

KINETIC THEORY OF FIELD EFFECTS IN NONUNIFORM MOLECULAR GASES

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Received 9 February 1983

Manuscript received in final form 25 April 1983

Dedicated to the memory of Hein Knaap

Effects of magnetic and electric fields on transport phenomena in dilute polyatomic gases are reviewed within the framework of first order Enskog theory. The established technique of approximate operator inversion is used to give first order approximations of the transport coefficients. Instead of the customary expansion of polarizations into orthogonal polynomials a more general treatment is chosen here so as to accommodate recent experimental observations. The polarizations produced by macroscopic fluxes are assumed to be eigenfunctions of the collision operator within the subspace of functions anisotropic in angular momentum. The formalism is extended to mixtures in a way to let the final expressions assume the same form as for pure gases. The obtained transport coefficients obey several symmetry relations and inequalities. Additional inequalities are now also derived for the matrix describing the saturated field effects.

1. Introduction

In 1930 Senftleben discovered that the thermal conductivity of oxygen changes in a magnetic field¹). The first analysis of this effect on the basis of a mean free path theory was given by Gorter^{2,3}) in 1938 and worked out in more detail by Zernike and Van Lier⁴) in 1939. In 1961 Kagan and Afanas'ev stated that, in a polyatomic gas, the presence of gradients gives rise to anisotropies not only in the velocity distribution, but also in the internal angular momentum distribution⁵). Subsequently, Kagan and Maksimov showed that the latter anisotropies, or polarizations, are the basic cause of field effects⁶).

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After the demonstration by Beenakker in 1962⁷⁾ that field effects are a general property of polyatomic gases and not only of paramagnetic molecules such as oxygen, these effects have been studied quite intensively both experimentally and theoretically. For a theoretical description the original form of the Boltzmann equation is no longer applicable since this equation does not take into account the internal degrees of freedom of the molecule. An adequate generalization was derived independently by Waldmann⁸⁾ and Snider⁹⁾. Solution procedures analogous to those for the classical Boltzmann equation have been developed. Waldmann and Hess presented a generalization of the moment method^{10,11)}. A generalization of the Chapman and Enskog procedure was given by McCourt and Snider^{12,13)} and by Snider^{14,15)}. A perturbation approach, formulated in terms of inverse operators, was first introduced by Kagan and Maksimov¹⁶⁾, extended by Tip, Levi and McCourt¹⁷⁾, and further developed by Coope and Snider¹⁸⁾.

The large amount of experimental information about field effects in dilute polyatomic gases accumulated in the last two decades has greatly contributed to the further development of the theory. It is the purpose of this paper to summarize the theory for transport phenomena in dilute polyatomic gases in the presence of external fields, taking into account the latest experimental results. One of the more fundamental differences with earlier presentations of the theory is the treatment of the dependence of polarizations upon the magnitude of the molecular velocity and the magnitude of the angular momentum. Some further new aspects are a modified formalism for gas mixtures and the derivation of an inequality for the magnitudes of the field effects on heat conductivity, thermal diffusion and diffusion.

For the sake of clarity, we shall first present in sections 2 through 4 the derivation of phenomenological coefficients for a pure gas, while section 5 contains a generalization of the scheme to mixtures.

The description will be restricted to dilute gases of diamagnetic symmetric top molecules. Moreover only rotational states are taken into account, since for most gases considered here vibrationally excited states do not play a significant role at room temperature.

2. The basic equations

The state of a molecular gas is described by a quantity f which is simultaneously a classical one-particle distribution function depending upon position \mathbf{r} , velocity \mathbf{c} and time t , and a statistical operator (density matrix) with respect to internal degrees of freedom. We may regard f as a partially Wignerized one-particle statistical operator^{12,19,20a)}. This operator f will simply be called the distribution function.

Under the usual conditions only rotation states of the molecules are excited. Moreover, we may safely assume that f is diagonal in the angular momentum quantum numbers. These numbers, J for linear molecules and J and K for symmetric top molecules, correspond to the total angular momentum and to its projection on the symmetry axis of the molecule, respectively. Physically the assumption is justified if, as is usually the case, the spacing between energy levels is large compared to \hbar -times the collision frequency of the molecules. Under such condition, during the time between collisions, matrix elements which are not diagonal in J and K , are destroyed by phase randomization^{5,21}).

Owing to its block-diagonality, f can be expressed as a function of the angular momentum operator $\hbar J$,

$$f = f(\mathbf{r}, \mathbf{c}, \mathbf{J}, t). \quad (1)$$

For a steady state and in the absence of external forces, the Waldmann–Snider version of the Boltzmann equation reads

$$\mathbf{c} \cdot \nabla f + \frac{i}{\hbar} [H_f, f] = C(f, f). \quad (2)$$

The influence of the external field upon the internal state is taken into account by the commutator with the field Hamiltonian H_f . An analogous term involving the rotational energy is missing, since H_{rot} commutes with the block-diagonal f . The collision term $C(f, f)$ represents the rate of change of f due to binary collisions. It is to be understood that this term is block-diagonalized in the sense explained before.

For most gases at ordinary temperature quasiclassical approximations are justified, so that f becomes an ordinary function also of angular momentum^{20a}). The Waldmann–Snider equation (2) is then replaced by a Boltzmann equation of classical appearance^{20b}). While keeping this option in mind, we shall continue to use the quantum language for the sake of greater generality.

The local Maxwellian is described by

$$f^0 = n \frac{1}{Z_{\text{rot}}} \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left\{ -W^2 - \frac{H_{\text{rot}}}{kT} \right\}, \quad (3)$$

with the reduced peculiar velocity

$$W = \sqrt{\frac{m}{2kT}} (\mathbf{c} - \mathbf{v}), \quad (4)$$

and with the rotational partition function obtained as a trace with respect to internal quantum numbers

$$Z_{\text{rot}} = \text{Tr} \exp \left\{ -\frac{H_{\text{rot}}}{kT} \right\}. \quad (5)$$

The symbols n , \mathbf{v} and T denote the local values of particle density, mean flow velocity and temperature, respectively, m the molecular mass and k the Boltzmann constant. The dependence of f^0 on the angular momentum \mathbf{J} is contained in the Hamiltonian. For symmetric top molecules one has

$$H_{\text{rot}} = \frac{\hbar^2}{2I_{\perp}} \left[\mathbf{J}^2 + \left(\frac{I_{\perp}}{I_{\parallel}} - 1 \right) J_{\parallel}^2 \right], \quad (6)$$

where J_{\parallel} is the component of \mathbf{J} along the symmetry axis of the molecule for linear molecules ($J_{\parallel} = 0$) and I_{\parallel} and I_{\perp} are the moments of inertia of the molecules with respect to an axis parallel and perpendicular to the symmetry axis.

For diamagnetic symmetric top molecules in magnetic and electric fields the field dependent part of the Hamiltonian is²²⁾

$$H_{f, \text{Zeeman}} = -\mu_{\text{N}} \left(\mathbf{g} \odot \frac{\overline{\mathbf{J}\mathbf{J}}}{J^2} \right) \mathbf{J} \cdot \mathbf{B} \quad (7)$$

and²³⁾

$$H_{f, \text{Stark}} = -\mu_{\text{e}} \frac{J_{\parallel}}{J^2} \mathbf{J} \cdot \mathbf{E}, \quad (8)$$

respectively. Here, μ_{N} and μ_{e} are the nuclear magneton and the electric dipole moment of the molecule, and \mathbf{g} the rotational Landé tensor,

$$\mathbf{g} = \begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix}, \quad (9)$$

where the symmetry axis of the molecule is taken in the third direction (for spherical top molecules $g_{\parallel} = g_{\perp}$). A double scalar product, denoted by \odot , with the symmetric traceless part $\overline{\mathbf{J}\mathbf{J}}$ of the tensor product $\mathbf{J}\mathbf{J}$ appears in eq. (7). Fractional notation is used here for products with inverse operators, with the excuse that the factors commute so that no ambiguity can arise.

For the calculation of transport coefficients it shall suffice to consider first-order Enskog approximations to nonequilibrium solutions of eq. (2). This means that we can write the distribution f in the form

$$f = f^0(1 + \phi), \quad (10)$$

where ϕ depends linearly on the first order gradients of the hydrodynamic quantities $n(\mathbf{r})$, $\mathbf{v}(\mathbf{r})$ and $T(\mathbf{r})$. The quantity ϕ is a selfadjoint operator commuting with f^0 and is considered to be "small" in the region of interest.

The solution for f may be used to determine the mean macroscopic values of

any observable quantity described by a selfadjoint operator A ,

$$\langle A \rangle = \frac{1}{n} \text{Tr} \int A f \, dc. \quad (11)$$

If the equilibrium average $\langle A \rangle_0$ vanishes we can rewrite $\langle A \rangle$ as follows:

$$\langle A \rangle = \frac{1}{n} \text{Tr} \int A f^0 \phi \, dc. \quad (12)$$

This leads us to introduce a Hilbert space of operators such as A and ϕ , with the weighted Hilbert–Schmidt inner product as in eq. (12),

$$\langle A | \phi \rangle = \frac{1}{n} \text{Tr} \int A^\dagger f^0 \phi \, dc. \quad (13)$$

The dagger has been added in case A is not selfadjoint. Since ϕ is selfadjoint we then have if $\langle A \rangle_0$ vanishes

$$\langle A \rangle \equiv \langle A^\dagger | \phi \rangle = \langle A | \phi \rangle^*. \quad (14)$$

With the Maxwellian f^0 varying from place to place, we have in fact introduced a whole collection of Hilbert spaces, one for each r . However, since only the state in the vicinity of an arbitrarily selected point will be of interest, we shall be satisfied with the Hilbert space belonging to that point.

By substituting the known zeroth-order (equilibrium) distribution f^0 into the left-hand side of the Waldmann–Snider equation (2) and retaining only linear terms with respect to ϕ in the rest of the equation, we obtain an inhomogeneous equation for ϕ of the following form:

$$\psi = -n(\mathcal{R} + i\mathcal{L})\phi. \quad (15)$$

The operators \mathcal{R} and \mathcal{L} and the term ψ will be explained below.

The linearized collision (super)operator \mathcal{R} is derived from the collision term in eq. (2)¹⁵.

$$-f^0 n \mathcal{R} \phi = C(f^0 \phi, f^0) + C(f^0, f^0 \phi). \quad (16)$$

The explicit form of \mathcal{R} is not important for the present discussion, the only properties required being its linearity, isotropy (rotational invariance) and its dissipative nature (positive semidefiniteness)¹⁵. In general \mathcal{R} is not selfadjoint; instead, by combining its properties under time reversal and space inversion²⁴, we obtain

$$\mathcal{R}^\dagger = R \mathcal{R} R, \quad (17)$$

where R is the angular momentum reversal operator,

$$R\chi(W, J) = \chi(W, -J). \quad (18)$$

One should moreover keep in mind that the collision operator has a 5-fold zero eigenvalue associated with the collisional invariants 1, W , and $W^2 + \mathcal{E}$, (where $\mathcal{E} = H_{\text{rot}}/kT$) as the hydrodynamic eigenfunctions.

The precession operator \mathcal{L} , which as part of the one-particle Liouville operator is selfadjoint, originates from the second term in eq. (2),

$$\frac{i}{\hbar} [H_{\text{rot}}, f^0 \phi] = f^0 n i \mathcal{L} \phi. \quad (19)$$

All isotropic-in- J functions, among them the hydrodynamic eigenfunctions of \mathcal{R} , belong to the zero eigenvalue of \mathcal{L} since they are not affected by precession. For a field in the z -direction, which henceforth will be our choice, we find that

$$n \mathcal{L} \phi = -\omega [J_z, \phi]. \quad (20)$$

The Larmor frequency ω (which by convention has the opposite sign of the precession frequency of the molecules) is

$$\omega = \frac{g_{\perp} \mu_N}{\hbar} \left[1 + \frac{g_{\parallel} - g_{\perp}}{g_{\perp}} \frac{K^2}{J(J+1)} \right] B \quad (21)$$

and

$$\omega = \frac{\mu_c}{\hbar} \frac{K}{J(J+1)} E \quad (22)$$

in magnetic and electric fields, respectively, cf. eqs. (7) and (8). Both for spherical-top and for linear molecules expression (22) as well as the K -dependent term in (21) vanish, because in the first case $g_{\parallel} = g_{\perp}$ and $\mu_c = 0$, while $K = 0$ in the second.

The inhomogeneous term ψ in eq. (15) stems from the gradient of the local Maxwellian^{12,19},

$$\begin{aligned} \mathbf{c} \cdot \nabla \ln f^0 \approx & T \sqrt{\frac{2kT}{m}} \mathbf{W} \left(W^2 - \frac{5}{2} + \mathcal{E} - \langle \mathcal{E} \rangle_0 \right) \frac{\nabla T}{T^2} + 2T \overline{\mathbf{W}\mathbf{W}} \odot \frac{\nabla \mathbf{v}}{T} \\ & + T \left[\left(\frac{5}{3} - \gamma \right) \left(W^2 - \frac{3}{2} \right) - (\gamma - 1) (\mathcal{E} - \langle \mathcal{E} \rangle_0) \right] \frac{\nabla \cdot \mathbf{v}}{T} \equiv \psi, \quad (23) \end{aligned}$$

where $\gamma = c_p/c_v$.

Since $\ln f^0$ is a linear combination of collisional invariants, it is not surprising to find ψ as a bilinear sum of products of microscopic fluxes Ψ^{α} and the

corresponding thermodynamic forces X^α ,

$$\psi = \sum_{\alpha} \Psi^{\alpha} \cdot X^{\alpha}, \quad (24)$$

with the factors given in the preceding explicit expression (see also table I). This can be seen more generally by evaluating the entropy source strength²⁵),

$$\begin{aligned} \sigma &= -k \int \ln f \left\{ C(f, f) - \frac{i}{\hbar} [H_f, f] \right\} dc \\ &= nk \int f^0 \ln f (\mathcal{R} + i\mathcal{L}) \phi \, dc \\ &= n^2 k \langle \ln f | (\mathcal{R} + i\mathcal{L}) \phi \rangle = -nk \langle \phi | \psi \rangle, \end{aligned} \quad (25)$$

where we have used eqs. (16), (20), (13), (10) and (15).

Substitution of eq. (23) yields the more familiar bilinear expression

$$\sigma = -p' \frac{\mathbf{V} \cdot \mathbf{v}}{T} - \mathbf{q} \cdot \frac{\nabla T}{T^2} - \overline{\Pi} \odot \frac{\overline{\nabla \mathbf{v}}}{T} \equiv - \sum_{\alpha} \mathbf{J}^{\alpha} \cdot X^{\alpha}. \quad (26)$$

The first term, related to bulk viscosity, has been simplified by aid of the relation

$$\langle \mathcal{E} \rangle - \langle \mathcal{E} \rangle_0 = - \left\langle W^2 - \frac{3}{2} \right\rangle \equiv - \frac{3}{2} \frac{p'}{nkT}. \quad (27)$$

Each term in (26) contains a macroscopic flux, which can be defined generally as

$$\mathbf{J}^{\alpha} = nk \langle \Psi^{\alpha} | \phi \rangle. \quad (28)$$

These fluxes are the heat flux, \mathbf{q} , the symmetric traceless part of the viscous pressure tensor, $\overline{\Pi}$, and a third of the trace of this tensor, p' . Inspection of eqs. (25) and (26), using eq. (28) shows the general validity of (24).

The formal solution of eq. (15) reads^{16,17,21})

$$\phi = - \frac{1}{n} (\mathcal{R} + i\mathcal{L})^{-1} \psi. \quad (29)$$

The inverse operator $(\mathcal{R} + i\mathcal{L})^{-1}$ appearing in eq. (29) is defined on the nonhydrodynamic subspace which is orthogonal to the collisional invariants. While ψ from eq. (23) already fulfills this condition, the definition of $(\mathcal{R} + i\mathcal{L})^{-1}$ demands the same for ϕ , i.e.,

$$\langle 1 | \phi \rangle = 0, \quad \langle W | \phi \rangle = 0, \quad \langle (W^2 + \mathcal{E}) | \phi \rangle = 0. \quad (30)$$

This coincides with the usual subsidiary condition that ϕ is not allowed to alter the values of n , \mathbf{v} and T prescribed by the local Maxwellian. Relation (27) follows from (30).

TABLE I

Fluxes J^α and forces X^α , microscopic fluxes $\Psi^\alpha = C^\alpha \psi^\alpha$ and normalized microscopic fluxes Φ^α for pure gases in the case of heat flux ($\alpha = q$) and momentum transport ($\alpha = \pi$). The constant r is defined by $r^2 = 2c_{\text{rot}}/5k$. The label $s = E$ refers to transport of energy

α	J^α	X^α	Ψ^α	Φ^α	C^α
$10E \equiv q$	q	$\frac{VT}{T^2}$	$T \sqrt{\frac{2kT}{m}} \left[W^2 - \frac{5}{2} + \mathcal{E} - \langle \mathcal{E} \rangle_0 \right] W$	$\left[\frac{5}{4}(1+r^2) \right]^{-1/2} \left[W^2 - \frac{5}{2} + \mathcal{E} - \langle \mathcal{E} \rangle_0 \right] [W]^{1/2}$	$T \sqrt{\frac{2kT}{m}} \left[\frac{5}{4}(1+r^2) \right]^{1/2}$
$20 \equiv \pi$	$\overline{\Pi}$	$\frac{\overline{V^2}}{T}$	$2T\overline{W^2}$	$\sqrt{2} [W]^2$	$T\sqrt{2}$

3. Formal expressions for phenomenological coefficients

The macroscopic irreversible fluxes \mathbf{J}^α , such as the heat flux \mathbf{q} and the viscous pressure tensor $\overline{\Pi}$ vanish in equilibrium. In nonequilibrium they obey linear phenomenological laws in the so-called linear regime. For vectorial forces and fluxes e.g., one has

$$\mathbf{J}^\alpha = - \sum_{\beta} \mathbf{L}^{\alpha\beta} \cdot \mathbf{X}^\beta, \quad (31)$$

where \mathbf{X}^β is the thermodynamic force conjugate (in the sense of Onsager, see e.g., ref. 25) to \mathbf{J}^β , and $\mathbf{L}^{\alpha\beta}$ is a phenomenological second rank tensor coupling the flux \mathbf{J}^α to the force \mathbf{X}^β . Likewise, if the force and flux are second-rank tensors, the phenomenological coefficient becomes a tensor of 4th rank. Such is the case of viscous flow, as specified by the third term in eq. (26) and by the bottom line of table I.

Only one force and one flux of each rank enter expression (26) for the entropy source in a pure gas; one pair of conjugate scalars, one pair of vectors, and one pair of second-rank tensors. This means that in the field-free case for pure gases, considering the \mathbf{J}^α and \mathbf{X}^β from eq. (31) we always have $\alpha = \beta$. The scheme will be kept more general, however, since occasionally additional fluxes, such as the flux of translational or rotational energy, may be of interest. Moreover, as we will see, in the case of a mixture diffusive fluxes and concentration gradients come in naturally as additional pairs of conjugate vectors.

Substituting the formal solution (29) with expression (24) into eq. (28) we obtain

$$\mathbf{J}^\alpha = -k \sum_{\beta} \langle \Psi^\alpha | (\mathcal{R} + i\mathcal{L})^{-1} \Psi^\beta \rangle^* \cdot \mathbf{X}^\beta, \quad (32)$$

so that

$$\mathbf{L}^{\alpha\beta} = k \langle \Psi^\alpha | (\mathcal{R} + i\mathcal{L})^{-1} \Psi^\beta \rangle^*. \quad (33)$$

For the actual evaluation of phenomenological coefficients it is convenient to introduce a basis \mathcal{H} of orthonormalized tensors to span the Hilbert space. Their general form is given by

$$\Phi^{pq_s} = \left(\frac{2^p}{p!} \right)^{1/2} [W]^p \mathcal{Y}^{(q)}(\mathbf{J}) P_s, \quad (34)$$

where $[W]^p$ is an irreducible tensor²⁶⁻²⁸⁾ of rank p in W , and $\mathcal{Y}^{(q)}$ a normalized irreducible tensor of rank q formed from the operator \mathbf{J} according to

$$\mathcal{Y}^{(q)} = (2q + 1)^{1/2} \frac{[\mathbf{J}]^q}{\{[\mathbf{J}]^q \odot [\mathbf{J}]^q\}^{1/2}}. \quad (35)$$

The \odot now denotes a q -fold scalar product. Since the submatrices of $[J]^q$ corresponding to $0 \leq J < \frac{1}{2}q$ vanish²⁴, the definition of $\mathcal{Y}^{(q)}$ is only meaningful within the subspace corresponding to $J \geq \frac{1}{2}q$. Hence the quantummechanical trace of an operator containing $\mathcal{Y}^{(q)}$ involves a summation over J beginning only with $J = \frac{1}{2}q$ or $\frac{1}{2}(q+1)$ (whichever is integer).

The last factor P_s in expression (34) is a scalar operator and may depend upon W^2 , J^2 and J_{\parallel} . One should actually write $P_s^{(pq)}(W^2, J^2, J_{\parallel})$, since the set is different for each pair (pq) . However, for the sake of brevity the superscripts will usually be omitted. Recent experiments^{28a}) have shown that the usual expansion into Sonine (associated Laguerre) and Wang–Chang–Uhlenbeck polynomials does not lead to a satisfactory description. Therefore a more general treatment will be given here and the form of P_s will not be specified in advance. While p and q stand for numbers $0, 1, \dots$, specific values of the label s will be designated by letters. For instance the basis function representing the total heat flux is²⁹)

$$\Phi^{10E} = \sqrt{2}[W]^1 \left[\frac{5}{2}(1+r^2) \right]^{-1/2} \left[W^2 - \frac{5}{2} + \mathcal{E} - \langle \mathcal{E} \rangle_0 \right] \equiv \sqrt{2}[W]^1 P_E, \quad (36)$$

where $r^2 = (2/5)c_{\text{rot}}/k$ and $p = 1$, $q = 0$, while the normalized scalar factor P_E is characterized by $s = E$ for energy.

The tensors Φ^{pqs} shall be normalized as follows;

$$\langle \Phi^{pqs} | \Phi^{p'q's'} \rangle = \delta_{pp'} \delta_{qq'} \delta_{ss'} \Delta^{(p)} \Delta^{(q)}, \quad (37)$$

where $\Delta^{(p)}$ is the projection tensor producing a symmetric traceless tensor of rank p from any tensor of that rank²⁸). Translated into spherical components the normalization condition reads*)

$$\langle \Phi_{\mu\nu}^{pqs} | \Phi_{\mu'\nu'}^{p'q's'} \rangle = \delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{\mu\mu'} \delta_{\nu\nu'}, \quad (38)$$

with

$$\Phi_{\mu\nu}^{pqs} = \left(\frac{2^p}{p!} \right)^{1/2} [W]_{\mu}^p \mathcal{Y}_{\nu}^{(q)} P_s. \quad (39)$$

For eqs. (37) and (38) to hold, the sets $\{P_s^{(pq)}\}$ must be orthonormalized as follows:

$$\frac{2^{2p} p!}{(2p+1)!} \langle W^p P_s^{(pq)} | W^p P_{s'}^{(pq)} \rangle = \delta_{ss'} \quad (40)$$

where the trace involved in $\langle \dots | \dots \rangle$ is carried out according to the value of q , as explained before. For instance, if $q = 2$ and if a particular $P_s^{(p2)}$ is to be a

* The relation between spherical and Cartesian components of a vector W is taken to be as in Edmonds³⁰), $W_0 = W_z$; $W_{\pm 1} = \mp \frac{1}{2\sqrt{2}}(W_x \pm iW_y)$, and is analogous for tensors where spherical harmonics or their operator analogs come into play.

constant, we must take $P_s^{(p2)} = (1 - Z_{\text{rot}}^{-1})^{1/2}$. However, such precaution is usually unimportant since the state with $J = 0$ only carries a small weight, except in hydrogen at low temperatures.

At this point some additional remarks concerning the choice of the basis (34) need to be made. First of all, the set of basis functions \mathcal{R} shall include the normalized microscopic fluxes

$$\Phi^\alpha = \frac{\Psi^\alpha}{C^\alpha}, \quad (41)$$

where C^α are normalization factors (see table I). Note that from now on labels of microscopic fluxes stand for triplets $\alpha = (r_\alpha, 0, s_\alpha)$ and $\beta = (r_\beta, 0, s_\beta)$. The two fluxes considered in (33) are isotropic in \mathbf{J} , hence $q = 0$, and both usually have the same rank ($r_\alpha = r_\beta$) in \mathbf{W} ; yet the scalar factors P_s may differ.

Basis functions which are anisotropic-in- \mathbf{J} are called polarizations. Occasionally one has to switch from one orthonormal basis $\{\Phi^{pq\bar{s}}\}$ to another one $\{\Phi^{pq\bar{s}}\}$ by choosing a different set of scalar factors, without changing the tensors. Basis functions of the different sets may then be transformed into one another by

$$\Phi_{\mu\nu}^{pq\bar{s}} = \sum_{\tilde{s}} a_{s\tilde{s}} \Phi_{\mu\nu}^{pq\tilde{s}}, \quad (42)$$

where the indices s and \tilde{s} refer to the two different sets, respectively. The coefficient

$$a_{s\tilde{s}} = \langle \Phi_{\mu\nu}^{pq\bar{s}} | \Phi_{\mu\nu}^{pq\tilde{s}} \rangle = \frac{2^{2p} p!}{(2p+1)!} \langle W^p P_s | W^p P_{\tilde{s}} \rangle. \quad (43)$$

represents the component of $\Phi_{\mu\nu}^{pq\bar{s}}$ proportional to $\Phi_{\mu\nu}^{pq\tilde{s}}$.

The matrix elements of the inverse operator $(\mathcal{R} + i\mathcal{L})^{-1}$ in eq. (33) will be approximated in terms of matrix elements of \mathcal{R} within a finite subset of the orthonormal basis. Because of the isotropy of \mathcal{R} , these matrix elements can be decomposed according to the Wigner-Eckart theorem into isotropic tensors and scalar factors, the so-called reduced matrix elements. This is done following the coupling scheme of Chen, Moraal and Snider²⁴), which is analogous to Russel-Saunders coupling in atomic physics and which is preferable for analogous reasons. As the effects of the nonspherical part of the intermolecular potential are small, first the velocity tensors are coupled, similarly the angular momentum tensors, and then the coupling between \mathbf{W} and \mathbf{J} is considered. Explicitly,

$$\begin{aligned} \langle \Phi_{\mu\nu}^{pq\bar{s}} | \mathcal{R} \Phi_{\mu'\nu'}^{p'q's'} \rangle &= \sum_{L,M} i^{p-p'+q-q'} (-1)^{L+p+q+\mu+\nu'} \sqrt{\Omega(pp'L)\Omega(qq'L)} \\ &\times \begin{pmatrix} p & p' & L \\ -\mu & \mu' & -M \end{pmatrix} \begin{pmatrix} q & q' & L \\ -\nu & \nu' & M \end{pmatrix} S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix}. \quad (44) \end{aligned}$$

The isotropic tensorial factor is represented in terms of $3j$ -symbols³⁰⁾ and the corresponding normalization coefficient

$$\Omega(l_1 l_2 l_3) = \frac{(l+1)!(l-2l_1)!(l-2l_2)!(l-2l_3)! 3 - (-1)^l}{(2l_1)!(2l_2)!(2l_3)! 2}, \quad (45)$$

with $l = l_1 + l_2 + l_3$. The reduced matrix element S_L is customarily expressed by an effective cross section \mathfrak{S}_L , which describes the collisional coupling of the pqs and the $p'q's'$ tensors,

$$S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} = \langle v \rangle_0 \mathfrak{S}_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix}, \quad (46)$$

where $\langle v \rangle_0$ is the average relative speed of a molecular pair,

$$\langle v \rangle_0 = \sqrt{\frac{16kT}{\pi m}}. \quad (47)$$

According to the established convention the subscript L in (44) is omitted if only one value is possible. Furthermore, if $pqs = p'q's'$ one row of indices is suppressed and similarly the last column if $P_s = P_{s'} = \text{const}$. A cross section with $pqs \neq p'q's'$ is called a production cross section when either q or q' equals zero, and a transfer cross section when neither q nor q' is zero. If $pqs = p'q's'$ and $q \neq 0$ it is called a decay cross section.

Next, we have

$$\mathcal{L} \Phi_{\mu\nu}^{pqs} = -\frac{1}{n} \omega v \Phi_{\mu\nu}^{pqs}, \quad (48)$$

and thus the matrix elements of the precession operator are

$$\langle \Phi_{\mu\nu}^{pqs} | \mathcal{L} \Phi_{\mu'\nu'}^{p'q's'} \rangle = -\delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{\mu\mu'} \delta_{\nu\nu'} \frac{1}{n} v \langle P_s^2 \omega \rangle_0. \quad (49)$$

The equilibrium average of P_s^2 is to be understood in the sense of eq. (40), hence with the additional weight $\propto W^{2p}$ included and, e.g., with the $J = 0$ term deleted if $q = 2$. For linear molecules ω does not depend on J so that $\langle P_s^2 \omega \rangle_0 = \omega$.

4. Perturbation scheme

Coupling between W and J can only be caused by a nonspherical potential. In the cases of interest here the result of this coupling averaged over all collisions is small as one can conclude from the observed magnitude of field effects. Therefore the complete set of tensors Φ^{pqs} (34) is split into a part \mathcal{H}_0 containing

all tensors which are isotropic in angular momentum ($q = 0$) and a complementary set \mathcal{H}_1 ($q \neq 0$). Also the collision operator is decomposed^{21,31,32,33}

$$\mathcal{R} = \mathcal{R}_d + \mathcal{R}_{nd}. \quad (50)$$

The block-diagonal part \mathcal{R}_d has nonvanishing matrix elements only within the subspaces spanned separately by \mathcal{H}_0 and by \mathcal{H}_1 , i.e. \mathcal{R}_d couples only the tensors within each of these subsets. The nondiagonal part \mathcal{R}_{nd} , on the other hand, accounts for the weaker coupling between tensors from \mathcal{H}_0 and those from \mathcal{H}_1 . Symbolically

$$\langle \mathcal{H}_0 | \mathcal{R}_d \mathcal{H}_1 \rangle = 0, \quad \langle \mathcal{H}_0 | \mathcal{R}_{nd} \mathcal{H}_0 \rangle = 0, \quad \langle \mathcal{H}_1 | \mathcal{R}_{nd} \mathcal{H}_1 \rangle = 0. \quad (51)$$

Treating \mathcal{R}_{nd} as a perturbation, we expand the operator $(\mathcal{R} + i\mathcal{L})^{-1}$ accordingly,

$$\begin{aligned} (\mathcal{R} + i\mathcal{L})^{-1} &= (\mathcal{R}_d + i\mathcal{L})^{-1} - (\mathcal{R}_d + i\mathcal{L})^{-1} \mathcal{R}_{nd} (\mathcal{R}_d + i\mathcal{L})^{-1} \\ &\quad + (\mathcal{R}_d + i\mathcal{L})^{-1} \mathcal{R}_{nd} (\mathcal{R}_d + i\mathcal{L})^{-1} \mathcal{R}_{nd} (\mathcal{R}_d + i\mathcal{L})^{-1} + \dots \end{aligned} \quad (52)$$

Since the microscopic fluxes Ψ^α and Ψ^β are isotropic-in- \mathbf{J} , the precession operator drops out from the zeroth-order contribution to $\mathbf{L}^{\alpha\beta}$. In spherical coordinates,

$$L_{\mu\mu}^{\alpha\beta(0)} = k \langle \Psi_\mu^\alpha | (\mathcal{R}_d + i\mathcal{L})^{-1} \Psi_\mu^\beta \rangle^* = k \langle \Psi_\mu^\alpha | \mathcal{R}_d^{-1} \Psi_\mu^\beta \rangle. \quad (53)$$

Because of the rotational invariance of \mathcal{R}_d , the tensor $\mathbf{L}^{\alpha\beta(0)}$ is isotropic. To a good approximation it represents the field-free value $\mathbf{L}_{B=0}^{\alpha\beta}$. We now re-express (53) in terms of matrix elements with respect to the chosen basis, and apply the Wigner–Eckart theorem (44),

$$L_{\mu\mu}^{\alpha\beta(0)} = k C^\alpha C^\beta \langle \Phi_\mu^\alpha | \mathcal{R}_d^{-1} \Phi_\mu^\beta \rangle = \delta_{\mu\mu} k C^\alpha C^\beta S^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \quad (54)$$

where $S^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ is the reduced matrix element of \mathcal{R}_d^{-1} . To obtain this element we first consider all the reduced matrix elements of \mathcal{R}_d with respect to \mathcal{H}_0 . These matrix elements constitute a matrix

$$S = \begin{pmatrix} S(\alpha) & S(\beta) & \dots \\ S(\alpha) & S(\beta) & \dots \\ \vdots & \vdots & \vdots \end{pmatrix} = \langle v \rangle_0 \begin{pmatrix} \mathfrak{S}(\alpha) & \mathfrak{S}(\beta) & \dots \\ \mathfrak{S}(\alpha) & \mathfrak{S}(\beta) & \dots \\ \vdots & \vdots & \vdots \end{pmatrix}. \quad (55)$$

In practice inversion is carried out with finite matrices constructed with a finite subset $\{\Phi^\alpha, \Phi^\beta, \dots\}$ from \mathcal{H}_0 , whereby approximations to $S^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$ are obtained. In the simplest approximation, i.e., if only one tensor Φ^α from \mathcal{H}_0 would be taken into account, we have

$$S^{-1}(\alpha) = \frac{1}{\langle v \rangle_0 \mathfrak{S}(\alpha)}. \quad (56)$$

If two tensors Φ^α and Φ^β are taken into account, then

$$S^{-1}(\beta) = -\frac{1}{\langle v \rangle_0} \frac{\mathfrak{S}(\beta)}{\mathfrak{S}(\alpha)\mathfrak{S}(\beta) - \mathfrak{S}(\alpha)\mathfrak{S}(\beta)}. \quad (57)$$

The first-order contribution $L_{\mu\mu}^{\alpha\beta[1]}$ vanishes, because the nondiagonal operator is sandwiched between two isotropic-in- \mathbf{J} factors. So we must include the second-order contribution, which to a good approximation contains the field dependent part of $L_{\mu\mu}^{\alpha\beta}$,

$$L_{\mu\mu}^{\alpha\beta[2]} = k \langle \Psi_\mu^\alpha | \mathcal{R}_d^{-1} \mathcal{R}_{nd} (\mathcal{R}_d + i\mathcal{L})^{-1} \mathcal{R}_{nd} \mathcal{R}_d^{-1} \Psi_\mu^\beta \rangle^*. \quad (58)$$

We are mainly interested in the change of phenomenological coefficients in a magnetic or electric field defined as

$$\Delta L_{\mu\mu}^{\alpha\beta} \equiv L_{\mu\mu}^{\alpha\beta}(B; E) - L_{\mu\mu}^{\alpha\beta}(0) \approx L_{\mu\mu}^{\alpha\beta[2]}(B; E) - L_{\mu\mu}^{\alpha\beta[2]}(0), \quad (59)$$

where $L(B; E)$ denotes a function of B or E . The factors

$$\chi^\alpha = \mathcal{R}_{nd} \mathcal{R}_d^{-1} \Psi^\alpha, \quad \chi^\beta = \mathcal{R}_{nd} \mathcal{R}_d^{-1} \Psi^\beta, \quad (60)$$

appearing in eq. (58) represent linear combinations of polarizations produced in collisions by the microscopic fluxes Ψ^α and Ψ^β , respectively. This can be stated as

$$\chi_\mu^\alpha = \sum_{pqs} \sum_{\mu'v} (2r+1)^{1/2} \begin{pmatrix} p & q & r \\ \mu' & v & -\mu \end{pmatrix} K \begin{pmatrix} \alpha \\ pqs \end{pmatrix} \Phi_{\mu',v}^{pqs}, \quad (61)$$

where r is the tensorial rank of Ψ^α . The coefficients are given by

$$(2r+1)^{1/2} \begin{pmatrix} p & q & r \\ \mu' & v & -\mu \end{pmatrix} K \begin{pmatrix} \alpha \\ pqs \end{pmatrix} = \langle \Phi_{\mu',v}^{pqs} | \chi_\mu^\alpha \rangle = C^\alpha \langle \Phi_{\mu',v}^{pqs} | \mathcal{R}_{nd} \mathcal{R}_d^{-1} \Phi_\mu^\alpha \rangle. \quad (62)$$

Expression (59) with (58) can now be simplified,

$$\Delta L_{\mu\mu}^{\alpha\beta} = k \langle R \chi_\mu^\alpha | [(\mathcal{R}_d + i\mathcal{L})^{-1} - \mathcal{R}_d^{-1}] \chi_\mu^\beta \rangle^*, \quad (63)$$

where we have used the adjoint from eq. (17).

In order to simplify the evaluation of the field dependence of phenomenological coefficients one usually makes the so-called spherical approximation in the calculation of the matrix elements such as in eq. (44). The approximation consists in neglecting there all terms with $L \neq 0$ whenever none of the p, p', q, q' equals 0,

$$\langle \Phi_{\mu\nu}^{pqs} | \mathcal{R}_d \Phi_{\mu'v'}^{p'q's'} \rangle = \delta_{\mu\mu'} \delta_{\nu\nu'} \delta_{pp'} \delta_{qq'} \langle v \rangle_0 \mathfrak{S}_0 \begin{pmatrix} pqs \\ pqs' \end{pmatrix}. \quad (64)$$

The name of the approximation refers to the fact that for an isotropic (spherical) potential all terms with $L \neq 0$ vanish³⁴). Generally the $L \neq 0$ contributions, which

measure the coupling between W and J , are expected to be much smaller than the spherical ($L = 0$) contribution. The spherical approximation allows a simple formula for the saturation values of field effects. Inserting expression (61) into (63) and by taking $\omega \rightarrow \infty$ we obtain

$$\Delta L_{\mu\mu}^{\alpha\beta}(\infty) = -k \langle R\tilde{\chi}_\mu^\alpha | \mathcal{R}_d^{-1} \tilde{\chi}_\mu^\beta \rangle. \quad (65)$$

Modified functions $\tilde{\chi}_\mu^\alpha$ must be substituted, differing from the original χ_μ^α insofar that the terms with $\nu = 0$ in the sum (61) are deleted. The formula will be useful in the discussion of general properties of phenomenological coefficients in section 6.

Experiments have furthermore shown that field effects can accurately be described with a very limited number of polarizations³⁵. For each allowed combination of p and q (cf. eq. (44)) the orthonormal set of scalar factors P_s can apparently always be chosen in such a way that in equation (61) only one tensor Φ^{pqs} has to be taken into account. In other words, the polarizations Φ^{pqs} produced by the microscopic fluxes are eigenfunctions of \mathcal{R}_d . This means that the collision operator is diagonal within the subset of \mathcal{H}_1 relevant for the representation of the χ^α . Thereby the matrix inversion of $(\mathcal{R}_d + i\mathcal{L})^{-1}$ is greatly simplified. One has

$$\langle \Phi_{\mu\nu}^{pqs} | (\mathcal{R}_d + i\mathcal{L}) \Phi_{\mu\nu}^{p'q's'} \rangle^* = \delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{\mu\mu'} \delta_{\nu\nu'} \left[S_0(pqs) + \frac{i}{n} v \langle P_s^2 \omega \rangle_0 \right], \quad (66)$$

so that

$$\begin{aligned} & \langle \Phi_{\mu\nu}^{pqs} | (\mathcal{R}_d + i\mathcal{L})^{-1} \Phi_{\mu\nu}^{p'q's'} \rangle^* \\ &= \delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{\mu\mu'} \delta_{\nu\nu'} \frac{1}{S_0(pqs)} \left\langle P_s^2 \left[1 + \frac{iv\omega}{nS_0(pqs)} \right]^{-1} \right\rangle_0. \end{aligned} \quad (67)$$

To evaluate the matrix elements of the operator product in eq. (58) we twice insert in Dirac fashion the unit operator in form of a complete set of projectors $\Sigma | \dots \rangle \langle \dots |$. With the diagonality of $(\mathcal{R}_d + i\mathcal{L})^{-1}$ within \mathcal{H}_1 taken into account, eq. (59) with (58) leads to

$$\begin{aligned} \Delta L^{\alpha\beta} &= k C^\alpha C^\beta \sum_{pqs} \langle \Phi^\alpha | \mathcal{R}_d^{-1} \mathcal{R}_{nd} \Phi^{pqs} \rangle \odot \langle \Phi^{pqs} | [(\mathcal{R}_d + i\mathcal{L})^{-1} - \mathcal{R}_d^{-1}] \Phi^{pqs} \rangle^* \\ &\odot \langle \Phi^{pqs} | \mathcal{R}_{nd} \mathcal{R}_d^{-1} \Phi^\beta \rangle. \end{aligned} \quad (68)$$

As before, α and β stand for triplets of labels: $\alpha = r_\alpha, 0, s_\alpha$ and $\beta = r_\beta, 0, s_\beta$. After insertion of two more sums of projectors between the \mathcal{R}_d^{-1} and \mathcal{R}_{nd} in (68),

application of eq. (44) with (67) yields (for $r_\alpha = r_\beta = r$)

$$\begin{aligned} \Delta L_{\mu\mu}^{\alpha\beta} &= \delta_{\mu\mu} k C^\alpha C^\beta \sum_{pqs} (-1)^{p+q+r} \Omega(pqr) \sum_{\kappa, \nu} \begin{pmatrix} p & p & r \\ \kappa & \nu & -\mu \end{pmatrix}^2 \\ &\times \sum_{i,j} S^{-1} \begin{pmatrix} \alpha \\ i \end{pmatrix} S \begin{pmatrix} i \\ pqs \end{pmatrix} \frac{1}{S_0(pqs)} \left\langle P_s^2 \left\{ \left[1 + i \frac{v\omega}{nS_0(pqs)} \right]^{-1} - 1 \right\} \right\rangle_0 \\ &\times S \begin{pmatrix} pqs \\ j \end{pmatrix} S^{-1} \begin{pmatrix} j \\ \beta \end{pmatrix}, \end{aligned} \quad (69)$$

where the summation over the intermediate triplets i, j refers to tensors Φ^i , $\Phi^j \in \mathcal{H}_0$. The expression for the relative magnitude of the field effect may now be written in the standard form

$$\begin{aligned} \frac{\Delta L_{\mu\mu}^{\alpha\beta}}{L_{\mu\mu}^{\alpha\beta}} &= - \sum_{pqs} \psi_{pqs} (1 + \delta_{p1} \delta_{q2}) (-1)^{p+q+r} \Omega(pqr) \sum_{\kappa, \nu} \begin{pmatrix} p & q & r \\ \kappa & \nu & -\mu \end{pmatrix}^2 \\ &\times \langle P_s^2 [f(v\xi_{pqs}) + ig(v\xi_{pqs})] \rangle_0, \end{aligned} \quad (70)$$

with the coefficient of the pqs -polarization defined as

$$\psi_{pqs} = \left(1 - \frac{1}{2} \delta_{p1} \delta_{q2} \right) \frac{\sum_{i,j} S^{-1} \begin{pmatrix} \alpha \\ i \end{pmatrix} S \begin{pmatrix} i \\ pqs \end{pmatrix} S \begin{pmatrix} pqs \\ j \end{pmatrix} S^{-1} \begin{pmatrix} j \\ \beta \end{pmatrix}}{S^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} S_0(pqs)} \quad (71)$$

and the field parameter

$$\xi_{pqs} = \omega \frac{1}{nS_0(pqs)} \equiv \omega \tau_{pqs}. \quad (72)$$

Factors containing Kronecker delta symbols have been incorporated in order to get ψ 's identical to the ones defined in the literature on this subject. The field dependent functions are given by

$$f(x) = \frac{x^2}{1+x^2}, \quad g(x) = \frac{x}{1+x^2}. \quad (73)$$

Specific examples of the field dependence (70) for linear molecules for $r = 1, 2$ and various values of pq can be found in refs. 36 and 37.

5. Mixtures

The microscopic state of an N -component mixture of dilute gases with internal degrees of freedom is specified by the distribution f_k for each molecular species

k . In steady state the $f_k(\mathbf{r}, \mathbf{c}_k, \mathbf{J})$ obey a system of Waldmann–Snider equations,

$$\mathbf{c}_k \cdot \nabla f_k + \frac{i}{\hbar} [H_{i,k}, f_k] = \sum_l C_k(f_k, f_l), \quad k, l = 1, 2, \dots, N, \quad (74)$$

where the collision terms now represent the rate of change of f_k resulting from binary collisions with particles of the same and of all other species. The local Maxwellian is

$$f_k^0 = n x_k \left(\frac{m_k}{2\pi k T} \right)^{3/2} \frac{1}{Z_{\text{rot},k}} \exp\{-W_k^2 - \mathcal{E}_k\}, \quad (75)$$

where $x_k = x_k(\mathbf{r})$ is the mole fraction of component k and

$$\mathbf{W}_k = \sqrt{\frac{m_k}{2kT}} (\mathbf{c}_k - \mathbf{v}). \quad (76)$$

In the nonequilibrium state, each f_k is considered to be close enough to equilibrium that f_k can be written in the form

$$f_k = f_k^0 (1 + \phi_k). \quad (77)$$

The barycentric flow velocity of the mixture is defined as

$$\mathbf{v} = \frac{\sum_k x_k m_k \mathbf{v}_k}{\sum_k x_k m_k}, \quad (78)$$

with

$$\mathbf{v}_k = \frac{1}{n x_k} \text{Tr} \int \mathbf{c}_k f_k d\mathbf{c}_k. \quad (79)$$

For a quantity A , which for each species is specified by A_k , the nonequilibrium average is calculated according to

$$\langle A \rangle = \frac{1}{n} \sum_k \text{Tr} \int A_k f_k d\mathbf{c}_k. \quad (80)$$

In analogy to the case of a pure gas it is useful to introduce a Hilbert space of arrays of operators such as $A = (A_1, A_2, \dots, A_N)$ and $\phi = (\phi_1, \phi_2, \dots, \phi_N)$, with the inner product

$$\langle A | \phi \rangle = \frac{1}{n} \sum_k \text{Tr} \int A_k^\dagger f_k^0 \phi_k d\mathbf{c}_k. \quad (81)$$

This definition will lead to final results of similar appearance as in the case of a pure gas. The deviations ϕ_k obey the linearized system of equations

$$\psi_k = -n \sum_l (\mathcal{R} + i\mathcal{L})_{kl} \phi_l, \quad (82)$$

or, in short

$$\psi = -n(\mathcal{R} + i\mathcal{L})\phi, \quad (83)$$

which is derived in the same way as eq. (15). The Waldmann–Snider collision operators \mathcal{R}_{kl} constitute a matrix \mathcal{R} of operators, while \mathcal{L} in (83) stands for a diagonal matrix of this kind. It is to be noticed that each diagonal element \mathcal{R}_{kk} still contains contributions from binary collisions with molecules of species other than k . In analogy with eq. (16) we notice that

$$-f_k^0 n \mathcal{R}_{kk} \phi_k = C_{kk}(f_k^0, f_k^0 \phi_k) + \sum_l C_{kl}(f_k^0 \phi_k, f_l^0), \quad (84)$$

$$-f_k^0 n \mathcal{R}_{kl} \phi_l = C_{kl}(f_k^0, f_l^0 \phi_l), \quad l \neq k. \quad (85)$$

Proceeding as for the pure gas, we obtain a formal solution of eq. (83),

$$\phi = -\frac{1}{n} (\mathcal{R} + i\mathcal{L})^{-1} \psi, \quad (86)$$

or explicitly

$$\phi_k = -\frac{1}{n} \sum_l [(\mathcal{R} + i\mathcal{L})^{-1}]_{kl} \psi_l, \quad (87)$$

with $[(\mathcal{R} + i\mathcal{L})^{-1}]_{kl}$ the kl -element of the inverse operator matrix $(\mathcal{R} + i\mathcal{L})^{-1}$ defined on the nonhydrodynamic subspace. The hydrodynamic subspace is richer now; for a binary mixture, e.g., it is 6-dimensional, with a basis consisting of the arrays $(1, 0)$, $(0, 1)$, $(m_1^{1/2} W_1, m_2^{1/2} W_2)$ and $(W_1^2 + \mathcal{E}_1, W_2^2 + \mathcal{E}_2)$.

The definition of $(\mathcal{R} + i\mathcal{L})^{-1}$ implies the orthogonality of ϕ to the hydrodynamic eigenfunctions. Thanks to the chosen inner product (81), this prescription coincides with the condition that ϕ in eq. (77) shall not alter the partial densities nor the flow velocity or mean energy of the mixture*).

The inhomogeneous term again has the form

$$\psi = \sum_{\alpha} \Psi^{\alpha} \cdot X^{\alpha}, \quad (88)$$

which now means that

$$\psi_k = \sum_{\alpha} \Psi^{\alpha|k} \cdot X^{\alpha}. \quad (89)$$

The relevant microscopic fluxes $\Psi^{\alpha|k}$ and the corresponding thermodynamic forces X^{α} for a binary mixture are listed in table II.

* With a different choice of the inner product, e.g. with different weights in the sum in (81), the mentioned coincidence is destroyed. If the matrix elements of \mathcal{R} are to remain the same, the definition of this operator matrix must also be modified, resulting in unnecessary complications, see e.g. ref. 32.

TABLE II
Fluxes and forces, microscopic fluxes and normalized microscopic fluxes for binary gas mixtures ($k = 1, 2$)

α	\mathbf{J}^α	χ^α	$\Psi^{\alpha ik} = C^{\alpha ik} \Phi^{\alpha ik}$	$\Phi^{\alpha ik}$	$C^{\alpha ik}$
$10E \equiv q$	\mathbf{q}	$\frac{VT}{T^2}$	$T \sqrt{\frac{2kT}{m_k}} \left[W_k^2 - \frac{5}{2} + \epsilon_k - \langle \epsilon_k \rangle_0 \right] W_k$	$\left[\frac{5}{4}(1+r_k^2) \right]^{-1/2} \left[W_k^2 - \frac{5}{2} + \epsilon_k - \langle \epsilon_k \rangle_0 \right] [W_k]^{1/2}$	$T \sqrt{\frac{2kT}{m_k}} \left[\frac{5}{4}(1+r_k^2) \right]^{1/2}$
$10 \equiv j$	$\mathbf{v}_1 - \mathbf{v}_2$	$nk \nabla x_1$	$(-1)^{k+1} \frac{\sqrt{2T}}{nx_k} W_k$	$\sqrt{2} [W_k]^{1/2}$	$\frac{(-1)^{k+1} \sqrt{T}}{nx_k} \sqrt{\frac{T}{m_k k}}$
$20 \equiv \pi$	$\overline{\Pi}$	$\frac{\overline{Vv}}{T}$	$2T \overline{W_k W_k}$	$\sqrt{2} [W_k]^2$	$T \sqrt{2}$

As before, the macroscopic fluxes are obtained from nonequilibrium averages of microscopic fluxes,

$$\mathbf{J}^\alpha = nk \langle \Psi^\alpha | \phi \rangle^* . \quad (90)$$

Substituting the solution (86) we see that

$$\mathbf{J}^\alpha = - \sum_{\beta} \mathbf{L}^{\alpha\beta} \cdot \mathbf{X}^\beta , \quad (91)$$

with

$$\mathbf{L}^{\alpha\beta} = k \langle \Psi^\alpha | (\mathcal{R} + i\mathcal{L})^{-1} \Psi^\beta \rangle^* . \quad (92)$$

In analogy to the case of a pure gas we consider a set of tensors (cf. eq. (34))

$$\Phi^{pqslk} = \left(\frac{2^p}{p!} \right)^{1/2} [W_k]^p \mathcal{Y}^{(q)} P_{s,k} . \quad (93)$$

In Hilbert space formulation, Φ^{pqslk} may be considered as an array consisting of zeros except for component k , which has the value indicated in (93). These arrays then satisfy the orthogonality relation

$$\langle \Phi_{\mu\nu}^{pqslk} | \Phi_{\mu'\nu'}^{p'q's'l'} \rangle = x_k \delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{kl} \delta_{\mu\mu'} \delta_{\nu\nu'} . \quad (94)$$

The normalization is to x_k instead of unity so as to have a concentration independent basis. The microscopic fluxes can now be written as a linear combination of such tensors,

$$\Psi^\alpha = \sum_k C^{\alpha|k} \Phi^{\alpha|k}, \quad \alpha = (r, 0, s), \quad (95)$$

which is actually an array with the elements from (93) multiplied by factors $C^{\alpha|k}$. Consequently, we can rewrite eq. (92) as a linear combination of matrix elements of the inverse collision operator within the basis \mathcal{H}_0

$$\mathbf{L}^{\alpha\beta} = k \sum_{k,l} C^{\alpha|k} C^{\beta|l} \langle \Phi^{\alpha|k} | (\mathcal{R} + i\mathcal{L})^{-1} \Phi^{\beta|l} \rangle^* . \quad (96)$$

The matrix elements of the collision operator are factorized as in eq. (44),

$$\begin{aligned} \langle \Phi_{\mu\nu}^{pqslk} | \mathcal{R} \Phi_{\mu'\nu'}^{p'q's'l'} \rangle &= \sum_{L,M} i^{p-p'+q-q'} (-1)^{L+p+q+\mu+\nu'} \sqrt{\Omega(pp'L)\Omega(qq'L)} \\ &\times \begin{pmatrix} p & p' & L \\ -\mu & \mu' & -M \end{pmatrix} \begin{pmatrix} q & q' & L \\ -\nu & \nu' & M \end{pmatrix} S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} k \\ l \end{matrix} . \end{aligned} \quad (97)$$

As can be seen from eqs. (97), (84) and (85), the reduced matrix elements $S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} k \\ l \end{matrix}$

now depend upon the concentrations. They may be expressed in terms of concentration-independent cross sections as follows:

$$S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} | \\ | \\ | \end{matrix} \begin{matrix} k \\ l \\ l \end{matrix} = x_k x_l \langle v_{kl} \rangle_0 \mathfrak{S}_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} | \\ | \\ | \end{matrix} \begin{matrix} k \\ l \\ l \end{matrix} \quad (k \neq l), \quad (98)$$

$$S_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} | \\ | \\ | \end{matrix} \begin{matrix} k \\ k \\ k \end{matrix} = \sum_l x_k x_l \langle v_{kl} \rangle_0 \mathfrak{S}_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} | \\ | \\ | \end{matrix} \begin{matrix} k \\ k \\ k \end{matrix}. \quad (99)$$

The cross section $\mathfrak{S}_L \begin{pmatrix} p & q & s \\ p' & q' & s' \end{pmatrix} \begin{matrix} | \\ | \\ | \end{matrix} \begin{matrix} k \\ l \\ l \end{matrix}$ describes the coupling between a pqs -polarization of a molecule of species k and a $p'q's'$ -polarization of a molecule of species l by collisions between species k and l , and $\langle v_{kl} \rangle_0$ is the corresponding average relative thermal speed,

$$\langle v_{kl} \rangle_0 = \sqrt{\frac{8kT}{\pi\mu_{kl}}}, \quad (100)$$

with μ_{kl} the reduced mass.

The matrix elements of the precession operator are

$$\langle \Phi_{\mu\nu}^{pqs|k} | \mathcal{L} \Phi_{\mu'\nu'}^{p'q's'|l} \rangle = -\delta_{pp'} \delta_{qq'} \delta_{ss'} \delta_{kl} \delta_{\mu\mu'} \delta_{\nu\nu'} \frac{x_k}{n} v \langle P_{s,k}^2 \omega_k \rangle_0, \quad (101)$$

with the Larmor frequency ω_k as before.

As an example we consider a binary gas mixture, consisting of a polyatomic gas (species 1) and a noble gas (species 2). As only component 1 has angular momentum, polarizations ($q \neq 0$) will exist only for this component. Thanks to the previously introduced formalism the evaluation of expression (96) for $\mathbf{L}^{\alpha\beta}$ follows the same scheme as in the case of a pure gas. First, the collision operator matrix is split into a diagonal and a nondiagonal part. Then the inverse $(\mathcal{R} + i\mathcal{L})^{-1}$ is expanded in terms of \mathcal{R}_{nd} , and the second-order contribution is calculated using the spherical approximation. The result for the relative change in the phenomenological coefficient has exactly the same form as before (eq. (70)), except for the more complicated expression for ψ_{pqs} ,

$$\psi_{pqs} = (1 - \frac{1}{2}\delta_{p1}\delta_{q2}) \frac{\sum_{k,l=1,2} \sum_{i,j} S^{-1} \begin{pmatrix} \alpha | k \\ i \end{pmatrix} S \begin{pmatrix} i \\ pqs | 1 \end{pmatrix} S \begin{pmatrix} pqs | 1 \\ j \end{pmatrix} S^{-1} \begin{pmatrix} j \\ \beta | l \end{pmatrix}}{S_0 \begin{pmatrix} pqs | 1 \\ pqs | 1 \end{pmatrix} \sum_{k,l=1,2} S^{-1} \begin{pmatrix} \alpha | k \\ \beta | l \end{pmatrix}}. \quad (102)$$

In approximating the elements of the inverse operator matrix S^{-1} by finite matrix inversion one has to keep in mind that the basis functions used are not normalized to unity, cf. eq. (94). The final results can be expressed in terms of concentration independent cross sections by means of eqs. (98) and (99). Explicit expressions for ψ_{pqs} for some transport coefficients are given in refs. 32 and 38.

For a binary mixture, the set of thermodynamic fluxes is enriched by the diffusive flux which is a polar vector just like the heat flux. The corresponding cross phenomena, thermal diffusion and the Dufour effect, may therefore also occur. The constitutive relations which describe these four phenomena, in addition to viscous flow, are

$$\mathbf{q} = -\lambda \cdot \nabla T - \frac{nkT}{x_1x_2} \mathcal{D} \cdot \nabla x_1, \quad (103)$$

$$\mathbf{v}_1 - \mathbf{v}_2 = -\frac{1}{x_1x_2T} \mathbf{D}_T \cdot \nabla T - \frac{1}{x_1x_2} \mathbf{D} \cdot \nabla x_1, \quad (104)$$

$$\overline{\Pi} = -2\eta \odot \overline{\nabla v}. \quad (105)$$

The difference of the velocities \mathbf{v}_1 and \mathbf{v}_2 from eq. (104) is used to describe the diffusive flux instead of the usual^{25,39)}

$$\mathbf{j}_1 = \frac{n^2 m_1 m_2}{\rho} x_1 x_2 (\mathbf{v}_1 - \mathbf{v}_2) = -\mathbf{j}_2, \quad (106)$$

with the total mass density given by

$$\rho = n \sum_i m_i x_i. \quad (107)$$

The coefficients \mathbf{D} , \mathbf{D}_T , \mathcal{D} and η are the diffusion, thermal diffusion, Dufour and viscosity tensors, respectively. By substituting the expressions of table II into eq. (96) we obtain explicit expressions for the coefficients $\mathbf{L}^{\alpha\beta}$. They are related to the conventional phenomenological coefficients by

$$\lambda = \frac{1}{T^2} \mathbf{L}^{qq}, \quad (108)$$

$$\mathbf{D}_T = \frac{x_1 x_2}{T} \mathbf{L}^{jq}, \quad (109)$$

$$\mathcal{D} = \frac{x_1 x_2}{T} \mathbf{L}^{qj}, \quad (110)$$

$$\mathbf{D} = x_1 x_2 nk \mathbf{L}^{jj}, \quad (111)$$

$$\eta = \frac{1}{2T} \mathbf{L}^{\pi\pi}, \quad (112)$$

as can be seen by comparing the gradients in eqs. (103) through (105) to the thermodynamic forces X^α listed in the tables.

6. General properties of phenomenological coefficients

In the absence of external fields the phenomenological coefficients are given by matrix elements of the inverse collision operator. This operator is isotropic and, if optically active molecules are excluded, also invariant against space inversion. Therefore only microscopic fluxes of the same tensorial rank and parity couple. The phenomenological coefficients are, just as the approximation $L_{\mu\mu}^{\alpha\beta(0)}$ in eq. (53), therefore real isotropic tensors²¹),

$$L_{\mu\mu}^{\alpha\beta} = \delta_{\mu\mu} L^{\alpha\beta}. \quad (113)$$

From the time reversal invariance of molecular interaction one obtains the Onsager relations

$$L^{\alpha\beta} = L^{\beta\alpha}, \quad (114)$$

where we have used the fact that \mathcal{R} couples only microscopic fluxes which have the same time reversal symmetry. Since \mathcal{R} is a positive semidefinite operator and its inverse is positive definite on the nonhydrodynamic subspace, we have

$$L^{\alpha\alpha} > 0 \quad (115)$$

and (from the Schwartz inequality)

$$(L^{\alpha\beta})^2 \leq L^{\alpha\alpha} L^{\beta\beta}. \quad (116)$$

Note that eqs. (115) and (116) are a consequence of the dissipative nature of the collision term, or equivalently, a consequence of the positive definiteness of entropy production, cf. eq. (26).

In the presence of an external field, $L_{\mu\mu}^{\alpha\beta}$ is given by (33). Since the operator $(\mathcal{R} + i\mathcal{L})^{-1}$ occurring in this equation is no longer isotropic, coupling between tensors of different rank becomes possible. For instance, cross effects between bulk and shear viscosity appear⁴⁰). On the other hand, the parity selection rule still holds. Therefore, e.g., heat flow cannot couple to viscous flow. The operator $(\mathcal{R} + i\mathcal{L})^{-1}$ is, however, still invariant with respect to rotations around the field direction. Therefore, since the polar axis was chosen along the field direction, the phenomenological tensors in the presence of an external magnetic or electric field are diagonal in spherical representation

$$L_{\mu\mu}^{\alpha\beta}(B; E) = \delta_{\mu\mu} L_{\mu\mu}^{\alpha\beta}(B; E). \quad (117)$$

Similarly, from a rotation of 180° around an axis perpendicular to the field it follows that

$$L_{\mu\mu}^{\alpha\beta}(B; E) = L_{\mu\mu}^{\alpha\beta*}(-B; -E), \quad (118)$$

which means that the real part of $L_{\mu\mu}^{\alpha\beta}$ is even and the imaginary part odd in the field.

From time reversal symmetry one obtains the Onsager–Casimir relations²⁵⁾

$$L_{\mu\mu}^{\alpha\beta}(\mathbf{B}; E) = L_{\mu\mu}^{\beta\alpha}(-\mathbf{B}; E). \quad (119)$$

Combination of eqs. (118) and (119) yields

$$L_{\mu\mu}^{\alpha\beta}(\mathbf{B}; E) = L_{\mu\mu}^{\beta\alpha}(\mathbf{B}; -E), \quad (120)$$

so that for $\alpha = \beta$ odd-in-field coefficients vanish in the electric field case.

If space inversion symmetry applies one also obtains

$$L_{\mu\mu}^{\alpha\beta}(\mathbf{B}; E) = L_{\mu\mu}^{\alpha\beta}(\mathbf{B}; -E), \quad (121)$$

so that then in the electric field case all odd-in-field coefficients vanish.

The saturation value of the field induced change in $L_{\mu\mu}^{\alpha\beta}$ is given by eq. (65). The operator \mathcal{R}_d occurring there is, just as \mathcal{R} itself, positive semidefinite since for any $\Phi = \Phi_0 + \Phi_1$, with $\Phi_0 \in \mathcal{H}_0$ and $\Phi_1 \in \mathcal{H}_1$,

$$\langle \Phi | \mathcal{R}_d \Phi \rangle = \langle \Phi_0 | \mathcal{R} \Phi_0 \rangle + \langle \Phi_1 | \mathcal{R} \Phi_1 \rangle \geq 0. \quad (122)$$

Consequently, for $\alpha = \beta$ and χ^α and thereby $\tilde{\chi}^\alpha$ even-in- \mathbf{J} , so that $R\tilde{\chi}^\alpha = \tilde{\chi}^\alpha$, we have

$$\Delta L_{\mu\mu}^{\alpha\alpha}(\infty) \leq 0. \quad (123)$$

On the other hand, if χ^α and thereby $\tilde{\chi}^\alpha$ are odd-in- \mathbf{J} the saturation value is positive,

$$\Delta L_{\mu\mu}^{\alpha\alpha}(\infty) > 0. \quad (124)$$

Let us now investigate the cross effects. The value of $\Delta L_{\mu\mu}^{\alpha\beta}(\infty)$ for $\alpha \neq \beta$ will be seen to obey a Schwartz inequality. For arbitrary a and b one has

$$\langle a\chi_\mu^\alpha - b\chi_\mu^\beta | \mathcal{R}_d^{-1}(a\chi_\mu^\alpha - b\chi_\mu^\beta) \rangle \geq 0. \quad (125)$$

Thus with

$$a = \langle \chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle^{1/2} \langle \chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle^{1/2} \quad (126)$$

and

$$b = \langle \chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle^{1/2} \langle \chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle^{1/2}, \quad (127)$$

it follows that

$$\langle \chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle \langle \chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle \geq \langle \chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle \langle \chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle. \quad (128)$$

If χ^α and χ^β are either both even or both odd-in- \mathbf{J} this inequality may be written as

$$\langle R\chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle \langle R\chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle \geq \langle R\chi_\mu^\alpha | \mathcal{R}_d^{-1} \chi_\mu^\beta \rangle \langle R\chi_\mu^\beta | \mathcal{R}_d^{-1} \chi_\mu^\alpha \rangle. \quad (129)$$

With $\chi_\mu^\alpha, \chi_\mu^\beta$ replaced by $\tilde{\chi}_\mu^\alpha, \tilde{\chi}_\mu^\beta$, we have

$$\Delta L_{\mu\mu}^{\alpha\alpha}(\infty)\Delta L_{\mu\mu}^{\beta\beta}(\infty) \geq [\Delta L_{\mu\mu}^{\alpha\beta}(\infty)]^2. \quad (130)$$

Equality holds only if χ^α is proportional to χ^β and consequently $\tilde{\chi}^\alpha$ to $\tilde{\chi}^\beta$, which implies that both microscopic fluxes couple to one and the same tensor or, in the usual jargon, both microscopic fluxes produce the same polarization. Equation (130) is then a generalization of the relation between thermal conductivity, diffusion and their cross effects derived by Eggermont, Vestner and Knaap³²). Experimental results for these three effects, however, satisfy the inequality rather than the equality^{28a}). On the other hand the same results show that the polarizations produced by heat and diffusive fluxes respectively have the same tensorial factor (i.e. the same values of p and q). Since the polarizations are not proportional to each other, this shows that the scalar factors must differ.

In order to derive a relation between these effects in this case we therefore need to consider two sets of basis functions $\{\Phi^\alpha, \Phi^\beta, \Phi^{pqA}, \dots\}$ and $\{\Phi^\alpha, \Phi^\beta, \Phi^{pqB}, \dots\}$. The sets are chosen in such a way that Φ^{pqA} is the only anisotropic-in- J basis function which couples to Φ^α , and Φ^{pqB} the only one to Φ^β . Hence both Φ^{pqA} and Φ^{pqB} are eigenfunctions of \mathcal{R}_d . Since this operator is selfadjoint, Φ^{pqA} and Φ^{pqB} must be orthogonal to each other, unless they belong to the same eigenvalue, $S(pqA) = S(pqB)$. These decay constants indeed appear equal in the sets of experiments carried out so far^{28a}). Moreover, nonorthogonality of the eigenfunctions is established by the nonvanishing infinite-field contribution to the corresponding cross phenomena.

With each set, the summation over p, q and s in (61) reduces to a single term, which we substitute into eq. (65). After using an orthogonality relation for the 3- j symbols³⁰) we find for $r_\alpha = r_\beta = r$ that

$$\Delta L_{\mu\mu}^{\alpha\alpha}(\infty) = (-1)^{q+1}k \left[1 - (2r+1) \begin{pmatrix} p & q & r \\ \mu & 0 & -\mu \end{pmatrix}^2 \right] \left[K \begin{pmatrix} \alpha \\ pqB \end{pmatrix} \right]^2 S^{-1}(pq), \quad (131)$$

$$\Delta L_{\mu\mu}^{\beta\beta}(\infty) = (-1)^{q+1}k \left[1 - (2r+1) \begin{pmatrix} p & q & r \\ \mu & 0 & -\mu \end{pmatrix}^2 \right] \left[K \begin{pmatrix} \beta \\ pqB \end{pmatrix} \right]^2 S^{-1}(pq), \quad (132)$$

$$\begin{aligned} \Delta L_{\mu\mu}^{\alpha\beta}(\infty) &= (-1)^{q+1}ka_{AB} \left[1 - (2r+1) \begin{pmatrix} p & q & r \\ \mu & 0 & -\mu \end{pmatrix}^2 \right] \\ &\quad \times K \begin{pmatrix} \alpha \\ pqA \end{pmatrix} K \begin{pmatrix} \beta \\ pqB \end{pmatrix} S^{-1}(pq), \end{aligned} \quad (133)$$

where $S(pq)$ is an abbreviation for $S(pqA) = S(pqB)$, and the overlap integral a_{AB}

is defined according to eq. (43). Obviously,

$$[\Delta L_{\mu\mu}^{\alpha\beta}(\infty)]^2 = a_{AB}^2 \Delta L_{\mu\mu}^{\alpha\alpha}(\infty) \Delta L_{\mu\mu}^{\beta\beta}(\infty), \quad (134)$$

which is in agreement with inequality (130) since $a_{AB}^2 \leq 1$. Eq. (134) makes it possible to use the observed saturation values of the three field effects for determining the coefficients a_{AB} .

The kinetic theory presented above coherently describes the large class of field effects which has been studied experimentally during the last two decades. Previously existing discrepancies between theory and experiment are eliminated by adapting the scalar factor of polarizations to the particular type of phenomenon under consideration, instead of the customary expansion in fixed orthogonal polynomials. The uniform reformulation of the theory, both for pure gases and gas mixtures, yields clear insight into the relations existing between the various field effects.

Acknowledgements

We wish to thank Professor F.R. McCourt for enlightening comments, and Mr. H. van Houten for helpful criticism.

The investigation was part of the program of the "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) and was supported by the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek" (ZWO), which also provided for inspiring visits of the first and last authors to Ljubljana and Leiden, respectively. The last author's contribution was supported by "Raziskovalna skupnost Slovenije".

References

- 1) H. Senftleben, Phys. Z. **31** (1930) 822, 961.
- 2) C.J. Gorter, Naturwissenschaften **26** (1938) 140.
- 3) C.J. Gorter, Ned. Tijdschr. Natuurk. **7** (1940) 89.
- 4) F. Zernike and C. van Lier, Physica **6** (1939) 961.
- 5) Yu.M. Kagan and A.M. Afanas'ev, Sov. Phys. JETP **14** (1962) 1096.
- 6) Yu.M. Kagan and L.A. Maksimov, Sov. Phys. JETP **14** (1962) 604.
- 7) J.J.M. Beenakker, G. Scoles, H.F.P. Knaap and R.M. Jonkman, Phys. Lett. **2** (1962) 5.
- 8) L. Waldmann, Z. Naturforsch. **12a** (1957) 660; **13a** (1958) 609.
- 9) R.F. Snider, J. Chem. Phys. **32** (1960) 1051.
- 10) L. Waldmann, Z. Naturforsch. **18a** (1963) 1033.
- 11) S. Hess and L. Waldmann, Z. Naturforsch. **21a** (1966) 1529.
- 12) F.R. McCourt and R.F. Snider, J. Chem. Phys. **41** (1964) 3185.
- 13) F.R. McCourt and R.F. Snider, J. Chem. Phys. **43** (1965) 2276.
- 14) R.F. Snider, J. Chem. Phys. **41** (1964) 591.

- 15) R.F. Snider, *J. Math. Phys.* **5** (1964) 1580.
- 16) Yu.M. Kagan and L.A. Maksimov, *Sov. Phys. JETP* **24** (1967) 1272.
- 17) A. Tip, A.C. Levi and F.R. McCourt, *Physica* **40** (1968) 435.
- 18) J.A.R. Coope and R.F. Snider, *J. Chem. Phys.* **57** (1972) 4266.
- 19) J.H. Ferziger and H.G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).
- 20a) I. Kuščer, H.F.P. Knaap and J.J.M. Beenakker, *Physica* **108A** (1981) 265.
b) C.F. Curtiss, *J. Chem. Phys.* **75** (1981) 376.
- 21) J.A.R. Coope and R.F. Snider, *J. Chem. Phys.* **56** (1972) 2056.
- 22) H. Moraal, *Phys. Rep.* **17C** (1975) 225.
- 23) A.C. Levi, F.R. McCourt and A. Tip, *Physica* **39** (1968) 165.
- 24) F.M. Chen, H. Moraal and R.F. Snider, *J. Chem. Phys.* **57** (1972) 542.
- 25) S.R. de Groot and P. Mazur, *Non-Equilibrium thermodynamics* (North-Holland, Amsterdam, 1962).
- 26) J.A.R. Coope, R.F. Snider and F.R. McCourt, *J. Chem. Phys.* **43** (1965) 2269.
- 27) J.A.R. Coope and R.F. Snider, *J. Math. Phys.* **11** (1970) 1003.
- 28) S. Hess and W.E. Köhler, *Formeln zur Tensor-Rechnung* (Palm & Enke, Erlangen, 1980).
a) E. Mazur, E. Viswat, L.J.F. Hermans and J.J.M. Beenakker, *Physica* **121A** (1983) 457; E. Mazur, H.J.M. Hijnen, L.J.F. Hermans and J.J.M. Beenakker, *Physica*, to be published.
- 29) B.J. Thijsse, G.W. 't Hooft, D.A. Coombe, H.F.P. Knaap and J.J.M. Beenakker, *Physica* **98A** (1979) 307.
- 30) A.R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton Univ. Press, Princeton, N.J., 1957).
- 31) F. Tommasini, A.C. Levi, G. Scoles, J.J. de Groot, J.W. van den Broeke, C.J.N. van den Meijdenberg and J.J.M. Beenakker, *Physica* **49** (1970) 299.
- 32) G.E.J. Eggermont, H. Vestner and H.F.P. Knaap, *Physica* **82A** (1976) 23.
- 33) W.E. Köhler, H.F.P. Knaap, G.E.J. Eggermont and G.W. 't Hooft, *Z. Naturforsch.* **33a** (1978) 761.
- 34) W.E. Köhler, *Z. Naturforsch.* **29a** (1974) 1705.
- 35) E. Mazur and J.J.M. Beenakker, *Physica*, to be published.
- 36) B.J. Thijsse, W.A.P. Denissen, L.J.F. Hermans, H.F.P. Knaap and J.J.M. Beenakker, *Physica* **97A** (1979) 467.
- 37) P.G. van Ditzhuyzen, B.J. Thijsse, L.K. van der Meij, L.J.F. Hermans and H.F.P. Knaap, *Physica* **88A** (1977) 53.
- 38) A.L.J. Burgmans, P.G. van Ditzhuyzen and H.F.P. Knaap, *Z. Naturforsch.* **28a** (1973) 849.
- 39) S. Chapman and T.G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge Univ. Press, London, 1970).
- 40) J. Korving, H. Hulsman, G. Scoles, H.F.P. Knaap and J.J.M. Beenakker, *Physica* **36** (1967) 177.