EFFECT OF A VARYING FIELD ON TRANSPORT PHENOMENA IN POLYATOMIC GASES

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The transfer coefficients for polyatomic gases in varying electric and magnetic fields are obtained by solving the kinetic equation for a gas with rotational degrees of freedom. The time dependence of the transfer coefficients in varying fields is oscillatory and the oscillation spectrum consists of frequencies that are multiples of the field frequency. The dependence of the time-averaged viscosity and thermal-conductivity coefficients on the field frequency is determined. Comparison of the dependence with the experimental data yields the magnitude of the eigenvalue of the collision integral.

A frequency dependence of the coefficient of thermal conductivity of the polar gas NF_3 in an alternating electric field was recently observed experimentally.[1] The relative change of the thermal-conductivity coefficient ($\epsilon = -\Delta\kappa/\kappa$) decreases noticeably at field-frequencies close to the molecule precession frequency. The effect was connected with a decrease in the angle of rotation of the vector of the rotation moment of a nonspherical molecule precessing about the field direction when the field frequency is increased. It was shown that the change in the thermal conductivity coefficient ϵ_ν/ϵ_0 (ϵ_0—relative change of the thermal conductivity coefficient at the frequency $\nu = 0$) is a function of any two ratios made up of the following three quantities: the field intensity E, the pressure P, and the frequency ν. In the region of small field values, i.e., at $E/P \ll 1$, the value of ϵ_ν/ϵ_0 is determined only by the ratio ν/P.

In this paper we consider the influence of an alternating field on transport phenomena in gases theoretically. The kinetic equation for a gas with rotational degrees of freedom in an alternating field is solved by the method developed in [2]. We investigate in detail the thermal conductivity and the viscosity of a polar gas with symmetrical-top molecules having nearly equal moments of inertia ($I_1 = I_2 \approx I_3$) in an alternating electric field, and of a paramagnetic gas with linear molecules in an alternating magnetic field.

The linearized kinetic equation for the polar gas with symmetrical-top molecules having nearly equal moments of inertia ($I_1 = I_2 \approx I_3$) and a dipole moment **d** in an alternating field $\mathbf{E} = \mathbf{E}_0 \cos \omega t$ is[2]

$$\frac{\partial\chi}{\partial t} + N + \gamma\cos\omega t\frac{\partial\chi}{\partial\varphi_M} = -\hat{I}\chi, \tag{1}$$

where

$$f = f_0(1+\chi), \quad f_0 = n\exp(-U^2 - M^2); \tag{2a}$$

$$\gamma = dE_0\sigma/M, \quad \sigma = \cos(\widehat{\mathbf{dM}}); \tag{2b}$$

$$N = \sum_{l,m} a_{lm}{}^* A_{lm}, \quad A_{1m} = (U^2 + M^2 - c_p)Y_{1m}(\mathbf{U}),$$
$$A_{2m} = Y_{2m}(\mathbf{U}), \quad A_{00} = {}^2/_3U^2 - \frac{1}{c_v}(U^2 + M^2); \tag{2c}$$

$$\hat{I}\chi = \int f_{01}[(\chi + \chi_1)W - (\chi' + \chi_1')W']\,d\Gamma_1\,d\Gamma'\,d\Gamma_1',$$
$$d\Gamma = \pi^{-3}U^2dUd\Omega_U M^2dMd\Omega_M. \tag{2d}$$

The quantities a_{lm} are given in [2]; U and M are the dimensionless velocity and angular momentum, and φ_M is the angle variable in momentum space. Equation (1) is written out in a spherical coordinate system in which the z axis is in the direction of the field **E**.

The linearized kinetic equation for a paramagnetic gas with linear molecules in an alternating magnetic field $\mathbf{H} = \mathbf{H}_0 \cos \omega t$ is similar in form to (1). The values of γ and of the phase volume for such molecules are

$$\gamma = \mu_0\sigma H_0 M^{-1}, \quad \sigma = 0, \pm 1;$$
$$d\Gamma = {}^1/_2\,\pi^{-5/2}U^2dUd\Omega_U MdMd\Omega_M$$

(μ_0 = Bohr magneton).

We seek a solution of (1) in the form

$$\chi = -\sum_{l,m} a_{lm}{}^*\chi_{lm} \tag{3}$$

Then the functions χ_{lm} should satisfy the equation

$$\partial\chi_{lm}/\partial t - A_{lm} + \gamma\cos\omega t\,\partial\chi_{lm}/\partial\varphi_M = -\hat{I}\chi_{lm}. \tag{4}$$

Let us consider the time-averaged variation of the transport coefficient in the alternating field.

Following [2], we break up the collision operator (2d) into two parts:

$$\hat{I} = \hat{I}^{(0)} + \varepsilon\hat{I}^{(1)}, \qquad (5)$$

where $\hat{I}^{(0)}$ describes collisions without allowance for the rotational degrees of freedom of the molecules, and $\epsilon I^{(1)}$ is a small operator which takes into account the dependence of the collision cross section on the molecule rotation (ϵ is a small parameter).

We shall assume that $\hat{I}^{(0)}$ corresponds to a Maxwellian molecule-interaction potential. The eigenfunctions of the operator $\hat{I}^{(0)}$ constitute a complete set of orthogonal normalized functions and are determined, together with the eigenvalues, by the following equations:

$$\psi_n = \psi_{l,m,l_1,l_2,r_1,r_2,s} = \sum_{m_1+m_2=m} C^{lm}_{l_1m_1l_2m_2} Y_{l_1m_1}(\mathbf{U}) \times Y_{l_2m_2}(\mathbf{M}) T_{r_1}{}^{l_1}(U^2) L_{r_2}{}^{l_2}(M^2)\varphi_s(\sigma), \qquad (6)$$

$$\lambda_n = \alpha_{l_1r_1}\delta_{r_20}\delta_{l_20}\delta_{s0} + \beta_{l_1r_1}(1-\delta_{r_20}\delta_{l_20}\delta_{s0}), \qquad (7)$$

where $C^{\cdots}_{\cdots}$ are Clebsch-Gordan coefficients, $L^{l_2}_{r_2}(M^2)$ are Laguerre polynomials of rank l_2 for linear molecules and of rank $l_2 + 1/2$ for symmetrical-top molecules, and $T^{l_1}_{r_1}(U^2)$ are Laguerre polynomials of rank $l_1 + 1/2$ in the case of a Maxwellian molecule-interaction potential. The eigenvalues (7) differ from those introduced in [2] by a factor n (n = density).

When (5) is taken into account, Eq. (4) for χ_{lm} takes the form

$$\hat{K}^{-1}\chi_{lm} = A_{lm} - \varepsilon\hat{I}^{(1)}\chi_{lm}, \qquad (8)$$

$$\hat{K}^{-1} = \partial/\partial t + \gamma\cos\omega t\,\partial/\partial\varphi_M + \hat{I}^{(0)}. \qquad (9)$$

A formal solution of Eq. (8) in the form of an expansion in the small parameter ϵ is

$$\chi_{lm} = \hat{K}A_{lm} - \varepsilon\hat{K}\hat{I}^{(1)}\hat{K}A_{lm} + \varepsilon^2\hat{K}\hat{I}^{(1)}\hat{K}\hat{I}^{(1)}\hat{K}A_{lm} - \cdots, \qquad (10)$$

where $\hat{K}$ is an operator inverse to $\hat{K}^{-1}$.

The operator $\hat{K}^{-1}$ differs from the corresponding operator in a constant field[2] in that it contains a time derivative and cos ωt in the second term, and operates in a function space of the form $\psi_n \exp(-ik\omega t)$ (k = integer). Therefore the field dependence of the time-averaged thermal-conductivity and viscosity coefficients is determined by expressions

$$\bar{c}^{(2)}_{lm,\,l'm} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} \varepsilon^2\langle A_{lm}, \hat{K}\hat{I}^{(1)}\hat{K}\hat{I}^{(1)}\hat{K}A_{l'm}\rangle\,dt, \qquad (11)$$

where in the case of an electric field we have

$$\langle F_1, F_2\rangle = \int\int f_0F_1F_2\,d\Gamma\,d\sigma.$$

In the case of a paramagnetic gas in a magnetic field, the integration with respect to σ is replaced by summation.

Using the explicit form of the coefficients A_{lm}, we rewrite (11) in the form

$$\bar{c}^{(2)}_{lm,\,l'm} = \varepsilon^2\sum_{n',n}\langle A_{lm}, \hat{K}\hat{I}^{(1)}\psi_{n'}\rangle\frac{\omega}{2\pi}\int_0^{2\pi/\omega} K_{n'n}dt\langle\psi_n, \hat{I}^{(1)}\hat{K}A_{l'm}\rangle, \qquad (12)$$

where

$$\langle A_{lm}, \hat{K}\hat{I}^{(1)}\psi_n\rangle = \sum_{n_0}\frac{1}{\lambda_{n_0}}I^{(1)}_{n_0n}\langle A_{lm}, \psi_{n_0}\rangle,$$
$$n_0 = (l, m, l_1, 0, r_1, r_2, 0). \qquad (13)$$

The dependence of the coefficients $\bar{c}^{(2)}_{lm,\,l'm}$ on the field is determined by the matrix elements

$$K_{n'n} = \langle\psi_{n'}, \hat{K}\psi_n\rangle. \qquad (14)$$

The action of the operator $\hat{K}$ on ψ_n is represented by

$$K\psi_n = Z_n(t)\psi_n, \qquad (15)$$

where the unknown function $Z_n(t)$ satisfies the equation

$$dZ_n/dt + \lambda_nZ_n + im_2\gamma\cos\omega tZ_n = 1. \qquad (16)$$

The periodic solution of this equation takes the form

$$Z_n = \exp\left(-\frac{im_2\gamma}{\omega}\sin\omega t - \lambda_nt\right) \times \int_{-\infty}^{t}\exp\left(\frac{im_2\gamma}{\omega}\sin\omega t' + \lambda_nt'\right)dt'. \qquad (17)$$

Performing the required time averaging in (12), we get

$$\bar{Z}_n = \frac{\omega}{2\pi}\int_0^{2\pi/\omega}\exp\left(-\frac{im_2\gamma}{\omega}\sin\omega t - \lambda_nt\right)dt \times \int_{-\infty}^{t}\exp\left(\frac{im_2\gamma}{\omega}\sin\omega t' + \lambda_nt'\right)dt'. \qquad (18)$$

Replacing the variable t′ by z = t′ − t and using the expansion

$$\exp(iz\sin\varphi) = \sum_{k=-\infty}^{\infty}J_k(z)e^{ik\varphi},$$

where $J_k(z)$ are Bessel functions, we get

$$\bar{Z}_n = \sum_{k=-\infty}^{\infty}J_k{}^2\left(\frac{m_2\gamma}{\omega}\right)\frac{1}{i\omega k + \lambda_n}. \qquad (19)$$

Let us substitute this expression in (15) and separate the field-dependent part $\Delta K_{n'n}$. Then, taking into account the explicit forms (6) of ψ_n and of γ, we get

$$K_{n'n} = \lambda_n^{-1}\delta_{n'n} + \Delta K_{n'n},$$

$$\Delta K_{n'n} = -\frac{1}{\lambda_n} \times \sum_{m_1+m_2=m} C^{lm}_{l_1m_1l_2m_2} C^{l'm}_{l_1m_1l_2m_2} \delta_{mm'}\delta_{l_1l_1'}\delta_{m_1m_1'}\delta_{l_2l_2'}\delta_{m_2m_2'}\delta_{r_1r_1'} \cdot \times \Big\langle 2L_{r_2}(M^2)\varphi_s(\sigma) \sum_{k=1} \frac{\omega^2k^2}{\omega^2k^2+\lambda_n^2} \times J_k^2\Big(\frac{m_2\gamma}{\omega}\Big) M^{2l_2} L_{r_2'}(M^2)\varphi_{s'}(\sigma)\Big\rangle . \quad (20)$$

To get (20), we used the identity

$$\sum_{k=-\infty}^{\infty} J_k^2(z) = 1.$$

Expressions (12) and (20) determine the dependence of the time-averaged changes of the thermal-conductivity and viscosity coefficients on the amplitude and frequency of the alternating field. The imaginary part of (20) vanishes. Therefore the time-averaged effects that are "odd" in the field vanish in an alternating field, as expected. Since $\lambda_n \sim P$, it follows, as is evident from (20), that the effect depends on the ratios E_0/ω (H_0/ω) and ω/P. It is obvious that the parameters that determine the change of the transport coefficients can be any two ratios of E_0 (H_0), ω, and P. This circumstance is confirmed by results of an experiment in which the thermal conductivity of the polar gas NF_3 was measured in an alternating electric field.[1]

Using (18), we can readily show that at field frequencies $\omega \to 0$ the quantity $\Delta K_{n'n}$ takes a form corresponding to the solution of the problem in a constant field. At field frequencies $\omega \to \infty$ we get $\Delta K_{n'n} \to 0$ and consequently the effect vanishes, since $J_k(1/\omega) \to 0$ $(k \neq 0)$ as $\omega \to \infty$. This corresponds to complete vanishing of the molecule precession.

Let us find the dependence of the time-averaged changes of the transport coefficients on the amplitude and frequency of the field in the case of weak fields $(\gamma/\lambda_n \ll 1)$. Using the expression for Bessel functions at small values of the argument

$$J_k(z) \approx \frac{1}{k!}\Big(\frac{z}{2}\Big)^k \qquad (k \neq 0)$$

and retaining the first term in the sum over k in (20), we get

$$\Delta K_{n'n} = -\frac{1}{\lambda_n} \sum_{m_1+m_2=m} C^{lm}_{l_1m_1l_2m_2} C^{l'm}_{l_1m_1l_2m_2} \times \Big\langle \Big(\frac{m_2\gamma}{\omega}\Big)^2 M^{2l_2}(L^{l_2}_{r_2}(M^2))^2 \varphi_s\varphi_{s'}\Big\rangle \frac{(\omega/\lambda_n)^2}{1+(\omega/\lambda_n)^2}. \quad (21)$$

Inasmuch as the changes of the transport coefficients in a constant field are proportional to $(\gamma/\lambda_n)^2$,[2] in the region $\gamma/\lambda_n \ll 1$,[2] it follows from (21) that the change in the effect with changing frequency does not depend on the field amplitude and is determined by the last factor of (21). Comparison of the theoretical frequency dependence of the change of the effect with the experimental data allows us to obtain the eigenvalue λ_n of the collision operator $\hat{I}^{(0)}$.

In order to carry out such a comparison, let us consider a collision model in which the matrix elements $I^{(1)}_{n'n}$ differ from zero only for n = (l, m, 2, 1, 0, 0, 0). With (7), (11), and (21) taken into account, the relative change of the thermal-conductivity coefficient with changing frequency is given by

$$\frac{\Delta\varkappa(\omega)}{\Delta\varkappa(\omega=0)} = \frac{1}{1+(\omega/n\beta_{10}')^2}, \quad \beta_{10} = n\beta_{10}'. \quad (22)$$

(It can be shown that formula (22) remains unchanged when account is taken of the difference of the moments of inertia of the molecules of the polar gas.) The figure shows a plot of (22) together with the data taken from [1]. We see that a dependence of the type (22) describes the observed regularity with the same accuracy that has been attained in the experiment. In this case β'_{10} is equal to 1.3×10^4 kT.

Let us examine the time dependence of the transport coefficients.[1)] We assume that the values of the momentum M in the quantity γ have been replaced by their mean values. This enables us to obtain qualitatively correct results and simplify the solution of (8). We represent χ_{lm}, as we have done in fact earlier in the derivation of (10), in the form of an expansion in the small parameter ϵ:

$$\chi_{lm} = \chi^{(0)}_{lm} + \varepsilon\chi^{(1)}_{lm} + \varepsilon^2\chi^{(2)}_{lm} + \ldots \quad (23)$$

Substituting (23) in (8) and solving successively the equations for $\chi^{(0)}_{lm}$ $\chi^{(1)}_{lm}$, and $\chi^{(2)}_{lm}$ we obtain the following expression for the function $\chi^{(2)}_{lm}$ and the coefficients $c^{(2)}_{lm,\,l'm}$, which give the dependence of the transport coefficients on the field:

$$\chi^{(2)}_{lm} = \sum_{n,\,n_0,\,n_0'} (\lambda_{n_0}, \lambda_{n_0'})^{-1}\psi_{n_0'}\langle A_{lm}, \psi_{n_0}\rangle I^{(1)}_{n_0n} I^{(1)}_{nn_0'} Z_{nn_0n_0'}(t); \quad (24)$$

$$c^{(2)}_{lm,\,l'm} = \sum_{n,\,n_0,\,n_0'} B^{lm,\,l'm}_{nn_0n_0'} Z_{nn_0n_0'}(t),$$
$$B^{lm,\,l'm}_{nn_0n_0'} = (\lambda_{n_0}\lambda_{n_0'})^{-1}\langle\psi_{n_0'}, A_{l'm}\rangle\langle A_{lm}, \psi_{n_0}\rangle I^{(1)}_{n_0n} I^{(1)}_{nn_0'}. \quad (25)$$

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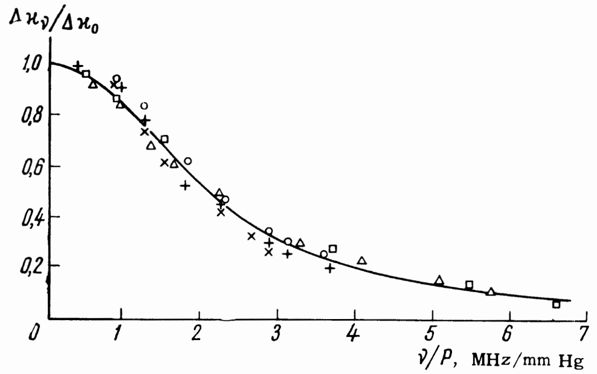
1)We are grateful to Yu. M. Kagan who called our attention to this aspect of the problem.



Dependence of $\Delta\kappa_n/\Delta\kappa_0$ on ν/P. Solid curve – calculation by means of formula (22), points – experimental: +,×) E/P = 102 (V/cm)/mm Hg, +) P = 0.6 mm Hg, ×) P = 0.87 mm Hg, o,△,□) E/P = 187 (V/cm)/mm Hg, o) P = 0.6 mm Hg, △) P = 0.33 mm Hg, □) P = 0.2 mm Hg.

The sets of numbers n_0 and n_0' are given in (13). The time-dependent functions $Z_{nn_0n_0'}$ are of the form

$$Z_{nn_0n_0'} = \sum_{k=-\infty}^{\infty} A_k e^{ik\omega t}, \tag{26}$$

$$A_k = \lambda_{n_0} \frac{1}{ik\omega + \lambda_{n_0'}} - \sum_{l=-\infty}^{\infty} \frac{1}{i\omega(k+l) + \lambda_n} J_l\left(\frac{m_2\gamma}{\omega}\right) J_{l+k}\left(\frac{m_2\gamma}{\omega}\right). \tag{27}$$

In accordance with (25)–(27), the variation of the transport coefficients of polyatomic gases in an alternating field has an oscillating character, owing to the periodic oscillations of the effective molecule-collision cross sections in the oscillating field. The spectrum of the transport-coefficient oscillations consists of a set of frequencies that are multiples of the field frequency.

When k = 0, expression (26) goes over into (19).

In the case of low frequencies ($\omega \ll \gamma$, λ_n) expressions (25)–(27) of the transport coefficients should obviously go over into the formulas of [2] for $c^{(2)}_{lm,l'm}$ in a constant field, when the substitution $H \to H_0 \cos \omega t$ is made.

In the case of high field frequencies ($\omega \ll \gamma$, λ_n) the series (26) converges rapidly ($A_k \sim (\gamma/\omega)^k$) and it suffices to retain the first few terms. Since in this approximation $A_{-k} = (-1)^k A_k$, it is obvious that Re $Z_{nn_0n_0'}$, and consequently also Re $c^{(2)}_{lm,l'm}$ will contain only even harmonics, and Im $Z_{nn_0n_0'}$ and Im $c^{(2)}_{lm,l'm}$ will contain only odd ones. Therefore the expression

$$\Delta \operatorname{Re} c^{(2)}_{lm,l'm} = -\frac{1}{16}\frac{\gamma^2}{\omega^4}\Lambda^{lm,l'm}\cos 2\omega t, \tag{28}$$

where

$$\Lambda^{lm,l'm} = \sum_{nn_0n_0'} m_2 B^{lm,l'm}_{nn_0n_0'},$$

describes small deviations from the mean values of effects that are even in the field, and

$$\Delta \operatorname{Im} c^{(2)}_{lm,l'm} = -\frac{1}{2}\frac{\gamma}{\omega^3}\Lambda^{lm,l'm}\sin \omega t \tag{29}$$

is the first non-vanishing term describing effects that are "odd" in the field and oscillate with the field.

The quantities (28) and (29) are quite small, but it may turn out that their measurement can serve to obtain additional information on molecule collisions in polyatomic gases.

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[2] Yu. M. Kagan and L. A. Maksimov, JETP 51, 1893 (1966), Soviet Phys. JETP 24, 1272 (1967).

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