Waldmann-Snider Collision Integrals and Nonspherical Molecular Interaction

I. Collision Integrals for Pure Gases

W. E. Köhler

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

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Collision integrals of the linearized Waldmann-Snider collision operator for pure gases are defined. General properties due to invariances of the molecular interaction are discussed. Effective cross sections are introduced and expressed in terms of convenient bracket symbols. The positive definiteness of the relaxation coefficients is proved. The approximation of small nonsphericity for the scattering amplitude is explained and consequences for the collision integrals are investigated. Molecular cross sections describing the orientation and reorientation of the molecular rotational angular momentum are defined. Expressions for effective cross sections relevant for the various nonequilibrium alignment phenomena are presented.

Introduction

The kinetic theory of dilute monatomic gases is based on the classical Boltzmann equation. Collision integrals of the linearized Boltzmann collision term determine the magnitudes of the transport coefficients, e. g. heat conductivity and viscosity [1]. The kinetic theory for dilute gases of polyatomic molecules is based on the Waldmann-Snider equation [2, 3] which treats the internal rotational degrees of freedom of a molecule quantum-mechanically. The distribution function obeying the Waldmann-Snider equation depends on the operator $\hbar \boldsymbol{J}$ of the rotational angular momentum as well. As a consequence, collision integrals of the linearized Waldmann-Snider collision operator determine not only the magnitudes of the scalar transport phenomena in molecular gases (heat conductivity, shear and bulk viscosity) but, in addition, the magnitudes of all tensorial phenomena, i. e. phenomena linked with a partial alignment of the rotational angular momenta. Such typical effects are for pure gases: Flow birefringence [4], heat flow birefringence [5], depolarized Rayleigh light scattering [6], alignment phenomena in atomic vapors [7], nuclear spin relaxation [8], electric polarization caused by a temperature gradient [9], and, finally, the Senftleben-Beenakker effect [10], i. e. the influence of external magnetic and electric fields on the transport properties. In binary gas mixtures, diffusio birefringence [11] and electric polarization caused by a concentration gradient [12] can occur in addition.

The Waldmann-Snider collision operator contains the binary scattering amplitude and its adjoint in a bilinear way [2, 3] which is, however, not a differential cross section. This scattering amplitude is still a matrix with respect to the degenerate rotational states. It is connected with the nonspherical intermolecular potential by the Lippmann-Schwinger integral equation. The collision integrals linked with the occurrence of the tensorial phenomena are determined by generalized molecular cross sections which describe the production and the decay of the angular momentum polarizations produced in a nonequilibrium situation. These orientation- and reorientation cross sections vanish for a purely central molecular potential. Thus they can give information on the nonspherical part of the interaction.

In practice, the scattering problem with a nonspherical potential can only be solved within some approximation. If the nonspherical part of the interaction is small compared with the spherical part the distorted wave Born approximation [13] (DWBA) can be used. Here, the scattering problem governed by the spherical potential is solved exactly, the nonsphericity is then treated in a first order perturbation theory.

In the last years several authors have directed their attention to the calculation of Waldmann-Snider collision integrals for diatomic diamagnetic molecules. The "nonspherical" scattering amplitude and its relevance for certain collision integrals has first been studied by Hess and Köhler [14] for energetically elastic and by Köhler, Hess and Waldmann [15] for inelastic molecular collisions in DWBA. Formal expressions for relaxation coefficients for

Reprint requests to Dr. W. Köhler, Institut für Theoretische Physik der Universität Erlangen-Nürnberg, *D-8520 Erlangen*, Glückstraße 6.

particles with spin and approximate relations (on the basis of the scattering amplitude of Ref. [14]) have been obtained by Hess and Waldmann [16]. Calculations of two collision integrals for HD at room temperature have been reported by the author [17]. They were followed by a paper concerning the calculation of the collision integral determining the magnitude of the Senftleben-Beenakker effect of the heat conductivity for $p-H_2$ at room temperature [18]. In both cases simple models of nonspherical potentials have been used. General procedures for the evaluation of Waldmann-Snider collision integrals in DWBA, in particular for high temperatures, have been stated by Moraal and Snider [19] and, in more detail, by Chen, Moraal and Snider [20]. Formal and approximate expressions for a number of collision integrals and various kinds of nonspherical potentials have recently been given by Moraal [21]. The same author also considered collision integrals for the quadrupole-quadrupole interaction [22] and presented results for transport- and relaxation coefficients for monatomic spin 1/2 gases [23]. Expressions for effective orientation and reorientation cross sections for the tensor polarization of $^2P_{3/2}$-atoms in Born approximation have been obtained by Köhler and Hess [7]. Finally, the kinetic theory calculation of the NMR relaxation time of dilute ^{3}He gas of Shizgal [24] should be mentioned.

The present work is the first of three papers mainly based on the author's thesis entitled "Transporterscheinungen in Gasen aus linearen Molekülen im äußeren Magnetfeld und nichtsphärische intermolekulare Wechselwirkung", Erlangen, January 1971. In it, Waldmann-Snider collision integrals for pure gases are considered. General properties following from rotational-, parity-, and time reversal invariance of the interaction are discussed. Effective cross sections are introduced and expressed in terms of convenient bracket symbols. The positive definiteness of the relaxation cross sections is proved and the "spherical approximation" is discussed. For the relaxation cross sections of J-multipolarizations and the coupling cross sections molecular cross sections are introduced which describe the orientation and reorientation of the rotational angular momentum. They are essentially connected with the nonspherical part of the interaction. Expressions for the special effective cross sections linked with the scalar and tensorial phenomena mentioned above are given. Their relation to experimentally observable quantities is briefly reviewed.

A second paper is concerned with the calculation of the scattering amplitude and the cross sections for linear molecules. A third paper will deal with the collision integrals occurring in the kinetic theory of mixtures of dilute gases [25].

I) Definition and General Properties of the Collision Integrals

1) Definitions

The temporal development of the distribution function f^{j_1} for molecules in the rotational state j_1 is governed by the Waldmann-Snider equation [2, 3]. The superscript j_1 shall indicate that f^{j_1} is a $(2\,j_1+1)\times(2\,j_1+1)$ matrix with respect to magnetic quantum numbers. With the help of the operator

$$P^j=\sum_m |\,j\,m\rangle\langle j\,m\,| \tag{1.1}$$

projecting on molecular states with rotational quantum number j, a distribution operator f^j is generally defined by

$$f^j(t,\boldsymbol{x},\boldsymbol{c})=P^j\,f(t,\boldsymbol{x},\boldsymbol{c},\boldsymbol{J})\,P^j\,, \tag{1.2}$$

where the distribution operator f depends on the operator (in units of $\hbar$) $\boldsymbol{J}$ for the rotational angular momentum as well. If Φ denotes the deviation of the distribution operator from the equilibrium distribution f_0 according to

$$f=f_0(1+\Phi)\,, \tag{1.3}$$

the linearized Waldmann-Snider equation in the absence of external fields is

$$\partial\Phi^{j_1}/\partial t+\boldsymbol{c}\cdot\partial\Phi^{j_1}/\partial\boldsymbol{x}+\omega(\Phi)^{j_1}=0\,. \tag{1.4}$$

In Eq. (1.4), $\omega(\Phi)^{j_1}$ is the linearized Waldmann-Snider collision (super-)operator, given by

$$\omega(\Phi)^{j_1}=-\sum_{j_2}\mathrm{tr}_2\int\mathrm{d}^3c_2\,f_{20}\left\{\sum_{j_1'j_2'}\int a^{j_1j_2,\,j_1'j_2'}\right.$$
$$(\Phi_1{}^{j_1'}+\Phi_2{}^{j_2'})\,a^{\dagger\,j_1'j_2',\,j_1j_2}\,g'\,\mathrm{d}^2e'-\frac{h}{i\,m_{12}}\,[a^{j_1j_2,\,j_1j_2}\,(0)$$
$$\left.(\Phi_1{}^{j_1}+\Phi_2{}^{j_2})\;-(\Phi_1{}^{j_1}+\Phi_2{}^{j_2})\,a^{\dagger\,j_1j_2,\,j_1j_2}\,(0)\,]\right\}. \tag{1.5}$$

In Eq. (1.5) the abbreviations

$$\Phi^{j'}=P^{j'}\,\Phi(t,\boldsymbol{x},\boldsymbol{c}',\boldsymbol{J})\,P^{j'},\;\Phi^{j}=P^{j}\,\Phi(t,\boldsymbol{x},\boldsymbol{c},\boldsymbol{J})\,P^{j} \tag{1.6}$$

have been used. The equilibrium distribution f_0 is given by

$$f_0(c,j) = n_0\,Q^{-1}(m/2\,\pi\,k_\mathrm{B}\,T_0)^{3/2} \cdot \exp\left\{-\frac{m\,c^2}{2\,k_\mathrm{B}\,T_0} - \frac{E(j)}{k_\mathrm{B}\,T_0}\right\}, \tag{1.7}$$

where n_0 is the equilibrium particle density, Q is the rotational partition sum and

$$E(j) = \hbar^2\,j(j+1)/2\,\Theta \tag{1.8}$$

is the rotational internal energy of the linear molecule with moment of inertia Θ. The trace over magnetic quantum numbers in (1.5) has been denoted by "tr"; $\boldsymbol{g} = g\,\boldsymbol{e} = \boldsymbol{c}_1 - \boldsymbol{c}_2$ is the relative velocity after the collision, $\boldsymbol{g}' = g'\,\boldsymbol{e}' = \boldsymbol{c}_1{}' - \boldsymbol{c}_2{}'$ before the collision. The most important quantity is the binary scattering amplitude $a^{j_1 j_2, j_1' j_2'}(\boldsymbol{e}, \boldsymbol{e}', g)$ which describes a transition $j_1{}' + j_2{}' \rightarrow j_1 + j_2$ in rotational quantum numbers and is again a matrix with respect to the magnetic quantum numbers. The scattering amplitude in forward direction $\boldsymbol{e} = \boldsymbol{e}'$ (angle of deflection in the c. m. system $\vartheta = 0$) is denoted by $a(0)$. Due to the conservation of normalization and the completeness of free particle states (unitarity of the S-matrix), the scattering amplitude obeys the optical theorem

$$\begin{aligned}\frac{h}{i\,m_{12}}\left[a^{j_1 j_2, j_1 j_2}(0) - a^{\dagger\, j_1 j_2, j_1 j_2}(0)\right] &= \sum_{j_1' j_2'} \int a^{j_1 j_2, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}')\, a^{\dagger\, j_1' j_2', j_1 j_2}(\boldsymbol{k}, \boldsymbol{k}')\, g'\,\mathrm{d}^2 e' \\ &= \sum_{j_1' j_2'} \int a^{\dagger\, j_1 j_2, j_1' j_2'}(\boldsymbol{k}', \boldsymbol{k})\, a^{j_1' j_2', j_1 j_2}(\boldsymbol{k}', \boldsymbol{k})\, g'\,\mathrm{d}^2 e'\,. \end{aligned} \tag{1.9}$$

where the wave vectors $\hbar\,\boldsymbol{k} = m_{12}\,\boldsymbol{g}$ etc. have been introduced (m_{12} is the reduced mass). The scattering amplitude $a^{j_1 j_2, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}')$ must again be understood as an abbreviation

$$a^{j_1 j_2, j_1' j_2'}(\boldsymbol{k}, \boldsymbol{k}') = P^{j_1 j_2}\,a(\boldsymbol{k}, \boldsymbol{k}')\,P^{j_1' j_2'}, \tag{1.10}$$

where $P^{j_1 j_2} = P^{j_1}\,P^{j_2}$ is the corresponding two particle projection operator. The scattering amplitude $a(\boldsymbol{k}, \boldsymbol{k}')$ is proportional to the matrix element between momentum eigenstates of the more familiar T-operator [13]

$$a(\boldsymbol{k}, \boldsymbol{k}') = -\frac{m_{12}}{2\,\pi\,\hbar^2}\,\langle \boldsymbol{k} \,|\, T \,|\, \boldsymbol{k}' \rangle, \tag{1.11}$$

which is connected with the interaction potential V via the Lippmann-Schwinger integral equation [13]

$$T = V + V(E - H_0 + i\,\eta)^{-1}\,T\,. \tag{1.12}$$

In (1.12), E is the total energy, H_0 is the free particle Hamiltonian and $(E - H_0 + i\,\eta)^{-1}$ denotes the Green's function for outgoing spherical waves at infinity. For the calculation of T in a reasonable approximation it is referred to the second paper.

The linearized Waldmann-Snider equation can be transformed into an (infinite) set of coupled differential equations (transport-relaxation-equations) by use of the moment method [25, 26]. For the application of the moment method, Φ has to be expanded in a complete set of orthonormal irreducible tensors built up of the molecular velocity $\boldsymbol{c}$ and the rotational angular momentum $\boldsymbol{J}$:

$$\Phi(t, \boldsymbol{x}, \mathbf{c}, \boldsymbol{J}) = \sum_{P=\pm 1} \sum_{l=0}^{\infty} \sum_{k=1}^{\infty} a^{(Pk)\mu_l}_{\mu_1 \ldots}(t, \boldsymbol{x})\,\Phi^{(Pk)}_{\mu_1 \ldots \mu_l}(\mathbf{c}, \boldsymbol{J})\,. \tag{1.13}$$

In Eq. (1.13), l is the tensor rank and P is the parity. The expansion tensors are orthonormalized according to

$$\langle \Phi^{(Pk)}_{\mu_1 \ldots \mu_l}\,\Phi^{(P'k')}_{\nu_1 \ldots \nu_{l'}} \rangle_0 = \delta_{ll'}\,\delta^{PP'}\,\delta^{kk'}\,\Delta^{(l)}_{\mu_1 \ldots \mu_l, \nu_1 \ldots \nu_l}, \tag{1.14}$$

where $\langle \cdots \rangle_0$ denotes an equilibrium average and $\Delta^{(l)}_{\mu_1 \ldots \mu_l, \nu_1 \ldots \nu_l}$ is an isotropic tensor which projects out the symmetric irreducible part if applied to an arbitrary l^th rank tensor. For properties of this tensor see Reference [27]. If the expansion (1.13) is inserted into Eq. (1.4), if the result is multiplied with a special expansion tensor $\Phi^{(Pk)}_{\mu_1 \ldots \mu_l}$, and if the equilibrium average is taken, one obtains the well known moment equations [25, 26]. We are interested here only in the collision term which is determined now by the matrix elements of the collision superoperator defined by

$$\begin{aligned}&\langle \Phi^{(Pk)}_{\mu_1 \ldots \mu_l}\,\omega(\Phi^{(P'k')}_{\nu_1 \ldots \nu_{l'}}) \rangle_0 \\ &\quad = \frac{1}{n_0} \sum_{j_1} \mathrm{tr}_1 \int \mathrm{d}^3 c_1\,f_{10}\,\Phi^{(Pk)j_1}_{\mu_1 \ldots \mu_l}\,\omega(\Phi^{(P'k')}_{\nu_1 \ldots \nu_{l'}})^{j_1}\,.\end{aligned} \tag{1.15}$$

2) Properties Following from Invariances

Since $\Phi^{(Pk)}_{\ldots}$ and $\omega(\Phi^{(P'k')}_{\ldots})$ are hermitean operators, the ω-matrix elements are real. Due to the rotational and parity invariance of the scattering amplitude the matrix element Eq. (1.15) can be factorized into a product of an isotropic tensor and a reduced matrix element (Wigner-Eckart theorem) which vanishes unless both tensors $\boldsymbol{\Phi}_l{}^{(Pk)}$ and $\boldsymbol{\Phi}_{l'}{}^{(P'k')}$ have the same tensor rank and parity

$$\langle \Phi^{(Pk)}_{\mu_1 \ldots \mu_l} \, \omega \, (\Phi^{(P'k')}_{\nu_1 \ldots \nu_{l'}}) \rangle_0 = \delta_{ll'} \, \delta^{PP'} \, \omega^{(kk')}_{Pl} \, \Delta^{(l)}_{\mu_1 \ldots \mu_l, \nu_1 \ldots \nu_l} \, . \tag{1.16}$$

The reduced matrix element $\omega^{(kk')}_{Pl}$ – in the following always called collision integral – can then be obtained by a total contraction over the l tensor indices (in the following abbreviated by a dot)

$$\omega^{(kk')}_{Pl} = \frac{1}{2\,l+1} \, \langle \boldsymbol{\Phi}_l{}^{(Pk)} \cdot \omega \, (\boldsymbol{\Phi}_l{}^{(Pk')}) \rangle_0 \, . \tag{1.17}$$

The time reversal invariance of the molecular interaction guarantees the following Onsager symmetries of the collision integrals (the proof is completely analogous to that in Ref. [26] and is thus omitted here):

$$\omega^{(kk')}_{Pl} = T^{(k)} \, T^{(k')} \, \omega^{(k'k)}_{Pl} \, , \tag{1.18}$$

where $T^{(k)}, T^{(k')} = \pm 1$ whenever $\boldsymbol{\Phi}_l{}^{(Pk)}$, $\boldsymbol{\Phi}_l{}^{(Pk')}$ is even or odd under time reversal.

If $\boldsymbol{\Phi}^j$ is a "classical" expansion tensor, i. e. proportional to the unit matrix in rotational angular momentum space and thus commuting with the scattering amplitude matrix, the optical theorem Eq. (1.9) can be applied to Eq. (1.5) to give

$$\omega \, (\boldsymbol{\Phi}_{\text{class}}) = \sum_{j_2} \text{tr}_2 \int \mathrm{d}^3 c_2 \, f_{20} \sum_{j_1' j_2'} \int a^{j_1 j_2, j_1' j_2'} \; a^{\dagger \, j_1' j_2', j_1 j_2} \; \Delta \boldsymbol{\Phi}_{\text{class}} \, g' \, \mathrm{d}^2 e' \, , \tag{1.19}$$

where

$$\Delta \boldsymbol{\Phi} = \boldsymbol{\Phi} \, (\mathbf{c}_1 , j_1) + \boldsymbol{\Phi} \, (\mathbf{c}_2 , j_2) - \boldsymbol{\Phi} \, (\mathbf{c}_1', j_1') - \boldsymbol{\Phi} \, (\mathbf{c}_2', j_2') \, . \tag{1.20}$$

If $\boldsymbol{\Phi}$ represents a collisional invariant

$$[\boldsymbol{\Phi} = 1, m \, \mathbf{c}, \tfrac{1}{2} \, m \, c^2 + E \, (j)]$$

one has $\Delta \boldsymbol{\Phi} = 0$ and the corresponding collision integral vanishes.

II) Evaluation of the Collision Integrals, Cross Sections

1) Reduced Variables, Effective Cross Sections, Bracket Symbols

For the further evaluation of the collision integrals (1.17) it is useful to introduce first dimensionless velocity variables by

$$\mathbf{V} = \sqrt{m/k_{\text{B}} \, T_0} \, (\mathbf{c}_1 + \mathbf{c}_2) = \sqrt{m/k_{\text{B}} \, T_0} \, (\mathbf{c}_1' + \mathbf{c}_2') \, , \tag{2.1}$$

which is a dimensionless center of mass velocity, and

$$\boldsymbol{\gamma}' = \tfrac{1}{2} \, g' \, \mathbf{e}' \, \sqrt{m/k_{\text{B}} \, T_0} \, , \quad \boldsymbol{\gamma} = \tfrac{1}{2} \, g \, \mathbf{e} \, \sqrt{m/k_{\text{B}} \, T_0} \, , \tag{2.2}$$

which are dimensionless relative velocities before and after the collision. The energy conservation in a molecular collision process $j_1' + j_2' \rightarrow j_1 + j_2$ is then expressed by

$$\gamma'^2 = \gamma^2 + \Delta \varepsilon \tag{2.3}$$

where

$$\Delta \varepsilon = \varepsilon \, (j_1) + \varepsilon \, (j_2) - \varepsilon \, (j_1') - \varepsilon \, (j_2') \, , \tag{2.4}$$

and

$$\varepsilon \, (j) = E \, (j) / k_{\text{B}} \, T_0 \tag{2.5}$$

is the dimensionless rotational energy. Using Eqs. (1.7), (2.1 – 5) we obtain

$$f_{10} \, f_{20} \, \mathrm{d}^3 c_1 \, \mathrm{d}^3 c_2 = n_0{}^2 \, Q^{-2} \, \pi^{-3} \, \exp \, (-V^2) \cdot \exp \{ -\gamma^2 - \varepsilon \, (j_1) - \varepsilon \, (j_2) \} \, \mathrm{d}^3 V \, \mathrm{d}^2 e \, \gamma^2 \, \mathrm{d} \gamma \, . \tag{2.6}$$

If furthermore a thermal velocity v_0 is introduced,

$$v_0 = \sqrt{8 \, k_{\text{B}} \, T_0 / \pi \, m_{12}} = 4 \sqrt{k_{\text{B}} \, T_0 / \pi \, m} \, , \tag{2.7}$$

the collision integrals can now be factorized as follows:

$$\omega^{(kk')}_{Pl} = n_0 \, v_0 \, \sigma^{(kk')}_{Pl} \, . \tag{2.8}$$

The $\sigma^{(kk')}_{Pl}$ are effective temperature dependent cross sections which are (for $k' \neq k$) not necessarily positive. They are, in general, given by

$$\begin{aligned} \sigma^{(kk')}_{Pl} = & - \frac{1}{2 \, (2 \, l+1)} \, \pi^{-5/2} \, Q^{-2} \sum_{j_1 j_2 j_1' j_2'} \text{tr}_1 \, \text{tr}_2 \iiint \exp \{ -V^2 \} \; \exp \{ -\gamma^2 - \varepsilon \, (j_1) - \varepsilon \, (j_2) \} \\ & \times \boldsymbol{\Phi}^{(Pk) j_1}_{1l} \cdot \{ \textstyle\int a^{j_1 j_2, j_1' j_2'} \, \boldsymbol{\Phi}^{(Pk') j_1' j_2'}_{12l} \, a^{\dagger \, j_1' j_2', j_1 j_2} \gamma' \, \mathrm{d}^2 e' - \delta^{j_1 j_1'} \, \delta^{j_2 j_2'} \, \dfrac{h}{i \, m_{12}} \\ & \times [a^{j_1 j_2, j_1 j_2} \, (0) \, \boldsymbol{\Phi}^{(Pk') j_1 j_2}_{12l} - \boldsymbol{\Phi}^{(Pk') j_1 j_2}_{12l} a^{\dagger \, j_1 j_2, j_1 j_2} (0)] \} \mathrm{d}^3 V \, \mathrm{d}^2 e \, \gamma^2 \, \mathrm{d} \gamma \, , \end{aligned} \tag{2.9}$$

where the abbreviation

$$\boldsymbol{\Phi}^{(Pk) j_1 j_2}_{12l} \equiv \boldsymbol{\Phi}^{(Pk) j_1}_{1l} + \boldsymbol{\Phi}^{(Pk) j_2}_{2l}$$

has been used.

For further reduction of the somewhat lengthy expression (2.9), the following bracket symbols are introduced:

$$\{ \cdots \} \equiv \pi^{-3/2} \int \exp \, (-V^2) \, (\cdots) \, \mathrm{d}^3 V \, , \tag{2.10}$$

which denotes an averaging over the center of mass velocity and can always be performed explicitly since the scattering amplitude does not depend on $\boldsymbol{V}$. If we make use of the fact that after evaluation of the $\boldsymbol{V}$-integration and of the spin traces the remaining scalar expression can depend on the unit vectors $\boldsymbol{e}$ and $\boldsymbol{e}'$ only by way of the scalar product $\boldsymbol{e}\cdot\boldsymbol{e}' = \cos\vartheta$ (ϑ is the angle of deflection in the c. m. system) we can finally reduce the integral $\iint \mathrm{d}^2e\,\mathrm{d}^2e' \ldots$ to $8\pi^2 \int \sin\vartheta\,\mathrm{d}\vartheta \ldots$ Then it is convenient to define another bracket symbol by

$$\llbracket \cdots \rrbracket \equiv 2\pi Q^{-2} \sum_{j_1 j_2 j_1' j_2'} (2j_1+1)(2j_2+1) \cdot \iint \exp\{-\gamma^2 - \varepsilon(j_1) - \varepsilon(j_2)\}\,\gamma^3 (\cdots) \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\gamma\,, \tag{2.11}$$

which describes a weighted averaging over γ and the postcollisional rotational quantum numbers j_1, j_2 as well as an integration over the solid angle ($2\pi\sin\vartheta\,\mathrm{d}\vartheta$) and a summation over the precollisional rotational quantum numbers j_1' and j_2'. Note that the γ-integration has to be performed such that always γ', γ are positive.

2) Relaxation Cross Sections

If $k = k'$ the collision integrals are called relaxation coefficients. The pertaining effective cross sections are the relaxation cross sections. Their positive definiteness can be shown as follows: In the loss term of the collision operator Eq. (1.5) the combination

$$a(0)\,\boldsymbol{\Phi}_{12l}^{(Pk)} - \boldsymbol{\Phi}_{12l}^{(Pk)}\,a(0)^\dagger = [a(0) - a(0)^\dagger]\,\boldsymbol{\Phi}_{12l}^{(Pk)} + [a(0)^\dagger, \boldsymbol{\Phi}_{12l}^{(Pk)}]_- \,. \tag{2.12}$$

occurs. Since

$$\mathrm{tr}_1\,\mathrm{tr}_2 [\boldsymbol{\Phi}_{1l}^{(Pk)} \cdot [a(0)^\dagger, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-] = 0\,, \tag{2.13}$$

and the optical theorem Eq. (1.9) (the first equation) can be used one finds

$$\sigma_{Pl}^{(kk)} = \frac{2}{2l+1} \left\{ \left\llbracket \frac{\gamma'}{\gamma} \frac{1}{(2j_1+1)(2j_2+1)}\, \mathrm{tr}_1\,\mathrm{tr}_2 [\boldsymbol{\Phi}_l{}^{(Pk)j_1}\, a^{j_1 j_2, j_1' j_2'} \cdot [a^\dagger, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{j_1' j_2', j_1 j_2}] \right\rrbracket \right\}, \tag{2.14}$$

where the generalized commutator has been defined by

$$[a, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{j_1 j_2, j_1' j_2'} = a^{j_1 j_2, j_1' j_2'}\,(\boldsymbol{\Phi}_{1l}{}^{(Pk)j_1'} + \boldsymbol{\Phi}_{2l}{}^{(Pk)j_2'}) - (\boldsymbol{\Phi}_{1l}{}^{(Pk)j_1} + \boldsymbol{\Phi}_{2l}{}^{(Pk)j_2})\,a^{j_1 j_2, j_1' j_2'}\,. \tag{2.15}$$

By use of the second equation of the optical theorem (1.9) in the loss term an expression similar to Eq. (2.14) is obtained. If in this expression primed and unprimed quantities are interchanged in the loss term one finds with $\gamma'\,\mathrm{d}\gamma' = \gamma\,\mathrm{d}\gamma$ an alternative expression

$$\sigma_{Pl}^{(kk)} = -\frac{2}{2l+1} \left\{ \left\llbracket \frac{\gamma'}{\gamma} \frac{1}{(2j_1+1)(2j_2+1)}\, \mathrm{tr}_1\,\mathrm{tr}_2 [[\boldsymbol{\Phi}_{1l}^{(Pk)}, a]_-{}^{j_1 j_2, j_1' j_2'} \cdot \boldsymbol{\Phi}_{12l}^{(Pk) j_1' j_2'}\, a^{\dagger\, j_1' j_2', j_1 j_2}] \right\rrbracket \right\}. \tag{2.16}$$

Renaming the indices $1 \longleftrightarrow 2$ in Eqs. (2.14), (2.16) and adding the four expressions for $\sigma_{Pl}^{(kk)}$ leads finally to the following expression for the relaxation cross section

$$\sigma_{Pl}^{(kk)} = \frac{1}{2(2l+1)} \left\{ \left\llbracket \frac{\gamma'}{\gamma} \frac{1}{(2j_1+1)(2j_2+1)}\, \mathrm{tr}_1\,\mathrm{tr}_2 [[a, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{j_1 j_2, j_1' j_2'} \cdot [a, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{\dagger\, j_1' j_2', j_1 j_2}] \right\rrbracket \right\} \tag{2.17}$$

which obviously is $\geqq 0$.

3) Coupling Cross Sections

The name "coupling cross section" will be used if $\boldsymbol{\Phi}_l{}^{(Pk')}$ is a classical expansion tensor and $\boldsymbol{\Phi}_l{}^{(Pk)}$ is a quantum mechanical one or vice versa. Because of the Onsager symmetry Eq. (1.18) only the first case has to be considered. The coupling cross sections are of crucial importance for the occurrence and the magnitudes of all nonequilibrium alignment phenomena in gases mentioned above. In this case $\boldsymbol{\Phi}_l{}^{(Pk')}$ commutes with the scattering amplitude and the first version of the optical theorem Eq. (1.9) can be applied yielding

$$\sigma_{Pl}^{(kk')} = \frac{2}{2l+1} \left\{ \left\llbracket \frac{\gamma'}{\gamma} \frac{1}{(2j_1+1)(2j_2+1)}\, \Delta\,\boldsymbol{\Phi}_l{}^{(Pk')} \cdot \mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2, j_1' j_2'}\, a^{\dagger\, j_1' j_2', j_1 j_2}\, \boldsymbol{\Phi}_l{}^{(Pk)j_1}] \right\rrbracket \right\}. \tag{2.18}$$

Since the trace of any quantum mechanical expansion tensor vanishes, the part of the scattering amplitude which is independent of the magnetic quantum numbers ("spherical part") gives no contributions to the cross section (2.18). The coupling cross sections are thus essentially connected with the nonspherical part of the molecular interaction.

4) Molecular Cross Sections and Scattering Amplitude in the Approximation of Small Nonsphericity

The notation can still be simplified and the underlying physics made clearer by introduction of molecular cross sections within the bracket symbol (2.11). An important special case for the relaxation cross section (2.17) appears if $\boldsymbol{\Phi}_l{}^{(Pk)}$ is a classical expansion tensor. In this case one has

$$[a, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{j_1 j_2, j_1' j_2'} = -a^{j_1 j_2, j_1' j_2'} \, \Delta \boldsymbol{\Phi}_l{}^{(Pk)} , \tag{2.19}$$

with $\Delta \boldsymbol{\Phi}_l{}^{(Pk)}$ given by Equation (1.20). It is now useful to introduce the molecular cross section

$$\sigma(j_1 j_2, j_1' j_2') = \frac{\gamma'}{\gamma} \frac{1}{(2 j_1 + 1)(2 j_2 + 1)} \operatorname{tr}_1 \operatorname{tr}_2 [a^{j_1 j_2, j_1' j_2'} \, a^{\dagger \, j_1' j_2', j_1 j_2}] \tag{2.20}$$

which is equal to the "unpolarized" differential cross section for the time reversed molecular collision process $j_1 + j_2 \rightarrow j_1' + j_2'$ averaged over initial and summed over final magnetic quantum numbers. With (2.20), the corresponding relaxation cross section can be cast into the simple form

$$\sigma_{Pl}^{(kk)} = \frac{1}{2(2l+1)} \, \{ [\![\sigma \Delta \boldsymbol{\Phi}_l{}^{(Pk)} \cdot \Delta \boldsymbol{\Phi}_l{}^{(Pk)}]\!] \} . \tag{2.21}$$

Equation (2.21) represents the Wang-Chang-Uhlenbeck-de Boer (WUB) form of the relaxation cross sections [28] and remains also valid for $k' \neq k$ if both expansion tensors involved are classical ones.

In the approximation of small nonsphericity (first order DWBA, see paper II) the scattering amplitude matrix is written as

$$a^{j_1 j_2, j_1' j_2'} = a_0 \, P^{j_1 j_2} \delta^{j_1 j_1'} \, \delta^{j_2 j_2'} + \varepsilon \, a_1{}^{j_1 j_2, j_1' j_2'} , \tag{2.22}$$

where a_0 is the part of the scattering amplitude due to a purely spherical interaction potential (only energetically elastic collisions without change of magnetic quantum numbers are possible), and $a_1{}^{j_1 j_2, j_1' j_2'}$ is the part of the scattering amplitude matrix due to the nonspherical part of the interaction. The scaling parameter ε measures the nonsphericity of the interaction if $|a_1|$ is considered to be of the same order of magnitude as $|a_0|$. In the so-called "spherical approximation" only terms independent of ε are retained, i. e. one has with $\sigma_0 = |a_0|^2$

$$\begin{aligned} \operatorname{tr}_1 \operatorname{tr}_2 [[a, \boldsymbol{\Phi}_{12l}^{(Pk)}]_-{}^{j_1 j_2, j_1' j_2'} \cdot [a, \boldsymbol{\Phi}_{12l}^{(Pk)}]^{\dagger \, j_1' j_2', j_1 j_2}] &= \delta^{j_1 j_1'} \, \delta^{j_2 j_2'} \operatorname{tr}_1 \operatorname{tr}_2 [\Delta \boldsymbol{\Phi}_l{}^{(Pk) j_1 j_2} \cdot \Delta \boldsymbol{\Phi}_l{}^{(Pk) j_1 j_2}] \, \sigma_0 \\ &\quad + \text{terms at least of } O(\varepsilon) . \end{aligned} \tag{2.23}$$

Since $\operatorname{tr}_1 \operatorname{tr}_2 [a_1{}^{j_1 j_2, j_1 j_2}] \equiv 0$ (see paper II) one has in particular in Eq. (2.20)

$$\sigma(j_1 j_2, j_1' j_2') = \sigma_0 \, \delta_{j_1 j_1'} \, \delta_{j_2 j_2'} + O(\varepsilon^2) , \tag{2.24}$$

and, of course, a corresponding relation for the effective relaxation cross section. The effective relaxation cross sections in spherical approximation (denoted by the subscript "$_0$" at the lower left)

$${}_0\sigma_{Pl}^{(kk)} = \frac{1}{2(2l+1)} \left\{ \left[\!\!\left[\sigma_0 \frac{1}{(2 j_1 + 1)(2 j_2 + 1)} \operatorname{tr}_1 \operatorname{tr}_2 [\Delta \boldsymbol{\Phi}_l{}^{(Pk) j_1 j_2} \cdot \Delta \boldsymbol{\Phi}_l{}^{(Pk) j_1 j_2}] \right]\!\!\right]_{\text{el}} \right\} \tag{2.25}$$

(the subscript "el" refers to energetically elastic collisions, i. e. $j_1' = j_1$, $j_2' = j_2$), can, after evaluation of the spin traces and j-summations, always be expressed in terms of well known Chapman-Cowling Ω-integrals [1] defined by

$$\Omega^{(l,r)} = \tfrac{1}{4} v_0 \, 2 \pi \int_0^\infty \mathrm{d}\gamma \exp\{-\gamma^2\} \gamma^{2r+3} \int_0^\pi (1 - \cos^l \vartheta) \, \sigma_0 \sin \vartheta \, \mathrm{d}\vartheta . \tag{2.26}$$

The spherical approximation is not possible for the coupling cross sections. They are at least of order ε and essentially determined by the so-called "orientation cross section tensors" for the l^{th} rank J-multipolarization *

$$\sigma^{(1)}_{\mu_1\ldots\mu_l} \equiv \frac{\gamma'}{\gamma}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\sqrt{\frac{(2\,l+1)\,!!}{l!}}\;\mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2,\,j_1' j_2'}\;a^{\dagger\,j_1' j_2',\,j_1 j_2}\,\overline{J_{1\mu_1}\ldots J_{1\mu_l}}]\,. \tag{2.27}$$

In particular, the molecular orientation cross section tensors for vector- and 2nd rank tensor polarizations are given by

$$\sigma^{(1)}_{\mu} = \frac{\gamma'}{\gamma}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\,\sqrt{3}\;\mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2,\,j_1' j_2'}\;a^{\dagger\,j_1' j_2',\,j_1 j_2}\,J_{1\mu}]\,, \tag{2.28}$$

$$\sigma^{(1)}_{\mu\nu} = \frac{\gamma'}{\gamma}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\,\sqrt{\tfrac{15}{2}}\;\mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2,\,j_1' j_2'}\;a^{\dagger\,j_1' j_2',\,j_1 j_2}\,\overline{J_{1\mu}\,J_{1\nu}}]\,. \tag{2.29}$$

The orientation cross section tensor $\sigma^{(1)}_{\mu_1\ldots\mu_l}$ is directly proportional to the multipolarization $\langle\overline{J_{\mu_1}\ldots J_{\mu_l}}\rangle_{j_1}$ produced in a molecular collision with unpolarized beams of molecules in the corresponding rotational states [15]. Scalar expressions are used later, e. g. $\sigma^{(1)}_{ee} = \sigma^{(1)}_{\mu\nu}\,e_\mu\,e_\nu$.

Likewise, the spherical approximation cannot be applied for relaxation cross sections which involve expansion tensors solely built up of components of $\boldsymbol{J}$ (J-multipolarizations). In this case the commutator (2.15) is at least linear in ε and thus the cross section Eq. (2.17) is at least of $0(\varepsilon^2)$. The relaxation cross sections for the J-multipolarizations are determined by so called molecular "reorientation cross sections" defined by

$${}_{\mathrm{re}}\sigma_l{}^{(1)} \equiv \frac{\gamma'}{\gamma}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\,\frac{(2\,l+1)\,!!}{l!}\;\mathrm{tr}_1\,\mathrm{tr}_2\,[\overline{J_{1\mu_1}\ldots J_{1\mu_l}}\,a^{j_1 j_2,\,j_1' j_2'}\,[a^\dagger,\overline{J_{1\mu_1}\ldots J_{1\mu_l}}]_-{}^{j_1' j_2',\,j_1 j_2}]\,. \tag{2.30}$$

They are a measure for the change of a polarization (reorientation) in the collision if there was already a polarization present before scattering. Also reorientation cross sections ${}_{\mathrm{re}}\sigma_l{}^{(2)}$ occur which differ from Eq. (2.30) by $\overline{J_{2\mu_1}\ldots J_{2\mu_l}}$ in the commutator instead of $\overline{J_{1\mu_1}\ldots J_{1\mu_l}}$.
Further evaluation of the relaxation cross sections of moments describing molecular velocity-rotational angular momentum correlations (e. g. the Kagan-vector [18]) makes the introduction of more general cross section tensors necessary. An orientation-correlation cross section tensor of rank $2(l-n)$ is defined by

$$\sigma^{(1,2)}_{l;\mu_{n+1}\ldots\mu_l,\nu_{n+1}\ldots\nu_l} = \frac{(2\,l+1)\,!!}{l!}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\,\frac{\gamma'}{\gamma}$$
$$\times\,\mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2,\,j_1' j_2'}\;a^{\dagger\,j_1' j_2',\,j_1 j_2}\,\overline{J_{1\mu_1}\ldots J_{1\mu_n}\,J_{1\mu_{n+1}}\ldots J_{1\mu_l}}\;\overline{J_{2\mu_1}\ldots J_{2\mu_n}\,J_{2\nu_{n+1}}\ldots J_{2\nu_l}}]\,. \tag{2.31}$$

Here, n is the number of contractions over tensor indices. The cross section (2.31) vanishes for a purely central interaction. Similarly, generalized reorientation cross section tensors $\sigma^{(1)}_{l;\ldots}$ and $\tilde{\sigma}^{(2)}_{l;\ldots}$ occur:

$$\tilde{\sigma}^{(1)}_{l;\mu_{n+1}\ldots\mu_l,\nu_{n+1}\ldots\nu_l} = \frac{(2\,l+1)\,!!}{l!}\,\frac{1}{(2\,j_1+1)\,(2\,j_2+1)}\,\frac{\gamma'}{\gamma}$$
$$\times\,\mathrm{tr}_1\,\mathrm{tr}_2\,[a^{j_1 j_2,\,j_1' j_2'}\,\overline{J_{1\mu_1}\ldots J_{1\mu_n}\,J_{1\mu_{n+1}}\ldots J_{1\mu_l}}\,a^{\dagger\,j_1' j_2',\,j_1 j_2}\,\overline{J_{1\mu_1}\ldots J_{1\mu_n}\,J_{1\nu_{n+1}}\ldots J_{1\nu_l}}]\,. \tag{2.32}$$

For $\tilde{\sigma}^{(2)}_{l;\mu_{n+1}\ldots\mu_l,\nu_{n+1}\ldots\nu_l}$, one has to replace the tensor $\overline{J_{1\mu_1}\ldots J_{1\mu_l}}$ in (2.32) by $\overline{J_{2\mu_1}\ldots J_{2\mu_l}}$. For a spherical potential $\tilde{\sigma}^{(2)}_{l;\ldots}$ vanishes and

$${}_0\tilde{\sigma}^{(1)}_{l,\mu_{n+1}\ldots\mu_l,\nu_{n+1}\ldots\nu_l} = \frac{2\,l+1}{2\,(l-n)+1}\;g_l^2\;(j_1)\;\sigma_0\,\delta_{j_1 j_1'}\,\delta_{j_2 j_2'}\;\Delta^{(l-n)}_{\mu_{n+1}\ldots\mu_l,\nu_{n+1}\ldots\nu_l}\,, \tag{2.33}$$

where the abbreviation

$$g_l{}^2(j) = \prod_{l'=0}^{l}\left(j\;(j+1) - \frac{l'}{2}\left(\frac{l'}{2}+1\right)\right) \tag{2.34}$$

has been introduced. Equation (2.33) must be observed if the spherical approximation is made for the relaxation cross sections of velocity-rotational angular momentum correlations.

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* In a more concise notation the indices j_1, j_2, j_1', j_2' are omitted in the symbols used for the various molecular cross sections. The symbol "$\overline{}$" means that the corresponding tensor is irreducible.

III) Special Effective Cross Sections

In this section, relaxation- and coupling cross sections of moments relevant for most of the transport-orientation- and relaxation phenomena in a dilute gas of linear molecules are considered. The integration over the center-of-mass velocity is performed explicitly, the remaining cross sections are represented in terms of the bracket symbols (2.11). Their magnitudes are estimated within the framework of small nonsphericity.

1) Relaxation and Coupling Cross Sections of Classical Moments

Relaxation- and coupling cross sections of classical moments (i. e. the pertaining expansion tensors commute with the scattering amplitude) give the major contributions to the scalar transport- and relaxation phenomena. They are essentially determined by the averaged cross section σ given by Equation (2.20).

First, the scalars

$$\Phi^{\text{tr}} = \sqrt{\frac{2}{3}} \left(\frac{m}{2\, k_{\text{B}}\, T_0}\, c^2 - \frac{3}{2} \right), \tag{3.1}$$

and

$$\Phi^{\text{rot}} = \sqrt{\frac{k_{\text{B}}}{c_{\text{rot}}}}\, (\varepsilon - \langle \varepsilon \rangle_0) \tag{3.2}$$

are considered. The rotational heat capacity per molecule at the equilibrium temperature T_0 has been denoted by c_{rot}. The averages of (3.1) and (3.2) determine the translational and rotational temperatures, viz.

$$\langle \Phi^{\text{tr}} \rangle = \sqrt{\tfrac{3}{2}}\, (T_{\text{tr}} - T_0)/T_0\,, \tag{3.3}$$

$$\langle \Phi^{\text{rot}} \rangle = \sqrt{c_{\text{rot}}/k_{\text{B}}}\, (T_{\text{rot}} - T_0)/T_0\,. \tag{3.4}$$

Instead of the $\sigma_{Pl}^{(kk')}$ we will in the following use the shorter symbols σ^{A} and $\sigma^{\text{A,B}}$ for relaxation- and coupling cross sections. The letters A, B are chosen such that they characterize uniquely the expansion tensors being involved. So, we find from Eqs. (2.21) and (3.1) for the relaxation cross section σ^{tr} of the translational temperature

$$\sigma^{\text{tr}} = \tfrac{1}{3}\, [\![\sigma\, (\Delta\varepsilon)^2]\!]\,. \tag{3.5}$$

From the conservation of total energy and the Onsager relation Eq. (1.18) the equality

$$\sigma^{\text{rot}} = -\sqrt{\frac{3\, k_{\text{B}}}{2\, c_{\text{rot}}}}\, \sigma^{\text{tr, rot}} = \frac{3\, k_{\text{B}}}{2\, c_{\text{rot}}}\, \sigma^{\text{tr}} \tag{3.6}$$

is derived. The relaxation coefficient of the temperature difference $\Theta = T_{\text{tr}} - \text{T}_{\text{rot}}$, $\omega_\Theta = n_0\, v_0\, \sigma_\Theta$, can be obtained from the transport-relaxation equations as

$$\omega_\Theta = (1 + 3\, k_{\text{B}}/2\, c_{\text{rot}})\, \omega^{\text{tr}}\,. \tag{3.7}$$

The bulk viscosity η_{V} is connected with ω_Θ by

$$\eta_{\text{V}} = \frac{2}{3}\, \frac{c_{\text{rot}}}{c_{\text{rot}} + 3\, k_{\text{B}}/2}\, \frac{p_0}{\omega_\Theta}\,, \tag{3.8}$$

where $p_0 = n_0\, k_{\text{B}}\, T_0$ is the equilibrium pressure. Since $\Delta\varepsilon$ vanishes for energetically elastic collisions, only the inelastic part of σ enters in (3.5). After Eq. (2.24), this part is quadratic in the nonsphericity. This explains why for hydrogen molecules (where the nonsphericity is very small) the temperature relaxation proceeds slowly and the bulk viscosity is extremely large.

Next, relaxation- and coupling cross sections of the translational and internal heat fluxes are considered. The pertaining expansion tensors are

$$\Phi_\mu{}^{\text{qtr}} = \frac{2}{\sqrt{5}} \sqrt{\frac{m}{2\, k_{\text{B}}\, T_0}} \left(\frac{m}{2\, k_{\text{B}}\, T_0}\, c^2 - \frac{5}{2} \right) c_\mu\,, \tag{3.9}$$

and

$$\Phi_\mu{}^{\text{qrot}} = \sqrt{\frac{m}{c_{\text{rot}}\, T_0}}\, (\varepsilon - \langle \varepsilon \rangle_0)\, c_\mu\,. \tag{3.10}$$

Their averages are proportional to the respective heat fluxes, viz.

$$q_\mu{}^{\text{tr}} = p_0\, \sqrt{5\, k_{\text{B}}\, T_0/2\, m}\, \langle \Phi_\mu{}^{\text{qtr}} \rangle\,, \tag{3.11}$$

$$q_\mu{}^{\text{rot}} = p_0\, \sqrt{c_{\text{rot}}\, T_0/m}\, \langle \Phi_\mu{}^{\text{qrot}} \rangle\,. \tag{3.12}$$

The ensuing relaxation cross sections are

$$\sigma^{\text{qtr}} = \tfrac{1}{30}\, [\![\sigma [11\, (\Delta\varepsilon)^2 + \gamma^2\, \gamma'^2\, 8\, (1 - \cos^2 \vartheta)]]\!]\,, \tag{3.13}$$

and

$$\sigma^{\text{qrot}} = \frac{k_{\text{B}}}{6\, c_{\text{rot}}}\, [\![\sigma\, [\tfrac{3}{2}\, (\Delta\varepsilon)^2 + \gamma^2 (\varepsilon_1 - \varepsilon_2)^2 + \gamma'^2 (\varepsilon_1{}' - \varepsilon_2{}')^2 - 2\, \gamma\, \gamma'\, (\varepsilon_1 - \varepsilon_2)\, (\varepsilon_1{}' - \varepsilon_2{}') \cos \vartheta]]\!]\,, \tag{3.14}$$

where the abbreviations $\varepsilon_1 = \varepsilon(j_1)$, $\varepsilon_1{}' = \varepsilon(j_1{}')$ etc. are used. The spherical approximation applied to the expressions (3.13) and (3.14) yields with the use of Eqs. (2.24) and (2.26)

$$ {}_0\sigma^{\mathrm{qtr}} = \tfrac{16}{15}\, v_0{}^{-1}\, \Omega^{(2,2)}\,, \qquad (3.15) \qquad\qquad {}_0\sigma^{\mathrm{qrot}} = \tfrac{8}{3}\, v_0{}^{-1}\, \Omega^{(1,1)}\,. \qquad (3.16)$$

Since $\Omega^{(1,1)}$ determines, on the other hand, the self diffusion coefficient[1], Eq. (3.16) can be understood such that in the spherical approximation (no inelastic collisions!) diffusion of rotational energy takes place. The coupling cross section of both heat fluxes is, from Eq. (2.21), obtained as

$$\sigma^{\mathrm{qtr,\,qrot}} = \tfrac{1}{6} \sqrt{\frac{5\, k_{\mathrm{B}}}{2\, c_{\mathrm{rot}}}}\, \llbracket \sigma (\Delta\varepsilon)^2 \rrbracket = \sqrt{\tfrac{5}{12}}\, \sigma^{\mathrm{tr,\,rot}}\,. \tag{3.17}$$

It is determined solely by the inelastic collisions and can thus be neglected compared with σ^{qtr}, σ^{qrot} if the nonsphericity is small. For completeness we recall the expression for the heat conductivity λ_{WUB} (orientation effects being ignored) in terms of the effective cross sections (3.13), (3.14) and (3.17)

$$\lambda_{\mathrm{WUB}} = \frac{k_{\mathrm{B}}{}^2 T_0}{m\, v_0} \left[\frac{5}{2}\, \sigma^{\mathrm{qrot}} + \frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}}\, \sigma^{\mathrm{qtr}} - \sqrt{\frac{10\, c_{\mathrm{rot}}}{k_{\mathrm{B}}}}\, \sigma^{\mathrm{qtr,\,qrot}} \right] \left[\sigma^{\mathrm{qtr}}\, \sigma^{\mathrm{qrot}} - (\sigma^{\mathrm{qtr,\,qrot}})^2 \right]^{-1}. \tag{3.18}$$

The average of the second rank tensor

$$\Phi^{\eta}_{\mu\nu} = \frac{1}{\sqrt{2}}\, \frac{m}{k_{\mathrm{B}} T_0}\, \overline{c_\mu\, c_\nu} \tag{3.19}$$

gives the friction pressure tensor

$$\overline{p_{\mu\nu}} = \sqrt{2}\, p_0\, \langle \Phi^{\eta}_{\mu\nu} \rangle\,. \tag{3.20}$$

The corresponding relaxation cross section is

$$\sigma^{\eta} = \tfrac{2}{15} \llbracket \sigma \left[\gamma^4 + \gamma'^4 + \gamma^2 \gamma'^2\, (1 - 3 \cos^2 \vartheta) \right] \rrbracket, \tag{3.21}$$

which, in spherical approximation reduces to

$${}_0\sigma^{\eta} = \tfrac{8}{5}\, v_0{}^{-1}\, \Omega^{(2,2)}\,. \tag{3.22}$$

The viscosity (for neglected orientation effects) is connected with the relaxation coefficient ω^{η} by

$$\eta = p_0 / \omega^{\eta}\,. \tag{3.23}$$

From Eqs. (3.5), (3.13) and (3.21) one infers the equality

$$\tfrac{5}{6}\, \sigma^{\mathrm{tr}} = \sigma^{\mathrm{qtr}} - \tfrac{2}{3}\, \sigma^{\eta}\,. \tag{3.24}$$

2) *Relaxation Cross Sections of Quantum Mechanical Moments*

While the relaxation coefficients of classical moments of the distribution function are mainly determined by the spherical part of the interaction (spherical approximation is possible), the relaxation coefficients of pure *J*-multipolarizations are essentially determined by the nonspherical part of the interaction. The most important moments of this kind are the vector- and 2nd rank tensor polarizations of the rotational angular momenta

$$\langle \Phi^{\mathrm{V}}_{\mu} \rangle = \sqrt{3 / \langle J^2 \rangle_0}\, \langle J_\mu \rangle\,, \tag{3.25}$$

and

$$\langle \Phi^{\mathrm{T}}_{\mu\nu} \rangle = \sqrt{15/2\, \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0}\, \langle \overline{J_\mu\, J_\nu} \rangle\,. \tag{3.26}$$

Using Eqs. (2.14) and (2.30) we obtain the effective relaxation cross sections of vector- and tensor polarization in terms of molecular reorientation cross sections as

$$\sigma^{\mathrm{V}} = \tfrac{2}{3}\, \langle J^2 \rangle_0{}^{-1} \llbracket {}_{\mathrm{re}}\sigma_1{}^{(1)} + {}_{\mathrm{re}}\sigma_1{}^{(2)} \rrbracket\,, \tag{3.27}$$

and

$$\sigma^{\mathrm{T}} = \tfrac{2}{5}\, \langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1} \llbracket {}_{\mathrm{re}}\sigma_2{}^{(1)} + {}_{\mathrm{re}}\sigma_2{}^{(2)} \rrbracket\,. \tag{3.28}$$

The part $\llbracket {}_{\mathrm{re}}\sigma_1{}^{(1)} \rrbracket$ of σ^{V} determines the nuclear spin relaxation times of spin-1/2-nuclei[8]. The cross section σ^{T} is important for the Senftleben-Beenakker effect of the viscosity[10], its part $\llbracket {}_{\mathrm{re}}\sigma_2{}^{(1)} \rrbracket$ for the nuclear spin relaxation times for molecular gases[8] with nuclear spin $\geqq 1$. If $\langle \Phi^{\mathrm{T}}_{\mu\nu} \rangle$ is replaced by

$$\langle \Phi^{\mathrm{T}'}_{\mu\nu} \rangle = \sqrt{\tfrac{15}{2}}\, \langle J^2 / (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1/2}\, \langle (J^2 - \tfrac{3}{4})^{-1}\, \overline{J_\mu\, J_\nu} \rangle \tag{3.29}$$

the corresponding relaxation cross section $\sigma^{\mathrm{T}'}$ determines the coefficient of flow birefringence[4] and the width of the depolarized Rayleigh line[6] in the high pressure limit. It shall be mentioned already here that for a nonspherical interaction of the special form (cf. paper II)

$$V(\boldsymbol{r}, \boldsymbol{u}_1, \boldsymbol{u}_2) = V_0(r) + V_{\mathrm{L}}(r) \cdot \left[P_{\mathrm{L}}(\boldsymbol{u}_1 \cdot \hat{\boldsymbol{r}}) + (-1)^{\mathrm{L}}\, P_{\mathrm{L}}(\boldsymbol{u}_2 \cdot \hat{\boldsymbol{r}}) \right] \tag{3.30}$$

($\boldsymbol{r} = r\, \hat{\boldsymbol{r}}$ is the vector connecting the centers of mass of the molecules, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are vectors in the directions of the respective molecular axes) with $\mathrm{L} = 1$ or 2 in first order DWBA the reorientation cross sections ${}_{\mathrm{re}}\sigma_1{}^{(2)}$, ${}_{\mathrm{re}}\sigma_2{}^{(2)}$ are zero so that in this case σ^{T} is already the correct expression used in nuclear spin relaxation theory. All cross sections mentioned above are at least quadratic in the nonsphericity.

The calculation of relaxation cross sections of velocity-rotational angular momentum correlations is somewhat more tedious. We restrict ourselves to two characteristic moments namely the azimuthal polarization ("Waldmann-vector")

$$\langle \Phi_\mu{}^{\mathrm{W}} \rangle = \sqrt{\frac{3\,m}{2\,k_{\mathrm{B}}\,T_0}}\,\langle J^2 \rangle_0{}^{-1/2}\,\langle \mathbf{c} \times \boldsymbol{J} \rangle_\mu\,, \tag{3.31}$$

and the Kagan-polarization

$$\langle \Phi_\mu{}^{\mathrm{K}} \rangle = 3\sqrt{\frac{m}{2\,k_{\mathrm{B}}\,T_0}}\,\langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1/2}\,\langle c_\nu\,\overline{J_\nu\,J_\mu} \rangle\,. \tag{3.32}$$

With the help of Eqs. (2.31), (2.32) we find the following expressions for their relaxation cross sections:

$$\begin{aligned}\sigma^{\mathrm{W}} = {} & \tfrac{1}{2}\,\sigma^{\mathrm{V}} + \tfrac{1}{3}\,\langle J^2 \rangle_0{}^{-1}\,\llbracket 2\,\gamma^2\,\sigma\,g_0{}^2(j_1) + \gamma\,\gamma'\,(\tilde{\sigma}^{(1)}_{1;ee'} - 3\,\sigma\cos\vartheta\,g_0{}^2(j_1))\,\rrbracket \\ & + \tfrac{1}{3}\,\langle J^2 \rangle_0{}^{-1}\,\llbracket \gamma^2\,(\sigma^{(1,2)}_{1;ee} - \tfrac{2}{3}\,\sigma^{(1,2)}_{1;\mu\mu} - \sqrt{\tfrac{6}{5}}\,\sigma^{(1)}_{ee}) + \gamma\,\gamma'[\cos\vartheta\,({}_{\mathrm{re}}\sigma_1{}^{(1)} - {}_{\mathrm{re}}\sigma_1{}^{(2)} + \sigma^{(1,2)}_{1;\mu\mu}) - \tilde{\sigma}^{(2)}_{1;ee'}]\,\rrbracket\,,\end{aligned} \tag{3.33}$$

and

$$\begin{aligned}\sigma^{\mathrm{K}} = {} & \tfrac{1}{2}\,\sigma^{\mathrm{T}} + \tfrac{2}{3}\,\langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1}\,\llbracket \gamma^2\,\sigma\,g_1{}^2(j_1) - \tfrac{3}{5}\,\gamma\,\gamma'\,\tilde{\sigma}^{(2)}_{2;ee'} \rrbracket \\ & + \tfrac{1}{5}\,\langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1}\,\llbracket \tfrac{\sqrt{30}}{3}\,\gamma^2\,\sigma^{(1)}_{ee}\,[g_0{}^2(j_1) - \tfrac{15}{4}] - 2\,\gamma^2\,\sigma^{(1,2)}_{2;ee} + 2\,\gamma\,\gamma'\,\sigma^{(2)}_{2;ee'} \rrbracket\,.\end{aligned} \tag{3.34}$$

In spherical approximation, σ^{V}, σ^{T} and the second bracket symbols of the r.h.s. of Eqs. (3.33), (3.34) vanish. Furthermore one has

$${}_0\sigma(j_1\,j_2, j_1'\,j_2') = \sigma_0\,\delta_{j_1 j_1'}\,\delta_{j_2 j_2'}\,, \tag{3.35 a}$$

$${}_0\tilde{\sigma}^{(1)}_{1;ee'}\,(j_1\,j_2, j_1'\,j_2') \equiv {}_0\tilde{\sigma}^{(1)}_{1;\mu\nu}\,e_\mu\,e_\nu' = g_0{}^2(j_1)\cos\vartheta\;\;\sigma_0\,\delta_{j_1 j_1'}\,\delta_{j_2 j_2'}\,, \tag{3.35 b}$$

$${}_0\tilde{\sigma}^{(1)}_{2;ee'}\,(j_1\,j_2, j_1'\,j_2') \equiv {}_0\tilde{\sigma}^{(1)}_{2;\mu\nu}\,e_\mu\,e_\nu' = \tfrac{5}{3}\,g_1{}^2(j_1)\cos\vartheta\;\;\sigma_0\,\delta_{j_1 j_1'}\,\delta_{j_2 j_2'}\,. \tag{3.35 c}$$

Thus from Eqs. (2.26), (3.33) – (3.35 c) the relation

$${}_0\sigma^{\mathrm{W}} = {}_0\sigma^{\mathrm{K}} = \tfrac{8}{3}\,v_0{}^{-1}\,\Omega^{(1,1)} \tag{3.36}$$

is inferred.

3) Coupling Cross Sections of Classical and Quantum Mechanical Moments

Since the coupling of different quantum mechanical moments gives only higher order corrections to the transport anisotropy effects, it is sufficient that we restrict ourselves to couplings between classical and quantum mechanical moments. The ensuing cross sections are of crucial importance for all direct (e. g. flow birefringence) and indirect (e. g. Senftleben-Beenakker effects) nonequilibrium alignment phenomena. They are determined by the molecular orientation cross sections Eq. (2.27) which vanish unless the potential contains a nonspherical part. Starting point for the evaluation of such coupling cross sections is Equation (2.18).

Firstly, the coupling between the azimuthal polarization and the heat fluxes is considered. After performance of the **V**-integration the coupling of azimuthal polarization and translational heat flux proves to be zero

$$\sigma^{\mathrm{W,qtr}} = 0\,, \tag{3.37}$$

independent of the form of the scattering amplitude. This surprising result has first been obtained by Hess [29] for spin particles. On the other hand, the coupling cross section of azimuthal polarization and rotational heat flux is nonzero:

$$\begin{aligned}\sigma^{\mathrm{W,qrot}} = {} & \tfrac{1}{3}\,(2\,k_{\mathrm{B}}/c_{\mathrm{rot}}\,\langle J^2 \rangle_0)^{1/2} \\ & \cdot \llbracket \sigma_{\mathrm{n}}{}^{(1)}\sin\vartheta\,\gamma\,\gamma'\,(\varepsilon_2' - \varepsilon_1')\,\rrbracket,\end{aligned} \tag{3.38}$$

where $\sigma_{\mathrm{n}}{}^{(1)} = \sigma_\mu{}^{(1)}\,n_\mu$

and
$$\boldsymbol{n} = (\boldsymbol{e}' \times \boldsymbol{e})/\sin\vartheta \tag{3.39}$$

is a unit vector in the direction of the normal to the scattering plane. For molecules with small nonsphericity $\sigma_{\mathrm{n}}{}^{(1)}$ is at least quadratic in the nonsphericity (cf. Ref. [14] and paper II).

The coupling cross section of the Kagan polarization and the translational heat flux is given by

$$\sigma^{\mathrm{K,qtr}} = \tfrac{2}{5}\sqrt{\tfrac{2}{3}}\,\langle J^2 (J^2 - \tfrac{3}{4}) \rangle_0{}^{-1/2}\,\llbracket \gamma^2\,\sigma^{(1)}_{ee} - \gamma'^2\,\sigma^{(1)}_{e'e'} \rrbracket. \tag{3.40}$$

For a nonspherical potential of the form Eq. (3.30) and in first order DWBA one has for elastic collisions $\sigma^{(1)}_{e'e'} = \sigma^{(1)}_{ee}$ (cf. Ref.[15] and paper II). The only contributions to (3.40) thus stem from energetically inelastic collisions and are quadratic in the nonsphericity. For the coupling cross section of the Kagan polarization with the rotational heat flux one obtains

$$\sigma^{\mathrm{K,qrot}} = 2\left(\frac{15\,c_{\mathrm{rot}}}{k_{\mathrm{B}}}\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0\right)^{-1/2} \llbracket \gamma^2(\varepsilon_1-\varepsilon_2)\,\sigma^{(1)}_{ee} - \gamma\,\gamma'(\varepsilon_1{}'-\varepsilon_2{}')\,\sigma^{(1)}_{ee'}\rrbracket\,. \qquad (3.41)$$

For a potential (3.30) with L = 2 as it should describe the interaction between homonuclear molecules (H_2, D_2, N_2) in good approximation there are contributions to (3.41) linear in the nonsphericity due to elastic collisions. In these cases one may neglect the inelastic contributions and finds for the elastic part

$$_{\mathrm{el}}\sigma^{\mathrm{K,qrot}} = 2\left(\frac{15}{k_{\mathrm{B}}}\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0\right)^{-1/2} \llbracket \gamma^2(\varepsilon_1-\varepsilon_2)\,(\sigma^{(1)}_{ee} - \sigma^{(1)}_{ee'})\,\rrbracket_{\mathrm{el}}\,, \qquad (3.42)$$

where the subscript "el" denotes that in the bracket (2.11) $j_1{}' = j_1$ and $j_2{}' = j_2$ has to be taken. The cross section Eq. (3.42) has recently been calculated by the author[18] for $p-H_2$ at room temperature and a potential of the form (3.30) with simple radial parts $V_0(r)$ and $V_2(r)$.

The coupling cross sections (3.40) and (3.41) determine the saturation value of the change of the heat conductivity in a magnetic field according to ($\sigma^{\mathrm{qtr,qrot}}$ being neglected[30-32])

$$\left(\frac{\Delta\lambda^{\perp}}{\lambda}\right)_{\mathrm{sat}} = \frac{3}{2}\left(\frac{\Delta\lambda^{\parallel}}{\lambda}\right)_{\mathrm{sat}} = -\frac{9}{10}\left[\sigma^{\mathrm{K,qtr}}\sqrt{\frac{5}{2}\,\frac{\sigma^{\mathrm{qrot}}}{\sigma^{\mathrm{K}}\,\sigma^{\mathrm{qtr}}}} + \sigma^{\mathrm{K,qrot}}\sqrt{\frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}}\,\frac{\sigma^{\mathrm{qtr}}}{\sigma^{\mathrm{K}}\,\sigma^{\mathrm{qrot}}}}\right]^2 \left[\frac{5}{2}\,\sigma^{\mathrm{qrot}} + \frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}}\,\sigma^{\mathrm{qtr}}\right]^{-1}. \qquad (3.43)$$

For H_2, D_2 molecules, $\sigma^{\mathrm{K,qtr}}$ can be neglected compared with $\sigma^{\mathrm{K,qrot}}$.
The experiments confirm very well the $(\Delta\lambda^{\perp}/\Delta\lambda^{\parallel})_{\mathrm{sat}} = 3/2$-relation so that contributions of the azimuthal polarization to (3.43) proportional to $(\sigma^{\mathrm{W,qrot}})^2$ play a minor role.

Finally, the important coupling cross section of the friction pressure tensor and the tensor polarization is obtained as

$$\sigma^{\mathrm{T},\eta} = \frac{2\sqrt{2}}{5}\,\langle J^2(J^2-\tfrac{3}{4})\rangle_0{}^{-1/2} \cdot \llbracket \gamma^2\,\sigma^{(1)}_{ee} - \gamma'^2\,\sigma^{(1)}_{e'e'}\rrbracket = \sqrt{3}\,\sigma^{\mathrm{K,qtr}}\,. \qquad (3.44)$$

This cross section determines the magnitude of the change of viscosity in a magnetic field (saturation value)[33, 34]:

$$(\Delta\eta/\eta)_{\mathrm{sat}} = -(\sigma^{\mathrm{T},\eta})^2/\sigma^{\eta}\,\sigma^{\mathrm{T}}\,. \qquad (3.45)$$

The corresponding cross section $\sigma^{\mathrm{T}',\eta}$ [with $\Phi^{\mathrm{T}'}_{\mu\nu}$ of Eq. (3.29)] is decisive for the magnitude of the flow birefringence coefficient β. After Hess[4] one has

$$\beta = 2\,\pi\,(\alpha_{\parallel}-\alpha_{\perp})\,\eta\,(\sqrt{15}\,k_{\mathrm{B}}\,T_0)^{-1} \cdot \langle J^2/(J^2-\tfrac{3}{4})\rangle_0{}^{1/2}\,\sigma^{\mathrm{T}',\eta}/\sigma^{\mathrm{T}'}\,, \qquad (3.46)$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities parallel and perpendicular to the molecular axis.

The calculation of some of these effective cross sections for linear molecules from a given nonspherical potential will be the subject of a following paper.

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