KINETIC THEORY OF GASES TAKING INTO ACCOUNT ROTATIONAL DEGREES OF FREEDOM IN AN EXTERNAL FIELD

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A general method is developed to study kinetic phenomena in polyatomic gases in a magnetic or electric field. Attention is paid to effects which change sign when the magnetic field does so. We obtain expressions for the viscosity, thermal conductivity, diffusion, and self-diffusion tensors.

1. INTRODUCTION

E ARLIER [2] the authors have developed a theory of transport phenomena for a diatomic paramagnetic gas in a magnetic field; this enabled us to consider consistently the Senftleben effect [1] for arbitrary values of the magnetic field. Recently a magnetic field dependence of kinetic effects has been discovered in non-paramagnetic gases [3-5] and similarly the influence of a static electric field upon transport phenomena in a polar gas. [6,7] This last effect is analogous to the case of a paramagnetic gas in a magnetic field. As far as the influence of a magnetic field on a non-paramagnetic gas is concerned, this is connected with the existence of a small magnetic moment which is caused by the rotation of the nuclei and which is not compensated for by the motion of the electron shell. [8]

These phenomena have all the same physical character: the external field leads to a precession of the rotational molecular moment which in turn causes an effective change in the collision cross-section of the molecules (the mechanism causing the precession is here unimportant, and only the precession frequency matters, or rather, the ratio of this frequency to the frequency of collisions between molecules). This change is connected with the fact that for molecules with rotational degrees of freedom (RDF) the collision cross-section depends not only on the relative velocity of the colliding molecules, but also on the orientation of their rotational moments.

For a quantitative description of transport phenomena in a gas with RDF we must take into account the dependence of the non-equilibrium distribution function not only on the velocity vector u but also on the rotational moment M. [9] We can in principle use for an analysis of transport phenomena in the cases considered the method de-

veloped in [2]. However, it seemed advisable to us to give the one more method, more general and canonical, to consider kinetic phenomena in gases with RDF.

We use an expansion of the non-equilibrium distribution function in terms of the eigenfunctions of the "ideal" collision operator, which takes into account only the change in the translational degrees of freedom in collisions. It is convenient then to change from a Cartesian system of coordinates to a spherical system in which the irreducible tensors of u and M are described by spherical polynomials. We develop a perturbation theory in terms of a small parameter, which in our case is the degree to which the complete collision operator deviates from the "ideal" one. As a result we reduce the calculation of the effect in an external field to finding the eigenfunctions of the ideal collision operator and determining the matrix elements of the perturbing collision operator. In the present paper these will be regarded as parameters whose magnitudes must be found experimentally.

We use the general method to determine the influence of a magnetic field on the first and second viscosity, thermal conductivity, diffusion, and self-diffusion in paramagnetic and non-paramagnetic gases. When analysing these phenomena we have found that in a magnetic field there are not only even effects (these effects do not change sign when the direction of the field changes) but also odd effects. [1] As a result the general viscosity

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[1]When we were finishing the present work, a paper [14] appeared in which the discovery of an odd effect in the viscosity was reported, and also a preprint of a paper by Knaap and Beenakker in which a theoretical description of this effect was given. These authors connect the odd effect in the case of a paramagnetic gas with the presence of a quantum correction to the effective magnetic moment. In the present paper the odd effect has a purely kinetic character.

tensor in a magnetic field has seven independent coefficients (five even and two odd ones), and the thermal conductivity, diffusion, and self-diffusion tensors three independent coefficients (two even and one odd). It is interesting that in an electric field the number of independent coefficients is reduced - all coefficients which are odd in the electric field vanish identically.

2. PRECESSION OF THE MOLECULES IN AN EXTERNAL FIELD

The external field does not act directly on the translational degrees of freedom in a neutral gas. Constant magnetic, $\mathbf{H}$, and electric, $\mathbf{E}$, fields lead to a precession of the rotational moment of the molecule. In the present paper we restrict ourselves to a consideration of processes at sufficiently high temperatures ($T \gg \hbar^2/2I$, I = moment of inertia), when we can use the classical equation of motion for the moment

$$\frac{d}{dt}\mathbf{M} = [\mu\mathbf{H}] + [\mathbf{dE}], \qquad (2.1)^*$$

averaged over the fast rotation around $\mathbf{M}$. However, it is more convenient to determine the precession of the rotational moment from the semi-classical limit of the quantum equation

$$\frac{d}{dt}\hat{\mathbf{M}} = \frac{1}{i\hbar}[\hat{\mathbf{M}}\hat{V} - \hat{V}\hat{\mathbf{M}}], \qquad (2.2)$$

where the energy of the molecule is $\hat{V} = -(\hat{\mu} \cdot \mathbf{H})$ in a magnetic field and $\hat{V} = -(\hat{\mathbf{d}} \cdot \mathbf{E})$ in an electric field.

In [2] we found that in the limit of large values of the rotational quantum number we have for a paramagnetic diatomic molecule with spin S

$$\dot{\mathbf{M}} = \gamma_1[\mathbf{MH}], \quad \gamma_1 = 2\mu_0\sigma M^{-1}, \quad \sigma = -S, -S+1, \ldots, S. \qquad (2.3)$$

Since the spin-orbit interaction of the nuclei is small already for fields $H \gtrsim 10$ Oe the spin and orbital motions of the nuclei of the molecules are, as a rule, decoupled, and for the average value of the precession of a non-paramagnetic molecule we have simply

$$\dot{\mathbf{M}} = \gamma_2[\mathbf{MH}], \quad \gamma_2 = \mu_{rot}/\hbar. \qquad (2.4)$$

The coefficient μ_{rot} is of the order of magnitude of a Bohr nuclear magneton and can be determined from the Zeeman splitting of the rotational levels of the molecule.[8]

If the rotational properties of a polar molecule are described by the model of a symmetric top with a dipole moment directed along the principal axis, we find easily, using the expressions for the matrix elements of the unit vector directed along

the principal axis (see[10]), that in the limit of large M:

$$\dot{\mathbf{M}} = \gamma_3[\mathbf{ME}], \quad \gamma_3 = d\sigma M^{-1}, \qquad (2.5)$$

where σ is the cosine of the angle between the direction of $\mathbf{M}$ and the direction of the principal axis.

If the polar molecule is diatomic or linear, the dipole and the rotational moments are perpendicular to each other and expression (2.5) tends identically to zero ($\sigma = 0$). To obtain a non-vanishing result in that case we must evaluate the average value of $\dot{\mathbf{M}}$ in the approximation which is quadratic in the electric field (see[10]):

$$\dot{\mathbf{M}} = \gamma_4[\mathbf{ME}], \quad \gamma_4 = {}^3/_2 d^2 I M^{-4}(\mathbf{ME}). \qquad (2.6)$$

When the dipole moments d in (2.5) and (2.6) are of the same order of magnitude, the magnitude of (2.6) is less than the magnitude of (2.5) by an order of magnitude Ed/T and the observation of the effect is in that case very difficult. An exception is the NO molecule the electronic ground state of which is $^2\Pi$, i.e., the component of the orbital momentum along the axis of the molecule is non-vanishing: $\Lambda = 1$. In that case the total moment of the molecule is not perpendicular to the molecular axis and the average value of the dipole moment is non-vanishing already in the zeroth approximation in the electric field:

$$\dot{\mathbf{M}} = \gamma_{NO}[\mathbf{ME}], \quad \gamma_{NO} = d\Lambda M^{-2}. \qquad (2.7)$$

However if the dipole moment and the moment of inertia are of the same order of magnitude as in the case (2.5), then at room temperatures, when $\overline{M} \sim 10\,\hbar$ the magnitude of (2.7) will be one order of magnitude less than the magnitude of (2.5).

Finally, in a polyatomic polar molecule of the asymmetric top type the average value of the dipole moment vanishes in the first approximation in the field, since the states of such a molecule are non-degenerate. The precession of the rotational moment $\mathbf{M}$ is thus quadratic in the field and the influence of the field on the transport phenomena is small. However, it was pointed out to us by V. Borman that if the asymmetry of the molecule is small we may, for sufficiently large values of the electric field, neglect the splitting of the rotational levels, and the effect becomes linear in the field. We may note the same also for polar linear molecules which have densely spaced levels for the transverse vibrations.

We see that Eqs. (2.3) to (2.7) are very similar to one another and that they determine the precession (averaged over the fast rotation around its

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*$[\mu\mathbf{H}] \equiv \mu \times \mathbf{H}$.

axis) of the rotational moment in an external field. The magnitude of the change in a transport coefficient in an external field depends essentially on the ratio ξ of the precessional frequency to the average collision frequency, which is proportional to the pressure p. This ratio behaves in the cases (2.3) to (2.5) and (2.7) as H/p or E/p. In the case (2.6) the magnitude of ξ is $\sim E^2/p$.

The effect reaches saturation when the parameter $\xi \gg 1$. It is clear that when saturation occurs the effect does not depend on the character of the cause of the precession of the moment, and the only differences are connected merely with the peculiarities of the interaction in the gas which has internal degrees of freedom.

3. DERIVATION OF THE BASIC EQUATIONS

When an external field is turned on, the kinetic equation averaged over the fast rotation of the molecule around its own axis is

$$\frac{\partial f}{\partial t} + (\mathbf{v}\nabla)f + \dot{\mathbf{M}}\frac{\partial}{\partial \mathbf{M}}f = I_{\text{coll}}. \qquad (3.1)$$

If the deviation from statistical equilibrium is small the kinetic equation becomes [2]

$$N + \gamma[\mathbf{MB}]\frac{\partial \chi}{\partial \mathbf{M}} = -n\hat{I}\chi,$$

$$f = nf_0(1+\chi), \quad f_0 = \exp(-u^2 - M^2), \quad n = p/T; \quad (3.2)$$

$$N = (u^2 + M^2 - c_p)u_i \sqrt{\frac{2T}{m}}(\nabla \ln T)_i$$

$$+ \left(u_i u_k - \frac{1}{3}\delta_{ik}u^2\right)\left(\frac{\partial v_{0k}}{\partial x_i} + \frac{\partial v_{0i}}{\partial x_k} - \frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{v}_0\right)$$

$$+ \left[\frac{2}{3}u^2 - \frac{1}{c_v}(u^2 + M^2)\right]\operatorname{div}\mathbf{v}_0; \qquad (3.3)$$

$$\hat{I}\chi = -\frac{I_{\text{coll}}}{n^2 f_0} = \iiint f_{01}[(\chi + \chi_1)W$$

$$- (\chi' + \chi_1')W']d\Gamma_1 d\Gamma' d\Gamma_1'. \qquad (3.4)$$

The velocity and the moment of the molecule are here measured, respectively, in units $(2T/m)^{1/2}$ and $(2IT)^{1/2}$. The coefficient γ, depending on the nature of the gas and of the external field (magnetic or electric), is defined by one of the expressions from the preceding section. The form of the equilibrium distribution function corresponds to the case of a diatomic (or linear) molecule and also of a top-type molecule with nearly equal moments of inertia ($I_A \approx I_B \approx I_C \approx I$). In the first case

$$d\Gamma = (2\pi^{5/2})^{-1}u^2 du M dM d\Omega_u d\Omega_M, \qquad (3.5)$$

and in the second case

$$d\Gamma = \pi^{-3}u^2 du M^2 dM d\Omega_u d\Omega_M. \qquad (3.6)$$

The integral sign includes averaging over the index σ. In the linearized kinetic equation (3.2) the collision integral is the linear integral operator (3.4). The functions W and W' in (3.4) describes the probabilities for direct and reverse collisions and satisfy the principle of detailed balancing.[11]

When solving Eq. (3.2) the dependence of the non-equilibrium distribution function on the directions of the velocity u and of the moment $\mathbf{M}$ turns out to be very important. It is therefore convenient to change to a spherical system of coordinates in which $\mathbf{B} \parallel \mathbf{z}$. In that system

$$\frac{1}{n}\gamma[\mathbf{MB}]\frac{\partial \chi}{\partial \mathbf{M}} = \tilde{\gamma}\frac{\partial}{\partial \varphi_M}\chi, \quad \tilde{\gamma} = \frac{\gamma B}{n}. \qquad (3.7)$$

The inhomogeneous part of (3.3) can be written in the form

$$N = n\sum_{lm} a_{lm}^* A_{lm}; \qquad (3.8)$$

$$A_{1m} = Y_{1m}(\mathbf{u})(u^2 + M^2 - c_p), \quad A_{2m} = Y_{2m}(\mathbf{u}),$$

$$A_{00} = {}^2\!/_3 u^2 - c_v^{-1}(u^2 + M^2),$$

$$a_{1m} = \frac{1}{n}\sqrt{\frac{2T}{m}}(\nabla \ln T)_i t_i^{1m}, \quad a_{2m} = \frac{1}{n}\left(\frac{\partial v_{0k}}{\partial x_i} + \frac{\partial v_{0i}}{\partial x_k}\right)t_{ik}^{2m},$$

$$a_{00} = \frac{1}{n}\left(\frac{\partial v_{0k}}{\partial x_i} + \frac{\partial v_{0i}}{\partial x_k}\right)t_{ik}^{00}, \quad Y_{lm}(\mathbf{u}) \equiv u^l Y_{lm}(\theta_u, \varphi_u). \qquad (3.9)$$

From the explicit form of (3,3) it follows that in the sum (3.8) only the terms with $l = 0$, 1, 2 and, correspondingly, $|m| \leq l$ do not vanish. We use here the coefficients for a change from a Cartesian to a spherical system of coordinates. If n is a unit vector,

$$t_i^{1m} = \frac{1}{4\pi}\int d\Omega\, Y_{1m}(\theta, \varphi)n_i, \quad t_{ik}^{lm} = \frac{1}{4\pi}\int d\Omega\, Y_{lm}(\theta, \varphi)n_i n_k,$$

$$t_{ik}^{l-m} = (-1)^m(t_{ik}^{lm})^*. \qquad (3.10)$$

Direct computation gives

$$t_i^{10} = \sqrt{1/3}\,\delta_{iz}, \quad t_i^{11} = -\sqrt{1/6}(\delta_{ix} + i\delta_{iy}),$$

$$t_{ik}^{00} = {}^1\!/_3\delta_{ik}, \quad t_{ik}^{20} = \sqrt{1/5}(\delta_{iz}\delta_{kz} - {}^1\!/_3\delta_{ik}),$$

$$t_{ik}^{21} = -\sqrt{1/30}[\delta_{iz}(\delta_{kx} + i\delta_{ky}) + \delta_{kz}(\delta_{ix} + i\delta_{iy})],$$

$$t_{ik}^{22} = \sqrt{1/30}(\delta_{ix} + i\delta_{iy})(\delta_{kx} + i\delta_{ky}). \qquad (3.10')$$

We look for a solution of Eq. (3.2) in the form

$$\chi = -\sum_{lm} a_{lm}^* \chi_{lm}. \qquad (3.11)$$

Substituting (3.7), (3.8), and (3.11) into (3.2) we find

$$\left(\hat{I} + \tilde{\gamma}\frac{\partial}{\partial \varphi_M}\right)\chi_{lm} = A_{lm}. \qquad (3.12)$$

The kinetic coefficients are defined in terms of

the magnitude of the energy or momentum current in the non-equilibrium state. Thus, in the thermal conductivity problem (see [2]) the heat current is equal to

$$q_i = nT \left(\frac{2T}{m}\right)^{1/2} \int d\Gamma f_0 u_i (u^2 + M^2 - c_p)\chi = -\varkappa_{ik}(\nabla T)_{k_1}$$

$$\varkappa_{ik} = \frac{2T}{m} \sum_{m,m'} t_i{}^{1m}(t_k{}^{1m'})^* \int d\Gamma f_0 A_{1m}{}^* \chi_{1m'}. \quad (3.13)$$

The tensor of viscous stresses is defined as

$$\sigma_{ik} = -nm\frac{2T}{m}\int d\Gamma f_0\chi u_i u_k = \eta_{ikpq}\left(\frac{\partial v_{0q}}{\partial x_p} + \frac{\partial v_{0p}}{\partial x_q}\right).$$

Using (3.8) to (3.11), we can write the general expression for the viscosity tensor in the form

$$\eta_{ikpq} = 2T \sum_{lm;\, l'm'} t_{ik}^{lm}(t_{pq}^{l'm'})^* \int d\Gamma f_0 A_{lm}{}^*\chi_{l'm'}, \quad l,\, l' = 0.\, 2. \quad (3.14)$$

To obtain this last expression we took it into account that the non-equilibrium distribution function must satisfy the conditions (see [2])

$$\int d\Gamma f_0\chi = 0, \qquad \int d\Gamma f_0\chi(u^2 + M^2) = 0,$$

$$\int d\Gamma f_0\chi \mathbf{u} = 0, \qquad \int d\Gamma f_0\chi \mathbf{M} = 0. \quad (3.15)$$

The expressions for the tensors (3.13) and (3.14) can be simplified if we use the fact that the quantities

$$c_{lm;\, l'm'} = \int d\Gamma f_0 A_{lm}{}^*\chi_{l'm'} \quad (3.16)$$

satisfy the following symmetry properties

$$c_{lm;\, l'm} = c^*{}_{l-m;\, l'-m}, \quad c_{lm;\, l'm'} = 0, \quad m \neq m'. \quad (3.17)$$

Taking (3.10) and (3.17) into account, the thermal conductivity tensor and the viscosity tensor (3.14) take the form ($h_i = H_i/H$, $h_{ik} = e_{ikp}h_p = \delta_{ix}\delta_{ky} - \delta_{iy}\delta_{kx}$):

$$\varkappa_{ik} = \frac{2T}{3m}\{\delta_{ik}\,\mathrm{Re}\,c_{11;\,11} + h_i h_k(c_{10;\,10} - \mathrm{Re}\,c_{11;\,11})$$

$$+ h_{ik}\,\mathrm{Im}\,c_{11;\,11}\}; \quad (3.18)$$

$$\eta_{ikpq} = {}^2/_{15}T\{3(h_i h_k - {}^1/_3\delta_{ik})(h_p h_q - {}^1/_3\delta_{pq})c_{20;\,20}$$

$$+ (h_i h_p\delta_{kq} + h_i h_q\delta_{kp} + h_k h_p\delta_{iq} + h_k h_q\delta_{ip}$$

$$- 4h_i h_k h_p h_q)\,\mathrm{Re}\,c_{21;\,21} + (h_i h_p h_{kq} + h_i h_q h_{kp} + h_k h_p h_{iq}$$

$$+ h_k h_q h_{ip})\,\mathrm{Im}\,c_{21;\,21} + [-h_{ip}h_{kq} + (\delta_{ip} - h_i h_p)$$

$$\times (\delta_{kq} - h_k h_q)]\,\mathrm{Re}\,c_{22;\,22} + [(\delta_{ip} - h_i h_p)h_{kq}$$

$$+ (\delta_{kq} - h_k h_q)h_{ip}]\,\mathrm{Im}\,c_{22;\,22} + \sqrt{5}(h_i h_k$$

$$- {}^1/_3\delta_{ik})\delta_{pq}c_{20;\,00} + \sqrt{5}(h_p h_q - {}^1/_3\delta_{pq})\delta_{ik}c_{00;\,20}$$

$$+ {}^5/_3\delta_{ik}\delta_{pq}c_{00;\,00}\}. \quad (3.19)$$

In accordance with the symmetry principle of transport coefficients, we have in a magnetic field

$$\varkappa_{ik}(\mathbf{H}) = \varkappa_{ki}(-\mathbf{H}), \quad \eta_{ikpq}(\mathbf{H}) = \eta_{pqik}(-\mathbf{H}), \quad (3.20)$$

and in an electric field

$$\varkappa_{ik} = \varkappa_{ki}, \quad \eta_{ikpq} = \eta_{pqik}. \quad (3.21)$$

Comparing (3.19) with (3.20) and (3.21) we see that the imaginary part $\mathrm{Im}\,c_{lm;\,lm}$ must be different from zero only for a magnetic field and must change sign when we replace $\mathbf{H}$ by $-\mathbf{H}$. In an electric field $\mathrm{Im}\,c_{lm;\,lm}$ must vanish. Moreover, it is necessary that

$$c_{20;\,00} = c_{00;\,20}. \quad (3.22)$$

We shall see below (Sec. 5) that the coefficients $c_{lm;l'm}$ satisfy these requirements. Hence it follows that the number of independent coefficients describing the behavior of the thermal conductivity in a magnetic field is three, and in an electric field is two. The corresponding number of the viscosity tensor is seven and five.

In [2] the third term of (3.18) was absent, since we used there a model for which $\mathrm{Im}\,c_{11;11} = 0$ (for details see Sec. 5).

When there is no external field we have

$$c_{lm;\,l'm'} = c_l\delta_{ll'}\delta_{mm'} \quad (3.23)$$

and (3.18) and (3.19) change to the usual expressions:

$$\varkappa_{ik} = \varkappa\delta_{ik}, \quad \varkappa = (2T/3m)c_1,$$

$$\eta_{iklm} = {}^1/_2\eta(-{}^2/_3\delta_{ik}\delta_{lm} + \delta_{il}\delta_{km} + \delta_{im}\delta_{kl}) + {}^1/_2\zeta\delta_{ik}\delta_{lm},$$

$$\eta = {}^4/_{15}Tc_2, \quad \zeta = {}^4/_9Tc_0. \quad (3.24)$$

4. PROPERTIES OF THE COLLISION OPERATOR

To evaluate the coefficients $c_{lm;l'm}$ which determine the transport effects we must find a solution of Eq. (3.12). It is clear that the function χ_{lm} and thus the transport coefficients will depend on the external field only when the functions χ_{lm} depends on the direction of the moment $\mathbf{M}$. To find this dependence we must take into account in the collision integral the correlation between the translational and rotational degrees of freedom. We shall assume that in (3.4)

$$W = W^{(0)} + \varepsilon W^{(1)}, \quad \varepsilon \ll 1 \quad (4.1)$$

and thus

$$I = I^{(0)} + \varepsilon I^{(1)}. \quad (4.2)$$

The first term in (4.1) and (4.2) does not affect the internal degrees of freedom and the second term takes into account the dependence of the collision cross-section on the rotational moments. Here and henceforth we denote by an index in brackets the order of smallness of the corresponding quantity as far as ϵ is concerned. We

assume that parameter to be small, which corresponds to a natural assumption of a relatively weak correlation between the internal and external degrees of freedom. In particular, this leads to a relatively weak dependence of the cross-section on the angle between $\mathbf{u}$ and $\mathbf{M}$.

The properties of the operator $\hat{I}^{(0)}$ are the same as those of the often-studied collision integral of monatomic gases. The eigenfunctions and eigenvalues of this operator are determined by the equation

$$\hat{I}^{(0)} \psi_n = \lambda_n^{(0)} \psi_n. \tag{4.3}$$

Under rather general assumptions about the character of $\hat{I}^{(0)}$ one may assume that the set of functions ψ_n is a complete system of functions which are orthogonal and normalized in the sense that

$$\langle \psi_n, \psi_{n'} \rangle = \delta_{nn'}, \tag{4.4}$$

where

$$\langle F_1, F_2 \rangle = \int d\Gamma \, f_0 F_1^* F_2. \tag{4.5}$$

As $\hat{I}^{(0)}$ is a scalar operator, the dependence of the eigenfunctions on the directions of $\mathbf{u}$ and $\mathbf{M}$ can be expressed in terms of the spherical polynomials (3.9):

$$\psi_n \propto \sum_{m_1+m_2=m} C_{l_1 m_1; l_2 m_2}^{lm} Y_{l_1 m_1}(\mathbf{u}) Y_{l_2 m_2}(\mathbf{M}), \tag{4.6}$$

where the $C_{l_1 m_1; l_2 m_2}^{l\,m}$ are Clebsch-Gordan coefficients.

If the functions ψ_n are independent of $\mathbf{M}$ and σ they are the same as the eigenfunctions of the corresponding collision operator of a monatomic gas and can be written in the form

$$T_r^{l_1}(u^2) Y_{l_1 m_1}(\mathbf{u}). \tag{4.7}$$

In the case of an interaction of the form of that between Maxwell molecules the functions $T_{r_1}^{l_1}$ are normalized Sonine (or Laguerre) polynomials of the appropriate type (see, for instance, [12]). The evaluation of these functions is not part of our problem and we shall assume that they and the corresponding eigenvalues $\alpha_{l_1 r_1}$ are known.

The functions ψ_n, which depend on $\mathbf{M}$ and σ, will be written as

$$\psi_n = F_1(\mathbf{M}, \sigma) F_2(\mathbf{u}), \qquad \int d\Gamma \, f_0 F_1(\mathbf{M}, \sigma) = 0. \tag{4.8}$$

Since in collisions described by $\hat{I}^{(0)}$ the internal degrees of freedom do not change, we have

$$I^{(0)} F_1(\mathbf{M}, \sigma) F_2(\mathbf{u}) = F_1(\mathbf{M}, \sigma) \hat{U} F_2(\mathbf{u}), \tag{4.9}$$

$$\hat{U} F(\mathbf{u}) \equiv \iiint f_{01} [F(\mathbf{u}) - F(\mathbf{u}')] W^{(0)} d\Gamma_1 \, d\Gamma' \, d\Gamma_1'. \tag{4.10}$$

Hence it follows that the eigenvalues corresponding to the eigenfunctions (4.8) are independent of the form of $F_1(\mathbf{M}, \sigma)$. The dependence of the functions ψ_n on $\mathbf{M}^2$ and σ is thus determined solely by the orthonormality conditions (4.4). The properties of the operator (4.10) are similar to those of $\hat{I}^{(0)}$. Its eigenfunctions have the form (4.7) and we shall assume that they and the corresponding eigenvalues $\beta_{l_1 r_1}$ are known.

We can thus write the eigenfunctions of the operator $I^{(0)}$ in the form

$$\psi_n = \sum_{m_1+m_2=m} C_{l_1 m_1;\, l_2 m_2}^{lm} Y_{l_1 m_1}(\mathbf{u}) Y_{l_2 m_2}(\mathbf{M}) T_{r_1}^{l_1}(u^2) L_{r_2}^{l_2}(M^2) \varphi_s(\sigma),$$
$$n = (lm; l_1 l_2; r_1 r_2; s). \tag{4.11}$$

Here L_r^l is a normalized Laguerre polynomial of rank l for linear molecules and of rank $l + \frac{1}{2}$ for top-type molecules. The functions $\varphi_s(\sigma)$ form an orthonormal system in the sense that

$$\frac{1}{2S+1} \sum_\sigma \varphi_s^*(\sigma) \varphi_{s'}(\sigma) = \delta_{ss'}, \quad s = 0, 1, 2, \ldots, 2S+1 \tag{4.12}$$

for paramagnetic molecules and in the sense that

$$\frac{1}{2} \int_{-1}^{1} d\sigma \, \varphi_s^*(\sigma) \varphi_{s'}(\sigma) = \delta_{ss'} \quad s = 0, 1, 2, \ldots \tag{4.12'}$$

for polar molecules of the symmetric top type. We shall number the functions $\varphi_s(\sigma)$ in such a way that $\varphi_0(\sigma) = 1$ and for even s the functions $\varphi_s(\sigma)$ are even and for odd s the functions $\varphi_s(\sigma)$ are odd. To the functions (4.11) correspond the eigenvalues

$$\lambda_n^{(0)} = \alpha_{l_1 r_1} \delta_{r_2 0} \delta_{l_2 0} \delta_{s0} + \beta_{l_1 r_1} (1 - \delta_{r_2 0} \delta_{l_2 0} \delta_{s0}). \tag{4.13}$$

The properties of the operator $\hat{I}^{(1)}$ – that part of the collision integral which takes into account that the internal and external degrees of freedom are mixed up in collisions – is completely characterized by its "matrix elements"

$$I_{nn'}^{(1)} = \langle \psi_n, \hat{I}^{(1)} \psi_{n'} \rangle, \qquad I_{nn'}^{(1)} = I_{n'n}^{(1)} = (I_{nn'}^{(1)})^*. \tag{4.14}$$

Since the operator $\hat{I}^{(1)}$ is scalar, i.e., it is invariant under rotations, inversion, and time reversal, we get the following "selection rules" (see the explicit form of (4.11)):

$$\begin{array}{ll} l = l', & m = m'; \\ l_1 - l_1' = \text{even}, & l_2 - l_2' = \text{even}. \end{array} \tag{4.15}$$

The quantity (4.14) is clearly independent of the value of m.

In a paramagnetic gas the index σ has the meaning of being the component of the spin of the molecule along its rotational moment, and is thus a true scalar. In a paramagnetic gas there is thus no "selection rule" when the index s changes. In a polar gas of the symmetric top type

$$\sigma = (\mathbf{dM}) / \sqrt{d^2 M^2}, \tag{4.16}$$

i.e., it is a pseudoscalar. If the interaction between the molecules is an even function of d, it leads to the "selection rule"

$$s - s' = \text{even}. \qquad (4.17)$$

In the opposite case "transitions" are allowed with odd values of this difference, which leads to a complication of (4.15):

$$l_2 - l_2' = \text{even},$$
$$l_1 - l_1' = \text{even}, \quad \text{if} \quad s - s' - \text{even}, \qquad (4.18)$$
$$l_1 - l_1' = \text{odd}, \quad \text{if} \quad s - s' - \text{odd}.$$

The system of functions (4.11) constructed above is a complete system in the sense that any function ψ of the variables u, M, and σ can be expanded in a series in terms of these functions provided the norm $\langle \psi, \psi \rangle$ is finite.

5. SOLUTION OF THE KINETIC EQUATION

We shall solve Eq. (3.12)

$$\left(\hat{I}^{(0)} + \varepsilon \hat{I}^{(1)} + \tilde{\gamma} \frac{\partial}{\partial \varphi_M} \right) \chi_{lm} = A_{lm} \qquad (5.1)$$

using perturbation theory methods. In our case the small parameter is the parameter ϵ in (4.2). To avoid division by zero we refer to the zeroth-approximation operator that part of the operator $\hat{I}^{(1)}$ which is determined by the relations

$$\hat{I}^{(1)} = \hat{I}_a^{(1)} + \hat{I}_b^{(1)}, \quad \hat{I}_a^{(1)} \psi_n = \begin{cases} 0, & \lambda_n^{(0)} \neq 0 \\ I_{nn}^{(1)} \psi_n, & \lambda_n^{(0)} = 0 \end{cases}. \qquad (5.2)$$

We bear in mind that because of the conditions (3.15) we shall not be interested in the eigenfunctions of the <u>total</u> collision operator which are of the form 1, <u>u</u>, M, or $u^2 + M^2$, for which

$$(\hat{I}^{(0)} + \varepsilon \hat{I}^{(1)}) \psi = 0.$$

The only eigenfunctions (4.11) with vanishing values of $\lambda_n^{(0)}$ will thus be functions with $l_1 = 0$ of the form $u^2 - \frac{3}{2}$, $\psi(M^2, \sigma)$, and $\psi(M/M, M^2, \sigma)$. For any physically reasonable model of the interaction transition between states with $\lambda_n^{(0)} = 0$ will be of much higher order of smallness than ϵ and for models with these properties we can use perturbation theory without reservations.

We choose thus as the zeroth approximation operator

$$\hat{K}^{-1} = \hat{I}^{(0)} + \varepsilon \hat{I}_a^{(1)} + \tilde{\gamma} \frac{\partial}{\partial \varphi_M}. \qquad (5.3)$$

The action of the operator which is the inverse of (5.3) is determined by the equation

$$\hat{K} \psi_n = \sum_{m_1 + m_2 = m} C_{l_1 m_1; \, l_2 m_2}^{lm} Y_{l_1 m_1}(\mathbf{u}) Y_{l_2 m_2}(\mathbf{M}) T_{r_1}^{l_1}(u^2)$$

$$\times L_{r_2}^{l_2}(M^2) \varphi_s(\sigma) (\lambda_n + im_2 \tilde{\gamma})^{-1},$$

$$\lambda_n = \lambda_n^{(0)} \text{ when } \lambda_n^{(0)} \neq 0, \quad \lambda_n = \varepsilon I_{nn}^{(1)} \text{ when } \lambda_n^{(0)} = 0. \quad (5.4)$$

We can easily write down a formal solution for Eq. (5.1) written in the form

$$\chi_{lm} = \hat{K} A_{lm} - \varepsilon \hat{K} \hat{I}_b^{(1)} \chi_{lm},$$

as an expansion in the parameter ϵ:

$$\chi_{lm} = \{ \hat{K} - \varepsilon \hat{K} \hat{I}_b^{(1)} \hat{K} + \varepsilon^2 \hat{K} \hat{I}_b^{(1)} \hat{K} \hat{I}_b^{(1)} \hat{K} - \ldots \} A_{lm}. \qquad (5.5)$$

Substituting this solution into (3.16) we find:

$$c_{lm; \, l'm} = \langle A_{lm}; \chi_{l'm} \rangle = \overset{(0)}{c}_{lm; \, l'm} + \overset{(1)}{c}_{lm; \, l'm} + \overset{(2)}{c}_{lm; \, lm'}, \qquad (5.6)$$

$$\overset{(0)}{c}_{lm; \, l'm} = \langle A_{lm}, \hat{K} A_{l'm} \rangle, \qquad (5.7)$$

$$\overset{(1)}{c}_{lm; \, l'm} = - \varepsilon \langle A_{lm}, \hat{K} \hat{I}_b^{(1)} \hat{K} A_{l'm} \rangle, \qquad (5.8)$$

$$\overset{(2)}{c}_{lm; \, l'm} = \varepsilon^2 \langle A_{lm}, \hat{K} \hat{I}_b^{(1)} \hat{K} \hat{I}_b^{(1)} \hat{K} A_{l'm} \rangle. \qquad (5.9)$$

The function A_{lm} is independent of the direction of the vector M and the index σ and its expansion in terms of the functions (4.11) contains only terms with $l_2 = m_2 = s = 0$:

$$A_{lm} = \sum_{n_0} \langle \psi_{n_0}, A_{lm} \rangle \psi_{n_0}, \quad n_0 = (lm; \, l0; \, r_1 r_2; \, 0). \qquad (5.10)$$

Hence it follows that

$$\hat{K} A_{lm} = \sum_{n_0} (\lambda_{n_0})^{-1} \langle \psi_{n_0}, A_{lm} \rangle \psi_{n_0} \qquad (5.11)$$

and the coefficients (5.7) and (5.8) are independent of the external field.

We can write Eq. (5.9) in the form

$$\overset{(2)}{c}_{lm; \, l'm} = \varepsilon^2 \sum_{nn'} \langle A_{lm}, \hat{K} \hat{I}_b^{(1)} \psi_n \rangle K_{nn'} \langle \psi_{n'}, \hat{I}_b^{(1)} \hat{K} A_{l'm} \rangle, \qquad (5.12)$$

where

$$\langle A_{lm} \hat{K} \hat{I}_b^{(1)} \psi_n \rangle = \sum_{n_0} \langle A_{lm}, \psi_{n_0} \rangle (\lambda_{n_0})^{-1} (I_b^{(1)})_{n_0 n} \qquad (5.13)$$

which is, indeed, independent of m. The last factor in (5.12) has a similar form.

The only quantity in Eq. (5.12) dependent on the external field is

$$K_{nn'} = \lambda_n^{-1} \delta_{nn'} + \Delta K_{nn'}, \qquad (5.14)$$

$$\Delta K_{nn'} = - \lambda_{n'}^{-1} \sum_{m_1 + m_2 = m} C_{l_1 m_1; \, l_2 m_2}^{lm} C_{l_1 m_1; \, l_2' m_2}^{l'm} \delta_{mm'} \delta_{l_1 l_1'} \delta_{m_1 m_1'}$$

$$\times \delta_{m_2 m_2'} \delta_{r_1 r_1'} \cdot \left\langle Y_{l_2 m_2}(\mathbf{M}) L_{r_2}^{l_2}(M^2) \varphi_s(\sigma), \right.$$

$$\times \frac{(m_2 \tilde{\gamma})^2 + im_2 \tilde{\gamma} \lambda_{n'}}{\lambda_{n'}^2 + (m_2 \tilde{\gamma})^2} Y_{l_2' m_2}(\mathbf{M})_{r_2'}^{l_2'}(M^2) \varphi_{s'}(\sigma) \right\rangle. \qquad (5.15)$$

Because of the selection rule (4.15), the numbers l, l', and m are the same as the corresponding indices in (5.12). In all cases except (2.6) the quantity $\tilde{\gamma}$ (see (3.7)) is independent of the direction of M and we can integrate in (5.15) over this direction and this leads to $l_2 = l_2'$. Clearly the change in (5.12) and hence in the transport

coefficients in an external field is determined (in the first non-vanishing approximation in ϵ) by Eq. (5.12), in which the matrix element K_{nn}' is replaced by $\Delta K_{nn}'$. The external field occurs in (5.15) through the parameter $\tilde{\gamma}$ and hence it follows that the transport coefficients are functions of the ratio B/n, i.e., B/p, in the cases (2.2), (2.4), or (2.5) and functions of E^2/p in the case (2.6).

The real part of (5.15) (and hence Re $c^{(2)}_{lm, l'm}$) is even in the external field and increases monotonically with increasing $\tilde{\gamma}$. For sufficiently small values of the field the magnitude of (5.15) is proportional to $(B/p)^2$ (the case (2.6) needs special considerations). For large values of the external field $(\tilde{\gamma} > \lambda_n')$ Re $\Delta K_{nn}'$ reaches saturation at a level which is independent of the nature of the external field and is determined solely by the properties of the interaction between the molecules.

The imaginary part of (5.15) leads to an effect which is odd in the external field. The quantity Im K_{nn}' can be non-vanishing in a magnetic field (when $H \neq 0$) both in a paramagnetic gas (case (2.2)), if the operator $\hat{I}^{(1)}$ does not prohibit transitions with odd values of the difference s − s', and in the general case (2.4) of a non-paramagnetic gas.

In an electric field Im $K_{nn}' \equiv 0$, as we can verify easily if in case (2.6) $(\gamma \approx (M \cdot E))$ we integrate explicitly in (5.15) over the direction of M; in the case (2.5), on the other hand, $\gamma \sim \sigma$ but then $l_2 = l_2'$ and the integration over σ again gives zero.

For small values of the magnetic field, Im K_{nn}' depends linearly on the ratio H/p, reaches somewhere $(<\tilde{\gamma}> \sim \lambda_n)$ a maximum, and for large values of H/p tends to zero as $(H/p)^{-1}$. Such a behavior in a magnetic field is characteristic of terms of the thermal conductivity tensor (3.18) and the viscosity tensor (3.19) which are odd in the field. We note that relation (3.22) follows immediately from the explicit form of the coefficients (5.12) (or (5.8)).

We note that the scheme worked out here allows us in principle to find the change in the kinetic coefficients in an external field with higher accuracy than ϵ^2. For instance,

$$c^{(3)}_{lm; l'm} = \epsilon^3 \langle A_{lm}, \hat{K}\hat{I}_b^{(1)}\hat{K}\hat{I}_b^{(1)}\hat{K}\hat{I}_b^{(1)}\hat{K}A_{l'm} \rangle. \quad (5.16)$$

In particular, we can use the expansion (5.6) also to evaluate with arbitrary accuracy the transport coefficients of the polyatomic gases when there are no external fields, in which case the

calculation can be appreciably simplified, for them

$$\hat{K}\psi_n = \lambda_n^{-1}\psi_n \quad (5.17)$$

and instead of the complicated Eq. (5.12) we have in the k-th approximation more simply

$$c^{(k)}_{lm; l'm} = \epsilon^k \sum_{n_0 n_0'} \langle A_{lm}, \psi_{n_0} \rangle \langle \psi_{n_0'}, A_{l'm} \rangle F_{n_0 n_0'}, \quad (5.18)$$

$$F_{n_0 n_0'} = \sum_{n_1 \cdots n_{k-1}} \lambda_{n_0}^{-1} (\hat{I}_b^{(1)})_{n_0 n_1} \lambda_{n_1}^{-1} \cdots (\hat{I}_b^{(1)})_{n_{k-1} n_0'} \lambda_{n_0'}^{-1}. \quad (5.19)$$

Strictly speaking, in all cases where $\tilde{\gamma}$ depends on M or σ the last bracket in (5.4) has only a symbolical meaning, indicating its limiting values as $\tilde{\gamma} \to 0$ and $\tilde{\gamma} \to \infty$, for functions ψ_n with $l_2 \neq 0$ of the form $\psi(M/M, M^2, \sigma)$. In practice one must replace the bracket by the matrix element $K_{n'n}$ determined from the equation

$$\epsilon I^{(1)}_{n'n'} K_{n'n} + i m_2 \sum_{n''} (\tilde{\gamma})_{n'n''} K_{n''n} = \delta_{n'n}. \quad (5.20)$$

If such states would play an important role, the change in transport coefficients such as the thermal conductivity and the first viscosity would be of relative order of magnitude ϵ and would reach saturation for relatively small values of the external field $(\tilde{\gamma} > \epsilon I_1)$. These consequences contradict experimental results, giving grounds for assuming that for real interactions matrix elements of the type

$$\langle \psi_{lm; l0; r_1 r_2; 0}, \hat{I}^{(1)}\psi_{lm; 0l; 0r_2'; s} \rangle$$

are very small and that we may neglect for an estimate of effects in an external field transitions into states with $l_1 = r_1 = 0$, $l_2 \neq 0$.

6. MODEL OF THE INTERACTION IN A PARAMAGNETIC DIATOMIC GAS

To illustrate the foregoing general method by concrete examples, and also to elucidate qualitatively (and to predict) the influence of a magnetic field on kinetic coefficients, it is sufficient to choose a very simple model, which leads to non-trivial results for all coefficients defining the behavior of the tensors (3.18) and (3.19).

We assume that the matrix element $(\hat{I}^{(1)}_b)_{n_0 n}$ in (5.13) is non-vanishing only for "transitions into states" with $l_2 = 2$, $r_1 = r_2 = 0$, s = 0 or 1 and only one value of l_1, which we shall later choose from symmetry considerations, i.e., for transitions to states

$$\psi_{lm}^{(0)} \equiv \psi_{lm; l_2; 00; 0} \sim \sum_{m_1 + m_2 = m} C^{lm}_{l_1 m_1; 2m_2} Y_{l_1 m_1}(\mathbf{u}) Y_{2m_2}(\mathbf{M}),$$

$$\psi_{lm}^{(1)} \equiv \psi_{lm;\, l,2;\, 00;\, 1} \sim \sigma \sum_{m_1+m_2=m} C_{l_1 m_1;\, 2m_2}^{lm} Y_{l_1 m_1}(\mathbf{u}) Y_{2m_2}(\mathbf{M}).$$
$$(6.1)$$

In this model, Eqs. (5.12) and (5.15) become

$$\Delta c_{lm;\, l'm} = -\Lambda_{ll'} \sum_{m_1+m_2=m} C_{l_1 m_1;\, 2m_2}^{lm} C_{l_1 m_1;\, 2m_2}^{l'm} f_{ll'}(m_2 \xi_{l_1}),$$

$$\Lambda_{ll'} = \langle A_{lm}, \hat{K}\hat{I}_b^{(1)} \psi_{lm}^{(0)} \rangle \langle \psi_{l'm}^{(0)}, \hat{I}_b^{(1)} \hat{K} A_{l'm} \rangle,$$

$$\langle A_{lm}, \hat{K}\hat{I}_b^{(1)} \psi_{lm}^{(0)} \rangle = a_l \langle A_{lm}, \hat{K}\hat{I}_b^{(1)} \psi_{lm}^{(0)} \rangle,$$

$$f_{ll'}(\xi) = \frac{1}{\nu \beta_{l,0}} \left\langle (1+a_l\sigma), \frac{(\sigma\xi)^2 + i\sigma\xi}{M^2 + (\sigma\xi)^2} M^4 (1 + a_{l'}\sigma) \right\rangle,$$

$$\xi_{l_1} = 2\mu_0 H \sqrt{T} / p\beta_{l,0}\sqrt{2I},$$

$$\nu^2 = \langle (1+a_l\sigma)^2 M^4 \rangle \langle (1+a_{l'}\sigma)^2 M^4 \rangle. \quad (6.2)$$

The determination of the quantities $\beta_{l_1 r_1}$ was given earlier in (4.13).

The real and imaginary parts of the function $f_{ll'}(\xi)$ are equal to

$$\mathrm{Re}\, f_{ll'}(\xi) = \frac{1}{2S+1} \frac{1}{\nu\beta_{l,0}} \sum_\sigma (1+a_l a_{l'}\sigma^2) \int_0^\infty \frac{x^2(\sigma\xi)^2}{x+(\sigma\xi)^2} e^{-x}\, dx,$$

$$\mathrm{Im}\, f_{ll'}(\xi) = a_l a_{l'} \frac{1}{2S+1} \frac{1}{\nu\beta_{l,0}} \sum_\sigma \sigma^2\xi \int_0^\infty \frac{x^{5/2}}{x+(\sigma\xi)^2} e^{-x}\, dx. \quad (6.3)$$

In the case (2.4) of a non-paramagnetic gas the form of the coefficient $\Delta c_{lm;\, l'm}$ remains the same, but Eqs. (6.3) must be replaced by simpler ones:

$$\mathrm{Re}\, f(\xi) = \frac{1}{2} \frac{\xi^2}{1+\xi^2}, \qquad \mathrm{Im}\, f(\xi) = \frac{1}{2} \frac{\xi}{1+\xi^2},$$

$$\xi_{l_1} = \frac{\mu_{\mathrm{rot}} HT}{p\beta_{l,0}\hbar}. \quad (6.4)$$

We can also describe approximately by formulas of this form the transition region in the case of a paramagnetic gas, since the functions (6.3) go over into (6.4) if in the former we put in the intergrand in the factor of the exponential x = 1. The qualitative conclusions about the behavior of transport effects in a magnetic field are thus the same for paramagnetic and non-paramagnetic gases.

The parameters $\Lambda_{ll'}$, a_l, and $\beta_{l,0}$ are independent of the magnetic field and are determined by the character of the interaction.

7. VISCOSITY

We apply the results obtained above to a calculation of the change in the viscosity tensor of a paramagnetic diatomic gas. To do this we must substitute Eq. (6.2) into (3.19), using the numerical values of the Clebsch-Gordon coefficients.

For the given problem

$$l, l' = 0, 2, \qquad l_1 = 2, \quad (7.1)$$

and the behavior of the viscosity tensor (3.19) in a magnetic field is determined by the equations

$$\Delta c_{20;\, 20} = -1/7\Lambda_{22}[\mathrm{Re}\, f_{22}(\xi_2) + 4\,\mathrm{Re}\, f_{22}(2\xi_2)],$$

$$\Delta\,\mathrm{Re}\, c_{21;\, 21} = -1/14\Lambda_{22}[7\,\mathrm{Re}\, f_{22}(\xi_2) + 6\,\mathrm{Re}\, f_{22}(2\xi_2)],$$

$$\mathrm{Im}\, c_{21;\, 21} = -1/14\Lambda_{22}[-5\,\mathrm{Im}\, f_{22}(\xi_2) + 6\,\mathrm{Im}\, f_{22}(2\xi_2)],$$

$$\Delta\,\mathrm{Re}\, c_{22;\, 22} = -1/7\Lambda_{22}[3\,\mathrm{Re}\, f_{22}(\xi_2) + \mathrm{Re}\, f_{22}(2\xi_2)],$$

$$\mathrm{Im}\, c_{22;\, 22} = -1/7\Lambda_{22}[3\,\mathrm{Im}\, f_{22}(\xi_2) + \mathrm{Im}\, f_{22}(2\xi_2)],$$

$$c_{20;\, 00} = c_{00;\, 20} = -\sqrt{2/21}\Lambda_{02}[\mathrm{Re}\, f_{20}(\xi_2) + 2\,\mathrm{Re}\, f_{20}(2\xi_2)].$$

$$\Delta c_{00;\, 00} = -2/3\Lambda_{00}[\mathrm{Re}\, f_{00}(\xi_2) + \mathrm{Re}\, f_{00}(2\xi_2)]. \quad (7.2)$$

The seven coefficients in (7.2) are functions of the ratio H/p and of the parameters Λ_{22}, Λ_{02}, Λ_{00}, a_2, and β_{20}. In the present limited state of our knowledge of the interactions between polyatomic molecules it is advisable not to attempt to evaluate numerical values of these parameters but to determine them directly from experiments. We note that the order of magnitude of the coefficients (7.2) and (3.24) in terms of the parameter ϵ is:

$$\eta \sim \epsilon^0, \quad \zeta \sim \epsilon^{-1}, \quad \Delta c_{2m;\, 2m} \sim \epsilon^2, \quad c_{20;\, 00} \sim \epsilon^1, \quad \Delta c_{00;\, 00} \sim \epsilon^0. \quad (7.3)$$

If we determine, as usual, the effective viscosity of a gas by measuring the pressure gradient along a flow in a tube of circular cross-section for different directions of the magnetic field, then we can determine three of the seven coefficients of (7.2).

To determine the odd effects and the coefficient $c_{00;\, 20}$ it is convenient to study transverse pressure gradients arising in viscous flow of the gas along the x axis between parallel walls perpendicular to the z axis:

$$\frac{dp}{dx} = (\nabla p)_0 \left\{ 1 + \frac{1}{c_2}[3h_x^2 h_z^2 \Delta c_{20;\, 20} + (h_x^2 + h_z^2 - 4h_x^2 h_z^2) \right.$$
$$\left. \times \Delta\,\mathrm{Re}\, c_{21;\, 21} + (h_y^2 + h_x^2 h_z^2)\,\Delta\,\mathrm{Re}\, c_{22;\, 22}] \right\},$$

$$\frac{dp}{dy} = (\nabla p)_0 \frac{1}{c_2}[3h_x h_y h_z^2 \Delta c_{20;\, 20} + h_x h_y(1 - 4h_z^2)\,\Delta\,\mathrm{Re}\, c_{21;\, 21}$$
$$+ h_x h_y(-1 + h_z^2)\,\Delta\,\mathrm{Re}\, c_{22;\, 22} + h_z(1 - 2h_z^2)\,\mathrm{Im}\, c_{21;\, 21}$$
$$- h_z(1 - h_z^2)\,\mathrm{Im}\, c_{22;\, 22}],$$

$$\frac{dp}{dz} = (\nabla p)_0 \frac{1}{c_2} \left\{ 3h_x h_z \left(h_z^2 - \frac{1}{3} \right) \Delta c_{20;\, 20} \right.$$

$$+ 2h_x h_z \left[(1 - 2h_z^2)\,\Delta\,\mathrm{Re}\, c_{21;\, 21} - \frac{1}{2}(1 - h_z^2)\,\Delta\,\mathrm{Re}\, c_{22;\, 22} \right]$$

$$+ 2h_y h_z^2\,\mathrm{Im}\, c_{21;\, 21} + h_y(1 - h_z^2)\,\mathrm{Im}\, c_{22;\, 22}$$

$$\left. + \sqrt{5}\, h_x h_z c_{00;\, 20} \right\}. \quad (7.4)$$

Here h = H/H, $c_2 = c_{2m;\, 2m}^{(0)}$ and $(\nabla p)_0$ is the value

of the pressure gradient when there is no magnetic field. It follows from (7.3) and (7.4) that the longitudinal effect (dp/dx) is an even function of the magnetic field and proportional to ϵ^2. The maximum value of the odd effects are of the order of ϵ^2, while the coefficient $c_{00;20}$ is linear in the parameter ϵ. However, an experimental determination of the latter is made difficult by the fact that it only occurs in the expression for the pressure gradient in a direction at right angles to parallel walls.

The last, seventh, coefficient in (7.2), $\Delta c_{00;00}$, determines the change of the second viscosity ζ in a magnetic field and can be determined from measurements of sound absorption. The relative change of the second viscosity coefficient is linear in the parameter ϵ, which explains apparently the magnitude of the relative change of the sound absorption in a magnetic field[13], which may reach 30%.

8. THERMAL CONDUCTIVITY OF A DIATOMIC PARAMAGNETIC GAS

We can describe the change in the thermal conductivity tensor (3.18) in a magnetic field by the equations of section 6 with $l = l' = l_1 = 1$:

$$\Delta c_{10;10} = -{}^3/_5 \Lambda_{11} \operatorname{Re} f_{11}(\xi_1),$$

$$\Delta \operatorname{Re} c_{11;11} = -\Lambda_{11}\{{}^3/_5 \operatorname{Re} f_{11}(\xi_1) + {}^3/_{10} \operatorname{Re} f_{11}(2\xi_1)\},$$

$$\operatorname{Im} c_{11;11} = -\Lambda_{11}\{{}^3/_5 \operatorname{Im} f_{11}(\xi_1) + {}^3/_{10} \operatorname{Im} f_{11}(2\xi_1)\}.$$

These equations describe the Senftleben effect more exactly than the formulas found in [2] by the usual method of moments. The difference consists mainly in the existence of the effect which is odd in the magnetic field and which is connected with $\operatorname{Im} c_{11;11}$. In our earlier paper[2] this term was absent, as we had there chosen a model of the interaction in which during the collision neither the rotational moment **M** nor (and this is the main point) the component of the spin along **M**, i.e., the index σ, changed. The presence of the odd effect leads to the appearance of a heat current in a direction at right angles to **H** and ∇T.

Another (unimportant) difference is that the function (6.3) describes more correctly the region where the transition from the quadratic dependence on the effect to saturation takes place, than a function of the form (6.4), which, strictly speaking, is correct only for the case (2.4) of a nonparamagnetic gas.

9. DIFFUSION AND SELF-DIFFUSION OF A PARAMAGNETIC GAS

We now find the change in a magnetic field of the diffusion of a paramagnetic gas into another

gas and the self-diffusion of paramagnetic molecules. This problem is most simply solved for small concentrations of the diffusing gas. In that case we can neglect the non-equilibrium of the gas of the medium and the effect considered is described by the equation

$$\sqrt{2T/m}\,\mathbf{u}\nabla \ln c + \gamma[\mathbf{MH}]\partial\chi/\partial\mathbf{M} = -n\hat{I}\chi,$$

$$\hat{I}\chi = \int f_{0A}(\chi - \chi')W d\Gamma' d\Gamma_A d\Gamma_A',$$

$$f = cn f_0(1 + \chi), \quad f_A = n f_{0A}. \quad (9.1)$$

Here f_0 and f_{0A} are the equilibrium distribution functions of the diffusing gas and of the medium, normalized to unit density, and W is the probability that a paramagnetic molecule is scattered by a molecule of the medium.

The diffusion (self-diffusion) coefficient of a paramagnetic gas in a magnetic field is a tensorial quantity and is determined in terms of the diffusion current of the paramagnetic gas

$$j_i = -nD_{ik}(\nabla c)_k = cn\sqrt{2T/m}\int f_{0\chi}u_i\,d\Gamma. \quad (9.2)$$

Formula (9.1) and Eq. (9.2) have the same form as the corresponding Eqs. (3.2) and (3.13) which describe the thermal conductivity of a one-component gas in an external field. The behavior of the diffusion (self-diffusion) tensor D_{ik} in an external field is thus identically the same as the behavior of the thermal conductivity tensor (see (3.18) and Sec. 8):

$$D_{ik} = \frac{2T}{3mn}\{\delta_{ik}\operatorname{Re} c_{11;11} + h_ih_k(c_{10;10} - \operatorname{Re} c_{11;11})$$

$$+ h_{ik}\operatorname{Im} c_{11;11}\}. \quad (9.3)$$

The expressions for the coefficients $c_{1m;1m}$ are in the general case described by the expressions of Sec. 5 in which we must put

$$A_{1m} = Y_{1m}(\mathbf{u}). \quad (9.4)$$

In the model, used above in Sec. 6, the coefficients $c_{1m;1m}$ for the diffusion of a paramagnetic diatomic gas in a magnetic field are described by the formulae of Sec. 8. The value of the factor Λ_{11} for diffusion have the same order of magnitude ϵ^2 as for thermal conductivity.

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