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Abstract

Full Text

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THEORY OF THE THERMOMOLECULAR PRESSURE DIFFERENCE AND THERMOOSMOSIS OF GASES IN WIDE CAPILLARIES

Maxwell' s work (^{1}) gave his followers grounds to interpret thermomechanical effects in nonuniformly heated gases on the basis of the assumption of thermal slip, i.e., a jump in velocity Δv between the gas and a solid wall. In this case it is assumed that $v = \frac{3}{4}\frac{\nu}{T}\,\mathrm{grad}\,T$, where $\mathrm{grad}\,T$ is the temperature gradient T along the surface of the wall, and ν is the kinematic viscosity of the gas. However, the formula derived by Epstein (^{2}) on this basis for the thermophoretic velocity of large particles (with radius r much greater than the mean free path of gas molecules λ) proved to contradict experiment. Namely, experiment does not confirm the sharp decrease (in the limit—to zero) in the thermophoretic velocity, following from Epstein' s formula, when the ratio of the thermal conductivity of the solid to the thermal conductivity of the gas increases (^{3}).

One of the reasons for this discrepancy between theory and experiment may be the insufficient rigor of Maxwell' s calculation method, which assumes that the velocity distribution of molecules striking different portions of the wall is the same as in the adjacent portions of the volume; in the presence of a temperature gradient near the wall this is impossible because of collisions experienced by the incident molecules with molecules reflected from the wall and retaining a different distribution in a layer of thickness λ. Strictly speaking, in this layer the velocity distribution function of the molecules must depend on two coordinates —one along and the other perpendicular to the surface—and finding this function to the necessary approximation is a rather difficult problem.

Therefore, a different, less direct path is simpler, in which one first calculates the heat transported in isothermal laminar flow in the surface layer of thickness λ. Knowing this "heat of transfer," one can, by applying the principle of symmetry of Onsager kinetic coefficients, find the thermal-slip velocity. As we showed earlier (^{4}), this method of calculation yields Maxwell' s formula, but with a coefficient 35 times smaller.

This unexpected result led us to suppose that, when solid bodies are flowed around by a gas, the main part of the heat is transported not in the wall layer of thickness λ, but in the volume of the gas or in a considerable part of it. The validity of this supposition is most easily examined using the example of

Poiseuille flow of a gas through a cylindrical tube. Here the isothermal flow of the gas along the walls, in contrast to the Couette flow considered earlier (4), is coupled with the appearance of a longitudinal pressure gradient.

To solve such a problem we shall use the methods of thermodynamics of irreversible processes. These proceed from the fact that the production (or dissipation) of entropy in any closed system can be represented in the form (see, for example, (5)):

$$\Delta s = I_Q X_Q + I_M X_M, \tag{1}$$

where Δs is the rate of production of entropy; I_Q and I_M are the fluxes of heat and matter; X_Q and X_M are the corresponding "thermodynamic forces."

Choosing the fluxes and "forces" in this way, one can write the phenomenological laws in the form

$$I_M = L_{11} X_M + L_{12} X_Q,$$

$$I_Q = L_{21} X_M + L_{22} X_Q. \tag{2}$$

Equations (2) mean that the flux, say, of heat is caused not only by the "force" X_Q (as in the usual Fourier law $I_Q = -\chi \operatorname{grad} T$), but also by the "force" X_M.

Let us now consider a concrete system consisting of two vessels with gas, connected by a "wide" tube (with a diameter much greater than λ). Suppose that in this system a temperature difference ΔT and a pressure difference Δp are maintained between the ends of the tube. Then equality (1) for this case takes the form:

$$\Delta s = I_M \frac{\Delta p}{\rho T} + I_Q \frac{\Delta T}{T^2}, \tag{1'}$$

and equations (2) can be written in the form

$$I_M = -L_{11} \frac{\Delta p}{\rho T} - L_{12} \frac{\Delta T}{T^2},$$

$$I_Q = -L_{21} \frac{\Delta p}{\rho T} - L_{22} \frac{\Delta T}{T^2}. \tag{2'}$$

The Onsager relations in this case read

$$L_{12} = L_{21}.$$

Let us now consider such a stationary state of the system in which there is no mass transfer. We have

$$\frac{\Delta p}{\Delta T} = -\frac{L_{12}}{L_{11}}\frac{\rho}{T}. \tag{3}$$

The ratio L_{12}/L_{11} is easily found by considering isothermal flow ($\Delta T = 0$). Taking the Onsager relation into account,

$$\frac{L_{12}}{L_{11}} = \left.\frac{I_Q}{I_M}\right|_T. \tag{4}$$

Hence

$$\frac{\Delta p}{\Delta T} = -\left.\frac{I_Q}{I_M}\right|_T \frac{\rho}{T}. \tag{5}$$

The quantity $I_Q\big|_T$ is the heat flux at constant temperature. For a gas consisting of elastic spheres, it was calculated by S. Chapman and T. Cowling (^{6}) in the third approximation of their theory and is equal to

$$I_Q\big|_T = {}^3/_2\eta\nu\pi r^2\left(\overrightarrow{\Delta v} + {}^1/_3\,\mathrm{grad\,div}\,\vec{v}\right), \tag{6}$$

where η is the dynamic viscosity of the gas. For sufficiently slow flows, with which we are dealing here, the gas may be regarded as incompressible, and therefore the second term on the right in formula (6) may be neglected.

On the other hand, for small $\vec{v}$ in the stationary case the Navier–Stokes equation takes the form:

$$\overrightarrow{\Delta v} = \frac{1}{\eta}\,\mathrm{grad}\,p. \tag{7}$$

In quantity (6), generally speaking, one should also add the heat of transfer in the wall layer, which is not taken into account here. It, as already

as was said, was calculated by us earlier^4 and is equal to

$$I'_\rho|T = kv\pi r^2\,\mathrm{grad}\,p, \tag{7'}$$

where $k = 0.0218\ldots$. Thus, for the total heat transfer we have here

$$I_Q|T + I'_Q|T = 1.52v\pi r^2\,\mathrm{grad}\,p. \tag{6'}$$

Fig. 1

Figure 1: Fig. 1

The flux of matter in the tube at constant temperature is determined by the Poiseuille formula

$$I_M|T = -\frac{\pi r^4}{8}\frac{1}{\nu}\,\mathrm{grad}\,p. \tag{8}$$

Substituting (6′), (7), (8) into (5), we obtain

$$\frac{\Delta p}{\Delta T} = \frac{12.2\eta v}{r^2 T} = 12.2\frac{\eta^2 R}{pMr^2}, \tag{9}$$

where M is the molecular weight of the gas, and R is the universal gas constant.

The formula obtained gives the desired thermomolecular effect in wide capillaries. In comparing it with experiment, the following circumstance must be borne in mind.

The viscosity of a gas depends rather strongly on its temperature. In particular, for hydrogen the semi-empirical formula is well confirmed,

$$\eta = \eta_0 \left(\frac{T}{273}\right)^{0.7}. \tag{10}$$

Fig. 1

In Knudsen' s experiment with hydrogen[7] the temperature varied in the interval 50–380° K. Consequently, formula (9) is not directly applicable to this case. It is valid for sections of the capillary of infinitesimally small length. The full effect is obtained by integrating (9), taking (10) into account, over the length of the capillary.

We have

$$p_1 - p_2 = \frac{12.2\eta^2 R}{Mr^2 p}\,\frac{T_2^{2.4} - T_1^{2.4}}{(273)^{1.4}\cdot 2.4}, \tag{11}$$

where T_1 and T_2 are the temperatures in the vessels; p_1 and p_2 are the pressures in them.

Figure 1 presents the theoretical course of Δp for specified T_1 and T_2 and compares it with Knudsen' s experiments in the pressure interval from ~ 7 mm to atmospheric pressure. The dashed curve is drawn according to Maxwell' s formula. The increase in the discrepancy between theory and experiment with increasing pressure is apparently explained by the imperfection of the model of noninteracting gas molecules at such pressures. For low pressures the theory agrees well with experiment, in contrast to calculations based on the Maxwell formula for thermal slip. These calculations give values that are underestimated by more than a factor of 2.

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

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