaxation [1], the distribution function acquires the structural form

$$\varphi_e^{(1)} = \mathbf{A}\frac{\partial T}{\partial \mathbf{r}} + \sum_{(i)} \mathbf{A}^{(i)}\frac{\partial T_i}{\partial \mathbf{r}} + \mathbf{B} : \frac{\partial \mathbf{v}}{\partial \mathbf{r}} + D\operatorname{div}\mathbf{v} + G, \tag{1.4}$$

where A and $A^{(i)}$ are vectors; B is a symmetric nondivergent tensor; D and G are scalars.

The quantities A, $A^{(i)}$, B, D, and G are functions of n, C, T_1, T_2, T_3, E_M, E_N, E_P, and E_V ($E_V = \theta_R V(V+1)$) and determine the various dissipative coefficients which can be calculated by solving the appropriate integral equations [1]. Since the main interest in the present case is the problem of determining boundary conditions for the equations of a boundary layer, terms associated with bulk viscosity (D div V) and relaxation pressure (G) [8, 9] in Eq. (1.4) will be unimportant in the following.

2. Equation (1.4) can be written in the form

$$\varphi_e^{(1)} = -AC_y\frac{\partial T}{\partial y} - \sum_{(i)} A^{(i)} C_y \frac{\partial T_i}{\partial y} - BC_x C_y \frac{\partial u}{\partial y}; \tag{2.1}$$

for plane flows in a boundary layer, where C_x and C_y are the projections of C on the tangential and normal directions with respect to the wall; v is the component of the mean-mass velocity along the x axis.

From an analysis of the exchange of vibrational energy in an adsorption layer [6], we assume that the gas molecules are reflected from a "nonequilibrium" wall with the distribution (1.3) in which $n=n_r$, $T=T_r$ $T_i=T_{ir}$ (r is a subscript denoting reflected molecules) where, in general, $T_r \neq T_{ir} \neq T_w$ (i=1, 2, 3,...) and the T_{ir} are different for different i. The distribution function for reflected molecules then takes the form

$$f_r = f_r^{(0)}(n = n_r, T = T_r, T_i = T_{ir}, u = v = 0). \tag{2.2}$$

It is obvious that the function (2.1) does not satisfy the kinetic boundary conditions (2.2). As in the flow of an ideal monatomic gas, therefore, it is necessary to consider a thick Knudsen layer on the upper boundary of which the distribution f agrees with $f^{(0)}(1 + \varphi_e^{(1)})$ in order to determine macroscopic boundary conditions.

In analogy with a monatomic gas [10], the generalized kinetic Boltzmann equation for the distribution function within the Knudsen layer can be written as

$$c_y\frac{\partial f}{\partial y_1} + \mathrm{Kn}\left[c_x\frac{\partial f}{\partial x} - \sum_{(V,I)}{}' \int (f'f_1' - ff_1)dP'\right] = \sum_{(A)} \int (f'f_1' - ff_1)\,dP, \tag{2.3}$$

where y_1 and x are dimensionless coordinates normalized, respectively, to the thickness l of the Knudson layer and the characteristic length L of the body.

Since the equilibrium distribution functions (1.3) and (2.2) satisfy Eq. (2.3) in the first approximation, i.e., for Kn → 0, and the function $\varphi_e \sim \sqrt{\mathrm{Kn}} \ll 1$ [1] on the outer boundary of the Knudsen layer, we seek a solution of Eq. (2.3) in the form

$$f = f_e^{(0)}(1 + \sqrt{\mathrm{Kn}}\,\varphi^{(1)} + \ldots), \tag{2.4}$$

where

$$f_e^{(0)} = f^{(0)}(n = n_e,\ T = T_r,\ T_i = T_{i_r},\ u = v = 0);$$

i=1, 2, 3,..., $n_e = p_e/kT_r$, and p_e is the pressure at the external boundary of the boundary layer.

For a rigorous formulation of the problem of determining $\varphi^{(1)}$ in the Knudsen layer we use (as in the case of a simple gas [8, 10]) matching of internal and external expansions. Then, substituting Eq. (2.4) into Eq. (2.1) and expanding the functions of $f^{(0)}(y_1 \to \infty)$ and $f_r^{(0)}$, we obtain the following boundary-value problem:

$$c_y\frac{\partial \varphi^{(1)}}{\partial y_1} = \mathscr{L}\left[\varphi^{(1)}\right]; \tag{2.5}$$

$$\varphi^{(1)}(y \to \infty) = \varphi_e^{(1)}(y \to 0) + y_1\frac{\partial f^{(0)}}{\partial y}(y \to 0) + 2\Delta u v_r^{-1}\zeta_x + \frac{\Delta T_r}{T_r}\left(\zeta^2 - \frac{5}{2} - P_V^{(1)}\right) - \sum_{(i)} \frac{\Delta T_{ir}}{T_{ir}} P_I^{(1)}\left(\frac{E_I}{kT_{ir}}\right); \tag{2.6}$$

$$\varphi^{(1)}(y_1 = 0,\ c_y > 0) = \frac{n_r - n_e}{n_e} = \frac{\Delta n_e}{n_e}, \tag{2.7}$$

where y is a dimensionless coordinate normalized to the thickness δ of the boundary layer; ΔT_r, ΔT_{ir}, and Δu are discontinuities of the gas parameters in the neighborhood of the wall:

$$\Delta T_r = T(y \to 0) - T_r; \quad \Delta T_{ir} = T_i(y \to 0) - T_{ir};$$
$$\Delta u = u(y \to 0); \quad v_r = \sqrt{2kT_r/m}; \quad \zeta^2 = \frac{mc^2}{2kT};$$
$$\frac{\Delta n_e}{n_e} = -\frac{2\sqrt{\pi}}{n_e v_r} \int f_e^{(0)} \varphi^{(1)}(y_1 = 0) \frac{1 - \operatorname{sign} c_y}{2} c_y d\mathbf{c};$$

$P_V^{(1)}$, and $P_I^{(1)}$ are polynomials in terms of a discrete set of values of the variables [1]

$$\frac{E_V}{kT}; \quad \frac{E_I}{kT_i}; \quad P_V^{(1)} = \frac{\varepsilon_V - E_V}{kT}; \quad P_I^{(1)} = \frac{\varepsilon_i - E_I}{kT_i};$$

ε_V and ε_i are the mean rotational and vibrational energies; $\mathscr{L}[\varphi^{(1)}]$ is the linearized integral for "fast" collisions, which are included in the left side of inequality (1.1).

It is well known that in the case of monatomic gas, the function $\varphi^{(1)}(y_1 = 0)$ is related to the quantities Δu and ΔT_r by the following exact relations [11]:

$$\langle c_y^2 c_x B \varphi^{(1)}(y_1 = 0) \rangle = -\frac{\mu}{kT_r} \Delta u; \tag{2.8}$$

$$\langle c_y^2 A \varphi^{(1)}(y_1 = 0) \rangle = -\frac{\lambda_t}{kT_r} \Delta T_r. \tag{2.9}$$

Here $\langle \psi\varphi^{(1)} \rangle = \int \psi\varphi^{(1)} f^{(0)} d\mathbf{c}$; μ is the coefficient of shear viscosity and λ_t is the coefficient of thermal conductivity associated with translational degrees of freedom.

We look for an analogy to Eqs. (2.8) and (2.9) for the present case of multitemperature relaxation. To do this, we multiply Eq. (2.5) successively by the functions $Bc_x c_y$, Ac_y, $A^{(i)}c_y$, and the invariants of binary collisions

$$\psi_j = 1, \ m\mathbf{c}, \ \frac{mc^2}{2} + E_V, E_M, E_N, E_P.$$

Averaging the composite products over velocity and internal-energy phase space and using the self-adjointness of the operator $\mathscr{L}[\varphi^{(1)}]$, demonstrated in [12],

$$\langle \varphi \mathscr{L}[\varphi^{(1)}] \rangle = \langle \varphi^{(1)} \mathscr{L}[\psi] \rangle,$$

we obtain

$$\frac{\partial}{\partial y_1} \langle c_y^2 c_x B \varphi^{(1)} \rangle = \langle c_y c_x B \mathscr{L}[\varphi^{(1)}] \rangle = \langle \varphi^{(1)} \mathscr{L}[c_y c_x B] \rangle;$$
$$\frac{\partial}{\partial y_1} \langle c_y^2 A \varphi^{(1)} \rangle = \langle c_y^2 A \mathscr{L}[\varphi^{(1)}] \rangle = \langle \varphi^{(1)} \mathscr{L}[c_y^2 A] \rangle;$$
$$\frac{\partial}{\partial y_1} \langle c_y^2 A^{(i)} \varphi^{(1)} \rangle = \langle c_y^2 A^{(i)} \mathscr{L}[\varphi^{(1)}] \rangle = \langle \varphi^{(1)} \mathscr{L}[c_y^2 A^{(i)}] \rangle;$$
$$\frac{\partial}{\partial y_1} \langle c_y \psi_j \rangle = 0.$$

Using the integral equations given in [1], we have

$$\frac{\partial}{\partial y_1} \langle c_y^2 c_x B \varphi^{(1)} \rangle = \langle \varphi^{(1)} D_3 \rangle; \quad \frac{\partial}{\partial y_1} \langle c_y^2 A \varphi^{(1)} \rangle = \langle \varphi^{(1)} D_1 \rangle; \quad \frac{\partial}{\partial y_1} \langle c_y^2 A^{(i)} \varphi^{(1)} \rangle = \langle \varphi^{(1)} D_2^{(i)} \rangle, \tag{2.10}$$

where

$$\langle g\varphi^{(1)} \rangle = \sum_{(V,I)} \int g\varphi^{(1)} f^{(0)} d\mathbf{c}; \quad D_3 = f^{(0)} \frac{m}{kT} c_y c_x;$$
$$D_1 = f^{(0)} c_y \left(\zeta^2 - \frac{5}{2} - P_V^{(1)} \right); \quad D_2^{(i)} = f^{(0)} c_y P_I^{(1)}, \ i = 1, 2, 3.$$

Converting to the integral form of Eqs. (2.10) and taking the matching conditions (2.6) into consideration, we obtain

$$\langle c_y^2 c_x B \varphi^{(1)}(y_1 = 0)\rangle = -\frac{\mu}{kT_r}\Delta u; \tag{2.11}$$

$$\langle c_y^2 A \varphi^{(1)}(y_1 = 0)\rangle = -\frac{\lambda_a}{kT_r}\Delta T_r; \tag{2.12}$$

$$\langle c_y^2 A^{(i)} \varphi^{(1)}(y_1 = 0)\rangle = -\frac{\lambda_i}{kT_{i_r}}\Delta T_{i_r}; \tag{2.13}$$

$$\langle c_y \psi_j \varphi^{(1)}(y_1 = 0)\rangle = \langle c_y \psi_j \varphi_e^{(1)}(y \to 0)\rangle, \tag{2.14}$$

where $\lambda_a = \lambda_t + \lambda_V$; λ_t ,λ_V and λ_i are dissipative coefficients similar to those determined in [1].

Equations (2.11)-(2.13) are the analogues of Eqs. (2.8) and (2.9) for the present case of multitemperature relaxation. In order to determine the magnitudes of the discontinuities ΔT_r, Δu and ΔT_{ir} by means of Eqs. (2.11)-(2.13), it is necessary to know the function $\varphi^{(1)}$ $(y_1 = 0)$, i.e., the solution of Eq. (2.5). We use the modified Maxwell [11] for an approximate determination of the discontinuities, approximating the function $\varphi(y_1 = 0,\ c_y < 0)$ in the following manner:

$$\varphi^{(1)}(y_1 = 0, c_y < 0) = \varphi_e + b_0 \zeta_x + b_1\left(\zeta^2 - \frac{5}{2} - P_V^{(1)}\right) - \sum_{(i)} b_{2i} P_I^{(1)}. \tag{2.15}$$

Substituting the approximation (2.15) in Eqs. (2.11)-(2.14), we obtain

$$\Delta u = \eta \frac{\partial u}{\partial y}; \quad \Delta T_r = \eta_a \frac{\partial T}{\partial y}; \quad \Delta T_{i_r} = \eta_i \frac{\partial T_i}{\partial y}; \quad \frac{\Delta n_e}{n_e} = -\eta_e \frac{\partial T}{\partial y}, \tag{2.16}$$

where

$$\eta = \left(0.5 + \frac{2}{\pi}\right)\frac{\sqrt{\pi}}{2}\frac{\mu v_r}{p_e};$$

$$\eta_a = \frac{\lambda_a \sqrt{\pi}}{\left(2 + c_v'\right) n_e v_r k}\left[\frac{1}{2} + \frac{26\left(2 + c_v'\right)}{25\pi\lambda_a^2}\lambda_t^2 + \frac{2\left(2 + c_v'\right)}{\pi c_v' \lambda_a^2}\lambda_V^2\right];$$

$$\eta_i = \frac{\lambda_i \sqrt{\pi}\,(1 + 4/\pi)}{2 c_i n_e v_r}; \quad c_i = \frac{d\varepsilon_i}{dT_i}; \quad c_v' = \frac{1}{k}\frac{d\varepsilon_V}{dT};$$

$$\eta_e = \lambda_a \sqrt{\pi}\left[2\left(2 + c_v'\right) n_e v_r kT\right]^{-1}.$$

For a final determination of the desired boundary conditions, i.e., the quantities $T_i(y \to 0) = T_{ir} + \Delta T_{ir}$, and $T(y \to 0) = T_r + \Delta T_r$, it is necessary to know the temperatures T_{ir} and T_r. To determine T_r in a beam of reflected molecules for a monatomic gas, one uses the so-called accommodation coefficients [13-15] which are introduced in the form of certain ratios of temperatures [13, 14] or of energy fluxes [8, 15] and which characterize the exchange of energy between molecules in the adsorbed state and the wall [13]. In the present case, one can use the following definitions for the accommodation coefficients by analogy with a simple gas:

$$\alpha_i = \frac{Q_i(y_1 = 0) - Q_{i_r}}{Q_i(y_1 = 0) - Q_{iw}}; \quad \alpha = \frac{Q(y_1 = 0) - Q_r}{Q(y_1 = 0) - Q_w}, \tag{2.17}$$

where

$$Q_i = -\langle c_y \tilde{f}(c_y < 0) E_I\rangle; \quad Q = -\left\langle c_y \tilde{f}(c_y < 0)\left(\frac{mc^2}{2} + E_V\right)\right\rangle;$$

$$Q_{i_r} = \langle c_y \tilde{f}(c_y > 0) E_I\rangle; \quad Q_r = \left\langle c_y \tilde{f}(c_y > 0)\left(\frac{mc^2}{2} + E_V\right)\right\rangle;$$

$$Q_{iw} = Q_{ir}(T_{ir} = T_r = T_w); \quad Q_w = Q_r(T_{ir} = T_r = T_w),$$

$$\tilde{f} = f f^{(0)-1}.$$

We consider the definitions (2.17). The quantity ($Q_i - Q_{ir}$) is equal to the total normal flux q_i of vibrational energy in mode i, and the quantity ($Q - Q_r$) is the total flux q of the translational—rotational energy $mc^2/2+E_V$.

In order to determine $q_i(y_1 = 0)$ and $q(y_1 = 0)$, we multiply Eq. (2.3) by the invariants E_I and $mc^2/2+E_V$ and average the results over the phase space of velocity and the energies E_I and E_V:

$$\frac{\partial q_i}{\partial y_1} + \mathrm{Kn}\,\Omega = 0;\quad \frac{\partial q}{\partial y_1} + \mathrm{Kn}\left\langle\left(\frac{mc^2}{2} + E_V\right) c_x \frac{\partial f}{\partial x}\right\rangle = 0, \tag{2.18}$$

where

$$\Omega = \left\langle E_I \left(\sum_{(V,I)}{}' \int (f'f_1' - ff_1)\, dp' + c_x \frac{\partial f}{\partial x}\right)\right\rangle.$$

Thus we have with an accuracy of the order of Kn

$$\frac{\partial q_i}{\partial y_1} = \frac{\partial q}{\partial y_1} = 0;\quad q_i(y_1 = 0) = q_i(y = 0);\quad q(y_1 = 0) = q(y = 0). \tag{2.19}$$

Calculating the fluxes $q_i(y \to 0)$ and $q(y \to 0)$ by means of Eqs. (2.6) and taking the definitions (2.17) into consideration, we obtain

$$\begin{aligned} \frac{\lambda_i}{c_i}\frac{\partial \varepsilon_i}{\partial y} &= \frac{\alpha_i}{2\sqrt{\pi}} n_r v_r [\varepsilon_{ir} - \varepsilon_{iw}] + \alpha_i \frac{\lambda_i}{c_i}\frac{\partial \varepsilon_i}{\partial y}; \\ \frac{\lambda_a}{c_a}\frac{\partial \varepsilon_a}{\partial y} &= \frac{\alpha}{2\sqrt{\pi}} n_r v_r [\varepsilon_{ar} - \varepsilon_{aw}] + \alpha \frac{\lambda_a}{c_a}\frac{\partial \varepsilon_a}{\partial y}, \end{aligned} \tag{2.20}$$

where

$$\varepsilon_{ir} = \varepsilon_i(T_{ir});\quad \varepsilon_{iw} = \varepsilon_i(T_w);\quad \varepsilon_a = 2kT + \varepsilon_V;$$

$$\varepsilon_{ar} = \varepsilon_a(T_r);\quad \varepsilon_{aw} = \varepsilon_a(T_w);\quad c_a = \frac{d\varepsilon_a}{dT}.$$

Estimating the orders of magnitude in Eqs. (2.20), we note that the temperature T_i and T can be determined to an accuracy of the order of $\sqrt{\mathrm{Kn}}$ from the boundary conditions

$$l_i \frac{\partial \varepsilon_i^{(0)}}{\partial y} = \frac{\alpha_i}{2\sqrt{\pi}}\left[\varepsilon_i^{(0)} - \varepsilon_{iw}\right];\quad l_a \frac{\partial \varepsilon_a^{(0)}}{\partial y} = \frac{\alpha}{2\sqrt{\pi}}\left[\varepsilon_a^{(0)} - \varepsilon_{aw}\right], \tag{2.21}$$

where

$$\varepsilon_i^{(0)} = \varepsilon_i\left(T_i^{(0)}\right);\quad \varepsilon_a^{(0)} = \varepsilon_a\left(T^{(0)}\right);\quad T_i = T_i^{(0)} + 0\left(\sqrt{\mathrm{Kn}}\right);$$

$$T = T^{(0)} + 0\left(\sqrt{\mathrm{Kn}}\right);$$

$$l_i = \lambda_i / n_e^{(0)} v_T c_i;\quad l_a = \lambda_a / n_e^{(0)} v_T c_a;$$

$$n_e^{(0)} = \frac{p_e}{kT^{(0)}};\quad v_T = \sqrt{\frac{2kT^{(0)}}{m}}.$$

We then obtain

1. $\varepsilon_i^{(0)} = \varepsilon_{iw};\ \varepsilon_a^{(0)} = \varepsilon_{aw}$ for $\alpha_i \approx \alpha \approx 1$;
2. $\frac{\partial \varepsilon_i^{(0)}}{\partial y} = \frac{\partial \varepsilon_a^{(0)}}{\partial y} = 0$ for $\alpha_i \approx \alpha \approx \mathrm{Kn}$;
3. $\left[\left(1 - \varepsilon_i^{(0)}\right)/\varepsilon_{iw}\right] \sim \left[\left(1 - \varepsilon_a^{(0)}\right)/\varepsilon_{aw}\right] \sim 1$ for $\alpha_i \approx \alpha \approx \sqrt{\mathrm{Kn}}$.

The set of values considered actually covers the entire range of the accommodation coefficients.

We analyze the physical significance of the conditions.

The first case corresponds to a wall at complete equilibrium, $T=T_1=T_2=T_3=T_w$.

The second case corresponds to a completely thermally insulated wall where the temperatures of the various vibrational modes may differ from one another and from the temperature T_w [5].

In the third case, all the vibrational temperatures differ in value from the wall temperature T_w.

In principle, cases are possible where the wall possesses different catalyticity with respect to the various vibrational modes.

In applications, surfaces which are favorable from the viewpoint of preservation of population inversion in gasdynamical flow may be of practical interest. For example, in physical adsorption of CO_2 molecules on a solid surface, relaxation of symmetric and deformation modes (i=1, 2) may take place in accordance with the first case, while relaxation of the antisymmetric mode may proceed in accordance with the second case, which is analogous to the vibrational relaxation processes on the surface of aerosol particles described in [6].

The determination of the boundary conditions in the first approximation of (2.21) does not require the solution of the kinetic problem involving the temperature discontinuities ΔT_{ir} or ΔT_r. The need for the solution of such a problem arises in the following approximation if it is necessary to differentiate T_i (i = 1, 2, 3,...) and T from temperatures T_{ir} and T_r in the reflected beam of molecules To establish these boundary conditions for the second approximation, we analyze Eq. (2.20) with the quantity $\mathrm{Kn}\Omega$ taken into consideration.

We consider as in Eq. (2.4) a Knudsen layer in which

$$f(y_1)=f^{(0)}(y=0)+0(\sqrt{\mathrm{Kn}}). \tag{2.22}$$

Substituting Eq. (2.22) into Eq. (2.18) and converting to integral notation, we obtain

$$q_i^{(2)}=-y_1\Omega^{(0)}+(\mathrm{const})_i, \tag{2.23}$$

where

$$\Omega^{(0)}=\Omega\left(f=f^{(0)}\right);\ q_i^{(2)}=\langle c_y E_I \varphi^{(2)}\rangle;\ \left[q_i^{(2)}/\varepsilon_i v_r\right]\sim \mathrm{Kn}.$$

To determine $(\mathrm{const})_i$, we consider the matching conditions for $y_1\to\infty$

$$\varphi^{(2)}(y_1\to\infty)=\frac{y_1^2}{2}\frac{\partial^2 f^{(0)}}{\partial y^2}(y\to 0)+y_1\frac{\partial\varphi_e^{(1)}}{\partial y}(y\to 0)+\varphi_e^{(2)}(y\to 0)$$

and write Eq. (2.23) at the upper $(y_1\to\infty)$ and lower $(y_1=0)$ boundaries of the Knudsen layer. Then

$$\frac{\partial^2}{\partial y^2}\langle c_y E_I\rangle\equiv 0;\quad y_1\frac{\partial}{\partial y}\langle c_y E_I\varphi_e\rangle=-y_1\Omega^{(0)};$$

$$\langle E_I c_y \varphi_e^{(2)}(y\to 0)\rangle=(\mathrm{const})_i;$$
$$\langle E_I c_y \varphi^{(2)}(y_1=0)\rangle=(\mathrm{const})_i.$$

Eliminating the $(\mathrm{const})_i$, we obtain

$$q_i^{(2)}(y_1=0)=q_i^{(2)}(y\to 0).$$

In analogy with the preceding, we obtain for the quantity $q^{(2)}=\left\langle c_y\left(\frac{mc^2}{2}+E_V\right)\varphi^{(2)}\right\rangle$

the result $q^{(2)}(y_1=0)=q^{(2)}(y\to 0)$.

Thus in a weakly nonequilibrium Knudsen layer, the conditions for the conservation of the energy fluxes q_i and q are valid to terms of the order of $\mathrm{Kn}\sqrt{\mathrm{Kn}}$.

The values of the fluxes $q_i^{(2)}$ and $q^{(2)}$ can be determined by the Chapman–Enskog method,

$$q_i^{(2)}(y\to 0)=\lambda_i(\Delta T,\Delta T_i)\frac{\partial T_i^{(0)}}{\partial y}+\lambda_i\left(T^{(0)},T_i^{(0)}\right)\frac{\partial\Delta T_i}{\partial y};$$
$$q_i^{(2)}(y\to 0)=\lambda_a(\Delta T)\frac{\partial T^{(0)}}{\partial y}+\lambda_a\left(T^{(0)}\right)\frac{\partial\Delta T}{\partial y}+\mu\Delta u\frac{\partial u}{\partial y},\tag{2.24}$$

where

$$\Delta T=T(y\to 0)-T^{(0)}(y\to 0);\quad \Delta T_i=T_i(y\to 0)-T_i^{(0)}(y\to 0);\quad T_i^{(0)},\ T^{(0)}$$

satisfy Eqs. (2.21).

Substituting Eq. (2.24) into Eq. (2.19) and taking ΔT_r and ΔT_{ir} into consideration [see Eq. (2.16)], we obtain the following boundary conditions for the corrections of ΔT and ΔT_i:

In the region $\alpha_i\sim 1$, $\alpha\sim 1$:

$$\Delta T_i=\left[\eta_i/l_i+(1/\alpha_i-1)\,2\sqrt{\pi}\right]l_i\frac{\partial T_i}{\partial y};$$
$$\Delta T=\left[\eta_a/l_a+(1/\alpha-1)\,2\sqrt{\pi}\right]l_a\frac{\partial T}{\partial y}.$$

In the region $\alpha_i\sim\sqrt{\mathrm{Kn}}$, $\alpha\sim\sqrt{\mathrm{Kn}}$:

$$\frac{\lambda_i(\Delta T,\Delta T_i)}{\lambda_i\left(T_i^{(0)},T^{(0)}\right)}+\left[\frac{\partial T_i^{(0)}}{\partial y}\right]^{-1}\frac{\partial\Delta T}{\partial y}=\frac{c_i(\Delta T_i-\Delta T_{ir})}{\varepsilon_i^{(0)}-\varepsilon_{iw}}+\frac{\Delta n_e}{n_e^{(0)}}-\frac{\Delta T-\Delta T_r}{2T^{(0)}}+\alpha_i;$$

$$\frac{\lambda_a(\Delta T)}{\lambda_a\left(T^{(0)}\right)}+\left[\frac{\partial T^{(0)}}{\partial y}\right]^{-1}\frac{\partial\Delta T}{\partial y}=\frac{c_a(\Delta T-\Delta T_r)}{\varepsilon_a^{(0)}-\varepsilon_{aw}}+\frac{\Delta n_e}{n_e^{(0)}}-\frac{\Delta T-\Delta T_r}{2T^{(0)}}+\alpha-\left[\lambda_a\frac{\partial T^{(0)}}{\partial y}\right]^{-1}\mu\Delta u\frac{\partial u}{\partial y}.$$

In the region $\alpha_i\ll\mathrm{Kn}$, $\alpha\ll\mathrm{Kn}$:

$$\lambda_i\frac{\partial\Delta T_i}{\partial y}=\frac{\alpha_i}{2\sqrt{\pi}}n_e^{(0)}v_T\left[\varepsilon_i^{(0)}-\varepsilon_{iw}\right];\quad \lambda_a\frac{\partial\Delta T}{\partial y}+\mu\Delta u\frac{\partial u}{\partial y}=0.$$

The expressions obtained solve the problem of determining the boundary conditions for the equations of a multitemperature boundary layer with strong vibrational nonequilibrium which can be used in evaluations of the role of boundary layers in flows of CO_2+N_2+H_2O(He) mixtures. Actually, $T_w=T_{iw}$ in grids ordinarily used and loss of amplification in boundary layers amounts to 15-20% [16]. In addition, these losses are propagated into the flow region in the cavity because of an expanding viscous wake. If indeed the wall is a nonequilibrium wall ($T_w\neq T_{iw}$), the nonequilibrium sublayer occupies a considerable portion of the thickness of the boundary layer even when $T_\infty=T_{i\infty}$ at the external boundary [5].

Since $T_\infty\pm T_{i\infty}(T_\infty\approx T_{i\infty},\ i=1,2;\ T_\infty\ll T_{i\infty},\ i=3,4)$, in a nonviscous flow core, inverse population and amplification may be maintained over the entire flow region with a nonequilibrium wall.

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