A kinetic theory is developed for the effects that arise when a free-molecular polyatomic gas flows between two surfaces in an external field. The influence of the field on the transport processes is due to the nonequilibrium polarization of the gas molecules when they are nonspherically scattered from the surface of a solid, and to the destruction of this polarization in the field. The change of the gas flow velocity in a channel in a magnetic field, and the onset of a transverse heat flux between the surfaces whose temperatures are equal is examined in detail. In contrast to the previously investigated thermomagnetic phenomena, the considered effects in a gas stream can occur when the molecules are scattered from the surface not only inelastically but also elastically. At the same time, these effects occur only if the interaction with the surface is such that the states of the molecule before and after the collision are correlated.

1. INTRODUCTION

The influence of a magnetic field on heat flow in a strongly rarefied ($I \gg L$, where $I$ is the molecule mean free path and $L$ is the characteristic dimension) polyatomic gas (the thermomagnetic effect) has already been observed and investigated earlier. Other possible effects in an inhomogeneously heating gas in a magnetic field were also analyzed, such as the appearance of transverse heat and mass fluxes in a gas contained between two surfaces having different temperatures, or of thermomagnetic forces acting on the walls. The physical causes common to the changes in the transport processes in a magnetic field are the polarization of the molecules (inelastically scattered from the solid surface and the precession of the magnetic moment of the molecule about the field direction. A distinguishing feature of the foregoing effects is the oscillatory character of the dependence of the macroscopic fluxes in the gas on the intensity of the constant external field at a fixed geometry of the problem. The concrete dependence of the macroscopic quantities on the intensity and orientation of the field is determined entirely by the law of nonspherical scattering of molecules by walls. Therefore the kinetic effects in a strongly rarefied gas in an external field serve as a unique source of information on the physical mechanism of the orientation-dependent interaction between molecules and the surface of a solid, and on the properties of the surface itself.

By virtue of the isotropy of the distribution of the molecules of the equilibrium gas with respect to their orientations and directions of motion, polarization of molecules reflected from the surface can occur only in a nonequilibrium gas. The effects listed above are due to the temperature inhomogeneity of the system. It can be assumed that the molecules reflected (elastically and inelastically) from the walls become polarized also in the case of gas flow. The presence of a predominant direction of the velocity of the molecules incident on the surface and the dependence of the probability of the scattering on the mutual orientation of the velocity $v$ and of the angular momentum $M$ of the molecule should make the distribution function dependent also on the orientation of the vector $M$, i.e., should lead to polarization of the molecules. The molecule precession produced when the external field is turned-on changes this dependence (it destroys partially the polarization). As a result, the kinetic properties of the system are altered in an external field; in particular, the scalar transport coefficients acquire a tensor character.

In this paper we construct a theory of the phenomena connected with the influence of an external field on the transport processes in a stream of strongly rarefied polyatomic gas. We solve the problem of the flow of collisionless gas in a channel made up of two infinite surfaces in a magnetic field. We investigate the change of the channel resistance in the field and the onset of heat flow between the surfaces (which have equal temperatures). These effects are the Knudsen analogs of the known viacomagnetic effect and of the effect of viacomagnetic heat flow, which take place if $I \lesssim L$. They are produced, however, by another physical mechanism, namely polarization of the molecules by nonspherical scattering from the surface.
The considered phenomena have a polarization-precession mechanism and are not sensitive to the kinetic part of the precession of the molecules. Therefore the expression obtained below for the nonequilibrium molecules in a magnetic field can be easily generalized to the case of paramagnetic molecules, as well as the case of dipole molecules in an electric field.

We must emphasize two substantial differences between the physical mechanisms responsible for the onset of the considered effects in a gas stream, and the mechanism of the previously investigated thermomagnetic effects. First, the field should influence the transport processes in a gas stream not only in inelastic but also in elastic scattering of molecules by wall, when the total energy of the molecule remains unchanged by the collision. Consequently, an investigation of these effects makes it possible to study additionally also the elastic interaction of polyatomic molecules with a surface. This possibility is of fundamental importance, since elastic scattering should depend only on the structure of the surface, while inelastic scattering should depend also on the spectrum of the surface phonons of the solid.

The other distinguishing feature of the considered effects is, as will be shown below, that they appear only if the scattering of the molecules by the surface is such that the states of the molecule before and after the collision are correlated. On the other hand, if the scattering law takes into account only the sticking of the molecule to the surface and its evaporation from it, then the field has no effect on the transport processes in a stream of a collisionless gas. It follows from this, in particular, that at sufficiently low temperatures (under conditions of strong physical adsorption) the considered effects (in contrast to the thermomagnetic ones) can vanish.

2. KINETIC THEORY OF FLOW OF COLLISIONLESS GAS IN A MAGNETIC FIELD

We consider the influence of a magnetic field \( \mathbf{H} \) on the flow of strongly rarefied gas \((\Gamma L \gg 1)\) in a channel between two infinite surfaces described by the equations \( z = 0 \) and \( z = L \). The gas moves along the \( x \)-axis under the influence of a specified density gradient \( \gamma_0 \) and \( \gamma \) a specified temperature gradient \( \gamma T \). The kinetic equation for the distribution function \( f \) of a gas with rotational degrees of freedom in a magnetic field takes in this case the form

\[
\frac{dE}{dt} + \frac{\partial}{\partial z} \left[ \frac{E}{E} \frac{\partial f}{\partial z} \right] = 0, \tag{1}
\]

where \( E = m\nu^2/2 + \frac{1}{2}(Mx^2 + My^2 + Mz^2) \) is the energy of the linear molecule, \( \gamma \) is the gyromagnetic ratio, and \( c_p \) is the specific heat. Equation (1) can be solved jointly with the system of the boundary conditions on the wall, which relate the distribution functions of the incident \( f_{in} \) and reflected \( f_{out} \) molecules, and which are written in the form

\[
\int_{-\infty}^{\infty} f_{out} dE = \int_{-\infty}^{\infty} f_{in} dE = 1. \tag{2}
\]

Here \( \Gamma = (v, M)/d\gamma v d/M \), \( k \) is the normal vector to the surface and \( W \) is the probability density of the scattering.

We integrate Eq. (1) along the characteristics in the range \( 0 < z < L \) and, using relations of the type (2) in the resultant boundary terms, we can change over to an integral equation, which we express in the following operator form:

\[
\phi(z) = \exp \left( -\frac{\gamma T z}{k} \right) \int_{0}^{L} dV \phi(L - z), \tag{3}
\]

where \( \phi(z) = f_{out}(z) - f_{in}(z) \), \( f_{in} = 0 \), \( f_{out} = 0 \).

The operators \( \hat{S}^+ \) and \( \hat{S}^- \) are determined by the general relation (3) and describe the scattering of the molecules respectively by the lower \((z = 0)\) and upper \((z = L)\) surfaces. The operators \( \hat{S}^+ \) and \( \hat{S}^- \) in (3) describe the precession of the molecules in the field as they move along the trajectory and are determined by the expressions

\[
\hat{S}^+ = p(z + L, k) = p(z, k), \tag{3a}
\]

\[
\hat{S}^- = p(z, k) = p(z - L, k), \tag{3b}
\]

where \( q_d \) and \( q_g \) are the spherical field-orientation angles. The first and second terms in the right-hand side of (3) describes the distributions of the molecules moving up \((z > 0)\) and down \((z < 0)\), respectively. The functions \( S^+ \) and \( S^- \) in (3) take into account the macroscopic motion of the gas. In the case \( \gamma T = 0 \), when \( S^+ = S^- \), Eq. (3) reduces to the previously obtained integral kinetic equation for a gas at rest in a magnetic field.

The error in (3), which manifests itself in the divergence of \( S^+ \) (4) as \( z \to L \), is due to the fact that the intermolecular collisions in the gas are not taken into account [the collision integral in (1) is set equal to zero]. This result corresponds to the known divergence in the problem of planar Poiseuille flow as \((L/\nu) \to 0\), when the gas velocity becomes infinite at a finite value of the pressure gradient. To obtain a finite value of the flow velocity, it must be recognized that the molecules with sufficiently small \( \nu \) manage to collide with other molecules before they reach the walls. We therefore put, neglecting intermolecular collisions,

\[
\nu = \nu_0 \exp \left( -\frac{\nu T}{\gamma} \right), \tag{4}
\]

where \( \nu_0 \) is the average thermal velocity of the molecules, and integrate in (3), which defines the operators \( \hat{S}^+ \), not over the half-space \( k \cdot v \to 0 \), but in the region \( k \cdot v < -\epsilon \) \( L/\nu \). As will be indicated below, the assumption (4) has no effect whatever on the dependences of the macroscopic fluxes on the magnetic field. The validity of the last statement is quite obvious, however, from general considerations, inasmuch as in accordance with the precession mechanism a substantial contribution to the effect should be made only by molecules with \( \epsilon \to 0 \).
In accordance with method, defining the expression for \( f \) in the \( n \)-th approximation as follows:

\[
f^{(n)}(v) = \sum_{\ell=0}^{\infty} \alpha_n(\ell) S^{(n)}(\ell), \quad \alpha_n(\ell) = a_1 a_2 \ldots a_\ell \prod_{k=1}^\ell a_k,
\]

where \( a_k \) is the coefficient of the probable or avoidable collision of the molecule with the surface. As the initial function \( f^{(0)} \) we choose the Maxwellian distribution \( f_M \). In accord with (1), the gas distribution function \( f \) is described by the local Maxwellian distribution corresponding to specified macroscopic gradients.

We consider first the distribution \( f^0 \) of molecules moving upward \( (v_x > 0) \). After an arbitrary \( k \)-th iteration we have

\[
f^{(k)} = f^0 + \sum_{\ell=1}^{\infty} \sum_{\ell_x=0}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k),
\]

where \( f^0 \) does not depend on the orientation of the angular momentum of the molecule, and the functions \( W_0 \), \( W_1 \), and \( W_2 \) describe the nonspherical interaction with the surface. The nonsphericity parameter \( \epsilon \) will be assumed small (the experimental value of \( \epsilon \) is less than 0.1) and that it is possible to retain in (10) any function \( S \) from among those on the right of the indicated operator combination.

For the analysis that follows, we represent the scattering probability in the form of the sum

\[
\sum_{\ell_x=0}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k),
\]

which is even. Next, the operators \( \mathcal{S}^0 \) and \( \mathcal{S}^n \) in the first combination \( \mathcal{S}^{0 \text{ or } n} \) on the right should be left out, since \( \mathcal{P}_0 f^{(k)} = f^{(k)} \) (the known conservation of the Maxwellian distribution), and \( \mathcal{P} \) is a unit operator in the subspace of functions that do not depend on the orientation of \( \mathcal{M} \).

The expression (10) reflects the physical mechanisms of the effect of the field on the transport processes, an explanation of which calls for allowance for at least two nonspherical collisions of the molecules with the walls. In the first of them the molecules become polarized (the polarization is specified in (10) by the operator \( \mathcal{P}_1 \)), while precession of the molecules in the field partially destroys this polarization (the action of \( \mathcal{P}_1 \)). The second nonspherical collision (the operator \( \mathcal{P}_2 \)) transforms the field-dependent distribution, which is anisotropic in \( \mathcal{M} \), into an isotropic distribution. The dependence of the latter on \( \mathcal{M} \) describes the change of the considered transport processes in the field.

We assume hereafter that the density and temperature gradients are small (\( \nabla n < n / T < T / \ell \)) and confine ourselves to an approximation linear in \( \nabla n \) and \( \nabla T \). We must then leave out of (10) all but one of the functions \( S \). Taking into account the relations \( \mathcal{P}_0 f^{(k)} = f^{(k)} \) and \( \mathcal{P}_x f^{(k)} = 0 \), we obtain

\[
|f^{(k)}|^2 = |f^0|^2 + \sum_{\ell_x=1}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k).
\]

The second summation in (11) implies sifting through all the possible operators \( \mathcal{P}_x \) on the right of the combination \( \mathcal{W}_r \mathcal{P}_n \mathcal{P}_1 \). This summation is the result of the fact that it is possible to retain in (10) any function \( S \) from among those on the right of the indicated operator combination.

It is easy to obtain in similar fashion an expression for the distribution \( f_{1 \text{ or } 2}^{(k)} \) of the molecules moving down \( (v_x < 0) \); this expression differs from (11) only in the interchange of the plus and minus indices.

We assume next that the surfaces are macroscopically isotropic (e.g., polycrystalline), i.e., there is no physically preferred direction in the plane of the surface. Then, as can be easily verified, the functions \( B_1 \) and \( B_2 \) calculated in accordance with the equations

\[
B_1 = \left\{ \begin{array}{l}
\mathcal{P}_1 f^{(k)} = f^{(k)}, \\
\mathcal{P}_2 f^{(k)} = 0
\end{array} \right.
\]

are independent of the tangential component of the velocity if the functions \( A_1 \) and \( A_2 \) are independent of it, and the function \( B \) is arbitrary.

Letting the number of iterations \( k \) in (11) go to infinity, and using relation (12) as well as the explicit forms of the operators \( \mathcal{P}_1 \), \( \mathcal{P}_2 \), and \( \mathcal{P}_x \), it is easy to obtain an expression for the field-dependent part of the macroscopic flux of the quantity \( A \) (\( A = 1 \), \( E \), or \( \nabla n \), \( \nabla T \), or \( \nabla \mathcal{M} \)) is arbitrary

\[
\begin{aligned}
\dot{A} &= -e \left\{ \sum_{\ell_x=1}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k) \right\} \mathcal{P}_1 f^{(k)} + \sum_{\ell_x=1}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k) \\
&= \left\{ \sum_{\ell_x=1}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k) \right\} \mathcal{P}_1 f^{(k)} + \sum_{\ell_x=1}^{\ell} \prod_{k=1}^{\ell_x} a_k S^{(n)}(\ell_x) \prod_{k=\ell_x+1}^{\ell} S^{(0)}(a_k)
\end{aligned}
\]

Therefore, the expression (10) reflects the physical mechanism of the transport processes in the field.
Here various orientations of \( H \) field by formula (14) leads to the following results at calculation of the change of the gas flow velocity in the channel resistance in a field can occur simply from physical considerations by using arguments previously advanced\(^2\) to explain the sign of the thermomagnetic effect. As shown by the analysis of (13), this result is typical of all those terms of the expansion (15) with \( I'_1 + I'_2 + I_1 + I_2 \) an even number, i.e., when the probability of scattering by the surface is invariant to reversal of the vectors \( v', v, M', M, \) and \( k. \)

The expansion terms with \( I'_1 + I'_2 + I_1 + I_2 \) odd, on the contrary, decrease the resistance of the channel in the field. We note that this general result can be obtained simply from physical considerations by using arguments previously advanced\(^2\) to explain the sign of the thermomagnetic effect.

As follows from (17), the gas velocity in the channel is determined by the parameter \( \omega T \), which is equal to the product of the molecule precession frequency in the field by the characteristic time of their travel between the walls. The dependence of \( \Delta(\omega T) \) on \( \omega T \) is similar to the corresponding dependences of the thermomagnetic effect\(^1\) and takes the form of damped oscillations. The first maximum is reached here at \( \omega T = 1 \), and \( \Delta(\omega T) \) saturates as \( \omega T \rightarrow \infty \). The magnitude of the effect at saturation is the same for the three different field orientations.

In accord with (17), the rate of flow of the gas in the channel decreases when the magnetic field is turned on. Since the gradients \( V_n \) and \( V_T \) are fixed, this means that the channel resistance decreases in the field.
equal to zero. In other words, a change in the resistance of the channel in the field takes place if the non-spherical scattering from both walls is such that the states of the molecules before and after the collision are correlated.

4. TRANSVERSE HEAT FLUX

Calculation of the heat flux \( \mathbf{q}(x, y, z) \) with the aid of relations (13)-(16) yields

\[
\mathbf{q} = \mathbf{u} T \left( \mathbf{C} - \frac{1}{3} \mathbf{m} \right) \cdot \mathbf{u} \quad \mathbf{C} = \frac{1}{2} \mathbf{m} \mathbf{m}^T + \frac{1}{2} \left( \mathbf{1} + \mathbf{u} \mathbf{u}^T \right)
\]

(19)

According to (10), energy transport is produced by turning on a field that is not collinear to the flow of gas between surfaces of equal temperature. The transverse heat flow is odd in the field and is an oscillating function of \( u \), reaching the maximum at \( u = -1 \) and tending to zero as \( u \to 0 \). The maximum heat flux in the flow of gas under the influence of, say, a temperature gradient is of the order of \( \mathbf{C} T \mathbf{m} [\mathbf{m} / T]\). Just as in the preceding case, this estimate is a lower bound, insomuch as allowance for the elastic scattering by the surfaces can increase the effect. In the case of pure elastic scattering of the molecules from both surfaces, however, this effect will not occur. To produce a transverse heat flux it is necessary that nonspherical scattering of the molecules from at least one of the walls be accompanied by energy exchange with the surface.

In contrast to the influence of the field on the gas flow, a transverse heat flux appears also if the scattering by one of the surfaces takes place without a correlation between the states of the molecule before and after the collision, i.e., it can be described with account taken of only the sticking and evaporation processes. There will be no effect, however, if this "correlationless" scattering is a characteristic of both surfaces (for example, under conditions of strong physical sorption).

We note that expression (19) coincides (accurate to within a factor of suitable dimensionality) with the expression for transverse thermomagnetic gas flow, as it should for crossovers effects in accord with the Onsager principle.

5. OTHER KINETIC EFFECTS IN A MAGNETIC FIELD

We have considered above two kinetic phenomena that are of greatest interest from the point of view of the possibility of their experimental investigation. The complete list of the possible effect in a stream of a strongly rarefied gas, which are different physical manifestations of nonequilibrium polarization of the molecules and its destruction in the field, is much larger. A magnetic field not collinear with the gas flow lifts the degeneracy of the system with respect to directions perpendicular to the flow. As a result, turning-on a field can give rise also to heat and mass fluxes in a direction perpendicular to the main gas flow (along the y axis), as well as to normal and tangential forces that act on the walls. The dependence of all the macrofluxes in the gas on the magnitude and orientation of the field follows from the general relation (13).

Without presenting here the detailed results of the calculations, we note only that the possible existence of various macrofluxes in a field in some particular direction and their general properties (e.g., whether they are even or odd in the field) can be explained by starting from simple considerations of the spatial symmetry of the system. To this end it is necessary to construct a phenomenological expression (of suitable tensor character) for the given macroscopic quantity out of the three characteristic vectors of the problem: the vector \( \mathbf{u} = \langle \mathbf{v} \rangle / \langle \mathbf{v} \rangle \) directed along the gas flow, the magnetic-field pseudovector \( \mathbf{H} \), and the vector \( \mathbf{K} \). The calculation of various macrofluxes can be found in (11) and (12). The kinetic theory constructed above can predict also the field dependence of the thermomolecular pressure difference (in the free-molecular limit). This effect consists of the onset of a pressure difference between two gas volumes connected by a sufficiently thin capillary and kept at different temperatures. It is easy to show that the dependence of the pressure difference on the field should coincide in form with the dependence of the gas-flow velocity described by expressions (15) and (17).

We note in conclusion that since the motion of the gas-mixture components in the free molecular regime is independent, the theory developed above can yield also without difficulty expressions for the diffusion and thermal-diffusion coefficients in a field.

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Closed equation for turbulent heat and mass transport

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1. INTRODUCTION

In view of the wide prevalence of turbulent flows, the problems of heat and mass transport in turbulent streams attract much attention. From the theoretical point of view, the principal problem is the closing of the averaged transport equations: the density $\rho_{\text{av}}$ of the turbulent flow of matter or of heat must be connected with the distribution of the average density of the matter or the average temperature $T$. As a rule, a local relation is assumed to exist between $\rho_{\text{av}}$ and the gradient of the average density or temperature $D_{\text{av}}$:

$$\rho_{\text{av}} = \rho_{\text{av}}(D_{\text{av}})$$

(1)

To be specific, we discuss below the mass-transport problem.

The phenomenologically introduced turbulent-diffusion coefficient $D_{\text{turb}}$ depends on the spatial coordinates, particularly on the distance to the solid surfaces. In some papers, several phenomenological quantities are introduced in the form of a tensor $D_{\text{turb}}$ that generalizes relation (1). To find the coefficient (or tensor) $D_{\text{turb}}$, it is customary to use the Reynolds analogy between $D_{\text{turb}}$ and the turbulent viscosity coefficient $\nu_{\text{turb}}$:

$$D_{\text{turb}} = \nu_{\text{turb}}(D_{\text{turb}})$$

(2)

For the last quantity, a power-law variation is usually postulated near the boundaries of solids:

$$\nu_{\text{turb}} = k^p$$

(3)

where a value 3 or 4 is assumed for the exponent $k$.

2. AVERAGED MASS-TRANSPORT EQUATIONS

The purpose of the present paper is to derive a relation between $D_{\text{turb}}$ and $\nu_{\text{turb}}$ on the basis of the initial (non-averaged) equation of convective diffusion in incompressible liquids:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

(4)

Here $\mathbf{v}$ is the instantaneous distribution of the velocity of the liquid, $D$ is the molecular-diffusion coefficient, and $\kappa$ is the field of the impurity densities. The latter is assumed to be too small to influence the hydrodynamic characteristics of the flow.

We resolve the velocity of the liquid and the density into averaged and pulsating components:

$$\mathbf{v}(t, \mathbf{x}) = \langle \mathbf{v}(t, \mathbf{x}) \rangle + \tilde{\mathbf{v}}(t, \mathbf{x})$$

$$\rho(t, \mathbf{x}) = \langle \rho(t, \mathbf{x}) \rangle + \tilde{\rho}(t, \mathbf{x})$$

(5)

Here and elsewhere, the brackets $\langle \cdots \rangle$ denote averaging, while the prime denotes pulsating quantities. Averaging of (4) leads to the fundamental equation of convective diffusion in turbulent flow:

$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$