GAS-DYNAMIC EQUATIONS INVOLVING VIBRATIONAL RELAXATION

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We derive the gas-dynamic equations in the Navier—Stokes approximation for weak excitation of molecular vibrational states. We determine the distribution function for the density of the numbers determining occupancy of the vibrational states of the molecules. We show that the relaxational pressure is proportional to the deviation of the vibrational energy density from its local-equilibrium value for the temperature of the translational and rotational degrees of freedom of the molecules.

The structure of the gas-dynamic equations in the presence of vibrational relaxation was considered in [1-6]. Depending on the degree of excitation of the vibrational states of the molecules, essential changes occur not only in the kinetic coefficients but also in the structure of the transport equations. Greatly detailed studies of the so-called "two-temperature approximation" have been made. In the general case [3, 6] such an approximation is not sufficient, so that it is necessary to supplement the known system of gas-dynamic equations with an equation for n_v, the number of molecules per unit volume existing at the vibrational level v.

It is known [3] that for the simplest model of vibrational transitions, the harmonic oscillator with single quantum jumps, it is sufficient merely to augment the gas-dynamic equations in the Euler approximation with a relaxational equation for the vibrational energy density, and there is no need to consider an equation for n_v. However, it is not clear whether this procedure is valid for the gas-dynamic equations in the Navier—Stokes approximation. In investigating this problem it is found that general concepts concerning the structure of the collision integral are no longer sufficient and that is necessary to consider a concrete model for the interaction between molecules and to obtain an explicit expression for the collision integral.

In the present paper we consider a diatomic gas for a weak excitation of the vibrational states of its molecules when the deviation ξ of the interatomic distance in the molecule from its equilibrium value is small. In this case, following [7], we can write the molecular interaction potential, and hence also the collision transition probabilities, in the form of a series in ξ. If in the collision integral we restrict ourselves to the contribution of terms of order ξ^2, we obtain a kinetic equation which takes into account single quantum vibrational transitions. We find that even for such a simple intermolecular interaction model it is necessary, in the Navier—Stokes approximation, to take into account an equation for n_v.

1. It is possible to determine the nonequilibrium state of a single-component polyatomic gas in the absence of external fields [8] if we know the monomolecular distribution function (Wigner function) $f(\mathbf{r}, \mathbf{p}; l, t)$, where $\mathbf{r}$ and $\mathbf{p}$ give the position and momentum of the center of mass of the molecule, and l is the total set of quantum numbers defining its internal energy E_l. Evolution of this function with the time t is determined from the kinetic equation

$$\left(\frac{\partial}{\partial t} + \frac{1}{m} \mathbf{p}_1 \operatorname{grad}_\mathbf{r} \right) f(1) = I(f, f) \tag{1.1}$$

where $f(1) = f(\mathbf{r}, \mathbf{p}_1; l_1, t)$,

$$I(f, f) = \int d1_0' \, d2_0' \, d2_0 w(12; 1'2') \, \delta(\Sigma p) [f^*(1') f^*(2') - f^*(1) f^*(2)] \tag{1.2}$$

$I(f, f)$ is the collision integral.

Here $w(12; 1'2')$ is the probability of a transition per unit time from the state $(\mathbf{p}_1'\mathbf{p}_2', l_1'l_2')$ to the state $(\mathbf{p}_1, \mathbf{p}_2, l_1 l_2)$, which is expressed in terms of the matrix elements of the T-operator in the space of the characteristic states of the noninteracting molecules 1 and 2 in the system of their center of inertia through the known relationship [9]

$$w(12; 1'2') = \frac{(2\pi)^2}{\hbar} \sum_{M_1 M_2 M_1' M_2'} \left| \left\langle \begin{matrix} l_1 M_1; \, l_2 M_2 \\ p_{21} \end{matrix} \, |T| \, \begin{matrix} l_1' M_1'; \, l_2' M_2' \\ p_{21}' \end{matrix} \right\rangle \right|^2$$
$$\delta\left(\frac{1}{2m} [p_1^2 + p_2^2 - p_1'^2 - p_2'^2] + E_{l_1} + E_{l_2} - E_{l_1'} - E_{l_2'} \right)$$

where $f^*(j) = g^{-1}(j) f(j)$, M_j are the quantum numbers for which the state corresponding to E_{l_j} is degenerate, and $g(j)$ is the multiplicity of the degeneracy of this state:

$$\int d1_0 = \sum_{l_1} \int d\mathbf{p}_1, \quad \delta(\Sigma p) = h^3 \delta(\mathbf{p}_1 + \mathbf{p}_2 - \mathbf{p}_1' - \mathbf{p}_2')$$

We consider the case in which the diatomic molecular interaction potential can be represented in the form

$$\Phi(12) = \sum_{i=1}^{2} \sum_{j=1}^{2} \Phi_{ij}(|\mathbf{r}_{1i} - \mathbf{r}_{2j}|) \tag{1.3}$$

where $\mathbf{r}_{ji}$ is the coordinate of the i-th atom in the j-th molecule. We denote by $\mathbf{r}_j, \xi_j$, and $\mathbf{u}_j$, respectively, the coordinate of the center of mass, the deviation of the interatomic distance from its equilibrium value R_0, and the unit vector directed from the second atom towards the first atom in the j-th molecule. We shall assume that $\xi_j/R_0 \ll 1$. Then, following [7], we can represent $\Phi(12)$ as a series in ξ_j. With accuracy up to the first order in ξ_j, from Eq. (1.3) we have

$$\Phi(12) = \Phi^{(0)}(12) + \sum_{j=1}^{2} \xi_j V(j) \tag{1.4}$$

Here $\Phi^{(0)}(12)$ is the interaction potential of (rigid) rotators, obtainable from Eq. (1.3) by replacing $\mathbf{r}_{ji}$ by

$$\mathbf{R}_{ji} = \mathbf{r}_j + (-1)^i \frac{R_0 \mu}{m_i} \mathbf{u}_j, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

and m_i is the mass of the i-th atom

$$V(j) = \sum_{k=1}^{2} \sum_{i=1}^{2} (-1)^i \frac{\mu \mathbf{u}_j}{m_i} \frac{\partial \Phi^{(0)}(|\mathbf{R}_{ji} - \mathbf{R}_{3-j,k}|)}{\partial(\mathbf{R}_{ji} - \mathbf{R}_{3-j,k})}$$

In the molecular internal energy operator we take into account terms of order ξ^2; i.e., we neglect the anharmonic vibrations and the relationship of vibrations with rotations. Then the internal state of the molecule is determined [10] by the quantum numbers J, M, and v, where J and M are the quantum numbers of the total internal moment and its projection on the z axis, and v is the vibrational quantum number. Moreover,

$$E_{Jv} = E_J + E_v, \quad E_J = \hbar^2 (2\mu R_0^2)^{-1} J(J+1), \quad E_v = h\nu(v + 1/2)$$

$$\langle v | \xi | v' \rangle = \delta_{v', v+1} \sqrt{\frac{\hbar}{4\pi \mu \nu}(v+1)}$$

ν is the characteristic frequency of the oscillator and $\delta_{\alpha, \alpha'}$ is the Kronecker symbol.

Taking note of the definition of the T-operator [9] and of the expression (1.4) for the molecular interaction potential, then, taking into account terms of the second order in ξ, we can write the collision integral in the form

$$I(f, f) = I^{(0)}(f, f) + I^{(1)}(f, f) + I^{(2)}(f, f) \tag{1.5}$$

Here the collision integral

$$I^{(0)}(f, f) = \sum_{v_2} \int d1' d2' d2 \, W^{(0)}(12; 1'2') \, [f_{v_1}^*(1') f_{v_2}^*(2') - f_{v_1}^*(1) f_{v_2}^*(2)] \tag{1.6}$$

only takes into account the contribution from collisions for which the vibrational states of the molecules do not change:

$$\int d1 = \sum_{J_1} d\mathbf{p}_1, \quad f_{v_1}(1) = f(\mathbf{r}, \mathbf{p}_1; J_1 v_1)$$

$$W^{(0)}(12; 1'2') = \frac{2\pi}{\hbar} \sum_{M_1 M_2 M_1' M_2'} \left| \left\langle \begin{matrix} \alpha_1, \alpha_2 \\ \mathbf{p}_{21} \end{matrix} \middle| T_r \middle| \begin{matrix} \alpha_1', \alpha_2' \\ \mathbf{p}_{21}' \end{matrix} \right\rangle \right|^2 \times \delta(\Sigma p) \, \delta(E_{J'} - E_J)$$

T_r is the T-operator for the model of rotators, $\alpha_j = (J_j M_j)$, and

$$E_J = \sum_{j=1}^{2} \left(\frac{1}{2m} p_j^2 + E_{J_j} \right)$$

The collision integral

$$I^{(1)}(f, f) = \sum_{i=1}^{2} \sum_{i \neq j} \sum_{v_2} \int d1' \, d2' \, d2 \, W_j^{(1)}(12; 1'2') \, \{[(v_j + 1) \, \delta(+) \overset{*}{f}_{v_j+1}(j') +$$

$$v_j \delta(-) \overset{*}{f}_{v_j-1}(j')] \, \overset{*}{f}_{v_i}(i') - [(v_j + 1) \, \delta(+) + v_j \delta(-)] \, \overset{*}{f}_{v_j}(j) \, \overset{*}{f}_{v_i}(i)\} \tag{1.7}$$

takes into account the contribution from collisions with single-quantum vibrational transitions, where

$$W_j^{(1)}(12; 1'2') = \frac{1}{2\mu v} \sum_{M_1 M_2 M_1' M_2'} \left| \left\langle \begin{matrix} \alpha_1, \alpha_2 \\ \mathbf{p}_{21} \end{matrix} \middle| \Omega^{(-)} V(j) \Omega^{(+)} \middle| \begin{matrix} \alpha_1', \alpha_2' \\ \mathbf{p}_{21}' \end{matrix} \right\rangle \right|^2 \delta(\Sigma p)$$

$\Omega^{(\pm)}$ are the Mellor operators [9] for the model of rotators, and $\delta(\pm) = \delta(E_{J'} - E_J \pm h\nu)$.

The collision integral $I^{(2)}(f, f)$ is obtained from $I^{(0)}(f, f)$ by replacing $W^{(0)}(12; 1'2')$ by

$$W^{(2)}(12; 1'2') = \lim_{\eta \to 0^+} \frac{1}{\mu v} \sum_{j=1}^{2} \sum_{M_1 M_2 M_1' M_2'} \mathrm{Re} \left\{ \left\langle \begin{matrix} \alpha_1, \alpha_2 \\ \mathbf{p}_{21} \end{matrix} \middle| T_r \middle| \begin{matrix} \alpha_1', \alpha_2' \\ \mathbf{p}_{21}' \end{matrix} \right\rangle \times \right.$$

$$\left. \times \left\langle \begin{matrix} \alpha_1', \alpha_2' \\ \mathbf{p}_{21}' \end{matrix} \middle| \Omega^{(+)} V(j) \left[\frac{v_j + 1}{E_{J'} - H - h\nu + i\eta} + \frac{v_j}{E_{J'} - H + h\nu - i\eta} \right] V(j) \Omega^{(-)} \middle| \begin{matrix} \alpha_1, \alpha_2 \\ \mathbf{p}_{21} \end{matrix} \right\rangle \right\} \delta(\Sigma p) \, \delta(E_{J'} - E_J)$$

where H is the total Hamiltonian of the two rotators in the system of their mass centers. From the invariance of H and V(j) relative to spatial reflections and time inversion [9], it follows that

$$W^{(k)}(12; 1'2') = W^{(k)}(1'2'; 12), \quad k = 0.2 \tag{1.8}$$

$$W_j^{(1)}(12; 1'2') = W_j^{(1)}(1'2'; 12)$$

2. We derive the gas-dynamic equations using the kinetic equation (1.1) with the collision integral in the form (1.5). We consider the case for which the "length of the vibrational relaxation" is of the order of the characteristic dimension of the spatial heterogeneity in the gas [1, 3, 11], i.e., for which the ratio of $I^{(1)}$ and $I^{(2)}$ to $I^{(0)}$ is of the order of the Knudsen number, which we may assume to be small.

From the expression (1.6) for $I^{(0)}$ it follows that

$$\sum_{v_1} \int d1 \, \psi_i I^{(0)}(f, f) = 0$$

for

$$\psi_1 = \delta_{v_1 v}, \quad \psi_2 = p_1, \quad \psi_3 = \frac{1}{2m} p_1^2 + E_{J_1} \tag{2.1}$$

Consequently, the following quantities vary slowly over times on the order of the free path time, defined for the translational and rotational states of the molecules: $n_v(\mathbf{r}, t)$, the number of molecules per unit volume which are in the vibrational state v; $u(\mathbf{r}, t)$, the mean speed of the molecules; and $e(\mathbf{r}, t)$, the internal energy (translational and rotational) density, calculated for a single molecule. We introduce the notation

$$N_1 = n_v, \quad N_2 = mn\mathbf{u}, \quad N_3 = n(e + {}^1\!/_2\, mu^2) \left(n = \sum_v n_v \right)$$

Then the local gas-dynamic variables may be defined in terms of the distribution function in the following way:

$$N_i = \sum_{v_1} \int d1\, \psi_i f_{v_1}(1) \quad (i = 1, 2, 3) \tag{2.2}$$

Taking the definition (2.2) into account, we obtain from Eq. (1.1), with the collision integral in the form (1.5), the system of gas-dynamic equations

$$\frac{Dn_v}{Dt} = -n_v \operatorname{div} \mathbf{u} - \operatorname{div} \mathbf{j}_v + Q_v$$

$$nm \frac{D\mathbf{u}}{Dt} = -\operatorname{Div} P \tag{2.3}$$

$$n \frac{De}{Dt} = -\operatorname{div} \mathbf{q} - P\operatorname{Grad} \mathbf{u} - Q_e \quad \left(\frac{D}{Dt} = \frac{\partial}{\partial t} + (\mathbf{u}\,\text{grad}) \right)$$

Here the stress tensor P and the energy flow $\mathbf{q}$ are defined in the usual way [8]

$$P^{ij} = \frac{1}{m} \sum_{v_1} \int d1\, p_1^{*i} p_1^{*j} f_{v_1}(1) \tag{2.4}$$

$$q^j = \frac{1}{m} \sum_{v_1} \int d1\, p_1^{*j} \left(\frac{1}{2m} (p_1^*)^2 + E_{J_1} \right) f_{v_1}(1) \; (i, j = 1, 2, 3, \; p^{*j} = p^j - mu^j)$$

while the current $\mathbf{j}_v$ and the source Q_v, in the equation for the transport of the density of vibrational states, as well as the source Q_e in the energy equation, are given by

$$j_v^{\,i} = \frac{1}{m} \int d1\, p_1^{*i} f_v(1) \tag{2.5}$$

$$Q_v = \int d_1 I^{(1)} (f, f), \quad Q_e = \sum_v h v n Q_v$$

We observe that the vibrational energy density per molecule for the model under consideration may be defined as follows:

$$e_k(\mathbf{r}, t) = n^{-1}(\mathbf{r}, t) \sum_v h v v n_v(\mathbf{r}, t)$$

To derive the gas-dynamic equations we use the Chapman–Enskog method. As the additional conditions on the coefficients in the expansion of f_v in a series with respect to the Knudsen number, we require that the local gas-dynamic variables be defined by a term of zero order. Moreover, in place of e we use the inverse local temperature, which we define in the usual way [8]

$$e = 3/2\beta + e_i(\beta)$$

where

$$e_i(\beta) = Q^{-1} \sum_{J_1} g(1) E_{J_1} \exp(-\beta E_{J_1}), \quad Q = \sum_{J_1} g(1) \exp(-\beta E_{J_1})$$

3. We consider the zeroth approximation with respect to the Knudsen number. The distribution function in this approximation satisfies the nonlinear system of integral equations

$$I^{(0)}\ (f^{(0)},\ f^{(0)}) = 0$$

Using the function

$$H = \sum_v \int d1 f_v(1) \ln\left[\frac{f_v(1)}{g(1)}\right]$$

the relations (1.8), and the definition of the local gas-dynamic variables, we can show similarly [2] that

$$f_v^{(0)}(1) = n_v F(1) \equiv n_v\ \frac{g(1)}{Q}\left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta\left(\frac{p_1^{*2}}{2m} + E_{J_1}\right)\right] \tag{3.1}$$

Then, noting the definition of the currents and sources in Eqs. (2.4) and (2.5), we obtain, in the zeroth approximation,

$$\mathbf{j}_v^{(0)} = 0, \quad \mathbf{q}^{(0)} = 0; \quad P^{(0)\ ij} = n\beta^{-1}\delta_{ij} \tag{3.2}$$

$$Q_v^{(0)} = \frac{1}{\tau}\left[(v+1)n_{v+1} + \gamma v n_{v-1} - \{\gamma(v+1) + v\}n_v\right] \tag{3.3}$$

$$Q_e^{(0)} = n\tau_k^{-1}(e_k - e_0)$$

Here $\gamma = \exp(-\beta h\nu)$, $e_0 = h\nu\gamma(1-\gamma)^{-1}$

$$\tau^{-1} = \frac{n}{2}\int d1'd2'd1\,d2\delta(+)F^*(1)F^*(2)\sum_{j=1}^{2}W_j^{(1)}(12;\,1'2'). \quad F^*(j) = g^{-1}(j)F(j)$$

$$\tau_k = \tau(1-\gamma)^{-1} \tag{3.4}$$

Consequently, in the Euler approximation the system of gas-dynamic equations has the form

$$\frac{Dn}{Dt} = -n\,\mathrm{div}\,\mathbf{u}, \quad nm\frac{D\mathbf{u}}{Dt} = -\,\mathrm{grad}\,(n\beta^{-1})$$

$$\frac{D\beta}{Dt} = -\beta^2\,\frac{e_k - e_0}{c_V\tau_k} + \beta c_V^{-1}\,\mathrm{div}\,\mathbf{u} \tag{3.5}$$

$$\frac{De_k}{Dt} = -\tau_k^{-1}(e_k - e_0), \quad \frac{Dn_v}{Dt} = -n_v\,\mathrm{div}\,\mathbf{u}$$

where the vibrational relaxation time τ_k is determined from the relation (3.4) and

$$c_V = \frac{3}{2} - \beta^2\frac{de_i}{d\beta}$$

4. We proceed now to determine the first order correction with respect to the Knudsen number to the distribution function. This function, which we denote by f_v^1, is determined from a nonhomogeneous system of linear integral equations with symmetric kernels (see relations (1.8))

$$\left[\frac{\partial}{\partial t} + \frac{1}{m}(\mathbf{p}_1\,\mathrm{grad}_r)\right]f_v^{(0)}(1) - I^{(1)}(f^{(0)}, f^{(0)}) - I^{(2)}(f^{(0)}, f^{(0)}) = I^{(0)}(f^{(1)}, f^{(0)}) + I^{(0)}(f^{(0)}, f^{(1)}) \tag{4.1}$$

subject to the additional conditions

$$\sum_{v_1}\int d1\psi_i f_{v_1}^{(1)}(1) = 0 \tag{4.2}$$

where the ψ_i are given by the relations (2.1). Taking note of the expression for $I^{(1)}$ and for $I^{(2)}$, we have

$$I^{(2)}\ (f^{(0)}, f^{(0)}) = 0$$

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$$I^{(1)}(f^{(0)}, f^{(0)}) = \sum_{v'} n_{v'} B_{v_1 v'} [\Delta_1^{(\pm)}] + n_{v_1}(1-\gamma)\frac{e_k - e_0}{h\nu} \sum_{j=1}^{2}(\Delta_j^{(+)} - \Delta_j^{(-)}) \tag{4.3}$$

where

$$B_{vv'}[\Delta^{(\pm)}] = v'\delta_{v', v_1 1}\Delta^{(+)} + \gamma(v'+1)\delta_{v', v-1}\Delta^{(-)} - \delta_{vv'}\left(\gamma(v'+1)\Delta^{(+)} \right.$$
$$\left. + v'\Delta^{(-)} + (1-\gamma)\frac{e_k - e_0}{h\nu}[\Delta^{(+)} - \Delta^{(-)}]\right) \tag{4.4}$$

$$\Delta_j^{(\pm)} = n\int d1'\,d2'\,d2\,W_j^{(1)}(12;\,1'2') \begin{cases} \delta(+)\,F^*(1')\,F^*(2') \\ \delta(-)\,F^*(1)\,F^*(2) \end{cases} \tag{4.5}$$

We remark that from Eq. (4.4) it follows that

$$\sum_{vv'} n_v B_{vv'} = 0$$

We proceed in the usual way [3] with the left side of the system of Eqs. (4.1), using the expression (3.1) for $f_v^{(0)}$ and the Euler Eq. (3.6). Then, taking note of the additional conditions (4.2), we can show that

$$f_{v_1}^{(1)}(1) = n_{v_1} F(1) \Phi_{v_1}(1) \tag{4.6}$$

where

$$\Phi_{v_1}(1) = \Phi^{(1)}(1) - \frac{1}{n^2}\sum_{v'} C_{v'v'}(1)\cdot p_1^* \operatorname{grad} n_{v_1} + \frac{1}{n} G_{v_1}(1) \tag{4.7}$$

Here $\Phi^{(1)}(1)$ is a known function of the first approximation [8], defined for the model of the rotators, and the functions $C_{vv'}(1)$ and $G_v(1)$ satisfy the systems of equations

$$\frac{p_1^*}{m} F(1) (\delta_{v_1|v'} - c_{v_1}) = \sum_{v_2} c_{v_1} c_{v_2} I_{v_1 v_2}(1/p^* C_{vv'}) \tag{4.8}$$

$$-c_{v_1} A(1)\varepsilon_k + \sum_{v'} c_{v'} B_{v_1 v'}[\lambda_1^{(\pm)}] = \sum_{v_2} c_{v_1} c_{v_2} I_{v_1 v_2}(1/G_v) \tag{4.9}$$

and the additional conditions

$$\sum_{v_1}\int d1\, n_{v_1} C_{v_1 v'}(1)\, p_1^{*2} F(1) = \sum_{v_1}\int d1\, \psi_i n_{v_1} G_{v_1}(1)\, F(1) = 0 \tag{4.10}$$

Here $c_v = n_v/n$, $\varepsilon_k = \beta^2(e_k - e_0)(c_V \tau_k)^{-1}$

$$A(1) = \left(\frac{1}{2m}p_1^{*2} - \frac{3}{2\beta} + E_{J_i} - e_i\right) - \frac{c_V \tau_k}{\beta^2 h\nu(1-\gamma)}\sum_{j=1}^{2}(\lambda_j^{(+)} - \lambda_j^{(-)}) \tag{4.11}$$

$$\lambda_j^{(\pm)} = \Delta_j^{(\pm)} - \tau^{-1} F(j) \tag{4.12}$$

$$I_{v_1 v_2}(1/H_{vv'}) = \int d1'\,d2'\,d2\,W^{(0)}(12;\,1'2')\,F^*(1)\,F^*(2)\,\{H_{v_1 v'}(1) + H_{v_2 v'}(2) - H_{v_1 v'}(1') - H_{v_2 v'}(2')\} \tag{4.13}$$

We may seek a solution of the system of Eqs. (4.8) in the form

$$C_{vv'}(1) = c_v^{-1}(\delta_{vv'} - c_v)\, C(1) \tag{4.14}$$

where the functions $C(1)$ are determined from the equations

$$\frac{p_1^*}{m} F(1) = I^{(1)}(1/p^*C) \equiv \int d1'\,d2'\,d2\,W^{(0)}(12;1'2')\,F^*(1)\,F^*(2)(p_1^* C(1) - p_1^{*'} C'(1)) \tag{4.15}$$

The additional conditions (4.10), as a consequence of Eq. (4.13), are satisfied identically.

We consider the solution of the system of Eqs. (4.9). We introduce the functions

$$G(1) = \sum_v c_v G_v(1), \quad \varphi_v(1) = G_v(1) - G(1)$$

for which we have, from Eq. (4.10), the equations

$$-A(1)\varepsilon_k = I(1/G), \quad \sum_{v'} c_{v'} B_{vv'}[\lambda_1^{(\pm)}] = c_v I^{(1)}(1/\varphi_v) \tag{4.16}$$

and the additional conditions

$$\int d1 \psi_i^\circ G(1) F(1) = \int d1 \varphi_v(1) F(1) = 0 \tag{4.17}$$

where ψ_i° is ψ_i [see Eqs. (2.1)] when $\psi_1 = 1$ (and not $\delta_{vv'}$); the integrals $I(1/G)$ and $I^{(1)}(1/\varphi_v)$ may be obtained from Eqs. (4.13) and (4.15) by replacing $H_{vv'}(i)$ by $G(i)$ and $p_1 * C(1)$ by $\varphi_v(1)$, respectively. In writing the Eqs. (4.16) we have accounted for the fact that, by definition,

$$\sum_v c_v \varphi_v = 0$$

From Eqs. (4.16) it follows that G and φ_v may be sought in the form

$$G(1) = -R(1)\varepsilon_k, \quad \varphi_v(1) = c_v^{-1} \sum_{v'} c_{v'} B_{vv'}[\omega_1^{(\pm)}]$$

The functions R and $\omega_1^{(\pm)}$ are determined from the equations

$$A(1) = I(1/R), \quad \lambda_1^{(\pm)} = I^{(1)}(1/\omega_1^{(\pm)}) \tag{4.18}$$

for the additional conditions (4.17), where in place of G and φ_v it is necessary to insert R and $\omega_1^{(\pm)}$, respectively. The functions $A(1)$ and $\lambda_1^{(\pm)}$ are determined from the relations (4.11) and (4.12).

Thus for the function of the first approximation with respect to the Knudsen number we have the following expression:

$$f_v^{(1)}(1) = n_v F(1) \Phi^{(1)}(1) - F(1) C(1) p_1 * \operatorname{grad} n_v/n - n_v F(1) R(1)\beta^2 \frac{e_k - e_0}{c_v \cdot n \tau_k} + $$
$$+ \frac{1}{n} F(1) \sum_{v'} n_{v'} B_{vv'}[\omega_1^{(\pm)}] \tag{4.19}$$

5. Using the expression (4.19) for $f_{v_1}^{(1)}(1)$, we can determine first-order corrections with respect to the Knudsen number to the currents and sources of the gas-dynamic equations and write the gas-dynamic equations in the Navier–Stokes approximation.

In accord with the definition (2.5), we have, taking Eq. (4.19) into account,

$$\mathbf{j}_v^{(1)} = -nD \operatorname{grad} n_v/n \tag{5.1}$$

where the "self-diffusion coefficient" D is given by

$$D = \frac{1}{3mn} \int d1 p_1 *^2 C(1) F(1)$$

The term proportional to the gradient β, on which the function $\Phi^{(1)}$ depends [8], does not contribute to Eq. (5.1) in view of the additional conditions for this function. If we assume that during a collision the rotational states are not excited and that there is merely an exchange taking place between the translational and vibrational states, then we obtain from Eq. (5.1) the expression for $\mathbf{j}_v$ obtained in [12].

The energy current can be written in the form

$$q^{(1)} = -\lambda \, \text{grad} \, T$$

where T is the temperature and λ is a known [8] thermal conductivity coefficient for the model of the rotators. As a consequence of Eq. (4.14), the term proportional to the gradient of n_V does not contribute to the current of energy.

We have the following expression for the stress tensor $P^{(1)}$:

$$P^{(1) \, ij} = -\eta \left(\frac{\partial u^i}{\partial r^j} + \frac{\partial u^j}{\partial r^i} - \frac{2}{3} \delta_{ij} \, \text{div} \, u \right) - \delta_{ij} (\eta_V \, \text{div} \, u - P_r)$$

where η_e and η_V are known [8] shear and volume viscosity coefficients for the rotator model, and P_r is the so-called relaxational pressure, defined as follows:

$$P_r = \frac{e_k - e_0}{c_V \tau_k} \beta^2 \frac{1}{3m} \int d1 \, p_1^{*2} R(1) F(1)$$

i.e., the relaxational pressure is proportional to the deviation of the vibrational energy density from its local-equilibrium value for the temperature of the translational and rotational degrees of freedom of the molecules. A dependence, similar in form, of the relaxational pressure on the vibrational energy density in the "two-temperature approximation" was obtained in [13] for the harmonic oscillator model in which exchanges between translational and vibrational degrees of freedom are not accompanied by a change in the rotational states of the molecules.

Substituting the expressions obtained, in the zeroth and first approximations with respect to the Knudsen number, for the currents and sources of the gas-dynamic variables into the system of Eqs. (2.2), we obtain the gas-dynamic equations in the Navier—Stokes approximation. Taking note of the expression for $Q_e^{(1)}$, we readily see that in this approximation the gas-dynamic equations cannot, as in the Euler approximation, be represented in the form of a closed system of equations for n, u, β, and e_k, and it is necessary to consider equations for n_V.

The determination of the relaxational pressure, the vibrational relaxation time, and also the sources Q_v and Q_e is tied in with the solution of the linear integral equations written out above. However, in solving these equations it is necessary to know the Mellor operators for the rigid rotators and not merely the corresponding transition probabilities. At the present time the solution of the quantum-mechanical problem is beset with considerable computational difficulty, so that quantitative estimates are not considered in this paper.

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