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ON THE KINETIC THEORY OF GASES WITH ROTATIONAL DEGREES OF FREEDOM

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The solution of the kinetic equation for molecules with rotational degrees of freedom (diatomic or linear molecules) is considered. The problem of the thermal conductivity and of the first and second viscosities is investigated.

1. INTRODUCTION

THE kinetic theory of gases with internal degrees of freedom is still in a rudimentary stage of development. The difficulties in setting up such a theory are mainly the sharp increase in the number of parameters characterizing the collisions between the molecules and the trouble in finding the explicit form of the collision integral taking into account inelastic processes. All these difficulties show up particularly clearly in a comparison with the kinetic theory developed for the monatomic gas.

The number of papers devoted to the study of the kinetic equation for molecules with internal degrees of freedom, in particular, rotational ones, is very small. Besides the traditional references to be found in the well known monographs, [1,2] the papers of Curtiss and Muckenfuss [3] deserve mention.

The papers in which the attempt is made to take account of the rotational degrees of freedom, start with assuming simple models of solid bodies for the description of the collisions and proceed then to translate the Chapman-Enskog-Barnett method, developed for the monatomic gas, to this case.

To which difficulties and actual errors this can give rise, may be seen by the example of the paper of Curtiss and Muckenfuss. [3] Regarding the molecule as a solid body with a center of symmetry, these authors keep as independent variables in the kinetic equation the phase angles, which vary strongly during the free flight. This leads, obviously, to an extremely complicated problem. On the other hand, when considering the problem of thermal conductivity and viscosity, the above-mentioned authors choose the solution in a form which contains tensors that are constructed entirely from components of the vector of the molecular velocity **V**. This is obviously wrong, since now the problem deals with two independent vectors, **V** and the angular momentum of the molecule **M** (more precisely, a vector and a pseudovector), and the general solution should contain all tensors of corresponding rank which can be formed from the components of these vectors.

In the present paper we investigate the kinetic theory of a diatomic gas in a region of temperatures where the vibrational degrees of freedom can be neglected. We make use of a kinetic equation which does not contain rapidly varying phases and solve the problem of thermal conductivity and of first and second viscosity.

2. KINETIC EQUATION

In the case of diatomic (linear) molecules the rotational motion is described by four quantities: two generalized momenta and the two corresponding generalized coordinates. However, it is convenient to choose as independent variables the three components of the angular momentum M_i and the angle ψ characterizing the position of the axis of the molecule in the plane perpendicular to **M**.

The classical kinetic equation in these variables is written in the form

$$\frac{\partial f}{\partial t} + \mathbf{V}\frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{V}}\frac{\partial f}{\partial \mathbf{V}} + \frac{\partial}{\partial \psi}(\dot{\psi} f) + \frac{\partial}{\partial \mathbf{M}}(\dot{\mathbf{M}} f) = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}. \tag{2.1}$$

It is easy to show that the phase volume corresponding to these variables is equal to

$$M dM d\Omega_{\mathbf{M}}\, d\psi = d\Gamma\, d\psi. \tag{2.2}$$

The equilibrium distribution function is written as

$$f^0 = n\left(\frac{\mu}{2\pi kT}\right)^{3/2}\frac{1}{4\pi IkT}\exp\left\{-\frac{\mu V^2}{2kT} - \frac{M^2}{2IkT}\right\}, \tag{2.3}$$

where I is the moment of inertia (all the remaining notations are standard).

The function (2.3) is normalized such that

$$\int f^0\, d\mathbf{V}\, d\Gamma = n. \tag{2.4}$$

One estimates easily that $1/\dot{\psi}$ is of the order of the collision time. But in deriving the kinetic equation for a monatomic function in the usual form one assumes explicitly that the gas is sufficiently rarefied and that the collision time is small compared with the time of free flight. Therefore, Eq. (2.1) reduces in first approximation to

$$\dot{\psi}\partial f/\partial\psi = 0.$$

Thus the function f is practically independent of ψ, and we find by integrating (2.1) over $d\psi$

$$\frac{\partial f}{\partial t} + \mathbf{V}\frac{\partial f}{\partial \mathbf{r}} + \dot{\mathbf{V}}\frac{\partial f}{\partial \mathbf{V}} + \frac{\partial}{\partial \mathbf{M}}(\dot{\mathbf{M}}f)$$
$$= \int (f'f_1' - ff_1)\, W d\mathbf{V}_1 d\mathbf{V}' d\mathbf{V}_1' d\Gamma_1 d\Gamma' d\Gamma_1'. \tag{2.5}$$

In writing down the righ-hand side of (2.5), we assumed that the collision probability is an even function of the angular momenta of the colliding molecules. We note that, if the model of a solid body is used in the description of the collisions of the molecules, W involves an average over ψ and ψ_1 and a sum over ψ' and ψ_1'.

Let us consider the case where there are no external forces. Assuming a small deviation from equilibrium, we shall seek the solution in the form

$$f = f^0(1+\chi), \tag{2.6}$$

where we choose for f^0 a quasi-equilibrium local distribution of the form (2.3) with V replaced by $\mathbf{U} = \mathbf{V} - \mathbf{V}_0$ ($\mathbf{V}_0$ is the macroscopic velocity of the gas at the given point). For each point in space we assume that there is no rotation of the gas as a whole.

The total distribution function is subject to the conditions

$$\int f d\mathbf{V}\, d\Gamma = n, \quad \int f\left(\frac{\mu U^2}{2} + \frac{M^2}{2I}\right) d\mathbf{V}\, d\Gamma = \frac{5}{2}kT,$$
$$\int f\mathbf{U} d\mathbf{V}\, d\Gamma = 0, \quad \int f\mathbf{M}\, d\mathbf{V}\, d\Gamma = 0. \tag{2.7}$$

Let us substitute (2.6) in (2.5). Keeping, as usual, only f^0 on the left and linearizing the collision integral, we find with the help of the conservation laws

$$f^0\left\{\left(u^2 + m^2 - \frac{7}{2}\right)\mathrm{U}\frac{\partial \ln T}{\partial \mathbf{r}} + u_i u_k\left(\frac{\partial V_{0i}}{\partial x_k} + \frac{\partial V_{0k}}{\partial x_i}\right.\right.$$
$$\left.\left. - \frac{2}{3}\delta_{ik}\frac{\partial V_{0l}}{\partial x_l}\right) + \frac{2}{5}\left(\frac{2}{3}u^2 - m^2\right)\frac{\partial V_{0l}}{\partial x_l}\right\}$$
$$= \int f^0 f_1^0 \{\chi\}\, W d\mathbf{V}_1 d\mathbf{V}' d\mathbf{V}_1' d\Gamma_1 d\Gamma' d\Gamma_1'. \tag{2.8}$$

Here

$$\mathbf{u} = \sqrt{\mu/2kT}\,\mathrm{U}, \qquad \mathbf{m} = \mathbf{M}/\sqrt{2IkT}, \tag{2.9}$$
$$\{\chi\} = \chi' + \chi_1' - \chi - \chi_1. \tag{2.10}$$

3. THERMAL CONDUCTIVITY

Let us now consider the problem of thermal conductivity. If the gradient of the macroscopic velocity vanishes, Eq. (2.8) reduces to

$$f^0\left(u^2 + m^2 - \frac{7}{2}\right)\tilde{\mathrm{U}}\nabla \ln T = J_{\mathrm{coll}}(\chi). \tag{3.1}$$

We write the solution of this equation in the form

$$\chi = -\mathbf{A}\nabla \ln T. \tag{3.2}$$

Substituting (3.2) in (3.1), we find

$$f^0\left(u^2 + m^2 - \frac{7}{2}\right)\mathrm{U} = -J_{\mathrm{coll}}(\mathbf{A}). \tag{3.3}$$

In the case of a monatomic gas only the vector **u** is available for constructing the vector **A**, and we therefore seek the solution in the form **A = uS**, where S is a scalar function of u^2. In the case of a gas with rotational degrees of freedom we have three independent vectors: **u**, **m(m · u)**, and **m × u**. Therefore **A** is in general written as

$$\mathbf{A} = \mathbf{u}S_1(u^2, m^2, t^2) + \mathbf{m}\,(\mathbf{mu})\, S_2(u^2, m^2, t^2)$$
$$+ [\mathbf{mu}]\, S_3(u^2, m^2, t^2), \tag{3.4}$$*

where

$$t^2 = (\mathbf{mu})^2/m^2u^2. \tag{3.5}$$

The left-hand side of (3.1) and the kernel of the collision integral are even functions of **M**. It is easy to show that then

$$S_3 \equiv 0. \tag{3.6}$$

Thus the problem of the thermal conductivity is determined by the two scalar functions S_1 and S_2.

Let us expand these functions in terms of orthogonal functions in the following way:

$$S_1 = \sum_{ikl} a_1^{ikl} S_i^{3/2}(u^2)\, S_k^0(m^2)\, P_l^0(t^2) \equiv \sum_{ikl} a_1^{ikl} R_{ikl}^1,$$
$$S_2 = \sum_{ikl} a_2^{ikl} S_i^{3/2}(u^2)\, S_k^1(m^2)\, P_l^1(t^2) \equiv \sum_{ikl} a_2^{ikl} R_{ikl}^2, \tag{3.7}$$

where the S_i^{α} are Sonine polynomials with the corresponding indices and the $P_l^{0,1}$ are polynomials which are orthogonal in the interval (– 1, 1), with weights 1 and t^2, respectively:

$$\int_{-1}^{1} P_l^0(t^2)\, P_{l'}(t^2)\, dt = \delta_{ll'}, \qquad \int_{-1}^{1} t^2 P_l^1(t^2)\, P_{l'}^1(t^2)\, dt = \delta_{ll'}.$$

If we consider only a finite number of terms in (3.7), the best variational solution is found from a system of algebraic equations which is obtained by multiplying (3.1) successively by $\mathbf{u}R_{ikl}^1$ and $\mathbf{m}(\mathbf{m}\cdot\mathbf{u})R_{ikl}^2$ and integrating over $d\mathbf{V}d\Gamma$.

We note that the choice of polynomials for the expansion of S_1 and S_2 is arbitrary and is dictated only by numerical simplicity. This arbitrariness stems from the fact that the variational principle does not even presuppose orthogonal polynomials.

The conditions (2.7) imply that not all coefficients in the expansion (3.7) are independent. Using (3.2), (3.4), and (3.7), we find

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*[**mu**] = **m × u**.

$$a_1^{000} + \tfrac{1}{3}a_2^{000} = 0. \tag{3.8}$$

Let us now define the heat current:

$$\mathbf{q} = \int f^0 \chi \mathbf{U} \left(\frac{\mu U^2}{2} + \frac{M^2}{2I}\right) d\mathbf{V}\, d\Gamma \equiv -\lambda \nabla T.$$

Substituting in this the value of χ, we obtain

$$\lambda = \frac{nk}{3}\left(\frac{2kT}{\mu}\right)^{1/2}\left[\frac{15}{4}a_1^{100} + \frac{3}{2}a_1^{010} + \frac{1}{2}a_2^{000} + \frac{5}{4}a_2^{100} + a_2^{010}\right]. \tag{3.9}$$

4. FIRST AND SECOND VISCOSITY

Assume now that $\nabla T = 0$. The solution of the general kinetic equation (2.8) will then be sought in the form

$$\chi = -B_{ik}\left(\frac{\partial V_{0i}}{\partial x_k} + \frac{\partial V_{0k}}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial V_{0l}}{\partial x_l}\right) - C\frac{\partial V_{0l}}{\partial x_l}, \tag{4.1}$$

where B_{ik} is a symmetric tensor with vanishing trace. Substituting (4.1) in (2.8), we find

$$f^0\left(u_i u_k - \tfrac{1}{3}\delta_{ik}u^2\right) = -J_{\text{coll}}(B_{ik}), \tag{4.2}$$

$$f^0\left(\tfrac{4}{15}u^2 - \tfrac{2}{5}m^2\right) = -J_{\text{coll}}(C). \tag{4.3}$$

In the most general case the tensor B_{ik} can be written as

$$\begin{aligned} B_{ik} = {} & B_1\left(u_i u_k - \tfrac{1}{3}\delta_{ik}u^2\right) + B_2\left(m_i m_k - \tfrac{1}{3}\delta_{ik}m^2\right) \\ & + B_3\left([\mathbf{mu}]_i[\mathbf{mu}]_k - \tfrac{1}{3}\delta_{ik}[\mathbf{mu}]^2\right) + B_4(\mathbf{mu})\left(m_i u_k\right. \\ & \left. + u_i m_k - \tfrac{2}{3}\delta_{ik}(\mathbf{mu})\right) + B_5\left(u_i[\mathbf{mu}]_k + u_k[\mathbf{mu}]_i\right) \\ & + B_6(\mathbf{mu})\left(m_i[\mathbf{mu}]_k + m_k[\mathbf{mu}]_i\right). \end{aligned} \tag{4.4}$$

Here the B_i are scalar functions of u^2, m^2, and t^2. Since the left-hand side of (4.2) is again an even function of $\mathbf{M}$, the evenness of the kernel of the collision integral leads to the relations

$$B_5 \equiv 0, \qquad B_6 \equiv 0. \tag{4.5}$$

We expand the quantities B_i in terms of orthogonal polynomials:

$$B_1 = \sum_{ikl} b_1^{ikl} S_i^{5/2}(u^2)\, S_k^0(m^2)\, P_l^0(t^2), \tag{4.6}$$

$$B_2 = \sum_{ikl} b_2^{ikl} S_i^{3/2}(u^2)\, S_k^1(m^2)\, P_l^0(t^2), \tag{4.7}$$

$$B_3 = \sum_{ikl} b_3^{ikl} S_i^{3/2}(u^2)\, S_k^1(m^2)\, P_l^{(0,1)}(t^2), \tag{4.8}$$

$$B_4 = \sum_{ikl} b_4^{ikl} S_i^{3/2}(u^2)\, S_k^1(m^2)\, P_l^1(t^2). \tag{4.9}$$

The $P_l^{(0,1)}$ are orthogonal with weight $1-t^2$. With B_{ik} defined as in (4.4), the conditions (2.7) are satisfied automatically.

We write the scalar function C which solves (4.3) in such a form that the conditions (2.7) are automatically fulfilled:

$$C = c_0\left(\tfrac{2}{3}u^2 - m^2\right) + \sum_{ikl} c^{ikl} S_i^{1/2}(u^2)\, S_k^0(m^2)\, P_l^0(t^2),$$
$$c^{000} = c^{100} = c^{010} = 0. \tag{4.10}$$

Let us now determine the expression for the stress tensor:

$$\sigma_{ik} = -\mu\int f^0 \chi\, U_i U_k\, d\mathbf{V}\, d\Gamma.$$

Substituting (4.1) and taking account of (4.4) to (4.10), we find

$$\sigma_{ik} = \eta\left(\frac{\partial V_{0i}}{\partial x_k} + \frac{\partial V_{0k}}{\partial x_i} - \frac{2}{3}\delta_{ik}\frac{\partial V_{0l}}{\partial x_l}\right) + \zeta\delta_{ik}\frac{\partial V_{0l}}{\partial x_l}, \tag{4.11}$$

where the first viscosity coefficient η is given by the expression

$$\eta = nkT\left(b_1^{000} + \left(\tfrac{2}{5}\right)^{3/2} b_2^{001} - \tfrac{1}{3}b_3^{000} + \tfrac{2}{3}b_4^{000}\right), \tag{4.12}$$

and the coefficient of second viscosity ζ by

$$\zeta = 2kT\, c_0/3. \tag{4.13}$$

The coefficients entering in (4.12) and (4.12) are determined approximately from a system of algebraic equations obtained from (4.2) and (4.3) by making use, as in the case of the thermal conductivity, of the usual variation procedure.

5. ON THE COLLISION INTEGRAL FOR THE MODEL OF SOLID BODIES

The results obtained in the preceding sections are very general and can be used for any type of interaction between the molecules.

In calculating the kinetic coefficients in the present paper, we describe the collisions between the molecules with the help of the model of elastic cylinder-spheres (see the following section). However, the use of the model of solid bodies necessitates a careful analysis of the collision integral. This is the more imperative as the expression for the collision integral given as exact in[3,4] is actually highly approximate and can in extreme cases lead to absurd results (see below).

For a complete description of the collision between two molecules with definite velocities $\mathbf{V}$, $\mathbf{V}_1$ and angular momenta $\mathbf{M}$, $\mathbf{M}_1$ we need only four variables: X, Y, the coordinates of the center of gravity of the incoming molecule in the plane perpendicular to the relative velocity $\mathbf{g} = \mathbf{V}_1 - \mathbf{V}$, and ψ_0, ψ_{01}, the values of the angles ψ, ψ_1 when the centers of gravity of the molecules are located at some fixed distance a from one another. Then we have for the part of the collision integral corresponding to emission from a given element of the phase volume

$$-\int f(\mathbf{VM})\, f(\mathbf{V}_1\mathbf{M}_1)\, g\, dX\, dY \frac{d\psi_0}{2\pi}\frac{d\psi_{01}}{2\pi}\, d\mathbf{V}_1 d\Gamma_1. \qquad (5.1)$$

The corresponding limits of integration are evidently closely connected with the geometry of the molecules. For molecules with a center of symmetry it is easy to obtain an expression for the inverse transitions. For this purpose we must use the connection between quantities before and after the collision (see [3]):

$$\begin{gathered}\mathbf{V}_1' = \mathbf{V}_1 - \xi(\mathbf{kG})\,\mathbf{k}, \qquad \mathbf{V}' = \mathbf{V} + \xi(\mathbf{kG})\,\mathbf{k},\\ \mathbf{M}_1' = \mathbf{M}_1 - \xi(\mathbf{kG})\,[\sigma_1\mathbf{k}], \quad \mathbf{M}' = \mathbf{M} + \xi(\mathbf{kG})\,[\sigma\mathbf{k}],\\ \xi = [1 + (m/2I)\{[\sigma\mathbf{k}]^2 + [\sigma_1\mathbf{k}]^2\}]^{-1}. \end{gathered} \qquad (5.2)$$

Here **k** is a unit vector normal to the surface of the molecules at the point of contact, $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}_1$ are the vectors from the centers of the corresponding molecules to the point of contact, and **G** is the relative velocity of the colliding molecules at the point of contact:

$$\mathbf{G} = \mathbf{V}_1 - \mathbf{V} + \left[\frac{\mathbf{M}_1}{I}\sigma_1\right] - \left[\frac{\mathbf{M}}{I}\sigma\right]. \qquad (5.3)$$

Let us now go over from the variables X, Y, ψ_0, ψ_{01} to the variables **k**, ψ, ψ_1 (ψ, ψ_1 are the angles at the time of collision), using the relations

$$\psi_0 = \psi - Mt_0/I, \qquad (5.4)$$

$$\psi_{01} = \psi_1 - M_1 t_0/I, \qquad (5.5)$$

$$\mathbf{R} = \mathbf{R}(\mathbf{k}, \psi, \psi_1, \mathbf{M}, \mathbf{M}_1), \qquad (5.6)$$

$$t_0 = (\mathbf{a} - \mathbf{R})\,\mathbf{g}/g^2, \qquad (5.7)$$

where $\mathbf{R}\{X, Y, Z\}$ is the radius vector connecting the centers of the molecules at the moment of the collision and **a** is an arbitrary vector. The form of (5.6) can be established immediately for any given geometry.

The Jacobian for making the transition from the old to the new variables is equal to (see the Appendix)

$$\partial(X, Y, \psi_0, \psi_{01})/\partial(\mathbf{k}, \psi, \psi_1) = \frac{\mathbf{kG}}{g} S(\mathbf{k}); \qquad (5.8)$$

$S(\mathbf{k})\,d\mathbf{k}$ is the surface element of the surface defined by (5.6) with constant ψ, ψ_1, **M**, and $\mathbf{M}_1$.

The expression for the collision integral in the new variables is

$$\int (f' f_1' - f f_1)\, |\mathbf{kG}|\, S(\mathbf{k})\, d\mathbf{k} \frac{d\psi}{2\pi}\frac{d\psi_1}{2\pi} d\mathbf{V}_1\, d\Gamma_1. \qquad (5.9)$$

It is easily seen that the region of integration is bounded by the condition

$$\mathbf{kG} < 0 \qquad (5.10)$$

(only those parts of the surface collide which move toward one another). However, condition (5.10) is not the only restriction on the region of possible values of **k**, ψ, and ψ_1. This has to do with the fact that in general **k**, ψ, and ψ_1 are multivalued functions of X, Y, ψ_0, and ψ_{01}. Of all the possible values one must evidently choose only that which corresponds to the smallest t_0. This implies a further restriction on the region of possible values of **k**, ψ, and ψ_1.

It is easily seen that the formula (5.9) with only the condition (5.10) is completely useless for $\dot{\psi} \gg g/l$, where l is a characteristic dimension of the molecules. [For $g = 0$ the molecules do not collide at all, while there is a nonvanishing contribution according to (5.9).] In the opposite limiting case the multivaluedness does not play a role, and we can use the formulas (5.9) and (5.10).

Thus it is clear that using a collision integral of the form (5.9) with the restriction (5.10) is in general only an approximate procedure. The determination of the exact region of integration in (5.9) for arbitrary $\dot{\psi}$ is a complicated problem. In view of the fact that in many actual cases $\dot{\psi} \lesssim g/l$, we have used (5.9) and (5.10) in all specific calculations.

In this case the use of a more exact region of integration should lead only to relatively small corrections.

6. CALCULATION OF THE KINETIC COEFFICIENTS. THE MODEL OF CYLINDER-SPHERES

Let us now go over to the direct determination of the kinetic coefficients, using the results of Secs. 3 and 4 with a collision integral of the form (5.9) and (5.10).

In calculating the coefficient of thermal conductivity, we restrict ourselves to the first three terms in the expansion of S_1 and to the first term in the expansion of S_2 [see (3.7)]:

$$S_1 = a_1^{000} + a_1^{100}\left(u^2 - \tfrac{5}{2}\right) + a_1^{010}(m^2 - 1), \qquad S_2 = a_2^{000}. \qquad (6.1)$$

Multiplying (3.1) by $\mathbf{u}(u^2 - 5/2)$, $\mathbf{u}(m^2 - 1)$, and $\mathbf{m}(\mathbf{m}\cdot\mathbf{u})$ and integrating over $d\mathbf{V}\,d\Gamma$, we obtain a system of equations for the determination of the coefficients a_1^{100}, a_1^{010}, and a_2^{000}:

$$\begin{gathered} C_1 = c_{11}a_1^{100} + c_{12}a_1^{010} + c_{13}a_2^{000}, \quad C_2 = c_{21}a_1^{100} + c_{22}a_1^{010}\\ + c_{23}a_2^{000}, \qquad C_3 = c_{31}a_1^{100} + c_{32}a_1^{010} + c_{33}a_2^{000}. \end{gathered} \qquad (6.2)$$

The coefficient a_1^{000} is determined by condition (3.8).

The computation of the coefficients C_i is elementary. The determination of the c_{ik} involves an integration over 16 variables. However, through a series of linear substitutions we can carry out the integration over 10 variables without reference to a particular model. The expression for c_{ik} is of the form

$$c_{ik} = \frac{\sqrt{2}\, n^2}{8\pi^2} \int \Phi_1^0 \Phi^0 \mathbf{A}_i \{\mathbf{A}_k\} \, |\mathbf{kw}| \, S(\mathbf{k}) \, d\mathbf{k} \, d\mathbf{u}_1 \, d\mathbf{u} \, d\tilde{\Gamma}_1 \, d\Gamma, \quad \mathbf{kw} < 0, \tag{6.3}$$

where

$$\mathbf{A}_1 = \left(u^2 - \tfrac{5}{2}\right)\mathbf{u}, \qquad \mathbf{A}_2 = (m^2 - 1)\,\mathbf{u}, \qquad \mathbf{A}_3 = \mathbf{m}\,(\mathbf{mu}),$$

$$\mathbf{w} = \left(\frac{2kT}{\mu}\right)^{1/2} \mathbf{G}, \qquad d\tilde{\Gamma} = m\,dm\, d\Omega_{\mathbf{m}}, \qquad \Phi^0 = \pi^{-5/2} e^{-u^2 - m^2}.$$

Let us first go over from the variables $\mathbf{m}$, ψ, $\mathbf{m}_1$, ψ_1 to the variables $\mathbf{l}$, m_n, m_τ, $\mathbf{l}_1$, m_{n_1}, m_{τ_1}, where $\mathbf{l}$ and $\mathbf{l}_1$ are unit vectors defining the direction of the axes of the molecules in space, m_n and m_{n_1} are the projections of the vectors $\mathbf{m}$ and $\mathbf{m}_1$ on the vector $\mathbf{l} \times \mathbf{l}_1$, m_τ is the projection of $\mathbf{m}$ on the vector $\mathbf{n} \times \mathbf{l}$, and m_{τ_1} is the projection of $\mathbf{m}_1$ on the vector $\mathbf{n} \times \mathbf{l}_1$.

It is easy to show that

$$d\tilde{\Gamma}\, d\psi = dm_n \, dm_\tau \, d\mathbf{l}. \tag{6.4}$$

Then we make the following substitutions:

$$\mathbf{u} = (\mathbf{Q} - \boldsymbol{\gamma})/\sqrt{2}, \quad \mathbf{u}_1 = (\mathbf{Q} + \boldsymbol{\gamma})/\sqrt{2}, \tag{6.5}$$

$$m_{\tau_1} = (r_1 x + r y)/\sqrt{r_1^2 + r^2}, \quad m_\tau = (-rx + r_1 y)/\sqrt{r_1^2 + r^2},$$
$$\gamma_3 = (t - \sqrt{r_1^2 + r^2}\, z) / \sqrt{1 + r_1^2 + r^2}, \tag{6.6}$$

$$x = (\sqrt{r_1^2 + r^2}\, t + z)/\sqrt{1 + r_1^2 + r^2}, \tag{6.7}$$

where

$$r^2 = \frac{\mu}{2I} [\boldsymbol{\sigma}\mathbf{k}]^2, \qquad r_1^2 = \frac{\mu}{2I} [\boldsymbol{\sigma}_1, \mathbf{k}]^2, \qquad \gamma_3 = \mathbf{k}\boldsymbol{\gamma}.$$

The product $\Phi^0 \Phi_1^0$ can be written in terms of the new variables:

$$\Phi^0 \Phi_1^0 = \pi^{-5} \exp\{-Q^2 - \gamma_1^2 - \gamma_2^2 - y^2 - t^2 - z^2 - m_n^2 - m_{n_1}^2\}, \tag{6.8}$$

where γ_1 and γ_2 are the projections of the vector $\boldsymbol{\gamma}$ on two mutually orthogonal axes perpendicular to the vector $\mathbf{k}$.

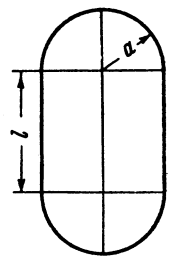
Taking account of the fact that $\mathbf{A}_i\{\mathbf{A}_k\}$ can be expressed as a sum of products of the type [we use (6.5) to (6.7) and (5.2)]

$$F(\mathbf{k}, \mathbf{l}\mathbf{l}_1)\, Q^n \gamma_1^m \gamma_2^l y^p t^q z^s m_n^f m_{n_1}^d \tag{6.9}$$

and that the region of integration (5.10) goes over into the region $t > 0$, we see easily that the integration over the variables

$$dQ\, d\gamma_1\, d\gamma_2\, dm_n\, dm_{n_1}\, dy\, dt\, dz$$

is completely trivial, and the final result can be expressed as a product of Γ functions.



Only the integration over $d\mathbf{k}\, d\mathbf{l}\, d\mathbf{l}_1$ remains to be done in (6.3). In order to carry out this integration, we must know the explicit form of $S(\mathbf{k})$.

We shall use the model of cylinder-spheres. In this model the collision of the molecules is described by the collision of solid bodies of cylindrical shape with hemispheres at each end (see the figure). Our model has some peculiarities which have to do with the fact that the vector $\mathbf{k}$ cannot define a point on the cylindrical surface uniquely. For collisions involving the cylindrical surfaces it is therefore advantageous to define the point of contact by two other parameters α_1 and α_2.

In collisions involving the cylindrical surfaces we can take for these parameters $\sigma_l = \boldsymbol{\sigma} \cdot \mathbf{l}$ and $\sigma_{l_1} = \boldsymbol{\sigma}_1 \cdot \mathbf{l}_1$, which define the point of contact for a given position of the molecules (except for the distinction between "from above" and "from below"). In this case $S(\mathbf{k})\,d\mathbf{k}$ goes over into

$$S(\sigma_l, \sigma_{l_1})\, d\sigma_l\, d\sigma_{l_1} = 2 \sin\Phi \, d\sigma_l\, d\sigma_{l_1}, \tag{6.10}$$

where

$$\sin\Phi = [\mathbf{l}\mathbf{l}_1].$$

For collisions involving the spherical surfaces we have

$$S(\mathbf{k})\, d\mathbf{k} = 4a^2\, d\mathbf{k}. \tag{6.11}$$

For mixed collisions we must write instead of $S(\mathbf{k})\,d\mathbf{k}$

$$S(z, \tilde{\varphi})\, dz\, d\tilde{\varphi} = 2a\,dz\, d\tilde{\varphi}, \tag{6.12}$$

where z and $\tilde{\varphi}$ are the cylindrical coordinates of the point of contact in a coordinate system with a Z axis along the axis of the molecule which collides at a point of its cylindrical surface.

The integral (6.3) thus separates into three integrals. All integrals are evaluated completely.*

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*We note that some of the resulting integrals have been computed in[3].

We shall not quote here the resulting complicated formulas for the c_{ik}. We give only the final expressions for the coefficients a_1^{100}, a_1^{010}, and a_2^{000} obtained as a solution of the system (6.2):

$$a_1^{100} \approx 0.34 \frac{1}{nl^2} \frac{1}{\beta^2 + \beta + 0.12}, \tag{6.13}$$

$$a_1^{010} \approx 0.48 \frac{1}{nl^2} \frac{1}{\beta^2 + \beta + 0.12}, \tag{6.14}$$

$$a_2^{000} \approx -0{,}17 \frac{1}{nl^2} \frac{1}{\beta^2 + \beta + 0{,}12}, \tag{6.15}$$

where $\beta = 2a/l$. These results refer to the case $\beta \gtrsim 1$, $\alpha = 4I/\mu l^2 = 1/2$. This value of the coefficient α corresponds to a diatomic molecule of the type A–A in which the atoms are located at a distance l from one another.

Information on the geometry of the molecules can be obtained if the virial coefficients are known.[2] It turns out that $\beta > 1$ in most cases.

Expressions for the coefficients a_1^{100}, a_1^{010}, and a_2^{000} can be found for arbitrary values of α and β. However, the general expressions are very complicated, and we shall be content with quoting only a particular example.

Substituting (6.13) to (6.15) in (3.9), we obtain an expression for the coefficient of thermal conductivity:

$$\lambda \approx 1.6\, k \left(\frac{kT}{\pi\mu}\right)^{1/2} \frac{1}{l^2} \frac{1}{\beta^2 + \beta + 0{,}12}. \tag{6.16}$$

It is interesting to note that all coefficients (6.13) to (6.15) are of the same order of magnitude, although their contributions to the coefficient of thermal conductivity are quite different [see formula (3.9)].

Finally, we give the final expressions for the first and second viscosity, obtained under the simplest assumptions:

$$B_1 = b_1^{000}, \qquad B_2 = B_3 = B_4 = 0, \qquad C = \left(\frac{2}{3}u^2 - m^2\right)c_0$$

[see formulas (4.6) to (4.9) and (4.10)]. For $\alpha = 1/2$ and $\beta \gtrsim 1$ we have

$$\eta \approx 0.32\, \mu \left(\frac{kT}{\pi\mu}\right)^{1/2} \frac{1}{l^2} \frac{1}{\beta^2 + \beta + 0.12}, \tag{6.17}$$

$$\zeta \approx 0{,}067\, \mu \left(\frac{kT}{\pi\mu}\right)^{1/2} \frac{1}{l^2} \frac{1}{\beta^2 + 0.87\beta + 0.12}. \tag{6.18}$$

APPENDIX

Here we determine the value of the Jacobian

$$J = \partial (X, Y, \psi_0, \psi_{01})/\partial (\cos\theta, \varphi, \psi, \psi_1), \tag{A.1}$$

where θ, φ are the angles which define the unit vector $\mathbf{k}$ in some coordinate system.

Using (5.4) to (5.6), we find easily

$$J = \frac{S(\mathbf{k})}{g}\left[\mathbf{gk} - \mathbf{k}\left(\frac{M}{I}\frac{\partial \mathbf{R}}{\partial \psi} + \frac{M_1}{I}\frac{\partial \mathbf{R}}{\partial \psi_1}\right)\right]. \tag{A.2}$$

We have made use of the fact that

$$S(\mathbf{k}) = \left[\left(\frac{\partial (XY)}{\partial (\cos\theta, \varphi)}\right)^2 + \left(\frac{\partial (Z, X)}{\partial (\cos\theta, \varphi)}\right)^2 + \left(\frac{\partial (Y, Z)}{\partial (\cos\theta, \varphi)}\right)^2\right]^{1/2},$$

$$k_x = \frac{1}{S(\mathbf{k})} \frac{\partial (Y, Z)}{\partial (\cos\theta, \varphi)}$$

and analogously for the other projections.

Let us now determine $(\partial \mathbf{R}/\partial \psi)_{\psi_1, \mathbf{k}}$. We see immediately that in general

$$\left(\frac{\partial \mathbf{R}}{\partial \psi}\right)_{\mathbf{k}, \psi_1} = \left[\frac{\mathbf{M}}{M}\sigma\right] + \mathbf{a}, \quad \left(\frac{\partial \mathbf{R}}{\partial \psi_1}\right)_{\mathbf{k}, \psi} = -\left[\frac{\mathbf{M}_1}{M_1}\sigma_1\right] + \mathbf{a}_1, \tag{A.3}$$

where $\mathbf{a}$ and $\mathbf{a}_1$ are vectors perpendicular to $\mathbf{k}$ which depend on the type of surface. Substituting (A.3) in (A.2), we find

$$J = \frac{S(\mathbf{k})}{g}\left\{\mathbf{gk} + \mathbf{k}\left(\left[\frac{\mathbf{M}_1}{I}\sigma_1\right] - \left[\frac{\mathbf{M}}{I}\sigma\right]\right)\right\}.$$

Using (5.3), we obtain (5.8).

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