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HETEROGENEOUS VIBRATIONAL RELAXATION UPON FREE MOLECULAR FLOW OF DIATOMIC GAS PAST CONCAVE BODIES

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The method of successive calculation of multiple reflections is used for investigating heterogeneous vibrational relaxation when a free molecular stream of diatomic gas flows past a concave body.

In the investigation of processes of heterogeneous relaxation in gases it is important to distinguish a class of problems in which this is the principal channel of relaxation. It must be taken into account that the importance of heterogeneous relaxation increases with decreasing gas pressure. Since the terrestrial atmosphere at altitudes $\gtrsim 150$ km is characterized by low densities and pressures, it may be expected that in the physicochemical aerodynamics of bodies flying in the atmosphere at such altitudes problems of nonequilibrium kinetics will arise in which the channel of heterogeneous relaxation is the decisive one.

Gashtol'd [1] distinguished a class of aerodynamic problems in which heterogeneous relaxation of translational energy is important, and a method was suggested for calculating the contribution of this process to the aerodynamic characteristics; this method was based on the successive calculation of multiple reflections.

The present work pinpoints a class of problems of the aerodynamics of the upper atmosphere, in which the principal role is played by the process of heterogeneous relaxation of the vibrational energy of gas molecules, and a method of solving them is suggested; this is analogous to the method used in [1].

We examine the external steady-state problem of flow of a free molecular single-component stream of diatomic gas past a concave body. The surface temperature of the body past which the gas flows is taken to be specified.

It is assumed that the mean translational energy of the molecules in a gas stream coming from infinity is much larger than the mean translational energy of molecules in a gas stream reflected with full accommodation and that it is

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also much larger than a quantum of vibrational energy of the gas molecules, but much smaller than a quantum of their electronic energy and their dissipation energy; this enables us to disregard the phenomena of dissociation, ionization, and electronic transitions upon impact of molecules on the surface. However, there is a considerable probability of transition of the translational energy of a molecule of a gas stream coming from infinity into internal rotational–vibrational energy upon its impact on the surface of a body.

The examination concerns gas of homonuclear molecules with dipole moment equal to zero (N_2, O_2). For such molecules the probabilities of radiational transitions between vibrational levels are very small, and during the process of flow past the body a change in the population density of their vibrational levels occurs practically only on account of impact on the surface.

Thus, in the problem under examination, the process of multiple reflections of a gas stream from the surface it flows past consists of two stages. During the first few reflections the vibrational motion of the gas molecules is excited, and a considerable vibrational disequilibrium forms in the system gas–surface of the body in the sense that the mean vibrational energy per molecule in the reflected gas stream is much larger than $\epsilon = \hbar\omega[\exp(\Theta/T_S)-1]^{-1}$ corresponding to reflection in thermal equilibrium with the surface. The process of further reflections is then a process of heterogeneous vibrational relaxation in which the distribution of molecules over the vibrational levels approaches the distribution corresponding to the state of equilibrium with the surface past which the flow occurs.

This process of heterogeneous vibrational relaxation is investigated in the present work on the assumption that the disequilibrium distribution of the molecules over the vibrational levels, which forms in the gas at the initial stage of the process of multiple reflections (at the stage of "excitation"), is known.

The investigation is carried out by the method of successive calculation of the multiple reflections in which the process of flow past is described by the sequence of distribution functions $f_\beta(\mathbf{r}, \mathbf{u}, \alpha, i)$. The subscript β characterizes the frequency of reflections, α is the number of the rotational level of the gas molecule, i is the number of its vibrational level. The function $f_\beta(\mathbf{r}, \mathbf{u}, \alpha, i)$ itself is the distribution function according to speeds and rotational–vibrational levels of the molecules β times colliding with the surface of the body past which the flow occurs.

At the point $\mathbf{r}_S$ of the surface past which the gas flows, the following relationships apply:

$$u_n f_{\beta+1}(\mathbf{r}_s, \mathbf{u}, \alpha, i) = \sum_{\alpha'} \sum_{j} \int_{v_n<0} |v_n| f_\beta(\mathbf{r}_s, \mathbf{v}, \alpha', j) W_\beta(\mathbf{v}, \alpha', j; \mathbf{u}, \alpha, i)\, d\mathbf{v}, \tag{1}$$

where $W_\beta(\mathbf{v}, \alpha', j; \mathbf{u}, \alpha, i)$ is the scattering function of the gas molecules on the surface corresponding to the transition $\mathbf{v}, \alpha', j \rightarrow \mathbf{u}, \alpha, i$; $\mathbf{n}$ is the normal to the surface at the point $\mathbf{r}_S$; $f_0 = f_\infty$.

If the scattering function W_β and the function f_∞ are known, then the sequence of relationships (1) characterizes the dependence of the distribution functions f_β on the parameter β, i.e., the change of the distribution function of the gas molecules according to speeds and rotational–vibrational levels in the process of multiple reflections of the gas stream by the surface.

Relationship (1) was written within the framework of the "quasiclassical" approach where the translational movement of the gas molecule is examined in the classical approximation, and the movement of the atoms in the molecule is examined from the point of view of quantum mechanics.

Determination of the type of the functions W_β for the molecules of different gases and at different conditions of flow against the body is one of the fundamental problems of the dynamics of scatter of a gas by a surface. In spite of the considerable number of investigations [2] dealing with the solution of this problem, we still lack at present a method of determining the scattering functions of polyatomic gases theoretically and experimentally with sufficient accuracy; this is connected basically with the insufficient amount of information on the nature of the interaction potentials of the gas molecule with a solid surface and with the difficulties of solving the problems in their accurate statement. However, the theory on the basis of the determinations and the most general facts alone enables us to assert that the function W_β in (1) satisfies the condition of nonnegativity and normalization, and the relationship of reciprocity [3].

Below we also take it that the function W_β satisfies the condition of "ensuring relaxation of reflected gas streams to the state of equilibrium with the surface" [1].

If we now examine only that part of the relationships of the sequence (1) which corresponds to the description of the process of heterogeneous relaxation of the vibrational energy of the gas molecules, then the form of each of these relationships can be substantially simplified.

Experimental investigations [4] showed that in multiple impacts of the homonuclear molecules N_2, O_2 against a surface, the change in their distribution according to vibrational levels occurs much more slowly than the change of their distribution according to speeds and rotational levels. This enables us in the first approximation (like in the examination of vibrational relaxation within the bulk of the gas) to examine heterogeneous vibrational relaxation in isolation, against the background of the already ending rapid processes of establishing equilibrium with the surface according to translational and rotational degrees of freedom. There the scattering function W does not depend on the parameter β, and the process of heterogeneous vibrational relaxation can be described in terms of the distribution functions averaged over speeds and rotational states.

As a result, the system of relations (1) can be written in the form

$$\nu_{\beta+1}^{+}(\mathbf{r}_s,\ i)=\sum_{j} P_{j,i}\nu_{\beta}^{-}(\mathbf{r}_s,\ j), \tag{2}$$

where

$$\nu_{\beta}^{-}(\mathbf{r}_s,\ j)=\sum_{\alpha'}\int_{v_n<0}|v_n|\,f_{\beta}(\mathbf{r}_s,\ \mathbf{v},\ \alpha',\ j)\,d\mathbf{v};$$

$$\nu_{\beta+1}^{+}(\mathbf{r}_s,\ i)=\sum_{\alpha}\int_{u_n>0}u_n f_{\beta+1}(\mathbf{r}_s,\ \mathbf{u},\ \alpha,\ i)\,d\mathbf{u}$$

are the streams of a number of gas molecules to the surface and from the surface (henceforth a plus sign always denotes streams from the surface, a minus sign streams to the surface);

$$P_{j,i}(\mathbf{r}_s)=\frac{1}{\nu_{\beta}^{-}}\sum_{\alpha}\sum_{\alpha'}\int_{u_n>0}\int_{v_n<0}|v_n|\,f_{\beta}(\mathbf{r}_s,\ \mathbf{v},\ \alpha',\ j)\,W(\mathbf{v},\ \alpha',\ j;\ \mathbf{u},\ \alpha,\ i)\,d\mathbf{v}d\mathbf{u}$$

is the probability of the transition j → i, averaged over speeds and rotational states, upon reflection from the surface near point r_s calculated for one gas molecule. The subscript β in (2) runs through the values corresponding to the stage of vibrational relaxation.

On account of their linear correlation with the function W, the probabilities $P_{j,i}$ satisfy the condition of nonnegativity, the condition of normalization

$$\sum_{i} P_{j,i}=1, \tag{3}$$

and also the relation of reciprocity

$$P_{j,i}\exp\left(-\frac{\varepsilon_j}{kT_s}\right)=P_{i,j}\exp\left(-\frac{\varepsilon_i}{kT_s}\right). \tag{4}$$

Strictly speaking, the theoretical calculation of the probability $P_{j,\,i}$ requires that the full scattering function W be known. However, in kinetic calculations dealing with the solution of equations of the type of (2) it is not indispensable to know the accurate form of the probability $P_{j,\,i}$. It suffices to know the explicit dependence of the value of $P_{j,\,i}$ on j, i, which is determined by the form of the function W. Further examination is conducted on the basis of the simplest assumptions concerning the nature of the dependence of $P_{j,\,i}$ on j, i. These assumptions are analogous to those usually made concerning the probabilities of vibrational transitions in the investigation of vibrational relaxation within the bulk of the gas.

It is believed that the process of heterogeneous relaxation occurs only on account of single-quantum vibrational transitions of gas molecules upon impact against the surface; this is justified when the temperature of the surface is moderate. With this assumption, Eqs. (2) and condition (3) assume the form

$$\nu_{\beta+1}^{+}(\mathbf{r}_s,\ i)=P_{i-1,i}\nu_{\beta}^{-}(\mathbf{r}_s,\ i-1)+P_{i,i}\nu_{\beta}^{-}(\mathbf{r}_s,\ i)+P_{i+1,i}\nu_{\beta}^{-}(\mathbf{r}_s,\ i+1), \tag{5}$$

$$P_{i,i-1}+P_{i,i}+P_{i,i+1}=1. \tag{6}$$

Now if we use the simplest model of a harmonic oscillator for describing the vibrations of the atoms in a molecule and consider the following relationships correct

$$P_{i,i+1}=(i+1)P_{0,1};\ P_{i,i-1}=iP_{1,0}, \tag{7}$$

then we obtain after multiplying Eq. (5) by $\hbar\omega i$ and summing over all i's the following relationship between the mean flows of vibrational energy from and to the surface:

$$E^{+}_{\beta+1} = (P_{0,1} - P_{1,0}) E^{-}_{\beta} + E^{-}_{\beta} + \hbar\omega P_{0,1} \nu^{-}_{\beta}, \tag{8}$$

where

$$E^{+}_{\beta+1} = \sum_{i} \hbar\omega i \nu^{+}_{\beta+1} (\mathbf{r}_s, i); \quad E^{-}_{\beta} = \sum_{i} \hbar\omega i \nu^{-}_{\beta} (\mathbf{r}_s, i);$$

$$\nu^{-}_{\beta} = \sum_{i} \nu^{-}_{\beta} (\mathbf{r}_s, i).$$

The probabilities $P_{0.1}$ and $P_{1.0}$ are correlated by the relation of reciprocity (4) which, for a harmonic oscillator, assumes the form

$$\frac{P_{0,1}}{P_{1,0}} = \exp\left(-\frac{\Theta}{T_s}\right). \tag{9}$$

Using relationship (9) and after some simple transformations we can obtain from (8) the expression for the accommodation coefficient of the vibrational energy

$$\gamma_{\beta} = \frac{E^{-}_{\beta} - E^{+}_{\beta+1}}{E^{-}_{\beta} - E^{+}_{s,\beta+1}} = \left[1 - \exp\left(-\frac{\Theta}{T_s}\right)\right] P_{1,0}, \tag{10}$$

where

$$E^{+}_{s,\beta+1} = \hbar\omega \nu^{+}_{\beta+1} \left[\exp\left(\frac{\Theta}{T_s}\right) - 1\right]^{-1}$$

is the flow of vibrational energy from the surface with full accommodation of the gas molecules according to vibrational degrees of freedom.

The derivation of Eq. (10) is almost completely analogous to the derivation of the relaxation equation for the vibrational energy in the examination of vibrational relaxation within the bulk of the gas. It may therefore be called the relaxation equation for the vibrational energy in the examined process of heterogeneous relaxation. Here the accommodation coefficient of the vibrational energy is analogous to the value $1/\tau_{VT}$, where τ_{VT} is the time of vibrational relaxation within the bulk of the gas.

Expression (10) contains the temperature dependence of the accommodation coefficient of vibrational energy, and also its dependence on the probability of deactivation of the first vibrational level. With the above assumptions, the probability $P_{1.0}$, and consequently also the coefficient of (10) do not depend on the parameter β. Henceforth we will therefore denote the accommodation coefficient of vibrational energy simply by γ.

Relationship (10) makes it possible to obtain the sequence of integral equations for vibrational energy corresponding to the given problem, the integral equations expressing the effect of different sections of the concave surface on each other. In deriving these equations it is assumed that in the time of passage of the gas molecules from one point of the surface to the other, their vibrational state does not change.

If we also take into account that to the above assumptions the following scattering function corresponds

$$W = \frac{2}{\pi} u_n h_s^2 Q_\alpha P_{j,i} \exp\left(-h_s u^2 - \frac{e_\alpha}{kT_s}\right), \tag{11}$$

where e_α is the rotational energy of a molecule calculated on the basis of the model of a rigid rotator, and $Q_\alpha = 2(2\alpha + 1)(\Theta_B/T_S)$, then for a stream of a number of molecules we can obtain the following system of integral relationships:

$$\nu^{-}_{\beta+1} (\mathbf{r}_s, i) = \sum_{j} \int_{S'} \nu^{-}_{\beta} (\mathbf{r}'_s, j) P_{j,i} (\mathbf{r}'_s) G(\mathbf{r}'_s, \mathbf{r}_s)\, dS', \tag{12}$$

where

$$G(\mathbf{r}'_s, \mathbf{r}_s) = \frac{1}{\pi} \frac{\mathbf{n}(\mathbf{r}'_s - \mathbf{r}_s)}{(\mathbf{r}'_s - \mathbf{r}_s)^2} \frac{\mathbf{n}(\mathbf{r}_s - \mathbf{r}'_s)}{(\mathbf{r}_s - \mathbf{r}'_s)^2};$$

S′ is the part of the surface in the flow through which the vector $\mathbf{r}'_S$ passes; dS′ is an element of the surface area near the point $\mathbf{r}'_S$.

Summing over i and taking (3) into account, we obtain from (12) a system of integral equations for the frequency of the impacts

$$\nu^{-}_{\beta+1}(\mathbf{r}_s) = \int\limits_{S'} \nu^{-}_{\beta}(\mathbf{r}'_s)\, G(\mathbf{r}'_s,\ \mathbf{r}_s)\, dS', \tag{13}$$

which is a characteristic trait of diffuse reflection.

If we make assumptions and carry out transformations analogous to those with whose aid we obtained (10) from (2), then the following sequence of integral equations for vibrational energy follows from (12):

$$E^{-}_{\beta+1}(\mathbf{r}_s) = \gamma E^{-}_{s,\beta+1}(\mathbf{r}_s) + (1-\gamma)\int\limits_{S'} \boldsymbol{E}^{-}_{\beta}(\mathbf{r}'_s)\, G(\mathbf{r}'_s,\ \mathbf{r}_s)\, dS', \tag{14}$$

where

$$E^{-}_{s,\beta+1} = \hbar\omega\left[\exp\left(\frac{\Theta}{T_s}\right) - 1\right]^{-1} \nu^{-}_{\beta+1}(\mathbf{r}_s).$$

In deriving Eq. (14), γ and T_S are considered constant on the entire surface in the flow.

The sequence of equations (14) together with (13) describes fully the process of heterogeneous relaxation of vibrational energy in the given problem.

In the same way we can in principle also investigate the initial stage of the process of multiple reflections of a gas stream from a surface (the stage of excitation of vibrations of the gas molecules). However, in this case the scattering function W depends largely on the parameter β (i.e., in fact on the mean flow speed), and this introduces substantial changes into the conclusions presented above.

NOTATION

f_∞, distribution function of speeds and rotational–vibrational levels of molecules in a gas stream coming from infinity; T_S, temperature of the surface in the flow; e, ϵ, rotational and vibrational energy, respectively, of the molecule; $\hbar\omega$, quantum of vibrational energy of a molecule; Θ_B, Θ, characteristic rotational and vibrational energy, respectively; $h_S = m/(2kT_S)$; m, molecular mass; k, Boltzmann constant.

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