Estimations of Rotational Relaxation Parameters in Diatomic Gases

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Abstract: 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 K 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 nitrogen flow in underexpanded jets and supersonic rarefied gas flow near a sphere.

Keywords: Chapman-Enskog method, nonequilibrium gasdynamic equations, relaxation time, transport coefficients, two-temperature relaxation model, underexpanded nitrogen jet, supersonic sphere
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INTRODUCTION

The problem of deriving the nonequilibrium gas dynamic equations from the first principles of the kinetic theory of gases was studied by Ferziger and Kaper [1] in the cases of near-equilibrium and slow-relaxation processes of the energy exchange between internal and translational degrees of molecular freedom. The case of the arbitrary energy exchange ratio was analyzed by Alekseev [2], Kogan and Makashev [3], Matsuk and Rykov [4], and Lebed and Riabov [5] for polyatomic gas mixtures.

In the present study the problem of redistribution of translational and rotational energy has been solved for diatomic gases within the framework of the Chapman-Enskog method [1], [5], [6] and the Parker model [7] 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 [5], [6]. The calculations of relaxation time, viscosity, thermal conductivity, and diffusion coefficients are carried out in the temperature range from 200 K to 10,000 K for nitrogen by using the technique of integral brackets [1], [4]. The calculated parameters and coefficients are compared with the values obtained by the Mason-Monchick approximate method [8] and data from experiments [9], [10] 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 for para-hydrogen at the rotational temperature range from 0 K to 1200 K is discussed. The numerical solutions of the Navier-Stokes equations are analyzed for spherical expanding nitrogen flow and supersonic rarefied gas flow near a sphere.

ROTATIONAL RELAXATION TIME

Two definitions of relaxation time are widely used. In the first case the expression for the temperature dependence of the relaxation time, $\tau_{R1}(T)$, is obtained by using the Chapman-Enskog iteration method of solving the Boltzmann equation for a gas of particles with internal degrees of freedom [1]. In the second case the relaxation

time, $\tau_{R2}(T)$, is found directly from the relaxation equation (see Eq. (17) from [6]) by calculating the rate of increase of the internal energy of the molecules that originally were not excited [11].
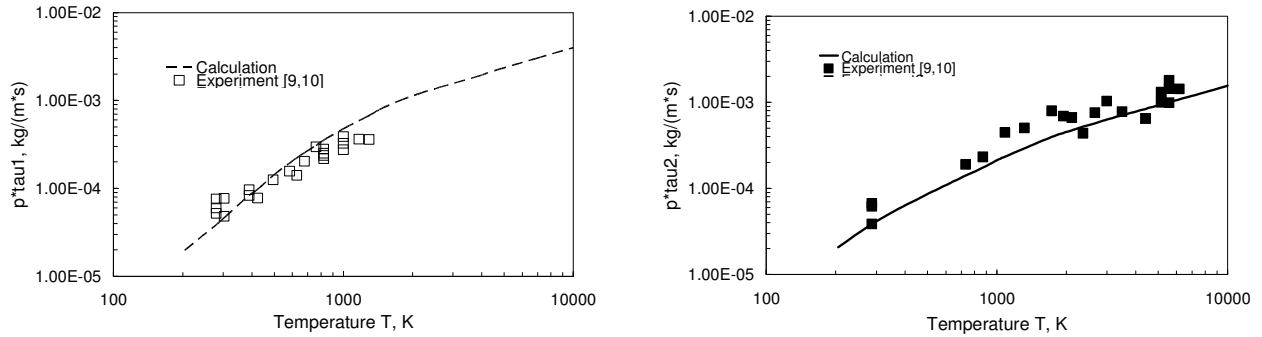
FIGURE 1. Parameters $p\tau_{R1}$ (*left*) and $p\tau_{R2}$ (*right*) vs. temperature T. Experimental data from [9], [10].

In the present study parameters $p\tau_{R1}(T)$ and $p\tau_{R2}(T)$ are calculated for nitrogen by formulas (18)-(20) from [6]. Multifold integrals are calculated at 200 points over the range of temperatures 200 K $\leq T \leq$ 10,000 K, using the Monte-Carlo technique [5], with 4000 tests at each point. The data for intermediate points are determined by means of the interpolation technique [6] 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 anisotropy parameter ε [6] in the molecule interaction potential make a substantial contribution at $T < 400$ K, and the accuracy of the calculations is lower under these conditions.

The results of calculations $p\tau_{R1}(T)$ and $p\tau_{R2}(T)$ are shown in Fig. 1 (dashed and solid lines, correspondingly). The experimental data (squares) were acquired by Brau and Jonkman [9], and Lordi and Mates [10]. 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 due to the adiabatic nature of the energy exchange between the highly excited rotational states of the molecules [5]. The effect of the initial energy distribution at rotational levels was not considered in this comparison.

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 [9]. The quantity $p\tau_{R2}(T)$ has been used for interpreting the data of experiments in shock tubes. The available experimental data [9], [10], 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 $p\tau_{R2}(T)$, as evident from Fig. 1.

THE EFFECT OF INITIAL ROTATIONAL ENERGY DISTRIBUTION

The effect of the initial energy distribution at rotational levels has been estimated in [5] under the assumption that at initial time the distribution corresponds to the Boltzmann distribution with rotational temperature $T_R > 0$. In this case, the translational-rotational relaxation time becomes a function not only of translational temperature T but of T_R as well [see Eq. (1.7) in Ref. 5]. The parameter $p\tau_{R2}(T, T_R)$, calculated for nitrogen at $T = 1000$ K, decreases from 2.13×10^{-4} kg/(m*s) for $T_R = 0$ K to 5.24×10^{-5} kg/(m*s) for $T_R = 800$ K.

The problem of a proper selection of the relaxation time [$\tau_{R2}(T)$ vs. $\tau_{R2}(T, T_R)$] for a more accurate description of the manner in which the system approaches equilibrium was studied in [5] for para-hydrogen. The solution of the kinetic equation in τ–approximation (see Eq. (17) from Ref. [6]) was compared with the exact solution obtained by numerical integration of the system of kinetic equations for the occupancies of the individual rotational levels [5]. In these calculations, the constants of the rotational-transfer rates for various rotational levels were estimated within the framework of the effective-potential method [12].

The results of the calculation are shown in Fig. 2, where parameters $p\tau_{R2}(T, T_R)$, estimated at constant temperature T = 400K, (triangles) are compared with the results of numerical integration of the system of kinetic equations for the occupancies (circles). The point $T_R = 0$ K of the first curve corresponds to $p\tau_{R2}(T)$. As in the case of the rotational relaxation of nitrogen, a strong dependence of the relaxation time on T_R has been found. Therefore, the use of a two-parameter function $p\tau_{R2}(T, T_R)$ significantly improves the approximate solution of the traditional

kinetic equation. These results indicate that the initial distribution of energy at rotational levels should be taken into account within the framework of the τ–approximation.
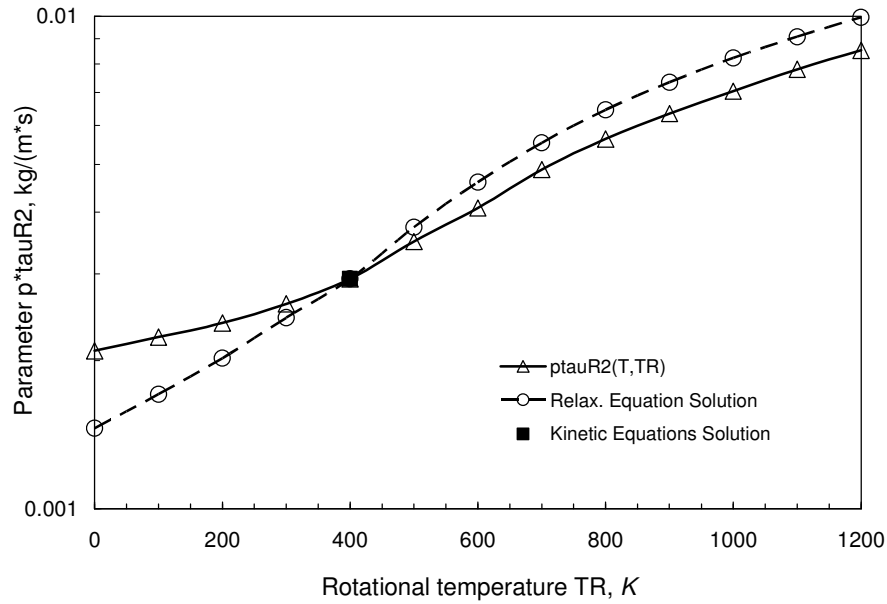

FIGURE 2. The rotational relaxation parameters $p\tau_{R2}$ (T, T_R) in para-hydrogen at constant temperature $T = 400K$.

ROTATIONAL RELAXATION IN FREELY EXPANDING GAS FLOWS

Marrone [13] and Borzenko et al. [14] studied the 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. The departure of the gas rotational energy from the equilibrium value was observed.

Lebed and Riabov [15] and Riabov [16] studied another cause for the rotational energy departure. At the decrease of kinetic temperature T_t, the Messy adiabatic parameter [17], which describes energy transfer between highly excited rotational levels unable to relax, becomes larger than unity. Adiabatic collision conditions [17] should be taken into account in this case. As T_t decreases, the relaxation time τ_R will increase due to the significant decrease of the rotational transfer probabilities.
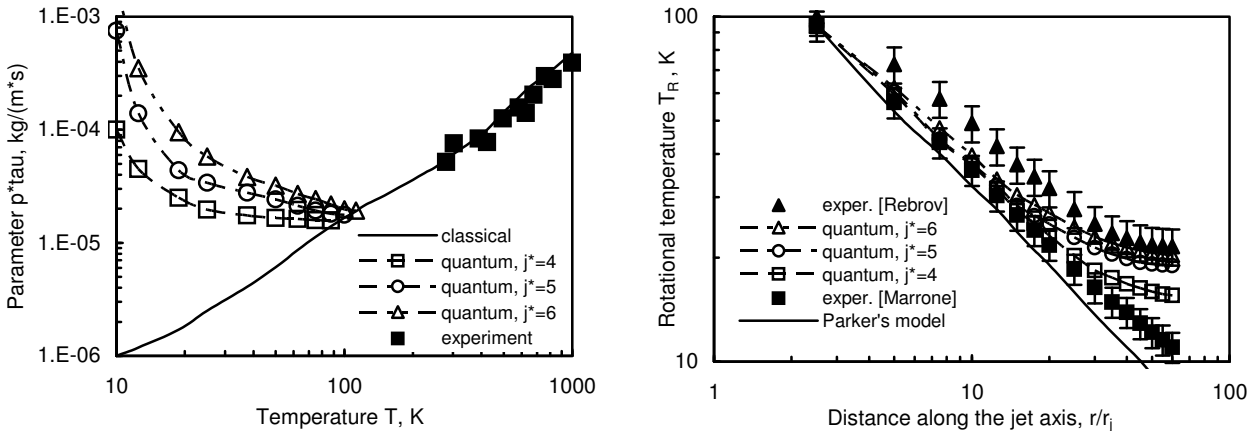

FIGURE 3. *Left*: The rotational relaxation parameters $p\tau_R$ (T_t) in nitrogen expanding into a vacuum. Experimental data from [9], [10]. *Right*: The rotational T_R and translational T_t temperatures in the underexpanded jets of nitrogen. Experimental data from [13], [14].

Using the technique of Lebed and Riabov [15], the rotational-translational relaxation times were calculated for nitrogen at stagnation temperature $T_0 = 290$ K [see Fig. 3 (left)] under the conditions of aerodynamic experiments in the underexpanded jets [13], [14], [16]. The relaxation times calculated by Parker [7] are shown in Fig. 3 (left) as the solid line. The calculations based on the classical-mechanics concept [7] do not show a tendency of increasing $p\tau_R$ with the decrease of T_t under adiabatic rotational energy exchange conditions. At temperatures $T_t > 273$ K, numerical results correlate well with experimental data [9], [10].

In the expansion of nitrogen, starting at a stagnation temperature $T_0 = 300$ K, the maximum population of molecules occurs at rotational levels j^* from 6 to 4. Following Refs. [15], [17], the results of calculating $p\tau_R$ for $j^* = 6$, 5, and 4 are shown in Fig. 3 (left) (empty triangles, circles, and squares, correspondingly). These values of $p\tau_R$ increase with decrease of T_t. At $T_t > 100$ K, the adiabatic condition breaks down, and the parameter $p\tau_R$ could be calculated by the Parker's classical-mechanics model [7].

For qualitative estimations, it is possible to replace the energy relaxation time by the relaxation time of the level j^*. This approximation method correctly represents the nature of the R-T nonequilibrium process, i.e., an increase of $p\tau_R$ with decreasing T_t. Figure 3 (right) shows the distributions of rotational temperature T_R along the axis of nitrogen jet. The result of using the classical mechanics concept [7] is shown there by the solid line. The curves marked by empty triangles, circles, and squares were obtained in terms of the quantum concept [15] for values of $p\tau_R$ at $j^* = 6$, 5, and 4, correspondingly. In the calculation it was assumed that the main R-T relaxation parameter was $K_* = \rho_* u_* r_*/(p\tau_R)_* = 2730$, $p_0 r_* = 240$ torr·mm and $T_0 = 290$ K.

The experimental data for T_R along the axis of a nitrogen jet, obtained by Marrone [13] (filled squares) and Borzenko et al. [14] (triangles), are upper and lower bounds on the distribution of rotational energy along the flow. Numerical results, based on the quantum concept of rotational energy exchange, correlate well with the experimental data [14]. The data contradicts the classical model predictions [7] of the T_R distributions along the jet axis.

The experimental and computational results demonstrate the necessity of considering the quantum concept in describing R-T relaxation in the underexpanded jets. This concept was used by Gochberg and Haas [18] in evaluating various rotational relaxation models in expanding low-density nitrogen flows.

TRANSPORT COEFFICIENTS IN NON-EQUILIBRIUM DIATOMIC GASES

The analytical formulas for various transport coefficients were found by Lebed and Riabov (see Eqs. (21-29) in [6]): the coefficients of shear viscosity corresponding to rotationally inelastic and elastic collisions, η and η_0; the corresponding values of the thermal conductivity, λ and λ_0; and the self-diffusion coefficient of the elastically colliding molecules, D_0.

The simplest approximations for the thermal conductivity coefficient λ were analyzed by Ferziger and Kaper [1], Mason and Monchick [8], and Lebed and Riabov [5], [6]. The first approximation [8] 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 for the thermal conductivity coefficient λ_2 (see Eqs. (30-32) in [6]).
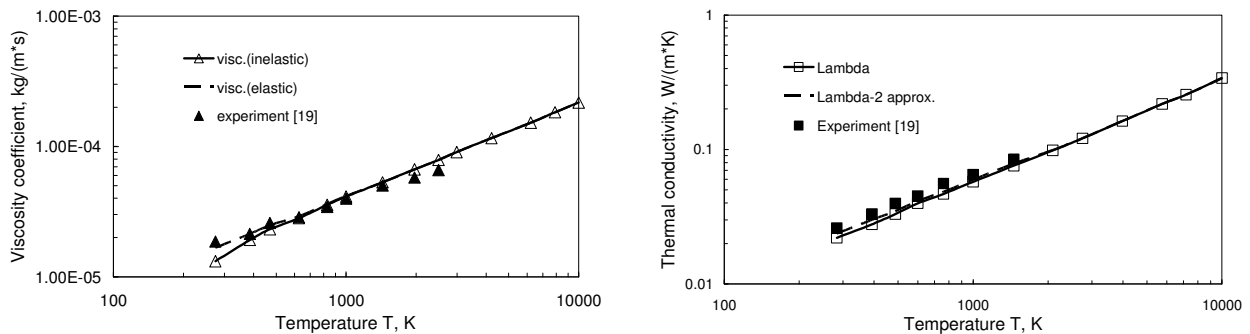
FIGURE 4. Viscosity (*left*) and conductivity coefficients (*right*) in nitrogen. Experimental data from [19].

The solid and dashed lines in Fig. 4 (left) show η and η_0, correspondingly, as given by Eqs. (21-29) from [6], while the filled triangles indicate the experimental data of Vargaftik [19]. 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 parameter $\rho D_0/\eta_0$ is approximately constant and equals to 1.20.

The solid line in Fig. 4 (right) shows λ, as given by Eqs. (21-29) from [6]. The dashed line corresponds to the Mason and Monchick's second approximation [8], λ_2. The filled squares indicate the experimental data of Vargaftik [19]. The present analysis shows that the correlation between the exact solution, the Mason and Monchick's second approximation [8], and experimental data [19] is acceptable. In both cases of η and λ, the small discrepancy between the theoretical values and experimental data (see Fig. 4) can be eliminated by a proper choice of the molecular potential and collision parameters [5] at $T < 1000$ K.

The closed system of the gas-dynamic equations (see Eq. (42-46) from [6]), which contains the coefficients η_0, λ_0, D_0, $p\tau_{R1}(T)$, and $p\tau_R$, could be used in various applications at any value of the Knudsen number, Kn_R.

ROTATIONAL RELAXATION IN VISCOUS GAS FLOWS NEAR A SPHERE

The combined effect of the rotational-translational relaxation and the viscosity and thermal conductivity processes is studied here by solving the full system of the Navier-Stokes equations and the relaxation equation (see Eq. (42-46) from [6]) with the implicit numerical technique described by Riabov [20] 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 conditions [20] were used.
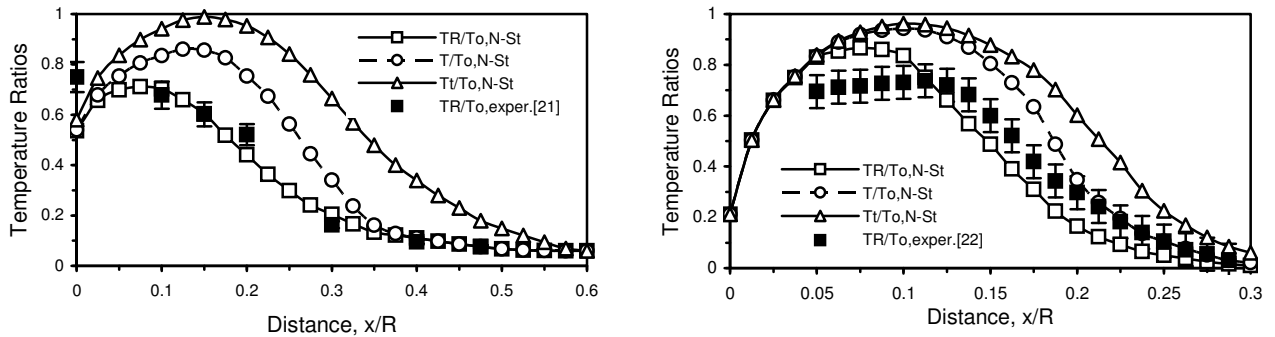
a) $Kn_{\infty,R} = 0.08$ $(Re_{0,R} = 16.86)$, $M_\infty = 9$, $T_0 = 298$ K, $t_w = 0.3$ **b)** $Kn_{\infty,R} = 0.017$ $(Re_{0,R} = 57.4)$, $M_\infty = 18.8$, $T_0 = 1600$ K, $t_w = 0.19$

FIGURE 5. Comparison of numerical solutions of the Navier-Stokes equations and experimental data [21, 22] for nonequilibrium rotational T_R, translational T_t, and equilibrium overall T temperatures on the stagnation stream line near a sphere.

The distribution of the nonequilibrium rotational (T_R, squares) and translational (T_t, triangles) temperatures are shown in Fig. 5a for rarefied upstream flow at 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 $t_w = T_w/T_0 = 0.3$. In the viscous shock layer near a sphere, a significant difference between the translational and rotational temperatures can be observed. The shock-layer becomes thicker under the nonequilibrium flow conditions than in the case of equilibrium flow at $T_R = T_t$ [see empty squares in Fig. 5a]. The numerical results for T_R, correlate well with the experimental data of Tirumalesa [21] (marked by filled squares in Fig. 5a), obtained in wind tunnels by the electron-beam diagnostics. A discrepancy of the results at the spherical surface can be explained by the strong influence of secondary electrons in the experiments [21] as well as by a chosen approximation of the slip and temperature jump conditions [20] in calculations.

In the viscous shock layer near a sphere under the continuum flow conditions at $Kn_{\infty,R} = 0.017$ $(Re_{0,R} = 57.4)$, $M_\infty = 18.8$, $T_0 = 1600$ K, $t_w = 0.19$, a significant difference between the translational and rotational temperatures still can be observed (see Fig. 5b). The shock-layer thickness becomes thicker under the nonequilibrium flow conditions than in the case of "equilibrium" flow at $T_R = T_t$ (see circles in Fig. 5b). The numerical results for T_R correlate well with the experimental data of Ahouse and Bogdonoff [22], obtained in wind tunnels by the electron-beam diagnostics.

CONCLUSIONS

The nonequilibrium gasdynamic 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, thermal conductivity, and diffusion coefficients were carried out by using the Monte-Carlo simulation technique in the temperature range $200 \leq T \leq 10,000$ K for nitrogen. The results are applied for the 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. The difference is apparently due to 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 computational results demonstrate the necessity of applying the quantum concept (that includes adiabatic collision conditions for highly excited rotational levels unable to relax at the sharp decrease of kinetic energy) in the analysis of the rotational-translational relaxation at $T_t < 100$K in the underexpanded jets of nitrogen.

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 τ-approximation technique, has been solved by the implicit numerical technique. The numerical and experimental data are well correlated.

ACKNOWLEDGEMENT

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