

EFFECT OF ELECTRIC FIELD ON THE TRANSPORT COEFFICIENTS OF POLAR GASES

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Submitted to JETP editor July 5, 1966; resubmitted November 9, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 1880-1892 (December, 1966)

We consider the solution of the kinetic equation for a gas of polar molecules of the symmetric-top type or of diatomic polar molecules in the presence of a constant electric field. The heat conduction and viscosity tensors are determined. The possibility of the appearance of viscous stresses in a gas with a temperature gradient is pointed out.

1. INTRODUCTION

RECENTLY a number of experimental works have appeared devoted to the effect of an electric field on the transport coefficients of polar gases.^[1-3] The observed effect supplements the well known phenomenon of the change of transport coefficients in a magnetic field (the Senftleben effect).

The maximum value of the electric field is limited by the possibility of sparkover. At temperatures for which the problem can be considered classical, it is always true that

$$dE / T \ll 1. \tag{1.1}$$

By virtue of this, the polarization in kinetic phenomena in a polar gas plays no role and the effect can be connected only with the precession of the rotational moment in an electric field. In a paramagnetic gas, precession is caused by the action of a magnetic field on the molecule spin, which is rigidly connected with the rotating molecule in space. In a polar gas, the effect of the field on the molecule is described by the equations:

$$\dot{\mathbf{M}} = [d\mathbf{E}], \quad \dot{\mathbf{d}} = [\Omega\mathbf{d}], \tag{1.2}^*$$

Ω is the angular velocity and \mathbf{d} the dipole moment.

The precession, averaged over the rapid rotation of the molecule, leads to macroscopic results. In this connection molecules of the top type lead to qualitatively different results, for which the mean value of the dipole moment over the rapid rotation differs from zero in the absence of a field, and diatomic molecules in which the dipole moment is strictly perpendicular to the axis of rotation and its mean value over the rapid rotation is equal to zero. In the first case, the problem is similar to the problem of a paramagnetic gas in a magnetic field and the effect depends universally on dE/p (p is the pressure). In the second case,

*[dE] = $\mathbf{d} \times \mathbf{E}$.

the average value differs from zero only in the approximation quadratic in \mathbf{E} , and the effect depends on E^2/p . We note that observation of the effect in a gas with linear molecules requires much greater fields than in the case of molecules of the top type.

2. THE KINETIC EQUATION

We consider the kinetic phenomena in a gas of molecules of a symmetric top type. The rotational energy of a symmetric top is

$$H = \frac{M^2}{2I_A} + \frac{1}{2} \left(\frac{1}{I_C} - \frac{1}{I_A} \right) M_C^2, \tag{2.1}$$

where I_A, I_B, I_C ($I_B = I_A$) are the principal moments of inertia of the molecule, M is the angular momentum, and M_C the projection of M on the C axis.

We shall assume that the dipole moment is directed along the C axis. The motion of a dipole in a field is described by Eq. (1.2) where

$$\Omega = \frac{1}{I_A} \mathbf{M} + \left(\frac{1}{I_C} - \frac{1}{I_A} \right) (\mathbf{M}\mathbf{d}) \frac{\mathbf{d}}{d^2}. \tag{2.2}$$

As independent variables, we choose the angular momentum \mathbf{M} , the angle α between \mathbf{d} and \mathbf{M} , and the angle φ which describes the motion of the dipole in a plane perpendicular to \mathbf{M} . In these variables, the element of canonical phase space is

$$d\Gamma = d\alpha d\mathbf{M} d\cos\alpha d\varphi, \tag{2.3}$$

the energy of rotational motion,

$$H = \frac{M^2}{2I_A} \left[\left(\frac{I_A}{I_C} - 1 \right) \cos^2 \alpha + 1 \right], \tag{2.4}$$

and the dipole moment,

$$\mathbf{d} = d \left\{ \cos \alpha \frac{\mathbf{M}}{M} + \sin \alpha \cos \varphi \frac{\mathbf{E} - (\mathbf{M}\mathbf{E})\mathbf{M}/M^2}{E \sin \theta} + \sin \alpha \sin \varphi \frac{[\mathbf{M}\mathbf{E}]}{ME \sin \theta} \right\}, \quad \cos \theta = \mathbf{M}\mathbf{E}/ME, \tag{2.5}$$

It follows from (1.2) that

$$\begin{aligned} \dot{\alpha} &= -M^{-1}dE \cos \alpha \sin \varphi \sin \theta, \\ \dot{\varphi} &= \frac{M}{I_A} + \frac{2dE}{M} \cos \alpha \cos \theta - \frac{\cos^2 \alpha}{M \sin \alpha} \cos \varphi dE - \frac{\sin \alpha}{\sin \theta} \\ &\times \cos \varphi \cos^2 \theta \frac{dE}{M}. \end{aligned} \quad (2.6)$$

The kinetic equation is described in the following fashion:

$$\frac{\partial f}{\partial t} + \mathbf{u} \frac{\partial f}{\partial \mathbf{r}} + [\mathbf{dE}] \frac{\partial f}{\partial \mathbf{M}} + \dot{\alpha} \frac{\partial f}{\partial \alpha} + \dot{\varphi} \frac{\partial f}{\partial \varphi} = \left[\frac{\partial f}{\partial t} \right]_{\text{cr}}. \quad (2.7)$$

The equilibrium distribution function is equal to

$$f_0 = \text{const} \exp \{ -T^{-1}(mu^2/2 + H - \mathbf{dE}) \}. \quad (2.8)$$

If the departures from equilibrium are small, then

$$f = nf_0(1 + \chi), \quad \chi \ll 1. \quad (2.9)$$

The following homogeneous conditions must be imposed on the function χ [4]:

$$\begin{aligned} \int f_0 \chi d\Gamma &= 0, \quad \int f_0 \chi (mu^2/2 + H) d\Gamma = 0, \\ \int f_0 \chi \mathbf{u} d\Gamma &= 0, \quad \int f_0 \chi \mathbf{M} d\Gamma = 0. \end{aligned} \quad (2.10)$$

In the approximation that is linear in χ , Eq. (2.7) takes the form

$$N + [\mathbf{dE}] \frac{\partial \chi}{\partial \mathbf{M}} + \dot{\alpha} \frac{\partial \chi}{\partial \alpha} + \dot{\varphi} \frac{\partial \chi}{\partial \varphi} = -n \hat{I} \chi, \quad (2.11)$$

$$\begin{aligned} N &= \mathbf{u} \left(\frac{mu^2}{2T} + \frac{H}{T} - 4 \right) \nabla \ln T + \frac{m}{2T} \left(u_i u_k - \frac{1}{3} \delta_{ik} u^2 \right) \\ &\times \left(\frac{\partial V_{0k}}{\partial x_i} + \frac{\partial V_{0i}}{\partial x_k} - \frac{2}{3} \delta_{ik} \text{div} V_0 \right) \\ &+ \frac{1}{3T} \left(\frac{mu^2}{2} - H \right) \text{div} V_0, \\ n \hat{I} \chi &= -\frac{1}{f_0} \left[\frac{\partial f}{\partial t} \right]_{\text{coll}}. \end{aligned} \quad (2.12)$$

The condition (1.1) permits us to neglect the term dE/T in the equilibrium distribution function (2.3). In the zeroth approximation in dE/T , the function does not depend on the angle φ . Averaging (2.11) over this angle, we obtain

$$\begin{aligned} \frac{1}{n} N + \gamma(\sigma) [\mathbf{Me}] \frac{\partial \chi}{\partial \mathbf{M}} &= -\hat{I} \chi; \\ \gamma(\sigma) &= \frac{\sigma dE}{Mn}, \quad \sigma = \cos \alpha, \quad \mathbf{e} = \frac{\mathbf{E}}{E}. \end{aligned} \quad (2.13)$$

This same function $\gamma(\sigma)$ is obtained by going to the classical limit in the expression for the quantum-mechanical mean value of the dipole moment of a symmetric top. In the derivation of this equation, one must satisfy the inequality (1.1). On the other hand, the ratio of the precession frequency of the momentum dE/M to the mean frequency of collision $1/\tau$,

$$dE\tau / \bar{M} = dE\tau / \sqrt{2IT},$$

can be arbitrary. Equation (2.13) differs formally from the corresponding equation for a paramagnetic gas in the magnetic field [4] only in the fact that in our case the value of σ runs through a continuous range of values ($-1 \leq \sigma \leq 1$).

3. SOLUTION OF THE KINETIC EQUATION

We shall solve Eq. (2.13) by the method put forth in [4]. We transform to nondimensional variables which differ from the previous one by the respective factors $\sqrt{m/2T}$ and $\sqrt{1/2I_A T}$, and write out the Eq. (2.13) in spherical coordinates, choosing \mathbf{E} along the z axis:

$$\begin{aligned} \frac{N}{n} + \gamma(\sigma) \frac{\partial \chi}{\partial \varphi_M} &= -\hat{I} \chi, \quad \gamma = \frac{\sigma}{M} \frac{E}{p} \left(\frac{T}{I_A} \right)^{1/2} d, \\ N &= \sum a_{lm}^* A_{lm}, \quad A_{lm} = V_{lm}(\mathbf{u}) (u^2 + H - 4), \\ A_{2m} &= Y_{2m}(\mathbf{u}), \quad A_{00} = 1/6(u^2 - H). \end{aligned} \quad (3.1)$$

The explicit form of a_{lm} is given in [4]. We seek the function χ in the form

$$\chi = -\sum_{lm} a_{lm}^* \chi_{lm}. \quad (3.2)$$

Substituting (3.2) and (3.1), we find

$$\left(\hat{I} + \gamma(\sigma) \frac{\partial}{\partial \varphi_M} \right) \chi_{lm} = \frac{1}{n} A_{lm}. \quad (3.3)$$

We represent the collision integral \hat{I} in the form

$$\hat{I} = \hat{I}^{(0)} + \epsilon \hat{I}^{(1)}, \quad (3.4)$$

where $\hat{I}^{(0)}$ is the collision integral for Maxwell molecules. Then $\epsilon \hat{I}^{(1)}$ is determined by two factors: the departure of the central interacting force from Maxwellian, and the nonsphericity of the molecule.

It was shown in [5-7] that for a broad class of molecular potentials the difference between \hat{I} and $\hat{I}^{(0)}$ can be regarded as small. In polar atomic gases, if the nonsphericity is small, we can assume as before that $\epsilon \ll 1$. But the properties of $\hat{I}^{(1)}$ are essentially different, inasmuch as the noncentral forces lead to a mixing of the external and internal degrees of freedom, and also to the appearance of correlation between the directions of the velocity and the momenta of the colliding molecules. The separation of $\hat{I}^{(0)}$ from \hat{I} is convenient in that the eigenfunctions $\psi_n(\mathbf{u})$ and the eigenvalues λ_n of the operator $\hat{I}^{(0)}$ are known. [8,9] Since \hat{M} is not changed by collisions with central forces, $\hat{I}^{(0)}$ possesses the following set of orthogonal eigenfunctions $\{\psi_n\}$ and eigenvalues $\{\lambda_n\}$:

$$\begin{aligned} \hat{I}^{(0)}\psi_n &= \lambda_n^{(0)}\psi_n, \quad \psi_n = \psi_{r_1 l_1 m_1; r_2 l_2 m_2} = L_{r_1}^{l_1+1/2}(u^2)L_{r_2}^{l_2+1/2}(u^2) \\ &\quad \times (H)Y_{l_1 m_1}(\mathbf{u})Y_{l_2 m_2}(\mathbf{M}), \\ \lambda_n^{(0)} &= \lambda_{r_1 l_1; r_2 l_2} = \alpha_{r_1 l_1} \delta_{r_2 0} \delta_{l_2 0} + \beta_{r_1 l_1} (1 - \delta_{r_2 0} \delta_{l_2 0}), \\ \alpha_{r l} &= \int_0^\pi \left[1 + \delta_{r 0} \delta_{r l} - \left(\cos \frac{\theta}{2} \right)^{2r+l} P_l \left(\cos \frac{\theta}{2} \right) \right. \\ &\quad \left. - \left(\sin \frac{\theta}{2} \right)^{2r+l} P_l \left(\sin \frac{\theta}{2} \right) \right] d\theta \sin \theta F(\theta), \\ \beta_{r l} &= \int_0^\pi \left[1 - \left(\cos \frac{\theta}{2} \right)^{2r+l} P_l \left(\cos \frac{\theta}{2} \right) \right] d\theta \sin \theta F(\theta), \\ g d\sigma^{(0)} &= F(\theta) \sin \theta d\theta, \end{aligned} \tag{3.5}$$

where L_n^α are the normalized Laguerre polynomials. We use the notation

$$\hat{K}^{-1} = \hat{I}^{(0)} + \gamma(\sigma) \frac{\partial}{\partial \varphi_M} + \varepsilon \hat{I}_0^{(4)}, \tag{3.6}$$

where

$$\begin{aligned} \hat{I}_0^{(4)}\psi_n &= \begin{cases} \varepsilon \lambda_0 \psi_n, & \text{if } n = (000, r_2 l_2 m_2) \text{ or } (100, 000), \\ 0, & \text{if } n \neq (000, r_2 l_2 m_2) \text{ or } (100, 000) \end{cases} \\ \lambda_0 &= (\psi_0, I^{(4)}\psi_0), \quad \psi_0 = L_1^{1/2}(u^2). \end{aligned}$$

Here and below the scalar product is defined by the expression

$$(\psi, f) = \int d\Gamma f_0 \psi^* f. \tag{3.7}$$

Then

$$\begin{aligned} \hat{K}\psi_n &= \frac{\psi_n}{\lambda_n + im_2 \gamma(\sigma)}, \\ \lambda_n &= \begin{cases} \varepsilon \lambda_0 & \text{for } n = (000, r_2 l_2 m_2) \text{ if } (100, 000) \\ \lambda_n^{(0)} & \text{for } n \neq (000, r_2 l_2 m_2) \text{ if } (100, 000) \end{cases}. \end{aligned} \tag{3.8}$$

With accuracy up to terms of order ε^2 , we find from (3.3)

$$\begin{aligned} \chi_{lm} &= [\hat{K} - \varepsilon \hat{K} I_1 \hat{K} + \varepsilon^2 \hat{K} I_1 \hat{K} I_1 \hat{K}] A_{lm}, \\ \hat{I}_1 &= \hat{I}^{(1)} - \hat{I}_0^{(1)} \end{aligned} \tag{3.9}$$

The transfer coefficients are determined by integrals of the type

$$c_{lm, l'm} = (A_{lm}, \chi_{l'm}). \tag{3.10}$$

Then, substituting the formal solution of the kinetic equation (3.9), we get

$$c = c^{(0)} + c^{(1)} + c^{(2)},$$

$$\begin{aligned} c_{nl, l'm}^{(0)} &= (A_{lm}, \hat{K} A_{l'm}), \quad c_{lm, l'm}^{(1)} = -\varepsilon \operatorname{Re} (A_{lm}, \hat{K} I_1 \hat{K} A_{l'm}), \\ c_{lm, l'm}^{(2)} &= \varepsilon^2 \operatorname{Re} (A_{lm}, \hat{K} I_1 \hat{K} I_1 \hat{K} A_{l'm}). \end{aligned} \tag{3.11}$$

The values of A_{lm} do not depend on the direction of \mathbf{M} ; therefore $C_{lm, l'm}^{(0)}$ and $C_{lm, l'm}^{(1)}$ do not depend on the external field. Recognizing that for

any f and ψ we have

$$(f, \hat{K}\psi) = (\hat{K}^* f, \psi), \quad (f, \hat{I}^{(1)}\psi) = (\hat{I}^{(1)} f, \psi), \tag{3.12}$$

we get for $c^{(2)}$

$$c_{lm, l'm}^{(2)} = (\hat{I}_1 \hat{K} A_{lm}, \hat{K} I_1 \hat{K} A_{l'm}). \tag{3.13}$$

It follows from the scalar nature of the integral \hat{I}_1 that

$$\begin{aligned} \hat{I}_1 Y_{lm}(\mathbf{u}) L_r^{l+1/2}(u^2) L_p^{1/2}(H) \\ = \sum_{l_1 l_2} \sum_{m_1 m_2} C_{l_1 m_1, l_2 m_2}^{lm} Y_{l_1 m_1}(\mathbf{u}) Y_{l_2 m_2}(\mathbf{M}) L_{r_1}^{l_1+1/2}(u^2) a_{r p r_1}^{l_1 l_2}, \end{aligned} \tag{3.14}$$

where $C_{l_1 m_1, l_2 m_2}^{lm}$ are the Clebsch-Gordan coefficients, l_2 takes on even values, and $a_{r p r_1}^{l_1 l_2}(M^2, \sigma)$, as a function of σ , is even for even $l - l_1$ and odd in the opposite case. The presence in (3.14) of terms with odd values of the difference $l - l_1$ is the most significant difference of the polar gas from the paramagnetic gas. This is associated with the fact that the quantity $\sigma = d\mathbf{M}/dM$ is a pseudoscalar and an odd function of it changes sign upon inversion.

Substituting (3.14) and (3.13), we find that the change of $c_{lm, l'm}$ in the field is determined by the following formulas:

$$\Delta c_{lm, l'm} = c_{lm, l'm}^{(2)}(E) - c_{lm, l'm}^{(2)}(0),$$

$$\begin{aligned} \Delta c_{lm, l'm} &= -\varepsilon^2 \delta_{mm'} \sum_h A_{lm}^{r p} A_{l'm}^{r' p'} \sum_{m_1+m_2=m} C_{l_1 m_1, l_2 m_2}^{lm} C_{l_1 m_1, l_2 m_2}^{l'm} \\ &\quad \times \frac{1}{\lambda_n^{(0)}} \frac{1}{\lambda_{n'}^{(0)}} \frac{1}{\beta_{r_1 l_1}} f_{km_2}; \\ \varkappa &= (r_1 l_1 p l_2, r' l' p'), \quad n = (r l m, p 00), \quad n' = (r' l' m', p' 00), \end{aligned}$$

$$f_{km_2} = \left(a_{r p r_1}^{l_1 l_2}, \frac{m_2^2 \xi_{r_1 l_1}^2 \sigma^2}{1 + m_2^2 \xi_{r_1 l_1}^2 \sigma^2 / M^2} M^{2l_2-2} a_{r' p' r_1}^{l_1' l_2'} \right), \tag{3.15}$$

$$\xi_{r_1 l_1} = \frac{dE \sqrt{T}}{p \beta_{r_1 l_1} \sqrt{I_A}}, \quad A_{lm} = \sum_{r p} A_{lm}^{r p} L_r^{l+1/2}(u^2) L_p^{1/2}(H).$$

The functions f_{km_2} are monotonically increasing functions of the ratio E/p . We find the asymptotic behavior of f_{km_2} in the region of small and large fields.

Inasmuch as f_{km_2} is a function of the type

$$\int_0^\infty \int_0^\infty e^{-x^2-y^2} \omega(x, y) dx dy,$$

where $x = M\sqrt{1 - \sigma^2}$, $y = M\sigma$, while $\omega(x, y)$ vanishes for $x = 0$ or $y = 0$, and increases at infinity much more slowly than exponentially, the

most significant regions of integration are those values of (x, y) close to $(1, 1)$, which corresponds to (M, σ) in the vicinity of the point

$$(M_0, \sigma_0) = \left(\frac{I_A^2 + I_C^2}{I_A^2}, \frac{I_C}{\sqrt{I_A^2 + I_C^2}} \right).$$

Therefore the condition of smallness of the field presupposes smallness (relative to unity) of the expression $m_2^2 \xi_{r_1} l_1^2 \sigma^2 / M^2$ at the point (M_1, σ_0) , that is, the condition

$$\xi_{r_1 l_1} \ll (I_A^2 + I_C^2) / I_A^{5/2} I_C \sqrt{I_A + I_C}; \quad (3.16)$$

here,

$$f_{hm_2} = m_2^2 \xi_{r_1 l_1}^2 (a_{r p r_1}^{l_1 l_2} M^{2l_2-2}, a_{r' p' r_1}^{l_1 l_2}). \quad (3.17)$$

and consequently, $|\Delta^c|$ at small E increases as $(E/p)^2$.

In the region of large fields, that is, for

$$\xi_{r_1 l_1} \gg \frac{(I_A^2 + I_C^2)^2}{I_A^{5/2} I_C \sqrt{I_A + I_C}}, \quad (3.18)$$

we have

$$f_{hm_2} = (a_{r p r_1}^{l_1 l_2} M^{l_2}, a_{r' p' r_1}^{l_1 l_2} M^{l_2}) \quad (3.19)$$

and consequently the quantities Δc reach saturation.

It is seen from Eq. (3.15) that the change of the kinetic coefficients in the field is explained by the presence in (3.14) of terms with $l_2 \neq 0$. The dependence of $a_{r p r_1}^{l_1 l_2}$ on σ and M^2 has no effect on the qualitative behavior of $\Delta c l_{m_1} l'_{m'}$. Determination of the specific form of $a_{r p r_1}^{l_1 l_2}$ requires a knowledge of the detailed structure of the collision integral. Inasmuch as there does not exist any detailed evidence at the present time as to the structure of the scattering cross section of monatomic molecules, we limit ourselves, for the determination of the dependence of the transport phenomena on the electric field, to the simplest model representations of the form of the quantities a , similar to what was done in the case of the magnetic field^[4].

4. THERMAL CONDUCTIVITY

The thermal conductivity tensor^[4] in the electric field is equal to

$$\kappa_{ih} = \kappa \delta_{ih} + \kappa' \frac{E_i E_h}{E^2} = \kappa_h \delta_{ih}, \quad (4.1)$$

$$\kappa_z = 1/3 (A_{10}, \chi_{10}), \quad \kappa_x = \kappa_y = 1/3 \text{Re} (A_{11}, \chi_{11}).$$

In the qualitative description of the phenomenon, we shall assume that a_{100}^{112} and a_{100}^{112} are independent of M^2 and σ . In the expansion (3.14), terms

with $l_1 > 1$ and $l_2 > 2$ describe the same correlation between u and M in the collision integral as with $l_1 = 1$, $l_2 = 2$. Therefore it is hardly likely that they would be significant.

Consequently, we can limit ourselves for $I_1 A_{1m}$ to terms with $l_1 = 1$ and $l_2 = 2$. Then, for

$$\Delta \kappa_h = \kappa_h(E) - \kappa_h(0) \quad (4.2)$$

we obtain

$$\Delta \kappa_z = \frac{3}{10} \frac{a^2 e^2}{\beta_{01}} f_1(\xi),$$

$$\Delta \kappa_x = \Delta \kappa_y = \frac{a^2 e^2}{\beta_{01}} \left[\frac{3}{20} f_1(\xi) + \frac{3}{10} f_2(\xi) \right],$$

$$a = \frac{\sqrt{5/2}}{\alpha_{11}} a_{100}^{112} + \frac{\sqrt{3/2}}{\beta_{01}} a_{010}^{112},$$

$$f_1(\xi) = \frac{1}{\sqrt{\pi}} \int_0^1 \int_0^\infty \frac{4 \xi^2 \sigma^2 M^4 \sqrt{I_A / I_C}}{1 + M^{-2} \sigma^2 \xi^2} \times \exp \left\{ -M^2 \left[1 + \sigma^2 \left(\frac{I_A}{I_C} - 1 \right) \right] \right\} dM d\sigma, \quad (4.3)$$

$$f_2(\xi) = f_1(2\xi), \quad \xi = dE \sqrt{T} / p \beta_{01} \sqrt{I_A}.$$

In the vicinity of (3.16),

$$f_1(\xi) = \xi^2 w_1(I_A / I_C),$$

$$w_1 = \frac{3}{2} \left(\left| \frac{I_A}{I_C} - 1 \right| \right)^{-1/2} \left| \frac{I_C}{I_A} - \left(\frac{I_C}{I_A} \right)^2 \right|, \quad (4.4)$$

$$\Delta \kappa_z = \frac{3}{10} \frac{a^2}{\beta_{01}} \xi^2 w_1, \quad \Delta \kappa_x = \Delta \kappa_y = 3/2 \Delta \kappa_z.$$

Upon satisfaction of (3.18), that is, in the region of E , we get

$$f_1(\infty) = f_2(\infty), \quad \Delta \kappa_x = \Delta \kappa_y = 3/2 \Delta \kappa_z. \quad (4.5)$$

5. FIRST AND SECOND VISCOSITY

The viscous-stress tensor^[4] can be expressed in terms of the quantity (3.11) by means of the coefficients of (3.2):

$$\sigma_{ih} = -2T \int d\Gamma f_0 u_i u_h \chi = \eta_{ih p q} \left(\frac{\partial V_{0q}}{\partial x_p} + \frac{\partial V_{0p}}{\partial x_q} \right), \quad (5.1)$$

$$\eta_{ih p q} = 2T \sum_{\substack{lm \\ l'm'}} t_{ik}^{lm} (t_{pq}^{l'm'})^* c_{lm, l'm'}, \quad l, l' = 0, 2. \quad (5.2)$$

In the expansion (3.14) we retain for $I_1 Y_{2m}(u)$ only terms with $l_2 = 2$. The presence of the term $a_{000}^{202} Y_{2m}(M)$, which has a significant effect on the viscosity, means that there should be partial saturation at fields of the order of $E_{\text{therm}}/\epsilon$, where E_{therm} is the field for which saturation is achieved in the experiment on the thermal conductivity.

A similar result should occur for a magnetic field. But in the case of a magnetic field, this is

not the case, as experiment has shown.^[10] Therefore, one must assume that a_{000}^{202} is close to zero, and assume as a simple model that

$$\begin{aligned} \hat{I}_1 Y_{2m}(\mathbf{u}) = & b_1 \sum_{m=m_1+m_2} C_{2m_1, 2m_2}^{2m} Y_{2m_1}(\mathbf{u}) Y_{2m_2}(\mathbf{M}) \\ & + b_2 Y_{2m}(M) \left(u^2 - \frac{3}{2} \right) \frac{1}{\sqrt{6}} + i b_3 \sigma \sum_{m=m_1+m_2} C_{1m_1, 2m_2}^{2m} Y_{1m_1} \\ & \times (\mathbf{u}) Y_{2m_2}(\mathbf{M}), \end{aligned} \quad (5.3)$$

$$\hat{I}_1(u^2 - H) = g_1 \sum_m C_{2m, 2-m}^{00} Y_{2m}(\mathbf{M}) Y_{2-m}(\mathbf{u}).$$

In these expressions, the last terms reflect the specific polar gas (pseudoscalar character of σ). For the change in viscosity, we have:

$$\begin{aligned} \Delta c_{2m, 2m'} = & \varepsilon^2 \delta_{mm'} \left\{ \frac{2b_1^2}{\alpha_{02}^2 \beta_{02}} \sum_{\substack{m=m_1+m_2 \\ m_2 > 0}} (C_{2m_1, 2m_2}^{2m})^2 f_{m_2}(\xi_1) \right. \\ & \left. + \frac{b_2^2}{\alpha_{02}^2 \beta_{10}} f_{|m|}(\xi_2) + \frac{b_3^2}{\alpha_{02}^2 \beta_{01}} \sum_{m=m_1+m_2} (C_{1m_1, 2m_2}^{2m})^2 f_{|m_2|}(\xi_3) \right\}, \\ c_{0000} = & \frac{2g_1^2}{\lambda_0^2 \beta_{02}} \sum_{m>0} (C_{2m, 2-m}^{20})^2 f_{m+2}(\xi_1), \end{aligned} \quad (5.4)$$

$$c_{2m00} = c_{002m} = \varepsilon \delta_{m0} \frac{1}{\lambda_0} \frac{2b_1 g_1}{\alpha_{02} \beta_{02}} \sum_{m>0} \frac{1}{5} f_{m+2}(\xi_1),$$

$$\xi_1 = \frac{dE \sqrt{T}}{p \beta_{02} \sqrt{I_A}}, \quad \xi_2 = \frac{dE \sqrt{T}}{p \beta_{10} \sqrt{I_A}}, \quad \xi_3 = \frac{dE \sqrt{T}}{p \beta_{01} \sqrt{I_A}},$$

$f_1(\xi)$ and $f_2(\xi)$ are defined in (4.3),

$$\begin{aligned} f_3(\xi) = & \frac{1}{\sqrt{\pi}} \int_0^\infty \int_0^1 \frac{4\xi^2 \sigma^4 M^4 \sqrt{I_A/I_C}}{1 + M^{-2} \sigma^2 \xi^2} \\ & \times \exp \left\{ -M^2 \left[1 + \sigma^2 \left(\frac{I_A}{I_C} - 1 \right) \right] \right\} dM d\sigma, \end{aligned}$$

$$f_4(\xi) = f_3(2\xi).$$

6. CROSSING EFFECT IN THE PHENOMENA OF VISCOSITY AND THERMAL CONDUCTIVITY

We have shown in Sec. 3 that in polar gases the invariance of the collision operator relative to time reversal makes it possible for the perturbed distribution function to possess terms with any parity relative to the velocity. This leads to the result that the following effect can be observed in principle in an electric field: by creating a temperature gradient one can obtain a change of the viscosity tensor, and conversely.

Let us consider this phenomenon. Let there be some ∇T , where the angle between ∇T and \mathbf{E} is

equal to θ . Then (the OX axis is in the plane of \mathbf{E} and ∇T) in (2.12)

$$\begin{aligned} N = & |\nabla T| \left\{ -i \cos \theta \sqrt{1/3} Y_{10}(\mathbf{u}) \right. \\ & \left. + i \sin \theta \sqrt{1/6} [Y_{11}(\mathbf{u}) + Y_{1-1}(\mathbf{u})] \right\} \left(\frac{mu^2}{2T} + \frac{M^2}{2IT} - 4 \right). \end{aligned} \quad (6.1)$$

Change of σ_{ik} in an electric field is described by the tensor

$$\sigma_{ik} = -2T \int u_i u_k f_0 \chi d\Gamma. \quad (6.2)$$

It is obvious that all the components σ_{ik} vanish, except $\sigma_{XZ} = \sigma_{ZX}$ and σ_{AA} . We calculate σ_{XZ} with accuracy up to terms of the order of ε^2 . Using (3.12), we have

$$\begin{aligned} \sigma_{XZ} = & \frac{\varepsilon^2}{\alpha_{02}} T |\nabla T| \left\{ [\sqrt{1/20} f(2\xi_1) + \sqrt{1/5} f(\xi_1)] ab_3 \right. \\ & \left. + [\sqrt{1/20} f(2\xi_2) + \sqrt{1/5} f(\xi_2)] bb_1 \right\} \sin \theta. \end{aligned} \quad (6.3)$$

Here

$$f(\xi) = (M^3, \sigma^2 \xi (1 + M^{-2} \sigma^2 \xi^2)^{-2}),$$

$$\xi_1 = \frac{dE \sqrt{T}}{p \beta_{01} \sqrt{I_A}}, \quad \xi_2 = \frac{dE \sqrt{T}}{p \beta_{02} \sqrt{I_A}},$$

$$b = \left(\sum_m C_{2m, 2-m}^{10} Y_{2m}(\mathbf{u}) Y_{2m}(\mathbf{M}) \sigma, \hat{I}_1 \hat{K} Y_{10}(\mathbf{u}) (u^2 + M^2 - 8) \right).$$

Similarly, in the case of viscous flow, that is, for $\partial V_{0i}/\partial x_k \neq 0$, heat flow arises:

$$\begin{aligned} Q_i = & T \sqrt{\frac{2T}{m}} e_{ikh} \left(\frac{\partial V_{0z}}{\partial x_h} + \frac{\partial V_{0h}}{\partial z} \right) \\ & \times \left\{ [\sqrt{1/20} f(2\xi_1) + \sqrt{1/5} f(\xi_1)] ab_3 + [\sqrt{1/20} f(2\xi_2) \right. \\ & \left. + \sqrt{1/5} f(\xi_2)] bb_1 \right\}. \end{aligned} \quad (6.4)$$

We note that b and b_3 differ from zero only when the interaction between the molecules includes terms which single out the direction d (for example, dipole-dipole interaction).

7. DIATOMIC LINEAR MOLECULE

For the description of the rotational motion in the case of a diatomic linear molecule, we choose as an independent variable the three components of the angular momentum and the angle φ which characterizes the position of the molecules in a plane perpendicular to \mathbf{M} . Then the kinetic equation for small departures of χ from equilibrium follows from (2.12) with $\alpha = \pi/2$, that is, it takes the form

$$\frac{N}{n} + \cos \varphi \hat{A}_1 \chi + \sin \varphi \hat{A}_2 \chi + \frac{1}{n} \left(\frac{M}{I} - \frac{dE}{M} \frac{\cos^2 \theta}{\sin \theta} \cos \varphi \right) \times \frac{\partial \chi}{\partial \varphi} = -\hat{I} \chi, \quad (7.1)$$

$$\hat{A} = \frac{d}{n} \cot \theta \frac{1}{M} [\mathbf{ME}] \frac{\partial}{\partial M}, \quad \hat{A}_2 = \frac{d}{n} \frac{[\mathbf{ME}] \mathbf{E}}{ME \sin \theta} \frac{\partial}{\partial M}.$$

We seek a solution of (7.1) in series form:

$$\chi = \chi_0 + \sum_{n=1}^{\infty} (a_n \cos n\varphi + b_n \sin n\varphi). \quad (7.2)$$

Since

$$\frac{M}{I} \frac{\partial \chi}{\partial \varphi} \sim \sqrt{\frac{T}{I}} \chi, \quad \hat{A}_1 \chi, \hat{A}_2 \chi \sim \frac{dE \chi}{\sqrt{IT}},$$

we get $a_n, b_n \sim (dE/T)^n$. Therefore, we limit ourselves in the expansion (7.2) to terms with $n = 0, 1$, that is, we assume that

$$\chi = \chi_0 + \chi_1 \cos \varphi + \chi_2 \sin \varphi. \quad (7.3)$$

We substitute (7.3) in (7.2). Multiplying the resultant equation successively by 1, $\cos \varphi$, and $\sin \varphi$, and integrating from 0 to 2π , we have

$$\begin{aligned} \frac{N}{n} + \frac{1}{2} (\hat{A}_1 \chi_1 + \hat{A}_2 \chi_2) - \frac{1}{2} \frac{dE \cos^2 \theta}{M \sin \theta} \chi_2 \\ = -(\hat{I}_{00} \chi_0 + \hat{I}_{01} \chi_1 + \hat{I}_{02} \chi_2), \\ \hat{A}_1 \chi_0 + I^{-1} M \chi_2 = -(\hat{I}_{11} \chi_1 + \hat{I}_{12} \chi_2 + \hat{I}_{10} \chi_0), \\ \hat{A}_2 \chi_0 + I^{-1} M \chi_1 = -(\hat{I}_{21} \chi_1 + \hat{I}_{22} \chi_2 + \hat{I}_{20} \chi_0). \end{aligned} \quad (7.4)$$

In (7.4),

$$\hat{I}_{ik} \chi_k = \frac{1}{2\pi} \int_0^{2\pi} \psi_i \hat{I} \psi_k \chi_k d\varphi, \quad (7.5)$$

$$\psi_0 = 1, \quad \psi_1 = \cos \varphi, \quad \psi_2 = \sin \varphi.$$

with accuracy to terms of the order $(dE/T)^2$, we find

$$\chi_2 = -\frac{I}{M} (\hat{A}_1 \chi_0 + \hat{I}_{10} \chi_0), \quad \chi_1 = \frac{I}{M} (\hat{A}_2 \chi_0 + \hat{I}_{20} \chi_0). \quad (7.6)$$

Substituting (7.6) in the first equation of (7.5), and noting that the terms

$$\hat{I}_{01} \chi_1, \quad \hat{I}_{02} \chi_2, \quad M^{-1} I \hat{A}_2 \hat{I}_{20} \chi_0, \quad M^{-1} I \hat{A}_1 \hat{I}_{10} \chi_0$$

are small in comparison with $\hat{I}_{00} \chi_0$, we obtain

$$\frac{1}{n} N + \gamma [\mathbf{M}, \mathbf{e}] \frac{\partial \chi_0}{\partial \mathbf{M}} = -\hat{I}_{00} \chi_0, \quad \gamma = \frac{3}{2} \frac{d^2 I E^2}{n M^4} (\mathbf{eM}). \quad (7.7)$$

This equation can also be obtained by going to the classical limit in the expression for the quantum-mechanical mean value of \mathbf{M} , computed in an approximation quadratic in \mathbf{E} . Equation (7.7) is similar to (2.13) with the following important differences. First, we now have $\sim E^2/p$. Second, this equation does not contain the independent variable

σ , whose role in (7.7) was played by the projection of the angular momentum on the electric field. In this connection, the expansion corresponding to (3.14) does not contain terms with odd values of $l - l_1$. Integration in the case of linear molecules is carried out over the phase volume:

$$d\Gamma = du d\mathbf{M} / M.$$

Third, the coefficient γ possesses an essential singularity as $M \rightarrow 0$, which leads (as we shall see below) to a nonanalytic dependence of the effect at small fields.

Keeping these remarks in mind, one can use the results obtained above for the description of the effect of the electric field on the transport phenomenon in gases of polar linear (diatomic) molecules.

Within the framework of the interaction model used in the case of the symmetric gyroscope, we get for the problem of thermal conductivity:

$$\begin{aligned} \Delta \kappa_z &= \frac{3}{10} \frac{a^2 e^2}{\beta_{01}} f_5(\xi), \\ \Delta \kappa_x = \Delta \kappa_y &= \frac{3}{10} \frac{a^2 e^2}{\beta_{01}} \left[\frac{1}{2} f_5(\xi) + f_6(\xi) \right], \\ \varepsilon &= \frac{d^2 E^2}{p \beta_{01}} \frac{1}{\sqrt{IT}}, \quad a = \frac{1}{\alpha_{11}} \sqrt{\frac{5}{2}} a_{100}^{112} + \frac{1}{\beta_{01}} \sqrt{\frac{3}{2}} a_{010}^{112}, \\ f_5(\xi) &= \int_0^\infty \int_0^\pi \frac{15}{2} \frac{e^{-M^2} dM}{M} \frac{\xi^2 \cos^4 \theta \sin^3 \theta d\theta}{[1 + \xi^2 \cos^2 \theta / M^6]}, \\ f_6(\xi) &= \int_0^\infty \int_0^\pi \frac{15}{2} \frac{e^{-M^2} dM}{M} \frac{\xi^2 \cos^2 \theta \sin^5 \theta d\theta}{1 + 4\xi^2 \cos^2 \theta / M^6}. \end{aligned} \quad (7.8)$$

In the region of small fields, that is, for

$$\xi \ll 1, \quad (7.9)$$

we have

$$f_5(\xi) = -^{2/7} \xi^2 \ln \xi, \quad f_6(\xi) = -^{8/21} \xi^2 \ln \xi. \quad (7.10)$$

Consequently, in this case,

$$\Delta \kappa_z = -\frac{3}{35} \frac{a^2 e^2}{\beta_{01}} \xi^2 \ln \xi, \quad \Delta \kappa_x = \Delta \kappa_y = \frac{11}{6} \Delta \kappa_z. \quad (7.11)$$

For large E , that is, for $\xi \gg 1$, we obtain

$$\begin{aligned} f_5(\xi) = f_6(\xi) &= \frac{15}{4}, \quad \Delta \kappa_z = \frac{9}{4} \frac{a^2 e^2}{\beta_{01}}, \\ \Delta \kappa_x = \Delta \kappa_y &= \frac{3}{2} \Delta \kappa_z. \end{aligned} \quad (7.12)$$

It is easy to see that Eqs. (5.7) for the viscosity will be valid also in this case if $f_1(\xi)$ and $f_2(\xi)$ are replaced by $f_5(\xi)$ and $f_6(\xi)$, respectively, where

$$\xi_1 = \frac{d^2 E^2}{p\beta_{02}\sqrt{IT}}, \quad \xi_2 = \frac{d^2 E^2}{p\beta_{10}\sqrt{IT}},$$

and b_3 and g_2 are equal to zero.

We note the following result. For small I_C/I_A , as follows from Sec. 3, the change in the transfer coefficients is fundamentally determined by the quantity $(I_C/I_A)(dE/p\beta_{r1})$. Therefore the molecule can be regarded as linear only if $I_C/I_A \ll dE/T$.

8. DISCUSSION OF THE RESULTS

The electric and magnetic effects in gases have a common physical origin: the precession of the angular momentum around the field. The mathematical expression for this is the term on the left side of the kinetic equation (2.13)

$$\dot{M}\partial f/\partial M = \gamma\partial f/\partial\varphi,$$

where φ is the angle of rotation around the field, and γ does not depend on φ . Two conclusions follow from this: First, there is a characteristic parameter which completely determines the phenomenon: $\xi = E^\alpha/p$, α is equal to 1 or 2; second, thanks to the fact that both operators included in (2.13) possess clearly expressed symmetry properties, the symmetry properties of the system play a significant role. These properties are different for a gas in an electric and in a magnetic field. We recall that a molecule in a magnetic field is characterized by velocity (\mathbf{u}), angular momentum (\mathbf{M}), and projection of the magnetic moment on the angular momentum of the molecule (s)^[4]. Relative to rotation and reflection in space, \mathbf{u} is a vector, \mathbf{M} a pseudovector and s a scalar. In an electric field, the corresponding quantities are \mathbf{u} , \mathbf{M} , and the pseudoscalar σ —the projection of the dipole moment on the angular momentum.

Certain components of the transport tensor are insensitive to this difference and behave in the same manner regardless of the type of molecule and field, changing monotonically and reaching saturation at high fields. But for other components, this connection is decisive and, just as in a magnetic field^[4], the scalar character of s determines an effect which is odd in H , and the pseudoscalar character of σ makes possible the existence of the crossing effect. In this connection it should be pointed out that Beenakker and Knaap^[12] suggested the existence of the crossing effect in a magnetic field at a definite interaction between the molecules. It is necessary to emphasize that symmetry considerations forbid this effect in a magnetic field no matter how the interaction between the molecules is chosen.

Borman and the Nikolaevs also investigated transport phenomena in a polar diatomic gas.^[13] It should be noted that the variational method used by them leads to unlikely results both in the region of high and of low fields.

In conclusion, we note the difficulty in principle which arises in considering the behavior of a diatomic polar gas in an electric field if the coefficients with $l_1 = r_1 = 0$, $l_2 \neq 0$ are different from zero. In this case, contradictions arise in the problem of first viscosity with the requirement

$$\bar{M} = \int M f_0 \chi d\Gamma.$$

We find it difficult to say whether this contradiction is connected with the fact that in the given case the electric field produces a macroscopic rotation of the gas or with the approximate character of the initial kinetic equation.

The authors express their gratitude to L. L. Gorelik and Yu. M. Kagan for interest in the research.

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