TRANSPORT COEFFICIENTS OF A GAS MIXTURE OF ATOMS
AND EXCITED MOLECULES

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We obtain compact analytical expressions for the transport coefficients.

The complexity of the problem of calculating the transport coefficients of an N-component gas mixture consisting of atoms and molecules is due to the necessity of taking into account in a systematic way the excited internal degrees of freedom of the molecules. The essence of the problem is as follows. In order to use the well-developed methods of calculating the kinetic coefficients of ideal gas mixtures [1] to solve this problem, where the transport coefficients are determined from the solution of a linear system of N algebraic equations, each i-th internal state of the molecule must be identified with a gas of the i-th kind. Then the effective number of gas components in the mixture and hence the amount of computation required greatly increase. An exception is the case when the distribution over the internal degrees of freedom can be described in terms of a certain temperature, which in general is different from the translational temperature of the gas. In this case the system of N algebraic equations is supplemented by only K additional equations, where K is the number of terms retained in the expansion of the first-order correction to the zero-order distribution function in the Chapman–Enskog method [2]. However even in this simple case the resulting system of equations is complicated and the author is unaware of a paper in which the equations are solved.

In practice, the approximation of [3] is widely used, in which the transport coefficients are calculated as for an N-component mixture of ideal gases. In [3] the dependence of the diffusion velocity of the molecules on their internal states is completely neglected, and the stress tensor and diffusion velocity reduce to the expressions obtained for a mixture of structureless particles. Diffusion of internal energy is taken into account only approximately in the expression for the heat flux.

The method used in the present paper is based on [4], in which an approximate method of calculating the transport coefficients of multi-component gas mixtures of structureless particles is given, and on [5], in which the transport coefficients of a rotationally excited gas are calculated. We consider the simplest case of a mixture consisting of a single atomic and single molecular component. The results are analyzed and compared with previous results and the accuracy of our results is estimated.

Following the generally used method, we identify the set of molecules in the i-th quantum state with a gas of the i-th kind. Let $i = 0$ correspond to the atomic component, and $i = 1, 2, \ldots, \infty$ correspond to the molecular component of a given kind. After transforming the semiclassical system of kinetic equations for the distribution function of particles of the i-th kind $f_i(t, x, \xi^i)$ to dimensionless form, these equations will contain the parameters Kn and Kn_Q, where Kn is equivalent to the Knudsen number, and Kn_Q represents a set of parameters equivalent to the average (per gas-kinetic collision) probabilities of the inelastic transitions $Q = R-R, R-T, V-V, V-T, V-R-T$ [6]. The case when any one of the parameters, for example Kn_{V-T}, is of order unity corresponds to so-called equilibrium exchange of the translational and vibrational energies, and the case $Kn_{V-T} \sim Kn$ corresponds to relaxational exchange. We first consider only the relaxational case, when all of the parameters Kn_Q are comparable to Kn. The equilibrium limit will be considered below.

At the hydrodynamical level the solution of the system of kinetic equations is written as an asymptotic series in the small parameter Kn. After eliminating the derivatives with respect to time (in correspondence with the Chapman–Enskog method) the equation for the first-

order correction $\phi\binom{1}{i}$ to the zeroth approximation distribution function $f_i^{(0)}$ takes the form [6]:

$$f_i^{(0)}\left[\left(\frac{m_i c^{i2}}{2kT}-\frac{5}{2}\right)c_r^i\frac{\partial\ln kT}{\partial x_r}+\frac{m_i}{kT}\left(c_r^i c_s^i-\frac{1}{3}c^{i2}\delta_{rs}\right)\frac{\partial u_r}{\partial x_s}+\right.$$

$$\left.+c_r^i\frac{n}{n_i}d_r^i+\frac{R_i}{n_i}-(nkT)^{-1}\left(\frac{m_i c^{i2}}{3kT}-1\right)\Sigma E_i R_i\right]-\frac{1}{2}I_i(f^{(0)},f^{(0)})=I_i(f^{(0)},f^{(0)}\varphi^{(1)});$$

(1)

$$R_i=\frac{1}{2}\int I_i(f^{(0)},f^{(0)})d\xi^i,\quad\frac{1}{2}I_i(f^{(0)},f^{(0)})=$$

$$=\sum_{jkl}\int(sf_k^{(0)}f_l^{(0)}-f_i^{(0)}f_j^{(0)})P_{ij-kl}vbdbd\varepsilon d\vec{\xi}^i,\quad I_i(f^{(0)},f^{(0)}\varphi^{(1)})=$$

$$==\sum_j f_i^{(0)}f_j^{(0)}(\varphi_i^{(1)\prime}+\varphi_j^{(1)\prime}-\varphi_i^{(1)}-\varphi_j^{(1)})P_{ij-ij}vbdbd\varepsilon d\vec{\xi}^j.$$

In (1) $f_i^{(0)}=n_i\left(\frac{m_i}{2\Pi kT}\right)^{3/2}\exp\left(-\frac{m_i c^{i2}}{2kT}\right)$; P_{ij-kl} is the probability of the transition $ij-kl$

per collision, and the type of inelastic transition (R-R, R-T, V-V, V-T, V-R-T) will be determined by the relation between the numbers i, j, k, ℓ, $s=g_i g_j/g_k g_\ell$ where g_i is the degeneracy of the i-th state; b, ε, v are the impact parameter, azimuthal angle and relative velocity of the pair of colliding particles, respectively; $c^i=\xi^i-u$, where u is the hydrodynamic velocity of the gas and T is the temperature defined in terms of the kinetic energy of the particles; n_i is the local density of particles of the i-th kind, $n_0=n_a$, $\sum_{i=1}^{\infty}n_i=n_M$, $n=n_a+n_M$, $m_0=m_a$ is the mass of an atom; $m_i=m_M$ (i = 1, 2, ..., ∞) is the mass of a molecule; E_i are the vibrational-rotational energy levels of the molecules; k is the Boltzmann constant.

The set of diffusion thermodynamic forces $d_r^i=\cdot\frac{\partial}{\partial x_r}\frac{n_i}{n}+\left(\frac{n_i}{n}-\frac{m_i n_i}{mn}\right)\frac{\partial\ln p}{\partial x_r}$ is not linearly independence since $\sum_{i=0}^{\infty}d_r^i=d_r^0+\sum_{i=1}^{\infty}d_r^i=d_r^a+d_r^M=0$. Following [4], we transform from d_r^a and d_r^M to a set $D_s^{(p)}$, using as the elements of the transformation matrix the orthonormal Waldman-Trubenbacher polynomials $P_j^{(p)}=\sum_{k=0}^{(p)}\alpha_k m_j^k$:

$$\frac{n}{n_j}d_r^j=\sum_p\frac{m_j}{m}P_j^{(p)}D_r^{(p)},\quad p=a,\,M,$$

(2)

where $\overline{m}=(m_a n_a+m_M n_M)/(n_a+n_M)$; $P_j^{(0)}=1$, $P_j^{(1)}=(m_j-\langle m\rangle)/(\langle m^2\rangle-\langle m\rangle^2)^{1/2}$, $\langle m^k\rangle=\sum_j m_j^{k+1}n_j/m\cdot n$.

Then because $d_r^a+d_r^M=0$, we have $D_r^{(0)}=0$.

Following (5), we transform the set of molecular vectors d_r^i (i = 1, 2, ..., ∞) to a set $\tilde{D}_s^{(p)}$, using as the elements of the transformation matrix the orthogonal Waldman-Trubenbacher polynomials $\tilde{\Pi}_i^{(p)}=\sum_{k=0}^p\tilde{\beta}_k E_i^k$.

$$\frac{n}{n_i}d_r^i=\sum_{p=0}^{\infty}\tilde{\Pi}_i^{(p)}\tilde{D}_r^{(p)}\quad i=1,2,\ldots,\infty,$$

(3)

where $\tilde{\Pi}_i^{(0)}=1$, $\tilde{\Pi}_i^{(1)}=(E_i-\langle E\rangle)/kT$, $\langle E^k\rangle=\sum_{i=1}^{\infty}E_i^k n_i/n_M$. Then the operator $\tilde{D}_r^{(0)}=\frac{n}{n_M}d_r^M$ turns out to be proportional to the operator $D_r^{(1)}$: $\tilde{D}_r^{(0)}=\frac{m_M}{m}P_M^{(1)}D_r^{(1)}$, and hence the set of operators

$D(\frac{1}{r})$, $\tilde{D}(\frac{i}{r})$ $(i = 1, 2, \ldots, \infty)$ will be linearly independent.

According to the Chapman–Enskog method, we write the general solution of the system (1) as a sum of a particular solution and the general solution of the homogeneous integral equation. The arbitrary constants in the general solution are chosen so that $\phi_i^{(1)}$ does not contribute to n_i, u, and T. Using the results of [4, 5], and also (2) and (3), we write the general solution of (1) in the form

$$\varphi_i^{(1)} = -\frac{1}{n} A^i \frac{m_i}{\overline{m}} c_r^i \frac{\partial \ln kT}{\partial x_r} - \frac{1}{n} B^i \frac{m_i}{\overline{m}} \left(c_r^i c_l^i - \frac{1}{3} c^{i2} \delta_{rl} \right) \frac{\partial u_l}{\partial x_r} +$$

$$+ A^{i(1)} \frac{m_i}{\overline{m}} c_r^i D_r^{(1)} + \sum_{p=1}^{\infty} \tilde{A}^{i(p)} c_r^i D_r^{(p)} + G^i, \quad i = 0, 1, 2, \ldots, \infty. \tag{4}$$

Conditions are imposed on the coefficients A^i, $A^i({}^1)$, $\tilde{A}^i(p)$, B^i, $G^i(\tilde{A}^0(P) = 0$, $p = 1, 2, \ldots, \infty)$, which obey integral equations obtained from (1) and (3), such that $\phi_i({}^1)$ does not contribute to n, u, T.

The coefficients of (4) are expanded in a double set of polynomials

$$A^{i(1)} = \sum_{s=0}^{1} \sum_{q=0}^{\infty} a_{sq}^{(1)} P_s^{(1)} S_{(3/2)i}^{(q)} \quad i = 0, 1, \ldots, \infty, \tag{5}$$

$$\tilde{A}^{i(p)} = \sum_{sq=0}^{\infty} \tilde{a}_{sq}^{(p)} \tilde{\Pi}_i^{(s)} S_{(3/2)i}^{(q)} \quad i = 1, 2, \ldots, \infty, \tag{5a}$$

$$L^i = \sum_{s=0}^{1} \sum_{q=0}^{\infty} l_{sq} \Pi_i^{(s)} S_{(j)i}^{(q)} \quad i = 0, 1, 2, \ldots, \infty. \tag{5b}$$

In (5b) L^i takes the values A^i and B^i, ℓ_{sq} takes the values $\underline{a}_{sq}$ and b_{sq}, $j = 3/2$ and $5/2$, $S\{_j^q\}_i$ are the Sonine polynomials, $\Pi_i^{(s)} = \sum\limits_{k=0}^{s} \beta_k m_i^k$ are the orthonormal Waldman–Trubenbacher polynomials, $\Pi_i^{(0)} = 1$, $\Pi_i^{(1)} = (m_i - \overline{m})/(\overline{m^2} - (\overline{m})^2)^{1/2}$, $\overline{m^k} = \sum\limits_{j=0}^{\infty} m^k_j n_j/n$. The scalar part of (4) G^i contributes to the rate constant of the vibrational-rotational transitions. The problem of obtaining an explicit expression for G^i and the reduction of this expression to one convenient for calculation is outside the scope of the present paper. We note that when the temperature T is defined in terms of the kinetic energy of the molecules, terms in the hydrodynamical equations corresponding to the bulk viscosity and relaxational pressure will be absent.

In the calculation of A^i, B^i, $A^i({}^1)$, we limit ourselves to the first nonvanishing terms of the series (5) a_{01}, b_{00}, $a_{10}^{(1)}$, which were called the dominant terms in the expansion (5) in [4]. In calculating $\tilde{A}^i(p)$, we use only the term $\tilde{\underline{a}}_{10}^{(p)}$. The quantities $\underline{a}_{01}$, b_{00}, $\underline{a}_{10}^{(1)}$, $\tilde{a}_{10}^{(p)}$ are found using a variational method and the maximum principle [1]. We then find:

$$a_{01} = -\frac{15\overline{m}}{16R}, \quad a_{10}^{(1)} = -\frac{3\overline{m}}{8nR^{(1)}},$$

$$b_{00} = \frac{5\overline{m}}{8nTG'}, \quad \tilde{a}_{10}^{(p)} = -\delta_{1p} \frac{m_M D_0}{kT} \frac{1}{1 + \dfrac{n_a D_0}{n D_{aM}}}. \tag{6}$$

The coefficients in (6) are functions of the Ω-integrals of [1], corresponding to elastic scattering of particles:

$$R = \sum_{ij} \frac{n_i n_j}{n^2} \frac{m_i m_j}{(m_i + m_j)^3} \left[\frac{55}{2} (m_i^2 - m_i m_j) \Omega_{ij}^{(1,1)} - 10 (m_i^2 - m_i m_j) \Omega_{ij}^{(1,2)} + 2 (m_i^2 - m_i m_j) \Omega_{ij}^{(1,3)} + 8 m_i m_j \Omega_{ij}^{(2,2)} \right],$$

$$R^{(1)} = \sum_{ij} \frac{n_i n_j}{n^2} \frac{m_i m_j}{(m_i + m_j)} (P_i^{(1)} - P_j^{(1)}) \Omega_{ij}^{(1,1)}, \tag{7}$$

$$G' = \sum_{ij} \frac{n_i n_j}{n^2} \Omega_{ij}^{(2,2)}, \quad i, j = a, \text{м},$$

$D_0 = \dfrac{3kT}{8n_{\text{м}} m_{\text{м}} \Omega_{\text{мм}}^{(1,1)}}$ is the coefficient of self-diffusion of the molecules, $D_{a\text{м}} = 3kT / 16 n \mu_{a\text{м}} \Omega_{a\text{м}}^{(1,1)}$ is the coefficient of binary diffusion, and $\mu_{a\text{м}} = m_a m_\text{м} / (m_a + m_\text{м})$.

The relations (4), with the calculated coefficients (6), can be used to find expressions for the velocity of diffusion V^i of particles of the i-th kind, the heat flux q, and the stress tensor P_{rs}:

$$V_r^q = -\frac{3kT}{8nR^{(1)}} \frac{m_a - \langle m \rangle}{\langle m^2 \rangle - \langle m \rangle^2} \left(\frac{\partial \overline{m}}{\partial x_r} + (\overline{m} - \langle m \rangle) \frac{\partial \ln p}{\partial x_r} \right),$$

$$V_r^i = -\frac{3kT}{8nR^{(1)}} \frac{m_\text{м} - \langle m \rangle}{\langle m^2 \rangle - \langle m \rangle^2} \left(\frac{\partial \overline{m}}{\partial x_r} + (\overline{m} - \langle m \rangle) \frac{\partial \ln p}{\partial x_r} \right) - \frac{E_i - \langle E \rangle}{\langle E^2 \rangle - \langle E \rangle^2} \frac{D_0}{\left(1 + \dfrac{n_a D_0}{n D_{a\text{м}}} \right)} \frac{\partial \langle E \rangle}{\partial x_r},$$

$$i = 1, 2, \ldots, \infty, \tag{8}$$

$$V_r^\text{м} = \frac{1}{n_\text{м}} \sum_{i=1}^{\infty} n_i V_r^i = -\frac{3kT}{8nR^{(1)}} \frac{m_\text{м} - \langle m \rangle}{\langle m^2 \rangle - \langle m \rangle^2} \left(\frac{\partial \overline{m}}{\partial x_r} + (\overline{m} - \langle m \rangle) \frac{\partial \ln p}{\partial x_r} \right),$$

$$q_r = -\frac{75}{32} \frac{kT}{R} \frac{\partial kT}{\partial x_r} - \frac{15}{16} \frac{(kT)^2}{R^{(1)}} \frac{(\overline{m} - \langle m \rangle)}{(\langle m^2 \rangle - \langle m \rangle^2)} \left(\frac{\partial \overline{m}}{\partial x_r} + \right.$$

$$\left. + (\overline{m} - \langle m \rangle) \frac{\partial \ln p}{\partial x_r} \right) - \frac{3kT}{8nR^{(1)}} \frac{n_\text{м}(m_\text{м} - \langle m \rangle)\langle E \rangle}{\langle m^2 \rangle - \langle m \rangle^2} \left(\frac{\partial \overline{m}}{\partial x_r} + (\overline{m} - \langle m \rangle) \frac{\partial \ln p}{\partial x_r} \right) - \frac{n_\text{м} D_0}{\left(1 + \dfrac{n_a D_0}{n D_{a\text{м}}} \right)} \frac{\partial \langle E \rangle}{\partial x_r},$$

$$P_{rs} = p \delta_{rs} - \frac{5kT}{8G'} \left(\frac{\partial u_r}{\partial x_s} + \frac{\partial u_s}{\partial x_r} - \frac{2}{3} \delta_{rs} \frac{\partial u_k}{\partial x_k} \right), \quad p = nkT.$$

Hence the system of gas-dynamical equations is now closed. Integrating (8) in terms of the usual relations:

$$V_r^i = -\sum_j D_{ij} d_r^j - D_i^T \frac{\partial}{\partial x_r} \ln kT, \quad q_r = -\lambda' \frac{\partial T}{\partial x_r} - p \sum_{i=0}^{\infty} D_i^T d_r^i + \sum_{i=0}^{\infty} \left(\frac{5}{2} kT + E_i \right) n_i V_r^i,$$

we find expressions for the coefficients of diffusion D_{ij}, thermodiffusion D_i^T, thermal conductivity λ', and viscosity η:

$$D_{ai} = \frac{3kT}{8nR^{(1)}} \frac{(m_a - \langle m \rangle)(m_i - \langle m \rangle)}{\langle m^2 \rangle - \langle m \rangle^2}, \quad i = a, \text{м},$$

$$D_{ij} = \frac{3kT}{8nR^{(1)}} \frac{(m_\text{м} - \langle m \rangle)^2}{\langle m^2 \rangle - \langle m \rangle^2} + \frac{n}{n_\text{м}} \frac{(E_i - \langle E \rangle)(E_j - \langle E \rangle)}{\langle E^2 \rangle - \langle E \rangle^2} \frac{D_0}{1 + \dfrac{n_a D_0}{n D_{a\text{м}}}}, \quad i, j \neq 0, \tag{9}$$

$$D_i^T = 0, \quad \eta = \frac{5kT}{8G'}, \quad \lambda' = \frac{75}{32} \frac{k^2 T}{R}.$$

We consider some limiting cases of these relations. When the molecules have no internal energy ($E_i = 0$, $i = 1, 2, \ldots, \infty$) the relations (8) with the coefficients (9) reduce to the corresponding expressions of [4] for a gas mixture of structureless particles. In the limit when the concentration of the molecular component $n_\text{м}$ goes to zero, (8) reduces to the well-known expressions for an ideal gas [1]. In the case when the concentration of the atomic component n_a goes to zero, (8) with the coefficients (9) reduces to the expressions of [5],

corresponding to the relaxational limit. If we consider the case where the total Hamiltonian of the system can be written as a sum of Hamiltonians corresponding to the separate vibrational and rotational degrees of freedom of the molecules, then $E_i = E_r + E_v$, $<E> = <E>_R + <E>_V$ (r is the rotational quantum number, and v is the vibrational quantum number).

We compare our results with those of [3], which are usually used in practical calculations. We note that in [3] the expression for the velocity of diffusion of a molecule in the i-th state does not contain the term involving $\sim\partial < E > /\partial x_r$, which dominates in the limit $\dot{n}_a \to 0$. In the expression for the heat flux the term proportional to $\partial < E > /\delta x_r$ is approximated by adding an additional term to the coefficient λ'.

We estimate the contributions of the terms that were dropped from the expansions in (5). In the calculation of $A^i(^1)$, A^i, B^i we kept the first nonvanishing terms $\underline{a}^1_{10}$, $\underline{a}_{01}$, b_{00} in the expansions (5) and (5b). These were called the dominant terms in [4], because they are the only terms in the expansions which contribute to the coefficient of diffusion, thermal conductivity, and the viscosity, respectively. The numerical results presented in [4] demonstrate the high degree of accuracy of this approximation. It is shown that the error in the transport coefficients is only of the order of several percent.

The expressions given here for the transport coefficients are obtained in the framework of the relaxational scheme for the internal states of the molecule. As shown in [5], where we go to the equilibrium regime corresponding to a simple exchange of energy between the internal and translational degrees of freedom of the molecules, additional terms appear in the expressions for the transport coefficients proportional to $(p\tau_R)^{-1}$ and $(p\tau_V)^{-1}$, where τ_R and τ_V are the vibrational and rotational relaxation times. It can be shown [5] that the contribution of these terms constitutes only several percent at room temperature, and is negligibly small at high temperatures. Therefore the expressions (8) and (9), obtained in the framework of the relaxational scheme, can be used over the entire range of the parameter Kn_Q.

In the calculation of $\hat{A}^i(p)$, we used only the first nonvanishing term $\tilde{a}^i_{10}(p)$ in the expansion (5a). In the equilibrium limit the additional terms in (5a) lead to additional terms in the expressions for the transport coefficients proportional to $(p\tau)^{-1}$, $(p\tau)^{-2}$, and so on, which do not contribute significantly to the coefficients, as pointed out above. Obviously, this approximation will also be satisfactory in the relaxation limit.

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