QUANTUM EFFECTS IN ROTATIONAL RELAXATION OF A FREELY EXPANDING GAS

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It is well known that the equilibrium between the translational and rotational degrees of freedom is disturbed in expansion of a molecular gas into a vacuum [1, 2]. Departure of the rotational energy of the gas from the equilibrium for a given kinetic temperature results from a sharp drop in the gas density downstream, leading to a decrease in the number of gas-kinetic collisions experienced by individual molecules.

There is another cause for the equilibrium being disturbed, of a purely quantum nature. In a sharp fall of kinetic temperature T_t, occurring when the gas expands in the vacuum, the Mess adiabatic parameter, describing energy transfer between highly excited rotational levels unable to relax, becomes larger than unity. Below a certain temperature (characteristic for a given rotational level) under adiabatic collision conditions, the probability of a rotational transfer begins to fall sharply [3, 4]. Thus, as T_t decreases, the relaxation time τ_R will increase.

In the available theoretical papers dealing with distribution of rotational energy in flow of expanding nitrogen (e.g., see [5-7]), τ_R is calculated on the basis of classical mechanics. However, when there is rapid cooling of a gas, T_t becomes less than the distance between the highly excited rotational levels, and one cannot regard the rotational spectrum of the molecule as being continuous. For the rotational levels N_2 which are effectively populated at room temperature the classical approach in calculating τ_R leads to an appreciable distortion of the result in the range $T_t < 100°K$.

This paper carries out a theoretical investigation of the distributions of rotational and translational energy along the axis of a jet of nitrogen expanding into vacuum. The system of gasdynamic equations for a model expansion from a spherical source is solved. The relaxation time of the gas in the low T_t range is calculated on the basis of quantum mechanics.

1. We consider the process of establishing equilibrium among rotational states in a steady-state expansion of inviscid, non-heat-conducting nitrogen from a spherical source. In the computations the N_2 molecule is approximated by a rigid rotator. The original system of equations includes the equations of continuity, momentum, energy and the equation of state [5]. The system is closed by the relaxation equation, written in the τ-approximation:

$$udT_R/dr = (T_t - T_R)/\tau_R,$$

where r is the distance from the center of the source; u is the flow velocity; and $T_R = E_R/R$ (R is the gas constant, and E_R is the rotational energy per mole of gas). We note that in the expansion process the Boltzmann nature of the rotational energy distribution is disturbed [2], and therefore T_R is not typical of the relative level populations.

It is convenient to reduce the original system of equations to dimensionless form, referring all the quantities to their values on the sonic sphere, where the Mach number M = 1. Then the unique similarity parameter of the problem becomes the dimensionless parameter $\alpha = \rho^* u^* r^*/p^* \tau_R^*$, where ρ and p are the gas density and pressure, and the superscript * is used to denote quantities on the sonic sphere.

The boundary conditions we take to be $r/r^* = 1$, $T_t/T^* = 1$, $T_R/T^* = 1, u = \sqrt{\frac{7}{5} RT^*} = 1$. We assume that in a certain δ-layer at the surface of the spherical source, whose boundary is given by the condition M = 1.15, the supersonic flow remains in equilibrium. The numerical integration of the closed system must begin from the boundary of the δ-layer. The numerical method used is similar to that applied in [5].

2. We estimate τ_R on the basis of approximate models. In the Parker model [8] a quantity, the reciprocal of τ_R, is defined as the ratio of the rotational energy obtained for a nonrotating rotator to the collisional

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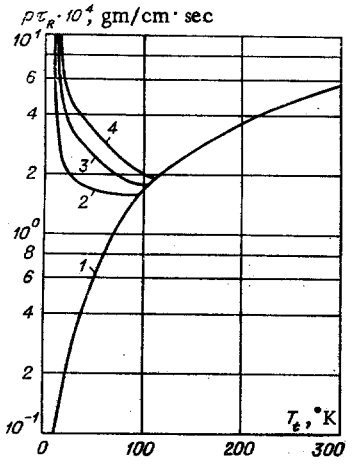

Fig. 1

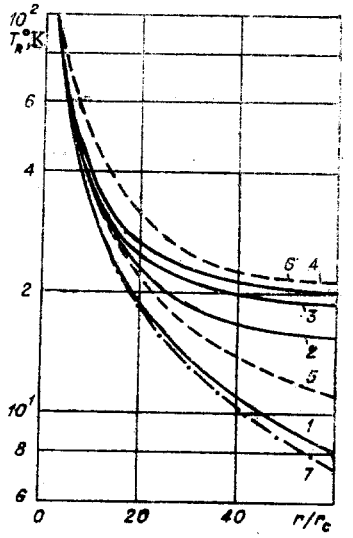

Fig. 2

energy. In the calculation, based on classical mechanics, it is assumed that the rotators lie in one plane; it is also assumed that each rotator has two centers of repulsion, which do not coincide with the centers of the atom, and one center of attraction, lying at the center of gravity of the model.

Curve 1 in Fig. 1 shows the calculated relaxation times from Eq. (43) of [8]. In calculating $p\tau_R$ we used the molecular interaction potential parameters, given in [8]. Curve 1 can be approximated by the power function

$$p\tau_R = CT_t^m$$

with the parameters m = 1 and $C = 1.65 \cdot 10^{-6}$ gm/cm · sec · °K, taken from [6].

As T_t tends to zero, $p\tau_R$ also tends to zero. The reason is that transfer of energy between molecules with larger moments of rotation is more difficult. As can be seen from Fig. 1, the value of $p\tau_R$ calculated classically does not show a tendency to increase with the decrease of T_t under conditions of adiabatic exchange of rotational energy.

It is known that the relaxation process is limited by transitions from the effectively populated highly excited rotational levels under the given conditions. Thus, in the low range of T_t the energy relaxation time τ_R can be approximated by the relaxation time for a certain rotational level j*

$$p\tau_R = \frac{kT_t}{\sigma_0}\left(\frac{\Pi\mu}{8kT_t}\right)^{1/2}\frac{1}{\langle P_{j^*,j^*-2}\rangle}; \qquad (2.1)$$

where k is the Boltzmann constant; σ_0 is the gas-kinetic cross section; μ is the reduced mass of the partners; and $\langle P_{j^*,j^*-2}\rangle$ is the average transition probability $j^* \rightarrow j^*-2$ in one gas-kinetic collision.

Before the start of discharge at room temperature the maximum population of nitrogen occurs for the j = 6 rotational level. Thus, if we put j* = 6, the estimate obtained will be an upper limit for τ_R. Apparently, the relaxation time for the j = 4 level in the case considered can be regarded as a lower bound on τ_R.

The general method of calculating the probabilities for rotational transitions has been described in [3, 4]. The calculation of $\langle P_{j^*,j^*-2}\rangle$ for j* = 4, 5, 6 was carried out using Eq. (14) of [4]. In the computation we used the potential parameters given in [8]. By allowing for the high degree of symmetry of the N_2 electron shell we can approximate to the anisotropy parameter of the first nonzero term c_2 in the expansion of the molecular potential in Legendre polynomials by the anisotropy parameter for the potential pair N_2-structureless particle: $c_2 = 0.5$ [9]. The unique condition for using Eq. (14) of [4] is the adiabatic condition, which holds up to temperatures as high as 100°K for j* = 4, 5, 6.

Curves 2-4 of Fig. 1 show the results of calculating $p\tau_R$ from Eq. (2.1) for j* = 4, 5, 6, respectively. It can be seen from Fig. 1 that $p\tau_R$, calculated using Eq. (2.1), increases with decrease of T_t. In the region of T_t where the adiabatic condition breaks down, curves 2-4 undergo a smooth transition to curve 1, which was calculated using the classical Parker model. By replacing the energy relaxation time by the relaxation time for level j*, in spite of the approximation, one can correctly represent the qualitative nature of the equilibrium establishment process with respect to rotational states, i.e., an increase of τ_R with reduction of T_t.

3. Figure 2 shows the distributions of T_R along the flow. Curve 1 shows τ_R, calculated using classical mechanics, and curves 2-4 were obtained using curves 2-4, respectively, of Fig. 1 for the value of $p\tau_R$. In the calculation it is assumed that $\alpha = 2730$.

If one takes into account that the solution of the gasdynamic equations describing expansion of the gas from a spherical source will satisfactorily represent the behavior of the flow near the axis of a jet issuing from a circular aperture, one can compare the calculated distributions with experimentally measured values. The critical source radius is uniquely related to the radius of the exit aperture of the jet r_c: $r^* = Ar_c$, $A = 1.15$ for N_2 [10]; $\alpha = 2730$ corresponds to $p_0 r_c = 240$ torr · mm for $T_0 = 290°K$, where p_0 and T_0 are the stagnation pressure and temperature. In the case considered we neglected the effect of viscosity on the gas flow parameters.

Curves 5 and 6 of Fig. 2 show the results of measurement of T_R along the flow (curve 5 was taken from [1], and curve 2 from [2]). We note that the results obtained in [1] are low, since the sensitivity of the experimental equipment did not allow recording of part of the luminescence spectrum which corresponds to the excited rotational N_2 levels. The results given in [2] are somewhat high, since the "hot" phonon gas either takes part in the relaxation process, slowing it down, or makes its own contribution to the luminescence spectrum.

Thus, the experimental curves 5 and 6 are upper and lower bounds on the distribution of rotational energy along the flow. They form a "fork" shape encompassing only curves calculated allowing for the quantum nature of rotational energy exchanged. It can be seen from Fig. 2 that the use of classical models in calculating τ_R leads to values of T_R which are several times too low.

Curve 7 of Fig. 2 is the temperature characteristic of an isentropic expansion of nitrogen from a circular aperture, calculated along the jet axis under the assumption that the distribution function for rotational states retains its Boltzmann form, i.e., $E_R = RT_t$.

The results of the calculations and the experiments shown in Fig. 2 demonstrate the presence of a considerable departure of rotational energy from the equilibrium value for the given temperature, and point to the need to use quantum methods in describing rotational relaxation in an expanding flow of nitrogen.

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