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KINETIC THEORY OF GASES WITH ROTATIONAL DEGREES OF FREEDOM

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An analysis is given of the kinetic equation for gases with rotational degrees of freedom without assuming the simplest form of the principle of detailed balancing—the equality of the probabilities of direct and inverse transitions, in particular when molecular stereoisomerism is present. An analysis is given of the general form of the solution of the kinetic equation which demonstrates, in particular, the existence of new nonvanishing mixed correlators of the velocity and the rotational angular momentum. It is shown that the switching on of an external field when the probabilities of direct and inverse processes are equal leads only to a decrease in the kinetic coefficients. The principle of detailed balance in the general form gives rise to the possibility of either sign for the variation of the kinetic coefficient with the field. An analysis is given of the general form of the solution in this case. It is found that so-called cross effects can exist when the lack of equilibrium of one kind of tensor quantities leads to fluxes of another kind of tensor quantities. Particular attention is paid to effects associated with molecular stereoisomerism. A generalized variational principle is analyzed which takes into account the nonselfconjugate nature of the collision operator in the case under consideration.

1. INTRODUCTION

IN preceding papers by the present authors[1-3] the kinetic theory of gases with rotational degrees of freedom was discussed. The principal feature which distinguishes this theory from the classical kinetic theory of a monatomic gas[4] was the introduction along with the velocity vector v, of the pseudovector of the rotational angular momentum of the molecule M as independent vectors on the basis of which any microscopic tensors have to be constructed. Another essential feature was the taking into account of the effect on the probability of collision W of the relative position of the vectors v and M of the colliding molecules. It is this taking into account of both circumstances that enabled us to explain and to predict a series of kinetic phenomena, particularly those associated with the behavior of molecular gases in external fields (cf., for example, the review[5]). In analyzing specific phenomena in these papers an assumption was made for the sake of simplification that W is an even function of the angular momenta of the colliding molecules. This led to the simplest variant of the principle of detailed balancing—to the equality of the probability of direct and inverse transitions (cf., for example,[6]):

$$W(\Gamma_1, \Gamma_2 \to \Gamma_1', \Gamma_2') = W(\Gamma_1', \Gamma_2' \to \Gamma_1, \Gamma_2), \qquad (1.1)$$

where $\Gamma = (\mathbf{v}, \mathbf{M})$.

All the effects that have been observed until recently were insensitive to the simplification of the collision integral resulting from (1.1). However, recently a discovery was made experimentally of the effect of an increase in the heat conductivity in an external field[7-9] instead of the usual falling off, and Levi and McCourt[10] and Waldmann[11] saw the possibility in principle of the appearance of such a rise based on an analysis of the quantum kinetic equation.

It can be shown that an increase in the heat conductivity in an external field can occur in principle only if relation (1.1) is violated (cf., below Sec. 5, subsection C). From this there arises in a natural manner the problem of a complete analysis of the picture of kinetic phenomena in a gas with rotational degrees of freedom in the case of the most general nature of the interaction between the molecules including also the case of molecular stereoisomerism.

The present paper is devoted to such an analysis. The whole discussion in this case is conducted on the basis of the classical kinetic equation. It seems to us that under the condition $T \gg \hbar^2/2I$ (I is the moment of inertia of the molecule), which is fulfilled practically always, with the exception perhaps only of hydrogen and of deuterium, the use of the classical kinetic equation is completely adequate for the problem. In particular, it will be shown that the appearance of a positive effect is by no means associated with the quantum nature of the rotational degrees of freedom. For the simplicity of discussion we will assume that a given rotational angular momentum M completely determines the internal state of the molecule, and the rotational energy is given by $E_{\text{rot}} = M^2/2I$. The necessary refinements will be introduced as required.

2. GENERAL PROPERTIES OF THE COLLISION INTEGRAL

A. We consider the properties of the collision integral arising in the general case when one gives up the conditions (1.1). From the symmetry of the equation of mechanics (or of quantum mechanics) with respect to time reversal we have in the most general form (cf., for example[6])

$$W(\Gamma_1, \Gamma_2 \to \Gamma_1', \Gamma_2') = W(\Gamma_1'^T, \Gamma_2'^T \to \Gamma_1^T, \Gamma_2^T); \qquad (2.1)$$

here $\Gamma^T = \hat{T}\Gamma = (-\mathbf{v}, -\mathbf{M})$.

If the interaction and, consequently, the transition probability is not altered when I is inverted, then W is an even function of the velocities and (2.1) can be transformed into the form

$$W(\Gamma_1, \Gamma_2 \to \Gamma_1', \Gamma_2') = W(\Gamma_1'^{TI}, \Gamma_2'^{TI} \to \Gamma_1^{TI}, \Gamma_2^{TI}). \qquad (2.2)$$

Finally, if in the general interaction between the molecules the terms of the rotational-orbital type are negligibly small, then W will be an even function of the angular momenta and (2.2) reduces to (1.1).

We note that the transition from (2.1) to (2.2) is impossible only in the absence of invariance of the interaction between the molecules with respect to the transformation of inversion, i.e., in fact only in the presence of molecular stereoisomerism. In the latter case in principle one can introduce an additional parameter—the pseudoscalar α, which changes sign under inversion (but $\hat{T}\alpha = \alpha$) and distinguishes between the right handed and the left handed states of stereoisomeric molecules:

$$\Gamma = (\mathbf{v}, \mathbf{M}, \alpha), \quad \Gamma^{TI} = \hat{T}\hat{I}\Gamma = (\mathbf{v}, -\mathbf{M}, -\alpha),$$

and one can utilize the relation between the probabilities in the form (2.2) in the general case.

B. Usually the general properties of the Boltzmann equation (in particular, the H-theorem) are proved on the basis of condition (1.1). Stückelberg[12] derived the H-theorem within the framework of a quantum mechanical discussion without utilizing (1.1). By a method close to that of[12] we will analyze the general properties of the classical equation for gases with internal degrees of freedom.

We utilize the usual local form of the collision integral:

$$J(\Gamma_1) = \int d\Gamma_2\, d\Gamma_1'\, d\Gamma_2' \{W f_1 f_2 - W' f_1' f_2'\};$$
$$W = W(\Gamma_1,\ \Gamma_2 \to \Gamma_1', \Gamma_2'), \quad W' = W(\Gamma_1', \Gamma_2' \to \Gamma_1, \Gamma_2). \tag{2.3}$$

As usual, we transfer the index characterizing the argument to the corresponding function.

Taking into account the obvious symmetry of W with respect to an interchange of the colliding molecules and utilizing a change of notation of the variables of integration we easily find that

$$\int d\Gamma\, AJ = \frac{1}{2}\int d\Gamma_1\, d\Gamma_2\, d\Gamma_1'\, d\Gamma_2'\, W' f_1' f_2' (A_1' + A_2' - A_1 - A_2). \tag{2.4}$$

From this it follows that $\int d\Gamma aJ$ vanishes when A is one of the integrals of the motion conserved in a collision (property I). We see that this property which lies at the basis of the derivation of the hydrodynamic equations from the Boltzmann equation is preserved in the general case[1)].

We shall utilize the identity which follows from the unitary nature of the scattering matrix[12]:

$$\int d\Gamma_1'\, d\Gamma_2'\, W = \int d\Gamma_1'\, d\Gamma_2'\, W'. \tag{2.5}$$

In fact this identity means that for conservative systems the total transition probabilities from and to a given state are equal to one another. Taking this result into account one can transform the collision integral (2.1) to the form

$$J(\Gamma_1) = \int d\Gamma_2\, d\Gamma_1'\, d\Gamma_2'\, W' (f_1 f_2 - f_1' f_2'). \tag{2.6}$$

The vanishing of this expression for the equilibrium distribution (property II) is obvious.

We now demonstrate how the H-theorem can be proved in the case of the most general form of the probability of collisions. The change of entropy due to collisions is determined by a quantity whose explicit form follows from (2.4), (2.6):

$$\int d\Gamma\, J \ln f = \frac{1}{2}\int d\Gamma_1\, d\Gamma_2\, d\Gamma_1'\, d\Gamma_2'\, W' f_1 f_2 [x \ln x + 1 - x],$$
$$x = f_1' f_2' / f_1 f_2. \tag{2.7}$$

From the nonnegative nature of the expression appearing in square brackets Boltzmann's H-theorem follows immediately (property III):

$$\int d\Gamma\, J \ln f \geqslant 0. \tag{2.8}$$

Thus, all three general properties (I, II, III) which are generally proved for a monotonic gas are a consequence of the general structure of the collision integral and are completely preserved when condition (1.1) is dropped. At the same time no limitations arise on the form of the scattering probability with the exception of (2.5).

C. We shall carry out the further analysis of the properties of the collision integral in the linear approximation with respect to a small deviation from equilibrium when

$$f = f^{(0)}(1 + \chi), \quad |\chi| \ll 1. \tag{2.9}$$

The collision integral in this case reduces to the linear integral operator $\hat{\Omega}$, operating on the function χ:

$$J(\Gamma_1) = f_1^{(0)}\, \hat{\Omega}\chi_1 = \int d\Gamma_2\, d\Gamma_1'\, d\Gamma_2'\, W' f_1^{(0)} f_2^{(0)} [\chi_1 + \chi_2 - \chi_1' - \chi_2']. \tag{2.10}$$

The behavior of the collision operator $\hat{\Omega}$ is completely determined by the properties of its matrix elements

$$\Omega_{mn} \equiv \langle \psi_m \hat{\Omega} \psi_n \rangle, \quad \langle \psi_m \psi_n \rangle \equiv \int d\Gamma\, f^{(0)} \psi_m \psi_n = \delta_{mn}. \tag{2.11}$$

Without restricting generality the complete set of state functions can be assumed to be orthonormal and possessing definite spatial (I) and temporal (T) parities:

$$\hat{I}\psi_m(\Gamma) = \psi_m(\Gamma^I) = \eta_m{}^I \psi_m(\Gamma), \quad \eta_m{}^I = \pm 1;$$
$$\hat{T}\psi_m(\Gamma) = \psi_m(\Gamma^T) = \eta_m{}^T \psi_m(\Gamma), \quad \eta_m{}^T = \pm 1. \tag{2.12}$$

First of all it is obvious that the matrix elements Ω_{mn} differ from zero only if ψ_m and ψ_n have the same tensor properties. This follows from the invariance of the scattering probability with respect to rotations of the coordinate system.

Another important property of the operator Ω reflects the temporal symmetry of the probability of a collision. Utilizing (2.1) and (2.5) we find that for any two functions φ and χ we have the equation

$$\langle \varphi \hat{\Omega} \chi \rangle = \langle \chi^T \hat{\Omega} \varphi^T \rangle. \tag{2.13}$$

For functions which have a definite temporal parity (2.12) this equation takes on the form

$$\Omega_{mn} = \eta_m{}^T \eta_n{}^T \Omega_{nm}. \tag{2.14}$$

From this it is clear that the operator $\hat{\Omega}$ is naturally separated into two parts:

$$\hat{\Omega} = \hat{\Omega}^{(+)} + \hat{\Omega}^{(-)}; \quad \Omega_{mn}^{(+)} = \Omega_{nm}^{(+)}, \quad \Omega_{mn}^{(-)} = -\Omega_{nm}^{(-)}, \tag{2.15}$$

[1)] In deriving the hydrodynamic system of equations in the case of polyatomic molecules in order to take into the account the exchange between the translational and the rotational degrees of freedom it is necessary to take into account the nonlocality of the collision integral. In this case (2.4) does not vanish identically for the integrals of the motion. However, the corrections associated with the nonlocal nature of J are very small for all the kinetic phenomena which are of interest to us, and we shall in future neglect them. Cf., the detailed discussion in [13].

where $\hat{\Omega}^{(+)}$ is a symmetric operator which does not alter the temporal parity of a function on which it operates, while $\hat{\Omega}^{(-)}$ is an antisymmetric operator which brings about transitions between states with different temporal parity. These operators have the form (2.10) where the role of W′ is played by the quantities

$$W^{(\pm)} = {}^1\!/_2(W' \pm W). \tag{2.16}$$

Expanding the nonequilibrium part of the distribution function (2.7) in terms of the complete system of functions:

$$\chi = \sum_m \chi_m \psi_m, \tag{2.17}$$

we obtain taking into account (2.8)

$$\int d\Gamma\, J \ln f = \langle \chi \hat{\Omega} \chi \rangle = \sum \Omega_{mn}^{(+)} \chi_m \chi_n \geqslant 0. \tag{2.18}$$

Thus, the matrix $\Omega_{mn}^{(+)}$ is positive definite. At the same time the law of increasing entropy does not impose any restrictions on the matrix elements of the operator $\Omega^{(-)}$

In the absence of stereoisomerism, when the scattering probability is not altered by inversion and, as a consequence, relation (2.2) is valid, the matrix elements Ω_{mn} vanish if the functions ψ_m and ψ_n have different spatial parity. But if relation (1.1) holds, then $\Omega^{(-)} = 0$, and Ω_{mn} differ from zero only if both the spatial and the temporal parities of ψ_m and ψ_n coincide ("selection rules").

3. TRANSPORT PHENOMENA IN THE ABSENCE OF EXTERNAL FIELDS

We consider how the suppression of relation (1.1) alters the nature of the general solution of the linearized kinetic equation in the absence of an external field

$$\hat{\Omega}\chi + N = 0. \tag{3.1}$$

The inhomogeneous term of this equation is equal to

$$N = N_i^{(1)} (\nabla \ln T)_i + N_{ik}^{(2)} \{\nabla_i V_k\} + N^{(0)} \operatorname{div} \mathbf{V}, \tag{3.2}$$

where

$$N_i^{(1)} = v_i \left(\frac{\varepsilon}{T} - c_P\right), \quad N_{ik}^{(2)} = \{v_i v_k\} \frac{m}{T},$$

$$N^{(0)} = \frac{mv^2}{2T} - \frac{\varepsilon}{c_V T},$$

$$\varepsilon = {}^1\!/_2 mv^2 + E_{\text{вр}}, \quad \{a_i b_k\} = {}^1\!/_2 (a_i b_k + a_k b_i - {}^2\!/_3 \delta_{ik} (\mathbf{ab})).$$

Writing the nonequilibrium part of the distribution function in the form

$$\chi = \chi_i^{(1)} (\nabla \ln T)_i + \chi_{ik}^{(2)} \{\nabla_i V_k\} + \chi^{(0)} \operatorname{div} \mathbf{V},$$

we can separate (3.1) into three independent equations:

$$\hat{\Omega}\chi^{(a)} + N^{(a)} = 0, \quad a = 0, 1, 2. \tag{3.3}$$

The functions $\chi^{(a)}$ uniquely determine the kinetic coefficients: the coefficient of heat conductivity

$$\varkappa = -{}^1\!/_3 \langle N_i^{(1)} \chi_i^{(1)} \rangle, \tag{3.4a}$$

the first viscosity coefficient

$$\eta = -{}^1\!/_{10} \langle N_{ik}^{(2)} \chi_{ik}^{(2)} \rangle, \tag{3.4b}$$

the second viscosity coefficient

$$\zeta = -T \langle N^{(0)} \chi^{(0)} \rangle. \tag{3.4c}$$

Below we shall give the name of a kinetic equation to one of equations (3.3) and the name of a kinetic coefficient to a quantity of the form (3.4) omitting the indices in this case.

We represent the function χ in the form of the expansion (2.17). Then the integral equation (3.3) goes over into the infinite system of algebraic equations equivalent to it

$$\sum_n \Omega_{mn} \chi_n + N_m = 0, \quad N_m = \langle \psi_m N \rangle. \tag{3.5}$$

If the relation (1.1) holds, then $\Omega = \Omega^{(+)}$ and Ω_{mn} differs from zero only for transitions with the same T- and I-parities. But then it immediately follows from (3.5) that the coefficients χ_n differ from zero only if the functions ψ_n and N have the same T- and I-parities.

When the relation (1.1) is violated and an operator $\hat{\Omega}^{(-)}$ different from zero arises, the collision operator connects functions of different parity, as a result of which there appear in the general solution of (3.3) terms with parity which does not coincide with the parity of N.

Let the temperature gradient be different from zero. In accordance with what has been stated above, and taking into account the explicit form of (3.2), we can assert that the vector $\chi^{(1)}$ will be determined by the set of vector functions of the following form:

a) in the case (1.1)

$$\mathbf{v}, \ \mathbf{M}(\mathbf{vM}); \tag{3.6a}$$

b) in the case (2.2) (the temporal parity of $\chi^{(1)}$ need not coincide with the T-parity of $\mathbf{N}^{(1)}$) to the functions (3.6a) there is added the function

$$[\mathbf{vM}]; \tag{3.6b}$$

c) in the general case (2.1) (when there is no "selection rule" with respect to the spatial parity) additional functions appear in the form

$$\mathbf{M}, \ \mathbf{v}(\mathbf{vM}), \ [\mathbf{vM}](\mathbf{vM}). \tag{3.6c}$$

Naturally all these quantities are assumed to be multiplied by scalar functions of scalar arguments v^2, M^2 and $(vM)^2$.

Thus, in the absence of stereoisomerism $\chi^{(1)}$ is determined by three independent polar vectors (3.6a), (3.6b), (cf.,[2]; specific calculations in the present paper were carried out on the assumption (1.1) in accordance with which the coefficient of the function (3.6b) was set equal to zero). It is interesting that in the presence of a temperature gradient an average flux of rotational angular momentum can arise of the form

$$\overline{[\mathbf{vM}]} = C_1 \nabla T, \quad \bar{A} = \int d\Gamma\, fA \Big/ \int d\Gamma\, f. \tag{3.7}$$

In the case of stereoisomerism the vector $\chi^{(1)}$ begins to depend also on three independent pseudovectors (3.6c). In this case the temperature gradient can lead even to the appearance of an average angular momentum

$$\overline{M} = C_2 \nabla T, \tag{3.8}$$

and at the same time, in principle, also to a rotation of the gas (cf.,[13]). We note that the kinetic coefficient C_2 is proportional to the pseudoscalar α and the polarization induced by the temperature gradient has a different sign for left-handed and right-handed stereoisomeric molecules.

In polar gases there can also arise the effect of polarization of the dipole moment of the gas

$$\bar{d} = C_3 \nabla T. \qquad (3.9)$$

We now let the divergence of the microscopic velocity be different from zero. In the case of such an inhomogeneity in addition to the usual solution corresponding to a scalar function of scalar arguments[2] there appears a pseudoscalar solution of the form

$$(\mathbf{vM}) F(v^2, M^2, (\mathbf{vM})^2), \qquad (3.10)$$

if the gas consists of stereoisomeric molecules. In this case there arises a flux of rotational angular momentum of the form

$$\overline{(\mathbf{vM})} = C_4 \operatorname{div} \mathbf{V}. \qquad (3.11)$$

We now examine the nature of the solution of the kinetic equation (3.3) with the inhomogeneity $N^{(2)}$. In this case in the expansion of $\chi^{(2)}$ nonvanishing coefficients can appear only multiplying the following irreducible tensors of the second rank (the scalar functions have been omitted):

$$\{v_i v_k\}, \quad \{M_i M_k\}, \quad \{v_i M_k\}(\mathbf{vM}); \qquad (3.12a)$$

$$\{v_i [\mathbf{vM}]_k\}, \quad \{M_i [\mathbf{vM}]_k\}(\mathbf{vM}); \qquad (3.12b)$$

$$\{v_i M_k\}, \quad \{v_i v_k\}(\mathbf{vM}), \quad \{M_i M_k\}(\mathbf{vM}), \quad \{M_i [\mathbf{vM}]_k\}, \quad \{v_i [\mathbf{vM}]_k\}(\mathbf{vM}). \qquad (3.12c)$$

In the absence of stereoisomerism $\chi^{(2)}$ is determined by tensors corresponding to (3.12a) and (3.12b) (cf.,[12]). In this case the three tensors (3.12a) which form a complete system when condition (1.1) is fulfilled have the same parity as $N^{(2)}$. If we give up temporal parity (condition (2.2)) the two tensors (3.12b) are added to this system. But in the case of stereoisomerism there appear five more independent pseudotensors (3.12c).

Thus, the inhomogeneous motion of a gas with rotational degrees of freedom when the tensor $\{\nabla_i V_k\} \neq 0$ can lead to the appearance (in addition to the usual viscous flux of momentum $\langle m\{v_i v_k\}\rangle$) of nonvanishing average values of a number of correlations enumerated in (3.11).

We note in conclusion that in constructing functions of tensor dimensionality l from polynomials in v and M of tensor dimensionalities l_1 and l_2 the correspondingly independent tensors are only tensors with $l_1 + l_2 = l$ and $l_1 + l_2 = l + 1$. The remaining tensors with $l_1 + l_2 \geq l + 2$ reduce to a linear combination of tensors with $l_1 + l_2 = l$ or $l_1 + l_2 = l + 1$. It is evident that the coefficients of this linear combination may depend on scalar expressions v^2, M^2 and (vM).

4. REMARKS CONCERNING THE VARIATIONAL PRINCIPLE

In finding an approximate solution of the linearized kinetic equation in the case of monatomic gases a significant role is played by the so-called variational principle which is a consequence of the law of increase of entropy and of the symmetry of the collision operator $\hat{\Omega}$. But on suppressing condition (1.1) the second condition is violated and the variational principle cannot be utilized in its ordinary form.

For kinetic problems with a nonselfconjugate operator, and also in the general case in obtaining the nondiagonal kinetic coefficients it is convenient to utilize the variational principle which is close to the method developed by Schwinger[14] (cf., also[15]). For this we introduce the functional

$$K_{PN} = -\{\langle \varphi \hat{\Omega} \chi \rangle + \langle \varphi N \rangle + \langle P \chi \rangle\}. \qquad (4.1)$$

Independent variation of this functional with respect to the functions φ and χ gives at the extremum

$$\hat{\Omega} \chi_N + N = 0, \quad \hat{\Omega}^+ \varphi_P + P = 0, \qquad (4.2)$$

where the first equation coincides with the kinetic equation. In this case the extremal value of (4.1)

$$K_{PN} = -\langle P \chi_N \rangle = -\langle \varphi_P N \rangle \qquad (4.3)$$

is equal to the value of the kinetic coefficient (up to a nonessential factor) corresponding to the flux of P under the condition that the inhomogeneity of the kinetic equation is equal to N.

In the case of a small deviation from the extremum we have

$$\delta^2 K_{PN} = -2\langle \delta\varphi \hat{\Omega} \delta\chi \rangle. \qquad (4.4)$$

For diagonal kinetic coefficients (P = N) and under the condition that the operator $\hat{\Omega}$ is selfconjugate both equations in (4.2) coincide and we arrive at the usual form of the variational principle, when (4.4) together (2.18) guarantee that the approximate value of the kinetic coefficient cannot exceed the exact one. This assertion is removed for nondiagonal kinetic coefficients in the general case, while for the diagonal ones it is removed in the case when (1.1) is suppressed. In this case the extremum of the functional (4.1) turns out to be a saddle point. But if the approximate value of the kinetic coefficient is evaluated by means of formula (4.1), then (4.4) gives us the possibility of asserting that the error in evaluating the kinetic coefficient is a quantity of the second order of smallness in terms of the deviation of the approximate solutions of equations (4.2) from the exact expressions χ_N and φ_P (cf., the analogous remark in[15]).

A search for an approximate solution of (4.2) in the form

$$\chi = \sum_{t=1}^{t_0} \chi_t \psi_t, \quad \varphi = \sum_{s=1}^{s_0} \varphi_s \psi_s' \qquad (4.5)$$

within the framework of the variational problem for the functional (4.1) leads to the system of equations

$$\sum_{t=1}^{t_0} \Omega_{st} \chi_t + N_s = 0, \quad \sum_{s=1}^{s_0} \varphi_s \Omega_{st} + P_t = 0, \qquad (4.6)$$

where the same notation has been adopted as in (3.5). Generally speaking the set of functions ψ_t and ψ_s' is different.

One can easily see that the system (4.6) will be compatible only under the conditions $s_0 = t_0$. In this case there arises a distinctive generalized method of moments. It is of interest that in each of systems (4.6) only matrix elements Ω_{st} between functions of different sets appear, and this reflects the internal connection of the two systems of equations (4.6).

We note that the approximate functions (4.5), just as the exact solutions of equations (4.2), satisfy the equation

$$\langle \varphi \hat{\Omega} \chi \rangle + \langle \varphi N \rangle = 0, \quad \langle \varphi \hat{\Omega} \chi \rangle + \langle P \chi \rangle = 0, \qquad (4.7)$$

and therefore the problem of the unconditional extremum of the functional (4.1) is equivalent to the problem of the conditional extremum of the functionals $\langle P\chi\rangle$, $\langle\varphi N\rangle$ or $\langle\varphi\hat\Omega\chi\rangle$, when the role of the subsidiary condition is played by one of the equations (4.7).

The function φ does not have a direct physical meaning. However its temporal reflection φ_P^T, as follows from (4.2) and (2.13), represents a perturbation of the distribution function due to the inhomogeneity of P^T. In this case the value of the dissipative flux is characterized by the kinetic coefficient

$$K_{N^T,\,P^T} = -\langle N^T\varphi_{P^T}\rangle = -\langle N\varphi_P\rangle. \tag{4.8}$$

This expression together with (4.3) yields

$$K_{PN} = K_{N^T P^T}. \tag{4.9}$$

We see that the Onsager principle follows directly from the kinetic equation.

5. PROPERTIES OF THE SOLUTION OF THE KINETIC EQUATION IN THE PRESENCE OF EXTERNAL FIELDS

A. We now analyze the manner in which the suppression of (1.1) affects the nature of the general solution the kinetic equation in the presence of an external field acting on the rotational degrees of freedom. If we denote the external field by **B**, then the kinetic equation in the general case can be written in the form[1-3]

$$(\hat\Omega + \hat\Omega_B)\chi_N + N = 0, \tag{5.1}$$

where the differential operator $\hat\Omega_B$ has the form

$$\hat\Omega_B\chi \equiv \dot{\mathbf{M}}\partial\chi/\partial\mathbf{M} = \gamma[\mathbf{MB}]\partial\chi/\partial\mathbf{M}. \tag{5.2}$$

Here γ is a quantity which has a definite value for each definite case and which is a scalar when **B** is a magnetic field, and a pseudoscalar when **B** is an electric field.

From the definition of the operator $\hat\Omega_B$ it follows directly that this operator is an antisymmetric operator:

$$\langle\varphi\hat\Omega_B\chi\rangle = -\langle\chi\hat\Omega_B\varphi\rangle. \tag{5.3}$$

Moreover, the operator $\hat\Omega_B$ is not changed on reflection and changes sign under time reversal. But from the point of view of the expansion of the function χ (2.18) in terms of a complete system of functions having a definite tensor dimensionality and parity the operator $\hat\Omega_B$ mixes states ψ_m of different tensor dimensionality, and this is associated with the presence of the external vector **B**. If the coefficient γ does not depend on **B**, then the operator $\hat\Omega_B$ does not alter the spatial and the temporal parities in the case of the magnetic field and changes both parities in the case of the electric field.

From this we see that the kinetic coefficient in an external field

$$K_{PN}(\mathbf{B}) = -\langle P\chi_N\rangle = \langle P(\hat\Omega + \hat\Omega_B)^{-1}N\rangle, \tag{5.4}$$

generally speaking differs from zero even if the inhomogeneity N and the flux P have different tensor dimensionality and parity.

The functions N and P are, generally speaking, components of corresponding tensors, and therefore the quantities K_{PN} are elements of a tensor constructed from one select vector—the vector of the external field.

We note that the variational principle formulated in the preceding section is preserved also in the case of an external field if we replace the operator $\hat\Omega$ by the operator $\hat\Omega(B) = \hat\Omega + \hat\Omega_B$. For this operator the principal property (2.13) is replaced by

$$\langle\varphi\hat\Omega(\mathbf{B})\chi\rangle = \langle\chi^T\hat\Omega(\mathbf{B}^T)\varphi^T\rangle, \quad \mathbf{B}^T = \pm\mathbf{B} \tag{5.5}$$

(the upper sign corresponds to the electric field, the lower sign to the magnetic field). In this case the relation (4.9) assumes the form of the generalized Onsager principle in an external field

$$K_{PN}(\mathbf{B}) = K_{N^T P^T}(\mathbf{B}^T). \tag{5.6}$$

B. Let first the external magnetic field be different from zero. In this case γ for the most interesting cases either simply represents a constant (nonparamagnetic gas in a magnetic field), or it is proportional to a discrete variable σ, which takes on values from $-S$ to $+S$ (S is the spin of the molecule) and which is a true scalar (a paramagnetic gas in a magnetic field). If we now take into account the properties of the operators $\hat\Omega$ and $\hat\Omega_B$, then this turns out to be sufficient in order to formulate certain general properties of the solution of equation (5.1).

We assume that the condition (1.1) is fulfilled. Then the solution of equation (5.1) will have the same temporal and spatial parity as the inhomogeneity N (we are speaking everywhere about parity with respect to the variables **v** and **M**). Again the subspace of functions with parity noncoincident with N is split off and does not participate in the construction of the nonequilibrium function χ_N. Within the framework of conservation of T- and I-parities the expansion can contain along with (3.6a) or (3.12a) terms of arbitrary tensor dimensionality with respect to **v** and **M**.

If the principle of detailed balance is fulfilled in the form (2.2), then as a result of the action of the operator $\hat\Omega^{(-)}$ temporal parity is not conserved and the action of the operator $\hat\Omega_B$ leads to the appearance in the expansion of terms of arbitrary tensor dimensionality, but with spatial parity coincident with N.

In those cases when the principle of detailed balance is fulfilled only in the form (2.1), terms of arbitrary parity and tensor dimensionality can appear in the expansion for χ_N.

Thus, on violation of condition (1.1) the simultaneous action of operators $\hat\Omega$ and $\hat\Omega_B$ leads to the appearance of "cross" effects, i.e., the microscopic nonequilibrium of definite tensor dimensionality and of definite parity $N^{(a)}$ gives rise to fluxes of different tensor dimensionality, which for $B = 0$ or $\hat\Omega^{(-)} = 0$ are brought about by an inhomogeneity of the kinetic equation of other parity (the other "a"). The only thing for which we have to watch out is the possibility of constructing (for the description of the flux) of the corresponding tensor from the given external macroscopic tensor and the axial vector **B**. In the case of stereoisomeric molecules no problems arise in general, since in the problem there always exists the pseudoscalar α.

The appearance of "cross" effects can be traced in a very clearcut manner by considering a gas with an inhomogeneous temperature. In the case of stereoisomeric molecules the action of the operator $\hat\Omega^{(-)}$ leads to the appearance in $\chi^{(1)}$ of terms even with respect to v (cf., (3.6c)), while the operator $\hat{\Omega}_B$ "builds up" their tensor dimensionality to $\{v_iv_k\}$ and v^2. This immediately leads to the appearance of the tensor of the flux of momentum—quantities of the form $\overline{\{v_iv_k\}}$ and $\overline{v^2}$. Naturally these are not the only effects. One can easily trace that in the presence of stereoisomerism the average correlators of all functions of the form (3.12) differ from zero.

In the converse case, when $\nabla_i V_k \neq 0$, in a gas consisting of stereoisomeric molecules a heat flux arises which is associated with the appearance of a nonvanishing correlation of the form $\overline{v_i(\epsilon - c_pT)}$.

Within the framework of the present analysis one can easily point out the conditions under which the existence of effects odd in the field is possible. Taking into account the fact that the corresponding term of the expansion of χ will contain γ to an odd power, and in the expression for the corresponding flux there will be contained a summation over the additional variable σ, it can be easily established that odd effects take place in a nonparamagnetic gas in the general case, and in a paramagnetic gas in the case of a consistent taking into account of the state with $\sigma = 0$[16] or of taking into account the change in σ in a collision[3].

One of the most interesting manifestations of the suppression of conditions (1.1) is the appearance of the "positive" effect[7-9,17]. The possibility of the existence of this effect and the reason for its appearance can be understood without resorting to a quantum discussion of the rotational degrees of freedom[10,11]. In order to do this we make use of the fact that the operator $\hat{\Omega}_B$ is an antisymmetric operator.

Multiplying the kinetic equation (5.1) by χ_N and integrating over $f^{(0)}d\Gamma$, we arrive at an equation of the form (4.7)

$$\langle\chi\hat{\Omega}\chi\rangle + \langle\chi N\rangle = 0, \tag{5.7}$$

which turns out to be valid both in the absence and in the presence of an external field. But, as we know (cf., above section 4), for $\hat{\Omega}^{(-)} = 0$ of all the functions satisfying (5.7) the maximum value is given to the quantity $K_{NN} = -\langle N\chi\rangle$ by the solution of the kinetic equation without a field (3.3). From this it follows immediately that when the principle of detailed balancing in the form of (1.1) is satisfied the kinetic coefficients K_{NN} (which for $B = 0$ are in fact a contraction of the corresponding tensors) are always diminished when an external field is switched on[2]. This is the usual "negative" Senftleben effect. Naturally this applies also to the diagonal elements of the kinetic tensors of heat conductivity and viscosity.

When condition (1.1) is replaced by (2.1) or (2.2), then the sign of the change in the kinetic coefficients in an external field in accordance with (4.4) becomes arbitrary. The sign of this deviation and, consequently, the sign in the change of the kinetic coefficient in an external field depends on the nature of the change generated by the operator $\hat{\Omega}_B$ in the relative weight of the functions of different parity in the expansion (2.17). If $\hat{\Omega}_B$ acts primarily on a state of the same parity as N, then the switching on of the field leads to a reduction in the kinetic coefficient. In the opposite case when $\hat{\Omega}_B$ alters primarily states of opposite parity, the kinetic coefficients in an external field increase and we arrive at a "positive" Senftleben effect. Since, as we have seen, the operator $\hat{\Omega}_B$ does not alter the temporal parity of the function, the appearance of a "positive" effect is associated in a decisive manner with the scale of the operator $\hat{\Omega}^{(-)}$ and always occurs in competition with the "negative" effect. From this, on the one hand, arises the difficulty of predicting a priori the sign of the change in the kinetic coefficient without a detailed knowledge of the nature of the interaction between molecules, and on the other hand there appears a possibility of a change in the sign as the magnitude of the field is varied.

The whole picture described above is manifested very clearly if we utilize the general formulas obtained in[3] on the assumption of weak nonsphericity. Thus, for example, in the case of a nonparamagnetic gas the change in the kinetic coefficient in an external field is determined by the expression (cf., formulas (5.12)—(5.15) in[3])

$$\begin{aligned}\operatorname{Re} c^{(2)}_{lm,lm} &= -\Omega_{NN}^{-2}\sum_n \Omega_{nn}^{-1}\langle N_{lm}\hat{\Omega}\psi_n\rangle\langle\psi_n\hat{\Omega}N_{lm}\rangle \\ &\times \sum_{m_2}\{C^{lm}_{l_1m_1l_2m_2}\}^2(m_2\gamma B)^2/[\Omega_{nn}{}^2 + (m_2\gamma B)^2].\end{aligned} \tag{5.8}$$

Here Ω_{NN} and Ω_{nn} are the diagonal matrix elements of the operator $\hat{\Omega}$ corresponding to N and ψ_n, $C^{lm}_{l_1m_1l_2m_2}$ are the Clebsch-Gordan coefficients, $n = (lm, l_1l_2, \ldots)$. We see that in agreement with (2.14) the terms of the sum with respect to n, for which the temporal parity of ψ_n coincides with N always enter with a negative sign. For small fields the common sign is determined by the sign of the sum

$$\sum_n \Omega_{Nn}\Omega_{nN}/\Omega_{nn}^3, \tag{5.9}$$

and for large fields by the sign of the sum

$$\sum_n \Omega_{Nn}\Omega_{nN}/\Omega_{nn}. \tag{5.10}$$

It is essential that the signs of (5.9) and (5.10) need not coincide. This manifested itself clearly in references[9,17] where it was found that a change in the coefficient of heat conductivity of CH_3CN in electric and magnetic fields changes sign in going from weak fields to saturation fields.

C. We now proceed to the case when the electric field differs from zero. We consider a gas of polar polyatomic molecules. In this case $\gamma \sim \sigma$ where $\sigma = (Md)(M^2d^2)^{-1/2}$ is a continuous variable taking on values from -1 to $+1$ (d is the dipole moment of the molecule)[3]. In this case $\Gamma = (v, M, \sigma)$, with $\hat{I}\sigma = -\sigma$ and $\hat{T}\sigma = -\sigma$. From this it can be seen that in the absence of stereoisomerism the probability of scattering is an even function with respect to the simultaneous replacement $v \to -v$ and $\sigma \to -\sigma$ (cf., (2.2) $\Gamma^{IT} = (v, -M, \sigma)$). Now let the set of functions in terms of which the function χ_N is expanded have definite T and I-parity, including also the variable σ. Then it follows from (5.2) that the operator $\hat{\Omega}_B$ in the case of the elec-

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[2] An analogous conclusion can be drawn for the coefficient of electrical conductivity in metals with a center of inversion if the spin-orbit interaction is small.

tric field differs from zero only for transitions between states with different temporal and spatial parities. It is clear that for effects even in terms of the electric field the analysis remains the same as in case of the magnetic field. But for effects odd in B the picture requires special consideration.

In the heat conductivity tensor κ_{ik} and the viscosity tensor $\eta_{ikl m}$ terms odd in the electric field are always absent. This is associated with the fact that in accordance with (5.6) these tensors are symmetric while the terms odd in the field lead to antisymmetry.

It is of interest that in the case of the electric field the "cross" effect can exist when the principle of detailed balance is realized in the form (2.2) or (1.1). This can be easily traced if we take into account the fact that in order to find the "cross" effect we must calculate an expression of the form (5.4) with P which differs in its symmetry properties from N. Considering again the phenomena of heat conductivity and of viscous momentum transfer and taking into account the fact that $N^{(1)}$ and $N^{(2)}$ have just the opposite temporal and spatial parities we find that there will exist a cross effect odd in the electric field even for $\hat{\Omega}^{(-)} = 0$. For example, in a weak field (cf.,[18]) $\kappa_{ik} \sim B_i(\nabla T)_k$. We note also the possibility in principle of the appearance of polarization in an electric field in the presence of a temperature gradient[14]:

$$\overline{\mathbf{M}} = [\mathbf{B}\nabla T]. \qquad (5.11)$$

In the remaining details the reconstruction of χ_N under the influence of an electric field when (1.1) is dropped has qualitatively the same character as in the case of a magnetic field; in particular, there is manifested to the full extent the possibility of the existence of a "positive" effect[7-9].

If the polar molecule is diatomic or linear[3], then $\gamma \sim (\mathbf{ME})$ and no additional variable arises. In this case the operator $\hat{\Omega}_B$ (5.2) connects functions of different temporal and coincident spatial parities. Consequently, in the expansion of the solution χ_N terms will appear of temporal parity which differs from N even when condition (1.1) is satisfied. But conservation of spatial parity leads to the fact that, for example, "cross" effects generally cannot be observed in this case (there is no stereoisomerism); as regards the "positive" effect, it is possible if $\hat{\Omega}^{(-)} \neq 0$. An analogous analysis can also be carried out for any more complicated case when the internal state of the molecule is described in addition to M by more than one parameter. The corresponding generalization can be carried out directly. No new characteristic features differing in principle arise in such a case.

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