RELAXATION PROCESSES IN GASES

Part II. Establishment of Rotational Equilibrium* (Survey)

A. L. Osipov

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§1. INTRODUCTION

In a number of respects the process of establishment of equilibrium in polyatomic gases differs importantly from the relaxation process in monatomic gases. In the latter, the basic relaxation process is associated with the formation of a Maxwellian distribution; electronic excitation may be neglected if the region of not very high temperatures is considered. In polyatomic gases, the process of establishment of total statistical equilibrium embraces all the degrees of freedom—translational, rotational, vibrational (and electronic); therefore, it is characterized by a spectrum of relaxation times.

The presence of several characteristic relaxation times complicates the equilibrium process. This is particularly clear in relation to shock waves. In a monatomic gas, a shock wave is a layer of finite thickness characterized by a process of establishment of equilibrium, with respect to translational degrees of freedom. In polyatomic gases, the shock wave structure is much more complicated. In this case, the shock wave may be represented as a more or less distinctly expressed multilayer formation, each layer having its own relaxation time characteristic of the excitation of some particular degree of freedom.

The existence of a relaxation-time spectrum is also confirmed by direct experiments. Especially convenient in this respect are the ultrasonic methods which in a number of cases make possible the precise determination of the characteristic times associated with the excitation of rotational, vibrational and electronic degrees of freedom (see, for example, [2, 3]).

The presence of several relaxation processes also modifies the dynamic behavior of gases. This is particularly apparent in relation to the transport coefficients. The thermal conductivity of polyatomic gases differs from that of monatomic gases owing to the additional energy flow associated with the internal degrees of freedom. This effect depends importantly on the characteristic time of energy transfer between translational and internal degrees of freedom [4]. The delay in the process of energy transfer from translational to internal degrees of freedom leads to another interesting effect in the theory of transport coefficients—in polyatomic gases the second viscosity is nonzero, whereas that of a perfect monatomic gas is zero.

The dynamic behavior of a nonequilibrium gas cannot always be described by means of transport coefficients. This applies both to monatomic (case of strong shock waves) and polyatomic gases. In particular, in order to describe a flow region whose dimensions are on the order of the relaxation zone, it may be necessary to use the equations of relaxation hydrodynamics [5]. The system of equations of relaxation hydrodynamics includes equations of equal validity describing the kinetics of the relaxation processes. Thus, in this case, too, statistical nonequilibrium affects the dynamic behavior of the gas.

In this article we propose to analyze one particular relaxation process—the establishment of equilibrium with respect to rotational degrees of freedom. Apart from the questions raised above, the study of rotational relaxation is also of specific importance. It has been established that certain chemical reactions lead to the appearance of products in an anomalously excited rotational (and vibrational) state. A typical example is the anomalous rotational excitation of the hydroxyl group OH observed in flames or in an arc discharge in water vapor [6, 7]. The practical application of such reactions has a promising future. In particular, the reaction H + Cl2 → HCl* + Cl + 45 kcal/mole has been used to create a vibrational-rotational population inversion and to obtain stimulated, coherent emission in the infrared [8]. A combined theoretical and experimental study of rotational relaxation also makes possible a more accurate analysis of the intermolecular potential (this applies in particular to the H2 and D2 molecules). Actually, the intermolecular potential of real molecules is always somewhat asymmetrical. The equilibrium properties and also the transport properties of gases are relatively insensitive to this asymmetrical component. This is not the case with the probabilities of rotational excitation of the molecules (or rotational relaxation times). They are wholly determined by the nonspherical part of the intermolecular potential.

§2. EXCITATION OF ROTATIONAL DEGREES OF FREEDOM. RELAXATION TIME

The excitation of rotational degrees of freedom leading to the formation of a Boltzmann distribution takes place as a result of energy transfer between the translational motion and rotation of the molecules. In order to estimate the relaxation time of this process (rotational relaxation time), we will consider the simplest system. We assume that a relaxing gas A with molecular mass m1 forms a small impurity in a monatomic gas B (with molecular mass m2), which has a Maxwellian velocity distribution and temperature T. We also assume that in this system the relaxation process is

*For Part I see [1].
described by the equation

\[
\frac{dE}{dt} = -\frac{E - E_0}{\tau},
\]

where \(E\) is the rotational energy of the gas per unit volume, \(E_0\) is the equilibrium value of that energy, and \(\tau\) the relaxation time.

Equation (1) may be regarded as an expression defining the relaxation time; accordingly we can write

\[
\tau = \frac{E_0}{\left(\frac{dE}{dt}\right)_{E=0}}.
\]

Equation (2) gives only the order of magnitude of the relaxation time; however, this estimate is sufficient.

We will find the relaxation time \(\tau\). In Eq. (2) \(E_0 \sim kTn_1\), where \(n_1\) is the number density of the molecules of gas A. It is assumed that \(T\) is greater than the characteristic rotational temperature, which for heavy gases is several degrees Kelvin. We find the rate of energy transfer from translational to rotational degrees of freedom \(\frac{dE}{dt}\) from the problem of the collision of a rotator and an atom. Collisions between rotators can be neglected in view of their low concentration. For simplicity we assume that all collisions occur under conditions most favorable to the conversion of translational into rotational energy. In such collisions the hitting atom moves along a straight line passing through one of the atoms of the rotator at right angles to the rotator axis (see figure). In accordance with Eq. (2), we calculate the increment of rotational energy on the assumption that the rotator does not rotate before impact \((E = 0)\), and that its center of gravity is at rest. For this model (interaction of elastic spheres) and the selected configuration, the collision process is so rapid that at the moment of impact the instantaneous axis of rotation of the rotator passes through the right-hand atom; therefore

\[
\Delta E = \frac{2m_1}{m_2} \cdot \frac{v_1^2}{2},
\]

\((d\) is the distance between the rotator atoms\), and the rotational energy

\[
E_r = \frac{\Delta E}{2} = \frac{m_1 m_2 v_1^2}{2(m_2 + m_1/2)},
\]

\((the\ moment\ of\ inertia\ I = m_d t^2/4)\).

The energy transferred to translational degrees of freedom

\[
E_t = E - E_r = \frac{m_1 m_2}{2(m_2 + m_1/2)} \cdot v_1^2.
\]

Thus, for the selected model and configuration the energy transferred to rotational degrees of freedom is exactly equal to the energy imparted to translational motion. If the result obtained is formulated as follows: when a molecule collides with an atom (or molecule) the energy acquired by the rotational and translational degrees of freedom of the molecules is of the same order, it is valid for a broader class of molecular models, in practice for all homonuclear molecules except the lightest, \(H_2\) and \(D_2\).

Now, if we use Eq. (2) to estimate the time required to establish a Maxwellian distribution, we can draw the following conclusion: the rotational relaxation time coincides in order of magnitude with the relaxation time for translational degrees of freedom. Indeed, in Eq. (2) the quantity \(E_0\), like \(\frac{dE}{dt}\) at \(E=0\), is of the same order for rotational and translational degrees of freedom. In reality, the rotational relaxation time is somewhat greater than the time required to establish a Maxwellian distribution, since not every collision is accompanied by rotational excitation. In particular, the rotational energy of the rotator is not affected by a head-on collision between the rotator and an atom.

The fact that the rotational relaxation time and the time required to establish a Maxwellian distribution coincide in order of magnitude leads to a number of important practical conclusions.

1. In pure gases and in mixtures in which the molecules of the different components are commensurate in mass the rotational relaxation time is of the order of the mean free time. Ultrasonic measurements confirm the correctness of this estimate. In spite of the scatter of the experimental data, it can be stated that at

\[
v = \frac{2m_1}{m_2 + m_1/2} \cdot v_1
\]