

# Thermophoresis in gases

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We analyze the mechanisms that cause the motion of objects suspended in inhomogeneously heated gases. We treat two limiting cases: a) a highly rarefied gas in which the mean free path  $\lambda$  of the gas molecules is large in comparison with the characteristic dimension  $R$  of the object, and b) a weakly rarefied gas that satisfies the condition  $\lambda \ll R$ . In both cases we assume that the characteristic scale of the temperature inhomogeneities in the gas obeys  $L \gg \lambda$ . The case of a weakly rarefied gas is of very great interest, primarily from the standpoint of studying the state of a gas near a gas-solid phase boundary in the Knudsen layer. The greater part of the review is devoted to this problem: we treat the methodology of obtaining the boundary conditions for hydrogasdynamics with slip, and present in detail a scheme for calculating the kinetic coefficients that generalizes the Chapman-Enskog method to the case in which the state of the gas inside the Knudsen layers plays a substantial role, and we discuss the problem of the applicability of the thermodynamics of irreversible processes to problems of this type and demonstrate the efficacy of its methods. In addition, we modify the well-known method of half-range expansions on the basis of some physical assumptions and express some ideas on the principles of construction of the system of moment equations in the kinetic theory of gases. We also propose a scheme of experiment for testing the validity of the presented concepts.

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## INTRODUCTION

The phenomenon that we shall discuss below was discovered experimentally more than one hundred years ago. Its essence is the following. Let one put a foreign body (for simplicity we shall treat this body henceforth as being a sphere of radius  $R$ ) into a gas in which a small temperature gradient is maintained by external heat sources. Then, in spite of the absence of external forces, the object will go into motion with a steady velocity proportional to the temperature gradient in the same direction as the heat flux arising from the heat conductivity of the gas. It has been rather easy since the creation of the kinetic theory of gases to explain and calculate this effect for objects of small dimensions ( $R \ll \lambda$ , where  $\lambda$  is the mean free path of the molecules of the gas). One would calculate the momentum imparted to the object by the molecules incident from the side of hotter gas, which proved greater than the total momentum of the "cold" molecules. Matters are far more

complicated in the case of an object of large dimensions, or as is equivalent, of a weakly rarefied gas, i.e., when  $R \gg \lambda$ . Within the scope of classical hydrodynamics, the velocity of motion of an object placed in an inhomogeneously heated gas proves to differ from zero only in the presence of external forces. A nonzero result was first obtained by Epstein.<sup>1</sup> Upon imposing boundary conditions on the surface of an object in a gas flow, he took account of the effect discovered by Reynolds<sup>2</sup> of thermal slip (creep). This study initiated the development of hydrogasdynamics involving slip, in which the classical condition of "attachment" of the gas to the surface of the object is replaced by the conditions of slip and discontinuity. Thus, the condition of proportionality of the velocity to the local tangential temperature gradient was assumed to hold for the tangential component of the velocity of the gas at the surface of the object in the gas flow. The proportionality coefficient, which is called the thermal slip coefficient, cannot of course be calculated within the framework of hydrogas-

dynamics itself. It must be found either by experiment or from independent theoretical treatment. Maxwell<sup>9</sup> undertook the first attempt at calculating a thermal slip coefficient on the basis of the just-created kinetic theory of gases.

Subsequently, during a rather prolonged period, principal attention was paid to studying transport processes in the volume of the gas far from the surfaces bounding the gas. Here substantial advances were made in developing methods for solving the problems of the kinetic theory.

Interest in the boundary conditions of the kinetic theory increased greatly in connection with the invention of aircraft for the upper layers of the Earth's atmosphere, and also with the intensive development of vacuum technique and the demands of chemical technology. It became necessary to generalize the kinetic theory to the case in which not only the collisions of the gas molecules with one another play an essential role in the phenomenon, but also their interaction with the surface bounding the gas.

At about this time results were already known of experiments to measure the velocity of thermophoresis of aerosols. They showed that Epstein's formula gives a depressed value of the velocity of thermophoresis, that it does not reveal its dependence on the nature of the interaction of the gas molecules with the surface of the object, and that it agrees poorly with experiment for objects of high heat conductivity. This sharp contradiction with experiment stimulated further theoretical study of the phenomenon of thermophoresis.

A contribution of no small importance to the construction of a theory of thermophoresis of large objects was made by using the methods of the thermodynamics of irreversible processes (TIP). They were first applied to studying thermophoresis in Refs. 4-6. Subsequently boundary conditions for hydrogasdynamics with slip were formulated<sup>7</sup> on the basis of concepts of TIP. Also an algorithm<sup>8</sup> was proposed that enables one to eliminate ambiguity in calculating the kinetic coefficients for boundary problems that arise in applying methods of polynomial expansions. Simultaneously the applicability of TIP to problems in which the properties of the gas inside the Knudsen layers plays an essential role was demonstrated<sup>8</sup> within the framework of the kinetic theory of gases. We give below a calculation of the velocity of thermophoresis, not only within the framework of hydrogasdynamics with slip, but also on the basis of TIP. Undoubtedly, the agreement of the results obtained by these two methods enhances the degree of faith in the procedure of the calculations, and also indicates the correctness of the formulation of the problem itself.

As for the experimental material, the literature mainly offers data of measurements performed on aerosols.<sup>9-19,42</sup> These systems are rather complicated in practice, and their properties depend strongly on the method of preparation and the parameters of the source material. Therefore the scatter in the results and errors of measurement are considerable. Moreover, experiments have not yet been performed in the range of

Knudsen numbers in which one can reliably compare them with the results of theoretical calculations.

We should stress that all of the arguments presented below hold at sufficiently small values of the temperature gradient  $\nabla T$ , when the characteristic scale  $L$  of the inhomogeneity is large in comparison with the mean free path  $\lambda$  of the gas molecules.

## 1. THERMOPHORESIS IN HIGHLY RAREFIED GASES (SMALL OBJECTS)

Two approaches have been developed for calculating the velocity of motion of small objects in an inhomogeneously heated gas.<sup>20</sup> One of them is based on viewing the system of "gas + small objects suspended in it" as a binary mixture of gases. As we know, a separation of components occurs in a binary gas mixture when acted on by a temperature gradient. This same effect occurs also in the studied system: inhomogeneous heating leads to relative motion of the gas proper and the objects suspended in it. This model has been applied widely in studying the flow of gases through porous objects<sup>21-25</sup> and the evolution of nonequilibrium aerosol systems.<sup>26-30</sup> It is sometimes given the name dusty-gas model in foreign literature.

The second approach consists in direct calculation of the impulse imparted to the object by the molecules of the gas surrounding it upon colliding with its surface and subsequent reflection. The established velocity of motion of the object is found by equating the total impulse to zero.<sup>20,31</sup>

### a) The "dusty-gas" model

The chief merit of the dust-gas model consists in its undoubted simplicity, which primarily involves the fact that one can apply the already available results obtained in the kinetic theory of gas mixtures for solving the posed problem. Actually, the velocity of motion of a small object with respect to the center of mass of a set of gas molecules under the acting of a temperature gradient coincides, within the scope of the treated model, with the velocity of thermal-diffusion separation of the components of a mixture. It is equal to<sup>32,33</sup>

$$v_T = \frac{n^2}{n_1 n_2} D^{(T)} \frac{\nabla T}{T_0}. \quad (1.1)$$

Here  $n_1$  and  $n_2$  are respectively the number of small objects and the number of gas molecules per unit volume,  $n = n_1 + n_2$ ,  $D^{(T)}$  is the "thermal-diffusion" coefficient in the studied binary system, and  $T_0$  is a certain mean temperature. For the calculations,  $D^{(T)}$  must be fixed by the laws of interaction of the gas molecules with one another and with the surface of the object. We can neglect the mutual collisions of the objects suspended in the gas.

Let us first treat the case in which all the collisions obey the law of collision of elastic spheres. Here we allow for the fact that the masses of the objects and their dimensions are large in comparison with the corresponding characteristics of the gas molecules (yet we recall that  $R \ll \lambda$ ), while their number per unit volume is small. Then after obvious transformations of the

known expressions,<sup>32,33</sup> we arrive at the following formula for the velocity of motion of a small sphere with respect to the center of mass of the gas

$$\mathbf{v}_T = -\frac{3}{4} \frac{\eta}{\rho} \frac{\nabla T}{T_0}. \quad (1.2)$$

Here  $\eta$  is the dynamic viscosity of the gas, and  $\rho$  is its density. Thus the velocity of thermophoresis in a highly rarefied gas does not depend on the dimensions of the object, and is inversely proportional to the gas pressure. Mason and Chapman<sup>26</sup> have tried to account for the dependence of the velocity of thermophoresis on the type of gas-surface interaction within the framework of this model. Upon treating scattering according to Lambert's law in addition to elastic interaction, they arrived at Eq. (1.2) in both cases. It is more complicated to generalize this method to the case of other models of interaction of the gas molecules with the surface of the object. It is more convenient to do this by a different method, namely, the model that has been applied involving free-molecular flow.

### b) The model of free-molecular flow

The model of free-molecular flow of a gas around a small object is based on the obvious idea that the state of the gas is weakly perturbed by the presence of the small object in it. Actually, if the dimensions of the object are small in comparison with the mean free path of the gas molecules, then the probability is also small that a gas molecule that has been reflected from the object upon colliding with it will again suffer such a collision. On the other hand, when the characteristic scale of the temperature inhomogeneity of the gas is large in comparison with the mean free path of the molecules, then the distribution function of the molecules at a large enough distance from the object can be found by expanding a function satisfying the Boltzmann equation in the small parameter  $\lambda/L$ .

The distribution function  $f^+(\mathbf{r}, \mathbf{v})$  of the reflected molecules is determined by the nature of their interaction with the surface of the object. Let us restrict the treatment to monatomic gases while not treating nonlinear effects involving adsorption of gases on the surface of the object. Then, in the steady-state case (in which we can treat the scattering of gas molecules by the surface as practically instantaneous), we can write the probability that a molecule having the initial velocity  $\mathbf{v}'$  will have after collision with the surface of the object a velocity lying in a volume element  $d\mathbf{v}$  of velocity space near the velocity  $\mathbf{v}$  of the form  $W(\mathbf{v}' \rightarrow \mathbf{v})d\mathbf{v}$ . The operator  $W(\mathbf{v}' \rightarrow \mathbf{v})$  must be nonnegative, and moreover must satisfy the normalization condition

$$\int_{(\mathbf{v}\hat{n}) > 0} W(\mathbf{v}' \rightarrow \mathbf{v}) d\mathbf{v} = 1.$$

The integration is performed here over the half-space in which the projection of the velocity of the molecules on the direction of the normal drawn out trail from the object is positive. The distribution function of the reflected molecules must satisfy the condition of non-penetration:

$$(\mathbf{v}\hat{n}) f^+(\mathbf{v}) = \int_{(\mathbf{v}'\hat{n}) < 0} |(\mathbf{v}'\hat{n})| f(\mathbf{v}') W(\mathbf{v}' \rightarrow \mathbf{v}) d\mathbf{v}'.$$

The scattering kernel  $W$  depends on the nature of the atoms of the gas and on the surface, and also on the temperature of the surface and the type of treatment that it has had. Here any scattering kernel must satisfy the principle of detailed balancing:<sup>34</sup>

$$|(\mathbf{v}'\hat{n})| W(\mathbf{v}' \rightarrow \mathbf{v}) \exp\left(-\frac{\rho v'^2}{2p}\right) = (\mathbf{v}\hat{n}) W(-\mathbf{v} \rightarrow -\mathbf{v}') \exp\left(-\frac{\rho v^2}{2p}\right). \quad (1.3)$$

The condition of nonnegativity, the normalization condition, and the principle of detailed balancing are the three fundamental relationships that determine the form of the scattering kernel admissible as a mathematical model of scattering of gas molecules by the surface of a phase boundary. Until recently only four very simple models were known<sup>35</sup> (and their linear combinations) that didn't violate these limitations:

1) specular reflection:

$$W(\mathbf{v}' \rightarrow \mathbf{v}) = \delta\{\mathbf{v}' - \mathbf{v} + 2\mathbf{n}(\mathbf{v}\hat{n})\} \quad (1.4)$$

[ $\delta(x)$  is the Dirac delta function];

2) total backscattering:

$$W(\mathbf{v}' \rightarrow \mathbf{v}) = \delta(\mathbf{v} + \mathbf{v}'); \quad (1.5)$$

3) diffuse reflection with complete accommodation:

$$W(\mathbf{v}' \rightarrow \mathbf{v}) = \frac{2}{\pi} \left(\frac{\rho}{2p}\right)^2 (\mathbf{v}\hat{n}) \exp\left(-\frac{\rho v^2}{2p}\right); \quad (1.6)$$

4) elastic scattering (without changing the modulus of the velocity) following the cosine (Lambert's) law:

$$W(\mathbf{v}' \rightarrow \mathbf{v}) = \frac{1}{\pi} \frac{(\mathbf{v}\hat{n})}{v^3} \delta(v - v'). \quad (1.7)$$

Maxwell<sup>3</sup> combined Eqs. (1.4) and (1.6) into a single-parameter family of models

$$W(\mathbf{v}' \rightarrow \mathbf{v}) = (1 - \varepsilon) \delta(\mathbf{v}' - \mathbf{v} + 2\mathbf{n}(\mathbf{v}\hat{n})) + \varepsilon \frac{2}{\pi} \left(\frac{\rho}{2p}\right)^2 (\mathbf{v}\hat{n}) \exp\left(-\frac{\rho v^2}{2p}\right). \quad (1.8)$$

Here  $\varepsilon$  is the fraction of diffusely reflected molecules. More flexible models have been proposed in Refs. 36-39, though we shall spend no time on them.

Specular reflection and total backscattering are rather hypothetical models. People often employ the latter for describing highly roughened surfaces. Scattering with complete accommodation is the approximation closest to reality, especially if the gas molecules are temporarily captured by the surface. Apparently elastic scattering by the cosine law is realized with a moderately rough surface if its atoms are heavy in comparison with those of the gas and if capture doesn't occur upon interaction.

Upon assigning a scattering model, it is easy to find the momentum of the molecules reflected from the surface of the sphere. When summed with the momentum of the incident molecules and integrated over the surface of the sphere, it determines the overall force of action of the gas on the object immersed in it. This force proves to be the same for the cases of specular reflection and total backscattering. A different value is obtained for the other two models. As for the velocity of thermophoresis, specular reflection, backscattering,

and cosine-law scattering all lead to the same value of the velocity, while the velocity proves to be smaller by a factor of  $1 + (\pi/8)$  for diffuse reflection with complete accommodation. This result can be conveniently written as the following formula [cf. (1.2)]:

$$v_T = -\frac{3}{4} \frac{\eta}{1 + (\pi/8)} \frac{\eta}{\rho} \frac{\nabla T}{T_0} \quad (1.9)$$

## 2. THERMOPHORESIS IN WEAKLY RAREFIED GASES

If the size of an object suspended in the gas is not vanishingly small in comparison with the mean free path of the gas molecules, then this object appreciably perturbs the flux of the molecules incident on its surface. Hence the approach developed in the last chapter for calculating the velocity of thermophoresis in such cases proves inapplicable. One can construct a theory that accounts for the weak  $|\sim R/\lambda|$  perturbation of the stated flux of molecules by the object. Such studies have been published;<sup>84,85</sup> however, their results differ even qualitatively.

There is a possibility of constructing a method of successive approximations in the other limiting case in which the size of the object appreciably exceeds that of the mean free path. This involves hydrogasdynamics with slip. As we have mentioned, the velocity of thermophoresis of large objects was first calculated in such a formulation by Epstein,<sup>1</sup> who obtained the following expression for  $v_T$ :

$$v_T = -\frac{3}{4} \frac{\eta}{\rho} \frac{1}{1 + (1/2)(\kappa_i/\kappa_g)} \frac{\nabla T}{T_0} \quad (2.1)$$

Here  $\kappa_i$  and  $\kappa_g$  are respectively the heat conductivity of the object and of the gas. Essentially, Eq. (2.1) differs from (1.9) only in the factor  $(1 + \frac{1}{2}\kappa_i/\kappa_g)^{-1}$ , which stems from the effect of the object on the temperature distribution in the gas. It is precisely the presence of this factor that sharply diminishes the theoretical value of  $v_T$  for highly heat-conductive objects of large dimensions, which is not observed experimentally. This discrepancy with experiment stimulated Brock<sup>40-42</sup> to seek a refinement of the Epstein approach along the line of accounting for terms of the order of the Knudsen number  $Kn = \lambda/R$  in the boundary conditions that were omitted in Ref. 1. An analogous method was employed also in Refs. 43-46, and here they refined the values of the numerical coefficients at the same time.

Along with this, a methodology was developed and refined for calculating the velocity of thermophoresis based on thermodynamics of irreversible processes.<sup>43,45,46</sup> However, we should note that, in spite of the progress attained, the results of calculation obtained by the direct and the thermodynamic routes still differed from one another. Analysis shows that the main reason for this discrepancy consists in the fact that not all of the terms of the first order in the Knudsen number were taken into account in formulating the boundary conditions within the framework of hydrogasdynamics with slip, but only part of them. Studies<sup>47-50</sup> later appeared where the writers wrote out the series in the boundary conditions containing powers of  $Kn$  up to the fifth. Yet without sufficient grounds they omitted certain terms that were linear in  $Kn$ .

In line with what we've said, we do not consider it superfluous to describe in detail the method of deriving correct boundary conditions and the scheme of solution of the posed problem in the approximation that is linear in  $Kn$ .

### a) Boundary conditions

Let an inhomogeneously heated gas flow around a surface of arbitrary shape. Far from this surface the gas is described by the equations of hydrogasdynamics. Let us restrict the treatment to the Navier-Stokes approximation. At any arbitrarily small Knudsen number, there is a region near the phase boundary where the equations of hydrogasdynamics are inapplicable. In this region the state of the gas is described by solving the Boltzmann equation with the true kinetic boundary conditions, which transform into the Navier-Stokes approximation as we go away from the boundary, which approximation is obtained with certain fictive macroscopic boundary conditions. Our problem consists in formulating these boundary conditions precisely. An analogous situation occurs in the problem of heat propagation, diffusion, etc.

Let us write the true velocity of the gas in the form

$$u = v + v^{(Kn)}$$

Here  $v$  is the velocity that satisfies the equations of hydrogasdynamics in the Navier-Stokes approximation if the latter are assumed to hold up to the phase boundary, and  $v^{(Kn)}$  is the correction to the velocity that arises when we account for the state of the gas in the Knudsen layer. At a sufficient distance from the boundary surface, we have  $v^{(Kn)} \rightarrow 0$ , and  $u \approx v$ . If adsorption or desorption of molecules does not occur at the surface of the condensed phase, and the surface is impenetrable to the gas molecules, then the normal component of the true velocity  $u$  at the surface  $\Sigma$  must vanish. The equation of continuity for  $u$  and  $v$  implies that the correction  $v^{(Kn)}$  also satisfies the same equation. Upon integrating the latter along the normal to the surface and allowing for the fact that  $v^{(Kn)}$  vanishes at an infinite distance from the phase boundary, we get a boundary condition for the normal component of the velocity of the form

$$v_n|_{\Sigma} = -\frac{1}{\rho} \frac{\partial}{\partial x} \hat{I}_v^{(m)} \quad (2.2)$$

Here the symbol  $\hat{I}_v^{(m)}$  denotes the density of the tangential flux of mass localized in the Knudsen layer, integrated over the normal to the phase-boundary surface:

$$\hat{I}_v^{(m)} = \int_0^{\infty} \rho v_v^{(Kn)} dn \quad (2.3)$$

Analogously, upon denoting the density of the tangential flux of energy localized in the Knudsen layer by the symbol  $\hat{I}_v^{(e)}$  and introducing the stress tensor  $p_{\mu\nu} = p\delta_{\mu\nu} + \sigma_{\mu\nu}$ , we have the following boundary condition for the heat fluxes normal to the phase boundary:

$$\left( I_{en}^{(g)} - I_{in}^{(g)} + \frac{3}{2} p v_n + v_n p_{vn} \right)_{\Sigma} = -\frac{\partial}{\partial x} \left( \hat{I}_v^{(e)} \right) \quad (2.4)$$

The subscripts  $e$  and  $i$  relate the respective quantities to the gas and to the condensed phase.

In order to obtain the rest of the boundary conditions,

as well as the relationships that express the connection between the fluxes  $\hat{I}_\tau^{(m)}$  and  $\hat{I}_\tau^{(e)}$  and the macrocharacteristics of the gas, let us turn to the ideas of thermodynamics of irreversible processes (TIP). As will be shown below, the sought expressions have the form of linear relationships between certain "fluxes" and "forces" calculated at the phase boundary. We know from the textbooks on TIP that a correct formulation of these relationships requires primarily finding the entropy production of the system. In our case the problem is the entropy production at the phase boundary. We can calculate it by integrating the difference of the normal fluxes of entropy in the gas and in the condensed phase over the phase-boundary surface  $\Sigma$ . This method was first proposed in Ref. 51. It has been subsequently extended to the case of liquids and multicomponent gas mixtures,<sup>52,53</sup> as well as rarefied gases.<sup>49,50</sup> This method allows one to account for the effects at the gas-condensed phase boundary in most general form.

In order to calculate the flux of entropy in the gas, we shall write the expressions for the fluxes of heat and momentum for sufficiently low velocities and temperature gradients in the form

$$I_{e\mu}^{(q)} = -\kappa_e \left( \frac{\partial T_e}{\partial r_\mu} + \frac{2}{5} \frac{T_0}{p} \frac{\partial \sigma_{\mu\nu}}{\partial r_\nu} \right), \quad (2.5)$$

$$\sigma_{\mu\nu} = -2\eta \nabla_\mu \left( v_\nu + \frac{2}{5p} I_{e\nu}^{(q)} \right). \quad (2.6)$$

Here we have retained certain terms that correspond to the approximation of Barnett (see Ref. 32). We take  $\nabla_\mu \cdot a_\nu$  to mean the combination

$$\nabla_\mu \cdot a_\nu = \frac{1}{2} \left( \frac{\partial a_\mu}{\partial r_\nu} + \frac{\partial a_\nu}{\partial r_\mu} \right) - \frac{1}{3} \delta_{\mu\nu} \frac{\partial a_k}{\partial r_k}. \quad (2.7)$$

The numerical coefficient 2/5 is calculated in the single-polynomial approximation by the Chapman-Enskog method for monatomic gases.

Upon writing the expression for the entropy production per unit volume of gas by using (2.5) and (2.6), employing the equation of entropy balance, and restricting the treatment to the case in which only heat fluxes occur inside the condensed phase, we get the entropy production at the phase boundary in the form

$$\Delta S_W = \int d\Sigma \left[ \frac{1}{2} (I_{en}^{(q)} + I_{in}^{(q)}) \left( \frac{1}{T_i} - \frac{1}{T_e} + \frac{2}{5pT_0} \sigma_{nn} \right) + \frac{\sigma_{\tau n}}{T_0} \left( v_\tau + \frac{2}{5p} I_{e\tau}^{(q)} \right) + \frac{\hat{I}_\tau^{(m)}}{p} \frac{1}{T_0} \frac{\partial}{\partial x} (p + \sigma_{nn}) - \frac{1}{2} \hat{I}_\tau^{(e)} \frac{\partial}{\partial x} \left( \frac{1}{T_e} + \frac{1}{T_i} - \frac{2}{5pT_0} \sigma_{nn} \right) \right]. \quad (2.8)$$

Now we can write the linear relationships between the "fluxes" and the "thermodynamic forces" taken at the phase boundary. Let us choose as the "fluxes" the expressions

$$I_0 = \frac{1}{T_i} - \frac{1}{T_e} + \frac{2}{5pT_0} \sigma_{nn}, \quad I_2 = \hat{I}_\tau^{(e)} = \hat{I}_\tau^{(e)} - \frac{5}{2} \frac{p}{\rho} \hat{I}_\tau^{(m)}, \quad (2.9)$$

$$I_1 = \frac{1}{T_0} \left( v_\tau + \frac{2}{5p} I_{e\tau}^{(q)} \right), \quad I_3 = \frac{\hat{I}_\tau^{(m)}}{p}.$$

Then the "forces" take on the form

$$X_0 = \frac{1}{2} (I_{en}^{(q)} + I_{in}^{(q)}), \quad X_2 = \frac{1}{2} \frac{\partial}{\partial x} \left( \frac{1}{T_i} + \frac{1}{T_e} - \frac{2}{5pT_0} \sigma_{nn} \right), \quad (2.10)$$

$$X_1 = \sigma_{\tau n}, \quad X_3 = \frac{1}{T_0} \frac{\partial}{\partial x} p_{nn}.$$

Hence we have

$$I_0 = L_{00} X_0, \quad (2.11)$$

$$I_k = \sum_{i=1}^3 L_{ik} X_i, \quad k=1, 2, 3. \quad (2.12)$$

According to the Onsager principle we have  $L_{ik} = L_{ki}$ . Equations (2.11) and (2.12) for  $k=1$  express two more boundary conditions, while Eq. (2.12) for  $k=2$  or 3 relates the fluxes  $\hat{I}_\tau^{(e)}$  and  $\hat{I}_\tau^{(m)}$  with the bulk characteristics of the gas.

## b) Velocity of thermophoresis

The problem of determining the velocity of thermophoresis consists in calculating the relative velocity of the gas and of the object embedded in it when a small, constant temperature gradient is maintained at a large enough distance from the latter. The procedure of calculation consists in determining the temperature field in the vicinity of the object and the gas-velocity field caused by its inhomogeneous heating, and equating to zero the total force with which the gas acts on the object. The temperature distribution in the gas and the condensed phase is found by solving the Laplace equation, while the velocity and pressure fields in the gas are found from the Navier-Stokes and continuity equations. The integration constants are determined by using the boundary conditions written above.

Let us introduce the notation

$$L_{00} = -\frac{R}{\kappa_e T_0} C_i \text{Kn}, \quad L_{11} = -\frac{R}{\eta T_0} C_m \text{Kn}, \quad (2.13)$$

$$L_{12} = \left( \frac{3}{2} - k_{TS} \right) \frac{\eta}{\rho}, \quad L_{22} = R \kappa_e T_0^2 C_0 \text{Kn}, \quad L_{32} = R \frac{\eta}{\rho} T_0 C_0 \text{Kn}.$$

Upon restricting the treatment to terms proportional to powers of the Knudsen number no higher than the first, we get the boundary conditions in the form

$$\left. \begin{aligned} v_r &= \text{Kn} C_0 \frac{\eta}{\rho T_0} \frac{1}{R} \left( \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} \right) \frac{1}{2} (T_e + T_i), \\ v_\theta &= k_{TS} \frac{\eta}{\rho T_0} \frac{1}{R} \frac{\partial T_e}{\partial \theta} - \frac{R}{\eta} C_m \text{Kn} \sigma_{\theta\theta} \\ &\quad - \left( \frac{3}{2} - k_{TS} \right) \frac{\eta}{\rho T_0} \frac{1}{2\kappa_e} C_i \text{Kn} \frac{\partial}{\partial \theta} \frac{1}{2} (I_{e\tau}^{(q)} + I_{i\tau}^{(q)}), \\ T_e - T_i &= -\frac{R}{\kappa_e} C_i \text{Kn} \frac{1}{2} (I_{e\tau}^{(q)} + I_{i\tau}^{(q)}), \\ -\kappa_e \frac{\partial T_e}{\partial r} + \kappa_i \frac{\partial T_i}{\partial r} &= -\text{Kn} C_0 \kappa_e \frac{1}{R} \left( \cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} \right) \frac{1}{2} (T_e + T_i). \end{aligned} \right\} \quad (2.14)$$

Elementary calculations lead to the formula for the velocity of thermophoresis:

$$v_T = -k_{TS} \frac{\eta}{\rho T_0} \nabla T \frac{1}{1 + (1/2)(\kappa_i/\kappa_e)} \left\{ 1 + \text{Kn} \left[ \frac{\kappa_i}{\kappa_e} \left( \frac{1}{2} C_i + \frac{3}{4k_{TS}} C_i - \frac{3}{k_{TS}} C_m \right) - \frac{C_0}{k_{TS}} + C_m \left( \frac{3}{k_{TS}} - 2 \right) + \frac{1}{1 + (1/2)(\kappa_i/\kappa_e)} \left( C_0 - \frac{\kappa_i}{\kappa_e} C_i \right) \right] \right\}. \quad (2.15)$$

When  $\text{Kn} = 0$ , Eq. (2.15) formally coincides with the Epstein formula (2.1). As we have pointed out above, the Epstein formula agrees poorly with experiment, especially for objects of high heat conductivity. Equation (2.15) implies (see also Refs. 40-46, 50) that when  $\kappa_i \gg \kappa_e$ , the velocity of thermophoresis does not depend on the ratio of the heat conductivities of the object and of the gas. At least qualitatively, experiment<sup>9-19</sup> reveals this specific behavior of highly heat-conductive objects in a temperature-gradient field.

Equation (2.15) implies another interesting result: when

$$C_t = \frac{6C_m}{k_{TS} + (3/2)}$$

the velocity of thermophoresis of highly heat-conductive objects must change sign (negative thermophoresis). This effect was not predicted in Refs. 40, 44, and 45. Brock<sup>42</sup> first pointed out the possibility of negative thermophoresis. Dwyer<sup>47</sup> has obtained a similar result. Vestner *et al.*<sup>49-50</sup> and Sone and Aoki<sup>54</sup> also note it. Experimentally the phenomenon of negative thermophoresis has not yet been observed in explicit form, so that the problem of its existence remains open.

### 3. KINETIC COEFFICIENTS

The coefficients of viscous (isothermal) slip  $C_m$ , and thermal slip  $k_{TS}$ , the temperature jump  $C_t$ , etc., can be calculated only within the framework of the kinetic theory of gases. An analogous situation exists in the problem of adjusting the equations of hydrogasdynamics by establishing the connections between the fluxes of matter, momentum and energy and the density, mass velocity and temperature. Yet a substantial distinction consists in the fact that here one should account for the collisions of the molecules with the boundary surface as well as for those with one another.

Maxwell<sup>3</sup> first solved such a problem. He noted the discontinuous nature of the distribution function of the gas molecules near the surface of objects bounding a gas, and he obtained a solution upon postulating that the molecules incident on the surface have a distribution that doesn't differ from the bulk distribution up to the very wall, while the reflected molecules are in equilibrium with the wall. In this model the thickness of the Knudsen layer, where the gas molecules gradually change their distribution, is taken to be zero. Nevertheless, even within the framework of this crude model, Maxwell obtained a rather good estimate of the coefficients of thermal and viscous slip. These calculations were subsequently refined.<sup>55-61</sup> We should note that, apart from the direct calculation of the stated coefficients, the structure of the Knudsen layer itself is of great interest. Possibilities have currently arisen of not only theoretical, but also experimental study of this structure.<sup>62, 63</sup>

The first attempt at theoretical analysis of the phenomena occurring in the layer of thickness of the order of the mean free path of the gas molecules near the surface of a solid was apparently the study of Gross *et al.*,<sup>64, 65</sup> where the method of half-range expansions proposed by Yvon<sup>66</sup> was applied to solving the Couette problem. Its essence amounts to the following. Let the small deviation of the distribution function from the Maxwellian value be a function of the distance from the phase boundary. Let us expand it in a series in certain polynomials in the velocity, similarly to what is done, e.g., in the Chapman-Enskog method. However, we assume the coefficients of the expansion to be functions of the distance from the boundary. It turns out that the method of half-range expansions in any approximation gives better results than the usual method of polynomial expansions (full range) in an approximation that is twice as high. However, the cost of this improvement is com-

plication of the system of equations.

However, it is physically obvious that the correction to the equilibrium distribution determined by solving the boundary problem must acquire a symmetrical form with increasing distance from the boundary that is the same for molecules of both types. Under the condition that the external perturbation is small, we can require that this correction coincides with the Chapman-Enskog distribution at a great enough distance from the boundary. On the one hand, this approach, which was proposed in Ref. 67 and was then developed in Refs. 68 and 69, permitted one to determine the form of the approximation of the distribution function, and on the other hand, to point out certain important connections between the coefficients of the expansion. The latter allowed them to simplify the system of equations substantially for determining these coefficients. Let us start with establishing these connections.

#### a) On some integral relationships

Let us seek the solution of the steady-state Boltzmann equation

$$c \frac{\partial f}{\partial r} = I(f, f) \quad (3.1)$$

in the form

$$f = f^{(0)} (1 + \varphi). \quad (3.2)$$

Here we have  $\varphi \ll 1$ . We shall assume that a good enough approximation of the function  $\phi(c, x)$  can be represented in the form of the series

$$\begin{aligned} \varphi^+(c, x) &= \sum_i a_i^+(x) P_i(c), \\ \varphi^-(c, x) &= \sum_i a_i^-(x) P_i(c). \end{aligned} \quad (3.3)$$

Here the  $P_i(c)$  are certain polynomials in the velocity of the molecule. The superscripts + and - refer respectively to molecules having  $c_x > 0$  and  $c_x < 0$ . (The  $x$  axis lies along the normal to the boundary surface inside the gas.) Thus we have

$$\varphi(c, x) = \frac{\varphi^+ + \varphi^-}{2} + \frac{\varphi^+ - \varphi^-}{2} \text{sign } c_x, \quad (3.4)$$

where

$$\text{sign } c_x = \frac{c_x}{|c_x|}.$$

Let us substitute (3.4) in Eq. (3.1), multiply by the polynomial  $P_k(c)$ , and integrate over the velocities. The moments of the Boltzmann collision integral that arise on the right-hand side of the system of equations obtained in this way (the recent literature<sup>71</sup> has termed them the integral brackets)

$$\mathcal{L}_{ik} = [P_i(c), P_k(c)] = \frac{1}{n^2} \int f^{(0)} P_i(c) I [P_k(c)] dc \quad (3.5)$$

constitute the object of study of this section.

A method of calculating integral brackets that don't contain the symbol "sign" has been presented in detail in the book (Ref. 31). The expressions with sign  $c_x$  (half-range integral brackets) for a simple monatomic gas were first calculated by Wang-Chang and Uhlenbeck.<sup>72</sup> The calculation of even the simplest of them proves to be a highly unwieldy matter. Numerical methods<sup>73</sup> have been proposed whose substantial flaw,

in our opinion, consists in the impossibility of determining *a priori* the necessary accuracy of calculations. Hence they require unwarranted large expenditures of machine time. The arguments presented below open up also a new pathway for estimating the necessary accuracy of calculations.

Let us study the Boltzmann equation in the Chapman-Enskog form<sup>32</sup>:

$$f^{(0)} \left[ \left( c^2 - \frac{5}{2} \right) c_i \frac{\partial \ln T}{\partial r_i} + 2 \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right) \frac{\partial v_i}{\partial r_j} \right] = f^{(0)} I(\varphi). \quad (3.6)$$

As we know, its solution in the bulk of the gas is sought in the form of series in Sonin-Laguerre polynomials. The method of successive approximations within the scope of a theory that is linear in the derivatives of the temperature and velocity consists in accounting for one, two, etc., terms of the expansion. In the one-polynomial approximation, the solution of Eq. (3.6) for any model of the interaction of the molecules has the form

$$\varphi = -\frac{1}{n} \left[ a_1 \left( \frac{5}{2} - c^2 \right) c_i \frac{\partial \ln T}{\partial r_i} + b_1 \left( c_i c_j - \frac{1}{3} \delta_{ij} c^2 \right) \frac{\partial v_i}{\partial r_j} \right]. \quad (3.7)$$

Here the coefficients  $a_1$  and  $b_1$  are connected by the relationship

$$-4a_1 = 3b_1. \quad (3.8)$$

We can calculate them upon assigning a model for the interaction of the molecules.

For convenience of further calculations, we shall introduce the notation:

$$\left. \begin{aligned} P_1(c) &= c_x \operatorname{sign} c_x, & P_4(c) &= c_x c_x^2, \\ P_2(c) &= c_x c_x, & P_5(c) &= c_x c_x^2 \operatorname{sign} c_x, \\ P_3(c) &= c_x c_x \operatorname{sign} c_x, & P_6(c) &= c_x \left( \frac{5}{2} - c^2 \right) \\ & & P_7 &= c_x \left( \frac{5}{2} - c^2 \right) \operatorname{sign} c_x. \end{aligned} \right\} \quad (3.9)$$

Let us examine two-dimensional isothermal shear flow. Equation (3.6) acquires the form

$$-\frac{2}{b_1} n f^{(0)} c_x c_x = f^{(0)} I(c_x c_x).$$

We multiply it successively by  $P_1$ ,  $P_2$ ,  $P_5$ , and  $P_7$ , and integrate it over velocity space. The integrals that are obtained on the left-hand side are calculated in elementary fashion. In line with (3.5), we get the integral brackets on the right-hand side. Consequently we have

$$\begin{aligned} -\frac{\pi}{b_1} &= [P_1, P_2], & -\frac{\pi}{b_1} &= [P_2, P_5], \\ -\frac{\pi \sqrt{\pi}}{2b_1} &= [P_2, P_2], & \frac{\pi}{2b_1} &= [P_2, P_7]. \end{aligned} \quad (3.10)$$

Now let us examine the one-dimensional problem of heat conductivity. We have from (3.6)

$$\frac{1}{a_1} f^{(0)} n \left( \frac{5}{2} - c^2 \right) c_x = f^{(0)} I \left[ \left( \frac{5}{2} - c^2 \right), c_x \right].$$

Upon multiplying by the polynomials  $P_3$  and  $P_6$  and integrating over the velocities, we get

$$-\frac{\pi}{4a_1} = [P_3, P_6], \quad \frac{5}{4} \frac{\pi \sqrt{\pi}}{a_1} = [P_6, P_6]. \quad (3.11)$$

By comparing (3.10) and (3.11) with allowance for (3.8), we get the equation

$$\mathcal{L}_{12} = \mathcal{L}_{25} = \frac{2}{\sqrt{\pi}} \mathcal{L}_{22} = -3\mathcal{L}_{36} = \frac{3}{5\sqrt{\pi}} \mathcal{L}_{66} = -2\mathcal{L}_{27}. \quad (3.12)$$

Analogously we can show that the following relationships

hold:

$$\sqrt{\pi} \mathcal{L}_{34} = \mathcal{L}_{44}, \quad \sqrt{\pi} \mathcal{L}_{36} = \mathcal{L}_{46}. \quad (3.13)$$

As the above derivation implies, Eqs. (3.12) and (3.13) are a direct consequence of the one-polynomial expansion of (3.7), and they hold for various models of the intermolecular interaction to some degree of accuracy.<sup>11</sup> Thus, for molecules that interact according to the law  $\sim r^{-5}$ , Eqs. (3.12) and (3.13) are exact. It is pertinent to note that, as a rule, the applications of the method of half-range expansions do not extend beyond the framework of the one-polynomial expansion. Hence, in solving boundary problems of the kinetic theory by the method of half-range expansions, one should treat a violation of Eqs. (3.12) and (3.13) as going beyond the accuracy of the theory.<sup>68,74</sup> The proposed modification of the method of half-range expansions enables the satisfaction of a far more important physical requirement at the cost of a certain coarsening of the numerical values of the sought coefficients, which can easily be estimated by comparison with the values obtained by other methods. Namely, it enables a correct limiting transition to the distribution function in the bulk of the gas far from walls. Moreover, the relationships (3.12) and (3.13) decrease by a factor of two the number of half-range integral brackets that must be directly calculated, and also they substantially simplify the system of equations for finding the coefficients of the expansion (3.3). Finally, one can use them to estimate the accuracy to which one is reasonably limited in performing numerical calculations of the values of  $L_{ik}$ .

### b) Nonisothermal Poiseuille flow in a planar channel

The solution of the flow of a gas in a plane-parallel channel of unit width when small constant longitudinal temperature and pressure gradients are maintained in it enables one to calculate a number of the kinetic coefficients entering into (2.15). Let the length  $L$  of the channel exceed considerably both the distance  $2d$  between the plates and the mean free path of the gas molecules. Let us draw the  $z$  axis along the axis of the channel and the  $x$  axis along the normal to the walls inside the gas, while taking as the origin the symmetry axis in the space between the plates. Here, as one can easily show,<sup>8,55</sup> the solution of the steady-state Boltzmann equation (3.1) is reduced to solving the chain of equations

$$c_x \frac{\partial f^{(0)}}{\partial x} = I(f^{(0)}, f^{(0)}), \quad (3.14)$$

$$c_z \frac{\partial f^{(0)}}{\partial z} + f^{(0)} c_x \frac{\partial \varphi}{\partial x} + c_x \varphi \frac{\partial f^{(0)}}{\partial x} = f^{(0)} I(\varphi), \quad (3.15)$$

etc.

Equation (3.1) is satisfied by the local Maxwell distribution, whose parameters do not depend on  $x$ . Let us use it as a zero-order approximation to the desired solution. Equation (3.15) is suitable for arbitrary values of

<sup>11</sup>Analogously it is not hard to find the relationships that are also satisfied by the integral when one employs more than one polynomial in the expansion of the solution of the Boltzmann equation.

the Knudsen number  $\text{Kn}_d = \lambda/d$ , and its solution allows one to determine the macrocharacteristics of the flow at arbitrary rarefactions at any distances from the surfaces bounding the gas. Indeed, one can get an exact solution of Eq. (3.15) only in certain special cases. Usually, however, people resort to various types of approximate methods when treating such problems. We shall employ here the modified method of half-range expansions of Sec. a) of Chap. 3.

Following Maxwell, we shall assume that the distribution function of the molecules near the surface of the walls of the channel suffers a discontinuity at  $c_x = 0$ . However, we shall require it to be continuous in the bulk of the gas for  $\text{Kn}_d \ll 1$  and to go over into the well-known Chapman-Enskog solution. This determines the form of approximation of the function  $\varphi(x, c)$ :

$$\varphi^\pm = c_x \left[ a_0^\pm(x) + c_x a_1^\pm(x) + \left(c^2 - \frac{5}{2}\right) a_2^\pm(x) + \left(c_x^2 - \frac{1}{2}\right) a_3^\pm(x) \right]. \quad (3.16)$$

The functions  $a_i^\pm(x)$  must satisfy the following symmetry conditions:

$$\begin{aligned} a_{0,2,3}^+(x) &= a_{0,2,3}^+(-x), \\ a_1^+(x) &= -a_1^+(-x), \end{aligned}$$

and certain boundary conditions, for which we shall take the Maxwellian conditions of (1.8):

$$\begin{cases} a_0^-(d) = (1-\varepsilon) a_0^+(d), \\ a_1^-(d) = -(1-\varepsilon) a_1^+(d), \\ a_2^-(d) = (1-\varepsilon) a_2^+(d), \\ a_3^-(d) = (1-\varepsilon) a_3^+(d). \end{cases}$$

Let us substitute the approximation (3.16) into Eq. (3.15) and multiply successively by the polynomials  $c_x(1 \pm \text{sign} c_x)$ ,  $c_x c_x(1 \pm \text{sign} c_x)$ ,  $c_x(c^2 - \frac{5}{2})(1 \pm \text{sign} c_x)$ , and  $c_x(c_x^2 - \frac{1}{2})(1 \pm \text{sign} c_x)$ , and integrate over the velocities. As a result we arrive at a system of eight differential equations for determining the function  $a_i^\pm(x)$ . Accounting for Eqs. (3.12) and (3.13) allows this system to be simplified, and makes it possible to get an analytic solution.<sup>8</sup> Hence we can easily calculate the mean velocity of the gas and the flux density of heat along the channel:

$$\begin{aligned} \frac{I_2^{(m)}(x)}{\rho} &= \frac{d^3}{2\eta} \left[ \left( \frac{x^3}{d^3} - 1 \right) - \frac{5\pi}{8} \text{Kn}_d \frac{2-\varepsilon}{\varepsilon} F_1(x, \varepsilon) \right] \frac{\partial p}{\partial x} \\ &\quad - \frac{15}{8} \frac{\eta}{\rho} F_2(x, \varepsilon) \frac{\partial \ln p}{\partial x} + \frac{3}{4} \frac{\eta}{\rho} F_3(x, \varepsilon) \frac{\partial \ln T}{\partial x}, \end{aligned} \quad (3.17)$$

$$\begin{aligned} I_2^{(q)} &= \frac{3}{2} \frac{\eta}{\rho} \left[ 1 + \frac{1}{2} \Phi_1(x, \varepsilon) + \frac{2-\varepsilon}{\varepsilon} \text{Kn}_d \Phi_2(x, \varepsilon) \right] \frac{\partial p}{\partial x} \\ &\quad - \kappa_e \left[ 1 + \frac{\varepsilon}{2-\varepsilon} \text{Kn}_d \Phi_3(x, \varepsilon) \right] \frac{\partial T}{\partial x}. \end{aligned} \quad (3.18)$$

Here  $F_i(x, \varepsilon)$  and  $\Phi_i(x, \varepsilon)$  are certain functions of the distance  $x$  from the wall of the channel and of the momentum accommodation coefficient  $\varepsilon$ . We get the following values for the coefficients of viscous and thermal slip from (3.17) with  $|x-d| \gg \lambda$  and from (2.14):

$$C_m = \frac{5\pi}{16} \frac{2-\varepsilon}{\varepsilon} F_1(0, \varepsilon), \quad k_{TS}^{(0)} = \frac{3}{4} F_3(0, \varepsilon).$$

The values of the numerical coefficients depend on the adopted model of interaction of the gas molecules. For a hard-sphere model<sup>8</sup> we have

$$C_m = \frac{5\pi}{16} \frac{2-\varepsilon}{\varepsilon} \left\{ 1 + \frac{1}{\Delta(\varepsilon)} \frac{\varepsilon}{2-\varepsilon} \left[ 0.358 + \frac{\varepsilon}{2-\varepsilon} 0.484 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^2 0.673 \right] \right\}, \quad (3.19)$$

$$k_{TS}^{(0)} = \frac{3}{4} \left\{ 1 + \frac{1}{\Delta(\varepsilon)} \frac{\varepsilon}{2-\varepsilon} \left[ 1.44 + \frac{\varepsilon}{2-\varepsilon} 3.75 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^2 2.46 \right] \right\}. \quad (3.20)$$

Here we have

$$\Delta(\varepsilon) = 1 + \frac{\varepsilon}{2-\varepsilon} 4.07 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^2 5.55 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^3 2.46. \quad (3.21)$$

The values of the corresponding coefficients derived by Maxwell<sup>8</sup> have been separated out as the factors in front of the brackets in (3.19) and (3.20). We see that they amount to the limiting values of  $C_m$  and  $k_{TS}^{(0)}$  as  $\varepsilon \rightarrow 0$  (almost specular reflection). In the other limiting case where  $\varepsilon = 1$  (diffuse reflection), we have  $C_m = 1.13$  and  $k_{TS}^{(0)} = 1.19$ . The relation of  $k_{TS}^{(0)}$  to  $\varepsilon$  is rather well approximated by a linear function throughout the range of variation of  $\varepsilon$ . This agrees well with the results of other calculations.<sup>55-61</sup>

We note that the thermal slip coefficient  $k_{TS}$  that enters into Eq. (2.15) differs from the corresponding value of  $k_{TS}^{(0)}$  from (3.20) for a plane surface in that it depends on  $\text{Kn}$  (effect of curvature of the surface on the velocity of thermal slip). In the studied approximation we have  $k_{TS} = k_{TS}^{(0)}(1 + a\text{Kn})$ . The calculations<sup>87,88</sup> for a model kinetic equation respectively gave  $a = 1.16$  and 4.06.

The term proportional to  $F_2(x, \varepsilon)$  in (3.17) describes second-order slip of the order of  $|\text{Kn}_d^2|$ ; its study lies outside the scope of the approximation developed here (see Refs. 55 and 75).

Now let us examine Eq. (3.17). The first component, which consists of three terms, describes the heat flux in the absence of a temperature gradient. It is sometimes called the isothermal heat transport. The component that does not depend on the coordinate (the bulk isothermal heat transport) is obtained in Burnett's approximation by the ordinary kinetic theory of gases.<sup>32</sup> The two other terms describe the heat flux localized in the Knudsen layer. This component of the flux explicitly contains a dependence on the law of interaction of the gas molecules with the wall of the channel. If we average Eqs. (3.17) and (3.18) across the channel, then we get a relationship expressing the symmetry of the kinetic coefficients

$$\frac{1}{2} \bar{F}_3 = 1 + \frac{1}{2} \bar{\Phi}_1 + \frac{\varepsilon}{2-\varepsilon} \text{Kn}_d \bar{\Phi}_2.$$

This is in full accord with the Onsager principle.

The second component of (3.18) also has an analogous structure: its first term describes the heat flux in the bulk of the gas (ordinary heat conductivity), and the second term describes the heat transport inside the Knudsen layer. It declines exponentially as we go away from the wall, and at high enough pressures its contribution to the heat transport along the channel becomes arbitrarily small. Yet it is precisely the fluxes of heat and matter localized in the Knudsen layer that determine the values of the coefficients  $C_q$  and  $C_v$  (see Eqs. (1.5) and (1.6)). Actually, let us integrate the surface ( $x$ -dependent) components of the fluxes of (3.17) and (3.18) over the thickness of the Knudsen layer. In line with the definitions of  $\hat{I}_T^{(q)}$  and  $\hat{I}_T^{(m)}$ , we have

$$C_q = 1.12 \frac{1}{\Delta(\varepsilon)} \frac{\varepsilon}{2-\varepsilon} \left[ 1 + \frac{\varepsilon}{2-\varepsilon} 3.08 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^2 1.72 \right], \quad (3.22)$$

$$C_v = 1.16 \frac{1}{\Delta(\varepsilon)} \frac{\varepsilon}{2-\varepsilon} \left[ 1 + \frac{\varepsilon}{2-\varepsilon} 3.23 + \left( \frac{\varepsilon}{2-\varepsilon} \right)^2 1.86 \right]. \quad (3.23)$$

In closing, let us give one of the results of calculating



the coefficient  $C_i$ . People usually find it by a method independent of the determination of the other coefficients, since  $C_i$  is associated with the energy accommodation coefficient  $\alpha$ , which differs from  $\varepsilon$ , which defines the accommodation of momentum.

The value of  $C_i$  obtained by solving the linearized Boltzmann equation by the variation method for a hard-sphere model<sup>86</sup> has the form

$$C_i = 1.78 \frac{2-\alpha}{\alpha} (1 + 0.162\alpha). \quad (3.24)$$

The reader can find a detailed review of the results of theoretical and experimental study of the temperature jump in Refs. 76 and 77.

#### 4. BOUNDARY PROBLEMS OF THE KINETIC THEORY AND THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

A somewhat independent method of treating the boundary problems of the kinetic theory was first proposed in Ref. 4. It is based on employing the concepts of the thermodynamics of irreversible processes. It has been subsequently applied also to solving problems of thermophoresis in weakly rarefied gases, and also in a number of other problems. Its essence is the following. Instead of directly calculating the effect of interest to us, one solves another problem that is, so to speak, symmetrical (in Onsager's sense) to that being treated. Then one writes down the sought result in line with the principle of symmetry of the kinetic coefficients. In addition to its purely methodological importance in allowing one to control the procedure of rather unwieldy calculations, this pathway is also of independent interest. It has led to the discovery of a hitherto unknown effect of thermal polarization of an object in a flux of rarefied gas and has suggested the idea of designing an experiment for studying the phenomenon of thermophoresis on a completely new basis, as well as studying the nature of the interaction of gas molecules with the surface of solid and liquid objects.

Moreover, there are cases in which such an indirect calculation is preferable to a direct one, since it allows one to deal with a smaller number of polynomials in the expansion of the distribution function in solving the kinetic equation. However, we note to avoid misunderstanding that, just as in the direct calculation, the thermodynamic method cannot dispense with the calculation of the kinetic coefficients by solving the Boltzmann equation (see Sec. b of Chap. 3).

In spite of the evident success of this approach, statements have appeared in the literature<sup>78-80</sup> that cast doubt on the validity of its application under conditions in which the mean free path of the gas molecules becomes comparable with the characteristic dimensions of the problem. The basis of these statements has been the fact that the connection between the kinetic theory and thermodynamics of irreversible processes has been established<sup>81</sup> only for processes that can be described within the framework of the Navier-Stokes approximation of the Chapman-Enskog method, which is not suitable for solving boundary problems.

Therefore we shall first take up the problem of the applicability of TIP to studying phenomena in which the essential role is played by the properties of the gas inside the Knudsen layers at the surface of the gas-condensed phase boundary and of the connection of the TIP with the kinetic theory of gases in treating such problems.

#### a) On the entropy production in a bounded volume of gas

Let us treat this problem with the example of solving the problem of nonisothermal Poiseuille flow. We turn to Eq. (3.15) and multiply both sides by  $\phi$ , integrate over the momenta of the molecules, and average over the volume of the gas. Apart from a constant factor, we get on the right-hand side the entropy production  $\Delta S$ . We employ the following expression for  $f^{(0)}$ :

$$f^{(0)} = \exp \left[ \frac{\rho}{p} \left( \mu - \frac{1}{2} v^2 \right) \right].$$

Here  $\mu$  is the chemical potential of the gas, and we introduce the following notation for the vectors of the flux of mass density  $\mathbf{I}^{(m)}$  and of energy  $\mathbf{I}^{(e)}$ :

$$\mathbf{I}^{(m)}(x) = m \int \phi f^{(0)} \mathbf{v} \, dp,$$

$$\mathbf{I}^{(e)}(x) = \frac{1}{2} m \int \phi f^{(0)} v v^2 \, dp.$$

Consequently, after averaging over the cross-section of the channel we get

$$\Delta S = (\mathbf{I}^{(e)} - \mu \mathbf{I}^{(m)}) \frac{\nabla T}{T_0^2} + \mathbf{I}^{(m)} \frac{\nabla \mu}{T_0} - \frac{1}{2d} \int f^{(0)} v_x \frac{v^2}{2} \, dp \Big|_{-d}^d. \quad (4.1)$$

Here  $\nabla T$  and  $\nabla \mu$  are the longitudinal gradients of the temperature and of the chemical potential.  $\mathbf{I}^{(m)}$  and  $\mathbf{I}^{(e)}$  are the fluxes of mass and energy averaged over the cross-section of the channel. Thus the entropy production differs from the classical expression by the presence of an additional term involving the properties of the gas inside the Knudsen layer at the walls of the channel. Now let us consider the fact that the gas molecules change their distribution upon colliding with the walls. Hence an additional entropy production arises here that must be added to Eq. (4.1) to obtain the total entropy production per unit volume of the channel. We shall proceed as follows to calculate this quantity. Let us find the difference of entropy fluxes that are carried by the gas molecules moving toward and away from the wall. Molecules having the distribution  $f^*$  are incident on the surface of the wall  $x = d$ ; the distribution of the scattered molecules is  $f^-$ . If the interaction follows a law differing from the specular law, then these functions differ substantially. The entropy flux carried to the wall by the gas molecules is<sup>33</sup>

$$I^{(S)}(0) = - \int_{v_x > 0} \mathbf{v} f^* \ln f^* \, dp.$$

The flux carried away by the reflected molecules is

$$I^{(S)}(\delta) = \int_{v_x < 0} \mathbf{v} f^- \ln f^- \, dp.$$

Here  $\delta$  is the arbitrary thickness of the layer of matter in the wall in which the transformation of the distribution function occurs. The balance equation

$$\text{div } \mathbf{I}^{(S)} = \Delta S_w$$

determines the desired entropy production  $\Delta S_w$  in the

layer  $\delta$ . The total entropy production in the surface layer per unit volume of gas exactly compensates the additional term in Eq. (4.1), and the entropy production in the gas acquires the classical form of a bilinear combination of thermodynamic forces and fluxes. The linear relationships between the fluxes and forces also conserve their form.<sup>2)</sup>

The obtained result solves positively the problem of the validity of applying TIP to problems in which the properties of the gas inside the Knudsen layer play an essential role.

Thermodynamics of irreversible processes enables one to solve another problem of no small importance that arises in solving the kinetic equation by the method of polynomial expansions. The problem is that of the ambiguous choice of velocity polynomials that must be employed for constructing the moment equations. Although this problem has already been discussed in the literature,<sup>56</sup> current practice has the choice of polynomials dictated by notions of convenience and simplicity of the calculations. Yet we shall show that the requirement that the distribution function found by the approximate method should satisfy the equation of entropy balance is equivalent to a certain condition determining the choice of polynomials that is sufficient, but generally not necessary.

In the steady-state case the equation of entropy balance is equivalent to the relationship

$$\int dp \varphi f^{(0)} \left[ v_z \frac{\partial \ln f^{(0)}}{\partial z} + v_x \frac{\partial \varphi}{\partial x} - I(\varphi) \right] = 0. \quad (4.2)$$

Naturally, the exact solution of Eq. (3.15) satisfies it. We shall require that the solution sought, while approximate, should nevertheless also satisfy (4.2). Let us write it as a series in polynomials in the velocity of the molecules:

$$\varphi = \sum a_i(x) P_i(c). \quad (4.3)$$

Upon substituting the expansion (4.3) into Eq. (4.2) and introducing the notation

$$I_i = \int dp f^{(0)} P_i(c) \left[ v_z \frac{\partial \ln f^{(0)}}{\partial z} + v_x \sum_k \frac{\partial a_k(x)}{\partial x} P_k(c) \right],$$

we represent the local entropy production in the form

$$\int dp \varphi f^{(0)} I(\varphi) = \sum_i a_i I_i.$$

Consequently we can write the linear relationships between the "fluxes" and the "forces"  $a_i$  in the form

$$I_i = \sum_k \mathcal{L}_{ik} a_k. \quad (4.4)$$

We can easily see that the equations (4.4) amount to the moment equations obtained from (3.15) by using the

<sup>2)</sup>We note that the derivation of the expression for the entropy production in a channel that was proposed in Ref. 81 generally loses validity for rarefied gases. This involves the fact that the calculations of Ref. 81 presume the absence of an entropy flux through the surface of the channel when the heat flux normal to the boundary surface is zero. Yet, as we see from what we've said above, the effects of rarefaction cause an entropy flux through the surface to occur in the presence of any inhomogeneity in the gas.

same polynomials with which the function  $\phi$  has been approximated, while the coefficients  $L_{ik}$  are the integral brackets of (3.5). As we know, the latter have the property of symmetry with respect to permutation of indices. We also know that this method of constructing the moment equations ensures that the condition of entropy balance will be satisfied, in contrast to the usual, formal method, in which one applies arbitrary polynomials in the velocity. The approximate distribution function found in this way determines the fluxes  $I_i$  in such a way that the proportionality coefficients relating them to the forces  $a_i$  satisfy the Onsager symmetry principle.

## b) The velocity of thermophoresis

Let us employ the methods of TIP to calculate the velocity of thermophoresis. Let us fix the velocity of relative motion of the gas and the sphere and calculate the change in temperature of the gas in the vicinity of the sphere caused by this motion. Then, upon employing the symmetry principle, we shall find the velocity of thermophoresis. We should stress that the problem in both cases is solved under the assumption that the Reynolds number is small. Thus the viscous heating is small, being proportional to  $Re^2$ . We note in passing that the thermostress effects treated in Ref. 82 are also small.

We shall begin by calculating the entropy production  $\Delta S_V$  in the gas when it is moving with respect to the sphere with the small constant velocity  $v_0$ , while a small temperature gradient is maintained at a sufficiently large distance from the sphere. In the system of coordinates associated with the sphere, the equation of entropy balance has the form

$$\text{div} (v_0 S + I^{(S)}) = \Delta S.$$

We integrate this equation over the volume of the gas. On the right-hand side we get the sought entropy production  $\Delta S_V$ . We now transform the left-hand side by Gauss' theorem into an integral over a surface surrounding the sphere. We can conveniently take as such a surface a cylinder of large enough radius with its center of symmetry coinciding with the center of the sphere and its axis lying along the temperature gradient ( $z$  axis). If we take the radius of the cylinder to be much larger than its altitude, then integration over the surface of the cylinder is reduced to integrating over its ends, i.e.,

$$\Delta S_V = 2\pi \int_0^\infty (v_{0z} S + I_z^{(S)}) r dr \Big|_{z=-H}^{z=H}.$$

Upon considering the constancy of the vector of energy flux density, we get

$$\Delta S_V = -2\pi \int_0^\infty r dr \left[ \frac{v_{0z}}{T_0} \Delta p + I_z^{(q)}(z=H) \frac{\Delta T}{T_0^2} \right]. \quad (4.5)$$

The symbols  $\Delta p$  and  $\Delta T$  denote the drop in pressure and temperature between the ends of the cylinder at the coordinates  $z=H$  and  $z=-H$ . The temperature of the gas in the vicinity of the sphere is expressed in the form

$$T = T_0 + \frac{(Br)}{r^2} + (\nabla T)r.$$

We shall use Eq. (2.5) for the heat flux density. We

transform (4.5), while keeping the terms quadratic with respect to the small deviation from equilibrium. After simple calculations we get

$$\Delta S_V = \frac{Fv_0}{T_0} + \frac{4\pi\kappa_e(BVT)}{T_0^2}.$$

Here  $\mathbf{F}$  is the total force that the gas exerts on the sphere. We can write the linear relationships between the "fluxes" and the "forces" in the form

$$\begin{aligned} v_0 &= \Lambda_{11} \frac{F}{T_0} + \Lambda_{12} \frac{\nabla T}{T_0^2}, \\ 4\pi\kappa_e \mathbf{B} &= \Lambda_{21} \frac{F}{T_0} + \Lambda_{22} \frac{\nabla T}{T_0^2}. \end{aligned} \quad (4.6)$$

The velocity of thermophoresis is (with reversed sign) the value of  $v_0$  at  $F=0$ , or

$$v_T = -\Lambda_{12} \frac{\nabla T}{T_0^2}.$$

We now find the proportionality coefficient  $\Lambda_{12}$  by calculating the change in temperature of the gas caused by its flow with respect to the sphere and by employing the symmetry principle. When  $\nabla T=0$ , the second equation of (4.6) implies that

$$\Lambda_{21} = 4\pi\kappa_e T_0 \frac{(\mathbf{B}\mathbf{F})}{F^2}.$$

Thus the calculation of the velocity of thermophoresis by the thermodynamic method is reduced in the studied formulation to determining the integration constants  $\mathbf{B}$  and  $\alpha$  from the corresponding boundary conditions for  $\nabla T=0$ . Naturally, in the approximation studied they must be written in some way that differs from (2.14). Actually, if the condition that the velocity jump at the phase boundary surface is proportional to the derivative of the temperature of the gas is satisfied in the direct calculation of the connection between the dynamical and thermal characteristics of the gas flow, then here it corresponds to the condition that the heat flux is proportional to the pressure gradient, or more exactly, to the derivative of the stress in the gas with respect to the coordinates, i.e., to the second derivative of the velocity of the gas. An account for this leads in the studied approximation to boundary conditions of the form

$$\begin{aligned} v_r &= 0, \\ v_\theta &= -C_m \mathbf{K} \mathbf{n} \frac{R}{\eta} \sigma_{\theta r}^{(g)}, \\ T_e - T_i &= 3C_m \mathbf{K} \mathbf{n} \frac{\eta}{\rho \kappa_e} R \frac{\partial p}{\partial r} - C_i \mathbf{K} \mathbf{n} \frac{R}{2\kappa_e} (I_{r'}^{(g)} + I_{i'}^{(g)}), \\ \kappa_i \frac{\partial T_i}{\partial r} - \kappa_e \frac{\partial T_e}{\partial r} &= k_{TS} \frac{\eta}{\rho} \frac{\partial p}{\partial r} \left[ 1 + \left( \frac{3}{k_{TS}} - 2 \right) C_m \mathbf{K} \mathbf{n} \right] \\ &+ \mathbf{K} \mathbf{n} \frac{1}{R} \left( \text{ctg } \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} \right) \left[ \frac{\eta}{\rho} \sigma_{r\theta}^{(g)} \left( C_v - \frac{3}{4} C_q \right) \right. \\ &\left. + \frac{\eta}{\rho} C_v p - \kappa_e C_q \frac{T_e + T_i}{2} \right]. \end{aligned}$$

Here we have used the complete expression of (2.5) for the heat flow in the gas, while we have used for the stress only the term corresponding to the viscous stresses.

Upon determining the integration constants from this in the usual way, we arrive at the desired expression for the velocity of thermophoresis with an accuracy coinciding with that of (2.15).

### c) Determination of the coefficient of thermal slip of a gas

We can also apply the thermodynamics of irreversible processes for determining the coefficient of thermal

slip  $k_{TS}^{(0)}$ .

For this purpose let us examine the flow of a gas in a planar slit formed by two parallel planes at a spacing of  $2d$ . They are brought into relative motion with the velocity  $\mathbf{v}$  under the action of a certain force. If we create a temperature field with a small constant temperature gradient  $\nabla T$  directed along the gap, then the entropy production per unit length of the channel can be written in the form

$$\Delta S = \frac{Fv}{T_0} + \int_{-d}^d I^{(q)}(x) dx \frac{\nabla T}{T_0^2}. \quad (4.7)$$

Here  $\mathbf{F}$  is the force per unit surface of the plate, and we have  $I^{(q)} = \mathbf{I}^{(e)} - (5/2)(p/\rho)\mathbf{I}^{(m)}$ . We shall write the linear relationships between the fluxes  $\mathbf{v}$  and  $\mathbf{q} = \int_{-d}^d \mathbf{I}^{(q)}(x) dx$  and the forces  $\mathbf{F}$  and  $\nabla T$  in the form

$$\mathbf{v} = L_{11} \frac{F}{T_0} + L_{12} \frac{\nabla T}{T_0^2}, \quad \mathbf{q} = L_{21} \frac{F}{T_0} + L_{22} \frac{\nabla T}{T_0^2}. \quad (4.8)$$

Upon using the kinetic theory to calculate the heat flux  $\mathbf{q}|_T$  at constant temperature and for a given force  $\mathbf{F}$ , we can easily find  $L_{21}$ . Then, by employing the symmetry principle, we can find the velocity  $\mathbf{v}$  for  $\mathbf{F}=0$  and for a given temperature gradient:

$$\mathbf{v} = \frac{(\mathbf{q}|_T \mathbf{F})}{F^2} \frac{\nabla T}{T_0}. \quad (4.9)$$

Thus the problem of determining the velocity of relative motion of the plates under the action of the temperature gradient is reduced in the given formulation to calculating the isothermal heat flux along the channel in the Couette problem from the kinetic theory.

Upon considering the equality  $\mathbf{F} = -\sigma_{xx}$ , we obtain the desired velocity of relative motion of the plates:

$$\mathbf{v} = - \int_{-d}^d \frac{I^{(q)}(x) dx}{\sigma_{xx}} \frac{\nabla T}{T_0}. \quad (4.10)$$

We note that the Couette flow is completely antisymmetric when the values of the accommodation coefficient at the surfaces of the two plates are identical, and that relative motion of the plates under the action of the temperature gradient does not arise. Now let us find the velocity of motion of the plates with respect to the center of mass of the gas (velocity of thermal slip). When  $\lambda/d \ll 1$ , we can neglect the overlap of the Knudsen layers next to the walls. Then we can write the relative velocity of the plates as the difference of the velocities of each of them with respect to the center of mass of the gas:  $v = v_{TS}^{(2)} - v_{TS}^{(1)}$ . That is, we represent the velocity of slip in the form

$$v_{TS}^{(0)} = \frac{\int_{-d}^d I^{(q)}(x) dx}{\sigma_{xx}} \frac{\nabla T}{T_0} + C_1. \quad (4.11)$$

Here  $C_1$  is a constant that does not depend on  $\varepsilon$ , which we can determine from the following considerations. When the molecules are reflected from the phase boundary according to a law close to specular, the gas slips along the surfaces under the action of the temperature gradient with the Maxwellian velocity<sup>57</sup> (see Sec. b of Chap. 3):

$$v_{TS}^{(M)} = \frac{3}{4} \frac{\eta}{\rho} \frac{\nabla T}{T_0}. \quad (4.12)$$

Upon calculating the flux of heat and momentum in the Couette-flow problem by the method presented in Sec. b of Chap. 3, transforming to the limit as  $\varepsilon \rightarrow 0$  in the expression (4.11), and comparing the result with (4.12), we find the constant  $C_1$ .

Consequently we obtain an expression for the velocity of thermal slip that coincides with (3.17).

## CONCLUSION

Without question, the theory of thermophoresis requires experimental verification. However, as we have noted above, the experiments, which have mainly been performed with aerosols, do not allow one to carry out a reliable comparison with theory, owing to the unusually large scatter in the properties of the object of the measurements and to purely experimental difficulties. Moreover, as we see from the arguments presented above, we need independent experiments to determine the accommodation coefficients of the momentum and energy of the gas molecules when they interact with the surface of an object existing in a gas. Actually, Eq. (1.9) implies that the velocity of thermophoresis of small objects depends on the accommodation coefficient  $\varepsilon$  of the momentum, whereas we see from (2.15) and (3.19)–(3.24) that we must know both the coefficients  $\varepsilon$  and  $\alpha$  to calculate the velocity of thermophoresis of large objects. Results are continually being published in the literature from measuring the values of these parameters for different gases, materials, and states of the surfaces of solids and liquids. Usually the employed method consists in measuring the resistance of the gas to flow in a tube (the Knudsen method), in viscosimetry of a sufficiently rarefied gas (the method of A. K. Timiryazev), and finally, in studying the viscous resistance of objects in the gas (the Millikan method). The value of the coefficient  $C_m$  is measured by these methods and then the parameter  $\varepsilon$  is calculated by Eq. (3.21). Apparently the Millikan method is the most accurate. It allows one to determine  $C_m$  with an error less than 3%.<sup>15</sup> The accommodation of energy in the interaction of a gas with the surface of objects is measured in experiments of a different type, namely by studying heat transport in sufficiently rarefied gases. Experiments performed in apparatus of various modifications have detected a sharp dependence of the energy accommodation coefficient on the type of gas, the material of the surface, and the nature of its treatment and degree of purity. The experimentally determined values of  $\alpha$  have proved to lie in the interval 0.15–1.00.<sup>77</sup> Unfortunately, we have not been able to find publications giving experimental values of  $\varepsilon$  and  $\alpha$  for the same gas-condensed phase pair. This deprives us of the opportunity of performing an unambiguous comparison of the theory presented above with experiment, at least for rather large objects.

As for small particles (or for a sufficiently rarefied gas), the experiments and calculations performed by various authors agree well.

As we see it, an experimental test of the theory in the range of small Knudsen numbers requires performing special experiments that envision the possibility of con-

trolled change of the accommodation coefficients of gas molecules at the surface of an object by an appropriate treatment and cleaning of the latter, and well as by the choice of the gas.

One of the possible schemes of such an experiment stems from the results of Sec. b of Chap. 4, where we showed that, in line with the symmetry principle, the motion of an object under the action of a temperature gradient in a gas corresponds to thermal polarization of the object as it moves in a homogeneous gas. Actually, when  $Re \ll 1$  (when we can neglect energy release owing to friction), the temperature difference  $\Delta T_i$  of two points of the surface of the sphere lying at opposite ends of a diameter parallel to the velocity of the ongoing flux can be expressed in the form

$$\frac{\Delta T_i}{T_0} = -\frac{KnM k_{TS}}{1+(1/2)(\alpha_i/\alpha_e)} \left\{ 1 + Kn \left[ 3C_m \left( \frac{3}{k_{TS}} - 1 \right) + C_i \left( 1 - \frac{3}{2k_{TS}} \right) - \frac{C_e}{k_{TS}} - \frac{(\alpha_i/\alpha_e) C_i - C_q}{1+(1/2)(\alpha_i/\alpha_e)} \right] \right\}.$$

Here  $M$  is the Mach number.

This temperature difference is simply related to the velocity of thermophoresis. Upon measuring it, one can decide on the validity of a theory of thermophoresis without measuring the velocity itself. This method is also attractive in that here one can experiment with objects of rather large size. Hence the potentialities are considerably expanded and the methodology of treatment and monitoring of the state of the surface of the object is simplified as compared with aerosols. Moreover, if the validity of the theory is proved by a series of experiments, then one can employ this method for experimental determination of one of the accommodation coefficients (the other one being known).

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