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COMPARISON OF MODELS WITH DIFFERENT AND IDENTICAL VIBRATIONAL TEMPERATURES OF MOLECULAR COMPONENTS

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UDC 533.6.011

During the entry of bodies into the Earth's atmosphere with a primary cosmic velocity the flow conditions at the fundamental thermal stress portion of designed trajectories are characterized by the absence of equilibrium between translational and vibrational degrees of freedom [1]. This result was obtained by using a model of one "averaged" vibrational temperature.

A model was considered in [2, 3], in which each molecular component corresponds to its vibrational temperature. These vibrational temperatures were found to differ insignificantly from each other, and the results practically coincide with calculation results using the "averaged" vibrational temperature. A number of simplifying assumptions were made in this case in [2, 3], including the neglect of the opposite effect of chemical reactions on vibrational relaxation, leading to a breakdown of the vibrational energy balance, resulting from not including its variations during generation and decay of molecules due to chemical reactions.

As shown in [1], with the development of dissociation the value of the corresponding source term is comparable with the value of the fundamental Landau–Teller term, and neglecting the effects mentioned above can lead to a substantial excess of the vibrational temperature over the translational one inside the shock layer, which was also observed in [2, 3].

In the present study we compare calculation results using an "averaged" model and different vibrational temperatures of molecular components for the example of flow in the vicinity of the critical line of the orbiting satellite "Buran."

1. Statement of the Problem. Consider stationary flow around an axially symmetric body due to a viscous chemically and thermodynamically nonequilibrium gas. We use the model of a thin viscous shock layer, being the asymptotic form of the Navier–Stokes equations for large Mach and Reynolds numbers, and density ratios before and after the shock wave, which is characteristic of the fundamental thermal stress portions of designed entry trajectories. Taking into account vibrational relaxation, the system of equations at the stagnation line can be written down as follows (y is the distance along the axis from the body):

$$\rho u+\frac{\partial}{\partial y}(\rho v)=0,\quad \rho Du=-2p_1+\frac{\partial}{\partial y}\left(\frac{\mu}{\mathrm{Re}_\infty}\frac{\partial u}{\partial y}\right); \tag{1.1}$$

$$\frac{\partial p}{\partial y}=0,\quad \frac{\partial p_1}{\partial y}=\rho u^2; \tag{1.2}$$

$$\rho c_p DT-\rho\sum_{k=1}^{M}DE_k^*-Dp=\frac{\partial}{\partial y}\left(\frac{\mu c_p}{\mathrm{Re}_\infty\sigma}\frac{\partial T}{\partial y}+\sum_{k=1}^{M}q_k^v\right)-\sum_{i=1}^{N}h_i\dot{w}_i-\left(\sum_{i=1}^{N}c_{pi}I_i\right)\frac{\partial T}{\partial y}; \tag{1.3}$$

Moscow. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, No. 1, pp. 12-18, January-February, 1993. Original article submitted June 27, 1991; revision submitted December 18, 1991.

$$\rho DE_k + \frac{\partial}{\partial y}(q_k^v) = Q_k^{VT} + Q_k^R + Q_k^{VV}, \quad k = 1, \ldots, M; \tag{1.4}$$

$$\rho Dc_i + \frac{\partial}{\partial y}(I_i) = \dot{w}_i, \quad \frac{\mu}{\mathrm{Re}_\infty}\frac{\partial}{\partial y}(mc_i) = \sum_{i=1}^{N} \frac{m^2}{m_j} \mathrm{S}_{ij}(c_i I_j - c_j I_i), \tag{1.5}$$

$$p = R_A \rho T \sum_{i=1}^{N} \frac{c_i}{m_i}, \quad \sum_{i=1}^{N} I_i = 0, \quad \sum_{i=1}^{N} c_i = 1, \quad D = v\frac{\partial}{\partial y},$$

$$E_k = c_k e_k = c_k \frac{R_A}{m_k} \frac{\theta_k}{\exp(\theta_k/T_{vk}) - 1}, \quad E_k^* = E_k(T) - E_k.$$

Here $V_\infty u$ and $V_\infty v$ are the physical components of the velocity vector in the x and y directions, $T_0 T$, $\rho_\infty V_\infty^2 p$, $\rho_\infty \rho$ are the translational temperature, the pressure and density of the gas mixture ($T_0 = V_\infty^2/c_{p\infty}$); $\mu_\infty \mu$, $c_{p\infty} c_p$, σ, m are the viscosity and heat capacity coefficients, the Prandtl number, and the molecular mass of the mixture, c_i, m_i, $c_{p\infty} T_0 h_i$, $c_{p\infty} c_{pi}$, $\rho_\infty V_\infty I_i$, $\rho_\infty V_\infty \dot{w}_i/R$ are the mass concentration, molecular mass, thermodynamic equilibrium specific enthalpy and heat capacity, the normal component of the diffusion flux vector, and the rate of formation of the i-th component mass, $c_{p\infty} T_0 E_k$, $T_0 \theta_k$, $T_0 T_{vk}$ are the vibrational energy, referenced to a unit mass of the mixture, and the characteristic and vibrational temperature of the k-th molecular component, $c_{p\infty} T_0 \rho_\infty V_\infty / RQ_k$ are source terms, $c_{p\infty} R_A$ is the universal gas constant, S_{ij} is the Schmidt number, V_∞ is the absolute value of the velocity vector of the surrounding flow, and N is the number of components, and M is the number of molecular components. All linear sizes refer to the blunt radius of curvature R, and the subscript ∞ refers to parameters in the surrounding flow.

The vibrational energy flux of molecular component k is

$$q_k^v = -\frac{\mu}{\mathrm{Re}_\infty \mathrm{S}_k}\frac{\partial}{\partial y}E_k^* + \frac{E_k^*}{\mathrm{S}_k}\sum_{i=1}^{N} \mathrm{S}_{ki}^0 I_i,$$

$$\mathrm{S}_k = m\sum_{i=1}^{N} \frac{c_i \mathrm{S}_{ki}}{m_i}, \quad \mathrm{S}_{ki}^0 = \frac{m}{m_k}\mathrm{S}_{ki} + \sum_{j=1}^{N} \mathrm{S}_{kj} c_j \left(\frac{m}{m_j} - \frac{m}{m_i}\right).$$

The equations of vibrational relaxation (1.4) were written down for molecules with different vibrational temperatures, and their number corresponds to the number of molecular components. Using the model with "averaged" vibrational temperature, it is necessary to sum Eq. (1.4) under the assumption of equal vibrational temperatures. In this case the unknown function is the vibrational temperature, while the equation of vibrational relaxation and the expression for q_k^v can be written as follows:

$$\rho\left(\sum_{k=1}^{M} c_k e_k'\right) DT_v + \left(\sum_{k=1}^{M} I_k e_k'\right)\frac{\partial T_v}{\partial y} =$$
$$= \frac{\partial}{\partial y}\left[\frac{\rho}{\mathrm{Re}_\infty}\left(\sum_{k=1}^{M} c_k D_k e_k'\right)\frac{\partial T_v}{\partial y}\right] + \sum_{k=1}^{M}(Q_k^{VT} - \dot{w}_k e_k + Q_k^R), \tag{1.6}$$

$$q_k^v = e_k^* I_k - \frac{\rho}{\mathrm{Re}_\infty} c_k D_k \frac{\partial e_k^*}{\partial y},$$

$$e_k' = \frac{\partial e_k}{\partial T_v}, \quad e_k^* = e_k(T) - e_k, \quad D_k = \frac{\mu}{\rho m}\sum_{i=1}^{N}\left(\frac{c_i}{m_i}\mathrm{S}_{ik}\right)^{-1}.$$

The boundary conditions at the surface of the body, expressed by the conditions of continuity, adhesion, heterogeneous flow of recombination reactions, and the thermal balance conditions, are written in the form

$$u = v = 0, \quad I_i = -\rho k_{wi} c_i, \quad q = \frac{\varepsilon \sigma_{\mathrm{B}} T_0^4}{\rho_\infty V_\infty^3} T_w^4,$$

$$q = \frac{\mu c_p}{\mathrm{Re}_\infty \sigma}\frac{\partial T}{\partial y} - \sum_{i=1}^{N} h_i I_i + \sum_{k=1}^{M} q_k^v,$$

where ε, $V_\infty k_{wi}$ are the coefficients of surface blackness and of catalytic recombination, σ_B is the Boltzmann constant, and T_w is the equilibrium temperature of the surface. The thermal flux from the body is neglected, since for the material of the thermal protection coverage of the orbiting satellite "Buran" its value is only several percent of q at $H \lesssim 90$ km.

For the vibrational temperature at the surface it is assumed that either the equilibrium condition or the condition of noncatalytic walls with respect to the internal degrees of freedom are satisfied:

$$T_{vk} = T_w; \tag{1.7}$$

$$\partial T_{vk}/\partial y = 0. \tag{1.8}$$

The generalized Rankine–Hugoniot relations are assigned as boundary conditions on the shock wave. In the shock layer one assumes the presence of the components N_2, O_2, NO, N, O, between whom occur reactions of dissociation, recombination, and exchange reactions with the rate constants of [4].

The action of nonequilibrium excitation of vibrational degrees of freedom on the dissociation reaction rate is manifested in terms of the two-temperature dependence of the dissociation rate constant [5]:

$$K_i^D(T, T_{vi}) = K_i^D(T)V_i(T, T_{vi}), \quad i = 1, \ldots, M,$$
$$V_i(T, T_{vi}) = \frac{Z_i(T)Z_i(T_{Fi})}{Z_i(T_{vi})Z_i(-U_i)}, \quad \frac{1}{T_{Fi}} = \frac{1}{T_{vi}} - \frac{1}{T} - \frac{1}{U_i}.$$

Here $K_i^D(T)$ is the dissociation constant in thermodynamic equilibrium, when $T_v = T$, Z_i is the partition function over vibrational levels, and U_i is a supplementary parameter, having the dimensionality of temperature and determining the extent of predominant dissociation from the upper levels in comparison with the lower ones. In the calculations we put $U_i = T_{Di}/6$ (T_{Di} is the dissociation temperature). In determining the recombination rate constants we took V = 1. The effect of vibrational relaxation on the exchange reaction rates was not taken into account.

The opposite effect of chemical reactions on vibrational relaxation was taken into account in terms of the source term Q_k^R [6]. For O_2 molecules, for example, it is expressed in the form

$$Q_k^R = -m_k\left(\frac{\rho}{m}\right)^2\left[\left(\sum_{i=1}^{N} K_{1i}x_i\right)\left(e_{Dk}\frac{K_{pi}}{p}V_i x_k - e_{Rk}x_{\mathrm{O}}^2\right) - \right.$$
$$\left. - K_2 e_k(K_{p2}x_{\mathrm{O}}x_{\mathrm{NO}} - x_{\mathrm{N}}x_k)\right],$$
$$k = \mathrm{O}_2, \quad x_i = \frac{mc_i}{m_i}, \quad e_{Dk} = e_k(T_{Fk}), \quad e_{Rk} = e_k(-U_k),$$

where K_{1i}, K_{p1} are the rate and equilibrium constants for the recombination reaction of oxygen, while K_2, K_{p2} are the exchange reaction rates with participation of oxygen, e_{Dk} is the mean value of vibrational energy, lost by O_2 molecules as a result of a single act of dissociation, and e_{Rk} is the mean value of vibrational energy, acquired by O_2 molecules as a result of a single act of recombination.

The energy transfer between translational and vibrational degrees of freedom Q_k^{VT} was calculated in the Landau–Teller form

$$Q_k^{VT} = \rho\frac{E_k(T) - E_k}{\tau_k^{VT}}.$$

To calculate the vibrational relaxation time of VT-exchange we used the Millikan–White τ_{ik}^{MW} approximation [7], and a correction for T > 8000 K suggested in [8]:

$$\frac{1}{\tau_k^{VT}} = \sum_{i=1}^{N}\frac{x_i}{\tau_{ik}^{MW}} + \sigma v_k n.$$

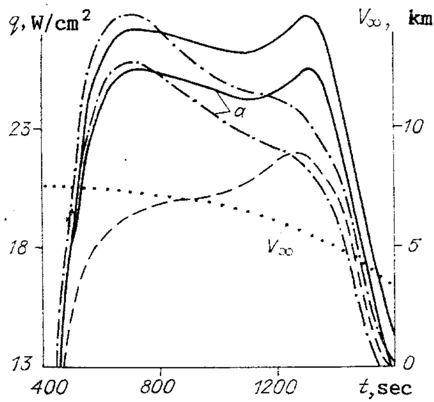

Fig. 1

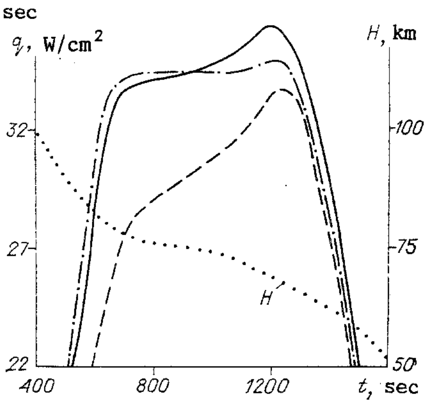

Fig. 2

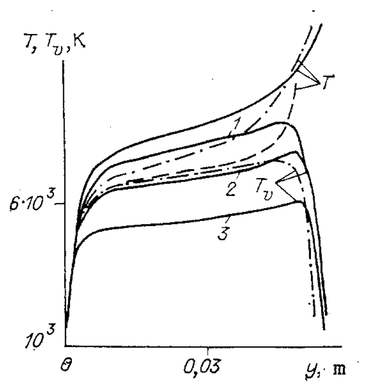

Fig. 3

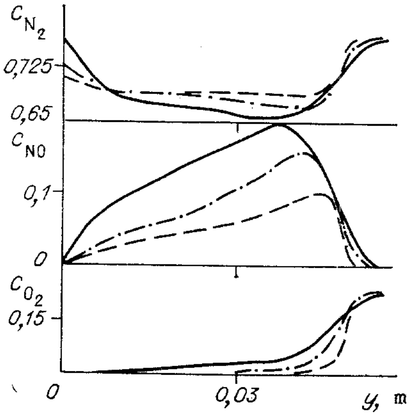

Fig. 4

Here and later v_k is the mean thermal velocity of molecules, n is the number of particles per unit volume, and σ is the effective transverse cross section of collisions, taken equal to 10^{-16} cm².

The exchange rate of vibrational energy due to VV'-processes can be written in the form

$$Q_k^{VV} = \rho c_k \frac{R_A \theta_k}{m_k} \sum_{i=1}^{M} \frac{(L_k+1) L_i \exp(t_i - t_k) - (L_i + 1) L_k}{t_i L_i (T) \tau_{ik}^{VV}},$$

$$t_i = \frac{\theta_i}{T_{vi}}, \quad L_i = (\exp(t_i) - 1)^{-1},$$

$$\tau_{ik}^{VV} = (nK_{10}^{ik})^{-1} + (\sigma v_k n)^{-1}, \quad K_{10}^{N_2-O_2} = K_{10}^{N_2-NO} = 0{,}1 K_{10}^{O_2-NO}.$$

In calculating the rate constant values of vibrational deactivation we used the approximation of experimental data obtained in [9]:

$$K_{10}^{N_2-O_2} = 2{,}5 \cdot 10^{-12} \exp(-131 T^{-1/3} + 489/T) T^{1/3} \text{ cm}^3/\text{sec}.$$

2. Analysis of Results.

Consider the flow in the vicinity of the critical line of the orbiting satellite "Buran" during its descent along the designed entry trajectory [10]. The conditions in the surrounding flow corresponded to a standard atmosphere. The surface blackness coefficient was taken equal to 0.8, with R = 0.83 m. The N_2, O_2, NO molecules correspond to the following values of characteristic and dissociation temperatures: θ_i = 3372, 2256, 2720 K, T_{Di} = 113,000, 59,500, 75,500 K. The method of numerical solution is similar to [11].

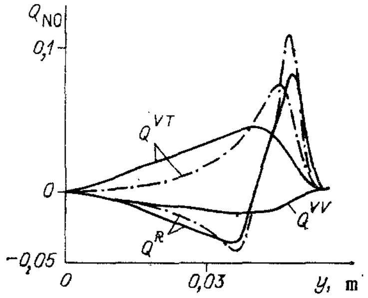

Fig. 5

Below are provided several calculation results. In the figures we use the following notations: the solid lines are results of calculating the system of equations (1.1)-(1.5) with different vibrational temperatures of the molecular components, and the dashed-dotted lines are calculations by the model with a single "averaged" vibrational temperature [the equation of vibrational relaxation (1.6)]. Results are provided for the boundary conditions (1.7), except the letter a notation in Fig. 1, when condition (1.8) was used for the vibrational temperature. The dashed lines are calculations under the assumption of thermodynamic equilibrium, i.e., when all internal degrees of freedom are equally excited and the vibrational temperature coincides with the translational, and the dotted lines in Figs. 1, 2 are the velocity and height values as functions of time of flight.

In Fig. 1 is given the dependence of the thermal flux on the time of descent of the orbiting satellite "Buran." The trajectory portion presented covers the height range H = 100-52 km, the body surface is assumed to be noncatalytic with respect to chemical recombination reactions.

The value of the thermal flux is higher at the initial portion of the trajectory in the case of a model with a single vibrational temperature. Considering the model with different vibrational temperatures of the molecular components, the thermodynamically nonequilibrium flow character is retained to a large extent. The difference between the models in the thermal flux values can reach 20%, while for an equilibrium temperature surface it is 80 K. This difference is mostly due to the effect of the source terms Q_k^R and to the lesser extent due to VV'-exchange processes, though they also lead to an increase in thermal flux. We note that the characteristic behavior of thermal flow shown in Fig. 1 is also similar for other calculated designed trajectories.

The application of the noncatalytic boundary condition (1.8) with respect to the vibrational degrees of freedom of the wall leads to reduction of the thermal flux. For the model with a single vibrational temperature the thermal flux in the lower part of the trajectory can be less than in the calculation under the assumption of thermodynamic equilibrium. For the model with different vibrational temperatures the thermal flux remains higher. Due to the uncertainty in boundary conditions for the vibrational temperature the thermal flux values can differ by 10%, and the surface temperatures — by 30 K.

Figure 2 shows the dependence of the thermal flux on the time of descent for a surface with rate constants of heterogeneous recombination $k_{wO} = k_{wN} = 3$ m/sec, $k_{wNO} = 0$, corresponding to catalytic activity of a surface covered by carbon, the carbon of the orbiting satellite "Buran." For this version the maximum difference between the models is 5% in the thermal flux values and up to 20 K in the equilibrium temperature of the surface.

Figure 3 presents the profiles of translational and vibrational temperatures at t = 1340 sec (H = 64.6 km, $V_\infty = 5.35$ km/sec). Lines 1-3 denote the vibrational temperatures of the molecular components N_2, NO, and O_2, respectively.

We name model 1 the model with a single "averaged" vibrational temperature, model 2 — the thermodynamically equilibrium model, when all internal degrees of freedom are equally excited, and model 3 — the one with different vibrational temperatures of the molecular components.

At the initial trajectory portion the vibrational temperature of model 1 practically corresponds to the vibrational temperature of N_2 molecules, while the temperatures of the molecular components O_2 and NO have substantially higher values. The translational temperature and the thickness of the shock layer for model 1 are somewhat higher than for model 3. The relative temperature arrangement varies with decreasing flight altitude: the state of N_2 molecules is closest to thermodynamic equilibrium, and the vibrational temperature of O_2 molecules is the lowest. The vibrational temperature values of NO molecules and of model 1 are located between them. The translational temperature of model 1 on the largest portion of the shock layer is below model 3.

Figure 4 shows mass concentration profiles of the molecular components at the same trajectory point. The concentration of N_2 molecules in the thermodynamic equilibrium case at the initial trajectory portion is lower than in the nonequilibrium case. A relative increase then occurs in the nitrogen content in the case of model 2 in comparison with nonequilibrium models. In the larger trajectory portion and in the case of model 3 nitrogen dissociates more strongly than in model 1. The content of nitrogen oxide molecules in the shock layer is quite higher for nonequilibrium models than for model 2. Oxygen also mostly dissociates in the thermodynamic equilibrium model. The content of O_2 molecules for model 1 and at the initial trajectory portion is higher, and then decreases in comparison with model 3 due to the relatively lower values of the vibrational temperature of oxygen.

Figure 5 shows profiles of the dimensionless source terms for the molecular component of nitrogen oxide at $t = 1340$ sec. As can be seen, the source term Q^R, corresponding to the inverse effect of chemical reactions on vibrational relaxation, is comparable in magnitude with the Landau–Teller Q^{VT} term during the development of dissociation. At the same time VV'-exchange processes contribute substantially less to the total balance, while the relative value of the source term Q^{VV} is substantially smaller for the other molecular components.

From the results provided above it follows that the vibrational temperatures of the molecular components can differ substantially. When using in the calculations models with different vibrational temperatures, the nonequilibrium excitation of vibrational degrees of freedom exerts a stronger effect on the flow characteristics at the thermal stress portion of designed entry trajectory than for models with a single "averaged" vibrational temperature. The difference in thermal flux values for the models considered can reach 20%.

The author is grateful to G. A. Tirskii for his help and interest in this study.

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