

A KNUDSEN LAYER IN A FLOW WITH TWO-TEMPERATURE RELAXATION

M. M. Kuznetsov

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The boundary conditions are considered for the hydrodynamic equation of [1, 2] for highly nonequilibrium diatomic gas with vibrational relaxation.

The behavior of an ideal monatomic gas indicates that one has to determine the boundary conditions by solving Boltzmann's equation in the Knudsen layer. To solve the analogous problem for a polyatomic gas with internal degrees of freedom one naturally uses the generalized Boltzmann kinetic equation [1]

$$\mathbf{c} \frac{\partial f}{\partial \mathbf{r}} = \sum_{(N_1, N_1', N')} \int_{(P)} (f' f_1' - f f_1) \alpha dP \quad (1)$$

Here  $f = f(\mathbf{r}, \mathbf{c}, N)$ ,  $\alpha dP = \alpha(g, \chi, b, N, N_1, N', N_1')$   $dbdb_\varepsilon d\mathbf{c}_1 dn$ , while  $g$  is the relative velocity of the colliding particles,  $\varepsilon$  and  $\chi$  are the angles between the directions of  $g$  and  $\mathbf{n}$ ,  $dn$  is an element of solid angle reckoned from the center of particle  $f_1$ ,  $\alpha$  is the probability of collision of two molecules involving change in  $N$  and  $N_1$  to  $N'$  and  $N_1'$ ,  $d\mathbf{c}_1$  is an element in velocity space for particle  $f_1$ , while the summation is taken over all values of the quantum numbers for the vibrational levels and it is assumed that degenerate states are absent.

Apart from (1) one needs to specify the distribution  $f_e$  in the region external to the Knudsen layer and the boundary condition for  $f$  at the surface of the body. The  $f_e$  for the case of a planar flow of diatomic gas takes [2] the form

$$f_e = f^{(0)}(1 + \varphi_e), \quad f^{(0)} = n \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ \sum_{(N)} \exp\left(-\frac{E_N}{kT_i}\right) \right]^{-1} \exp\left(-\frac{mC^2}{2kT} - \frac{E_N}{kT_i}\right),$$

$$\varphi_e = A_1(C, E_N, T, T_i) \mathbf{C} \frac{\partial T}{\partial \mathbf{r}} + A_2(C, E_N, T, T_i) \mathbf{C} \frac{\partial T_i}{\partial \mathbf{r}} + B(C, E_N, T, T_i) \mathbf{C} \mathbf{C} : \frac{\partial \mathbf{V}}{\partial \mathbf{r}} + A_3(C, E_N, T, T_i) \quad (2)$$

Here  $\mathbf{C} = \mathbf{c} - \mathbf{V}$  is the velocity of the random motion, while  $T$  and  $T_i$  are the temperatures of the translational and vibrational degrees of freedom,  $A_1, A_2, A_3, B$  are scalars,  $\mathbf{C} \mathbf{C}$  is a symmetrical nondivergent tensor, and  $E_N$  is the internal vibrational energy in state  $N$ :

$$\mathbf{C} \partial / \partial \mathbf{r} = C_x \partial / \partial x + C_y \partial / \partial y$$

$\mathbf{C} \mathbf{C} : \partial \mathbf{V} / \partial \mathbf{r}$  is the bistable product of the tensors  $\mathbf{C} \mathbf{C}$  and  $\partial \mathbf{V} / \partial \mathbf{r}$  ( $x, y, z$ ) is a rectangular system of spatial coordinates.

As the kinetic boundary condition we assume that a fraction  $(1 - \sigma)$  of the incident molecules is reflected specularly, while the other part  $\sigma$  is at first adsorbed and then is emitted by the wall with a Maxwellian distribution  $f^{(0)}$  at different temperatures  $T_w$  and  $T_{iw}$  for the translational and vibrational degrees of freedom:

$$f^+(c_x, c_y, c_z, E_N) = (1 - \sigma) f^-(c_x, -c_y, c_z, E_N) + \sigma \left( \frac{m}{2\pi kT_w} \right)^{3/2} \times$$

$$\times \left[ \sum_{(N)} \exp\left(-\frac{E_N}{kT_i}\right) \right]^{-1} \exp\left(-\frac{mc^2}{2kT_w} - \frac{E_N}{kT_{iw}}\right) \quad (3)$$

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Here  $(x, y, z)$  is a rectangular coordinate system in the planar flow around the surface  $y=0$  (the  $y$  axis is directed along the exterior normal, while the  $x$  axis lies along the flow direction).

Boundary condition (3) coincides to 0 ( $\varphi_e$ ) for  $T_w=T_{1w}$  with the condition used in [3]; we note here that the derivation of the boundary conditions for a polyatomic gas given in [3] does not contain an analysis of the solution to the kinetic equation in the Knudsen layer and so cannot be rigorous.

We use linked asymptotic expansions to show [4] that the distribution in the Knudsen layer may be found as a superposition of the function of (2) and the function  $f^{(0)h}$  that satisfies the linearized kinetic equation

$$c_y \frac{\partial h}{\partial y} = J(h), \quad J(h) \equiv \sum_{(N', N_1', N_1)} \int_{(P)} f_1^{(0)} (h' + h_1' - h - h_1) \alpha dP \quad (4)$$

The linearized collision into integral of (4) for molecules vibrating as harmonic oscillators with 1-quantum transitions takes the following form:

$$J(h) = \sum_{(N_1)} \int_{(P)} f_1^{(0)} \{ [h'_{N+1} + h'_{N-1} - h_N - h_{N_1}] (N+1) N_1 p_{01} + [h'_{N-1} + h'_{N+1} - h_N - h_{N_1}] (N_1+1) N p_{01} + [h_{N'} + h_{N_1'} - h_N - h_{N_1}] [1 - N_1(N+1) p_{01} - N(N_1+1) p_{01}] \} dP \quad (5)$$

Here  $p_{01}(g)$  is the probability of resonant transition of an oscillator from the ground state to the first excited state [5].

We seek the solution to (4) with (5) in the form

$$h(c, y, E_N) = \sum_{n=0}^{\infty} q^{(n)}(c, y) P_N^{(n)} \left( \frac{E_N}{kT_i} \right) \quad (6)$$

Here  $P_N^{(n)}(E_N/kT_i)$  are orthogonal polynomials specified for a discrete manifold of values of  $E_N$  [6], with

$$P_N^{(0)} = 1, \quad P_N^{(1)} = \frac{\varepsilon_i - E_N}{kT_i}, \quad \varepsilon_i = \langle E \rangle$$

$$\langle E_N \rangle = \left[ \sum_{(N)} E_N \exp \left( -\frac{E_N}{kT_i} \right) \right] \left[ \sum_{(N)} \exp \left( -\frac{E_N}{kT_i} \right) \right]^{-1}, \quad \langle P_N^{(1)*} \rangle = \frac{c_v}{k}$$

and  $\varepsilon_i$  is the mean vibrational energy, while  $c_v$  is the specific heat of the vibrational degrees of freedom. The following is the matrix representation of the collision integral of (5):

$$L^{(m)}(c, y) = \left\langle P_N^{(m)} \sum_{n=0}^{\infty} J(q^{(n)} P_N^{(n)}) \right\rangle \quad (m=0, 1, \dots) \quad (7)$$

In view of the orthogonality of the combination

$$\langle N_1 \rangle (N+1) [P_{N+1}^{(n)} - P_N^{(n)}] + \langle N_1+1 \rangle N [P_{N-1}^{(n)} - P_N^{(n)}] \quad (8)$$

for all the polynomials  $P_N^{(m)}$  with  $m \neq n$ , we get

$$L^{(0)} = \int_{(P)} f_M^{(0)}(c_1) [q^{(0)'} + q_1^{(0)'} - q^{(0)} - q_1^{(0)}] dP \quad (9)$$

$$L^{(1)} = \frac{c_v}{k} \int_{(P)} f_M^{(0)}(c_1) [(1 - p_{01}) q^{(1)'} + p_{01} q_1^{(1)'} - q^{(1)}] dP \quad (10)$$

$$L^{(l)} = \langle P_N^{(l)*} \rangle \int_{(P)} f_M^{(0)}(c_1) [(1 - p_{01}) q^{(l)'} - q^{(l)}] dP \quad (11)$$

Here  $l=2, 3, \dots$ ,  $f_M^{(0)}(c)$  is the Maxwell distribution [7]. Then for each  $l$  we have an independent kinetic equation

$$c_y \frac{\partial q^{(l)}}{\partial y} = L^{(l)}(q^{(l)}) \quad (12)$$

The distribution  $\varphi_e$ , and also  $h$ , may be put in the form of (6); in fact [8]

$$\begin{aligned} A_1 &= a_1(T, T_i) P_N^{(0)} \left( \frac{E_N}{kT_i} \right) S_{1/2}^{(1)}(\xi^2), \quad A_2 = a_2 P_N^{(1)} S_{1/2}^{(0)} \\ B &= b P_N^{(0)} S_{1/2}^{(0)}, \quad S_l^{(m)}(x) = \sum_{j=0}^l \frac{(-1)^j (m+j)!}{(m+j)! (l-j)! j!} x^j \\ \xi &= \frac{mC^2}{2kT} \end{aligned} \quad (13)$$

Here  $S_l^{(m)}(x)$  are the Sonin polynomials [7].

To determine the scalar  $A_3$  we need to solve the following linear integral equation [2]:

$$\begin{aligned} f^{(0)} \left( \frac{mC^2}{3k^2T^2} - \frac{1}{kT} - \frac{E_N - \varepsilon_i}{kT_i^2 \varepsilon_i} \right) \frac{\Omega}{n} + \sum' \Big|_{f=f^{(0)}} = J(A_3) \\ \Omega = \frac{\varepsilon(T) - \varepsilon_i(T_i)}{\tau}, \quad \sum' \Big|_{f=f^{(0)}} = \sum_{(N', N_i', N_i)} \int_{(P)} (f^{(0)'} f_1^{(0)'} - f^{(0)} f_1^{(0)}) \alpha dP \end{aligned} \quad (14)$$

Here  $\Sigma'$  is the part of the collision integral in (1) related to the inelastic exchange of vibrational quanta, while  $\tau$  is the relaxation time [9]. As the left side of (14) is orthogonal for all  $P_N^{(m)}$  for a harmonic oscillator [2, 9], apart from  $P_N^{(1)}$  and  $P_N^{(0)}$ , we use the property of (8) to seek  $A_3$  in the form

$$A_3 = P_N^{(1)} \left( \frac{E_N}{kT_i} \right) \sum_{(n)}^{l-1} a_3^{(n)}(T, T_i, \xi) S_{1/2}^{(n)}(\xi^2) \quad (15)$$

The coefficients  $a_3^{(n)}$  may be found from (14) by Ritz's method; but this converges rapidly [8], so it is best to restrict oneself to the first nonzero coefficient in the series of (15), and then we get

$$a_3^{(1)} = - \frac{r_i}{c_v(T_i) T_i} \frac{\varepsilon(T) - \varepsilon_i(T_i)}{r_{it}} \quad (16)$$

Here  $r_i$ ,  $r_{it}$  are quantities having the dimensions of length, with  $r_i/r_{it} \sim l_i/l_{it}$ , where  $l_i$  and  $l_{it}$  are the lengths for the resonant and inelastic exchange of energy quanta [1]:

$$\begin{aligned} r_i &= n\gamma v / I_5, \quad r_{it} = \tau v, \quad v = (8kT / \pi m)^{1/2}, \quad \gamma = \gamma(T, T_i) \\ \gamma(T, T_i) &= \gamma_0 \left[ \gamma_1 \exp\left(\frac{h\nu}{kT_i} - \frac{h\nu}{kT}\right) - 1 \right] \left[ \exp\left(\frac{h\nu}{kT_i}\right) - 1 \right]^{-1} \\ \gamma_0 &= \left[ \frac{1}{2} \int_0^\infty \exp(-G^2) (2 - G^2) p_{01}(G, G') G^3 dG \right] \left[ \int_0^\infty \exp(-G^2) p_{01}(G, G') G^3 dG \right]^{-1} \\ \gamma_1 &= \left[ \int_0^\infty \exp(-G^2) (2 - G^2) p_{10}(G, G') G^3 dG \right] \left[ \int_0^\infty \exp(-G^2) (2 - G^2) p_{01} \times \right. \\ &\quad \left. \times (G, G') G^3 dG \right]^{-1}, \quad G = g / \sqrt{2kT/m} \\ I_5 &= [S_{1/2}^{(1)}, S_{1/2}^{(1)}]_1, \quad [A, B]_1 = \int_{(\xi)} e^{-\xi^2} A L^{(1)}(B) d\xi \end{aligned}$$

while  $p_{01}(G, G')$  and  $p_{10}(G, G')$  are the probabilities of transition from the first levels in inelastic collision [5, 9], while a prime refers to  $G$  after collision.

Then superposition of the solutions  $q^{(l)}$  of (12) provides a complete solution to (4) subject to the boundary conditions of (2) and (3).

It is readily seen that the boundary conditions for the velocity and the temperature step defined by means of  $q^{(0)}$  will be as for an ideal monatomic gas.

Consider the case  $l=1$ ; in accordance with the simplified form of the method of semispatial polynomial expansions [10], we represent  $q^{(1)}(y, \mathbf{c})$  in the form

$$\begin{aligned} q^{(1)}(y, \mathbf{c}) &= q^{(1)}(y, \mathbf{c}) \left( \frac{1 + \text{sign } c_y}{2} \right) + q^{(1)}(y, \mathbf{c}) \left( \frac{1 - \text{sign } c_y}{2} \right) \\ q^{(1)} &= q_0^{(1)} + q_1^{(1)} + q_2^{(1)} + q_3^{(1)}, \quad q_0^{(1)\pm} = a_0^\pm(y), \quad q_1^{(1)\pm} = a_1^\pm(y) \xi_y \\ q_2^{(1)\pm} &= a_2^\pm(y) \xi_y, \quad q_3^{(1)\pm} = a_3^\pm(y) S_{1/2}^{(1)}(\xi^2) \end{aligned} \quad (17)$$

where  $a_i \pm (y)$  satisfy the following equations:

$$\begin{aligned} \pm 2 \frac{da_0^\pm}{dy} + \sqrt{\pi} \frac{da_1^\pm}{dy} &= \pm (a_1^+ + a_1^-) \frac{I_2}{\pi} \pm (a_0^+ - a_0^-) \frac{I_1}{\pi} \\ \sqrt{\pi} \frac{da_0^\pm}{dy} \pm 2 \frac{da_1^\pm}{dy} &= (a_1^+ + a_1^-) \frac{I_3}{\pi} + (a_0^+ - a_0^-) \frac{I_3}{\pi} \pm (a_1^+ - a_1^-) \frac{I_4}{\pi} \\ \pm 2 \frac{da_2^\pm}{dy} &= (a_2^+ + a_2^-) \frac{I_3}{\pi} \pm (a_2^+ - a_2^-) \frac{I_4}{\pi} \\ \pm \frac{9}{2} \frac{da_3^\pm}{dy} &= (a_3^+ + a_3^-) \frac{I_5}{\pi} \pm (a_3^+ - a_3^-) \frac{I_6}{\pi} \end{aligned} \quad (18)$$

Here

$$\begin{aligned} I_1 &= [\text{sign } c_y, \text{sign } c_y]_1, \quad I_2 = [\text{sign } c_y, c_y]_1, \quad I_3 = [c_y, c_y]_1 \\ I_5 &= [{}^3/2 - c^2, {}^3/2 - c^2]_1, \quad I_4 = [c_y \text{sign } c_y, c_y \text{sign } c_y]_1 \\ I_6 &= [S_{i_z}^{(1)}(c^2) \text{sign } c_y, S_{i_z}^{(1)}(c^2) \text{sign } c_y]_1 \end{aligned}$$

We integrate system (18) to get

$$\begin{aligned} a_0^\pm &= b_0^\pm e^{-\alpha_1 y} + c_0, \quad a_1^\pm = b_1^\pm e^{-\alpha_1 y} \\ a_2^\pm &= b_2^\pm e^{-\alpha_2 y}, \quad a_3^\pm = b_3^\pm e^{-\alpha_3 y} \end{aligned} \quad (19)$$

The constants  $b_0^\pm$ ,  $b_1^\pm$ ,  $b_2^\pm$ ,  $b_3^\pm$ , and  $c_0$  are determined from the boundary condition of (3), (13), and (15) together with the condition for conservation of the normal component of the flux of internal energy:

$$\int_{(c)} f_M^{(0)} c_y \langle E_N h(y=0) \rangle dc = \int_{(c)} f_M^{(0)} c_y \langle E_N h(y \rightarrow \infty) \rangle dc \quad (20)$$

where condition (20) is not necessary from the viewpoint of the exact solution to (12) with  $l=1$  since it follows from the transport equation for  $E_N$ ; also,  $\alpha_i > 0$  is found from (18).

By virtue of (19), there is at the upper boundary of the Knudsen layer ( $y \rightarrow \infty$ ) a temperature step in the vibrational degrees of freedom:

$$\Delta T_i = \frac{kT_i}{c_v(T_i)} \int_{(c)} f_M^{(0)} \left\langle h(c, y \rightarrow \infty) P_N^{(1)} \left( \frac{E_N}{kT_i} \right) \right\rangle dc \quad (21)$$

$$\Delta T_i = \eta_1(\sigma) \frac{\lambda_i(T_w, T_{iw})}{n\nu c_v(T_{iw})} \frac{\partial T_{iw}}{\partial y} + \eta_2(\sigma) \frac{r_i}{c_v(T_{iw})} \frac{\varepsilon(T_w) - \varepsilon_i(T_{iw})}{r_{it}} \quad (22)$$

Here  $\eta_1(\sigma)$  and  $\eta_2(\sigma)$  are numerical factors dependent on the diffuseness parameter  $\sigma$  and the intermolecular interaction potential.

The first term in (22) may be derived from elementary considerations, if we incorporate the further coefficient  $\eta_1(\sigma)$ , on the assumption that the flux of molecules incident on the wall carries energy  $\varepsilon_1 = kT_1$ .

The second term in (22) cannot be derived in this way, so two-temperature relaxation is not described by the elementary theory of transport phenomena.

In conclusion we consider the derivation of the boundary conditions for a flow in a boundary layer [2]. In this case the distribution of (2) does not contain  $A_3$ , so in (17) and (18) we need to put  $a_2^\pm = a_3^\pm = 0$ . The integrals  $I_1 - I_4$  can be calculated analytically by using a collision model [11] for the resonant transitions:

$$\begin{aligned} I_1 &= -[\sqrt{2} + \theta^2(\sqrt{2} - 5/4)](\pi/l), \quad I_2 = -[1 + \pi/4 + \theta^2(\pi/4 + 5/6)](\pi/l) \\ I_3 &= -(2/3)[1 - \theta^2](\pi/l), \quad I_4 = -[2/3 - \sqrt{2/4} + \theta^2(2/3 - \sqrt{34/48})](\pi/l) \\ \theta^2 &= (\alpha/\pi\nu)^2 (kT/m) \end{aligned} \quad (23)$$

Here  $l = (\pi n d^2 \sqrt{2})^{-1}$ , while  $d$  is the effective diameter of the molecule in the form of a solid sphere with the Lennard-Jones potential [11]; while  $\alpha$  is a constant chosen from the characteristics of the Lennard-Jones potential [5] and  $\nu$  is the frequency of a quantum.

The coefficient  $\eta_1(\sigma)$  in this case is

$$\eta_1(\sigma) = \left( \frac{\pi}{4} \frac{2-\sigma}{\sigma} + 0.7052 - 0.91800\sigma \right) \frac{(2-\sigma)4D/(1-\theta^2)}{2-\sigma-1.783\sigma(1-1.98130\sigma^2)} \quad (24)$$

$$\eta_1(1) = (0.8427 + 0.3866\theta^2)(2D / (1 - \theta^2)) \quad (25)$$

$$D = \frac{3}{8na^2}(kT / \pi m)^{1/2}$$

Here  $D$  is the self-diffusion coefficient [7].

It is readily seen that the resonant transitions increase  $\eta_1$  by a factor proportional to  $\sim \theta^2$ .

Then in the boundary layer with  $(1 - T_{IW}/T_W) \sim 1$  (highly nonequilibrium wall) the conditions for the velocity and temperature step for the translational degrees of freedom are as for a monatomic ideal gas. Also, there is a temperature discontinuity  $\Delta T_1$  in the vibrational degrees of freedom, which is responsible in the general case for a temperature gradient in  $T_1$ , and also for the relaxation.

If  $T_W = T_{IW}$  (equilibrium wall), we get from (22) that the part of  $\Delta T$  responsible for the transport of internal energy is proportional only to  $\lambda_1(T_W) \partial T_W / \partial y$ ; this agrees with the result of [3] apart from the factor  $\eta_1(\sigma)$  if we bear in mind that the bulk viscosity coefficient  $\zeta$  appearing in (43) in [3] for  $\Delta T$  is zero for the present model for the medium [2].

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