

# Kinetic Theory for Mixtures of Dilute Gases of Linear Rotating Molecules

## II. The Senftleben–Beenakker Effect of the Heat Conductivity

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The system of transport relaxation equations obtained from the linearized Waldmann-Snider equation is the starting point for the kinetic treatment of the heat conductivity for mixtures of linear diamagnetic molecules in an external homogeneous magnetic field. The connection of the occurring collision integrals with certain molecular cross sections is discussed and order of magnitude considerations are made for molecules with small nonsphericity of their interaction. With the Kagan polarization as the decisive rotational angular momentum anisotropy term in the molecular distribution function, an expression for the heat conductivity in the presence of a magnetic field is derived for mixtures with an arbitrary number of components. The mole fraction dependence of the saturation values is studied for binary mixtures of rotating molecules and noble gas atoms for a simplified model. As an example, the system  $\text{o-D}_2/\text{He}$  is considered.

### Introduction

In a recent paper<sup>1</sup>, the moment method<sup>2</sup> has been used to obtain the (infinite) system of coupled transport relaxation equations (in the following abbreviated by TRE) for mixtures of dilute gases of linear diamagnetic molecules from the linearized Waldmann-Snider equations<sup>3,4</sup>. A special scheme of expansion tensors (trial functions) built from the dimensionless molecular velocity  $\mathbf{C}$ , the dimensionless operator for the rotational angular momentum,  $\mathbf{J}$ , and the dimensionless internal rotational energy  $\mathcal{E}(J)$  has been introduced<sup>1</sup>. The truncated system of special TRE has been written down up to third rank tensor equations<sup>1</sup>.

The special system of TRE can be used as the starting point for the theoretical treatment of transport and relaxation phenomena in mixtures of dilute gases (which may consist of an arbitrary number of components) of linear molecules in an external homogeneous magnetic field. Experimental work on the magnetic field effects on transport properties in mixtures has been done for diffusion<sup>5</sup>, thermal diffusion<sup>6</sup> (in both cases without a measurable effect having been found), viscosity<sup>7</sup>, and is in progress for the heat conductivity<sup>8</sup>. The influence of an electric field on the heat conductivity of polar gas —  $\text{N}_2$  mixtures has recently been experimentally investigated by DE GROOT et al.<sup>9</sup>.

The present paper is concerned with the Senftleben–Beenakker effect (SBE)<sup>10</sup> of the heat con-

ductivity in mixtures, in particular binary mixtures of linear molecules with noble gas atoms. In contrast to the viscosity case which for mixtures has been studied theoretically by TIP<sup>11</sup> in a classical treatment, there is, to our knowledge, no corresponding quantum mechanical treatment of the heat conductivity problem. Recently, the viscosity of mixtures of polar gases with argon and helium has been investigated for the electric field case experimentally as well as theoretically by LEVI, SCOLES and TOMMASINI<sup>12</sup> who followed Tip's work.

As in the pure gas case, the changes in the heat conductivity due to the magnetic field are related to certain collision integrals of the linearized Waldmann-Snider collision term. The calculation of these integrals from first principles, i.e. from a given nonspherical molecular interaction is a difficult task which will not be considered here (cf. Refs.<sup>13,14</sup>). On the other hand, these collision integrals can, for a fixed temperature, be used as parameters to be determined from the experiment. The mole fraction dependence of the saturation values  $(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}}$  and  $(\Delta\lambda_{\perp}/\lambda)_{\text{sat}}$  from which these collision integrals could, in principle, be extracted, is experimentally studied by HEEMSKERK<sup>8</sup>, in particular for mixtures of rotating molecules with noble gas atoms.

In the following, the system of special TRE needed for the treatment of the magnetic field effects on the heat conductivity is selected from Ref.<sup>1</sup>. The relevant collision brackets are discussed

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and their orders of magnitude are estimated for molecules with small nonsphericity. In that case the relaxation coefficients can approximately be expressed in terms of Chapman-Cowling integrals<sup>15</sup>. The connection of the cross coefficients with molecular orientation cross sections for the 2nd rank tensor polarization of the rotational angular momenta is discussed. An expression for the heat conductivity tensor is derived. In the last section, the mole fraction dependence of the saturation value of the SBE is investigated for binary mixtures of linear molecules with noble gas atoms. In order to simplify the calculation and to avoid the introduction of more than one adjustable parameter, a simple model is used. In it, only the coupling of the Kagan polarization<sup>16</sup> with the rotational heat flux is taken into account. The remaining parameter then is the ratio of an effective cross section for the production of the tensor polarization in molecule-atom collisions and the corresponding effective cross section for molecule-molecule collisions. As an example, the o-D<sub>2</sub>-He mixture at room temperature is considered. The relaxation coefficients are evaluated for the classical rigid sphere model. The mole fraction dependence of  $\Delta\lambda/\lambda$  is finally plotted for different values of the above parameter.

### I. The Special Transport Relaxation Equations for the Thermal Conductivity in Mixtures

A gas mixture consisting of  $K$  species of linear molecules (species label  $i = 1, \dots, K$ ) in a homogeneous magnetic field is considered. Starting points for the treatment of the heat conductivity problem are the vector equations in Table 2 of Ref.<sup>1</sup>, taken for the stationary case. In first order hydrodynamics the gradients of all quantities except of those which obey the local conservation laws are put equal to zero. Experimental arrangements are considered where the mean mass velocity of the gas is zero (no convection) and the diffusion fluxes vanish. This implies that the average velocities  $\langle \mathbf{c}_i \rangle \propto \mathbf{a}_i^{(1)}$  can be put equal to zero.

In the stationary state, the individual temperatures (translational and rotational temperature of each species) have relaxed to a common temperature  $T(\mathbf{x})$ ; a temperature gradient  $\partial T/\partial \mathbf{x}$  in the gas is caused by a temperature difference maintained externally. Thus we can put in the vector equations of Ref.<sup>1</sup>

$$\nabla a_i^{(2)} \approx \frac{1}{T_0} \sqrt{\frac{3}{2}} \nabla T(\mathbf{x}), \quad (1.1a)$$

$$\nabla a_i^{(3)} \approx \frac{1}{T_0} \sqrt{\frac{c_{\text{rot},i}}{k_B}} \nabla T(\mathbf{x}), \quad (1.1b)$$

where  $T_0$  is the equilibrium temperature (the deviation of the gas from thermal equilibrium being small),  $c_{\text{rot},i}$  is the rotational heat capacity per molecule at the temperature  $T_0$  for the species  $i$ , and  $k_B$  is Boltzmann's constant.

The heat fluxes  $\mathbf{q}_{\text{trans}}$  and  $\mathbf{q}_{\text{rot}}$  can be expressed in terms of the vectors  $\mathbf{a}_i^{(3)}$  and  $\mathbf{a}_i^{(4)}$  by<sup>1</sup>

$$\mathbf{q}_{\text{trans}} = \sqrt{\frac{5}{6}} k_B T_0 \sum_{i=1}^K d_i \mathbf{a}_i^{(3)}, \quad (1.2a)$$

$$\mathbf{q}_{\text{rot}} = \frac{1}{\sqrt{3}} k_B T_0 \sum_{i=1}^K \hat{d}_i \mathbf{a}_i^{(4)}. \quad (1.2b)$$

The abbreviations

$$d_i = n_{i0} c_i, \quad \hat{d}_i = n_{i0} \hat{c}_i, \quad (1.3a)$$

have been used in Eqs. (1.2a, b). The thermal velocities  $c_i$  and  $\hat{c}_i$  are defined by

$$c_i = \sqrt{3 k_B T_0 / m_i}, \quad \hat{c}_i = \sqrt{\frac{c_{\text{rot},i}}{k_B}} c_i. \quad (1.3b)$$

The equilibrium particle density of species  $i$  has been denoted by  $n_{i0}$ . The total heat flux  $\mathbf{q}$  is the sum of  $\mathbf{q}_{\text{trans}}$  and  $\mathbf{q}_{\text{rot}}$ .

For the situation considered, the relevant vector TRE are the following:

$$\sqrt{\frac{2}{3}} \omega_{H,i} h_\mu b_i^{(1)} + \frac{1}{2} \omega_{H,i} (\mathbf{h} \times \mathbf{a}_i^{(2)})_\mu \quad (1.4a)$$

$$- \frac{1}{\sqrt{2}} \omega_{H,i} h_\nu b_{i\mu\nu}^{(1)} + \sum_{j=1}^K \sum_{k'=2}^5 -1 \omega_{ij}^{(2k')} a_{j\mu}^{(k')} = 0,$$

$$\sqrt{\frac{5}{6}} \frac{c_i}{T_0} \nabla_\mu T + \sum_{j=1}^K \sum_{k'=2}^5 -1 \omega_{ij}^{(3k')} a_{j\mu}^{(k')} = 0, \quad (1.4b)$$

$$\frac{1}{\sqrt{3}} \frac{\hat{c}_i}{T_0} \nabla_\mu T + \sum_{j=1}^K \sum_{k'=2}^5 -1 \omega_{ij}^{(4k')} a_{j\mu}^{(k')} = 0, \quad (1.4c)$$

$$\begin{aligned} \frac{3}{2} \omega_{H,i} (\mathbf{h} \times \mathbf{a}_i^{(5)})_\mu + \frac{3}{\sqrt{10}} \omega_{H,i} h_\nu b_{i\mu\nu}^{(2)} \\ + \sum_{j=1}^K \sum_{k'=2}^5 -1 \omega_{ij}^{(5k')} a_{j\mu}^{(k')} = 0. \end{aligned} \quad (1.4d)$$

The vectors  $\mathbf{a}_i^{(2)} \propto \langle \mathbf{c} \times \mathbf{J} \rangle_i$  and  $\mathbf{a}_i^{(5)} \propto \langle \mathbf{J} \mathbf{J} \cdot \mathbf{c} \rangle_i$  both describe nonequilibrium correlations between the molecular velocity  $\mathbf{c}$  and the molecular rotational angular momentum  $\hbar \mathbf{J}$ ; the symmetric traceless tensor built from the components of  $\mathbf{J}$  is denoted by  $\overline{\mathbf{J} \mathbf{J}}$ . The vector  $\mathbf{a}^{(2)}$  is called "azimuthal

polarization", the vector  $\mathbf{a}^{(5)}$  is called "Kagan polarization". As can be seen from Eq. (1.4a), the azimuthal polarization is coupled by way of the precession term —  $\omega_{H,i}$  is the precession frequency of the magnetic moment of a molecule "i",  $\mathbf{h}$  is a unit vector in the direction of the magnetic field  $\mathbf{H}$  — to the pseudoscalar  $b_i^{(1)}$  and to the 2nd rank pseudotensor  $b_{i\mu\nu}^{(1)}$ , the physical meaning of which has been explained in <sup>1</sup>. Thus, in addition, the following two equations have to be considered:

$$-\sqrt{\frac{2}{3}} \omega_{H,i} h_\mu a_{i\mu}^{(2)} + \sum_{j=1}^K -\omega_{ij}^{(11)} b_j^{(1)} = 0, \quad (1.5a)$$

$$\frac{\omega_{H,i}}{\sqrt{2}} \overline{h_\mu a_{i\nu}^{(2)}} + \omega_{H,i} \square_{\mu\nu, \lambda, \mu'\nu'}^{(2)} h_\lambda b_{i\mu'\nu'}^{(1)} + \sum_{j=1}^K -2\omega_{ij}^{(11)} b_{j\mu\nu}^{(1)} = 0. \quad (1.5b)$$

The tensors  $\square_{\dots, \lambda, \dots}^{(l)} h_\lambda$  describe the infinitesimal rotation of an  $l$ th rank tensor about  $\mathbf{h}$  and have been used in Ref. <sup>1</sup>.

In the same manner the Kagan vector is coupled in Eq. (1.4d) by way of the precession term to the pseudotensor  $b_{i\mu\nu}^{(2)}$ , so that Eqs. (1.4) have to be supplemented by the following equation for the pseudotensor

$$-\frac{3}{\sqrt{10}} \omega_{H,i} \overline{h_\mu a_{i\nu}^{(5)}} + \frac{5}{3} \omega_{H,i} \square_{\mu\nu, \lambda, \mu'\nu'}^{(2)} h_\lambda b_{i\mu'\nu'}^{(2)} + \sqrt{\frac{2}{3}} \omega_{H,i} h_\lambda a_{i\mu\nu\lambda}^{(2)} + \sum_{j=1}^K -2\omega_{ij}^{(22)} b_{j\mu\nu}^{(2)} = 0. \quad (1.6)$$

In Eq. (1.6) the third rank tensor  $a_{i\mu\nu\lambda}^{(2)}$  appears. Therefore we must also take into account the second of the third rank tensor equations of Table 2 in <sup>1</sup>:

$$-\sqrt{\frac{2}{3}} \omega_{H,i} \overline{h_\mu b_{i\nu\lambda}^{(2)}} + 2\omega_{H,i} \square_{\mu\nu\lambda, \kappa, \mu'\nu'\lambda'}^{(3)} h_\kappa a_{i\mu'\nu'\lambda'}^{(2)} + \sum_{j=1}^K -3\omega_{ij}^{(22)} a_{j\mu\nu\lambda}^{(2)} = 0. \quad (1.7)$$

The physical meaning of the tensors  $b_{i\mu\nu}^{(2)}$  and  $a_{i\mu\nu\lambda}^{(2)}$  can be inferred from Ref. <sup>1</sup>; together with the Kagan vector these tensors are essentially the irreducible components of the flux of the tensor polarization.

The set of Eqs. (1.4)–(1.7) is sufficient for the calculation of the SBE of the heat conductivity for gas mixtures with an arbitrary number of components. In the Eqs. (1.5)–(1.7), the cross collision brackets  $\omega_{ij}^{(kk')}$ ,  $k \neq k'$ , have tacitly been neglected compared with the relaxation coefficients ( $k = k'$ ). This is certainly correct for molecules with a small

nonsphericity of their interaction (see the following chapter). Nevertheless, the Eqs. (1.4)–(1.7) are still too unwieldy and further simplifications will have to be made. Firstly, the coupling between the azimuthal polarization and the Kagan vector will be neglected since it would lead to higher order corrections in the (small) nonsphericity. Secondly, a "spherical" approximation for the relaxation coefficients will be made. This procedure is explained in the following chapter; one important result following from the spherical approximation is the equality of the relaxation coefficients of the irreducible components of a reducible tensor, e.g. the flux of tensor polarization.

## II. Collision Brackets

In this chapter the reduced collision brackets  $P_l \omega_{ij}^{(kk')}$  of the linearized Waldmann-Snider collision operator relevant for the heat conductivity problem are discussed, in particular for molecules with small nonsphericity of their interaction. We recall that the reduced collision brackets  $P_l \omega_{ij}^{(kk')}$  are abbreviations for sums of the more basic brackets  $P_l \omega_{ij}^{(kk')\top}$  and  $P_l \omega_{ij}^{(kk')\top\top}$  which arise directly from the linearized collision term [cf. Eqs. (3.4)–(3.6) of Ref <sup>1</sup>], viz.

$$P_l \omega_{ij}^{(kk')} = P_l \omega_{ij}^{(kk')\top\top} + \delta_{ij} \sum_j P_l \omega_{ij}^{(kk')\top},$$

Eq. (4.12) of Ref. <sup>1</sup>

where  $P$  and  $l$  denote parity and tensor rank of the expansion tensors (labelled with  $k$  and  $k'$ ) involved.

For further treatment, it is convenient to introduce the following dimensionless molecular quantities:

Dimensionless center-of-mass velocity:

$$\mathbf{V} = \sqrt{(m_i + m_j)/2k_B T_0} \tilde{\mathbf{c}}, \quad (2.1)$$

where  $\tilde{\mathbf{c}}$  is the center-of-mass velocity.

Dimensionless relative velocities before and after the collision, respectively:

$$\begin{aligned} \mathbf{V}' &= \mathbf{v}' \mathbf{e}' = \sqrt{m_{ij}/2k_B T_0} \mathbf{g}', \\ \mathbf{V} &= \mathbf{v} \mathbf{e} = \sqrt{m_{ij}/2k_B T_0} \mathbf{g}, \end{aligned} \quad (2.2)$$

where  $m_{ij}$  is the reduced mass,  $\mathbf{g}' = \mathbf{g}' \mathbf{e}' = \mathbf{c}'_I - \mathbf{c}'_{II}$ ,  $\mathbf{g} = \mathbf{g} \mathbf{e} = \mathbf{c}_I - \mathbf{c}_{II}$ . Since a possibility of confusion does not exist, it is not necessary to supply  $\mathbf{V}$ ,  $\mathbf{V}'$ ,  $\mathbf{g}$ , and  $\mathbf{g}'$  with species labels  $ij$ .

Dimensionless internal rotational energy:

$$\mathcal{E}_{iI} = E_i(J_I)/k_B T_0 \quad \text{etc.}, \quad (2.3)$$

where  $E_i(J) = \hbar^2 J(J+1)/2\Theta_i$ .

By use of the abbreviations

$$M_i = \sqrt{m_i/(m_i + m_j)}, \quad M_j = \sqrt{m_j/(m_i + m_j)}, \\ C_{iI} = \sqrt{m_i/2k_B T_0} \mathbf{c}_I, \quad \text{etc.} \quad (2.4)$$

the kinematic collision equations are

$$C_{iI} = M_i \mathbf{V} + M_j \gamma \mathbf{e}, \quad C_{jII} = M_j \mathbf{V} - M_i \gamma \mathbf{e}, \quad (2.5a)$$

$$C'_{iI} = M_i \mathbf{V} + M_j \gamma' \mathbf{e}', \quad C'_{jII} = M_j \mathbf{V} - M_i \gamma' \mathbf{e}'. \quad (2.5b)$$

With the energy transfer

$$\Delta \mathcal{E} = \mathcal{E}_{iI} + \mathcal{E}_{jII} - \mathcal{E}_{iI'} - \mathcal{E}_{jII'}, \quad (2.6)$$

the energy conservation in a collision is expressed by

$$\gamma'^2 = \gamma^2 + \Delta \mathcal{E}. \quad (2.7)$$

With the use of Eqs. (2.1), (2.2) and with Eq. (3.1) of Ref. <sup>1</sup> we obtain the following relation for the product of two equilibrium distribution functions

$$f_{iI}^{(0)} f_{jII}^{(0)} d^3 c_I d^3 c_{II} = n_{i0} n_{j0} (Q_i Q_j)^{-1} \pi^{-3} \quad (2.8)$$

$$\exp(-V^2) \exp(-\gamma^2 - \mathcal{E}_{iI} - \mathcal{E}_{jII}) d^3 V \gamma^2 d\gamma d^2 e.$$

Next, the following molecular cross sections which will occur in the expressions of the special collision brackets, are defined.

a) The "unpolarized differential cross section"  $\sigma_{ij}(I II, I' II')$  which is equal to the differential cross section averaged over the initial and summed over the final magnetic quantum numbers for the time reversed collision process (cf. <sup>13</sup>), viz.

$J_I + J_{II} \rightarrow J'_I + J'_{II}$ , is given by

$$\sigma_{ij} = (2J_I + 1)^{-1} (2J_{II} + 1)^{-1} \frac{\gamma'}{\gamma} \\ \cdot \text{tr}_I \text{tr}_{II} \{ a_{ij}^{I II, I' II'} a_{ij}^{I' II', I II} \}. \quad (2.9)$$

In Eq. (2.9),  $a_{ij}^{I II, I' II'}$  is the single channel scattering amplitude (matrix with respect to magnetic quantum numbers; remember that the matrix property is expressed by the superscripts I, II, etc. <sup>1</sup>), introduced in Ref. <sup>1</sup>, and "tr" is the trace over the magnetic quantum numbers.

b) The "orientation cross section for vector polarization" is defined by

$$\sigma_{ij}^{(n)} = (2J_I + 1)^{-1} (2J_{II} + 1)^{-1} \frac{\gamma'}{\gamma} \\ \cdot \sqrt{3} \text{tr}_I \text{tr}_{II} \{ a_{ij}^{I II, I' II'} a_{ij}^{I' II', I II} \mathbf{J}^I \cdot \mathbf{n} \}, \quad (2.10)$$

where  $\mathbf{n} = (\mathbf{e}' \times \mathbf{e})/\sin \chi$  is the vector normal to the scattering plane and  $\chi = \arccos(\mathbf{e}' \cdot \mathbf{e})$  is the angle of deflection.

c) "Orientation cross sections for the 2nd rank tensor polarization" of the molecular rotational angular momenta are defined by

$$\sigma_{ij}^{(ee)} = (2J_I + 1)^{-1} (2J_{II} + 1)^{-1} \frac{\gamma'}{\gamma} \\ \cdot \text{tr}_I \text{tr}_{II} \left\{ a_{ij}^{I II, I' II'} a_{ij}^{I' II', I II} \sqrt{\frac{15}{2}} \overline{J_{\mu}^I J_{\nu}^I} e_{\mu} e_{\nu} \right\}, \quad (2.11)$$

and, analogously, for  $\sigma_{ij}^{(ee')}$ ,  $\sigma_{ij}^{(e'e')}$ .

d) "Reorientation cross sections" for the  $l$ th rank tensor polarization:

$$\text{re}\sigma_{ij}^{(l)} = (2J_I + 1)^{-1} (2J_{II} + 1)^{-1} \frac{\gamma'}{\gamma} \frac{(2l+1)!!}{l!} \\ \cdot \text{tr}_I \text{tr}_{II} \{ \overline{J_{\mu_1}^I \dots J_{\mu_l}^I} a_{ij}^{I II, I' II'} [a_{ij}^{I' II', I II} \overline{J_{\mu_1}^I \dots J_{\mu_l}^I}] - \}, \quad (2.12)$$

where  $\overline{J_{\mu_1}^I \dots J_{\mu_l}^I}$  is the  $l$ th rank irreducible Cartesian tensor operator built up from the rotational angular momentum vector  $\mathbf{J}^I$  for molecules "I". The analogous expression  $\text{re}\sigma_{ij}^{(l)}$  is defined by replacing  $\mathbf{J}^I$  by  $\mathbf{J}^{II}$  in the commutator in (2.12). The arguments I, II, I', II' of the cross sections denoting their rotational quantum number dependence have been omitted for simplicity.

The orientation cross sections describe the production of various sorts of alignment of the rotational angular momenta of the molecules "I" in a collision process  $J'_I + J'_{II} \rightarrow J_I + J_{II}$ . (rotational quantum numbers). Since the trace of an irreducible tensor vanishes, they are connected with the magnetic quantum number dependent part of the binary scattering amplitude and thus with the nonspherical part of the intermolecular potential. The reorientation cross sections describe, roughly speaking, the change of an already existing alignment of the rotational angular momenta. They vanish also for a purely spherical interaction, because in this case the commutator in (2.12) is zero.

For molecules with small nonspherical interaction, the scattering amplitude can be written approximately (up to linear terms in a scaling parameter  $\varepsilon$  which essentially measures the ratio of the nonspherical and the spherical part of the potential<sup>13,14</sup>) as

$$a_{ij}^{I II, I' II'} = a_{ij}^{(0)} P^{I II} \delta_{I II, I' II'} + \varepsilon a_{ij}^{(1) I II, I' II'}, \quad (2.13)$$

where  $a_{ij}^{(0)}$  is the magnetic and rotational quantum number independent ("spherical") part of the



scattering amplitude,  $P_{II}$  is the two-particle projection operator in rotational angular momentum space [see Eq. (1.7) of Ref. 1], and  $\varepsilon a_{ij}^{(1)II, I'II'}$  is the first order DWBA "nonspherical" part of the scattering amplitude ( $\varepsilon \ll 1$ , valid e.g. for the hydrogen molecules). As can be shown in the first order distorted wave Born approximation (DWBA) for scattering of linear rotating molecules<sup>13, 14</sup>, the trace  $\text{tr}_I \text{tr}_{II} \{a_{ij}^{(1)II, I'II'}\}$  vanishes. Thus we have by means of (2.10)

$$\sigma_{ij}(II, I'II') = \sigma_{ij}^{(0)} \delta_{II, I'II'} + 0(\varepsilon^2);$$

$$\sigma_{ij}^{(0)} = |a_{ij}^{(0)}|^2, \quad (2.14)$$

where the  $\delta$ -symbol expresses that the spherical part of the scattering amplitude is connected only with energetically elastic collisions. Furthermore, it can be shown within the same approximation<sup>13, 14</sup> that the orientation cross section for the vector polarization is at least of the order  $\varepsilon^2$  due to inelastic collisions while the orientation cross sections for the tensor polarization are linear in  $\varepsilon$  for elastic collisions and quadratic for inelastic ones. In any case, the reorientation cross sections (2.12) are at least of  $0(\varepsilon^2)$  because the commutator is linear in  $\varepsilon$ . These statements are useful for estimating the orders of magnitude of the various collision brackets for molecules with small nonsphericity.

The reduced collision brackets  $P_I \omega_{ij}^{(kk')} \sqsupset$  and  $P_I \omega_{ij}^{(kk')} \sqsupset \sqsupset$ , defined in <sup>1</sup> by the Eqs. (3.4), (3.5), (4.10) can, in general, be factorized in the following way

$$P_I \omega_{ij}^{(kk')} \sqsupset, \sqsupset \sqsupset = n_{j0} v_0 \cdot P_I \sigma_{ij}^{(kk')} \sqsupset, \sqsupset \sqsupset, \quad (2.15)$$

where  $n_{j0}$  is the equilibrium particle density of species  $j$ ,  $v_0 = \sqrt{8 k_B T_0 / \pi m_{ij}}$  is a mean thermal velocity, and the quantities  $P_I \sigma_{ij}^{(kk')}$  are effective, temperature dependent cross sections which are (for  $k \neq k'$ ) not necessarily positive.

Next, general expressions for the effective cross sections are given. It is useful, to introduce the following bracket symbols

$$\{\cdots\} \equiv \pi^{-3/2} \int \exp(-V^2) (\cdots) d^3V, \quad (2.16)$$

and

$$[\cdots] \equiv 2\pi (Q_I Q_J)^{-1} \sum_{J_I, J_{II}, J_{I'}, J_{II'}} (2J_I + 1) (2J_{II} + 1)$$

$$\times \iint \exp(-\mathcal{E}_{II} - \mathcal{E}_{JII} - \gamma^2) \gamma^3 (\cdots) \sin \chi d\chi d\gamma. \quad (2.17)$$

The first bracket symbol, Eq. (2.16), denotes an averaging over the center of mass velocity. The

second one, Eq. (2.17), describes a weighted averaging over  $\gamma$  and the postcollisional rotational quantum numbers  $J_I, J_{II}$ , as well as an integration over the angle of deflection  $\chi$  and a summation over the precollisional rotational quantum numbers  $J'_I, J'_{II}$ . In the following we restrict ourselves to the discussion of three relevant cases:

a) Let  $\Phi_{i\mu_1 \dots \mu_l}^{(Pk)}$  and  $\Phi_{i\mu_1 \dots \mu_l}^{(Pk')}$  be "classical" expansion tensors, i.e.  $c$ -numbers in rotational angular momentum space depending only on  $C_i$  and  $\mathcal{E}_i$ . By application of the optical theorem to the expressions (3.4) of Ref. <sup>1</sup> and with the use of Eqs. (2.8)–(2.17) we obtain

$$P_I \sigma_{ij}^{(kk')} \sqsupset = 2(2l + 1)^{-1} \cdot [\sigma_{ij} \{ \Phi_{i\mu_1 \dots \mu_l}^{(Pk)} (\Phi_{i\mu_1 \dots \mu_l}^{(Pk')} - \Phi_{i\mu_1 \dots \mu_l}^{(Pk')} ) \}], \quad (2.18)$$

and the corresponding effective cross section  $P_I \sigma_{ij}^{(kk')} \sqsupset \sqsupset$  is obtained if in (2.18) the term  $(\Phi_{iI} - \Phi_{iI'})$  is replaced by  $(\Phi_{jII} - \Phi_{jII'})$ .

b) Now let  $\Phi_{i\mu_1 \dots \mu_l}^{(Pk')}$  be a "classical" expansion tensor and  $\Phi_{i\mu_1 \dots \mu_l}^{(Pk)}$  a "quantum mechanical" one, i.e. the latter shall depend on  $J$ . Then one finds

$$P_I \sigma_{ij}^{(kk')} \sqsupset = 2(2l + 1)^{-1} [(\gamma'/\gamma) \{ (\Phi_{i\mu_1 \dots \mu_l}^{(Pk')} - \Phi_{i\mu_1 \dots \mu_l}^{(Pk')} ) \times \text{tr}_I \text{tr}_{II} [\Phi_{i\mu_1 \dots \mu_l}^{(Pk)} a_{ij}^{II, I'II'} a_{ij}^{I'II, III'}] \}]. \quad (2.19)$$

The expression for  $P_I \sigma_{ij}^{(kk')} \sqsupset \sqsupset$  differs from (2.19) by  $(\Phi_{jII} - \Phi_{jII'})$  occurring instead of  $(\Phi_{iI} - \Phi_{iI'})$ .

c) Finally, the expansion tensor  $\Phi_{i\mu_1 \dots \mu_l}^{(Pk)}$  shall be a "quantum mechanical" one. The effective relaxation cross section is then given by

$$P_I \sigma_{ij}^{(kk)} \sqsupset = 2(2l + 1)^{-1} \times [(\gamma'/\gamma) \{ \text{tr}_I \text{tr}_{II} [\Phi_{i\mu_1 \dots \mu_l}^{(Pk)} a_{ij}^{II, I'II} \times [a_{ij}^{I'II, III} \Phi_{i\mu_1 \dots \mu_l}^{(Pk)} - \Phi_{i\mu_1 \dots \mu_l}^{(Pk)} a_{ij}^{I'II, III}]] \} ], \quad (2.20)$$

and  $P_I \sigma_{ij}^{(kk)} \sqsupset \sqsupset$  is obtained if one replaces  $\Phi_i^I, \Phi_i^{I'}$  in the commutator by  $\Phi_j^{II}, \Phi_j^{II'}$ . Since we are not interested in the coupling of two different "quantum mechanical" expansion tensors we do not deal with this more general case. In (2.18)–(2.20) we have used the fact that after evaluation of the integration over  $V$  and the spin traces, the remaining scalar expression can depend on the unit vectors  $e$  and  $e'$  only by way of the scalar product  $e \cdot e' = \cos \chi$ . It is possible then to reduce the integral  $\int d^2e d^2e' \dots$  of Ref. <sup>1</sup> by  $8\pi^2 \int \sin \chi d\chi \dots$  and to apply Eq. (2.17).

For  $i = j$  one recovers easily in all cases that

$$P_I \omega_i^{(kk')} \sqsupset + P_I \omega_i^{(kk')} \sqsupset \sqsupset = \omega_{Pl, i}^{(kk')},$$

where  $\omega_{Pl,i}^{(kk')}$  is the corresponding collision bracket for the pure gas of species  $i$  which has been defined in Refs. 17.

For molecules with small nonsphericity, a "spherical" approximation for the collision integrals (only the "spherical" part of the scattering amplitude is considered) can be made for certain cases of a) and c), viz. always when the resulting expressions are unequal to zero. This approximation can, however, never be made in case b) because the trace is always of order  $\varepsilon$  or  $\varepsilon^2$  due to the nonspherical part of the scattering amplitude. In the "spherical" approximation one has only elastic collisions, i.e.  $\gamma' = \gamma$ ,  $J'_I = J_I$ ,  $J'_{II} = J_{II}$ . Since the "spherical" part of the scattering amplitude,  $a_{ij}^{(0)}$ , does not depend on magnetic and rotational quantum numbers, the spin traces and  $J$ -summations can easily be performed as well as the  $V$ -integration. The remaining expressions for (2.18), (2.20) can then be written in terms of Chapman-Cowling integrals<sup>15</sup> which are defined by

$$\Omega_{ij}^{(l,r)} = \frac{v_0}{4} 2\pi \int_0^\infty \exp(-\gamma^2) \gamma^{2r+3} \times \int_0^\pi (1 - \cos^l \chi) \sigma_{ij}^{(0)} \sin \chi d\chi d\gamma, \quad (2.21)$$

where  $\sigma_{ij}^{(0)}$  has been defined in Equation (2.14).

Now let us consider the special effective cross sections occurring in the heat conductivity for molecules with small nonsphericity. Without terms in  $O(\varepsilon^2)$  (i.e. in "spherical approximation") the following are the relaxation cross sections of "classical" expansion tensors, obtained from Eqs. (2.18) and (2.21):

1) Relaxation cross sections for the translational heat flux

$$\begin{aligned} {}_{-1}^{\text{sph}}\sigma_{ij}^{(33)}\top = M_i^4 M_j^2 v_0^{-1} & \left[ \left( 16 + \frac{40}{3} \left( \frac{m_j}{m_i} \right)^2 \Omega_{ij}^{(1,1)} \right. \right. \\ & \left. \left. - \frac{32}{3} \left( \frac{m_j}{m_i} \right)^2 \Omega_{ij}^{(1,2)} + \frac{32}{15} \left( \frac{m_j}{m_i} \right)^2 \Omega_{ij}^{(1,3)} + \frac{64}{15} \frac{m_j}{m_i} \Omega_{ij}^{(2,2)} \right], \end{aligned} \quad (2.22)$$

$$\begin{aligned} {}_{-1}^{\text{sph}}\sigma_{ij}^{(33)}\top\top = (M_i M_j)^3 v_0^{-1} & \left[ -\frac{88}{3} \Omega_{ij}^{(1,1)} + \frac{32}{3} \Omega_{ij}^{(1,2)} \right. \\ & \left. - \frac{32}{15} \Omega_{ij}^{(1,3)} + \frac{64}{15} \Omega_{ij}^{(2,2)} \right]. \end{aligned} \quad (2.23)$$

2) Relaxation cross sections for the rotational heat flux

2) Coupling cross sections between azimuthal polarization and rotational heat flux

$$-1\sigma_{ij}^{(24)}\top = \frac{2}{3} \sqrt{\frac{2k_B}{c_{\text{rot},i}}} M_j^2 \alpha_{1i} \llbracket \gamma \gamma' (\langle \mathcal{E}_i \rangle_0 - \mathcal{E}_{iI'}) \sigma_{1i}^{(n)} \sin \chi \rrbracket, \quad (2.30a)$$

$$-1\sigma_{ij}^{(24)}\top\top = \frac{2}{3} \sqrt{\frac{2k_B}{c_{\text{rot},j}}} M_i M_j \alpha_{1i} \llbracket \gamma \gamma' (\mathcal{E}_{jII'} - \langle \mathcal{E}_j \rangle_0) \sigma_{1i}^{(n)} \sin \chi \rrbracket. \quad (2.30b)$$

$${}_{-1}^{\text{sph}}\sigma_{ij}^{(44)}\top = \frac{16}{3} M_j^2 v_0^{-1} \Omega_{ij}^{(1,1)}, \quad (2.24)$$

$${}_{-1}^{\text{sph}}\sigma_{ij}^{(4,4)}\top\top = 0. \quad (2.25)$$

The cross sections which couple the translational and rotational heat fluxes are linked with inelastic collisions only. Thus they are of order  $\varepsilon^2$  and can be neglected compared with the "diagonal" relaxation coefficients.

3) Relaxation cross sections of the azimuthal polarization and the Kagan polarization:

$${}_{-1}^{\text{sph}}\sigma_{ij}^{(22)}\top = {}_{-1}^{\text{sph}}\sigma_{ij}^{(55)}\top = \frac{16}{3} M_j^2 v_0^{-1} \Omega_{ij}^{(1,1)}. \quad (2.26)$$

The corresponding cross sections  ${}_{-1}^{\text{sph}}\sigma_{ij}^{\top\top}$  vanish since one has (cf. (2.20))  $\text{tr}_I(\Phi_{i\mu_1 \dots \mu_n}^I) \equiv 0$ . Furthermore, we have

$${}_{-0}^{\text{sph}}\sigma_{ij}^{(11)}\top = {}_{-2}^{\text{sph}}\sigma_{ij}^{(11)}\top = {}_{-1}^{\text{sph}}\sigma_{ij}^{(1,1)}\top, \quad (2.27a)$$

$${}_{-2}^{\text{sph}}\sigma_{ij}^{(22)}\top = {}_{-3}^{\text{sph}}\sigma_{ij}^{(22)}\top = {}_{-1}^{\text{sph}}\sigma_{ij}^{(55)}\top. \quad (2.27b)$$

Equations (2.27a, b) express the fact, that in "spherical" approximation the relaxation cross sections of the irreducible parts of a tensor are equal; reorientation cross sections (2.12) do not occur within this approximation.

Next, the coupling cross sections between azimuthal polarization and Kagan vector on the one side, and translational and rotational heat flux on the other side are discussed. Abbreviations for equilibrium mean values of  $J^2$  and  $J^2(J^2 - 3/4)$  for species  $i$  are introduced by

$$\alpha_{1i} \equiv \langle J^2 \rangle_{i0}^{-1/2}, \quad \alpha_{2i} \equiv \langle J^2(J^2 - 3/4) \rangle_{i0}^{-1/2}. \quad (2.28)$$

Then from Eqs. (2.16), (2.17), (2.19) and with the definitions of the orientation cross sections for vector- and tensor polarization, Eqs. (2.10), (2.11), the following expressions for the coupling cross sections are obtained:

1) Coupling cross sections between azimuthal polarization and translational heat flux

$$-1\sigma_{ij}^{(23)}\top = \frac{4}{3\sqrt{5}} M_j^4 \alpha_{1i} \llbracket \gamma \gamma' (5/2 - \gamma'^2) \sigma_{1i}^{(n)} \sin \chi \rrbracket, \quad (2.29a)$$

$$-1\sigma_{ij}^{(23)}\top\top = - (M_i/M_j)^3 {}_{-1}\sigma_{ij}^{(23)}\top. \quad (2.29b)$$

## 3) Coupling cross sections between Kagan polarization and translational heat flux

$$-1\sigma_{ij}^{(53)\top} = \frac{4}{5} \sqrt{\frac{9}{8}} M_j^2 \alpha_{2i} [\gamma^2 (1 + M_j^2 (\gamma^2 - 7/2)) \sigma_{ij}^{(ee)} - M_i^2 \gamma'^2 \sigma_{ij}^{(e'e')} + M_j^2 \gamma \gamma' (5/2 - \gamma'^2) \sigma_{ij}^{(ee')}], \quad (2.31a)$$

$$-1\sigma_{ij}^{(53)\top\top} = \frac{4}{5} \sqrt{\frac{9}{8}} M_i^3 M_j \alpha_{2i} [\gamma^2 (7/2 - \gamma^2) \sigma_{ij}^{(ee)} - \gamma'^2 \sigma_{ij}^{(e'e')} - \gamma \gamma' (5/2 - \gamma'^2) \sigma_{ij}^{(ee')}]. \quad (2.31b)$$

## 4) Coupling cross sections between Kagan polarization and rotational heat flux

$$-1\sigma_{ij}^{(54)\top} = 4 \sqrt{\frac{k_B}{15 c_{\text{rot}, i}}} M_j^2 \alpha_{2i} [\gamma^2 (\mathcal{E}_{iI} - \langle \mathcal{E}_i \rangle_0) \sigma_{ij}^{(ee)} - \gamma \gamma' (\mathcal{E}_{iI} - \langle \mathcal{E}_i \rangle_0) \sigma_{ij}^{(ee')}], \quad (2.32a)$$

$$-1\sigma_{ij}^{(54)\top\top} = 4 \sqrt{\frac{k_B}{15 c_{\text{rot}, j}}} M_i M_j \alpha_{2i} [\gamma^2 (\langle \mathcal{E}_j \rangle_0 - \mathcal{E}_{jII}) \sigma_{ij}^{(ee)} + \gamma \gamma' (\mathcal{E}_{jII} - \langle \mathcal{E}_j \rangle_0) \sigma_{ij}^{(ee')}]. \quad (2.32b)$$

For homonuclear molecules, the orientation cross sections for tensor polarization (2.11) contain contributions linear in the non-sphericity parameter  $\varepsilon$  due to elastic collisions<sup>13,14</sup> while the orientation cross section for vector polarization, Eq. (2.10), is at least quadratic in  $\varepsilon$ . Thus the coupling cross sections (2.31), (2.32) are one order of magnitude larger than the cross sections (2.29), (2.30). It can also be shown in DWBA<sup>13,14</sup> that, linear in  $\varepsilon$ , we have  $\sigma_{ij}^{(ee)} = \sigma_{ij}^{(e'e')} \mp \sigma_{ij}^{(ee')}$  which implies, e.g., that

$$-1\sigma_{ij}^{(53)\top\top} = - (M_i/M_j)^3 -1\sigma_{ij}^{(53)\top} + O(\varepsilon^2). \quad (2.33)$$

Thus, in the case of homonuclear molecules (with a P<sub>2</sub>-type nonspherical interaction<sup>13,14</sup>) the dominant contributions to the SBE of heat conductivity will be determined by the coupling of the Kagan vector with the heat fluxes. This statement, however, seems also to be true for heteronuclear molecules, such as HD, as one can infer from the experiments.

Finally, we mention that the effective cross sections  $-1\sigma_{ij}^{(k'k)}$  with  $k'=3,4$  and  $k=2,5$  can be obtained from Eqs. (2.29–2.32) with the help of the Onsager symmetry relation, Eq. (4.14), of Ref.<sup>1</sup>.

### III. The Heat Conductivity in the Presence of an External Magnetic Field

The system of transport relaxation Eqs. (1.4a) to (1.7) is considered once more. Using the results of the last chapter we can neglect the contributions of the azimuthal polarization to the SBE certainly for homonuclear molecules with small nonsphericity, such as H<sub>2</sub>, D<sub>2</sub>. The experiments<sup>10</sup> show, however that this neglect can also be made for arbitrary linear molecules. Thus the Kagan polarization is the decisive rotational angular momentum anisotropy term in the molecular distribution function. Furthermore, the cross coefficients coupling the translational

and rotational heat flux vectors are neglected compared with their relaxation coefficients. The matrix  $-1\omega_{ij}^{(55)}$  becomes — according to the results of Chapter II — diagonal with respect to  $i, j$  in the “spherical” approximation for which also the relation, Eq. (2.27b) holds. This relation will greatly simplify the calculation of the heat conductivity tensor.

Next, some remarks on the notation have to be made. In the following, matrices with respect to the species labels ( $i, j$ ) will be denoted by boldface Greek letters (e.g.  $\omega$ ) and columns with respect to the species labels by boldface Latin letters (e.g.  $\mathbf{a}_\mu^{(5)}$ ). The dot “ $\circ$ ” will denote the matrix multiplication (e.g.  $\omega \circ \varphi$  which is again a matrix or  $\omega \circ \mathbf{a}_\mu^{(5)}$  which is a column). The inverse matrix of  $\omega$  is denoted by  $\mathbf{x}$ , i.e.  $\mathbf{x} \circ \omega = \mathbf{1}$  where  $\mathbf{1}$  is the unit matrix. The Greek index notation for Cartesian vectors, tensors etc. will be maintained. Since in the following only Pl = −1 will occur, the subscripts “−1” on the left side of  $\omega_{..}$  and  $\mathbf{x}_{..}$  will be dropped for simplicity.

It is convenient to introduce a matrix  $\varphi$  by

$$\varphi_{ij} = \omega_{Hi} \cdot \text{sph} \chi_{ij}^{(55)}, \quad (3.1)$$

where  $\omega_{Hi} = \gamma_i H$  is the precession frequency ( $\gamma_i$  is the gyromagnetic ratio) for the magnetic moment of the molecule “ $i$ ”. Two Cartesian vectors  $\mathbf{B}_\mu$  and  $\mathbf{A}_\mu$  which are columns in the index space are also introduced by

$$\mathbf{B}_\mu = \mathbf{b}_{\mu\nu}^{(2)} h_\nu, \quad \mathbf{A}_\mu = \mathbf{a}_{\mu\nu\lambda}^{(2)} h_\nu h_\lambda. \quad (3.2)$$

If Eq. (1.6) is multiplied with  $h_\nu \text{sph} \mathbf{x}^{(55)}$  and Eq. (1.7) with  $h_\nu h_\lambda \text{sph} \mathbf{x}^{(55)}$  from the left and the definitions (3.1), (3.2) are observed then the system of transport relaxation equations can be rewritten in the form (for  $\mathbf{c}$ ,  $\hat{\mathbf{c}}$  see Eq. (1.3b))

$$\sqrt{\frac{5}{6}} \frac{\mathbf{c}}{T_0} \nabla_\mu T + \omega^{(33)} \circ \mathbf{a}_\mu^{(3)} + \omega^{(35)} \circ \mathbf{a}_\mu^{(5)} = 0, \quad (3.3a)$$

$$\frac{1}{\sqrt{3}} \frac{\hat{c}}{T_0} \nabla_\mu T + \omega^{(44)} \circ \mathbf{a}_\mu^{(4)} + \omega^{(45)} \circ \mathbf{a}_\mu^{(5)} = 0, \quad (3.3b)$$

$$-\frac{3}{2} \boldsymbol{\varphi} \circ \mathbf{a}_\nu^{(5)} \varepsilon_{\mu\nu\lambda} h_\lambda + \frac{3}{\sqrt{10}} \boldsymbol{\varphi} \circ \mathbf{B}_\mu + \mathbf{a}_\mu^{(5)} \quad (3.3c)$$

$$+ \boldsymbol{\chi}^{(55)} \circ \omega^{(53)} \circ \mathbf{a}_\mu^{(3)} + \boldsymbol{\chi}^{(55)} \circ \omega^{(54)} \circ \mathbf{a}_\mu^{(4)} = 0,$$

$$-\frac{3}{\sqrt{10}} \boldsymbol{\varphi} \circ \overline{\mathbf{a}_\mu^{(5)} h_\nu} - \frac{5}{6} \boldsymbol{\varphi} \circ \mathbf{B}_\nu \varepsilon_{\mu\nu\lambda} h_\lambda + \mathbf{B}_\mu$$

$$+ \sqrt{\frac{2}{3}} \mathbf{A}_\mu = 0, \quad (3.3d)$$

$$-\sqrt{\frac{2}{3}} \boldsymbol{\varphi} \circ \overline{\mathbf{B}_\nu h_\mu} - \frac{2}{3} \boldsymbol{\varphi} \circ \mathbf{A}_\nu \varepsilon_{\mu\nu\lambda} h_\lambda + \mathbf{A}_\mu = 0. \quad (3.3e)$$

In order to solve this system of coupled vector equations, i.e. to express  $\mathbf{a}_\mu^{(k)}$  in terms of the temperature gradient  $\nabla_\mu T$ , second rank tensors are introduced which act as projection operators<sup>17</sup>

$$P_{\mu\nu}^{(\pm 1)} = \frac{1}{2} (\delta_{\mu\nu} - h_\mu h_\nu \pm i \varepsilon_{\mu\lambda\nu} h_\lambda), \quad P_{\mu\nu}^{(0)} = h_\mu h_\nu. \quad (3.4)$$

They have the following properties<sup>17</sup>

$$P_{\mu\nu}^{(m)} P_{\nu\lambda}^{(n)} = \delta^{(mn)} P_{\mu\lambda}^{(n)}, \quad P_{\mu\nu}^{(m)*} = P_{\mu\nu}^{(-m)}, \quad \sum_m P_{\mu\nu}^{(m)} = \delta_{\mu\nu}. \quad (3.5)$$

The vector equation

$$\sum_m f^{(m)} P_{\mu\nu}^{(m)} a_\nu = b_\mu \quad (3.6)$$

(with  $f^{(m)}$  being arbitrary complex functions) then has the solution

$$a_\mu = \sum_m (f^{(m)})^{-1} P_{\mu\nu}^{(m)} b_\nu. \quad (3.7)$$

Furthermore, one has

$$a_\nu h_\nu h_\mu = P_{\mu\nu}^{(0)} a_\nu, \quad \varepsilon_{\mu\nu\lambda} h_\lambda a_\nu = i (P_{\mu\nu}^{(1)} - P_{\mu\nu}^{(-1)}) a_\nu. \quad (3.8)$$

Using Eqs. (3.5)–(3.8) we first express the vector  $\mathbf{A}_\mu$  in (3.3e) in terms of the vector  $\mathbf{B}_\mu$ . Next we

insert the result into Eq. (3.3d), express  $\mathbf{B}_\mu$  in terms of  $\mathbf{a}_\mu^{(5)}$  and, finally,  $\mathbf{a}_\mu^{(5)}$  in terms of  $\mathbf{a}_\mu^{(3)}$ ,  $\mathbf{a}_\mu^{(4)}$ . One obtains

$$\mathbf{a}_\mu^{(5)} = \tau^{\parallel} P_{\mu\nu}^{\parallel} + \tau^{\perp} P_{\mu\nu}^{\perp} + \tau^{\text{tr}} P_{\mu\nu}^{\text{tr}} \quad (3.9)$$

$$\circ (\boldsymbol{\chi}^{(55)} \circ \omega^{(53)} \circ \mathbf{a}_\mu^{(3)} + \boldsymbol{\chi}^{(55)} \circ \omega^{(54)} \circ \mathbf{a}_\mu^{(4)}),$$

where

$$P_{\mu\nu}^{\parallel} = P_{\mu\nu}^{(0)}, \quad P_{\mu\nu}^{\perp} = P_{\mu\nu}^{(1)} + P_{\mu\nu}^{(-1)},$$

$$P_{\mu\nu}^{\text{tr}} = -i (P_{\mu\nu}^{(1)} - P_{\mu\nu}^{(-1)}) \quad (3.10)$$

are projection operators which project out the components of an arbitrary vector  $\mathbf{a}$  in the direction of  $\mathbf{h}$ , perpendicular to the  $\mathbf{h}$ -direction, and in the transverse direction  $\mathbf{h} \times \mathbf{a}$ , respectively. In Eq. (3.9) the following abbreviations have been introduced:

$$\tau^{\parallel} = (\mathbf{1} + \boldsymbol{\varphi} \circ \boldsymbol{\varphi})^{-1} \circ (\mathbf{1} + \frac{2}{5} \boldsymbol{\varphi} \circ \boldsymbol{\varphi}), \quad (3.11a)$$

$$\tau^{\perp} = \{ \mathbf{1} - \frac{3}{10} [\boldsymbol{\varphi} \circ \boldsymbol{\varphi} \circ (\mathbf{1} + \boldsymbol{\varphi} \circ \boldsymbol{\varphi})^{-1} + 8 \boldsymbol{\varphi} \circ \boldsymbol{\varphi} \circ (\mathbf{1} + 4 \boldsymbol{\varphi} \circ \boldsymbol{\varphi})^{-1}] \}, \quad (3.11b)$$

$$\tau^{\text{tr}} = -\frac{3}{10} \boldsymbol{\varphi} \circ [(\mathbf{1} + \boldsymbol{\varphi} \circ \boldsymbol{\varphi})^{-1} + 4(\mathbf{1} + 4 \boldsymbol{\varphi} \circ \boldsymbol{\varphi})^{-1}]. \quad (3.11c)$$

If Eq. (3.9) is inserted into Eqs. (3.3a, b) and  $\sqrt{5/6} k_B T_0 \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(33)} \circ$  is applied from the left to Eq. (3.3a) and  $(1/\sqrt{3}) k_B T_0 \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(44)} \circ$  to Eq. (3.3b) (for  $\mathbf{d}$  and  $\hat{\mathbf{d}}$  see Eq. (1.3a), the “†” sign denotes the transposed column, i.e. a row) and the results are added, an expression for the heat flux is obtained. But the right hand side of this expression still contains the vectors  $\mathbf{a}_\mu^{(3)}$  and  $\mathbf{a}_\mu^{(4)}$ . Since, however, the corrections due to the Kagan polarization are small, the first step of an iteration is sufficient. One obtains for the total heat flux

$$q_\mu = -\lambda_{\mu\nu}(\mathbf{H}) \nabla_\nu T, \quad (3.12)$$

with the heat conductivity tensor

$$\lambda_{\mu\nu}(\mathbf{H}) = \lambda(H=0) \{ \delta_{\mu\nu} + [\frac{5}{2} \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(33)} \circ \mathbf{e} + \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(44)} \circ \hat{\mathbf{e}}]^{-1} \times \left( \sqrt{\frac{5}{2}} \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(33)} \circ \omega^{(35)} + \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(44)} \circ \omega^{(45)} \right) \circ \tau_{\mu\nu} \circ \boldsymbol{\chi}^{(55)} \left( \sqrt{\frac{5}{2}} \omega^{(53)} \circ \boldsymbol{\chi}^{(33)} \circ \mathbf{e} + \omega^{(54)} \circ \boldsymbol{\chi}^{(44)} \circ \hat{\mathbf{e}} \right) \}. \quad (3.13)$$

The tensor  $\tau_{\mu\nu}$  is defined by

$$\tau_{\mu\nu} = P_{\mu\nu}^{\parallel} (\tau^{\parallel} - \mathbf{1}) + P_{\mu\nu}^{\perp} (\tau^{\perp} - \mathbf{1}) + P_{\mu\nu}^{\text{tr}} \tau^{\text{tr}}, \quad (3.14)$$

( $\tau_{\mu\nu}(\boldsymbol{\varphi} = 0) \equiv 0$ ) and the zero field thermal conductivity is given by

$$\lambda(H=0) = \frac{k_B}{3} \left[ \frac{5}{2} \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(33)} \circ \mathbf{e} + \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(44)} \circ \hat{\mathbf{e}} + \left( \sqrt{\frac{5}{2}} \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(33)} \circ \omega^{(35)} + \hat{\mathbf{d}}^\dagger \circ \boldsymbol{\chi}^{(44)} \circ \omega^{(45)} \right) \circ \boldsymbol{\chi}^{(55)} \right. \\ \left. \circ \left( \sqrt{\frac{5}{2}} \omega^{(53)} \circ \boldsymbol{\chi}^{(33)} \circ \mathbf{e} + \omega^{(54)} \circ \boldsymbol{\chi}^{(44)} \circ \hat{\mathbf{e}} \right) \right]. \quad (3.15)$$



Equation (3.13) is valid for mixtures of an arbitrary number of components consisting of linear rotating molecules with small nonsphericity of their interaction. The formal expressions for the saturation values for the parallel and perpendicular SBE

$$(\Delta\lambda^{\parallel}/\lambda(H=0))_{\text{sat}} = (\lambda^{\parallel}(H \rightarrow \infty) - \lambda(H=0))/\lambda(H=0), \quad (3.16)$$

and, analogously for  $(\Delta\lambda^{\perp}/\lambda(H=0))_{\text{sat}}$  can easily be extracted from (3.13) if one observes that

$$\tau_{\mu\nu}(\varphi \rightarrow \infty) = (-\frac{3}{5} P_{\mu\nu}^{\parallel} - \frac{9}{10} P_{\mu\nu}^{\perp}) \mathbf{1}. \quad (3.17)$$

Then, for fixed mole fractions, also the relation  $\Delta\lambda^{\perp}/\Delta\lambda^{\parallel} = 3/2$  holds as well as in the pure gas case<sup>14, 18, 19</sup>.

Of course, Eqs. (3.13)–(3.15) must cover the pure gas case. Indeed, the columns, rows, and matrices with respect to species labels then become single numbers and one obtains the well known result<sup>19</sup>

$$\lambda_{\mu\nu}^{\text{pure}}(H) = \lambda^{\text{pure}}(H=0) \left\{ \delta_{\mu\nu} + [5/2 \omega_{-1}^{(33)} + c_{\text{rot}}/k_B \omega_{-1}^{(44)}]^{-1} (\omega_{-1}^{(55)})^{-1} \left[ \sqrt{\frac{5}{2}} \omega_{-1}^{(53)}/\omega_{-1}^{(33)} + \sqrt{\frac{c_{\text{rot}}}{k_B}} \omega_{-1}^{(54)}/\omega_{-1}^{(44)} \right]^2 \tau_{\mu\nu}(\varphi) \right\}. \quad (3.18)$$

In (3.18), the precession angle is  $\varphi = \omega_H/\omega_{-1}^{(55)}$  and Eq. (3.15) gives

$$\lambda^{\text{pure}}(H=0) = \frac{n_0 k_B^2 T_0}{m} \left[ 5/2 \omega_{-1}^{(33)} + c_{\text{rot}}/k_B \omega_{-1}^{(44)} + (\omega_{-1}^{(55)})^{-1} \left( \sqrt{\frac{5}{2}} \omega_{-1}^{(53)}/\omega_{-1}^{(33)} + \sqrt{\frac{c_{\text{rot}}}{k_B}} \omega_{-1}^{(54)}/\omega_{-1}^{(44)} \right)^2 \right]. \quad (3.19)$$

To obtain (3.18), (3.19), use has also been made of the Onsager symmetries  $\omega_{-1}^{(53)} = \omega_{-1}^{(35)}$  and  $\omega_{-1}^{(54)} = \omega_{-1}^{(45)}$  (cf. Refs.<sup>14, 17</sup>).

#### IV. Concentration Dependence of the Senftleben–Beenakker Effect for a Binary Mixture of Rotating Molecules and Atoms

The dependence of the SBE on the mole fractions is complicated, in general, since the  $\omega$ ,  $\kappa$ ,  $\varphi$  matrices as well as the quantities  $\mathbf{d}$ ,  $\hat{\mathbf{d}}$  are concentration dependent. To get some insight into the structure of the mole fraction dependence, a particular binary mixture is considered consisting of linear rotating molecules (“1”) and noble gas atoms (“2”). Although the expression (3.13) for the heat conductivity tensor is considerably simplified in this case, the explicit expressions for the saturation values

$$[\Delta\lambda/\lambda(H=0)]_{\text{sat}}$$

(with  $\Delta\lambda = \Delta\lambda^{\parallel}$  or  $\Delta\lambda^{\perp}$ ) contain still too many unknown parameters. Since the occurring relaxation coefficients can — in “spherical” approximation — be expressed in terms of  $\mathcal{Q}$ -integrals (see Chapter III) the unknown parameters are the effective orientation cross sections

$$\sigma_{ij}^{(53)\top, \top\top}, \quad \sigma_{ij}^{(54)\top, \top\top} \quad (i, j = 1, 2).$$

The calculation of these cross sections from a nonspherical potential is a formidable task<sup>13, 14</sup> and will not be considered in this paper. Therefore these coupling cross sections are treated as parameters.

The fact that  $c_{\text{rot}}$  and the vectors  $\Phi_{\mu}^{(4)}$ ,  $\Phi_{\mu}^{(5)}$  (rotational heat flux, Kagan vector) are equal to zero for the noble gas reduces the number of parameters, but still too many are left.

This difficulty is overcome by the following model assumption: The coupling of the rotational heat flux  $\Phi_{1\mu}^{(4)}$  with the Kagan polarization  $\Phi_{1\mu}^{(5)}$  gives the dominant contribution to the effect, the coupling of the translational heat flux with the Kagan vector is neglected. This assumption (which is in good agreement with experiments for pure  $H_2$ ,  $D_2$ ) may be approximately valid for homonuclear molecule-atom mixtures and reduces the number of unknown parameters to two, namely the coupling cross sections  $\sigma_1^{(54)} = \sigma_{11}^{(54)\top} + \sigma_{11}^{(54)\top\top}$  (effective orientation cross section for the pure gas of molecules “1”) and  $\sigma_{12}^{(54)\top}$  which involves the molecule-atom collisions. If the mole fraction is introduced by

$$x = n_{20}/(n_{10} + n_{20}), \quad (4.1)$$

( $x=0$  if only molecules are present,  $x=1$  for the pure noble gas) then in the “normalized” expression  $(\Delta\lambda/\lambda)_{\text{sat}}(x)/(\Delta\lambda/\lambda)_{\text{sat}}(x=0)$  only one parameter appears, viz. the ratio of the two orientation cross sections  $\sigma_{12}^{(54)\top}/\sigma_1^{(54)}$ . This ratio is a measure of the effectiveness of the molecule-atom collisions relative to the molecule-molecule collisions for producing a tensor polarization of the molecules if a heat

flow is present. It has thus a direct physical meaning. The model calculations give insight into the characteristic features of the mole fraction dependence of the saturation values for the parallel and perpendicular effect and may be considered to be representative also for the more general case.

Starting from Eq. (3.13) we obtain in our model for  $(\Delta\lambda^\parallel/\lambda)_{\text{sat}}$  e.g. ( $\lambda = \lambda(H = 0)$ )

$$(\Delta\lambda^\parallel/\lambda)_{\text{sat}} = -\frac{3}{5} [\frac{5}{2} \mathbf{d}^\dagger \circ \mathbf{x}^{(33)} \circ \mathbf{c} + \hat{d}_1 \hat{c}_1 / \omega_{11}^{(44)}]^{-1} \times \hat{d}_1 (\omega_{11}^{(45)} \omega_{11}^{(54)} / \omega_{11}^{(44)} \omega_{11}^{(55)} \omega_{11}^{(44)}) \hat{c}_1. \quad (4.2)$$

In deriving Eq. (4.2) use has been made of the fact that the quantities  $\hat{\mathbf{c}}, \hat{\mathbf{d}}, \omega^{(44)}, \omega^{(45)}, \omega^{(54)}, \omega^{(55)}$  have to be treated as numbers in the species label space (this can be inferred from the system of TRE, Eq. (1.4)). Next, we observe that any  $\omega_{ij}^{(kk')}$  diagonal in the species labels can be written in the following form [cf. Eq. (4.12) of<sup>1</sup>]

$$\omega_{ii}^{(kk')} = n_{i0} v_{i0} (\sigma_{ii}^{(kk')\top} + \sigma_{ii}^{(kk')\top\top}) + \sum_{j' \neq i} n_{j'0} v_{j'0} \sigma_{ij'}^{(kk')\top}, \quad (4.3)$$

and any non-diagonal collision bracket as

$$\omega_{ij}^{(kk')} = n_{j0} v_0 \sigma_{ij}^{(kk')\top\top}, \quad i \neq j. \quad (4.4)$$

In Eqs. (4.3), (4.4),

$$v_{i0} = \sqrt{16 k_B T_0 / \pi m_i}, \quad v_{j'0} = \sqrt{8 k_B T_0 / \pi m_{ij'}}, \quad \text{and} \\ v_0 = \sqrt{8 k_B T_0 / \pi m_{ij}}.$$

The effective cross sections  $\sigma_{ij}$  are independent of concentration; the notation  $\sigma_{ii} = \sigma_{ii}^\top + \sigma_{ii}^{\top\top}$  will be used. After some algebra one obtains

$$\left( \frac{\Delta\lambda}{\lambda} \right)_{\text{sat}}(x) / \left( \frac{\Delta\lambda}{\lambda} \right)_{\text{sat}}(x=0) = \frac{A(x)}{A(0)} \frac{A(0) + B(0)}{A(x) + B(x)} \frac{C(x)}{C(0)}, \quad (4.5)$$

where the functions  $A(x)$ ,  $B(x)$  and  $C(x)$  are

$$A(x) = (c_{\text{rot}}/k_B) (1-x) [(\beta_1 \sigma_1^{(33)} (1-x) + \sigma_{12}^{(33)\top} x) \cdot (\beta_2 \sigma_2^{(33)} x + \sigma_{21}^{(33)\top} (1-x)) - x(1-x) (\sigma_{12}^{(33)\top\top} x)^2], \quad (4.6)$$

$$B(x) = \frac{5}{2} (\sigma_{12}^{(44)\top} x + \beta_1 \sigma_1^{(44)} (1-x)) [(1-x) (\sigma_{21}^{(33)\top} (1-x) + \beta_2 \sigma_2^{(33)} x) - x(1-x) 2\beta_2 \beta_1^{-1} \sigma_{12}^{(33)\top\top} + \beta_2^2 \beta_1^{-2} x (\sigma_{12}^{(33)\top} x + \beta_1 \sigma_1^{(33)} (1-x))], \quad (4.7)$$

$$C(x) = (\beta_1 (1-x) + b x)^2 (\beta_1 \sigma_1^{(55)} (1-x) + \sigma_{12}^{(55)\top} x)^{-1} \cdot \sigma_1^{(54)^2} (\beta_1 (1-x) \sigma_1^{(44)} + \sigma_{12}^{(44)\top} x)^{-1}. \quad (4.8)$$

The abbreviations

$$\beta_1 = (v_{10}/v_0) = (2m_2/(m_1 + m_2))^{1/2}, \\ \beta_2 = (v_{20}/v_0) = (2m_1/(m_1 + m_2))^{1/2}, \quad (4.9)$$

and

$$b = \sigma_{12}^{(54)\top} / \sigma_1^{(54)} \quad (4.10)$$

have been used. The diagonal effective cross sections can, in "spherical" approximation, most easily be calculated for the classical rigid sphere model. The results are ( $i, j = 1, 2$ )

$$\sigma_i^{(33)} = \frac{8\pi}{15} a_i^2, \quad (4.11a)$$

$$\sigma_{ij}^{(33)\top} = \frac{2\pi}{15} \frac{m_i^2 m_j}{(m_i + m_j)^3} \left( 30 + 16 \frac{m_j}{m_i} + 13 \frac{m_j^2}{m_i^2} \right) a_{ij}^2. \quad (4.11b)$$

$$\sigma_{ij}^{(33)\top\top} = -\frac{18\pi}{5} \frac{(m_i m_j)^{3/2}}{(m_i + m_j)^3} \cdot a_{ij}^2, \quad (4.11c)$$

$$\sigma_i^{(44)} = \sigma_i^{(55)} = \frac{2\pi}{3} \cdot a_i^2, \quad (4.11d)$$

$$\sigma_{ij}^{(44)\top} = \sigma_{ij}^{(55)\top} = \frac{4\pi}{3} \cdot \frac{m_j}{m_i + m_j} \cdot a_{ij}^2, \quad (4.11e)$$

where  $a_1$  is the diameter of the molecule,  $a_2$  is the diameter of the noble gas atom and  $a_{12} = (a_1 + a_2)/2$ .

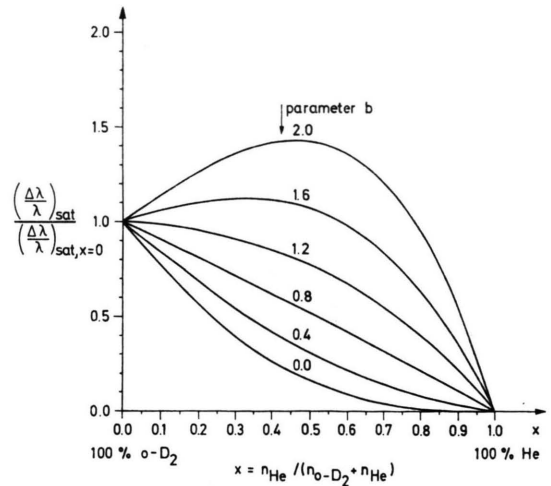


Fig. 1. Relative change at saturation of heat conductivity for He/o-D<sub>2</sub> mixture versus mole-fraction for several values of the parameter  $b$  defined in Equation (4.10).

As an example, the system o-D<sub>2</sub>/He has been chosen. Calculations have been performed for room temperature ( $c_{\text{rot}}/k_B \approx 1$ ). The values  $a_1 = 2.76 \text{ \AA}$ ,  $a_2 = 2.18 \text{ \AA}$ ,  $a_{12} = 2.47 \text{ \AA}$  have been taken from the rigid sphere viscosity cross sections for room tem-

perature<sup>15</sup>. In Fig. 1,  $(\Delta\lambda/\lambda)_{\text{sat}}(x)/(\Delta\lambda/\lambda)_{\text{sat}}(x=0)$  is plotted versus  $x = n_{\text{He}}/(n_{\text{D}_2} + n_{\text{He}})$  for several values of the parameter  $b$ . A noticeable fact is that the curvature changes the sign with increasing values of the parameter  $b$  (which could, in principle, also be negative) so that a maximum appears for larger  $b$  values. The preliminary experimental curves<sup>7</sup> for linear molecule-noble gas atom mixtures all show a concave behavior. Provided that our

model is a good approximation to the real situation, this would lead to the conclusion that  $\sigma_{12}^{(54)\top} < \sigma_1^{(54)}$ , i.e. for the orientation effects the molecule-atom collisions are less effective.

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- <sup>1</sup> H. H. RAUM and W. E. KÖHLER, *Z. Naturforsch.* **25a**, 1178 [1970].
- <sup>2</sup> H. GRAD, *Comm. Pure Appl. Math.* **2**, 331 [1949]. — L. WALDMANN, *Z. Naturforsch.* **18a**, 1033 [1963].
- <sup>3</sup> L. WALDMANN, *Z. Naturforsch.* **12a**, 660 [1957]; **13a**, 609 [1958].
- <sup>4</sup> R. F. SNIDER, *J. Chem. Phys.* **32**, 1051 [1960].
- <sup>5</sup> H. F. VUGTS, A. TIP, and J. LOS, *Physica* **38**, 579 [1968].
- <sup>6</sup> M. A. HIDALGO, J. M. SAVIRON, and D. GONZALEZ, *Physica* **46**, 41 [1970].
- <sup>7</sup> A. L. J. BURGMANS, Thesis, Leiden 1972.
- <sup>8</sup> J. P. J. HEEMSKERK, to be published.
- <sup>9</sup> J. J. DE GROOT, J. W. VAN DEN BROEKE, H. J. MARTINIUS, and C. J. N. VAN DEN MEIJDENBERG, *Physica* **49**, 342 [1970]; *Physica* **56**, 388 [1971].
- <sup>10</sup> H. SENFTLEBEN, *Phys. Z.* **31**, 822, 961 [1930]; J. J. M. BEENAKKER, G. SCOLES, H. F. P. KNAAP, and R. M. JONKMAN, *Phys. Letters* **2**, 5 [1962]; For a review see J. J. M. BEENAKKER and F. R. McCOURT, *Ann. Rev. Phys. Chem.* **21**, 136 [1970].
- <sup>11</sup> A. TIP, *Physica* **34**, 411 [1967].
- <sup>12</sup> A. C. LEVI, G. SCOLES, and F. TOMMASINI, *Z. Naturforsch.* **25a**, 1213 [1970].
- <sup>13</sup> W. E. KÖHLER, S. HESS, and L. WALDMANN, *Z. Naturforsch.* **25a**, 336 [1970].
- <sup>14</sup> W. E. KÖHLER, Thesis, Erlangen 1971 (unpublished).
- <sup>15</sup> S. CHAPMAN and T. G. COWLING, *The Mathematical Theory of Non-Uniform Gases*, Cambridge University Press, 1964. — L. WALDMANN, In: *Handbuch der Physik*, Vol. **12**, ed. S. FLÜGGE, Springer-Verlag, Berlin 1958. — J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD, *Molecular Theory of Gases and Liquids*, John Wiley, New York 1964.
- <sup>16</sup> Y. M. KAGAN and L. A. MAKSIMOV, *Sov. Phys. JETP* **14**, 604 [1962]; **24**, 1272 [1967].
- <sup>17</sup> S. HESS and L. WALDMANN, *Z. Naturforsch.* **21a**, 1529 [1966]; **23a**, 1893 [1968]; **26a**, 1057 [1971].
- <sup>18</sup> L. WALDMANN, In: *Fundamental problems in Statistical Mechanics II*, Ed. E. G. D. COHEN, North Holland Publ. Amsterdam 1968.
- <sup>19</sup> F. R. McCOURT and R. F. SNIDER, *J. Chem. Phys.* **46**, 2387 [1967]. — A. C. LEVI and F. R. McCOURT, *Physica* **38**, 415 [1968].