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Abstract

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ON THE TEMPERATURE JUMP IN POLYATOMIC GASES

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1. If a gas and the surface of a solid body bounding it are in thermodynamic equilibrium, then the influence of the surface on the distribution function of the gas molecules disappears outside the region of direct interaction of the molecules with the surface. Within this region only the density of the number of molecules changes. The situation is different for a nonuniformly heated gas. In the case of a monatomic gas, the influence of the wall is felt at distances of the order of the mean free path l_0, distorting in this region the temperature field, which beyond it may be regarded as a linear function of distance.

Extrapolation of the linear course of the temperature directly to the surface leads to a temperature value different from the true temperature of the surface. The difference δT of these temperature values—the temperature jump—is, for not too large gradients, proportional to the derivative $\partial T/\partial x$ in the region of the linear course of the temperature,

$$\delta T = g\,\partial T/\partial x, \tag{1}$$

where the positive direction of the x-axis, normal to the surface, is taken to be the direction from the wall into the gas (^{1}). The quantity g (of dimension length) —the temperature-jump coefficient—is of the order of l_0 and depends on the accommodation coefficient (^{1,2}), which characterizes the degree of equalization of the (gas-kinetic) temperature of the molecules reflected from the wall and the temperature of the wall.

Usually these results are extended to polyatomic gases (^{2}). In doing so, an essential premise, sometimes made implicitly, is the characterization of the exchange of energy between the gas molecules and the wall by means of some effective accommodation coefficient, common to all degrees of freedom. In this case the theory contains only one quantity of dimension length—the mean free path l_0—which determines the order of magnitude of g.

However, the situation changes substantially if the accommodation coefficient for some type of internal energy differs appreciably from the accommodation coefficient for translational energy. In this case, in the immediate vicinity of the wall the equilibrium distribution of energy between the internal and translational degrees of freedom is disturbed. If by τ we denote the relaxation time (the establishment of statistical equilibrium between the internal and translational degrees of freedom) and by D^* the diffusion coefficient determining the transfer of internal energy, then the length $l \sim \sqrt{D^* \tau}$ gives the width of the zone of nonequilibrium energy distribution. In (^{3}) the influence of retarded exchange of translational and vibrational energy on the values of thermal conductivity obtained by the heated-filament method was considered. Below we consider the influence of the zone l on the boundary conditions, formulated as a temperature jump, assuming $l \ll L$, where L is the characteristic size of the temperature field.

2. Let us assume that the f degrees of freedom of a molecule can be divided into two groups: $f = f_1 + f_2$. For the group f_1, which includes, for example, the translational and rotational degrees of freedom, a relaxation time of the order of the free-path time τ_0 is characteristic, with

$$\tau_0 \ll \tau, \tag{2}$$

where τ is the time for equilibrium to be established between the f_1 and f_2 degrees of freedom. By f_2 one may understand, for example, the vibrational degrees of freedom. Let the accommodation coefficient for the group f_2 be smaller than for the group f_1.

The region near the wall can be divided into three zones. In zone I, whose width a is of order l_0, the (gas-kinetic) temperatures T_1 and T of the first and second groups of degrees of freedom, respectively, vary in a complicated manner, and Fourier' s equation for the heat flux is not applicable. The conditions at the boundary of this zone can be written in the form:

$$\delta_1 T_1 = g_1 \partial T_1 / \partial x \big|_{x \sim a}, \tag{3}$$

$$\delta_2 T = g_2 \partial T / \partial x \big|_{x \sim a}, \tag{3'}$$

where $\delta_1 T_1$, $\delta_2 T$, g_1, g_2 are the temperature jumps, defined in the usual way, and their coefficients for the groups f_1 and f_2 of degrees of freedom, respectively.

The quantity g_1 can be related in the usual way (see, for example, (^{2})) to the accommodation coefficient a_1 for the f_1 degrees of freedom, since in zone I, by virtue of (2), the energy exchange between the groups f_1 and f_2 may be neglected. The quantity g_2 depends in principle on the accommodation coefficients a_1 and a_2 for both groups, since the transfer of energy of the f_2 degrees of freedom is also determined by the distribution of energy over the f_1 degrees of freedom. In our treatment we shall characterize the processes in zone I directly by the quantities g_1 and g_2, since the main interest lies in elucidating the role of zone II.

3. In this zone, whose width $l \gg l_0$, there occurs a relatively slow process of equalization of the temperatures T_1 and T. The heat-flux density $\mathbf{q}$ can be represented in the form

$$\mathbf{q} = \mathbf{q}_1 + \mathbf{q}_2, \tag{4}$$

where $\mathbf{q}_i = n\overline{\varepsilon_i \mathbf{C}}$; n is the number density of molecules; ε_i is the energy of the f_i degrees of freedom; $\mathbf{C}$ is the thermal velocity; the bar denotes averaging with the distribution function at the given point.

In the relations (one-dimensional problem)

$$q_1 = -\lambda_1 \frac{\partial T_1}{\partial x}, \quad q_2 = -\lambda_2 \frac{\partial T}{\partial x}. \tag{5}$$

λ_1 is the coefficient of thermal conductivity of a gas whose molecules would possess only the degrees of freedom of the group f_1. For the transfer of the energy ε_2 one may adopt a diffusion mechanism (4) and set

$$\lambda_2 = D^* n c_v^{(2)}. \tag{6}$$

Here $c_v^{(i)}$ is the heat capacity of the f_i degrees of freedom at constant volume, referred to one molecule; D^* is a certain effective diffusion coefficient, differing from the ordinary self-diffusion coefficient D by taking into account a possible "relay" transfer of the energy ε_2, and depending on T_1 and T.

In the stationary state, T_1 and T outside zone I satisfy the equations

$$\lambda_1 \frac{d^2 T_1}{dx^2} + A\frac{T - T_1}{\tau} = 0, \tag{7}$$

$$\lambda_2 \frac{d^2 T}{dx^2} - A\frac{T - T_1}{\tau} = 0, \tag{7'}$$

where λ_1 and λ_2 are taken to be constant. The second term in (7) represents the energy transferred from the f_2 degrees of freedom to the group f_1 per unit volume per unit time.

The quantity A is equal to

$$A = n c_v^{(1)} c_v^{(2)} / c_v^{(0)}, \tag{8}$$

where $c_v^{(0)} = c_v^{(1)} + c_v^{(2)}$. From (7) and (7′), taking into account that $T - T_1 \to 0$ as $x \to \infty$, we find

$$T - T_1 = C e^{-x/\alpha}; \tag{9}$$

$$\alpha^2 = \frac{\lambda_1 \lambda_2}{A\lambda}\tau; \tag{10}$$

$$T_1 = C\frac{\lambda_2}{\lambda} e^{-x/\alpha} + Bx + E, \tag{11}$$

where the constants B, C, E are determined from the boundary conditions. The length α gives the refined width of zone II, which, with increasing x, passes into the region of a constant temperature gradient (common to all degrees of freedom)

$$\left.\frac{dT_1}{dx}\right|_{x\to\infty} = B. \tag{12}$$

Extrapolating the asymptotic behavior of the temperature T_1

$$T_1 = Bx + E \tag{13}$$

to the values $x \to 0$, we obtain

$$T_{\text{st}} + \delta = E, \tag{14}$$

where T_{st} is the wall temperature, and δ is the effective temperature jump. In view of the inequality $1 - e^{-a/\alpha} \ll 1$, in equation (3) one may substitute the expression $\delta_1 T_1 = T_1(0) - T_{\text{st}}$ and replace the derivative $dT_1/dx|_{x\sim a}$ by the quantity $dT_1/dx|_{x=0}$; here $T_1(0)$ and $dT_1/dx|_{x=0}$ are calculated from (11). In this way, on the basis of (14), we obtain

$$-C\frac{\lambda_2}{\lambda} + \delta = g_1 C \frac{\lambda_2}{\lambda}\frac{1}{\alpha} + g_1 B. \tag{15}$$

Similarly, from (3′), (9), (11), and (14) we obtain

$$C\frac{\lambda_1}{\lambda} + \delta = -g_2 C \frac{\lambda_1}{\lambda}\frac{1}{\alpha} + g_2 B. \tag{16}$$

Eliminating C from (15) and (16), we obtain

$$\delta = g\, dT_1/dx \quad \left(dT_1/dx \equiv dT_1/dx|_{x\to\infty}\right), \tag{17}$$

where the coefficient g of the (effective) temperature jump is equal to

$$g = \alpha \left[\frac{\lambda_1}{\lambda} \frac{g_1}{\alpha} + \frac{g_1 g_2}{\alpha^2} + \frac{\lambda_2}{\lambda} \frac{g_2}{\alpha} \right] \Big/ \left[1 + \frac{\lambda_1}{\lambda} \frac{g_2}{\alpha} + \frac{\lambda_2}{\lambda} \frac{g_1}{\alpha} \right]. \tag{18}$$

4. The quantity g_1 is usually of the order of the free-path length l_0. An estimate of the order of magnitude of α gives

$$\alpha \sim l_0 \sqrt{\tau/\tau_0}, \tag{19}$$

where τ_0 is the free-flight time. Usually $\tau/\tau_0 \gg 1$; for example, for the equalization of the energies of the translational and rotational degrees of freedom, a time of the order 10^2-$10^5 \tau_0$ is required. Therefore one may take $g_1 \ll \alpha$.

If g_1 and g_2 are quantities of the same order, then approximately we have

$$g = \frac{\lambda_1}{\lambda} g_1 + \frac{\lambda_2}{\lambda} g_2. \tag{20}$$

For $g_2 \sim a$ (which is possible for a sufficiently small accommodation coefficient for the f_2 degrees of freedom) we obtain

$$g = \frac{\lambda_2 g_2}{\lambda a + \lambda_1 g_2}\, a. \tag{21}$$

For $g_2 \to \infty$ (the internal degrees of freedom f_2 are practically excluded from direct heat exchange between the gas and the wall)

$$g = g_1 + \frac{\lambda_2}{\lambda} (a + g_1). \tag{22}$$

5. Usually the condition for applicability of the concept of a temperature jump (without taking into account the influence of relaxation zone II considered here) is the inequality $l_0 \ll L$, where L is the characteristic size of the temperature field. In this case the quantity g in equality (1) does not depend on L and is inversely proportional to the gas pressure. When, as the dimensions of the apparatus or the gas pressure p decrease, l_0 becomes comparable with L, an additional dependence of the (formally introduced) temperature jump on L and p arises.

Result (18) was obtained under the assumption $L \gg a \gg l_0$. Therefore analogous anomalies in the behavior of the temperature jump in polyatomic gases may appear already at considerably higher pressures and dimensions L. This circumstance could be regarded as experimental confirmation of the influence of the relaxation zone.

In conclusion we note that the results presented can be extended to the case when the role of zone II is played by the region in which chemical equilibrium (in a gas mixture), disturbed by the wall, is restored.

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Note: Figure translations are in progress. See original paper for figures.

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