ANALYTICAL SOLUTION OF THE PROBLEM ON THERMAL SLIP OF SECOND ORDER FOR MOLECULAR GASES

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Results obtained using exact analytical methods in the problem on thermal slip of second order for molecular gases with allowance for the rotational degrees of freedom of molecules have been presented. Numerical calculations of the thermal-slip coefficient for a number of molecular gases have been carried out. The dependence of the velocity of thermal slip of second order of a molecular gas on the Prandtl number has been shown. The found value of the coefficient of thermal slip of second order theoretically confirms the existence of negative (in the direction of the temperature gradient) thermophoresis for molecular gases.

Processes occurring in molecular gases are fundamentally of a more complex character than those in elementary (monatomic) gases [1]. In the latter case, the distribution function is a function of the coordinates of the centers of inertia of gas molecules $\mathbf{r}'$ and the velocities of their translational motion $\mathbf{v}$. In the case of a molecular gas, the dependence of the distribution function on the rotational and vibrational degrees of freedom of molecules is added. The translational motion of molecules invariably follows the laws of the classical kinetic theory of gases. The rotational degrees of freedom of gas molecules are described in an analogous manner (except for extremely low temperatures). The vibrational degrees of freedom are invariably quantized. However, for a fairly wide range of temperatures (about 10–1000 K), it may be considered that the vibrational degrees of freedom are unexcited and the gas molecules are in the ground energy state [2].

A Boltzmann equation is used as the basic equation in kinetic theory of a rarefied gas [2]. In the case where the vibrational degrees of freedom of the gas molecules are "frozen" and the rotational ones are described based on the classical kinetic theory of gases, the Boltzmann steady-state equation, in the absence of mass forces, has the form [1]

$$\mathbf{C}\nabla f = \int (f' f_1' - f f_1)\, g d\sigma d^3 \mathbf{v}_1 d\omega_{1\theta} d\omega_{1\varphi} . \tag{1}$$

Here the molecules of a polyatomic gas have been considered as rigid rotators having five degrees of freedom. It seems generally impossible to obtain the solution of (1) in view of the nonlinearity of the sevenfold collision integral on the right-hand side of the equation. The main problem is in determining the differential cross section of scattering of colliding gas molecules $d\sigma$. For monatomic gases, it has turned out to be quite efficient to interpret gas molecules as hard spheres. Such an approach made it possible to compute analytically a number of bracket integrals and to solve numerous boundary-value problems of kinetic theory of a rarefied gas based on the method of half-space moments [3]. However, such an interpretation is unlikely to apply to a molecular gas. Allowance for the internal degrees of freedom of gas molecules by using the model of rough spheres and ovaloids appears equally unsuitable (see, e.g., [4] and the references therein). By virtue of this fact, the use of model kinetic equations (1) which make it possible to elucidate the structure of slow flows of rarefied molecular gases along hard surfaces is topical as before.

The work presented seeks to construct the exact analytical solution of the problem on thermal slip of second order as applied to molecular gases. The BGK (Bhatnagar, Gross, and Krook) model of the Boltzmann equation, which has been generalized in [5] to the case of allowance for the rotational degrees of freedom of gas molecules, is used as the basic equation. The gas molecules are assumed to be diffusely reflected by the surface.

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The problem on thermal slip of second order has repeatedly been considered by different authors for monatomic gases. This problem for monatomic gases was analyzed by numerical methods in [6–8]. The BGK model of the Boltzmann kinetic equation was used in [6], the ellipsoidal-statistical model was employed in [7], and the linearized Boltzmann equation for elastic spheres was used in [8]. In [9], the problem was solved by the method of half-space moments based on the linearized Boltzmann equation for rigid-sphere molecules. Exact analytical solutions of the problem in question were constructed in [10–12] respectively with the use of the BGK and ellipsoidal-statistical models of the Boltzmann kinetic equation as well as the Williams model. This problem was solved for the first time for polyatomic gases.

Formulation of the Problem. Derivation of the Basic Equations. Let us consider a spherical aerosol particle suspended in a rarefied molecular gas irregular in temperature. We tie a spherical coordinate system whose polar axis is guided along the temperature gradient in an unperturbed part of the gas flow to the center of a particle. We assume that the component (normal to the particle surface) of the temperature gradient $\partial T/\partial r$ slowly varies along the surface and is not constant. Thus, the quantity $\partial^2 T/\partial r \partial \theta$ will be nonzero in the problem, which leads to the so-called thermal slip of second order.

For small temperature gradients, the velocity of thermal slip of second order is determined by the expression [9]

$$U_0' = K_T \beta \operatorname{Kn} \nu_g \frac{1}{T_s} \frac{\partial^2 T}{\partial r \partial \theta} . \tag{2}$$

The quantity K_T for molecular gases has been found in [5] ($K_T = 0.7662/\mathrm{Pr}$). Thus, the problem formulated above is reduced to finding β.

The temperature gradient will be considered to be small. Then the problem allows linearization and the distribution function of gas particles by coordinate and velocity may be written in the form $f = f^{(0)}[1 + Y(\mathbf{r}, \mathbf{C}, \nu)]$, where $\mathbf{r} = (\mathrm{Pr}\sqrt{\pi}/2)\,(\mathbf{r}'/\lambda)$, $\lambda = \nu_g\sqrt{\pi m/2 k_B T_s}$, $\mathbf{C} = \mathbf{v}\sqrt{m/2k_B T_s}$, $\nu = \omega\sqrt{J/2k_B T_s}$, and $Y(\mathbf{r}, \mathbf{C}, \nu)$ is the solution of the equation [5] written in the spherical system whose origin coincides with the center of the spherical particle:

$$C_r \frac{\partial Y}{\partial r} + Y(\mathbf{r}, \mathbf{C}, \nu) + k\left[C_\theta \frac{\partial Y}{\partial \theta} + \frac{C_\varphi}{\sin \theta}\frac{\partial Y}{\partial \varphi} + (C_\theta^2 + C_\varphi^2)\frac{\partial Y}{\partial C_r} + (C_\varphi^2 \operatorname{ctg}\theta - C_r C_\theta)\frac{\partial Y}{\partial C_\theta} - \right.$$

$$\left. - (C_\varphi C_\theta \operatorname{ctg}\theta + C_r C_\varphi)\frac{\partial Y}{\partial C_\varphi} \right] = \int k\left(\mathbf{C}, \nu, \mathbf{C}', \nu'\right) Y\left(\mathbf{r}, \mathbf{C}', \nu'\right) d\Omega , \tag{3}$$

$$k\left(\mathbf{C}, \nu, \mathbf{C}', \nu'\right) = 1 + 2\mathbf{C}\mathbf{C}' + \frac{1}{l+1/2}\left(C^2 + \nu^2 - l - \frac{1}{2}\right)\left(C'^2 + \nu'^2 - l - \frac{1}{2}\right).$$

Here $l = 2$ and $d\Omega = 2\pi^{-3/2}\exp(-C^2 - \nu^2)\nu d\nu d^3C$ for a diatomic gas, $l = 5/2$ and $d\Omega = 2\pi^{-3}\exp(-C^2 - \nu^2)d^3\nu d^3C$ for an N atomic gas ($N \geq 3$), and $k = 2\mathrm{Kn}/(\sqrt{\pi}\,\mathrm{Pr})$, $\mathrm{Kn} = \lambda/R'$.

Following [6], we seek $Y(\mathbf{r}, \mathbf{C}, \nu)$ in the form of an expansion in parameter k:

$$Y(\mathbf{r}, \mathbf{C}, \nu) = Y_1(\mathbf{r}, \mathbf{C}, \nu) + k Y_2(\mathbf{r}, \mathbf{C}, \nu) + \dots . \tag{4}$$

Taking account of (4), we also expand the hydrodynamic characteristics of the gas flow, in particular, the component of the mass velocity U_θ tangential to the particle surface, in k:

$$U_\theta = U_\theta^{(1)} + k U_\theta^{(2)} .$$

Substituting (4) into (3) and equating the terms of k, we arrive at an equation for finding the function $Y_2(x, \mathbf{C}, \nu)$:

$$C_r \frac{\partial Y_2}{\partial x} + Y_2(x, \mathbf{C}, \nu) = \int k(\mathbf{C}, \nu, \mathbf{C}', \nu')\, Y_2(x, \mathbf{C}', \nu')\, d\Omega - \left[(C_\theta^2 + C_\varphi^2)\frac{\partial Y_1}{\partial C_r} + \right.$$

$$+ (C_\varphi^2 \, \text{ctg} \, \theta - C_r C_\theta) \frac{\partial Y_1}{\partial C_\theta} - (C_\varphi C_\theta \, \text{ctg} \, \theta + C_r C_\varphi) \frac{\partial Y_1}{\partial C_\varphi} \Bigg] - C_\theta \frac{\partial Y_1}{\partial \theta} , \tag{5}$$

$$Y_1 (x, \mathbf{C}, v) = \left[Z_1 (x, \mu) + \gamma (C^2 + v^2 - l - 1/2) \, Z_2 (x, \mu) \right] \frac{1}{T_s} \frac{\partial T}{\partial r} , \tag{6}$$

$$\gamma^2 = 1/(l + 1/2) , \quad Z (x, \mu) = \int_0^{+\infty} \exp (- x/\eta) \, F (\eta, \mu) \, A (\eta) \, d\eta ,$$

$$F (\eta, \mu) = \eta P \frac{1}{\eta - \mu} E + \exp (\eta^2) \, \Omega (\mu) \, \delta (\eta - \mu) , \quad x = r - R , \quad \mu = C_r ,$$

$$\Omega (\eta) = \lambda (\eta) E + \frac{1}{2l} \begin{pmatrix} 1/2 - \eta^2 & 1/2 + l - \eta^2 \\ 1 & 1 \end{pmatrix} , \quad \lambda (z) = 1 + \frac{1}{\sqrt{\pi}} z \int_{-\infty}^{+\infty} \frac{\exp (- \mu^2) \, d\mu}{\mu - z} ,$$

$$A (\eta) = [A_1 (\eta), A_2 (\eta)]^t , \quad Z (x, \mu) = [Z_1 (x, \mu), Z_2 (x, \mu)]^t .$$

The solution of Eq. (5) is sought in the form

$$Y_2 (x, \mathbf{C}, v) = C_\theta \varphi (x, \mu) + C_\theta (v^2 - l + 1) \, \varphi_1 (x, \mu) + \sum_k b_k (C_\theta, C_\varphi) \, \phi_k (x, \mu, v) , \tag{7}$$

where C_θ, together with $b_k(C_\theta, C_\varphi)$, form a complete system of orthogonal polynomials in the velocity space. By the orthogonality of the polynomials $g(\mathbf{C})$ and $f(\mathbf{C})$ in the velocity space we mean the equality of the integral $\int \exp (-C^2) g(\mathbf{C}) f(\mathbf{C}) d\mathbf{C}$ to zero.

Let us substitute (6) and (7) into (5). In the case of the diatomic gas we multiply the equality obtained by $v \exp (-v^2 - C_\theta^2 - C_\varphi^2)$ and integrate for v going from 0 to $+\infty$ and for C_θ and C_φ going from $-\infty$ to $+\infty$. In the case of the polyatomic gas, the equality obtained will be multiplied by $\exp (-v^2 - C_\theta^2 - C_\varphi^2)$ and will be integrated for v, C_θ, and C_φ going from $-\infty$ to $+\infty$. In both cases we arrive at the same system for finding $\varphi(x, \mu)$ and $\varphi_1(x, \mu)$:

$$\mu \frac{\partial \varphi}{\partial x} + \varphi (x, \mu) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\varphi} \exp (- \tau^2) \, \varphi (x, \tau) \, d\tau - k_T [Z_1 (x, \mu) + \gamma (\mu^2 + 1/2) \, Z_2 (x, \mu)] , \tag{8}$$

$$\mu \frac{\partial \varphi_1}{\partial x} + \varphi_1 (x, \mu) = - k_T Z_2 (x, \mu) , \quad k_T = \frac{1}{T_s} \frac{\partial^2 T}{\partial r \partial \theta} .$$

The gas molecules are assumed to be reflected from the surface of an aerosol particle diffusely. Then boundary conditions for the functions $\varphi(x, \mu)$ and $\varphi_1(x, \mu)$ sought will be written in the form

$$\varphi(0, \mu) = -2U_0 , \quad \mu > 0 , \tag{9}$$

$$\varphi (+ \infty, \mu) = 0 , \tag{10}$$

$$\varphi_1 (0, \mu) = 0 , \quad \mu > 0 , \quad \varphi_1 (+ \infty, \mu) = 0 .$$

Since the slip velocity U_0 sought is involved only in the boundary conditions for the function $\varphi(x, \mu)$, in what follows we may restrict ourselves to solution of Eq. (8) with boundary conditions (9) and (10).

Calculation of the Velocity of Thermal Slip of Second Order. We rewrite expressions (8) and (9) in vector form for an unknown column vector $\Phi(x, \mu) = [\varphi(x, \mu), 0]^t$:

$$\mu \frac{\partial \Phi}{\partial x} + \Phi(x, \mu) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \exp(-\tau^2) \Phi(x, \tau)\, d\tau - k_T K(\mu) Z(x, \mu), \tag{11}$$

$$\Phi(0, \mu) = [-2U_0, 0]^t, \quad \mu > 0, \quad \Phi(+\infty, \mu) = [0, 0]^t, \quad K(\mu) = \begin{bmatrix} 1 & \gamma(\mu^2 + 1/2) \\ 0 & 0 \end{bmatrix}.$$

The general solution of (11) will be given without derivation:

$$\Phi(x, \mu) = B_0 + B_1(x - \mu) + \int_0^{+\infty} \exp(-x/\eta) \Psi(\eta, \mu) B(\eta)\, d\eta +$$

$$+ k_T K(\mu) \int_0^{+\infty} \exp(-x/\eta) \eta P \frac{1}{\eta - \mu} F(\eta, \mu) A(\eta)\, d\eta,$$

$$\Psi(\eta, \mu) = \eta P \frac{1}{\eta - \mu} + \exp(\eta^2) \lambda(\mu) \delta(\eta - \mu).$$

The solution constructed for $B_0 = [0, 0]^t$ and $B_1[0, 0]^t$ satisfies boundary condition (10). We find the value of an unknown parameter U_0 with account for boundary condition (9) using the theory of boundary-value problems:

$$U_0 = -\frac{k_T}{2} [\varepsilon_n - Q_1 + 2Q_3 - (Q_2 - 1/2)\varepsilon_T]. \tag{12}$$

Here $Q_1 = -1.01619$, $Q_2 = -1.2663$, and $Q_3 = -1.8207$ [13]. The parameters ε_T and ε_n for the Boltzmann-equation model used in this work have been computed in [5]. We have $\varepsilon_T = 1.2168$ and $\varepsilon_n = -0.6716$ for diatomic gases and $\varepsilon_T = 1.1914$ and $\varepsilon_n = -0.6525$ for polyatomic gases. Substituting the above values into (12), we find $U_0 = 0.5738k_T$ for diatomic gases and $U_0 = 0.5867k_T$ for polyatomic gases.

In the case of a monatomic gas, we have obtained (in [10]) the velocity of thermal slip of second order based on the BGK model of the Boltzmann equation:

$$U_0 = -\frac{k_T}{2} [-\varepsilon_n - Q_1 + 2Q_3 - (Q_2 + 1/2)\varepsilon_T].$$

Here the values of the parameters $\varepsilon_T = 1.3013$ and $\varepsilon_n = -0.5633$ are computed based on the results obtained in [14]. Thus, for monatomic gases the BGK model yields the value of the velocity of thermal slip of second order $U_0 = 0.5323k_T$.

Passing to dimensional quantities in (12) and using (2), we find $\beta = 1.6934/\text{Pr}$ for diatomic gases and $\beta = 1.7299/\text{Pr}$ for polyatomic gases. Thus, e.g., the coefficient of thermal slip of second order for chlorine Cl_2 (Pr = 0.64) and carbon monoxide CO (Pr = 0.74) is equal to 2.6459 and 2.2884 respectively. For methane CH_4 (Pr = 0.75), sulfur dioxide SO_2 (Pr = 0.85), and ammonia NH_3 (Pr = 0.93), it is equal, respectively, to 2.3065, 2.0352, and 1.8201. Thus, the coefficient of thermal slip of second order for polyatomic gases (unlike monatomic ones) depends on the Prandtl number. For monatomic gases we have $\beta = 2.3524$ [10].

The result obtained in the work presented makes it possible to calculate the velocity of thermophoresis of high-thermal-conductivity aerosol particles for low values of the Knudsen number. Taking into account that [9]

$$\mathbf{U}_T' = \tau \nu_g \, \mathrm{Kn} \, \nabla T, \quad \tau = -2K_T(C_T + \beta - \beta_{Ba}),$$

where, according to [5], $C_T = 2\varepsilon_T/(\sqrt{\pi} \, \mathrm{Pr})$ and $\beta_{Ba} = 3.8662/\mathrm{Pr}^2$, we find $\tau = 1.2257/\mathrm{Pr}^2$ for the diatomic gas and $\tau = 1.2137/\mathrm{Pr}^2$ for the polyatomic gas. Thus, in particular, we have $\tau = 2.9924$ for Cl_2 and $\tau = 2.2383$ for CO. For CH_4, SO_2, and NH_3, the coefficient τ is equal to 2.1577, 1.6799, and 1.4032 respectively. For the monatomic gas we have obtained $\tau = 2.8544$ with the use of the BGK model. It is noteworthy that the value of the coefficient β that has been found for the gases indicated above theoretically confirms the existence of negative (in the direction of the temperature gradient) thermophoresis for molecular gases.

Thus, in the work, we have computed the velocity of thermal slip of second order of a rarefied polyatomic gas with the use of exact analytical methods based on a generalization of the BGK model of the Boltzmann kinetic equation to the case of allowance for the rotational degrees of freedom of the gas molecules. It has been established that, for polyatomic gases, the coefficient of thermal slip of second order depends on the Prandtl number. The found value of the coefficient of thermal slip of second order theoretically confirms the existence of negative (in the direction of the temperature gradient) thermophoresis for molecular gases.

NOTATION

$A_1(\eta)$ and $A_2(\eta)$, coefficients in the expansion of the solution of the problem on temperature jump at the boundary of a hard plane surface in the eigenvectors of a continuous spectrum; $\mathbf{C}$, dimensionless translational velocity of gas molecules; C_T, coefficient of temperature jump of a rarefied gas at the boundary of a hard plane surface; E, unit matrix; $f^{(0)}$, equilibrium distribution function in the gas volume at a large distance from the surface of an aerosol particle; f, f_1, and f', f_1', distribution functions of molecules before and after the collision; $F(\eta, \mu)$, eigenvectors of a continuous spectrum from the problem on temperature jump; g, impact parameter; J, moment of inertia of gas molecules, kg·m^2; Kn, Knudsen number; k_B, Boltzmann constant; K_T, coefficient of thermal slip of a rarefied gas along a hard plane surface; k_T, second mixed derivative of temperature, referred to the surface temperature; $K(\mu)$, matrix from the problem on thermal slip of second order; m, mass of gas molecules, kg; N, number of atoms in a molecule; Pr, Prandtl number; Px^{-1}, distribution in the sense of the principal value in integrating x^{-1}; Q_1, Q_2, and Q_3, Loyalka integrals; R', dimensional radius of an aerosol particle, m; R, dimensionless radius of an aerosol particle; r, radial coordinate of the spherical coordinate system; $\mathbf{r}'$, dimensional radius vector, m; $\mathbf{r}$, dimensionless radius vector; T, gas temperature, K; T_s, particle-surface temperature, K; $\mathbf{U}'$, dimensional mass velocity of the gas, m/sec; $\mathbf{U}_T'$, velocity of thermophoresis of high-thermal-conductivity aerosol particles, m; U_0', dimensional velocity of thermal slip of second order, m/sec; U_0, dimensionless velocity of thermal slip of second order; $\mathbf{v}$, dimensional translational velocity of gas molecules, m/sec; $\mathbf{v}_1$, velocity of the incident molecule before the collision; $Y(\mathbf{r}, \mathbf{C}, \nu)$, correction allowing for the deviation of the distribution function in the Knudsen layer from the distribution function in the gas volume; $Z_1(x, \mu)$ and $Z_2(x, \mu)$, functions constructed in the problem on temperature jump at the boundary of a hard plane surface; β, coefficient of thermal slip of second order; β_{Ba}, Barnett-slip coefficient; $\delta(x)$, Dirac delta function; θ, azimuthal angle of the spherical coordinate system; λ, mean free path of gas molecules, m; $\lambda(z)$, Cercignani dispersion function; ν, dimensional rotational velocity of gas molecules; ν_g, kinematic viscosity of the gas; ω, dimensional rotational velocity of gas molecules, rad/sec; $\Omega(\eta)$, dispersion matrix; $d\sigma$, differential scattering cross section of colliding gas molecules; $\omega_{1\theta}$ and $\omega_{1\varphi}$, projections of the angular rotational velocity of the incident molecule before the collision; ε_T, temperature jump on the particle surface; ε_n, parameter found in the problem on temperature jump from the surface-impermeability condition for gas molecules; $\Psi(\eta, \mu)$, eigenvectors of a continuous spectrum from the problem on thermal slip of second order; t, transposition. Subscripts: g, gas; n, number concentration; r, θ, φ, projections onto the axes of the spherical coordinate system; s, sphere surface.

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