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Abstract

Full Text

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Theory of Thermophoresis of Large Solid Aerosol Particles

As is known, the existing theory of thermophoresis—the motion, under the influence of an external temperature gradient, of aerosol particles with radius R much greater than the mean free path of gas molecules ⁽¹⁾λ—contradicts experiment, leading, in particular, to the conclusion that with increasing thermal conductivity of the particles the thermophoretic velocity should tend to zero. It is natural to suspect that the reason for this discrepancy is the Maxwell (2) concept used in (1) of thermal slip at the particle surface, proportional to the tangential temperature gradient. We have shown that, first, a more rigorous calculation reduces the Maxwell coefficient of "pure thermal slip" by a factor of 35 (3). Second, for the case of heat flow in a capillary it was shown that Maxwell' s theory disagrees with experiment, whereas agreement is obtained with an essentially different method of approach (4).

Let us apply this more rigorous approach, which has proved itself and is based on the methods of the thermodynamics of irreversible processes, to calculating the thermophoretic velocity for the case $R \gg \lambda$. This approach makes it possible to reduce the problem to the simpler case of isothermal flow around a sphere by a gas stream (by isothermal we here mean a process in which there is no external temperature field). For this purpose let us consider a porous partition constructed of spheres of radius R, arranged at random and rigidly fixed in space. According to the methods of the thermodynamics of irreversible processes, during gas flow through any partition the rate of production (or dissipation) of entropy $\Delta\dot{S}$ in a closed system may be represented in the form (5)

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

where I_Q and I_M are the fluxes of heat and matter; X_Q and X_M are the corresponding "thermodynamic forces." From this relation one can write the phenomenological laws in the form

$$\begin{aligned} I_M &= -L_{11} X_M - L_{12} X_Q, \\ I_Q &= -L_{21} X_M - L_{22} X_Q. \end{aligned} \tag{2}$$

Let temperature and pressure differences ΔT and Δp be maintained at the ends of the porous partition. Then the rate of change of entropy is written in the form

$$\Delta \dot{S} = I_M \Delta p/\rho T + I_Q \Delta T/T^2, \tag{1'}$$

and equation (2) may be written as

$$I_M = -L_{11}\Delta p/\rho T - L_{12}\Delta T/T^2, \qquad I_Q = -L_{21}\Delta p/\rho T - L_{22}\Delta T/T^2. \tag{2'}$$

The Onsager relation states that $L_{12} = L_{21}$.

Let us now consider such a state in which mass transfer through the cross section of the partition occurs at constant pressure. We have

$$I_M = -L_{12}\Delta T/T^2. \tag{3}$$

The value of the coefficient L_{12} can be found by calculating the heat transfer at constant temperature (this quantity is usually called the "heat of transfer")

$$I_Q\big|_T = Q\big|_T = -L_{21}\Delta p/\rho T. \tag{4}$$

Thus,

$$I_M\big|_p = \frac{\rho}{T}\,Q\big|_T\,\frac{\Delta T}{\Delta p}. \tag{5}$$

From relation (5) it is easy to obtain the velocity of gas flow through the cross section of the partition at constant pressure and $\Delta T \neq 0$. We note that this quantity (with the opposite sign) simultaneously gives us the desired thermophoretic velocity of large particles

$$v = \frac{Q\big|_T}{T}\,\frac{\Delta T}{\Delta p}. \tag{6}$$

To calculate the coefficient $Q\big|_T$ in formula (6), let us first consider the steady flow, at small Reynolds numbers, of a gas past a sphere with thermal conductivity χ_i, the thermal conductivity of the gas being χ_e. The Chapman-Enskog method for solving the kinetic equation (6) makes it possible to calculate (as a third approximation) the isothermal heat transfer in a gas flow when the spatial derivatives of the velocity gradient are not zero. This calculation, with allowance for the Navier-Stokes equation $\eta \Delta \mathbf{v} = dp/d\mathbf{r}$, gives

$$\mathbf{Q} = \frac{3}{2}\,\frac{\eta}{\rho}\,\frac{dp}{d\mathbf{r}}. \tag{7}$$

In addition, as we have shown earlier (3), there exists an isothermal heat transfer in a surface layer of thickness of order λ, proportional to the velocity gradient. However, as was shown earlier in considering gas flow in a tube (4), this heat flux is small compared with the volume flux, and therefore in the present work we shall not take it into account.

As is known, in Stokes flow of a sphere the pressure in the gas is distributed according to the law

$$p = p_0 - \frac{3}{2}\eta u R\cos\theta/r^2 = p_0 - \frac{3}{2}\eta R\,(\mathbf{u}\cdot\mathbf{r})/r^3,$$

where $\mathbf{u}$ is the velocity of the gas at infinity,

$$\frac{dp}{d\mathbf{r}} = 3\eta R\left[3\frac{(\mathbf{u}\cdot\mathbf{r})}{r^5}\mathbf{r} - \frac{\mathbf{u}}{r^3}\right]. \tag{8}$$

It follows from this that at the very surface of the sphere we have

$$Q_r\big|_{r=R} = \frac{9}{2}\,\frac{\eta^2}{\rho}\,\frac{1}{R^2}\,(\mathbf{u}\cdot\mathbf{r}) = (\vec{\alpha}\cdot\mathbf{r}_0), \tag{9}$$

where

$$\vec{\alpha} = \frac{9}{2}\,\frac{\eta^2}{\rho}\,\frac{1}{R^2}\mathbf{u};$$

$\mathbf{r}_0$ is the unit vector in the direction of $\mathbf{r}$.

Thus, in isothermal flow of a gas around a sphere, heat Q_r is released at its surface (but not in the volume, since $\operatorname{div}\mathbf{Q} = 0$), associated with dissipation of energy as a result of viscous friction.

Let us find the temperature distribution inside and outside the sphere under the condition that at infinity the temperature remains unchanged. At small Péclet numbers, the steady temperature distribution outside and inside the sphere is described by the Laplace equation $\Delta T = 0$.

At the boundaries the conditions $T_e|_\infty = 0$, $T_i|_0$ finite, are satisfied. At $r = R$ we have: $T_e = T_i$, $-\chi_e \partial T_e/\partial r + Q_r = -\chi_i \partial T_i/\partial r$.

As usual, the solution is sought in the form

$$T_i = \sum_{n=0}^{\infty} a_n r^n P_n(\cos\theta), \quad r < R; \qquad T_e = \sum_{n=0}^{\infty} b_n \frac{1}{r^n} P_n(\cos\theta), \quad r > R,$$

where P_n are Legendre polynomials, and θ is the polar angle relative to the velocity vector $\mathbf{u}$.

Using the orthogonality condition for Legendre polynomials and matching the solution at $r = R$, we obtain

$$T_i = -\frac{(\vec{\alpha} \cdot \mathbf{r})}{(2\chi_e + \chi_i)}; \qquad T_e = -\frac{(\vec{\alpha}\mathbf{r})}{(2\chi_e + \chi_i)}. \tag{10}$$

Let us first consider the case when $\chi_i \gg \chi_e$ (the spheres are infinitely heat-conducting). Then inside each sphere we have

$$-\frac{dT_i}{dz} = \operatorname{grad} T_i = -\frac{\vec{\alpha}}{2\chi_e + \chi_i} \simeq -\frac{\vec{\alpha}}{\chi_i}$$

(the z-axis is directed along $\mathbf{u}$), and the heat flux through a unit cross section of the sphere is

$$q_i = -\chi_i \operatorname{grad} T_i = \vec{\alpha}. \tag{11}$$

For a completely random arrangement of the spheres, the total area of their cross sections by any plane will be equal to the area of the plane multiplied by the volume filling of space by the spheres. Hence, from (7), it follows that through 1 cm^2 of an arbitrary plane cutting the porous partition perpendicular to the gas flow, in this case the amount of heat $Q|_T$ is transported equal to

$$Q|_T = -\frac{3}{2}\frac{\eta}{\rho}\overline{\frac{dp}{dz}} + \vec{\alpha}\frac{4}{3}\pi R^3 N, \tag{12}$$

where N is the number of spheres per unit volume of the partition, and $\overline{dp}/dz$ is the mean pressure gradient.

We further take into account that the resistance of the partition to the gas flow, according to Stokes' law, is

$$F = \overline{\frac{dp}{dz}} = 6\pi\eta R N u. \tag{13}$$

Substituting (12) into (11), with (9) taken into account, we have

$$Q^{(1)}|_T = -\frac{1}{2}\frac{\eta}{\rho}\overline{\frac{dp}{dz}}. \tag{14}$$

Hence, according to (6),

$$v = -\frac{1}{2}\frac{\eta}{\rho T}\overline{\frac{dT}{dz}}. \tag{15}$$

Let us now pass to the case when the magnitude χ_i is comparable with χ_e. In this case, around each sphere, as the gas flows past it, there arises a temperature field distributed according to the law of a dipole with "dipole moment"

$$\mathbf{p} = -\vec{\alpha}R^3/(2\chi_e + \chi_i). \tag{16}$$

As a result, by analogy with the problem of polarization of a dielectric, the whole partition acquires a "moment" $P = N\mathbf{p}$. Consequently, at the ends of the partition there instantaneously arises a temperature difference

$$\Delta T = 4\pi H\vec{\alpha}NR^3/(2\chi_e + \chi_i), \tag{17}$$

and inside the partition in the gas there is a mean temperature gradient

$$\overline{\operatorname{grad} T_e} = -4\pi\mathbf{P}.$$

The temperature jump ΔT will violate the requirement of equality of temperatures on both sides of the partition, which is necessary for determining the transported heat Q appearing in equation (4), by the methods of the thermodynamics of stationary processes. To eliminate this violation of "isothermality on the average" of the gas flow through our partition, it is necessary to supply to both its surfaces certain amounts of heat, producing a counter temperature jump that exactly compensates that calculated in formula (17).

These amounts (sources and sinks) of heat must be supplied at the ends of the partition in addition to those which compensate the transported heat calculated above. Thus, the total transported heat will be obtained,

adding to the heat Q the heat flux carried as a result of the occurrence of "thermal polarization" and equal to

$$Q_a = -\varkappa_e \operatorname{grad} T_e = -\frac{3\varkappa_e}{(2\varkappa_e + \varkappa_i)}\frac{\eta}{\rho}\overline{\frac{dp}{dz}}. \tag{18}$$

There arises, however, the question: will the value of Q previously calculated in (14) now change, when $\varkappa_e$ and $\varkappa_i$ are of the same order, since, in comparison

Fig. 1. Field of local temperatures around a sphere in Stokes flow

Figure 1: Fig. 1. Field of local temperatures around a sphere in Stokes flow

with $\vec{\alpha}$, the density of the heat flux through the section of the spheres by our plane will decrease? This question should be answered in the negative, since the power and distribution of the heat sources covering the surface of the spheres do not depend on the thermal conductivities $\varkappa_e$ and $\varkappa_i$, and therefore only the pattern of distribution of the heat fluxes penetrating the cutting plane near the sphere under consideration will change; the total heat flux will not change (see Fig. 1). To remove any ambiguity, it should be noted that that part of the heat flux passing between the two hemispheres of the spheres, which reaches the boundary of the partition and, being expended on producing the temperature difference ΔT in formula (17), does not intersect our plane, is very small for positions of the latter not too close to the surfaces of the partition.

Fig. 1. Field of local temperatures around a sphere in Stokes flow

The complete "heat of transfer" Q_{Res} will thus be found as the sum of two terms expressed, respectively, by formulas (14) and (18). It is equal to

$$Q_{\mathrm{Res}|T} = -\frac{4\varkappa_e + \frac{1}{2}\varkappa_i}{2\varkappa_e + \varkappa_i}\frac{\eta}{\rho}\frac{\overline{dp}}{dz}, \tag{19}$$

and the thermophoretic velocity (taking into account the opposite sign of the velocity vector of the spheres) is

$$v_T = \frac{(4\varkappa_e + \frac{1}{2}\varkappa_i)}{(2\varkappa_e + \varkappa_i)}\frac{\eta}{\rho T}\frac{dT}{dz}. \tag{20}$$

For comparison, we give Epstein' s formula (^{1})

$$v_T^{(\mathrm{E})} = \frac{3}{2}\frac{\varkappa_e}{(2\varkappa_e + \varkappa_i)}\frac{\eta}{\rho T}\frac{dT}{dz}. \tag{21}$$

We see that the new formula agrees with observations considerably better, since it does not lead to the disappearance of v_T as $\varkappa_i$ increases. At the same time, taking into account that, as a rule, $\varkappa_i$ is much greater than $\varkappa_e$, formula (20) explains the small, but apparently real, dependence of $\frac{\rho}{\eta}v_T$ on the kind of gas (the greatest value was obtained for hydrogen).

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CITED LITERATURE

1. P. Epstein, *Zs. Phys.*, **54**, 537 (1929).
2. J. C. Maxwell, *Phil. Trans. Roy. Soc.*, **170**, p. 1, 231 (1879).
3. B. V. Deryagin, S. P. Bakanov, *DAN*, **141**, 384 (1961).
4. B. V. Deryagin, S. P. Bakanov, *DAN*, **144**, 535 (1962).
5. S. R. de Groot, *Thermodynamics of Irreversible Processes*, Moscow, 1956.
6. S. Chapman, T. Cowling, *The Mathematical Theory of Non-uniform Gases*, Moscow, 1960.

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