# On the Behaviour of Rarefied Polyatomic Gases in a Static Magnetic Field

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Dedicated to Prof. Dr. L. Waldmann on the occasion of his 60th birthday

The behaviour of rarefied polyatomic gases is described by transport relaxation equations obtained from the Waldmann-Snider equation and by an appropriate set of boundary conditions which are derived from the interfacial entropy production. The influence of the magnetic field on the transport properties of the gas is due to the coupling of the tensor polarization and the tensor polarization flux with the frictional pressure tensor and the heat fluxes respectively. As an application the flow and the heat conduction of a gas between parallel plates in the presence of a magnetic field are treated, and from this two major results are obtained:

(a) Knudsen corrections for the Senftleben-Beenakker effect of viscosity,

(b) a theory of the thermomagnetic pressure difference.

A comparison with experimental data of Hulsman e. a. and Hermans e. a. yields boundary coefficients which describe both phenomena rather well for the gases HD,  $CH_4$ , CO and  $N_2$ .

The quantum mechanical kinetic equation due to Waldmann and Snider 1 is the starting point for the description of nonequilibrium processes in polyatomic gases. By an application of the moment method 2 to the linearized Waldmann-Snider equation an infinite system of coupled partial differential equations for the mean values is obtained. For all practical purposes this system has to be truncated so that only a few moments which specify the macroscopic state of the gas are retained. Such a special system of transport relaxation equations can for example be used for a treatment of the Senftleben-Beenakker effect (SBE) of viscosity and thermal conductivity<sup>3</sup>: In a streaming or heat conducting polyatomic gas polarizations are set up by collisions and partially destroyed by an external magnetic field. From experiments it is known that the only important types of alignment in such a gas are the tensor polarization for the SBE of viscosity 4-6 (with the exception of NH3 7) and the tensor polarization flux for the SBE of thermal conductivity 8. As has been shown by Hess these polarizations give rise to streaming 9 and heat-flow birefringence 10, 11 in polyatomic gases. Furthermore their fluctuations around the equilibrium value zero cause the depolarized Rayleigh scattering 9, 12. All these effects are typical for the behaviour of dilute polyatomic gases where only the collisions of the molecules with each other are of importance and where the collisions of the

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molecules with the wall are negligible. The situation is different when the mean free path of a molecule in the gas is comparable with the dimensions of the measuring device, since then the gas-wall collisions may influence the transport processes in the gas or even may give rise to new phenomena which do not exist in a dilute gas. This shows up for example in SBE measurements at lower pressures  $^{4-6,\,8}$  where deviations from the ordinary H/p-dependence of the transport coefficients are observed: The effective relaxation constants contain not only the gas-gas collisions (which are proportional to pressure p) but also the gas-wall collisions (which are independent of p).

The thermomagnetic torque, first observed by Scott et al. 13, is typical for a rarefied polyatomic gas in a magnetic field. Two possible contributions to the torque are discussed: Levi et al. 14 took into account the thermal stresses which occur in a rarefied gas and which consist of second order derivatives of temperature contributing to the pressure tensor (these "Burnett terms" are determined by gasgas collisions). On the other hand, Waldmann 15 stressed the importance of slip effects (i. e. of gaswall collisions) and postulated the existence of a polarization induced slip velocity. This "thermomagnetic slip" contains only first order derivatives of temperature and should therefore also occur in a heat conducting polyatomic gas between parallel plates, and consequently a pressure gradient perpendicular to the temperature gradient and the magnetic field should be observed 15. Because of the plane



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geometry second order derivatives of temperature play no role for the "thermomagnetic pressure difference", it is (in first approximation) only due to slip effects. In 1972 Hulsman et al.  $^{16}$  measured the effect for  $N_2$  and found the predicted  $^{15}$  order of magnitude. Further investigations with other gases are conducted by Hermans et al.  $^{17}$  in Leiden.

This paper proceeds as follows. In the stationary case a special system of transport relaxation equations is reduced to (a) constitutive laws for the heat fluxes, for the frictional pressure tensor and the flux of tensor polarization, and (b) differential equations for the temperature, the flow velocity and the tensor polarization. Then a set of boundary conditions for these quantities is derived from the entropy production at the interface between the gas and a solid body following Waldmann's thermodynamic method <sup>18</sup>. As an application the behaviour of a rarefied polyatomic gas between parallel plates in a magnetic field is studied: From the flow of the gas under the influence of a pressure gradient Knudsen corrections for the SBE of viscosity are derived. The investigation of the heat conducting gas leads to a theory of the thermomagnetic pressure difference <sup>19</sup>. The comparison of theoretical results with experimental data of Hulsman et al. 5,6 and Hermans et al. 17 gives a set of surface parameters which can account for both phenomena with the gases HD, CH<sub>4</sub>, CO and N<sub>2</sub>. A more detailed treatment is found in Reference 20.

## I. General Considerations

## 1. Differential Equations and Constitutive Laws

A gas of diatomic rotating molecules in a homogeneous magnetic field is considered. For small deviations from equilibrium which is characterized by the temperature  $T_0$ , the density  $n_0$  and the pressure  $p_0$ , the moment method  $^2$  is applied to the linearized Waldmann-Snider equation. It works as follows: The nonequilibrium distribution function is expanded into a complete set of irreducible tensors built up from the molecular velocity  $\boldsymbol{c}$  and the (dimension-

less) rotational angular momentum  $\boldsymbol{J}$  of the molecules. This expansion shall  $^{20}$  be restricted to the simplest tensors, the mean values of which correspond to the density n, the translational and rotational temperatures  $T_{\text{trans}}$ ,  $T_{\text{rot}}$ , the flow velocity  $\boldsymbol{v}$ , the translational and rotational heat fluxes  $\boldsymbol{q}_{\text{trans}}$ ,  $\boldsymbol{q}_{\text{rot}}$ , the frictional pressure tensor  $\bar{\mathbf{p}}$ , the tensor polarization  $\boldsymbol{a}$  and the tensor polarization flux  $\underline{\boldsymbol{b}}$ . The latter quantities are defined by

$$a_{\mu\nu} = \langle \Phi_{\mu\nu} \rangle, \quad b_{\lambda, \, \mu\nu} = (\sqrt{3}/c_0) \langle c_{\lambda} \Phi_{\mu\nu} \rangle,$$
 (1.1)

where  $c_0 = \sqrt{3 k T_0/M}$ , M is the molecular mass and k is Boltzmann's constant. The second rank expansion tensor  $\Phi_{uv}$  is given by

$$\Phi_{\mu\nu} = \sqrt{15/2} \, R(J^2) \, J_{\mu} J_{\nu} \,, \tag{1.2}$$

and  $R(J^2)$  obeys the normalization condition

$$\langle R^2 J^2 (J^2 - \frac{3}{4}) \rangle_0 = 1$$
.

Since only the formal structure of the moment equations is of importance in this connection,  $R(J^2)$  has not to be specified. In connection with birefringence

$$R(J^2) = (J^2 - \tfrac{3}{4})^{-1} \left( \left\langle J^2 (J^2 - \tfrac{3}{4})^{-1} \right\rangle_0 \right)^{-1/2}$$

has to be used 9, 11.

The symbol ... denotes the symmetric irreducible part of a tensor, e. g.

$$\overline{J_{\mu}J_{\nu}} = \frac{1}{2} (J_{\mu}J_{\nu} + J_{\nu}J_{\mu}) - \frac{1}{3} \delta_{\mu\nu}J^{2},$$

the bracket (...) refers to an average over the nonequilibrium distribution function,  $\langle \ldots \rangle_0$  is evaluated with the equilibrium distribution, respectively. It is assumed throughout that the relaxation constants for the three irreducible components 2 of the tensor  $b_{\lambda,\mu\nu}$  are equal, i. e. the "spherical approximation" <sup>21</sup> shall be valid. For the mean values of the expansion tensors a set of coupled partial differential equations is obtained from the linearized Waldmann-Snider equation, the transport relaxation equations. In the stationary case they yield constitutive laws for  $\mathbf{\bar{p}}$ ,  $oldsymbol{q}_{ ext{trans}}$  ,  $oldsymbol{q}_{ ext{rot}}$  and  $oldsymbol{\underline{b}}$  on one side and differential equations for v,  $T_{\rm trans}$ ,  $T_{\rm rot}$  and  ${\bf a}$  on the other side. In the one-temperature approximation  $(T_{\rm trans} \approx T_{\rm rot})$  $\approx T$ ) one gets the following constitutive laws <sup>20</sup> for the frictional pressure tensor

$$\mathbf{p} = -2 \eta_{\rm iso} \left( \overline{\nabla v} + \frac{2}{5} \cdot \frac{1}{p_0} \overline{\nabla q}_{\rm trans} \right) - p_0 \sqrt{2} \frac{\omega_{\eta T}}{\omega_{\eta}} \mathbf{a} , \qquad (1.3)$$

the translational heat flux

$$\boldsymbol{q}_{\text{trans}} = -\lambda_{\text{iso}}^{\text{trans}} \nabla T - \frac{2}{5} \lambda_{\text{iso}}^{\text{t}} \frac{T_0}{p_0} \nabla \cdot \vec{\mathbf{p}} - \frac{p_0 c_0}{\sqrt{2}} \boldsymbol{B} a_{\text{bt}} \sqrt{\frac{\omega_b}{\omega_t}} (1 - A_{\text{tr}})^{-1/2}, \qquad (1.4)$$

the total heat flux  $\boldsymbol{q} = \boldsymbol{q}_{\text{trans}} + \boldsymbol{q}_{\text{rot}}$ 

$$\boldsymbol{q} = -\lambda_{\rm iso} \nabla T - \frac{2}{5} \lambda_{\rm iso}^{\rm trans} \frac{T_0}{p_0} \nabla \cdot \mathbf{p} - \frac{p_0 c_0}{\sqrt{2}} \boldsymbol{B} a_{\rm rbt} \sqrt{\frac{\omega_b}{\omega_t}} \frac{\lambda_{\rm iso}}{\lambda_{\rm iso}^t} (1 - A_{\rm tr})^{-1/2}, \qquad (1.5)$$

and the tensor polarization flux

$$b_{\lambda,\,\mu\nu} = \sum_{m=-2}^{+2} \frac{1}{1+i\,m\,\varphi_{\rm b}} \,\mathcal{P}_{\mu\nu,\mu'\nu'}^{(m)} \left( -l_{\rm b} \,\frac{\partial a_{\mu'\nu'}}{\partial x_{\lambda}} + \Delta_{\mu'\nu',\,\lambda'\lambda} \,a_{\lambda'}^{\rm rt} \right). \tag{1.6}$$

The "Kagan vector"  $\mathbf{B}$  is derived from the third rank tensor  $\underline{\mathbf{b}}$  by contraction  $B_{\mu} = b_{\nu,\nu\mu}$ .

The isotropic transport coefficients  $\eta_{\rm iso}$ ,  $\lambda_{\rm iso}$ ,  $\lambda_{\rm iso}^{\rm t}$ ,  $\lambda_{\rm iso}^{\rm trans}$  can be expressed by the relaxation constants  $\omega_{\eta}$ ,  $\omega_{\rm t}$ ,  $\omega_{\rm r}$  for  $\dot{\bf p}$ ,  $\dot{\bf q}_{\rm trans}$ ,  $\dot{\bf q}_{\rm rot}$  and by  $\omega_{\rm tr}$  which characterizes the mutual coupling between  $\dot{\bf q}_{\rm trans}$  and  $\dot{\bf q}_{\rm rot}$ :

$$\eta_{\rm iso} = p_0/\omega_{\eta} \,, \tag{1.7}$$

$$\lambda_{\rm iso}^{\rm t} = \frac{5}{2} \frac{k}{M} \frac{p_0}{\omega_{\rm t}} (1 - A_{\rm tr})^{-1}, \ \lambda_{\rm iso}^{\rm trans} = \lambda_{\rm iso}^{\rm t} \left(1 - \frac{\omega_{\rm tr}}{\omega_{\rm r}}\right), \tag{1.8}$$

$$\lambda_{\rm iso} = \frac{5}{2} \frac{k}{M} p_0 (1 - A_{\rm tr})^{-1} \left( \frac{1}{\omega_{\rm t}} + \frac{1}{\omega_{\rm r}} - 2 \frac{\omega_{\rm tr}}{\omega_{\rm t} \omega_{\rm r}} \right), \quad A_{\rm tr} = \frac{\omega_{\rm tr}^2}{\omega_{\rm t} \omega_{\rm r}}.$$
 (1.9)

The influence of the anisotropic polarizations  $\bf a$  and  $\bf \underline{\bf b}$  on the transport phenomena in polyatomic gas is due to their coupling with the frictional pressure tensor and the heat fluxes which is expressed by the coefficients  $\omega_{\rm nT}/\omega_{\rm n}$  and by

$$a_{\rm bt} = (1 - A_{\rm tr})^{-1/2} \sqrt{\frac{5}{3}} \left( \frac{\omega_{\rm bt}}{V \omega_{\rm b} \omega_{\rm t}} - \frac{\omega_{\rm br}}{V \omega_{\rm b} \omega_{\rm r}} \frac{\omega_{\rm tr}}{V \omega_{\rm t} \omega_{\rm r}} \right), \tag{1.10}$$

$$a_{\rm rbt} = \sqrt{\lambda_{\rm iso}^{\rm t}/\lambda_{\rm iso}} \left(a_{\rm bt} + \sqrt{\omega_{\rm t}/\omega_{\rm r}} a_{\rm br}\right), \qquad (1.11)$$

where  $a_{\rm br}$  is obtained from  $a_{\rm bt}$  by replacing the subscript "t" by "r" and "r" by "t". Here  $\omega_{\rm b}$  characterizes the relaxation of  $\underline{\bf b}$  and  $\omega_{\rm bt}$ ,  $\omega_{\rm br}$  its coupling with  ${\bf q}_{\rm trans}$  and  ${\bf q}_{\rm rot}$ . On the other hand, the tensor polarization flux is determined by derivatives of the tensor polarization and by the heat fluxes  ${\bf q}_{\rm trans}$  and  ${\bf q}_{\rm rot}$ . The vector  ${\bf q}^{\rm rt}$  occurring in Eq. (1.6) is defined by

$$\boldsymbol{a}^{\text{rt}} = \frac{3}{5} \frac{\sqrt{2}}{p_0 c_0} \lambda_{\text{iso}} \sqrt{\frac{\omega_t}{\omega_b}} \frac{\lambda_{\text{iso}}^t}{\lambda_{\text{iso}}} (1 - A_{\text{tr}}) \left( a_{\text{rbt}} \nabla T + \frac{2}{5} \frac{T_0}{p_0} \nabla \cdot \overrightarrow{\mathbf{p}} a_{\text{bt}} \sqrt{\frac{\lambda_{\text{iso}}^t}{\lambda_{\text{iso}}}} \right), \tag{1.12}$$

here Eqs. (1.4), (1.5) have been used, but **B** has been neglected. The relaxation constants can be expressed by collision integrals obtained from the linearized Waldmann-Snider collision operator <sup>2, 11, 21</sup>. For a comparison with the work of Hess <sup>11</sup> it is noticed that  $\omega_t$ ,  $\omega_\eta$ ,  $\omega_{\eta T}$  and  $\omega_T$  (the relaxation constant of the tensor polarization) have the same meaning in this paper; for the remaining constants the following correspondence holds

$$\omega_{\mathrm{tr}} = r \, \omega_{\mathrm{ti}}, \qquad \omega_{\mathrm{r}} = r^2 \, \omega_{\mathrm{i}}, \omega_{\mathrm{h}} = \omega_{\mathrm{K}}, \qquad \omega_{\mathrm{hr}} = \sqrt{\frac{3}{5}} \, \omega_{\mathrm{Kt}}, \quad \omega_{\mathrm{hr}} = \sqrt{\frac{3}{5}} \, r \, \omega_{\mathrm{Ki}},$$

where  $r = \sqrt{5 \ k/2 \ c_i}$  and  $c_i$  denotes the rotational heat capacity per molecule.

The fourth rank tensor  $\Delta_{\mu\nu,\,\mu'\nu'} = \frac{1}{2} (\delta_{\mu\mu'} \, \delta_{\nu\nu'} + \delta_{\mu\nu'} \, \delta_{\nu\mu'}) - \frac{1}{3} \, \delta_{\mu\nu} \, \delta_{\mu'\nu'}$  projects any second rank tensor on its irreducible part;  $l_{\rm b}$  is a mean free path  $l_{\rm b} = c_0/(\sqrt{3} \, \omega_{\rm b})$ .

A magnetic field  $\mathbf{H} = H \mathbf{h} (\mathbf{h} \cdot \mathbf{h} = 1)$  can act on the polarizations via the magnetic moment which is connected with the angular momentum  $\mathbf{J}$ ,  $\omega_{\mathbf{H}} = g_{\mathbf{r}}(\mu_{\mathbf{N}}/\hbar) H$  is the precession frequency and  $g_{\mathbf{r}}$  the rotational g-factor. The dependence of  $\mathbf{a}$  and  $\mathbf{b}$  on the field strength H is contained in the precession angles

$$\varphi_{\rm T} = \omega_{\rm H}/\omega_{\rm T}, \quad \varphi_{\rm b} = \omega_{\rm H}/\omega_{\rm b},$$
 (1.13)

whereas the dependence on the field direction  $\boldsymbol{h}$  is expressed by the fourth rank projection tensors  $\mathcal{P}_{\mu\nu,\,\mu'\nu'}^{(m)}$  introduced by Hess <sup>9, 22</sup>.

Insertion of the constitutive laws (1.3) - (1.6) into the transport relaxation equations for **a**, **v** and **T** yields <sup>20</sup> differential equations for the tensor polarization

$$(1 - L_m^2 \nabla \cdot \nabla) \mathcal{P}_{\mu r, \mu' r'}^{(m)} a_{\mu' r'} = \frac{1}{1 + i \, m \, \varphi_{\mathrm{T}}} \mathcal{P}_{\mu r, \mu' r'}^{(m)} \left[ \frac{\omega_{\eta \mathrm{T}}}{\omega_{\mathrm{T}}} \frac{\sqrt{2} \, \eta_{\mathrm{iso}}}{p_0} \left( \overline{\nabla \boldsymbol{v}} + \frac{2}{5} \cdot \frac{1}{p_0} \, \overline{\nabla \boldsymbol{q}}_{\mathrm{trans}} \right) \right. \\ \left. - \frac{l_{\mathrm{T}}}{1 + i \, m \, \varphi_{\mathrm{b}}} \, \overline{\nabla \boldsymbol{q}}^{\mathrm{rt}} \right|_{\mu' r'}, \qquad (m = 0, \, \pm 1, \, \pm 2), \tag{1.14}$$

a modified Navier-Stokes equation

$$\frac{1}{\eta_{\rm iso}} \nabla p - \nabla \cdot \nabla \boldsymbol{v} = \frac{p_0}{\eta_{\rm iso}} V \overline{2} \frac{\omega_{\eta \rm T}}{\omega_{\eta}} \nabla \cdot \mathbf{a} + \frac{2}{5} \frac{c_0}{V \overline{2}} \sqrt{\frac{\omega_{\rm b}}{\omega_{\rm t}}} (1 - A_{\rm tr})^{-1/2} a_{\rm bt} \cdot (\nabla \nabla \cdot \boldsymbol{B} - \nabla \cdot \nabla \boldsymbol{B}), \quad (1.15)$$

and a modified Fourier equation

$$\nabla \cdot \nabla T = \frac{2}{5} T_0 \frac{\lambda_{\text{iso}}^{\text{trans}}}{\lambda_{\text{iso}}} \sqrt{2} \frac{\omega_{\eta \text{T}}}{\omega_{\eta}} \nabla \cdot (\nabla \cdot \mathbf{a}) - \frac{p_0 c_0}{\sqrt{2}} \frac{(1 - A_{\text{tr}})^{-1/2}}{\sqrt{\lambda_{\text{iso}}} \lambda_{\text{iso}}^{t}} \sqrt{\frac{\omega_b}{\omega_t}} a_{\text{rbt}} \nabla \cdot \mathbf{B}.$$
 (1.16)

The continuity equation reduces to

$$\nabla \cdot \boldsymbol{v} = 0. \tag{1.17}$$

The following mean free paths of a molecule in the gas have been used:

$$l_{\rm T} = c_0/(\sqrt{3} \,\omega_{\rm T}), \quad L_m = \frac{\sqrt{l_{\rm T}} \,l_{\rm b}}{\left[\left(1 + i\,m\,\varphi_{\rm T}\right)\left(1 + i\,m\,\varphi_{\rm b}\right)\right]^{1/2}}, \qquad (m = 0, \pm 1, \pm 2).$$
 (1.18)

In the hydrodynamic limit only the lowest order in  $1/p_0$  is retained on both sides of (1.14) so that

$$a_{\mu\nu} = \sum_{m=-2}^{+2} \mathcal{P}^{(m)}_{\mu
u,\,\mu'
u'} \, a_{\mu'
u'}$$

can directly be expressed by  $\nabla v$ . According to (1.3) the frictional pressure tensor is also proportional to  $\nabla v$  and the field free viscosity is v22

$$\eta = \eta_{\rm iso} (1 + A_{\eta \rm T}), \ A_{\eta \rm T} = \omega_{\eta \rm T}^2 / (\omega_{\eta} \ \omega_{\rm T}).$$
(1.19)

Similarly from (1.6) the "Kagan vector" can be expressed by  $\nabla T$  alone and (1.5) shows that the heat flux is determined by  $\nabla T$  only <sup>21</sup>; the field free value of the thermal conductivity is

$$\lambda = \lambda_{\rm iso} \left( 1 + a_{\rm rbt}^2 \right). \tag{1.20}$$

The influence of a magnetic field on flow and heat conduction is of the same order of magnitude as the deviation of the field free values of viscosity and thermal conductivity from the isotropic values, i. e. of the order  $A_{\eta T}$  (SBE of viscosity),  $a_{\text{rbt}}^2$  (SBE of thermal conductivity) respectively. In this approximation the SBE depends on the field strength H and on pressure  $p_0$  only via  $\varphi_T$ ,  $\varphi_b \propto g_r H/p_0$ . It is the purpose of this paper, however, to investigate the deviations from this simple behaviour. To this end the differential equations for  $\mathbf{a}$ ,  $\mathbf{v}$  and T have to be solved for any special arrangement. This is only possible if boundary conditions for these quantities are available.

### 2. Boundary Conditions

Following Waldmann's idea <sup>18</sup> we derive an appropriate set of boundary conditions from the entropy production  $\Theta$  at the interface  $\sigma$  between the gas and a solid body. This interfacial entropy production consists of a discontinuity of the entropy fluxes from both media at  $\sigma$ :

$$\Theta = -\int d\sigma \left( \mathbf{s} - \mathbf{s}_{\text{solid}} \right) \cdot \mathbf{n} , \qquad (1.21)$$

n is the outer unit normal of the gas. The entropy flux within the solid is simply given by

$$\mathbf{s}_{\text{solid}} = (\mathbf{q}/T)_{\text{solid}},$$
 (1.22)

and the entropy flux within the gas is calculated according to

$$\mathbf{s} = -n \, k \, \langle \, (\mathbf{c} - \mathbf{v}) \log (1/e) \, (h/M)^3 \, f \rangle \tag{1.23}$$

from the expansion of the distribution function f. In the above mentioned approximation it is given by  $^{20}$ 

$$\mathbf{s} = \frac{1}{T_{\text{trans}}} \mathbf{q}_{\text{trans}} + \frac{1}{T_{\text{rot}}} \mathbf{q}_{\text{rot}} - \frac{2}{5} \cdot \frac{1}{T_0 p_0} \mathbf{p} \cdot \mathbf{q}_{\text{trans}} - n_0 k \frac{c_0}{\sqrt{3}} \mathbf{b} : \mathbf{a}.$$
 (1.24)

Besides the heat fluxes and temperatures the entropy flux contains a Burnett-term,

$$-\frac{2}{5}\frac{1}{T_0p_0}\mathbf{\bar{p}}\cdot\boldsymbol{q}_{\mathrm{trans}},$$

and a contribution due to the polarizations  $\bf a$  and  $\bf b$ . Now  $\bf s$  and  $\bf s_{\rm solid}$  are inserted into (1.21) and (by the use of the energy conservation at  $\sigma$ )  $\Theta$  is transformed into a surface integral over bilinear products of independent "fluxes" (e. g. the tangential velocity) and "forces" (e. g. the tangential force per unit area) at the interface  $^{20}$ . Similar to the ordinary theory of irreversible processes in the bulk fluid linear relations between "fluxes" and "forces" are set up, and these are the boundary conditions  $^{18}$ . In the one-temperature approximation ( $T_{\rm trans} \approx T_{\rm rot} \approx T$ ) a suitable simplified set consists of  $^{20}$  a temperature jump condition

$$T - T_{\text{solid}} = C_{\text{t}}(l/\lambda_{\text{iso}}) \mathbf{q} \cdot \mathbf{n} + T_{0} \zeta C_{\text{ta}} \mathbf{n} \cdot \mathbf{b} : (\mathbf{n} \mathbf{n}), \tag{1.25}$$

a velocity slip condition

$$\left(\boldsymbol{v} + \frac{2}{5} \cdot \frac{1}{p_0} \boldsymbol{q}_{\text{trans}}\right)^{\text{tan}} = C_{\text{m}} \frac{l}{\eta_{\text{iso}}} \boldsymbol{k}^{\text{tan}} + \frac{c_0}{\sqrt{3}} C_{\text{ma}} (\boldsymbol{n} \cdot \underline{\boldsymbol{b}} \cdot \boldsymbol{n})^{\text{tan}}, \qquad (1.26)$$

and a condition for the tensor polarization

$$\mathbf{a} = C_{\text{at}} \frac{l}{T_0 \, \lambda_{\text{iso}}} \, \mathbf{q} \cdot \mathbf{n} \, \frac{3}{2} \, \overline{\mathbf{n} \, \mathbf{n}} + C_{\text{am}} \, \frac{1}{p_0} \, \overline{\mathbf{n} \, \mathbf{k}}^{\text{tan}} + C_{\text{a}} \, \mathbf{n} \cdot \underline{\mathbf{b}} \, . \tag{1.27}$$

By  $\mathbf{k} = \mathbf{p} \cdot \mathbf{n}$  the force per unit area is denoted,

$$l = \frac{8}{5} \sqrt{\frac{2}{\pi}} \frac{c_0}{\sqrt{3} \omega_n}$$

is the viscosity mean free path. Furthermore the continuity of normal velocity and normal heat fluxes is required:

$$\boldsymbol{v} \cdot \boldsymbol{n} = 0$$
,  $\boldsymbol{q}_{\text{solid}} \cdot \boldsymbol{n} = \boldsymbol{q} \cdot \boldsymbol{n}$ . (1.28)

The quantities  $C_{\perp}$  are dimensionless surface parameters:  $C_{\rm m}$  is the wellknown mechanical slip coefficient,  $C_{\rm t}$  the temperature jump coefficient, and  $C_{\rm a}$  characterizes the accommodation of tensor polarization at the wall. The nondiagonal coefficients  $C_{\rm am}$ ,  $C_{\rm at}$ ,  $C_{\rm ma}$ ,  $C_{\rm ta}$  are a measure for the mutual coupling between the ordinary flow variables  $\boldsymbol{v}$ , T and the polarizations  $\boldsymbol{a}$ ,  $\boldsymbol{b}$  at the wall; they are related by the Onsager-symmetries

$$C_{ta} = C_{at}, \quad C_{ma} = -C_{am}.$$
 (1.29)

Since the interfacial entropy production  $\Theta$  has to be positive there are further restrictions on the surface parameters:

$$C_{\rm a}, C_{\rm m}, C_{\rm t} \ge 0, C_{\rm a} C_{\rm t} - \zeta C_{\rm at}^2 \ge 0, \zeta = \frac{12}{5} \sqrt{\frac{2}{\pi}} \frac{k}{M} \frac{\eta}{\lambda}.$$
 (1.30)

In contrast to a monatomic gas where only a thermal slip  $\left[-\frac{2}{5}\frac{1}{p_0} \mathbf{q}_{\rm trans}^{\rm tan}\right]$  and a mechanical slip  $(C_{\rm m} l/\eta_{\rm iso} \mathbf{k}^{\rm tan})$  exist, in a polyatomic gas there is also a polarization induced <sup>15</sup> "thermomagnetic slip"  $[c_0/\sqrt{3} C_{\rm ma}(\mathbf{n} \cdot \mathbf{b} \cdot \mathbf{n})^{\rm tan}]$ . Then, according to Onsager-symmetry it should be possible that a tensor polarization is created at the wall by a tangential force  $\mathbf{k}^{\rm tan}$ . Similarly a tensor polarization can be built up by normal heat fluxes at the wall, and on the other side a temperature jump can occur according to normal components of the tensor polarization flux.

From a boundary condition for the distribution function Halbritter <sup>23</sup> has derived a slip condition and a simplified condition for the tensor polarization similar to (1.26), (1.27). Furthermore he was able to relate the surface parameters  $C_{\rm a}$  and  $C_{\rm ma}$  to the interaction potential between a gas molecule and the wall. In a special approximation he calculated  $C_{\rm a}$  and  $C_{\rm ma}$  with the result:  $C_{\rm a} \sim 1$ ,  $C_{\rm ma} \sim 10^{-2} - 10^{-3}$ .

As is known from SBE <sup>3</sup> the polarization induced effects are rather small (e. g.  $A_{\rm NT} \sim 10^{-2} - 10^{-3}$ ) so that the system of differential equations and boundary conditions can be approximately solved for any special geometry by a perturbation method: From the "isotropic" solutions (where **a** and **b** have been neglected) for  $\boldsymbol{v}$  and T the tensor polarization and its flux are calculated and then the modified (field dependent) temperature and velocity fields are obtained.

## II. Knudsen Corrections for the Senftleben-Beenakker Effect of Viscosity

In the hydrodynamic limit the SBE of viscosity and thermal conductivity depends on the strength H of the magnetic field and on the mean pressure  $p_0$  only via the precession angles  $\varphi_T$ ,  $\varphi_b \propto g_r H/p_0$ . If at lower pressures the mean free path l of a molecule becomes comparable with macroscopic dimensions of the measuring device then an additional dependence on pressure occurs: For decreasing pressure the magnitude of the effect (as a function of  $H/p_0$ ) decreases and the curves are shifted to higher  $H/p_0$ -values. Experimentally these Knudsen corrections have been measured by Hermans et al. § for thermal conductivity and Korving 4 and Hulsman et al. §, 6 for viscosity. Using different orientations of the magnetic field all five visvosity coefficients  $\eta_1, \ldots, \eta_5$  (in the notation of De Groot-Mazur) could be measured with the flow of a gas in a rectangular capillary  $^{5, 6}$  (see Figure 1). In order to explain the observed Knudsen corrections the flow of a gas between infinite parallel plates of distance  $D_y = 2 d$  (which may be a suitable approximation of the real apparatus of Figure 1) is treated in this section. By e the flow direction (z-direction) without magnetic field is denoted, e0 is the direction perpendicular to the plates (y-direction), e1 and e2 is the direction perpendicular to the plates (e2 direction), e3 and e4 is the direction perpendicular to the plates (e3 direction), e4 and e4 is the direction perpendicular to the plates (e3 direction).

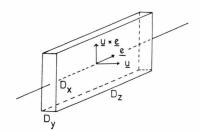


Fig. 1. Narrow rectangular capillary for the measurement of all five viscosity coefficients  $^{5, 6}$ ; the relation  $D_z \gg D_x \gg D_y$  = 2 d applies.

are unit vectors. Without a magnetic field the constant pressure gradient

$$\nabla p^{(0)} = \boldsymbol{e} \left( \mathrm{d} p / \mathrm{d} z \right)_{0} \tag{2.1}$$

shall be applied; the temperature is constant and equals  $T_0$ .

If all polarization effects are neglected the "isotropic" flow velocity  $v_{\rm iso}$  can easily be calculated from the Navier-Stokes Equation (1.15)

$$(1/\eta_{
m iso}) \ igtriangledown p^{(0)} - igtriangledown \cdot igtriangledown v_{
m iso}^{
m tan} = \mathcal{C}_{
m m} (l/\eta_{
m iso}) \ m{k}_{
m iso}^{
m tan}$$

and the slip condition

which is obtained from (1.26) by neglection of  $\boldsymbol{n} \cdot \underline{\boldsymbol{b}} \cdot \boldsymbol{n}$  and of  $(\boldsymbol{q}_{\text{trans}})_{\text{iso}}$ , i. e. only terms linear in l/d are retained. Notice that then  $\boldsymbol{k}_{\text{iso}}^{\text{tan}} = (\overline{\boldsymbol{p}}_{\text{iso}} \cdot \boldsymbol{n})^{\text{tan}}$  and  $\overline{\boldsymbol{p}}_{\text{iso}} = -2 \eta_{\text{iso}} \nabla \overline{\boldsymbol{v}}_{\text{iso}}$ , where the outer unit normal of the gas is given by  $\boldsymbol{n} = \pm \boldsymbol{u}$  for  $y = \pm d$ . The well-known result for the flow velocity is

$$\mathbf{v}_{\rm iso}(y) = -\left(d^2/2\,\eta_{\rm iso}\right) \left[1 - (y/d)^2 + 2\left(l/d\right)\,C_{\rm m}\right] \,(\mathrm{d}p/\mathrm{d}z)_{\,0}\,\mathbf{e}\,\,,\tag{2.2}$$

and the mean flow velocity is given by

$$\overline{\boldsymbol{v}_{\text{iso}}} = -\left(\frac{d^2}{3} \, \eta_{\text{iso}}\right) \left[1 + 3\left(\frac{l}{d}\right) \, C_{\text{m}}\right] \, \left(\frac{dp}{dz}\right)_{0} \, \boldsymbol{e} \,. \tag{2.3}$$

Now the tensor polarization  $\bf a$  and its flux  $\bf \underline{\bf b}$  are approximately calculated with this isotropic velocity, i. e. the differential equations (1.14)

$$\left( 1 - L_m^2 \, \frac{d^2}{\mathrm{d}y^2} \right) \mathcal{P}_{\mu\nu,\mu'\nu'}^{(m)} \, a_{\mu'\nu'} = \frac{1}{1 + i \, m \, \varphi_\mathrm{T}} \, \mathcal{P}_{\mu\nu,\mu'\nu'}^{(m)} \, \frac{\omega_{n\mathrm{T}}}{\omega_\mathrm{T}} \, \frac{\sqrt{2} \, \eta_\mathrm{iso}}{p_0} \, \left( \overline{\nabla v}_\mathrm{iso} \right)_{\mu'\nu'} \, d\nu' \,$$

are solved 20 using the boundary condition (1.27)

$$\mathbf{a} = C_{\text{am}} (1/p_0) \ \overline{\boldsymbol{n} \, \boldsymbol{k}_{\text{iso}}^{\text{tan}}} + C_{\text{a}} \, \boldsymbol{n} \cdot \underline{\boldsymbol{b}} , \text{ with } (1.6) \quad b_{\lambda, \, \mu\nu} = -l_b \frac{\partial}{\partial x_i} \sum_{m=-2}^{+2} \frac{1}{1+i \, m \, \varphi_b} \mathcal{P}_{\mu\nu, \, \mu'\nu'}^{(m)} \, a_{\mu'\nu'}.$$

Then the field dependent modifications of the flow velocity and the pressure gradient due to the polarizations can be determined. The total flow field (v) is split up into an isotropic  $(v_{iso})$  and an anisotropic part  $(v_1)$ :

$$v(y, H) = v_{iso}(y) + v_1(y, H), v_1 \cdot u = 0,$$
 (2.4)

and the pressure gradient is written as

$$\nabla p = \nabla p^{(0)} + \mathbf{u} \frac{\partial p}{\partial y} + \mathbf{P}, \quad \mathbf{P} \cdot \mathbf{u} = 0.$$
 (2.5)

For vanishing magnetic field the anisotropic parts  $\boldsymbol{u} \cdot \partial p/\partial y$  and  $\boldsymbol{P}$  of  $\nabla p$  vanish too, but  $\boldsymbol{v}_1(y, \boldsymbol{\theta})$  is not zero, viz.

$$\boldsymbol{v}(y,\boldsymbol{\theta}) = \boldsymbol{v}_{iso}(y) + \boldsymbol{v}_1(y,\boldsymbol{\theta})$$

is the field-free flow velocity. For  $l/d \to 0$  it is obtained from (2.2) if  $\eta_{\rm iso}$  is replaced by  $\eta = \eta_{\rm iso}(1 + A_{\eta \rm T})$ . Since  $\nabla p$  does not depend on  $x = (\boldsymbol{u} \times \boldsymbol{e}) \cdot \boldsymbol{x}$  and  $z = \boldsymbol{e} \cdot \boldsymbol{x}$  the vector  $\boldsymbol{P}$  has to be constant

$$\mathbf{P} = \text{const} = \mathbf{P}(\mathbf{H}), \quad \mathbf{P}(\mathbf{0}) = \mathbf{0}, \quad \mathbf{P} \cdot \mathbf{u} = 0.$$
 (2.6)

From **P** the observed pressure differences can be derived,  $\partial p/\partial y$  is not important and will not be calculated.

The constant pressure gradient P shall be determined up to terms linear in the Knudsen number l/d, then the Kagan vector B can be neglected in the modified Navier-Stokes Eq. (1.15) for  $v_1$ 

$$(1/\eta_{\rm iso}) \mathbf{P} - \nabla \cdot \nabla \mathbf{v}_1 = (p_0/\eta_{\rm iso}) \sqrt{2} (\omega_{nT}/\omega_n) (\nabla \cdot \mathbf{a} - \mathbf{u} \nabla \cdot (\mathbf{a} \cdot \mathbf{u})),$$

which is solved with the boundary condition (1.26)

$$\mathbf{v}_1 = C_m (l/\eta_{iso}) \mathbf{k}_1^{\tan} + (c_0/\sqrt{3}) C_{mo} (\mathbf{n} \cdot \mathbf{b} \cdot \mathbf{n})^{\tan}$$

Thermal slip has been neglected since it would give terms of the order  $(l/d)^2$  in P;  $k_1^{\text{tan}}$  has to be calculated from  $\overline{p}_1$  with (1.3)

$$\mathbf{p}_1 = -2 \, \eta_{\rm iso} \, \overline{\nabla v_1} - p_0 \, \sqrt{2} \, (\omega_{nT}/\omega_n) \, \mathbf{a} \, .$$

For  $v_1$  two additional conditions have to be used. One of them comes from the fact that the real apparatus is a rectangular capillary which is closed in  $u \times e$  direction, so that the mean velocity in this direction is zero. For the flow between parallel plates (which are open in  $u \times e$  direction) this should also be valid

$$\overline{\boldsymbol{v}_1} \cdot (\boldsymbol{u} \times \boldsymbol{e}) = 0. \tag{2.7}$$

Furthermore the measuring capillary is part of a gas-flow Wheatstone bridge 5, 6 and the gas flow is kept constant when the magnetic field is switched on

$$\mathbf{e} \cdot \overline{\mathbf{v}_1(y, \mathbf{H})} - \mathbf{e} \cdot \overline{\mathbf{v}_1(y, \mathbf{\theta})} = 0.$$
 (2.8)

The flow field  $v_1$  and the pressure gradient **P** can then be calculated  $^{20}$  with the following result for **P**:

$$\mathbf{P} \cdot \mathbf{e} \equiv P_z = (\mathrm{d}p/\mathrm{d}z)_0 \left[ E_1 (h_y^2 + h_z^2 - 4 h_y^2 h_z^2) + E_2 (1 - h_y^2) (1 - h_z^2) \right], \tag{2.9}$$

$$\mathbf{P} \cdot (\mathbf{u} \times \mathbf{e}) \equiv P_x = (\mathrm{d}p/\mathrm{d}z)_0 h_x h_z [E_1(1-4h_y^2) - E_2(1-h_y^2) - E_1^{\mathrm{tr}} h_y (1-2h_y^2) + E_2^{\mathrm{tr}} h_y (1-h_y^2)],$$
(2.10)

where  $h_x$ ,  $h_y$ ,  $h_z$  are defined by  $h_x = \mathbf{h} \cdot (\mathbf{u} \times \mathbf{e})$ ,  $h_y = \mathbf{h} \cdot \mathbf{u}$ ,  $h_z = \mathbf{h} \cdot \mathbf{e}$ .

The dimensionless quantities  $E_m$  and  $E_m^{\text{tr}}$  are the real and imaginary parts of a complex function of  $\varphi_b$ ,  $\varphi_T$  and l/d:

$$E_{m} + i E_{m}^{\text{tr}} = -\frac{A_{\eta T}}{1 + 3 (l/d) C_{m}} \left[ \frac{(m \varphi_{T})^{2}}{1 + (m \varphi_{T})^{2}} + i \frac{m \varphi_{T}}{1 + (m \varphi_{T})^{2}} \right] - 3 \frac{L_{0}}{d} A_{\eta T} \left[ \frac{\left(\frac{1}{1 + i m \varphi_{T}} - \widetilde{C}_{ma}\right)^{2}}{\widetilde{C}_{a} + \sqrt{\frac{1 + i m \varphi_{b}}{1 + i m \varphi_{T}}}} - \frac{(1 - \widetilde{C}_{ma})^{2}}{\widetilde{C}_{a} + 1} \right], \qquad m = 0, \pm 1, \pm 2.$$
 (2.11)

For convenience the coefficients  $\widetilde{C}_a$ ,  $\widetilde{C}_{ma}$  have been used instead of  $C_a$ ,  $C_{ma}$ :

$$C_{\rm a} = \sqrt{\omega_{\rm b}/\omega_{\rm T}} \, \widetilde{C}_{\rm a} \,, \quad C_{ma} = \sqrt{2} \left(\omega_{\rm \eta T}/\omega_{\rm T}\right) \, \widetilde{C}_{ma} \,, \tag{2.12}$$

for 
$$L_0$$
 see (1.18) 
$$L_0 = c_0 / (\sqrt{3} \sqrt{\omega_T \omega_b}) = l(5/8) \sqrt{\pi/2} \sqrt{\omega_\eta^2 / \omega_T \omega_b}.$$

For vanishing Knudsen number, l/d = 0, Eqs. (2.9) - (2.11) reduce to the wellknown formulae <sup>22, 24</sup> which relate the viscosity coefficients to the pressure differences:

$$\varepsilon_m \equiv (E_m)_{l/d=0} = -A_{\eta T} \frac{(m \, \varphi_T)^2}{1 + (m \, \varphi_T)^2}, \qquad \varepsilon_m^{\text{tr}} \equiv (E_m^{\text{tr}})_{l/d=0} = -A_{\eta T} \frac{m \, \varphi_T}{1 + (m \, \varphi_T)^2}, \qquad (2.13)$$

and the viscosity coefficients of Waldmann and Hess 22 are given by

$$\eta^{(m)} = \eta \left( 1 + \varepsilon_m + i \, \varepsilon_m^{\text{tr}} \right), \qquad m = 0, \pm 1, \pm 2.$$

Up to terms linear in l/d the angular dependence of  ${\bf P}$  is the same as for l/d=0, only the quantities  $\varepsilon_m$ ,  $\varepsilon_m^{\rm tr}$  are replaced by  $E_m$ ,  $E_m^{\rm tr}$ . The nature of these Knudsen corrections can most clearly be seen from the discussion of the simple case that  ${\bf z}\equiv \omega_{\rm T}/\omega_{\rm b}=1$ , i. e.  $\varphi_{\rm b}=\varphi_{\rm T}$ . Then  $E_m$ ,  $E_m^{\rm tr}$  can be written in the following form

$$\varepsilon'_{m} \equiv (E_{m})_{z=1} = -A'_{\eta T} \frac{(m \, \varphi'_{T})^{2}}{1 + (m \, \varphi'_{T})^{2}}, \qquad \varepsilon'_{m}^{\text{tr}} \equiv (E_{m}^{\text{tr}})_{z=1} = -A'_{\eta T} \frac{m \, \varphi'_{T}}{1 + (m \, \varphi'_{T})^{2}}, \qquad (2.14)$$

where the prime indicates that  $\omega_{\eta}$ ,  $\omega_{T}$ ,  $\omega_{\eta T}$  have to be replaced by the effective relaxation constants  $\omega_{\eta}^{'}$ ,  $\omega_{T}^{'}$ ,  $\omega_{\eta T}^{'}$ :

$$\omega_{\eta}' = \omega_{\eta} \left( 1 + 3 \frac{l}{d} C_{m} \right), \quad \omega_{\mathrm{T}}' = \omega_{\mathrm{T}} \left( 1 + 3 \frac{L_{0}}{d} \frac{1}{1 + \widetilde{C}_{a}} \right), \quad \omega_{\eta \mathrm{T}}' = \omega_{\eta \mathrm{T}} \left( 1 + \varepsilon \frac{L_{0}}{d} \frac{\widetilde{C}_{ma}}{1 + \widetilde{C}_{a}} \right). \tag{2.15}$$

They consist of two contributions with different pressure dependence: a gas collision frequency which is proportional to pressure, e. g.

$$\omega_{\eta} = \frac{4}{5} \sqrt{\frac{8 \, k \, T_0}{\pi \, M}} \, \frac{1}{l} \, \propto p_0 \, ,$$

and a pressure independent wall collision frequency, e. g.

$$(\omega_{\eta})_{\text{Wall}} = \frac{4}{5} \sqrt{\frac{8 k T_0}{\pi M}} \frac{3 C_m}{d},$$

$$\begin{aligned} \omega_{\eta}^{'} &= \omega_{\eta} + \left(\omega_{\eta}\right)_{\mathrm{Wall}}.\\ \mathrm{From} \quad \varphi_{\mathrm{T}}^{'} &= \varphi_{\mathrm{T}} \Bigg/ \left(1 + 3\,\frac{L_{0}}{d}\,\frac{1}{1 + \widetilde{C}_{\mathrm{a}}}\right), \\ \mathrm{and} \quad A_{\eta\mathrm{T}}^{'} &= A_{\eta\mathrm{T}} \Bigg/ \left(1 + 3\,\frac{l}{d}\,\,C_{m} + 3\,\frac{L_{0}}{d}\,\frac{1 - 2\,\widetilde{C}_{m\mathrm{a}}}{1 + \widetilde{C}_{\mathrm{a}}}\right) \end{aligned}$$

one can see that  $A_{\eta \mathrm{T}}^{'}$  (which determines the magnitude of  $\varepsilon_{m}^{'}$ ,  $\varepsilon_{m}^{'}$  decreases with increasing Knudsen

number l/d, and the curves  $\varepsilon_m'(\varphi_T)$ ,  $\varepsilon_m'^{\rm tr}(\varphi_T)$  are 0.50 shifted to higher  $\varphi_T$ -values. This corresponds exactly to the corrections made by Hulsman et al. <sup>5, 6</sup> with their measurements of the SBE of viscosity: The magnitude is reduced by a factor  $1 + n_\beta \cdot l/2 d$ , the  $H/p_0$ -axis is stretched by a factor  $1 + n_\gamma \cdot l/2 d$ , thus

$$\frac{1}{6} n_{\beta} = C_m + \frac{L_0}{l} \frac{1 - 2\widetilde{C}_{ma}}{1 + \widetilde{C}_a}, \quad \frac{1}{6} n_{\nu} = \frac{L_0}{l} \frac{1}{1 + \widetilde{C}_a}.$$
(2.18)

It should be noticed that for z = 1 the corrections are the same for  $E_m$  and  $E_m^{\text{tr}}$ . This is, in general, not true; different Knudsen parameters are observed for longitudinal  $(n_{\beta}^{\text{long}}, n_{\gamma}^{\text{long}})$  and transverse effects  $(n_{\beta}^{\text{tr}}, n_{\gamma}^{\text{tr}})$ . For the gases considered here  $\varkappa < 1$ applies, then  $E_m$ ,  $E_m^{\rm tr}$  are functions of  $\varphi_{\rm T}$ ,  $\varkappa$ , l/dand as a consequence the reduction of the effect depends on the  $\varphi_T$ -value and is different for longitudinal  $(E_m)$  and transverse  $(E_m^{\text{tr}})$  effects. A fit of (2.11) to experimental results obtained by Hulsman et al. 5, 6 yields values for the surface parameters  $C_{\rm m}$ ,  $C_{\rm a}$  and  $C_{\rm ma}$ . One possible set is given in Table 1, it describes experimental data 5,6 in the range  $0.005 \le l/d \le 0.05^{20}$  within 7% for HD and 3% for CH4, CO, N2 which roughly corresponds to measuring accuracy.

The parameter  $C_{\rm a}$  which describes the accommodation of the tensor polarization is of the order 1, whereas  $C_{\rm ma}$  (which describes thermomagnetic slip) is about two orders of magnitude smaller, in accordance with Halbritter's  $^{23}$  result. The coefficient  $C_{\rm ma}$  has its largest value for HD, for CH<sub>4</sub>, CO and N<sub>2</sub> it is at least smaller by a factor of 10 and can be put equal to zero. In Fig. 2 the effect of Knudsen corrections on  $E_m^{\rm tr}$  is plotted for HD; it is obtained from (2.11) with the parameters of Table 1;  $s_{\rm t}$  is the sign of  $\omega_{\rm vT}$  and  $\omega_{\rm bt} = (1/\sqrt{5}) \; \omega_{\rm vT}$ .

### III. Thermomagnetic Pressure Difference

Thermomagnetic pressure difference is an effect typical for rarefied polyatomic gases in a magnetic

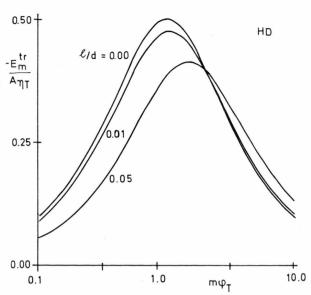


Fig. 2. Knudsen corrections for the SBE of viscosity;  $\tilde{E}_{m}^{\text{tr}}$  is calculated for HD from Eq. (2.11) with the parameters  $\tilde{C}_{a}$ = 0.40,  $\tilde{C}_{m\,a}$ =0.40 (corresponding to  $C_{a}$ ,  $C_{m\,a}$  from Table 1) and  $C_{m}$ =1.0.

field. It vanishes in the hydrodynamic limit and when the magnetic field is switched off. For a monatomic gas it does not exist at all. The effect has been predicted by Waldmann 15 in 1967 and has been observed for the first time in 1972 by Hulsman et al. 16 for N2; further experiments are made by Hermans et al. 17. In Fig. 3 the schematic experimental arrangement is shown together with the direction of the pressure gradient observed for N<sub>2</sub> <sup>16</sup>: The temperature gradient has the u-direction. A pressure gradient is found in the e-direction if a magnetic field  $\mathbf{H} = H \mathbf{h} (\mathbf{h} \cdot \mathbf{h} = 1)$  is applied in the  $\boldsymbol{u} \times \boldsymbol{e}$ -direction. For the gas CO the pressure gradient has the same direction as for N2 but for HD and CH<sub>4</sub> the opposite direction is measured, according to the different sign of the rotational g-factor  $g_{\rm r}$  16, 17 ( $g_{\rm r} > 0$  for HD, CH<sub>4</sub>,  $g_{\rm r} < 0$  for CO, N<sub>2</sub>).

For a theoretical treatment of thermomagnetic pressure difference a heat conducting gas between infinite parallel plates of distance  $D_y = 2 d$  is con-

	×	$L_0/l$	$n_{eta}^{\mathrm{long}}$	g 6 $n_{\gamma}$ long	6 n <sub>β</sub> tr 5	$n_{\gamma}{ m tr}$	5 Cm	$C_{\mathrm{a}}$	$C_{m a}$
HD	0.16	2.68	6	14	10	12	1.0	1.00	s <sub>t</sub> * 0.07
$CH_4$	0.56	0.78	9	3	10	3	1.0	0.80	0.00
CO	0.64	0.71	10	2	10	2	1.2	1.38	0.00
$N_2$	0.47	0.85	12	4	10	2	1.2	1.46	0.00

Table 1. Experimental <sup>5, 6</sup> and theoretical <sup>20</sup> results for the Knudsen corrections of the SBE of viscosity.

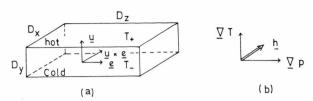


Fig. 3. Thermomagnetic pressure difference: (a) schematic experimental arrangement  $^{16, 17}$ , the relation  $D_z \gg D_x \gg D_y$  = 2 d applies; (b) direction of the pressure gradient for  $N_2$  as observed by Hulsman et alias  $^{16}$ .

sidered. The unit vector  $\boldsymbol{u}$  is perpendicular to the plates (y-direction), the unit vector  $\boldsymbol{e}$  is pointing in the z-direction in which the pressure gradients are observed. The magnetic field may have arbitrary directions, in experiments <sup>17</sup> it is varied in the  $(\boldsymbol{u}, \boldsymbol{u} \times \boldsymbol{e})$ -plane.

In the absence of a magnetic field the gas is at rest, therefore the isotropic flow velocity vanishes, viz.  $\boldsymbol{v}_{\mathrm{iso}} = \boldsymbol{0}$ , and in the one-temperature approximation  $(T_{\mathrm{trans}} \approx T_{\mathrm{rot}} \approx T)$  the isotropic pressure  $\boldsymbol{p}_{\mathrm{iso}}$  is constant and equals  $\boldsymbol{p}_0$ . The isotropic temperature distribution is obtained from the differential equation (1.16)  $\nabla \cdot \nabla T_{\mathrm{iso}} = 0$  and the boundary condition (1.25)  $T_{\mathrm{iso}} - T_{\mathrm{solid}} = C_{\mathrm{t}}(l/\lambda_{\mathrm{iso}})$   $\boldsymbol{q}_{\mathrm{iso}} \cdot \boldsymbol{n}$ :

$$T_{\rm iso}(y) = \frac{T_+ + T_-}{2} + \frac{y}{2 d} \frac{\delta T}{1 + (l/d) C_t},$$
 (3.1)

where  $T_{\rm solid}(y=\pm\,d)=T_{\,\pm}$  and  $\delta T=T_{\,+}-T_{\,-}$  have been used.

Then the tensor polarization can be determined by solving the homogeneous differential equation (1.14)  $[1-L_m^2(d^2/dy^2)] \mathcal{P}^{(m)}: \mathbf{a} = \mathbf{0}$  with the inhomogeneous boundary condition (1.27)

$$\mathbf{a} = C_{\mathrm{a}} \, \mathbf{n} \cdot \underline{\mathbf{b}} + C_{\mathrm{at}} \frac{l}{T_{\mathrm{o}} \, \lambda_{\mathrm{iso}}} \, \mathbf{q}_{\mathrm{iso}} \cdot \mathbf{n} \, \frac{3}{2} \, \overline{\mathbf{n} \, \mathbf{n}}.$$

Notice that v,  $q_{\text{trans}}$ , q and  $a^{\text{rt}}$  have been replaced by their constant isotropic values  $v_{\text{iso}} = \theta$ ,  $(q_{\text{trans}})_{\text{iso}}$ ,  $q_{\text{iso}}$  and

$$m{a}_{
m iso}^{
m rt} = rac{3}{5} \, rac{\sqrt{2}}{p_0 \, c_0} \, \lambda_{
m iso} \, \, \sqrt{rac{\omega_{
m t}}{\omega_{
m b}}} \, rac{\lambda_{
m iso}^{
m t}}{\lambda_{
m iso}} \, (1-A_{
m tr}) \, \, a_{
m rbt} \, 
abla T_{
m iso} \, .$$

When  $\mathbf{a}$  and  $\mathbf{b}$  are known the magnetic field dependent flow velocity  $\mathbf{v}(y, \mathbf{H})$  and the pressure gradient

$$\nabla p = \boldsymbol{u} (\partial p/\partial y) + \boldsymbol{P}, \quad \boldsymbol{u} \cdot \boldsymbol{P} = 0$$
 (3.2)

can be calculated. For vanishing magnetic field the vectors v and P are zero; the pressure gradient does not depend on x and z, thus P is constant:

$$\mathbf{P} = \text{const} = \mathbf{P}(\mathbf{H}), \quad \mathbf{P}(\mathbf{0}) = \mathbf{0}, \quad \mathbf{v}(\mathbf{y}, \mathbf{0}) = \mathbf{0}.$$
 (3.3)

From inspection of the velocity slip condition (1.26) it can be understood how a thermomagnetic pressure difference can be built up: In a magnetic field the translational heat flux  $q_{\rm trans}$  and the tensor polarization flux  $n \cdot \underline{b} \cdot n$  have components tangential to the wall. As a consequence the gas is set into motion at the plates due to thermal and thermomagnetic slip, thus creating a pressure gradient. The resulting viscous back-flow in the middle of the capillary establishes the stationary state such that no net gas flow exists:

$$\overline{\boldsymbol{v}} = \boldsymbol{\theta} . \tag{3.4}$$

Since the modification of temperature by a magnetic field plays no role in the differential equation (1.15) and in the boundary condition (1.26) the flow velocity and the pressure gradient  $\boldsymbol{P}$  can be obtained without a solution of the full temperature problem.

The thermomagnetic pressure difference observed over the distance  $D_z$  is given by  $\delta p = D_z \, \boldsymbol{e} \cdot \boldsymbol{P}$ ; for small Knudsen numbers it is inversely proportional to the mean pressure  $p_0$ , thus the quantity  $p_0 \, \delta p / \delta T$  has a nonzero limit for l/d = 0. In general it can be written as

$$p_0 \, \delta p / \delta T = -A \, s_t \, s_{rt} \, F \,, \tag{3.5}$$

where the positive factor A depends on the size of the measuring box and on the properties of the gas:

$$A = \frac{D_z}{(2d)^3} 9 \sqrt{2} \frac{k}{M} \eta_{\rm iso}^2 \sqrt{\frac{\lambda_{\rm iso}}{\frac{15}{4} (k/M) \eta_{\rm iso}}} \sqrt{\frac{\omega_n}{\omega_b} \frac{|\omega_{\eta \rm T}|}{\omega_{\rm T}}} |a_{\rm rbt}|.$$
 (3.6)

The signs  $s_{\rm t}$  of  $\omega_{\rm \eta T}$ ,  $\omega_{\rm bt} = \omega_{\rm \eta T}/\sqrt{5}$  and  $s_{\rm rt}$  of  $a_{\rm rbt}$  could be inferred  $^{9-11}$  from measurements of flow and heat-flow birefringence, respectively, but not from SBE measurements, since this effect is determined by  $\omega_{\rm \eta T}^2$  and  $a_{\rm rbt}^2$ . Flow birefringence has been measured by Baas  $^{25}$  for  ${\rm CO_2}$ , further results for other gases are to be published.

The dependence of thermomagnetic pressure difference on the direction and magnitude of the magnetic field and on the Knudsen number l/d is contained in the (dimensionless) function  $F = F(\mathbf{h}, \varphi_b, l/d)$ . For

a comparison with experiments <sup>16, 17</sup> F is stated for the special case  $\mathbf{h} \cdot \mathbf{e} = 0$ , l/d = 0 <sup>20</sup>:

$$F = \cos \Phi \left[ a_{\text{Tt}} \left( \frac{\varphi_{\text{b}}}{1 + \varphi_{\text{b}}^{2}} + \frac{4 \varphi_{\text{b}}}{1 + 4 \varphi_{\text{b}}^{2}} \right) + F_{1}^{\text{tr}} 2 \sin^{2} \Phi \right] + F_{2}^{\text{tr}} \cos^{2} \Phi \right], \tag{3.7}$$

where  $\Phi$  is the angle between h and  $u \times e$ , i. e.  $h \cdot (u \times e) = \cos \Phi$ ,  $h \cdot u = \sin \Phi$ .

The first term in Eq. (3.7) is due to thermal slip. Its relative importance for thermomagnetic pressure difference is determined by the magnitude of

$$a_{\text{Tt}} = \frac{1}{5} \frac{\omega_{\text{T}}}{\omega_{\text{t}}} \left( 1 - \frac{\omega_{\text{br}}}{\omega_{\text{pt}}} \cdot \frac{\omega_{\text{tr}}}{\omega_{\text{r}}} \right) (1 - A_{\text{tr}})^{-1}, \tag{3.8}$$

which depends on the relative sign of  $\omega_{\rm bt}$  and  $\omega_{\rm br}$ . The sign of  $\omega_{\rm br}$  is equal to that of  $a_{\rm rbt}$  (i. e.  $s_{\rm rt}$ ) for the gases HD, CH<sub>4</sub>, CO and N<sub>2</sub>. Then for  $s_{\rm rt}=s_{\rm t}$  the quantity  $a_{\rm Tt}$  is of the order of <sup>20</sup> 0.04 for HD and 0.3 to 0.4 for CH<sub>4</sub>, CO, N<sub>2</sub>. The functions  $F_1^{\rm tr}$ ,  $F_2^{\rm tr}$  in Eq. (3.7) describe the influence of the tensor polarization on thermomagnetic pressure difference. They are the imaginary parts of the complex functions

$$F_{m} + i F_{m}^{tr} = \left[ -\frac{\widetilde{C}_{a}}{(1 + i m \varphi_{T}) (1 + i m \varphi_{b})} - \frac{\widetilde{C}_{ma}}{V (1 + i m \varphi_{T}) (1 + i m \varphi_{b})} + \frac{\widetilde{C}_{at}}{1 + i m \varphi_{T}} - \widetilde{C}_{at} \widetilde{C}_{ma} \right] \cdot \left[ \widetilde{C}_{a} + \sqrt{\frac{1 + i m \varphi_{b}}{1 + i m \varphi_{T}}} \right]^{-1}.$$
(3.9)

Their real parts  $F_1$ ,  $F_2$  contribute to F only if both  $h \cdot e$  and  $h \cdot u$  are nonzero, see Ref. <sup>20</sup>.

If  $F_m^{\rm tr}$  is written as a function of  $\varphi_b$  the precession angle  $\varphi_T$  has to be replaced by  $(1/\varkappa)$   $\varphi_b$   $(\varkappa = \omega_T/\omega_b)$ . For convenience  $\widetilde{C}_{\rm at}$  has been used, it is related to  $C_{\rm at}$  by

$$C_{\rm at} = \widetilde{C}_{\rm at} \frac{L_0}{l} \sqrt{\frac{\omega_{\rm b}}{\omega_{\rm \eta}}} \sqrt{\frac{\lambda_{\rm iso}}{\frac{15}{4} (k/M) \eta_{\rm iso}}} a_{\rm rbt}, \qquad (3.10)$$

for  $\widetilde{C}_a$ ,  $\widetilde{C}_{am}$  see Equation (2.12). Now some characteristic features of thermomagnetic pressure difference are discussed by use of Equations (3.7), (3.9).

First it is noticed that  $F_m{}^{\rm tr}$  is an odd function of  $\varphi_{\rm b} \propto g_{\rm r} \, H/p_0$ , hence it vanishes for zero magnetic field. The sign of  $p_0 \, \delta p/\delta T$  as a function of  $H/p_0$  depends on the sign of the rotational g-factor  $g_{\rm r}$ . This is confirmed by experiments  $^{16, 17}$ .

There is no effect if the magnetic field is parallel to the temperature gradient (i. e.  $\Phi = \pi/2$ ).

The first experiments  $^{16, 17}$  have been done for  $\boldsymbol{h} \cdot \boldsymbol{e} = 0$  and  $\boldsymbol{\Phi} = 0$ . In this case only thermal slip and the function  $F_2^{\text{tr}}$  contribute to thermomagnetic pressure difference. But for increasing angle  $\boldsymbol{\Phi}$  (and  $\boldsymbol{h} \cdot \boldsymbol{e} = 0$ )  $F_1^{\text{tr}}$  becomes important too, and as a consequence the maximum value  $F_{\text{max}}$  of F decreases and is reached at higher  $\varphi_b$ -values. This is observed in experiments by Hermans et al.  $^{17}$ . If the tensor polarization is neglected (putting  $C_a = 0 = C_{\text{ma}} = C_{\text{at}}$ ) thermal slip alone determines thermomagnetic pressure difference. Then for  $\boldsymbol{h} \cdot \boldsymbol{e} = 0$  its magnitude

varies with  $\cos \Phi$ , but the maximum value

$$(F_{\rm max})^{
m th.sl.} = 1.425 \ a_{
m Tt} \cos \Phi$$

is for all angles  $\Phi$  reached at  $(\varphi_b)^{\text{th.sl.}} = 0.6158$  (where the transverse heat conductivity is maximal), in contradiction to experiments <sup>17</sup>.

As an illustration the gas  $N_2$  is considered with the corresponding experimental data obtained for  $\mathbf{h} \cdot \mathbf{e} = 0$ ,  $\Phi = 0$  by Hermans <sup>17</sup> and extrapolated to l/d = 0. The maximum value

$$(p_0 \delta p/\delta T)_{\text{max}}^0 = +1.84 \cdot 10^{-4} \text{ Torr}^2 \text{ K}^{-1}$$

of thermomagnetic pressure difference is reached at  $(H/p_0)_{\rm max}^0=2.48~{\rm kOe\,Torr^{-1}}$  which corresponds to  $^{20}$   $(\varphi_b)_{\rm max}^0=-0.34$   $(\varphi_b$  is negative since  $g_r<0$ ). With  $D_z=340$  cm,  $D_y=2$  d=1.75 mm and the values for  $|\omega_{\eta \rm T}|/\omega_{\rm T}=0.065, |a_{\rm rbt}|=0.116$  extracted  $^{20}$  from SBE data on viscosity  $^{4-6}$  and on thermal conductivity  $^8$  the factor A is found to be

$$A = 3.24 \cdot 10^{-4} \text{ Torr}^2 \text{ K}^{-1}$$
.

Then from Eq. (3.5)  $s_t \cdot s_{rt} \cdot F_{max}^0 = -0.57$  is found. Since  $a_{Tt} = 0.34$  for  $s_{rt} = s_t$  thermal slip accounts for about 85% of  $F_{max}^0$ . The parameters  $\widetilde{C}_a = 1.00$  and  $\widetilde{C}_{ma} = 0.00$  (corresponding to  $C_a$ ,  $C_{ma}$  from Table 1) are already known from Knudsen corrections for the SBE of viscosity. The remaining parameter  $\widetilde{C}_{at}$  is then determined such that the theoretical value of  $F_{max}$  as calculated from Eqs. (3.7) and

(3.9) agrees with the experimental value  $F_{\rm max}^0$ . The result is  $\widetilde{C}_{\rm at} = 0.44$ , i. e.  $C_{\rm at} = s_{\rm t}$  0.056. Then the position of the maximum is predicted as

$$(\varphi_{\rm b})_{\rm max} = -0.35$$

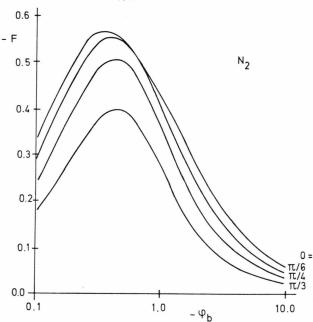


Fig. 4. Dependence of thermomagnetic pressure difference on the orientation of the magnetic field for  $\mathbf{h} \cdot \mathbf{e} = 0$ . The angle  $\Phi$  is defined by  $\mathbf{h} \cdot (\mathbf{u} \times \mathbf{e}) = \cos \Phi, \mathbf{h} \cdot \mathbf{u} = \sin \Phi$ . The function F is calculated for  $N_2$  from Eqs. (3.7), (3.9) with  $a_{\mathrm{T}t} = 0.34$  (i. e.  $s_{\mathrm{r}t} = s_t$ ) and the parameters  $\widetilde{C}_a = 1.00$ ,  $\widetilde{C}_{m\,a} = 0.00$  (corresponding to  $C_a$ ,  $C_{m\,a}$  from Table 1) and  $\widetilde{C}_{at} = 0.44$ , i. e.  $C_{at} = s_t \ 0.056$ .

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.

With these parameters the function  $F(\varphi_b)$  is calculated for different angles  $\Phi$  and  $\boldsymbol{h} \cdot \boldsymbol{e} = 0$  as is shown in Figure 4.

A similar analysis can be performed for other gases, details for HD, CH<sub>4</sub>, and CO can be found in Reference <sup>20</sup>.

In conclusion it can be stated that thermomagnetic pressure difference as well as Knudsen corrections for the SBE of viscosity can be described by the same set of surface parameters  $C_a$ ,  $C_{\rm ma}$  and  $C_{\rm at}$  which contain information on the influence of gas-wall collisions on the tensor polarization. A wide variety of effects typical for rarefied polyatomic gases in a magnetic field may be treated with the system of constitutive laws, differential equations and boundary conditions developed in Section I. Interesting examples are the Scott effect <sup>13, 14</sup> and 0 =  $\phi$  the pressure dependence of flow and heat-flow birefringence <sup>11</sup>.

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