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# *THE POSSIBLE EXISTENCE OF CROSS EFFECTS IN GASES WITH OPTICALLY ACTIVE MOLECULES*

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We consider the behavior of a gas of polyatomic molecules of the optical isomer type in external fields. We establish a selection rule for the matrix elements of the collision operator and obtain expressions for the kinetic cross coefficients in a field. We show that in the case of optical isomers cross effects in a magnetic field are possible. The magnitude of these effects should be different for dextro- and levo-rotatory isomers.

## 1. INTRODUCTION

IT is well known that the behavior of the transport coefficients of a number of polyatomic gases in electrical and magnetic fields shows an anomalous character.[1-3] To explain such a behavior of the transport coefficients we must assume that collisions with $W \neq W'$ are characteristic for these gases ($W$ and $W'$ are the probabilities for direct and inverse collisions [4,5] ). Such an assumption enables us, in particular, to obtain an expression for the thermal conductivity tensor which describes positive and negative effects in a field.

In gases with optically active molecules the collision probability is not invariant under an inversion transformation.[6] Cross effects which will be considered in the present paper are thus possible in such gases in external fields. In[5,7,8] the cross effect connecting the viscosity and the thermal conductivity in an electric field was considered for symmetric-top type optically-inactive molecules. It was shown that the effect is possible only under conditions when $W$ is not an even function of $\sigma$ (the component of the dipole moment along the angular momentum). For optically active molecules in an electric field this condition is not necessary.

## 2. INFLUENCE OF SPATIAL SYMMETRY ON THE PHENOMENOLOGICAL (KINETIC) COEFFICIENTS

It is convenient to use for the consideration of cross effects the relations of non-equilibrium thermodynamics.[9] Because of its generality this procedure makes it possible to take into account possible symmetry properties. Amongst such properties is spatial symmetry and also symmetry with respect to time reversal. A consistent use of this symmetry makes it possible to find the most general form possible of all kinetic coefficients.

We must introduce into the set of equations of non-equilibrium thermodynamics a pseudoscalar current $J^p$ and a pseudoscalar thermodynamic force $X^p$ since it is possible that scalar effects such as chemical reactions are different for dextro- and levo-rotatory isomers. We must note that although the molecules possess a non-zero angular momentum we assume that the average moment of the whole system is equal to zero, i.e., we do not consider rotation of the gas as a whole. The viscous stresses tensor is thus symmetric and we need not consider the "rotational" viscosity.[9,10]

In contrast to the isotropic system considered in[9] when there is no external field, it is necessary in the case of an optically active gas to consider merely symmetry with respect to arbitrary rotations since there is for such a gas no symmetry under an inversion of the coordinates. This symmetry can easily be taken into account if we use the properties of irreducible Cartesion tensors.[11]

After a few transformations we can see that the set of equations of non-equilibrium thermodynamics for the case of a gas with optically active molecules has the following form (when there is no field):

$$J^s = L^{ss}X^s + L^{sp}X^p, \quad J^p = L^{ps}X^s + L^{pp}X^p,$$
$$J_i^v = a_1 X_i^v + a_2 X_i^a, \quad J_i^a = a_3 X_i^v + a_4 X_i^a,$$
$$J_{ij}^t = a_5 X_{ij}^t, \tag{2.1}$$

where

$$a_1 = {}^1/_3 L_{ii}^{vv}, \quad a_2 = {}^1/_3 L_{ii}^{va}, \quad a_3 = {}^1/_3 L_{ii}^{av}, \quad a_4 = {}^1/_3 L_{ii}^{aa}, \quad a_5 = {}^1/_5 L^{tt}{}_{ik,\,kl}.$$

The notation used in (2.1) is the same as in[9].

From the form of the set (2.1) we can conclude that when there are no external fields there can not be any effects coupling viscosity and thermal conductivity. If the external field is non-vanishing the properties of the system are not invariant under arbitrary rotations and symmetry considerations do not forbid such kinds of an effect.

The system has axial symmetry in an external field. Consideration of this symmetry can be made in a way similar to the procedure used for the thermal conductivity and viscosity in a magnetic field.[9] Using this symmetry, the relation between $J_i^v$ and $X_{jk}^t$ takes the following form:

$$\begin{array}{c|cccccc} & X_{11}^t & X_{22}^t & X_{33}^t & X_{12}^t & X_{13}^t & X_{23}^t \\ \hline J_1^v & 0 & 0 & 0 & 0 & L_{113}^{vt} & L_{123}^{vt} \\ J_2^v & 0 & 0 & 0 & 0 & L_{213}^{vt} & L_{223}^{vt} \\ J_3^v & L_{311}^{vt} & L_{322}^{vt} & L_{333}^{vt} & 0 & 0 & 0 \end{array},$$

$L_{123}^{vt} = -L_{213}^{vt}$, $L_{113}^{vt} = L_{223}^{vt}$, $L_{311}^{vt} = L_{322}^{vt}$, $L_{333}^{vt} + L_{322}^{vt} + L_{311}^{vt} = 0$. $L_{311}^{vt}$, $L_{322}^{vt}$, $L_{333}^{vt}$, $L_{113}^{vt}$, and $L_{223}^{vt}$ are odd in the field, and $L_{213}^{vt}$ and $L_{123}^{vt}$ even. One can show that when there is no field the cross effects coupling the viscosity and the thermal conductivity must be absent when the properties of the system are invariant under a coordinate inversion. Bearing in mind that the electric field strength is a polar vector we see that the cross coefficients will be non-vanishing only if they are odd in the field. In a magnetic field these coefficients are non-vanishing in the case when the interaction potential of the molecules is non-invariant under a coordinate inversion.

## 3. SELECTION RULE FOR THE MATRIX ELEMENTS OF THE COLLISION OPERATOR

The basic condition for the optical activity of molecules is that there is for them no equilibrium configuration of the following symmetry elements: plane of symmetry and center of symmetry.[12] In that case $W \neq \hat{S}W$ and $W \neq \hat{P}W$ (here $\hat{S}$ is the operator of the coordinate inversion and $\hat{P}$ the operator of taking the reflection in an arbitrary plane). To establish a selection rule for the matrix elements we need thus consider only the symmetry under time reversal.

We write the collision operator $\hat{I}$ in the following form:[13]

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

The parameter $\epsilon$ characterizes the smallness of the off-diagonal matrix elements of the operator $\hat{I}$ and corresponds to the small parameter used in[14] for decomposing the interaction potential of diatomic molecules into a spherical and a non-spherical part; $\hat{I}^{(0)}$ is an operator which is diagonal in the functional space $\Psi_n$. The eigenfunctions $|\Psi_n\rangle$ of the operator $\hat{I}^{(0)}$ were given in ref.[13] and have the form

$$|\Psi_n\rangle = |lm, l_1 l_2, r_1 r_2\rangle = \sum_{m_1+m_2=m} C^{lm}_{l_1 m_1 l_2 m_2} Y_{l_1 m_1}(\mathbf{u})\, Y_{l_2 m_2}(\mathbf{M})\, T_{r_1}^{l_1}(u^2)\, L_{r_2}^{l_2}(M^2).$$

We assume that the eigenvalues $\lambda_n$ of the operator $\hat{I}^{(0)}$ form a discrete spectrum ($\lambda_n = \lambda_{l_1 l_2 r_1 r_2}$). The functions $\Psi_n$ are orthonormalized:

$$\langle \Psi_n, \Psi_{n'}\rangle = \int d\Gamma f_0 \Psi_n^* \Psi_{n'} \delta_{nn'}.$$

We write the operator $\hat{I}^{(1)}$ as a sum[3]

$$\hat{I}^{(1)} = \hat{I}_c^{(1)} + \hat{I}_a^{(1)}.$$

Here

$$\hat{I}_c^{(1)}\Psi_n = \int f_{01}(\Psi_n + \Psi_{1n} - \Psi_n' - \Psi_{1n}')\, W_c\, d\Gamma_1\, d\Gamma'\, d\Gamma_1',$$

$$\hat{I}_a^{(1)}\Psi_n = \int f_{01}(\Psi_n + \Psi_{1n} + \Psi_n' + \Psi_{1n}')\, W_a\, d\Gamma_1\, d\Gamma'\, d\Gamma_1'.$$

Using the symmetry properties of the collision integral[15] we see that the matrix elements of the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ have the following properties:

$$\langle \Psi_n | \hat{I}_c^{(1)} | \Psi_{n'}\rangle = \langle \Psi_n' | \hat{I}_c^{(1)} | \Psi_{n'}'\rangle, \tag{3.1}$$

$$\langle \Psi_n | \hat{I}_a^{(1)} | \Psi_{n'}\rangle = -\langle \Psi_n' | \hat{I}_a^{(1)} | \Psi_{n'}'\rangle. \tag{3.2}$$

Bearing in mind that the matrix elements of the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ can not change under time reversal and also Eqs. (3.1) and (3.2) we get the following selection rules:

for $\hat{I}_c^{(1)}$: if $l_1 + l_2$ is even, then $l_1' + l_2'$ is even, (3.3)
if $l_1 + l_2$ is odd, then $l_1' + l_2'$ is odd;

for $\hat{I}_a^{(1)}$: if $l_1 + l_2$ is even, then $l_1' + l_2'$ is odd, (3.4)
if $l_1 + l_2$ is odd, then $l_1' + l_2'$ is even.

In the case of molecules with higher symmetry it is necessary to consider also the invariance of the matrix elements under inversion. Bearing in mind that in that case $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ commute with the inversion operator we can obtain a selection rule which agrees with the one obtained in[3].

For a polar gas the eigenfunctions of the operator $\hat{I}^{(0)}$ have the form

$$|\Phi_n\rangle = |\Psi_n \varphi_s(\sigma)\rangle,$$

where the functions $\varphi_s(\sigma)$ are real and satisfy the relation

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

for even s the functions $\varphi_s(\sigma)$ are even and for odd s they are odd. Here $\sigma$ has the meaning of the component of the dipole moment along the angular momentum. We write the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ in the following form:

$$\hat{I}_c^{(1)} = \hat{\mathscr{P}}_c^{(1)} + \hat{Q}_c^{(1)}, \quad \hat{I}_a^{(1)} = \hat{\mathscr{P}}_a^{(1)} + \hat{Q}_a^{(1)}. \tag{3.5}$$

The division (3.5) corresponds to the assumption that the collision probability can be written in the form

$$W^{(1)} = W^{(1)}_{\text{even}} + W^{(1)}_{\text{odd}}$$

where $W^{(1)}_{\text{even}}$ and $W^{(1)}_{\text{odd}}$ are, respectively, even and odd functions in $\sigma$.

The selection rule for the operators $\hat{\mathscr{P}}^{(1)}$ and $\hat{Q}^{(1)}$ can be obtained by taking into account the invariance of the matrix elements of these operators under time reversal and coordinate inversion. For the matrix elements of the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ the condition $l = l'$ and $m = m'$ must be satisfied. (Since the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ commute with any rotation in the space of the N particles they do not change the dimensionality of the representation according to which $\Psi_n$ or $\Phi_n$ transform under rotations.)

We now establish some properties of the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$. We show that the operator $\hat{I}_c^{(1)}$ is Hermitean and $\hat{I}_a^{(1)}$ anti-Hermitean. Using the symmetry properties of the collision integral we have

$$\langle \Psi_n | \hat{I}_c^{(1)} | \Psi_{n'}\rangle = \langle \Psi_{n'} | \hat{I}_c^{(1)} | \Psi_n\rangle^*. \tag{3.6}$$

Comparing (3.6) with the matrix element of the transposed operator we get

$$(\hat{I}_c^{(1)})^* = \tilde{\hat{I}}_c^{(1)},$$

i.e., the operator $\hat{I}_c^{(1)}$ is Hermitean. By means of the relation

$$\int W d\Gamma' d\Gamma_1' = \int W' d\Gamma' d\Gamma_1'$$

we can obtain the following property of the matrix elements of the operator $\hat{I}_a^{(1)}$:

$$\langle \Psi_n | \hat{I}_a^{(1)} | \Psi_{n'}\rangle = -\langle \Psi_{n'} | \hat{I}_a^{(1)} | \Psi_n\rangle^*. \tag{3.7}$$

From (3.7) it follows that

$$(\hat{I}_a^{(1)})^* = -\tilde{\hat{I}}_a^{(1)}. \tag{3.8}$$

We conclude from (3.8) that the operator $\hat{I}_a^{(1)}$ is anti-Hermitean.

## 4. CROSS EFFECTS IN A MAGNETIC FIELD

The linearized kinetic equation, averaged over the fast rotation of the molecules has the form[13]

$$N+\gamma[\mathbf{MB}]\frac{\partial\chi}{\partial\mathbf{M}}=-n(\hat{I}^{(0)}+\varepsilon\hat{I}^{(1)})\chi. \qquad (4.1)^*$$

Following[13], we write Eq. (4.1) in a spherical system of coordinates (we take B ∥ z). We write the expression for N in the following form:

$$N=n\sum_{l,m}a_{lm}{}^*A_{lm},\qquad l=0,1,2,\qquad |m|\leqslant l. \qquad (4.2)$$

The quantities $A_{lm}$ in (4.2) are defined by means of the functions $\Theta_{lm}$ which differ from the ones used in[13] by the presence of a phase factor $i^l$ and normalization to $4\pi/(2l+1)$. This choice of phase factor is more natural from the point of view of the addition of angular momenta.[16,17] The coefficients $a_{lm}$ are determined as follows:

$$a_{00}=\frac{1}{n}\operatorname{div}\mathbf{v}_0,\qquad a_{2m}=\frac{1}{n}t_{ik}^{2m}\left(\frac{\partial v_{0k}}{\partial x_i}+\frac{\partial v_{0i}}{\partial x_k}-\frac{2}{3}\delta_{ik}\frac{\partial v_{0l}}{\partial x_l}\right).$$

The expression for $a_{lm}$ is the same as the one given in[13]. We can obtain the values of the coefficients $t_{ik}^{lm}$ and $t_i^{lm}$ in the same way as was done in[13]; The values of the coefficients $a_{lm}$ in (4.2) are chosen such that the volume viscosity and the cross coefficients connected with it are taken into account.

We can look for the solution of the equation in the form

$$\chi=-\sum_{l,m}a_{lm}{}^*\chi_{lm}. \qquad (4.3)$$

Substituting (4.3) into (4.1) and using (4.2) we get

$$\left(\hat{I}^{(0)}+\varepsilon\hat{I}^{(1)}-\tilde{\gamma}\frac{\partial}{\partial\varphi_M}\right)\chi_{lm}=A_{lm}. \qquad (4.4)$$

Equation (4.4) differs from the analogous equation given in[13] by the sign in front of $\tilde{\gamma}\partial/\partial\varphi_M$ but this does not lead to any essential change. We can solve Eq. (4.4) by the method developed in[13].

Substituting the expression for $\chi_{lm}$ into (4.3) and bearing in mind that $\chi$ is a real function we see that the matrix elements of the operators $\hat{I}_c^{(1)}$ and $\hat{I}_a^{(1)}$ are real numbers. The equations (3.6) and (3.7) now take the following form:

$$\langle\Psi_n|\hat{I}_c^{(1)}|\Psi_{n'}\rangle=\langle\Psi_{n'}|\hat{I}_c^{(1)}|\Psi_n\rangle, \qquad (4.5)$$

$$\langle\Psi_n|\hat{I}_a^{(1)}|\Psi_{n'}\rangle=-\langle\Psi_{n'}|\hat{I}_a^{(1)}|\Psi_n\rangle. \qquad (4.6)$$

For the evaluation of the kinetic coefficients it is necessary to determine the energy and momentum currents. The expressions for the heat current and the viscous tensions tensor have the form[13]

$$q_i=nT\sqrt{\frac{2T}{m}}\int d\Gamma f_0u_i(u^2+M^2-c_p)\chi,$$

$$\sigma_{ik}=2nT\int d\Gamma f_0\chi u_iu_k=\sigma_{ik}{}^{\mathrm{I}}+\sigma^{\mathrm{II}}\delta_{ik}, \qquad (4.7)$$

$\sigma_{ik}^{\mathrm{I}}$ corresponds to the usual viscous flux while $\sigma^{\mathrm{II}}$ is the viscous flux connected with the second (volume) viscosity. Substituting (4.3) into (4.7) we can see that

$$q_i=q_i{}^{\mathrm{I}}+q_i{}^{\mathrm{II}}+q_i^{\mathrm{III}},\qquad \sigma^{\mathrm{II}}=\sigma_1{}^{\mathrm{II}}+\sigma_2{}^{\mathrm{II}}+\sigma_3^{\mathrm{III}},\qquad \sigma_{ik}{}^{\mathrm{I}}=\sigma_{ik1}^{\mathrm{I}}+\sigma_{ik2}^{\mathrm{I}}+\sigma_{ik3}^{\mathrm{I}},$$

which corresponds to $l = 0, 1, 2$ in (4.3).

In correspondence with the phenomenological equations

$$q_i{}^{\mathrm{I}}=-c_{ikl}(D_{kl}-{}^1\!/_3\delta_{kl}D_{\alpha\alpha}),\qquad D_{kl}={}^1\!/_2(\partial v_{0l}/\partial x_k+\partial v_{0k}/\partial x_l),$$

$$q_i{}^{II}=-\varkappa_{ik}\nabla_kT/T,\qquad q_i^{\mathrm{III}}=-d_i\operatorname{div}\mathbf{v}_0,\qquad \sigma_1{}^{\mathrm{II}}=-\mu\operatorname{div}\mathbf{v}_0,$$

$$\sigma_2{}^{\mathrm{II}}=-d_i'\nabla_iT/T,\qquad \sigma_3{}^{\mathrm{II}}=-\xi'_{ik}(D_{ik}-{}^1\!/_3\delta_{ik}D_{ll}),$$

$$\sigma_{ik1}^{\mathrm{I}}=-\xi_{ik}\operatorname{div}\mathbf{v}_0,\qquad \sigma_{ik2}^{\mathrm{I}}=-c_{ikl}'\nabla_lT/T,$$

$$\sigma_{ik3}=-\eta_{ikpq}(D_{pq}-{}^1\!/_3\delta_{pq}D_{ll})$$

the expressions for the kinetic coefficients have the following form:

$$\begin{aligned}c_{ikl}&=2T\sqrt{2T/m}[-ih_i(h_kh_l-{}^1\!/_3\delta_{kl})C_{10,\,20}+\sqrt{{}^1\!/_3}(h_kh_{li}+\\&+h_lh_{ki})\operatorname{Re}C_{11,\,21}+\sqrt{{}^1\!/_3}(\delta_{li}h_k+\delta_{ki}h_l-2h_kh_lh_i)\operatorname{Im}C_{11,\,21}]\\d_i&=T\sqrt{2T/m}h_iiC_{10,\,00},\ \mu=TC_{00,\,00},\ d_i'=-T\sqrt{2T/m}h_iiC_{00,\,10},\\\xi_{ik}'&=-2T(h_ih_k-{}^1\!/_3\delta_{ik})C_{00,\,20},\qquad \xi_{ik}=-2T(h_ih_k-{}^1\!/_3\delta_{ik})C_{20,\,10},\\c'_{ikl}&=2T\sqrt{2T/m}[ih_l(h_kh_i-{}^1\!/_3\delta_{ik})C_{20,\,10}+\sqrt{{}^1\!/_3}(h_kh_{il}+\\&+h_ih_{kl})\operatorname{Re}C_{21,\,11}-\sqrt{{}^1\!/_3}(\delta_{li}h_k+\delta_{kl}h_i-2h_kh_lh_i)\operatorname{Im}C_{21,\,11}]\end{aligned} \qquad (4.8)$$

Here

$$h_i=H_i/H(\text{or }\ E_i/E),\ h_{ik}=\varepsilon_{ikp}h_p=\delta_{ix}\delta_{ky}-\delta_{iy}\delta_{kx}.$$

In obtaining (4.8) we used the relations

$$C_{lm,\,l'm}=\langle A_{lm},\chi_{l'm}\rangle=(-1)^{l+l'}C^*{}_{l-m,\,l'-m},$$

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

One verifies easily that the kinetic coefficients (4.8) satisfy the symmetry requirements established in Sec. 2. The expressions for the heat conductivity and viscosity tensors $\kappa_{ik}$ and $\eta_{ikpq}$ were given in[13]. We note that if we take into account the form of the tensor $\eta_{ikpq}$ when there is no field[9] we can prove that

$$C_{20,\,20}=-\operatorname{Re}C_{22,\,22}.$$

The kinetic coefficients (4.8) must satisfy the reciprocity relations. In a magnetic field these relations look as follows:

$$d_i(\mathbf{H})=-d_i'(-\mathbf{H}),\qquad \varkappa_{ik}(\mathbf{H})=\varkappa_{ki}(-\mathbf{H}),\qquad \xi_{ik}(\mathbf{H})=\xi_{ki}'(-\mathbf{H}),$$

$$c_{ikl}(\mathbf{H})=-c_{lki}(-\mathbf{H}),\qquad \eta_{ikpq}(\mathbf{H})=\eta_{pqik}(-\mathbf{H}). \qquad (4.9)$$

We note that the reciprocity relation for the coefficients $c_{ikl}$ and $c'_{ikl}$ can be obtained directly from the kinetic equation in a way similar to what was done in[5] for the case of an electric field. The reciprocity relations in an electric field will look as follows:

$$d_i=-d_i',\qquad \varkappa_{ik}=\varkappa_{ki},\qquad \xi_{ik}=\xi_{ki}',\qquad c_{ikl}=-c'_{lki},\qquad \eta_{ikpq}=\eta_{pqik}. \qquad (4.10)$$

It follows from Eqs. (10) that in an electric field $\operatorname{Im}C_{11,11}=\operatorname{Im}C_{21,21}=\operatorname{Im}C_{22,22}=0$. We shall show below that this equation is indeed satisfied.

We note that the Onsager relations are based upon the invariance of the laws of mechanics under time reversal. This invariance holds for a gas whatever the structure of the molecules and because of this the reciprocity relations are true also for an optically active gas. The effect which is odd in the field for the thermal

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*[MB] ≡ M × B.

conductivity and the viscosity must therefore be absent in an electric field.

We calculate the components of $\kappa_{ik}$ in a magnetic field. On the basis of the selection rules (3.3) and (3.4) we can choose such a model for the interaction between the molecules that transitions into the states $|1m, 11\rangle$ and $|1m, 22\rangle$ are allowed for $\hat{I}_a^{(1)}$ and into the states $|1m, 12\rangle$ and $|1m, 21\rangle$ for $\hat{I}_c^{(1)}$. For molecular-non-isomers transitions into the states $|1m, 22\rangle$ and $|1m, 21\rangle$ will be forbidden. (The indices $r_1$ and $r_2$ are not taken into account to simplify the notation.)

Using the chosen model we obtain easily expressions for $\Delta C_{11,11}^{(2)}$ and $\Delta C_{10,10}^{(2)}$ which describe the change in the components of the heat conductivity tensor in a magnetic field. However, because of their complexity we do not give these expressions in the present paper. Using Eqs. (4.5) and (4.6) in the expressions for $\Delta C_{11,11}^{(2)}$ and $\Delta C_{10,10}^{(2)}$ we can split off terms $\Delta C^+$ and $\Delta C^-$ describing positive and negative changes in the heat conductivity tensor components.

We consider now the case of an electric field. On the basis of the selection rules we can choose the following model: transitions into the states $|1m, 11, 0\rangle$, $|1m, 21, 1\rangle$, $|1m, 12, 1\rangle$, and $|1m, 22, 0\rangle$ are allowed for $\hat{I}_a^{(1)}$, and for $\hat{I}_c^{(1)}$ transitions into the states $|1m, 11, 1\rangle$, $|1m, 12, 0\rangle$, $|1m, 21, 0\rangle$, and $|1m, 22, 1\rangle$ are allowed.

Using the explicit form of the operator $\hat{K}$ in an electric field we can prove that

$$\langle\Phi_n|\hat{K}|\Phi_{n'}\rangle = \frac{1}{\lambda_n} - \frac{1}{\lambda_n}\sum_{m_1+m_2=m}(C_{l_1m_1l_2m_2}^{lm})^2$$

$$\times\left\langle L_0^{l_2}(M^2)M^{2l_2}\varphi_s(\sigma),\ \frac{(m_2\tilde{\gamma}\sigma)^2 - im_2\tilde{\gamma}\sigma M\lambda_n}{\lambda_n^2M^2 + (m_2\tilde{\gamma}\sigma)^2}L_0^{l_2}(M^2)\varphi_{s'}(\sigma)\right\rangle. \quad (4.11)$$

Here

$$l = l', \quad \tilde{\gamma} = dE/n.$$

It is clear from (4.11) that Im $C_{11,11}$ will vanish if the functions $\varphi_S(\sigma)$ and $\varphi_{S'}(\sigma)$ have the same parity in $\sigma$.

We consider the case when the functions $\varphi_S(\sigma)$ and $\varphi_{S'}(\sigma)$ have different parity in $\sigma$. Corresponding to the chosen model we have

$$C_{11,11}^{\prime(2)} = \varepsilon^2\sum_{\alpha,\beta}\Lambda_{11,11}\{\langle 11, 10, 0|\hat{I}_c^{(1)}|11, \alpha\beta, \gamma\rangle\langle 11, \alpha\beta, \delta|\hat{I}_a^{(1)}|11, 10, 0\rangle$$

$$\times\langle 11, \alpha\beta, \gamma|\hat{K}|11, \alpha\beta, \delta\rangle + \langle 11, 10, 0|\hat{I}_a^{(1)}|11, \alpha\beta, \delta\rangle$$

$$\times\langle 11, \alpha\beta, \gamma|\hat{I}_c^{(1)}|11, 10, 0\rangle\langle 11, \alpha\beta, \delta|\hat{K}|11, \alpha\beta, \gamma\rangle\}. \quad (4.12)$$

Here $\alpha$, $\beta$ = 1, 2; $\delta = |\gamma - 1|$;

$$\gamma = \begin{cases} 1 \text{ when } (\alpha+\beta) \text{ is even} \\ 0 \text{ when } (\alpha+\beta) \text{ is odd;} \end{cases}$$

$$\Lambda_{lm,\,l'm} = \sum_{n_{l0}n_{l'0}}\lambda_{n_{l0}}^{-1}\lambda_{n_{l'0}}^{-1}\langle\Phi_{n_{l0}},\ A_{lm}\rangle\langle\Phi_{n_{l'0}},\ A_{l'm}\rangle,$$

$$n_{l0} \equiv |lm,\ l0,\ r_1r_2, 0\rangle.$$

We get easily from (4.11) that

$$\langle 11, \alpha\beta, \gamma|\hat{K}|11, \alpha\beta, \delta\rangle = \langle 11, \alpha\beta, \delta|\hat{K}|11, \alpha\beta, \gamma\rangle. \quad (4.13)$$

Using (4.5), (4.6), and (4.13) we see that $C_{11,11}^{\prime(2)} = 0$. We verify easily that $C_{11,11}^{\prime(2)}$ vanishes for any possible interaction model. The functions $\varphi_S(\sigma)$ and $\varphi_{S'}(\sigma)$ in (4.11) can thus only be of the same parity in $\sigma$ and Im $C_{11,11}$ vanishes thus in an electric field. One can show similarly that Im $C_{21,21}$ and Im $C_{22,22}$, which determine the effect odd in the field for the viscosity tensor components, vanish in an electric field.

As in the case of a magnetic field we can in the expressions for $\Delta C_{11,11}^{(2)}$ and $\Delta C_{10,10}^{(2)}$ split off $\Delta C^+$ and $\Delta C^-$ which describe respectively the positive and negative changes in the thermal conductivity. In[18] the relation $(T/\kappa_0 m)(\Delta C_{10,10}^{(2)} + \text{Re}\ \Delta C_{11,11}^{(2)}) = \varphi(E/p)$ was studied for the optically active gas $C_4H_9OH$ (secondary butyl alcohol). It was shown that this relation has an anomalous nature. The measured quantity showed a maximum ($-0.32 \times 10^{-5}$) for E/p = 30 V/cm mm Hg and changed sign for E/p = 65 V/cm mm Hg. The anomalous character of the observed relation can be explained if the coefficients $\Delta C_{11,11}^{(2)+}$, $\Delta C_{11,11}^{(2)-}$, $\Delta C_{10,10}^{(2)+}$, and $\Delta C_{10,10}^{(2)-}$ in the expression for the heat conductivity tensor, which are different functions of E/p, are of the same order of magnitude.

We consider now the expressions for the cross coefficients in a magnetic field. One can show that in zeroth and first approximations in $\epsilon$ the expressions for the cross coefficients vanish. In second approximation in $\epsilon$ we can obtain for the coefficient $C_{11,21}^{(2)}$ in $c_{ikl}$ the expression

$$C_{11,21}^{(2)} = \varepsilon^2\sum_{\alpha\beta,pp',k}\Lambda_{11,21}(-1)^{\alpha+\beta}\langle 11, 10|\hat{I}_p^{(1)}|11, \alpha\beta\rangle\cdot$$

$$\times\langle 21, 20|\hat{I}_{p'}^{(1)}|21, \alpha\beta\rangle\Phi_k^H(\xi), \quad (4.14)$$

$$\alpha, \beta = 1, 2; \begin{cases}\alpha \neq 2 \\ \beta \neq 2\end{cases}; p, p' = c, a; p \neq p';$$

$$p = \begin{cases} c, \text{ if } (\alpha+\beta) \text{ is odd} \\ a, \text{ if } (\alpha+\beta) \text{ is even}\end{cases}, \quad k = \begin{cases} 1 \text{ for } \alpha = 1,\ \beta = 1 \\ 2 \text{ for } \alpha = 1,\ \beta = 2. \\ 3 \text{ for } \alpha = 2,\ \beta = 1\end{cases}$$

In deriving (4.14) we used Eqs. (4.5) and (4.6). The model used in (4.14) assumes that transitions into states with $l_1 = 2$ and $l_2 = 2$ have a small probability as was established in[19].

The functions $\Phi_k^H(\xi)$ have the form

$$\Phi_1^H = \frac{1}{2\lambda_{11}}\frac{\xi^2 - i\lambda_{11}\xi}{\lambda_{11}^2 + \xi^2},$$

$$\Phi_2^H = -\frac{1}{\lambda_{12}\sqrt{5}}\left[\frac{1}{2}\frac{\xi^2 - i\lambda_{12}\xi}{\lambda_{12}^2 + \xi^2} - \frac{4\xi^2 - 2i\lambda_{12}\xi}{\lambda_{12}^2 + 4\xi^2}\right],$$

$$\Phi_3^H = -\frac{1}{2\sqrt{5}\lambda_{21}}\left[\frac{\xi^2}{\lambda_{21}^2 + \xi^2} + \frac{3i\lambda_{21}\xi}{\lambda_{21}^2 + \xi^2}\right]. \quad (4.15)$$

From the form of (4.14) and (4.15) it is clear that when $\xi = 0$ (when there is no field) $c_{ikl}$ vanishes as we already noted in Sec. 2.

We note that when obtaining an expression for $C_{11,21}^{(2)}$ we took into account that in the presence of a field the operator $\hat{K}$ is not a scalar and transitions with a change in $l$ ($l = l_1 + l_2$) are allowed. We prove the reciprocity relations (4.9) for the cross coefficients $c_{ikl}$ and $c'_{ikl}$. Using the expression for $c'_{ikl}$ we get

$$c'_{lki}(-\mathbf{H}) = 2T\sqrt{\frac{2T}{m}}\left[-ih_i\left(h_kh_l - \frac{1}{3}\delta_{kl}\right)C_{20,10} + \sqrt{\frac{1}{3}}[h_kh_{li}\right.$$

$$\left.+ h_lh_{ki}]\,\text{Re}\,C_{21,11} + \sqrt{\frac{1}{3}}(\delta_{il}h_k + \delta_{ki}h_l - 2h_ih_kh_l)\right]\text{Im}\,C_{21,11}. \quad (4.16)$$

From (4.14), (4.15), and Eqs. (4.5) and (4.6) we find

$$C_{10,20} = -C_{20,10},\ C_{11,21} = -C_{21,11}. \tag{4.17}$$

Substituting (4.17) into (4.16) we find that the cross coefficients $c_{ikl}$ and $c'_{ikl}$ satisfy the Onsager relations in a magnetic field.

We can similarly obtain expressions and prove the reciprocity relations also for the other cross coefficients. We note that the coefficients $c_{ikl}$ and $c'_{ikl}$, $d_i$ and $d'_i$ will be non-vanishing only if the coordinate inversion is not a symmetry element of the operator $\hat{I}$. This agrees with the conclusions of Sec. 2. It turns out, however, that the coefficient $C^{(2)}_{20,00}$ which determines the cross coefficient $\xi_{ik}$ will be non-vanishing when the system is invariant under coordinate inversion (the selection rules for the operators $\hat{I}^{(1)}_c$ and $\hat{I}^{(1)}_a$ for that case were given in[3]). The expression for the coefficient $C^{(2)}_{20,00}$ which determines $\xi_{ik}$ has the following form:

$$C^{(2)}_{20,00} = \varepsilon^2 \Lambda_{20,00} \langle 20, 20 | \hat{I}_c^{(1)} | 20, 22 \rangle \langle 00, 00 | \hat{I}_c^{(1)} | 00, 22 \rangle \mathscr{L}_1{}^H(\xi),$$

$$\mathscr{L}_1{}^H(\xi) = -\sqrt{\frac{2}{35}} \frac{1}{\lambda_{22}} \left[ \frac{8\xi^2}{\lambda_{22}{}^2 + 4\xi^2} - \frac{\xi^2}{\lambda_{22}{}^2 + \xi^2} \right]. \tag{4.18}$$

We note that the coefficient $C_{20,00}$ vanishes when there is no field. The coefficient $\xi_{ik}$ corresponds in the general set of equations of non-equilibrium thermodynamics to the coefficient $L^{ts}_{ik}$ which is non-vanishing when there is a field even if the system is invariant under a coordinate inversion (in that case $\xi_{ik}$ must be even in the field).

It follows from Eq. (4.18) that the coefficients $\xi_{ik}$ and $\xi'_{ik}$ are determined only by "transitions" into states with $l_1 = l_2 = 2$. As we noted already, transitions into such states have a low probability and evidently these kinetic coefficients are small compared with the ones we consider.

By means of the selection rules for the operators $\hat{\mathscr{P}}^{(1)}$ and $\hat{Q}^{(1)}$ of (3.5) we can obtain the following expression for the coefficient $C^{(2)}_{11,21}$ for the case of optically inactive polar molecules in an electric field:

$$\begin{aligned} C^{(2)}_{11,21} = \varepsilon^2 \Lambda_{11,21} \{ & \langle 11, 10, 0 | \hat{\mathscr{P}}_a^{(1)} | 11, 11, 0 \rangle \langle 21, 20, 0 | \hat{Q}_a^{(1)} | 21, 11, 1 \rangle F_1{}^E(\tilde{\gamma}) \\ & - \langle 11, 10, 0 | \hat{\mathscr{P}}_c^{(1)} | 11, 12, 0 \rangle \langle 21, 20, 0, | \hat{Q}_c^{(1)} | 21, 12, 1 \rangle F_2{}^E(\tilde{\gamma}) \\ & - \langle 11, 10, 0 | \hat{Q}_a^{(1)} | 11, 21, 1 \rangle \langle 21, 20, 0 | \hat{\mathscr{P}}_a^{(1)} | 21, 21, 0 \rangle F_3{}^E(\tilde{\gamma}) \}, \end{aligned} \tag{4.19}$$

$$F_1{}^E(\tilde{\gamma}) = -\frac{i}{2} \left\langle L_0^{3/2}(M^2) \varphi_0(\sigma), \frac{\tilde{\gamma}\sigma M^3}{\lambda_{11}{}^2 M^2 + (\tilde{\gamma}\sigma)^2} L_0^{3/2}(M^2) \varphi_1(\sigma) \right\rangle,$$

$$F_2{}^E(\tilde{\gamma}) = \frac{i}{\sqrt{5}} \Big\langle L_0^{5/2}(M^2) \varphi_0(\sigma),$$

$$\left[ \frac{\tilde{\gamma}\sigma M^5}{\lambda_{12}{}^2 M^2 + (\tilde{\gamma}\sigma)^2} - \frac{2\tilde{\gamma}\sigma M^5}{\lambda_{12}{}^2 M^2 + 4(\tilde{\gamma}\sigma)^2} \right] L_0^{5/2}(M^2) \varphi_1(\sigma) \Big\rangle,$$

$$F_3{}^E(\tilde{\gamma}) = -\frac{3}{2\sqrt{5}} i \left\langle L_0^{3/2}(M^2) \varphi_1(\sigma), \frac{\tilde{\gamma}\sigma M^3}{\lambda_{21}{}^2 M^2 + (\tilde{\gamma}\sigma)^2} L_0^{3/2}(M^2) \varphi_0(\sigma) \right\rangle. \tag{4.20}$$

In exactly the same way we can obtain an expression for $C^{(2)}_{10,20}$.

The coefficients $C_{20,10}$ and $C_{21,11}$ satisfy the relations

$$C_{20,10} = C_{10,20},\ C_{21,11} = C_{11,21}. \tag{4.21}$$

Using (4.21) one can show that the reciprocity relations for the coefficients $c_{ikl}$ and $c'_{ikl}$ are satisfied. It follows from (4.19) and (4.20) that $c_{ikl}$ and $c'_{ikl}$ are odd in the field as was already noted in Sec. 2. One can prove that the coefficients $d_i$ and $d'_i$ are also odd in the field. We note that the cross coefficients are non-vanishing also in the case when $W = W'(\hat{\mathscr{P}}^{(1)}_a = \hat{Q}^{(1)}_a = 0)$, as was shown in[7]. This statement is valid only for an electric field; in a magnetic field the cross coefficients vanish when $W = W'$.

We note that (4.19) and (4.20) are the classical analogue of the quantum mechanical expressions obtained in[5].

We can similarly obtain expressions for $c_{ikl}$ and $c'_{ikl}$ in an electric field for optically active polar molecules and in these expressions there will occur terms which are even in the field. One can prove the reciprocity relations in that case, if we bear in mind that

$$C_{20,10} = C_{10,20},\ \operatorname{Re} C_{21,11} = -\operatorname{Re} C_{11,21},\ \operatorname{Im} C_{21,11} = \operatorname{Im} C_{11,21}.$$

In conclusion we consider different effects for gases the molecules of which have rotational powers which differ in sign. We write the operator $\hat{I}^{(1)}$ as a sum:

$$\hat{I}_c^{(1)} = \hat{I}_+^{(1)} + \hat{I}_-^{(1)},$$

where the operators $\hat{I}^{(1)}_+$ and $\hat{I}^{(1)}_-$ are defined as follows:

$$\hat{I}_+^{(1)} \Psi_n = \frac{1}{2} \int f_{01} (\Psi_n + \Psi_{1n} - \Psi_n' - \Psi_{1n}') (W_c + \hat{P} W_c) d\Gamma_1 \, d\Gamma' \, d\Gamma_1', \tag{4.22}$$

$$\hat{I}_-^{(1)} \Psi_n = \frac{1}{2} \int f_{01} (\Psi_n + \Psi_{1n} - \Psi_n' - \Psi_{1n}') (W_c - \hat{P} W_c) d\Gamma_1 \, d\Gamma' \, d\Gamma_1'. \tag{4.23}$$

For the sake of simplicity we assume that the operator $\hat{P}$ is the operator for the reflection into the x,y-plane. We conclude from the form of (4.22) and (4.23) that $\hat{I}^{(1)}_+$ commutes and $\hat{I}^{(1)}_-$ anticommutes with the operator $\hat{P}$. Acting with the operator $\hat{P}$ on the matrix element of the operator $\hat{I}^{(1)}_c$ we get

$$\langle \hat{P}\Psi_n,\ \hat{P}\hat{I}_c^{(1)}\Psi_{n'} \rangle = (-1)^{l_1 + l_1'} [\langle \Psi_n,\ \hat{I}_+^{(1)} \Psi_{n'} \rangle - \langle \Psi_n,\ \hat{I}_-^{(1)} \Psi_{n'} \rangle]. \tag{4.24}$$

We can conclude from (4.24) that for a gas consisting of molecules which are mirror images the matrix elements of the operator $\hat{I}^{(1)}_c$ change in magnitude (similar considerations refer equally to the operator $\hat{I}^{(1)}_a$). On the other hand, it is known that the rotational powers of two molecules which are mirror images have the same magnitude, but opposite signs[12] so that the above considered effects for such gases will be different.

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