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NONEQUILIBRIUM GAS DYNAMIC EQUATIONS AND TRANSFER COEFFICIENTS IN DIATOMIC GAS

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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. The nonequilibrium gasdynamic equations were obtained for rotational-translational processes in diatomic gas. The calculations of relaxation time, viscosity and thermal conductivity coefficients were carried out in the temperature range $200 \leq T \leq 10{,}000$ K for nitrogen. The calculated parameters and coefficients were compared with the values obtained by the Mason-Monchick approximate method as well as experimental data under the testing conditions 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 was discussed. The solution of the obtained system of the Navier-Stokes equations was analyzed for the case of spherical expanding nitrogen flow in rarefied gas media.

Introduction

The gas dynamic equations and transfer coefficients were received by Ferziger and Kaper,[1] and Kogan[2] for nonequilibrium polyatomic gas mixtures by using the Chapman-Enskog iteration method to solve the Boltzmann equation in the simple cases of near-equilibrium and slow-relaxation processes of the energy exchange between internal and translational degrees of molecular freedom. This technique was developed by Alekseev,[3] Galkin et al.,[4] Matsuk and Rykov,[5] and Kogan and Makashev[6] for the case of the arbitrary energy exchange ratio. However, these studies had more academic interest. The practical results were received by Matsuk and Rykov[5] for the model system of equations.

In this study the general case of the arbitrary energy exchange ratio is considered for the real diatomic gas with rotational degrees of freedom.

The transfer coefficients and reaction rates for rotational excited gas are received by using the technique of integral brackets.[1] In calculating of the correction term to the distribution function of the zero approximation, the linear-dependence transformation of the diffusion thermodynamic force vectors to the linear-independence vector set was done by the linear transformation method of Matsuk and Rykov.[5] The matrix transformation elements are the Waldmann-Trubenbaher polynomials. Integral brackets were calculated in terms of classical mechanics. The collision molecule model is based on the Parker concept.[7] The energy and momentum parameters could be presented in the analytical form in this case. The form was used for calculations.

The collision model was applied for prediction of the rotational-translational relaxation time τ_R. The six multiple integrals were evaluated by the Monte-Carlo technique in the temperature range from 200 to 10,000 K for nitrogen. The viscosity and thermal conductivity are compared with experimental data and the Mason-Monchick approximations.[8] The conditions of one- and two-temperature approximations for the relaxation time are considered for nitrogen. The two-temperature approximation was analyzed by Lebed' and Riabov[9,10] for parahydrogen. The applications of the theory are discussed for testing in ultrasonic devices, shock-wave tubes, and underexpanded jets in vacuum chambers.

The thermodynamic force transformation technique and the Mason-Monchick approximation were used to receive the analytical expressions for heat flux and diffusion

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velocity of the rotational levels.

The Chapman-Enskog iteration method to solve the Boltzmann equation for this case was described by Lebed' and Riabov[9] in detail. The calculating of rotational relaxation time and transfer coefficients was done by the technique of Lebed' and Riabov[10].

The 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[9]. The introducing of the Knudsen number *Kn* and parameter Kn_R, which characterizes the ratio of the specific non-elastic 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 according to the small parameter *Kn*. The first approximation term was received by Galkin et al.[4] The analysis of Galkin et al.,[4] Kogan and Makashev,[6] and Lebed' and Riabov[9] indicated that the elastic collision term and the non-elastic collision one have the order of the unit and $O(Kn_R)$, respectively.

The set of diffusion thermodynamic forces is linearly dependent. According to the technique of Matsuk and Rykov,[5] and using the Waldmann-Trubenbaher polynomials, we create the new set of linearly independent vectors for solving the problem on this stage. The general solution of the problem was found as the sum of the particular solution and the general solution of the uniform equation. This solution is as the following:[9]

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

The coefficients A^i, B^i, $A^{i(p)}$, and G_i are the roots of the integral equations given in the study by Lebed' and Riabov.[9] The solutions of the integral equations could be found as series of the Sohnin ($S_{(k)i}{}^{(t)}$) and Waldmann-Trubenbaher $P_i{}^{(p)}$ polynomials:[1,4-6,9]

$$\begin{aligned} A^i &= \sum_{p=0}^{\infty} \sum_{t=0}^{\infty} a_{pt} P_i{}^{(p)} S_{(3/2)i}{}^{(t)}; \\ B^i &= \sum_{p=0}^{\infty} \sum_{t=0}^{\infty} b_{pt} P_i{}^{(p)} S_{(5/2)i}{}^{(t)}; \\ A^{i(q)} &= \sum_{p=0}^{\infty} \sum_{t=0}^{\infty} a_{pt}{}^{(q)} P_i{}^{(p)} S_{(3/2)i}{}^{(t)}; \\ G_i &= \sum_{p=0}^{\infty} \sum_{t=0}^{\infty} g_{pt} P_i{}^{(p)} S_{(1/2)i}{}^{(t)} \end{aligned} \qquad (2)$$

In calculations we used two first non-zero terms in the series (2). The linear system of second order equations was solved by the maximum principle and variation technique.[1,3-5] Using equations (1) - (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 as the following:[9]

$$\begin{aligned} V_r{}^i &= -a_{10} \frac{E_i - \langle E \rangle}{\rho} \frac{\partial \ln kT}{\partial x_r} + a_{10}{}^{(1)} \left(\frac{kT}{m} \right) \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \frac{\partial \langle E \rangle}{\partial x_r}; \\ q_r &= -\left(a_{01} \frac{5}{2} \frac{kT}{m} + a_{10} \frac{kT}{m} \frac{\langle E^2 \rangle - \langle E \rangle^2}{(kT)^2} \right) \frac{\partial kT}{\partial x_r} + \\ &\quad + \left(a_{10}{}^{(1)} \frac{p}{m} + a_{01}{}^{(1)} \frac{\frac{5}{2} p (kT)^2}{\langle E^2 \rangle - \langle E \rangle^2} \right) \frac{\partial \langle E \rangle}{\partial x_r}; \\ P_{rs} &= p \delta_{rs} - \frac{(kT)^2}{m} b_{00} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_l}{\partial x_l} \right), \quad p = nkT \end{aligned} \qquad (3)$$

The scaler term of the solution (1) can be used for evaluation of the correction terms in the rotational rates.[9] The transfer coefficients can be found by the coefficients of the equations (3).

The Interaction Potential Model for Diatomic Molecules

Within the framework of the Parker model,[7] 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. Expansion of the short-acting part of the potential in a Fourier series let 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 was justified by the fact that anisotropy parameter $\varepsilon = 2I_2(y)/I_0(y)$ is small; here $y = \alpha d^*/2$, α is the inverse radius of action of the intermolecular forces, I_0 and I_2 are modified Bessel functions.

The interaction potential is represented in the form:[7]

$$V_r = Q e^{-\alpha r}(1 + \varepsilon\cos 2\theta_i + \varepsilon\cos 2\theta_j) \tag{4}$$

where Q is a constant, r is the intermolecular distance, and 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 potential (4) developed by Parker[7] was 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.[10] 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,[11] is replaced with the constant value $\mu v^2 b^2/2r_0^2$, where μ is the mass of an atom of the molecule, b is a target parameter, v is the velocity of relative motion of the participating entities which do not act on each other, r_0 is a parameter which takes on a value in a narrow range $1/\alpha$ around the point of turning r_p.

In the first order of the theory of perturbations with respect to the parameter ε, analytic expressions for the resulting angular velocities of the molecules are:[9,10]

$$\begin{gathered}
\varphi_i = -\frac{16\pi l_i \sin 2\psi_i}{\alpha^2 d^2 sh^2 \varkappa_i};\\
\varkappa_i = \frac{2\pi l_i}{\alpha g\sqrt{1 - q^2 + \dfrac{2\varepsilon_0}{g^2 kT}}};\\
\psi_i = \varphi_i - \arcsin q; \quad q = \frac{b}{r_0};\\
l_i = \sqrt{2}p_i d - \frac{qg}{r_0}; \quad g = \sqrt{\frac{\mu}{kT}}v
\end{gathered} \tag{5}$$

where p_i and φ_i are the initial reduced angular momenta and initial phases counted from the direction of the initial velocity of relative motion of the molecules.

The additional acceleration in the region of interaction as a result of the remote-acting forces is taken into account in Eq. 5 according to the study of Nikitin and Osipov[11] by replacing $\mu^2/2$ with $\mu v^2/2 + \varepsilon_0$, where ε_0 = 96.6 K is the depth of the potential well.[12,13]

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:[9,10]

$$\begin{gathered}
\Delta E_i = \frac{128\pi^2\varepsilon^2 l_i^2 \sin^2 2\psi_i}{\alpha^4 d^2 g^2 sh^2 \varkappa_i} - \frac{16\sqrt{2}\pi\varepsilon p_i l_i \sin 2\psi_i}{\alpha^2 d g^2 sh\varkappa_i};\\
\Delta M_i = -\frac{8\pi\varepsilon l_i \sin 2\psi_i}{\alpha^2 g r_0 sh\varkappa_i}
\end{gathered} \tag{6}$$

The isotropic interaction potential for the nitrogen molecules, $V_0(r)$, was approximated by data from the study of Belyaev et al.[12] in the range $r > 3.1096$Å. The short-acting branch of $V_0(r)$ was approximated by the exponential function $Q\exp(-\alpha r)$ at each point of turning r_p. The value of the parameter α was evaluated as $\alpha(r_p) = -d\ln V_0(r)/dr$ at r_p. The parameter r_0 was equated to the integral $\sqrt{\Omega^{(2,2)*}}$, calculated by Belyaev et al.[12] for the exact potential $V_0(r)$ at $r \sim 1/\alpha$.

The functions of $\alpha(T)$, $\varepsilon(T)$, $r_p(T)$, and $r_0(T)$, corresponding to $d^* = 0.62$ were calculated by Lebed′ and Riabov.[9,10]

The angle of elastic scattering for a short-acting potential was approximated by the angle of scattering of solid spheres as in the studies of Lebed′ and Riabov,[9,10] and Nikitin and Osipov.[11] The calculations of the angle of scattering is carried out on the assumption that the energy transfer from the translational to the rotational degrees of freedom takes place instantaneously at the point r_0.

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 to solve 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.[11]

To describe the rotational relaxation of a gas of homonuclear diatomic molecules, the specific models of the intermolecular interaction were used for calculating the redistribution of the rotational and translational energies upon collision. The main disadvantage of such models[13] 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 shape. 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. This fact contradicts the experimental data.[13]

The parameter $Z_{R2}(T) = \tau_{R2}/\tau$, calculated in Parker[7] and obtained more precisely by Brau and Jonkman,[14] corresponding to the plane collision of the initially unperturbed rotators, increased 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.[15]

The values of $Z_{R1}(T)$, and $Z_{R2}(T)$ for nitrogen were calculated by Lebed′ and Riabov[9,10] at $T \geq 300$ K.

The process of establishing equilibrium with respect to the rotational degrees of freedom in terms of the τ-approximation was described by the relaxation equation:[16]

$$\frac{d\varepsilon_R}{dt} = \frac{\left(\varepsilon_R{}^0 - \varepsilon_R\right)}{\tau_R} \tag{7}$$

where ε_R is the rotational energy per molecule and $\varepsilon_R{}^\circ$ is its equilibrium value. It was noted,[10,16] that Eq. 7 holds for small deviations from equilibrium $(\varepsilon_R{}^\circ - \varepsilon_R)/\varepsilon_R{}^\circ \ll 1$. Parameter $\tau_{R2}(T)$ could be determined from Eq. 7 as the ratio of $\varepsilon_R{}^\circ$ to the rate of growth of the energy of the initially unexcited rotators.[16] In the case considered here, this rate can be determined by averaging of the parameters in Eqs. 6, in which we must set $p_1 = p_2 = 0$:

$$p\,\tau_{R2}(T) = \frac{5}{I}\left(\frac{\alpha^2 d r_0}{128\pi\varepsilon}\right)^2; \quad \varkappa_0 = \varkappa_i\big|_{p_i=0}; \tag{8}$$

$$I = \frac{2}{\sqrt{2\pi\mu kT}}\int_0^{r_0}\int_0^{\infty}\left(\frac{b}{r_0}\right)^2\frac{g^5}{8}\exp\left(\frac{-g^2}{2}\right)sh^{-2}\varkappa_0\, b\,db\,dg$$

The effect of the initial distribution with respect to the rotational states was estimated by Lebed′ and Riabov.[9,10] They assumed that at time $t = 0$ this distribution corresponds to the Boltzmann distribution with some temperature $T_R \neq 0$. Under these conditions, the time of rotational relaxation 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 Riabov[10] for nitrogen and parahydrogen at $0 \leq T_R \leq 1200$ K.

As in the case of the rotational relaxation of nitrogen, investigated by Lebed′ and Riabov,[10] a strong dependence of the relaxation time τ_R on T_R in parahydrogen was found.[10] The use of two-parameter function $\tau_R(T, T_R)$ *improves the approximate calculation obtained with Eq.* (7). The results[9,10] indicated that the initial distribution according to rotational levels must be taken into account within the framework of the τ-approximation.

The rotational-translational energy exchange process was considered at $Kn_R \sim 1$, and $\tau < \tau_{R1}(T) \ll \theta$, where θ is the characteristic time of flow. Under the considered conditions, the rotational energy parameters $\varepsilon_R{}^\circ$ and ε_R differ from each other by a small quantity proportional to the Knudsen number Kn. The general expression for $p\tau_{R1}(T)$ is found by solving the Boltzmann equation, using the Chapman-Enskog method:[1,9,10]

$$\frac{1}{p\,\tau_{RI}(T)} = \frac{2}{\pi^2\sqrt{2\pi\mu kT}}\int_0^{r_0}\int_0^{\infty}\int_0^{\pi}\int_0^{\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Delta E^2 \times \times\exp\left(-\frac{g^2+p_i{}^2+p_j{}^2}{2}\right)b\,db\,\frac{g^7}{16}\,dg\,d\varphi_i\,d\varphi_j\,dp_i\,dp_j \tag{9}$$

The temperature was determined on the basis of the total molecular energy. Formula (9) differs by factor of 5/3 from the corresponding quantity obtained in determining the temperature on the basis of the kinetic energy of the molecules.[16]

Numerical Method

The sixfold integrals were calculated at 200 points of the range of temperatures 200 K $\leq T \leq$ 10,000 K, using the Monte-Carlo technique,[10] with 4000 tests at each point. The data were drawn by means of the interpolation technique[9,17] 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.

Numerical Results

The results of calculations $p\tau_{R2}(T)$ and $p\tau_{R1}(T)$ according to formulas (8) and (9) are shown in Figs. 1, and 2, correspondingly (solid lines and empty squares). The experimental data (filled squares) were received by Brau and Jonkman,[14] and Lordi and Mates.[18]

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.[10] The quantity $p\tau_{R1}(T)$ was 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.[14] The quantity $p\tau_{R2}(T)$ was used for interpreting the data of experiments in shock tubes. The effect of the initial distribution according to rotational levels was not considered in this comparison.

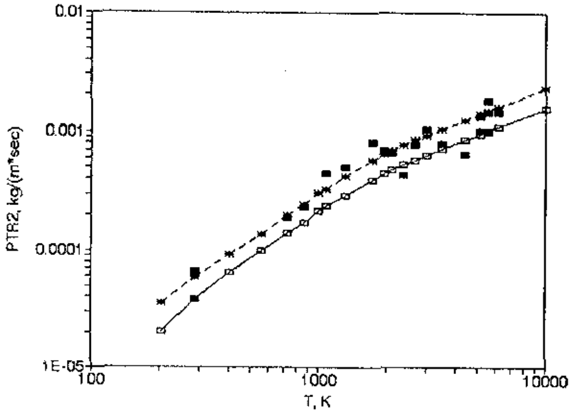

Fig. 1 The parameter $p\tau_{R2}(T)$ as a function of temperature: ▫ - solution of Eq. (8) at $d^* = 0.62$; * - solution of Eq. (8) at $d^* = 0.557$; ▪ - experimental data.[14,18]

The influence of the parameters α and d^* on $Z_{R2}(T)$ and $Z_{R1}(T)$ was analyzed by Lebed' and Riabov.[9,10] As it is shown in Fig. 1 (dashed line and asterisk correspond to $d^* = 0.557$), a decrease in d^* causes an increase in $p\tau_{R2}(T)$. It was noted by Lebed' and Riabov,[10] that for constant α both $Z_{R2}(T)$ and $Z_{R1}(T)$ remains 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 available experimental data,[14,18] 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 $p\tau_{R2}(T)$.

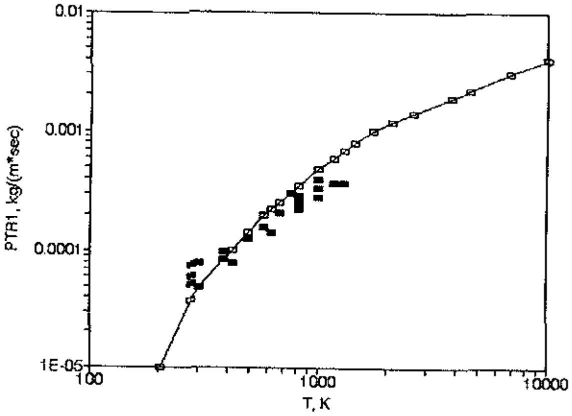

Fig. 2 The parameter $p\tau_{R1}(T)$ as a function of temperature: ▫ - solution of Eq. (9) at $d^* = 0.62$; ▪ - experimental data.[14,18]

The calculated values of rotational-translational relaxation time were used by Molodtsov and Riabov[19] in the analysis of the molecular nitrogen flow near a sphere. A significant difference between rotational energy and translational temperature distributions was discussed.

Rotational relaxation of a freely expanding gas

Marrone,[20] and Borzenko et al.[21] 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 $\varepsilon_R{}^{\circ}$ is observed.

Lebed' and Riabov[22] studied another cause for the rotational energy departure. At the decrease of kinetic temperature T_t, the Messy adiabatic parameter,[23] describing energy transfer between highly excited rotational levels unable to relax, becomes larger than unity. Adiabatic collision conditions[23,24] should be taken into account. As T_t decreases, the relaxation time τ_R will increase due to the significant decrease of the rotational transfer probabilities.

Using technique of Lebed' and Riabov,[22] the rotational-translational relaxation times were calculated for nitrogen at conditions of aerodynamic experiment in underexpanded jets.[25]

The analysis presented by Lebed' and Riabov[22] 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,[19] Riabov,[25-27] Skovorodko,[28] and Rebrov and Chekmarev[29] in terms of the full system of the Navier-Stokes equations and the relaxation equation (τ - approximation).

Transfer Coefficients in Near-Equilibrium Diatomic Gases

The general expressions for the transfer coefficients were analyzed by Lebed' and Riabov,[9,10] Lordi and Mates,[18] and Taxman.[30] Using formulas from Eq. (3), these expressions are:[9,10]

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

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

$$X=\frac{5}{2}\frac{1}{\eta}+\frac{5}{4}\frac{1}{p\tau_{RI}(T)};\quad Y=\frac{3}{4}\frac{1}{p\tau_{RI}(T)};$$

$$Z=\frac{3}{2}\frac{1}{\rho D_0}+\int[\frac{3}{4}g^2\Delta E^2+(p_i^2-p_j^2)\times$$

$$\times(p_i^2\cos\chi_0-(p_i^2+g^2\Delta E_i)\cos\chi\sqrt{1-\Delta E})]dw;\quad (10)$$

$$\frac{1}{\eta_0}=\frac{16\pi r_0^2}{5\sqrt{2\pi\mu kT}};\quad \lambda_0=\frac{15}{8}\frac{k}{\mu}\eta_0;$$

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

$$\int(\ )dw=\frac{1}{\pi^2\sqrt{2\pi\mu kT}}\int_0^\infty\int_0^{r_0}\int_0^\pi\int_0^\pi\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}(\ )\times$$

$$\times\exp\left(-\frac{g^2+p_i^2+p_j^2}{2}\right)\frac{g^5}{8}dg\,b\,db\,d\varphi_i\,d\varphi_j\,dp_i\,dp_j$$

In Eq. (10) η and η_0 are the coefficients of shear viscosity corresponding to rotationally inelastic and elastic collisions; λ and λ_0 are corresponding values of the thermal conductivity; ρ is the gas density; D_0 is the self-diffusion coefficient of the elastically colliding molecules.

The simplest approximations for the thermal conductivity coefficient λ were analyzed by Ferziger and Kaper,[1] Mason and Monchick,[8] Lebed' and Riabov,[9,10] and Hirshfelder et al.[13]

Mason and Monchick,[8] analyzing the relations (10), set $\Delta E = 0$ in the first approximation. This approximation 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 $(3/2)\rho D_0$ 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 as the following:

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

$$f_{tr}^{(2)}=\frac{5}{2}\left[1-\frac{5}{6}\left(1-\frac{2}{5}\frac{\rho D_0}{\eta}\right)\frac{\eta}{p\tau_{RI}(T)}\right];\qquad (11)$$

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

In the second approximation $\sin^2\chi$ was approximated by its value averaged over the unit sphere which was equal to 2/3; thus, $\eta = \eta_0$.[10]

The calculation technique and expressions for ΔE (Eq. 6) and χ were discussed above and in the study of Lebed' and Riabov.[9,10]

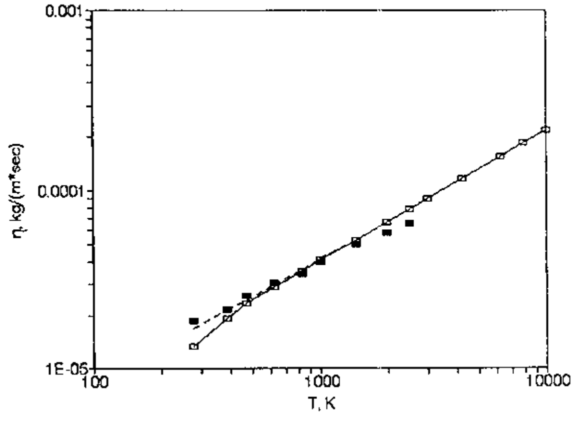

Fig. 3 The viscosity coefficient in nitrogen: □ - η, dashed line - η_0, ■ - experimental data.[31]

The solid and dashed lines in Fig. 3 show η and η_0, correspondingly, as given by Eq. (10), while the filled squares indicate the experimental data of Vargaftik.[31] 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.

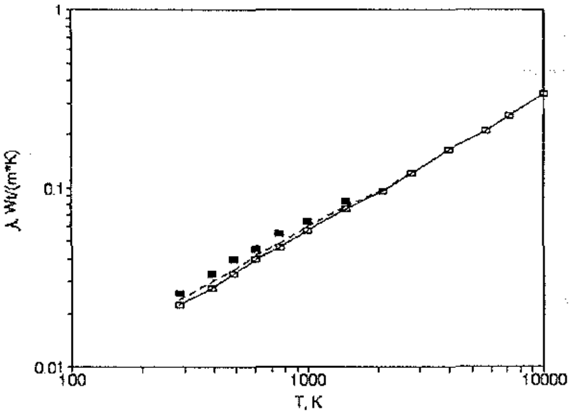

Fig. 4 The thermal conductivity coefficient in nitrogen: □ - λ, dashed line - λ_2, ■ - experimental data.[31]

The solid line in Fig. 4 shows λ, as given by Eq. (10). The dashed line corresponds to the Mason and Monchick's second approximation, λ_2. The filled squares indicate the experimental data of Vargaftik.[31] The Mason and Monchick's first approximation[8] as well as the Aiken approximation[1] were analyzed by Lebed′ and Riabov[9,10] in detail. The correlation between the exact solution, the Mason and Monchick' second approximation,[8] and experimental data[31] 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.

Transfer Coefficients in Nonequilibrium Diatomic Gases

The Mason and Monchick's second-order approximation technique[8] was used for calculating the transfer coefficients in the nonequilibrium case of the arbitrary value of Kn_R. As it was demonstrated above, this approximation is very good in the near-equilibrium case. The procedure of obtaining the coefficients is described by Lebed′ and Riabov[9,10] in detail. Using the fact that the relaxation terms in transfer coefficient formulas are small and they could be omitted, we find from Eq. (3) the following expressions:

$$\begin{aligned}
V_r{}^i &= -\frac{5}{4}\frac{\eta_0 D_0}{p\tau_{RI}(T)}\frac{E_i-\langle E\rangle}{\langle E^2\rangle-\langle E\rangle^2}\frac{\partial kT}{\partial x_r} - \\
&\quad -D_0\left(1-\frac{\rho D_0}{2p\tau_{RI}(T)}\right)\frac{E_i-\langle E\rangle}{\langle E^2\rangle-\langle E\rangle^2}\frac{\partial\langle E\rangle}{x_r};\\
q_r &= -\frac{15}{4}\frac{k}{m}\eta_0\left(1-\frac{\frac{5}{6}\eta_0-\frac{1}{3}\rho D_0}{p\tau_{RI}(T)}\right)\frac{\partial T}{\partial x_r} - \\
&\quad -nD_0\left(1-\frac{\rho D_0-\frac{5}{2}\eta_0}{2p\tau_{RI}(T)}\right)\frac{\partial\langle E\rangle}{\partial x_r};\\
P_{rs} &= p\delta_{rs}-\eta_0\left(\frac{\partial u_r}{\partial x_s}+\frac{\partial u_s}{\partial x_r}-\frac{2}{3}\delta_{rs}\frac{\partial u_l}{\partial x_l}\right)
\end{aligned} \tag{12}$$

In the nonequilibrium case,[1] the expressions for V_r^i and q_r are:[9]

$$\begin{aligned}
V_r{}^i &= \sum_j D_{ij}\frac{\partial n_i/n}{\partial x_r} - D_i{}^T\frac{\partial \ln kT}{\partial x_r};\\
q_r &= -\lambda^*\frac{\partial T}{\partial x_r}+\sum_i\left(E_i n_i + pk_i{}^T\right)V_r{}^i;\\
D_{ij} &= D_0\left[1-\frac{\rho D_0}{2p\tau_{RI}(T)}\right]\frac{(E_i-\langle E\rangle)(E_j-\langle E\rangle)}{\langle E^2\rangle-\langle E\rangle^2};\\
D_i{}^T &= \frac{5}{4}\frac{\eta_0 D_0 kT}{p\tau_{RI}(T)}\frac{E_i-\langle E\rangle}{\langle E^2\rangle-\langle E\rangle^2};\\
\sum_j &\frac{E_j-\langle E\rangle}{kT}k_j{}^T = \frac{5\eta_0}{4p\tau_{RI}(T)};\\
\lambda^* &= \frac{15}{4}\frac{k}{m}\eta_0\left[1-\frac{5}{6}\frac{\eta_0}{p\tau_{RI}(T)}\right]
\end{aligned} \tag{13}$$

In the equilibrium case the parameters $<E>$ and $<E^2>$ in Eqs. (12), and (13) should be changed on their equilibrium values. In the relaxation case the small values well-proportioned to $1/p\tau_{RI}(T)$ should be omitted.

It was noticed,[9] that the expressions for V_r^i and q_r from Eqs. (13) have only the gradients of values $<E>$ 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. (13) is very convenient for applications.[19,25-27] The similar expressions were found by Lebed′ and Riabov,[32] and Riabov[33,34] for multicomponent gas mixtures.

In equilibrium case the expressions in Eqs. (12), and (13) are the same as in the study of Ferziger and Kaper.[1]

Using Eqs. (12), and (13), we can find the gas dynamic equations in the common case as the following:[9]

$$\frac{\partial n_i}{\partial t}+\frac{\partial n_i u_r}{\partial x_r}-\frac{\partial}{\partial x_r}\Big\{\frac{n_i(E_i-\langle E\rangle)}{\langle E^2\rangle-\langle E\rangle^2}\Big[\frac{5}{4}\frac{\eta_0 D_0}{p\tau_{RI}(T)}\frac{\partial kT}{\partial x_r}+$$

$$+D_0\left(1-\frac{\rho D_0}{2p\tau_{RI}(T)}\right)\frac{\partial\langle E\rangle}{\partial x_r}\Big]\Big\}=\frac{n_i^{(p)}-n_i}{\tau_R};$$

$$\frac{\partial n}{\partial t}+\frac{\partial n u_r}{x_r}=0;$$

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

$$\left(\frac{\partial}{\partial t}+u_r\frac{\partial}{\partial x_r}\right)\left(\frac{3}{2}kT+\langle E\rangle\right)=\frac{1}{n}\frac{\partial}{\partial x_r}\left[\lambda_0\left(1-\frac{\frac{5}{6}\eta_0-\frac{1}{3}\rho D_0}{p\tau_{RI}(T)}\right)\frac{\partial T}{\partial x_r}-\right.$$

$$\left.-nD_0\left(1-\frac{\rho D_0-\frac{5}{2}\eta_0}{2p\tau_{RI}(T)}\right)\frac{\partial\langle E\rangle}{x_r}\right]-kT\frac{\partial u_k}{x_k}+ \qquad (14)$$

$$+\frac{\eta_0}{n}\left(\frac{\partial u_k}{\partial x_r}+\frac{\partial u_r}{\partial x_k}-\frac{2}{3}\delta_{rk}\frac{\partial u_l}{\partial x_l}\right)\frac{\partial u_k}{\partial x_r};$$

$$\left(\frac{\partial}{\partial t}+u_r\frac{\partial}{\partial x_r}\right)\langle E\rangle-\frac{1}{n}\frac{\partial}{\partial x_r}\Big|\frac{5}{4}\frac{\eta_0 n D_0}{p\tau_{RI}(T)}\frac{\partial kT}{x_r}+$$

$$+nD_0\left(1-\frac{\rho D_0}{2p\tau_{RI}(T)}\right)\frac{\partial\langle E\rangle}{\partial x_r}\Big|=\frac{kT-\langle E\rangle}{\tau_R}$$

In the formulas of Eq. (14), we used the τ-approximation method.[9] The relaxation time of the i-th rotational level was approximated by the value of the relaxation time of the rotational energy τ_R. The parameter τ_R should be selected after special analysis in each case, as it was done, for example, by Lebed' and Riabov.[9,22]

The closed system of the equations (14) contains the coefficients η_0, λ_0, D_0, $p\tau_{RI}(T)$, and $p\tau_R$, which are given in Figs. 1-4 for nitrogen at temperature from 200 K to 10,000 K. The parameter $\rho D_0/\eta_0$ is approximately constant and equals to 1.20.

The system (14) could be applied at any value of parameter Kn_R.

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,[19] Riabov,[25-27] Skovorodko,[28] and Rebrov and Chekmarev.[29] The full system of the Navier-Stokes equations and the relaxation equation (14), based on τ-approximation technique, has been solved by the implicit technique described by Riabov[27] in detail. The structure of spherically expended flows and underexpanded viscous jets was analyzed by Riabov.[25]

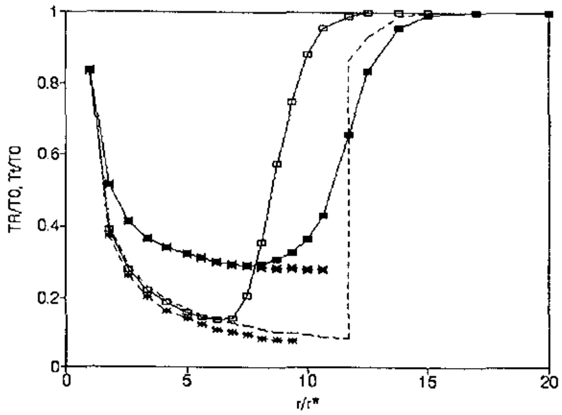

Fig. 5 The rotational T_R and translational T_t temperatures in spherically expanding flow of nitrogen: ▪ - T_R and ▫ - T_t in viscous flow; × - T_R and * - T_t in inviscid flow; dashed line - equilibrium flow (T_R = T_t) at γ = 1.4.

The changes of T_R and T_t in the spherically expending 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_∞ = 41.67; T_{t*} = T_{R*}, and $T_{0\infty}$ = 1.2T_* is shown by filled squares (T_R) and empty squares (T_t). Asterisk indicates the parameters at sonic conditions. The results for inviscid nonequilibrium flow (marker × for T_R and asterisk * for T_t) were obtained by the method of Lebed' and Riabov.[22] The dashed line in Fig. 5 corresponds to equilibrium values (T_t = T_R) at the specific heat ratio γ = 1.4.

The numerical results confirmed the earlier discovered delay[27-29] 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, 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 $T_{0\infty}$.

Concluding Remarks

The nonequilibrium gas dynamic equations were found for rotational-translational processes in diatomic gas for arbitrary value of parameter Kn_R. The calculations of relaxation time, viscosity and thermal conductivity coefficients were carried out in the temperature 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. It is important to use quantum effects in the latter case. The applicability of one- and two-temperature relaxation models was discussed. The presented results indicated that the initial distribution according to rotational levels must be taken into account within the frame work of the τ-approximation in parahydrogen.[10] The theoretical and experimental data are well correlated.

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