

Gas Dynamic Equations, Transport Coefficients, and Effects in Nonequilibrium Diatomic Gas Flows

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The problem of redistribution of translational and rotational energy has been solved for diatomic gases within the framework of the Chapman–Enskog method and the Parker model in the general case of the arbitrary energy exchange ratio. The nonequilibrium gasdynamic equations, transport coefficients, and relaxation time have been found for rotational-translational processes in a diatomic gas. The calculations of relaxation time, viscosity, thermal conductivity, and diffusion coefficients are carried out in the temperature range from 200 to 10,000 K for nitrogen. The calculated parameters and coefficients are compared with the values obtained by the Mason–Monchick approximate method as well as data from experiments in ultrasonic, shock-wave, and vacuum devices. The correlation of the theoretical and experimental data is satisfactory. The applicability of one- and two-temperature relaxation models is discussed. The numerical solutions of the obtained system of the Navier–Stokes equations are analyzed for the cases of spherical expanding nitrogen flow and supersonic rarefied gas flow near a sphere.

Nomenclature

A^i, B^i	= roots of the integral equations; Eqs. (2–5)
$A^{i(p)}, G_i$	
b	= impact parameter, m; Eq. (12)
D_0	= self-diffusion coefficient, m ² /s; Eq. (28)
d	= internuclear distance, m
d^*	= distance between centers of mass and force, m
E	= energy, J
I_0, I_2	= modified Bessel functions
Kn	= Knudsen number
Kn_R	= Knudsen relaxation parameter
M	= momentum of momentum, kg · m ² /s
$P_i^{(p)}$	= Waldmann–Trubenbaher polynomials; Eqs. (2–5)
P_{rs}	= components of viscous stress tensor, N/m ² ; Eqs. (8) and (35)
p	= static pressure, N/m ²
p_i	= initial reduced angular momenta; Eq. (13)
Q	= constant; Eq. (9)
q_r	= components of heat-flux vector, W/m ² ; Eqs. (7) and (34)
r	= intermolecular distance, m; Eq. (9)
r_p	= parameter of the turning point, m
r_0	= parameter that takes on a value in a narrow range $1/\alpha$ around r_p ; Eq. (12)
$S_{(k)i}^{(r)}$	= Sonine polynomials; Eqs. (2–5)
$T^{(k)i}$	= temperature, K
V_r^i	= components of diffusion velocity vector, m/s; Eqs. (6) and (33)
V_0	= isotropic interaction potential
v	= velocity of relative motion, m/s
y	= intermolecular force parameter, $\alpha d^*/2$
Z_R	= average number of collisions
α	= inverse radius of action of the intermolecular forces, m ⁻¹ ; Eq. (9)
ε	= anisotropy parameter, $2I_2(y)/I_0(y)$; Eq. (9)
ε_R	= rotational energy per molecule, J/mol
ε_0	= depth of the potential energy well, 96.6 K
η	= dynamic viscosity, kg/(m s)

Θ	= characteristic time of flow, s
θ	= angle between the intermolecular and interatomic axes, rad; Eq. (9)
λ	= thermal conductivity, W/(m K)
μ	= mass of an atom of the molecule, kg
ρ	= gas density, kg/m ³
τ_R	= rotational-translational relaxation time, s
φ_i	= initial phases; Eq. (10)
$\varphi_i^{(1)}$	= solution of the Boltzmann equation; Eq. (1)
χ	= angle of elastic scattering, rad; Eq. (16)

I. Introduction

SEVERAL attempts had been made in the past in deriving the nonequilibrium gas dynamic equations from the first principles of the kinetic theory of gases. In the simple cases of near-equilibrium and slow-relaxation processes of the energy exchange between internal and translational degrees of molecular freedom, the gas dynamic equations and transport coefficients were derived by Ferziger and Kaper¹ and Kogan² for nonequilibrium polyatomic gas mixtures by using the Chapman–Enskog iteration method to solve the Boltzmann equation. This technique was developed by Alekseev,³ Galkin et al.,⁴ Matsuk and Rykov,⁵ and Kogan and Makashev⁶ for the case of the arbitrary energy exchange ratio. However, these studies had mostly academic interest. Practical results were only obtained by Matsuk and Rykov⁵ for the system of model equations.

In the present study the general case of the arbitrary energy exchange ratio is considered for the real diatomic gas molecules with rotational degrees of freedom (see Sec. II). The transport coefficients and reaction rates for rotationally excited gas are obtained by using the technique of integral brackets.^{1,7,8} In calculating of the correction term related to the distribution function of the zeroth approximation, the linear-dependence transformation of the diffusion thermodynamic force vectors to the linear independent vector set has been done by the linear transformation method of Matsuk and Rykov.⁵ In this case the matrix transformation elements are the Waldmann–Trubenbaher polynomials. Integral brackets are calculated in terms of classical mechanics.^{7,8} The molecular collision model is based on the Parker concept.⁹ The analytical form of the energy and momentum parameters is found in this case (see Sec. III). The form is used for calculations.

In Sec. IV the collision model is applied for evaluation of the rotational-translational relaxation time τ_R . The sixfold integrals are evaluated by the Monte Carlo technique (see Sec. V) in the temperature range from 200 to 10,000 K for nitrogen. The conditions of one- and two-temperature approximations for the relaxation time are

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considered for nitrogen. The two-temperature approximation was also analyzed by Lebed and Riabov^{10,11} for para-hydrogen ($p\text{-H}_2$). Willauer and Varghese¹² studied rotational relaxation in $p\text{-H}_2$ using a direct simulation Monte Carlo method with state-to-state collision cross sections. The rotational relaxation times for molecular hydrogen were calculated by Sharma¹³ using a coupled rotation-vibration-dissociation model. In the present study the rotational relaxation processes for molecular nitrogen and applications of the theory are discussed for testing in ultrasonic devices, shock-wave tubes (see Sec. VI) and underexpanded jets in vacuum chambers (Sec. VII).

The thermodynamic force transformation technique and the Mason–Monchick approximation are used in this study (Sec. VIII) to find analytical expressions for heat flux and diffusion velocity of rotational levels. The Chapman–Enskog iteration method of solving the Boltzmann equation in this case was described by Lebed and Riabov¹⁰ in detail. A set of the nonequilibrium gas dynamic equations is found in Sec. IX for the general case of the arbitrary energy exchange ratio. Rotational relaxation time and transfer coefficients have been calculated by the technique of Lebed and Riabov.¹¹ The viscosity and thermal conductivity are compared with experimental data and the Mason–Monchick approximations.¹⁴

The combined effect of the rotational-translational relaxation and the viscosity and thermal conductivity processes has been numerically studied in Sec. X in cases of spherically expanding flows and nonequilibrium gas flow near a sphere. In the last case a good correlation between numerical and experimental data has been found.

II. Chapman–Enskog Method and Rotational Relaxation

To solve the Boltzmann equation in the case of rotational-translational relaxation, we will follow the technique described by Galkin et al.,⁴ Matsuk and Rykov,⁵ Kogan and Makashev,⁶ and Lebed and Riabov.¹⁰ The introduction of the Knudsen number Kn and parameter Kn_R , which characterizes the ratio of the specific nonelastic collision probability to the specific elastic one, is necessary to apply the Chapman–Enskog iteration technique.

At the hydrodynamic stage the solution of the Boltzmann equation is presented as an asymptotic series based on the small parameter Kn . The first approximation term was obtained by Galkin et al.⁴ The analysis of Galkin et al.,⁴ Kogan and Makashev,⁶ Lebed and Riabov,¹⁰ and Riabov¹⁵ indicated that the elastic collision term and the nonelastic collision one have the order of unity and $\mathcal{O}(Kn_R)$, respectively.

The set of diffusion thermodynamic forces is linearly dependent. Following the technique of Matsuk and Rykov⁵ and using the Waldmann–Trubebaher polynomials, a new set of linearly independent vectors for solving the problem has been introduced at this stage. The general solution of the problem is found as the sum of the particular solution and the general solution of the uniform equation. This solution is the following¹⁰:

$$\begin{aligned} \varphi_i^{(1)} = & -\frac{1}{n} A^i c_r^i \frac{\partial \ln kT}{\partial x_r} + \sum_{p=1}^{\infty} A^{i(p)} c_r^i D_r^{(p)} \\ & - \frac{1}{n} B^i \left(c_r^i c_s^i - \frac{1}{3} c^{i2} \delta_{rs} \right) \frac{\partial u_r}{\partial x_s} + G_i \end{aligned} \quad (1)$$

The coefficients A^i , B^i , $A^{i(p)}$, and G_i are the roots of the integral equations given in the study of Lebed and Riabov.¹⁰ The solutions of the integral equations could be found as series of the Sonine ($S_{(k)l}^{(r)}$) and Waldmann–Trubebaher $P_i^{(p)}$ polynomials^{1,4–8,10}:

$$A^i = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} a_{pl} P_i^{(p)} S_{(\frac{3}{2})l}^{(r)} \quad (2)$$

$$B^i = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} b_{pl} P_i^{(p)} S_{(\frac{3}{2})l}^{(r)} \quad (3)$$

$$A^{i(q)} = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} a_{pl} P_i^{(p)} S_{(\frac{3}{2})l}^{(r)} \quad (4)$$

$$G_i = \sum_{p=0}^{\infty} \sum_{l=0}^{\infty} g_{pl} P_i^{(p)} S_{(\frac{3}{2})l}^{(r)} \quad (5)$$

In calculations we used the two first nonzero terms in the series (2–5). The linear system of second-order equations has been solved by the maximum principle^{1,4,5} and variation technique.^{1,3–5} Using Eqs. (1) and (2), the expressions for the components of diffusion velocity vector V_r^i , heat-flux vector q_r , and viscous stress tensor P_{rs} are the following:

$$V_r^i = -a_{10} \frac{E_i - \langle E \rangle}{\rho} \frac{\partial \ln kT}{\partial x_r} + a_{10}^{(1)} \left(\frac{kT}{m} \right) \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \frac{\partial \langle E \rangle}{\partial x_r} \quad (6)$$

$$\begin{aligned} q_r = & - \left(a_{01} \frac{5}{2} \frac{kT}{m} + a_{10} \frac{kT \langle E^2 \rangle - \langle E \rangle^2}{(kT)^2} \right) \frac{\partial kT}{\partial x_r} \\ & + \left(a_{10}^{(1)} \frac{p}{m} + a_{01}^{(1)} \frac{\frac{5}{2} p (kT)^2}{\langle E^2 \rangle - \langle E \rangle^2} \right) \frac{\partial \langle E \rangle}{\partial x_r} \end{aligned} \quad (7)$$

$$P_{rs} = p \delta_{rs} - \frac{(kT)^2}{m} b_{00} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_l}{\partial x_l} \right), \quad p = nkT \quad (8)$$

The scalar term of solution (1) can be used for evaluation of the correction terms in the rotational rates.¹⁰ The transport coefficients can be found by comparing terms and coefficients of Eqs. (6–8).

III. Interaction Potential Model for Diatomic Molecules

Within the framework of the Parker model,⁹ the interaction potential of the molecules is represented as the sum of the exponential attraction between the centers of mass and the exponential repulsion between the centers of force, placed on the internuclear axis at a distance $d^* < d$ from each other, where d is the internuclear distance. The value of the parameter d^* can be estimated from experiments^{10,11} and is in the range from 0.557 to 0.62.

Expansion of the short-acting part of the potential in a Fourier series led to the generally accepted form of an expansion in powers of the cosines of the angles between the interatomic and intermolecular axes. The retention of only the first two terms of this expansion is justified by the fact that anisotropy parameter $\varepsilon = 2I_2(y)/I_0(y)$ is small.

The interaction potential is represented in the form⁹

$$V_r = Q e^{-\alpha r} (1 + \varepsilon \cos 2\theta_i + \varepsilon \cos 2\theta_j) \quad (9)$$

where θ_i and θ_j are the angles between the intermolecular and interatomic axes of the molecules i and j .

The system of classical equations of motion with a potential [Eq. (9)] developed by Parker⁹ is solved within the framework of the theory of perturbations with respect to the parameter ε . In the zeroth approximation the rotational state of the molecules does not change as a result of the collision.¹¹ In the narrow range of action of the intermolecular potential at $r \sim 1/\alpha$, the centrifugal energy $\mu v^2 b^2 / 2r^2$, which varies only slightly with r , in accordance with the effective-wave-number approximation developed by Nikitin and Osipov,¹⁶ is replaced with the constant value $\mu v^2 b^2 / 2r_0^2$.

In the first order of the theory of perturbations^{10,11,15} with respect to the parameter ε , analytic expressions for the resulting angular velocities of the molecules are

$$\varphi_i = -\frac{16\pi l_i \sin 2\psi_i}{\alpha^2 d^2 s h^2 \aleph_i} \quad (10)$$

$$\aleph_i = \frac{2\pi l_i}{\alpha g \sqrt{1 - q^2 + 2\varepsilon_0} g^2 kT} \quad (11)$$

$$\psi_i = \varphi_i - \arcsin q, \quad q = b/r_0 \quad (12)$$

$$l_i = \sqrt{2} p_i d - q g / r_0, \quad g = \sqrt{\mu / k T} v \quad (13)$$

The additional acceleration in the region of interaction as a result of the remote-acting forces is taken into account in Eqs. (10–13) according to the study of Nikitin and Osipov¹⁶ by replacing $\mu^2/2$ with $\mu v^2/2 + \varepsilon_0$, where $\varepsilon_0 = 96.6$ K is the depth of the potential well^{8,17} (also see Refs. 11 and 15).

The expressions for the energy $\Delta E = \Delta E' / \mu v^2/2 = \Delta E_i + \Delta E_j$ and the momentum $\Delta M = \Delta M' / \mu v r_0 = \Delta M_i + \Delta M_j$ transferred at the time of collision from the translational to the rotational degrees of freedom take the form

$$\Delta E_i = \frac{128\pi^2 \varepsilon_l^2 \sin^2 2\psi_i}{\alpha^4 d^2 g^2 s h^2 \aleph_i} - \frac{16\sqrt{2}\pi \varepsilon p_i l_i \sin 2\psi_i}{\alpha^2 d g^2 s h \aleph_i} \quad (14)$$

$$\Delta M_i = -\frac{8\pi \varepsilon l_i \sin 2\psi_i}{\alpha^2 g r_0 s h \aleph_i} \quad (15)$$

Nikitin and Osipov¹⁶ found that the angle of elastic scattering χ for a short-acting potential can be approximated by the angle of elastic scattering of solid spheres. At the condition that the calculated values of ΔE are much smaller than kT , the angle of scattering is calculated on the assumption that the transfer of energy from the translational to the rotational degrees of freedom takes place instantaneously at the point r_p . As a result, we have

$$\chi = \beta - \phi, \quad \phi = \arcsin\left(\frac{\sin \beta - \Delta M}{\sqrt{1 - \Delta E}}\right) \quad (16)$$

Here $\beta = \arcsin(q)$ is the angle between the velocity vector v of the relative motion of the noninteracting molecules and the vector drawn from the center of scattering to the point r_p .

The isotropic interaction potential for the nitrogen molecules $V_0(r)$ is approximated by data from the study of Belyaev et al.¹⁷ in the range $r > 3.1096\text{\AA}$. The short-acting branch of $V_0(r)$ is approximated by the exponential function $Q \exp(-\alpha r)$ at each point of turning r_p . The value of the parameter α is calculated as $\alpha(r_p) = -d \ln V_0(r)/dr$ at r_p . The parameter r_0 is equated to the integral $(\mathfrak{Q}^{(2,2)})^{1/2}$, calculated by Belyaev et al.¹⁷ for the exact potential $V_0(r)$ at $r \sim 1/\alpha$. The functions $\alpha(T)$, $\varepsilon(T)$, $r_p(T)$, and $r_0(T)$, corresponding to $d^* = 0.62$ were calculated by Lebed and Riabov.^{10,11}

IV. Rotational Relaxation Time

Two independent definitions of relaxation time are widely used. In the first case the general expression for the temperature dependence of the rotation time $\tau_{R1}(T)$ is obtained by using the Chapman–Enskog iteration method of solving the Boltzmann equation for a gas of particles, which possess internal degrees of freedom.¹ In the second case the relaxation time $\tau_{R2}(T)$ is found directly from the relaxation equation by calculating the rate of increase of the internal energy of the molecules, which originally were not internally excited.¹⁶

To describe the rotational relaxation of a gas of homonuclear diatomic molecules, the specific models of the intermolecular interaction have been used for calculating the redistribution of the rotational and translational energies upon collision. The main disadvantage of such models⁸ like the rough-sphere, loaded-sphere, spherocylinder, and ellipsoid models is that the real intermolecular interaction potential is replaced with the potential of rigid frames of different shapes. As a result, the average number of collisions calculated by means of these models, which is required to put the system into equilibrium with respect to the rotational degrees of freedom, $Z_{R1}(T) = \tau_{R1}/\tau$, where τ is the translational relaxation time, is independent of the temperature (see also comments in Ref. 18). This fact contradicts the experimental data.^{8,19}

The parameter $Z_{R2}(T) = \tau_{R2}/\tau$, calculated by Parker⁹ and obtained more precisely by Brau and Jonkman¹⁹ corresponding to the plane collision of the initially unperturbed rotators, increases monotonically with the increase in temperature because of the potential

well. This effect in the range of temperatures tens of times as high as the potential well depth was explained by Nyeland.²⁰ The values of $Z_{R1}(T)$ and $Z_{R2}(T)$ for nitrogen were calculated by Lebed and Riabov^{10,11} at $T \geq 300$ K.

The process of establishing equilibrium with respect to the rotational degrees of freedom in terms of the τ approximation can be described by the relaxation equation²¹

$$\frac{d\varepsilon_R}{dt} = \frac{(\varepsilon_R^0 - \varepsilon_R)}{\tau_R} \quad (17)$$

where ε_R is the specific rotational energy and ε_R^0 is its equilibrium value. It was noted^{11,15,21} that Eq. (17) holds for small deviations from equilibrium $(\varepsilon_R^0 - \varepsilon_R)/\varepsilon_R^0 \ll 1$. Parameter $\tau_{R2}(T)$ could be determined from Eq. (17) as the ratio of ε_R^0 to the rate of growth of the energy of the initially unexcited rotators.²¹ In the case considered here, this rate can be determined by averaging of the parameters in Eqs. (14) and (15), in which we must set $p_1 = p_2 = 0$:

$$p\tau_{R2}(T) = \frac{5}{I} \left(\frac{\alpha^2 dr_0}{128\pi \varepsilon} \right)^2, \quad \aleph_0 = \aleph_i|_{p_i=0} \quad (18)$$

$$I = \frac{2}{\sqrt{2\pi\mu kT}} \int_0^{r_0} \int_0^\infty \left(\frac{b}{r_0} \right)^2 \frac{g^5}{8} \exp\left(\frac{-g^2}{2}\right) s h^{-2} \aleph_0 b db dg \quad (19)$$

The effect of the initial distribution with respect to the rotational states was estimated by Lebed and Riabov.^{10,11} They assumed that at time $t=0$ this distribution corresponds to the Boltzmann distribution with the temperature $T_R \neq 0$. Under these conditions the rotational relaxation time τ_R becomes a function not only T but T_R as well. The values of $p\tau_R(T, T_R)$ and $Z_R(T, T_R)$ were calculated by Lebed and Riabov¹¹ for nitrogen and para-hydrogen at $0 \leq T_R \leq 1200$ K.

As in the case of the rotational relaxation of nitrogen investigated by Lebed and Riabov,¹¹ a strong dependence of the relaxation time τ_R on T_R in para-hydrogen was found.^{11,12} The use of the two-parameter function $\tau_R(T, T_R)$ improves the approximate calculation obtained with Eq. (17). The results^{10,11} indicated that the initial distribution according to rotational levels must be taken into account within the framework of the τ approximation.

The applicability of the Eq. (17) for rarefied hypersonic flows had been reviewed by Lumpkin et al.²² Following the technique of Rahn and Palmer²³ and Koszykowski et al.,²⁴ they developed a new algorithm that involves solving the master equation for stationary adiabatic rotational relaxation and the empirically fit relations for the upward and downward transition rates.

In the present study the rotational-translational energy exchange process is considered at $Kn_R \sim 1$, and $\tau < \tau_{R1}(T) \ll \Theta$. Under the considered conditions the rotational energy parameters ε_R^0 and ε_R differ from each other by a small quantity proportional to the Knudsen number Kn . The general expression^{1,10,11,15} for $p\tau_{R1}(T)$ is found by solving the Boltzmann equation, using the Chapman–Enskog method:

$$\frac{1}{p\tau_{R1}(T)} = \frac{2}{\pi^2 \sqrt{2\pi\mu kT}} \int_0^{r_0} \int_0^\infty \int_0^\pi \int_0^\pi \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Delta E^2 \times \exp\left(-\frac{g^2 + p_i^2 + p_j^2}{2}\right) b db \frac{g^7}{16} dg d\varphi_i d\varphi_j dp_i dp_j \quad (20)$$

The temperature is determined on the basis of the total molecular energy. Formula (20) differs by factor of 5/3 from the corresponding quantity obtained in Ref. 21 by determining the temperature on the basis of the kinetic energy of the molecules.

V. Numerical Method

The sixfold integrals are calculated at 200 points over the range of temperatures $200 \text{ K} \leq T \leq 10,000 \text{ K}$, using the Monte Carlo technique,¹¹ with 4000 tests at each point. The data for intermediate

points are determined by means of the interpolation technique^{10,25} using cubic splines of defect 1 with smoothing. The resulting estimated accuracy of the calculations is 1.5%. The higher orders of the theory of perturbations with respect to the parameter ε make a substantial contribution at $T < 400$ K, and the accuracy of the calculations is lower under these conditions.

VI. Numerical Results

The results of calculations $p\tau_{R2}(T)$ and $p\tau_{R1}(T)$ according to formulas (18–20) are shown in Figs. 1 and 2, correspondingly (solid lines and empty squares). The experimental data (filled squares) acquired by Brau and Jonkman¹⁹ and Lordi and Mates²⁶ are also shown.

The calculations show that, at $200 \leq T \leq 10,000$ K, $p\tau_{R1}(T)$ is 2 or 2.5 times as large as $p\tau_{R2}(T)$. This difference is apparently a result of the adiabatic nature of the energy exchange between the highly excited rotational states of the molecules.¹¹ The effect of the initial distribution according to rotational levels was not considered in this comparison.

The influence of the parameters α and d^* on $Z_{R2}(T)$ and $Z_{R1}(T)$ was analyzed by Lebed and Riabov.^{10,11} As is shown in Fig. 1 (dashed line and triangles correspond to $d^* = 0.557$), a decrease in d^* causes an increase in $p\tau_{R2}(T)$. Lebed and Riabov¹¹ noted that for constant α both $Z_{R2}(T)$ and $Z_{R1}(T)$ remain approximately constant everywhere except at low temperatures, where the additional acceleration of the molecules caused by the remote-acting forces should be taken into account. The quantity $p\tau_{R1}(T)$ has been used for interpreting the experimental data on the scattering and absorption of ultrasound, where the effect of the ultrasound frequency on $p\tau_{R1}(T)$ was disregarded.¹⁹ The quantity $p\tau_{R2}(T)$ has been used for interpreting the data of experiments in shock tubes. The available experimental data,^{19,26} both on ultrasound [$Z_{R1}(T)$] and on shock waves [$Z_{R2}(T)$], differ from one another by 200–300%, which is ap-

proximately equal to the difference between $p\tau_{R1}(T)$ and $p\tau_{R2}(T)$, as evident from Figs. 1 and 2.

VII. Specific Features of Rotational Relaxation in Freely Expanding Gas Flows

Marrone²⁷ and Borzenko et al.²⁸ studied the translational-rotational relaxation in expansion of a molecular gas into a vacuum. A significant decrease of the gas density downstream leads to a decrease in the number of molecular collisions. As a result, the departure of the rotational energy of the gas ε_R from the equilibrium value ε_R^0 is observed.

Lebed and Riabov²⁹ and Riabov³⁰ studied another cause for the rotational energy departure. At the decrease of kinetic temperature T_t , the Messy adiabatic parameter,³¹ describing energy transfer between highly excited rotational levels unable to relax, becomes larger than unity. Adiabatic collision conditions^{31,32} should be taken into account in this case. As T_t decreases, the relaxation time τ_R will increase because of the significant decrease of the rotational transfer probabilities.

Using the technique of Lebed and Riabov,²⁹ the rotational-translational relaxation times were calculated for nitrogen at conditions of aerodynamic experiments in underexpanded jets.³⁰ The analysis presented by Lebed and Riabov^{29,30} demonstrated the considerable departure of rotational energy from the equilibrium value at temperature $T \leq 100$ K and pointed to take into account the quantum methods under the conditions of experiments in an expanding flow of nitrogen. The rotational-translational nonequilibrium processes were studied by Molodtsov and Riabov,³³ Riabov,^{15,30,34,35} Olynick et al.,³⁶ Skovorodko,³⁷ and Rebrov and Chekmarev³⁸ in terms of the full system of the Navier-Stokes equations and the relaxation equation (τ approximation). New solutions have been found in the present study (see Sec. X.A).

VIII. Transport Coefficients in Near-Equilibrium Diatomic Gases

The general expressions for the transport coefficients were analyzed by Lebed and Riabov,^{10,11} Riabov,¹⁵ Lordi and Mates,²⁶ and Taxman.³⁹ Using formulas from Eqs. (6–8), these expressions are

$$\frac{1}{\eta} = \frac{8}{5} \int \left(\sin^2 \chi - \frac{\Delta E^2}{2} \sin^2 \chi + \frac{\Delta E^2}{3} \right) \frac{g^2}{2} dw \quad (21)$$

$$\lambda \left(1 - \frac{Y^2}{XZ} \right) = \left(\frac{75}{16} \frac{1}{X} + \frac{15}{4} \frac{Y}{XZ} + \frac{3}{4} \frac{1}{Z} \right) \frac{k}{\mu} \quad (22)$$

$$X = \frac{5}{2} \frac{1}{\eta} + \frac{5}{4} \frac{1}{p\tau_{R1}(T)} \quad (23)$$

$$Y = \frac{3}{4} \frac{1}{p\tau_{R1}(T)} \quad (24)$$

$$Z = \frac{3}{2} \frac{1}{\rho D_0} + \int \left\{ \frac{3}{4} g^2 \Delta E^2 + (p_i^2 - p_j^2) \times \left[p_i^2 \cos \chi_0 - (p_i^2 + g^2 \Delta E_i) \cos \chi \sqrt{1 - \Delta E} \right] \right\} dw \quad (25)$$

$$\frac{1}{\eta_0} = \frac{16\pi r_0^2}{5\sqrt{2\pi\mu kT}} \quad (26)$$

$$\lambda_0 = \frac{15}{8} \frac{k}{\mu} \eta_0 \quad (27)$$

$$\frac{1}{\rho D_0} = \frac{8}{3} \int (1 - \cos \chi_0) dw \quad (28)$$

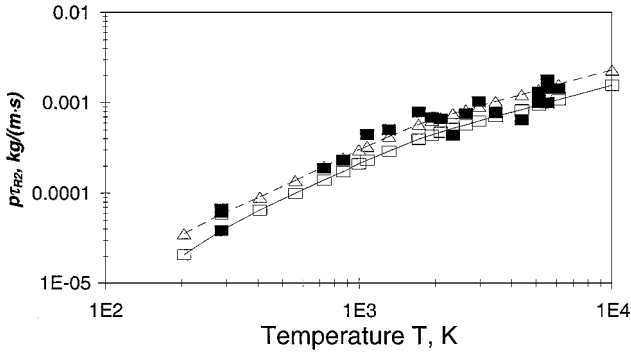


Fig. 1 Parameter $p\tau_{R2}(T)$ as a function of temperature: \square , solution of Eq. (18) at $d^* = 0.62$; \triangle , solution of Eq. (18) at $d^* = 0.557$; and \blacksquare , experimental data.^{19,26}

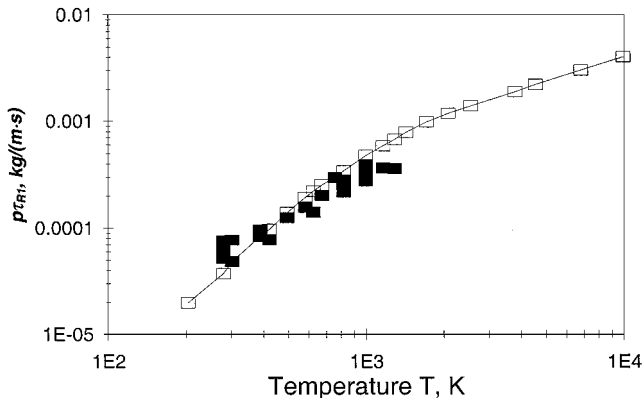


Fig. 2 Parameter $p\tau_{R1}(T)$ as a function of temperature: \square , solution of Eq. (20) at $d^* = 0.62$; and \blacksquare , experimental data.^{19,26}

$$\int (\cdot) dw = \frac{1}{\pi^2 \sqrt{2\pi\mu kT}} \int_0^\infty \int_0^{r_0} \int_0^\pi \int_0^\pi \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (\cdot) \times \exp\left(-\frac{g^2 + p_i^2 + p_j^2}{2}\right) \frac{g^5}{8} dg db d\varphi_i d\varphi_j dp_i dp_j \quad (29)$$

In Eqs. (21–29) η and η_0 are the coefficients of shear viscosity corresponding to rotationally inelastic and elastic collisions, and λ and λ_0 are corresponding values of the thermal conductivity.

The simplest approximations for the thermal conductivity coefficient λ were analyzed by Ferziger and Kaper,¹ Hirshfelder et al.,⁸ Mason and Monchick,¹⁴ and Lebed and Riabov.^{10,11} Mason and Monchick,¹⁴ analyzing the relations (21–29), set $\Delta E = 0$ in the first approximation. This approximation was based on the diffusive transfer, but it disregarded the relaxation of the rotational energy. The relaxation was taken into account partially in the next, second approximation, in which the term for Z contains not only $(\frac{3}{2})\rho D_0$ but also the first term of the sum under the integral sign. As a result, the expression for the thermal conductivity coefficient λ_2 is the following:

$$\lambda_2 = \left(\frac{3}{2}f_{tr}^{(2)} + f_{in}^{(2)}\right)(k/m)\eta \quad (30)$$

$$f_{tr}^{(2)} = \frac{5}{2} \left(1 - \frac{5}{6} \left(1 - \frac{2}{5} \frac{\rho D_0}{\eta}\right) \frac{\eta}{p\tau_{R1}(T)}\right) \quad (31)$$

$$f_{in}^{(2)} = \frac{\rho D_0}{\eta} \left(1 + \frac{5}{4} \left(1 - \frac{2}{5} \frac{\rho D_0}{\eta}\right) \frac{\eta}{p\tau_{R1}(T)}\right) \quad (32)$$

In the second approximation the parameter $\sin^2\chi$ was approximated by its value averaged over the unit sphere, which was equal to $2/3$; thus, $\eta = \eta_0$ (Ref. 11). The calculation technique and expressions for ΔE [Eqs. (14) and (15)] and χ [Eq. (16)] were just discussed (also see Refs. 10 and 11).

The solid and dashed lines in Fig. 3 show η and η_0 , correspondingly, as given by Eqs. (21–29), whereas the filled squares indicate the experimental data of Vargaftik.⁴⁰ The difference between η and η_0 is evaluated as 5% in the low-temperature regime. At temperature $T > 1000$ K these values correlate well with each other.

The solid line in Fig. 4 shows λ , as given by Eqs. (21–29). The dashed line corresponds to the Mason and Monchick's second approximation λ_2 . The filled squares indicate the experimental data of Vargaftik.⁴⁰ Mason–Monchick's first approximation¹⁴ and the Aiken approximation¹ were analyzed by Lebed and Riabov^{10,11} in detail. The present analysis shows that the correlation between the exact solution, Mason and Monchick's second approximation,¹⁴ and experimental data⁴⁰ is acceptable. The small discrepancy between the theoretical values of η and λ and the experimental data (see Figs. 3 and 4) can be eliminated by a proper choice of the potential at $T < 1000$ K.

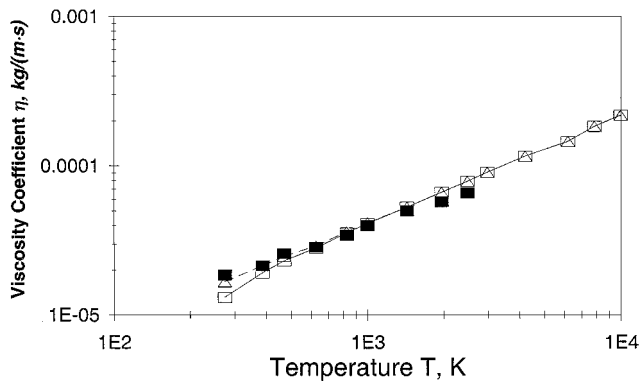


Fig. 3 Viscosity coefficient in nitrogen: □, η , solution of Eq. (21); ---, η_0 , solution of Eq. (26); and ■, experimental data.⁴⁰

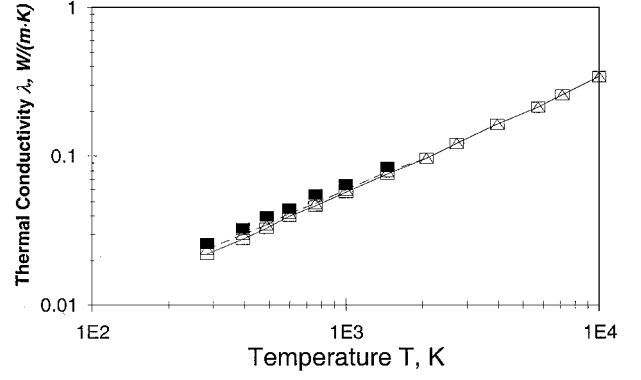


Fig. 4 Thermal conductivity coefficient in nitrogen: □, λ , solution of Eq. (22); ---, (△), λ_2 , solution of Eq. (30); and ■, experimental data.⁴⁰

IX. Transport Coefficients in Nonequilibrium Diatomic Gases (General Case)

Mason and Monchick's second-order approximation technique¹⁴ has been used for calculating the transport coefficients in the nonequilibrium case of the arbitrary value of Kn_R . As it was just demonstrated, this approximation is very good in the near-equilibrium case. The procedure of obtaining the coefficients is described by Lebed and Riabov^{10,11} in detail. Using the fact that the relaxation terms in transport coefficient formulas are small and they could be omitted, we find from Eqs. (6–8) the following expressions:

$$V_r^i = -\frac{5}{4} \frac{\eta_0 D_0}{p\tau_{R1}(T)} \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \frac{\partial kT}{\partial x_r} - D_0 \left(1 - \frac{\rho D_0}{2p\tau_{R1}(T)}\right) \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \frac{\partial \langle E \rangle}{\partial x_r} \quad (33)$$

$$q_r = -\frac{15}{4} \frac{k}{m} \eta_0 \left(1 - \frac{\frac{5}{6}\eta_0 - \frac{1}{3}\rho D_0}{p\tau_{R1}(T)}\right) \frac{\partial T}{\partial x_r} - n D_0 \left(1 - \frac{\rho D_0 - \frac{5}{2}\eta_0}{2p\tau_{R1}(T)}\right) \frac{\partial \langle E \rangle}{\partial x_r} \quad (34)$$

$$P_{ts} = p\delta_{ts} - \eta_0 \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3}\delta_{rs} \frac{\partial u_l}{\partial x_l}\right) \quad (35)$$

In the nonequilibrium case^{1,10,15} the expressions for V_r^i and q_r are

$$V_r^i = \sum_j D_{ij} \frac{\partial n_i/n}{\partial x_r} - D_i^T \frac{\partial \ell_n kT}{\partial x_r} \quad (36)$$

$$q_r = -\lambda_{R1} \frac{\partial T}{\partial x_r} + \sum_i (E_i n_i + p k_i^T) V_r^i \quad (37)$$

$$D_{ij} = D_0 \left(1 - \frac{\rho D_0}{2p\tau_{R1}(T)}\right) \frac{(E_i - \langle E \rangle)(E_j - \langle E \rangle)}{\langle E^2 \rangle - \langle E \rangle^2} \quad (38)$$

$$D_i^T = \frac{5}{4} \frac{\eta_0 D_0 kT}{p\tau_{R1}(T)} \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \quad (39)$$

$$\sum_j \frac{E_j - \langle E \rangle}{kT} k_j^T = \frac{5\eta_0}{4p\tau_{R1}(T)} \quad (40)$$

$$\lambda_{R1} = \frac{15}{4} \frac{k}{m} \eta_0 \left(1 - \frac{5}{6} \frac{\eta_0}{p\tau_{R1}(T)}\right) \quad (41)$$

In the equilibrium case the parameters $\langle E \rangle$ and $\langle E^2 \rangle$ in Eqs. (33–35) and (36–41) should be changed to their equilibrium values. In the relaxation case the small values well proportioned to $1/p\tau_{R1}(T)$

should be omitted. It was noticed^{10,15} that the expressions for V_i and q_r from Eqs. (36–41) have only the gradients of values $\langle E \rangle$ and kT , which characterize the system as a whole. In addition, the coefficients at these gradients are the functions of parameters of the i th level and the system as well. This property of the system of Eqs. (36–41) is very convenient for applications.^{29,33–35} The similar expressions were found by Lebed and Riabov⁴¹ and Riabov^{42–44} for multicomponent gas mixtures. In equilibrium case the expressions in Eqs. (33–35) and (36–41) are the same as in the study of Ferziger and Kaper.¹

Using Eqs. (33–35) and (36–41), we can find the gas dynamic equations in the common case as the following:

$$\frac{\partial n}{\partial t} + \frac{\partial nu_r}{\partial x_r} = 0 \quad (42)$$

$$\begin{aligned} \frac{\partial n_i}{\partial t} + \frac{\partial n_i u_r}{\partial x_r} - \frac{n_i^{(0)} - n_i}{\tau_R} = \frac{\partial}{\partial x_r} \left\{ n_i (E_i - \langle E \rangle) \left(\frac{5}{4} \frac{\eta_0 D_0}{p \tau_{R1}(T)} \frac{\partial kT}{\partial x_r} \right. \right. \\ \left. \left. + D_0 \left(1 - \frac{\rho D_0}{2p \tau_{R1}(T)} \right) \frac{\partial \langle E \rangle}{\partial x_r} \right) \right\} \end{aligned} \quad (43)$$

$$\frac{\partial u_s}{\partial t} + u_r \frac{\partial u_s}{\partial x_r} = -\frac{1}{\rho} \frac{\partial p}{\partial x_r} + \frac{1}{\rho} \frac{\partial}{\partial x_r} \eta_0 \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_l}{\partial x_l} \right) \quad (44)$$

$$\begin{aligned} \left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r} \right) \left(\frac{3}{2} kT + \langle E \rangle \right) \\ = \frac{1}{n} \frac{\partial}{\partial x_r} \left(\lambda_0 \left(1 - \frac{\frac{5}{6} \eta_0 - \frac{1}{3} \rho D_0}{p \tau_{R1}(T)} \right) \frac{\partial T}{\partial x_r} \right. \\ \left. - n D_0 \left(1 - \frac{\rho D_0 - \frac{5}{2} \eta_0}{2p \tau_{R1}(T)} \right) \frac{\partial \langle E \rangle}{\partial x_r} \right) \\ - kT \frac{\partial u_k}{\partial x_k} + \frac{\eta_0}{n} \left(\frac{\partial u_k}{\partial x_r} + \frac{\partial u_r}{\partial x_k} - \frac{2}{3} \delta_{rk} \frac{\partial u_l}{\partial x_l} \right) \frac{\partial u_k}{\partial x_r} \end{aligned} \quad (45)$$

$$\begin{aligned} \left(\frac{\partial}{\partial t} + u_r \frac{\partial}{\partial x_r} \right) \langle E \rangle - \frac{kT - \langle E \rangle}{\tau_R} \\ = \frac{1}{n} \frac{\partial}{\partial x_r} \left(\frac{5}{4} \frac{\eta_0 n D_0}{p \tau_{R1}(T)} \frac{\partial kT}{\partial x_r} + n D_0 \left(1 - \frac{\rho D_0}{2p \tau_{R1}(T)} \right) \frac{\partial \langle E \rangle}{\partial x_r} \right) \end{aligned} \quad (46)$$

In the formulas of Eqs. (42–46), we have used the τ -approximation method.¹⁰ The relaxation time of the i th rotational level has been approximated by the value of the relaxation time of the rotational energy τ_R . The parameter τ_R should be selected after an analysis of the rotational-translational relaxation conditions, as it was done, for example, by Lebed and Riabov.^{10,29}

The closed system of Eqs. (42–46) contains the coefficients η_0 , λ_0 , D_0 , $p \tau_{R1}(T)$, and $p \tau_R$, which are given in Figs. 1–4 for nitrogen at temperatures from 200 to 10,000 K. The parameter $\rho D_0 / \eta_0$ is approximately constant and equals 1.20. The system of Eqs. (42–46) could be applied at any value of parameter Kn_R .

X. Two Cases of Rotational Relaxation in Viscous Gas Flows

The combined effect of the rotational-translational relaxation and the viscosity and thermal conductivity processes was studied by Molodtsov and Riabov,³³ Riabov,^{15,29,34,35} Olynick et al.,³⁶ Skovorodko,³⁷ and Rebrov and Chekmarev.³⁸ The full system of the Navier–Stokes equations and the relaxation equation (42–26), based on τ -approximation technique, has been solved by the implicit

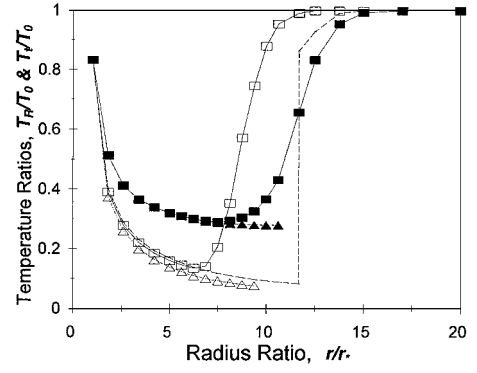


Fig. 5 Rotational T_R and translational T_t temperatures in spherically expanding flow of nitrogen: ■, T_R and □, T_t in viscous flow; ▲, T_R and △, T_t in inviscid flow; and ---, equilibrium inviscid flow ($T_R = T_t$) at $\gamma = 1.4$.

technique described by Riabov³⁵ in detail. The structure of spherical expanded flows and underexpanded viscous jets was analyzed by Riabov.^{15,29,35}

In the present study the system of Eqs. (42–46) has been numerically solved in two cases of spherically expanding flows and nonequilibrium gas flow near a sphere. The quantity $p \tau_{R2}(T)$ has been used in calculations.

A. Spherical Expanded Flows of a Viscous Gas

The changes of T_R and T_t in the spherical expanding flow of nitrogen are shown in Fig. 5. The result of computations for the Reynolds number $Re_* = \rho_* u_* r_* / \eta(T_*) = 161.83$; $K_* = \rho_* u_* r_* / p_* \tau_R(T_*) = 28.4$; $p_*/p_\infty = 41.67$; $T_{t*} = T_{R*}$, and $T_{0\infty} = 1.2 \cdot T_*$ is shown by filled squares (T_R) and empty squares (T_t). An asterisk indicates the parameters at sonic conditions. The results for inviscid nonequilibrium flow (filled triangles for T_R and empty triangles for T_t) are obtained by the method of Lebed and Riabov.²⁹ The dashed line in Fig. 5 corresponds to equilibrium values ($T_t = T_R$) for inviscid gas flow at the specific heat ratio $\gamma = 1.4$.

The numerical results confirm the earlier discovered lagging^{35,37,38} of rotational temperature compared to translational one. The speed of decrease of T_R slows down with the gas expanding in the inner supersonic area of the flow. Rotational-translational equilibrium never exists in front of the shock wave in such flow and $T_R > T_t$ both in the viscous and inviscid gas flows.

As the result of gas compression in the shock wave, a fast increase of translational and rotational temperatures occurs. In the subsonic area of the flow behind the shock wave, the temperatures reach the value of the stagnation temperature $T_{0\infty}$.

B. Nonequilibrium Flows of a Viscous Gas near a Sphere

The flow near a front area of a sphere might be considered as an example of a compressing nonequilibrium viscous flow. The calculated values of rotational-translational relaxation time [Eq. (18)] were used by Molodtsov and Riabov³³ in the analysis of the molecular nitrogen flow near a sphere. A significant difference between rotational energy and translational temperature distributions was discussed. The similar effect was studied by Olynick et al.³⁶ comparing Monte Carlo methods and Navier–Stokes equations approach for reentry flows near the continuum limit. The study of Boyd¹⁸ indicates a significant influence of the rotational-relaxation time model on the flow structure within shock waves in diatomic gases.

In the present study the full system of the Navier–Stokes equations and the relaxation equations (42–46), based on τ -approximation technique, has been solved by the implicit numerical technique described by Riabov³⁴ and Molodtsov and Riabov³³ in detail. The gas flow of molecular nitrogen was assumed to be undisturbed on the outer boundary of the computational region located at the distance of radius of the sphere R from the spherical surface. At the body surface the slip, temperature, and rotational energy jump conditions³⁴ were used.

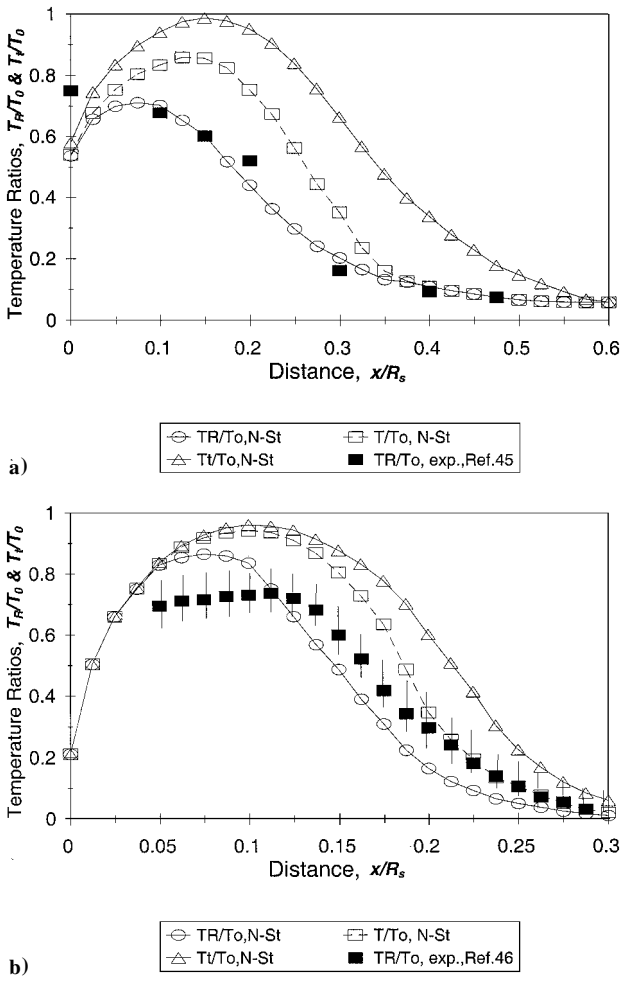


Fig. 6 Nonequilibrium rotational T_R , translational T_t , and equilibrium overall T temperatures at the stagnation stream line near a sphere: a) $Kn_{\infty,R} = 0.08$ ($Re_{0,R} = 16.86$), $M_{\infty} = 9$, $T_0 = 298$ K, $t_w = 0.3$; ■, experimental data⁴⁵; and b) $Kn_{\infty,R} = 0.017$ ($Re_{0,R} = 57.4$), $M_{\infty} = 18.8$, $T_0 = 1600$ K, $t_w = 0.19$; ■, experimental data.⁴⁶

The distribution of the nonequilibrium rotational (T_R , circles) and translational (T_t , triangles) temperatures are shown in Fig. 6 for two cases of rarefied upstream flow: a) Knudsen number $Kn_{\infty,R} = 0.08$ (or Reynolds number $Re_{0,R} = 16.86$), Mach number $M_{\infty} = 9$, stagnation temperature $T_0 = 298$ K, and temperature factor $t_w = 0.3$, and b) $Kn_{\infty,R} = 0.017$ ($Re_{0,R} = 57.4$), $M_{\infty} = 18.8$, $T_0 = 1600$ K, $t_w = 0.19$. In the viscous shock layer near a sphere, a significant difference between the translational and rotational temperatures can be observed. The shock-layer thickness becomes bigger under the nonequilibrium flow conditions than in the case of equilibrium flow at $T_R = T_t$ (see empty squares in Fig. 6). The numerical results for T_R correlate well with the experimental data of Tirumalesa⁴⁵ and Ahouse and Bogdonoff⁴⁶ (marked by filled squares in Fig. 6), obtained in wind tunnels by the electron-beam diagnostics. A discrepancy of the results at the leading stagnation point of the sphere can be explained by the strong influence of secondary electrons in the experiments^{45,46} as well as by a chosen approximation of the slip and temperature jump conditions in calculations.

XI. Conclusions

The nonequilibrium gas dynamic equations have been derived for rotational-translational processes in diatomic gases in the general case of the arbitrary energy exchange ratio, which is characterized by parameter Kn_R . The analytical form of the energy and momentum parameters is found in this case based on the Parker's molecular collision model. The calculations of relaxation time, viscosity and thermal conductivity, and diffusion coefficients have been carried out by using the Monte Carlo simulation technique in the tempera-

ture range $200 \leq T \leq 10,000$ K for nitrogen. The results are applied for different conditions of ultrasound, shock-wave, and underexpanded jet experiments.

The calculations show that the rotational relaxation time τ_{R1} , obtained by using the Chapman-Enskog iteration method, is 2 or 2.5 times as large as the time τ_{R2} , which is found directly from the relaxation equation by calculating the increased rate of the internal energy of molecules, which originally were not internally excited. The difference is apparently caused by the adiabatic nature of the energy exchange between the highly excited rotational states of the molecules. The quantity $p\tau_{R1}(T)$ has been used for interpreting the experimental data on the scattering and absorption of ultrasound. The quantity $p\tau_{R2}(T)$ has been used for interpreting the data of experiments in shock tubes. The available experimental data, both on ultrasound and on shock waves, differ from one another by 200–300%, which is approximately equal to the difference between $p\tau_{R1}(T)$ and $p\tau_{R2}(T)$.

The nonequilibrium viscous gas flow near a sphere has been studied. The full system of the Navier-Stokes equations and the relaxation equation, based on the τ -approximation technique, has been solved by the implicit numerical technique. The numerical and experimental data are well correlated.

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