THE TEMPERATURE DEPENDENCE OF FLOW BIREFRINGENCE IN GASES
AND THE SCALAR FACTOR OF ANGULAR MOMENTUM POLARIZATION IN VISCOUS FLOW

H. VAN HOUTEN, E. MAZUR [1] and J.J.M. BEENAKKER

Huygens Laboratorium der Rijksuniversiteit, Leyden, The Netherlands

Flow birefringence measurements have been performed for several linear molecules between 90 and 293 K. From a comparison with viscomagnetic effect data, information is obtained about the scalar factor of the angular momentum polarization present in viscous flow, of which only the tensorial factor had been determined. Experiments on hydrogen isotopes, for which only one rotational level is excited, confirm the assumption that the polarization does not depend on the translational energy.

1. Introduction

It is well known that in viscous flow of a gas consisting of polyatomic molecules, alignment of the angular momenta J occurs. Experiments on the viscomagnetic effect (VME, a Senftleben—Beenakker effect [1–4]), have shown that for linear molecules a single angular momentum polarization is produced in viscous flow. It was found that its tensorial factor could be represented by the second-rank irreducible tensor in J. The dependence of the polarization on the rotational and translational energy (J^2 and W^2 with W the reduced peculiar velocity) is usually taken into account by a single scalar factor which may depend on these quantities (single moment approximation). In the appendix an outline of the kinetic theory of angular momentum alignment is given.

We denote the scalar factor is viscous flow by P_π, so that the angular momentum polarization is

$$\phi^{02\pi} = P_\pi \phi^{02}, \tag{1}$$

with

$$\phi^{02} = (\tfrac{15}{2})^{1/2} \overline{JJ} / \langle J^2(J^2 - \tfrac{3}{4}) \rangle_0^{1/2}. \tag{2}$$

For $j = 0$ the tensor $\overline{JJ}$ has no meaning. It is here implicitly understood that in this case ϕ^{02} vanishes. The tensors $\phi^{02\pi}$ and ϕ^{02} are both normalized:

$$\langle \phi^{02\pi} : \phi^{02\pi} \rangle_0 = \langle \phi^{02} : \phi^{02} \rangle_0 = 5, \tag{3}$$

leading to a condition for P_π:

$$\langle P_\pi^2 J^2(J^2 - \tfrac{3}{4}) \rangle_0 = \langle J^2(J^2 - \tfrac{3}{4}) \rangle_0. \tag{4}$$

It is not possible to obtain information on the scalar factor from experiments on the viscomagnetic effect alone. Additional information can be obtained from flow birefringence experiments (FBR), which were first performed by Baas [5,6]. A theory of this phenomenon was given by Hess [7] in 1969. In 1974 Hess [8] suggested that information on the J^2 dependence of the scalar factor of the polarization could be obtained in the form of an overlap integral by combining FBR and VME data.

To do so we proceed in the following way. From measurements of the viscomagnetic effect the following inverse matrix element of the Waldmann—Snider collision operator $\mathcal{R}$ [11] can be calculated,

$$S^{-1}\binom{02\pi}{20} \equiv \tfrac{1}{5} \langle \phi^{02\pi} : \mathcal{R}^{-1} \phi^{20} \rangle_0. \tag{5}$$

Although in flow birefringence experiments the same polarization is produced, only the non-equilibrium average of the diagonal in J part of the molecular alignment tensor $\overline{uu}$ is observed (with u the unit vector along the figure axis of the molecule). This part

can be represented by the normalized tensor [7]

$$\phi^{0\hat{2}} = (\tfrac{15}{2})^{1/2} \langle J^2/(J^2 - \tfrac{3}{4})\rangle_0^{-1/2} \overline{JJ}/(J^2 - \tfrac{3}{4}). \qquad (6)$$

The experimental flow birefringence data directly give the following inverse matrix element:

$$S^{-1}\genfrac(){0pt}{}{0\hat{2}}{20} \equiv \tfrac{1}{5}\langle \phi^{0\hat{2}} : \mathcal{R}^{-1} \phi^{20}\rangle_0. \qquad (7)$$

As $\phi^{02\pi}$ is the only polarization produced in viscous flow, it is possible to write

$$\langle \phi^{0\hat{2}} : \mathcal{R}^{-1} \phi^{20}\rangle_0 = \tfrac{1}{5}\langle \phi^{0\hat{2}} : \phi^{02\pi}\rangle_0 \langle \phi^{02\pi} : \mathcal{R}^{-1} \phi^{20}\rangle_0, (8)$$

so that the overlap integral

$$a_\pi \equiv \tfrac{1}{5}\langle \phi^{0\hat{2}} : \phi^{02\pi}\rangle_0 \qquad (9)$$

can be determined by combining the results of both experiments. The sign of a_π is unknown, since the sign of $S^{-1}\genfrac(){0pt}{}{02\pi}{20}$ cannot be determined from the viscomagnetic effect. Essentially, a_π is a slightly modified thermal average of the scalar factor P_π:

$$a_\pi = [\langle J^2/(J^2 - \tfrac{3}{4})\rangle_0 \langle J^2(J^2 - \tfrac{3}{4})\rangle_0]^{-1/2}\langle P_\pi J^2\rangle_0. \quad (10)$$

If only a single rotational level is excited $a_\pi = \langle P_\pi\rangle_0$. Clearly P_π does not depend on J^2 in such a case, but it may still depend on W^2. If P_π does not depend on W^2, as is usually assumed, a_π must be equal to one in the single-level case.

Values for a_π for several gases at room temperature can be found in table 1, together with the rotational temperatures θ. The results show that $a_\pi \leqslant 1$ for all

molecules, as required by the fact that a_π is an overlap integral between two normalized tensors (eq. (9)).

2. Temperature dependence of a_π

In order to obtain further information on the scalar factor, an apparatus has been built which allowed us to measure the temperature dependence of flow birefringence in the region between 90 K and room temperature. VME data in the same temperature region were already available [2,3]. A detailed description of the experiment will be presented in a forthcoming paper [9].

From the measurements the relevant inverse matrix elements could be determined as a function of temperature. In fig. 1 results are shown for N_2 as an example of a "classical" molecule and in fig. 2 for ortho-deuterium as an example of a molecule for which the quantum-mechanical treatment is necessary. For N_2 also the resulting values for a_π are shown, which were calculated using eq. (8). Clearly, a_π does not depend on the temperature in the range investigated. Similar results have been obtained for CO. For ortho-deuterium $S^{-1}\genfrac(){0pt}{}{0\hat{2}}{20}$ and $S^{-1}\genfrac(){0pt}{}{02\pi}{20}$ are equal within the experimental uncertainties (see fig. 2), so that $a_\pi \approx 1$.
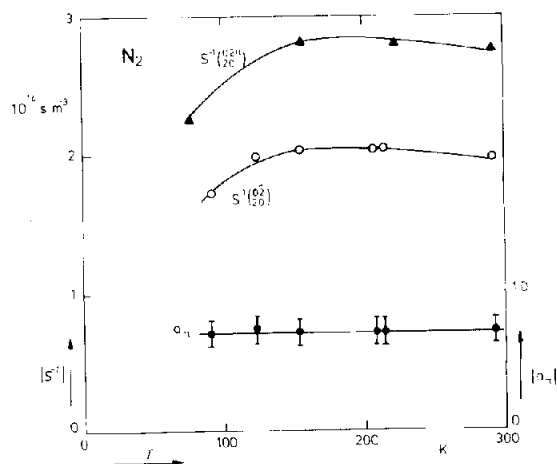
Table 1
The rotational temperature θ and the overlap integral a_π for some linear molecules at 293 K. Estimated error 7% for the "classical" linear molecules and HD, and 12% for para-hydrogen and ortho-deuterium (viscomagnetic effect data have been used from refs. [2,3] and flow birefringence data from ref. [9])

Gas	θ (K)	a_π
N_2	2.88	0.72
CO	2.78	0.73
N_2O	0.60	0.68
CO_2	0.56	0.67
OCS	0.29	0.66
HD	64.3	0.83
p-H_2	85.3	0.92
o-D_2	43.0	0.97

Fig. 1. Results for N_2. ▲: $S^{-1}\genfrac(){0pt}{}{02\pi}{20}$ obtained from the viscomagnetic effect [2] (estimated error 4%). ○: $S^{-1}\genfrac(){0pt}{}{0\hat{2}}{20}$ obtained from flow birefringence (estimated error 7%). ●: a_π as a function of temperature.
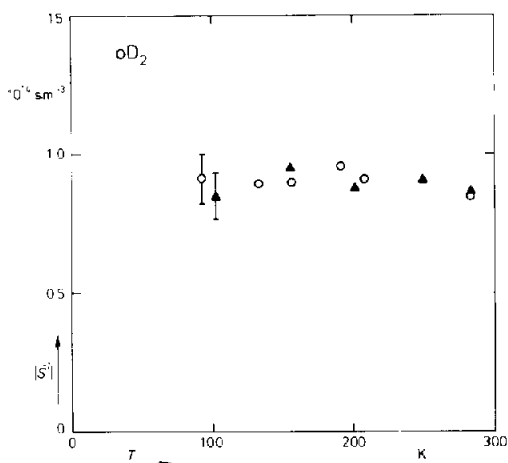
Fig. 2. Results for ortho-deuterium. $\blacktriangle$: $S^{-1}(^{02\pi}_{20})$ obtained from the viscomagnetic effect [3]. $\circ$: $S^{-1}(^{02}_{20})$ obtained from flow birefringence. Typical error bars are drawn. $a_\pi = S^{-1}(^{02}_{20})/S^{-1}(^{02\pi}_{20}) \approx 1$ over the temperature range investigated (not drawn).

3. Discussion

The results obtained for a_π for different gases at room temperature (see table 1), combined with the data obtained from this study on the temperature dependence, lead to the following conclusions. For "classical" linear molecules the data show that, within the experimental uncertainties, a_π has a constant value of about 0.70. This fact supports a hypothesis that in the classical region $(T \gg \theta)$ the scalar factor of the tensor polarization produced in viscous flow is the same for all linear molecules.

From the value of a_π even more specific information about the scalar factor may be obtained. It is usually assumed that P_π does not depend on W^2. Until now two different suggestions for P_π have been put forward:

$$P_\pi = \frac{\langle J^2(J^2 - \tfrac{3}{4})\rangle_0^{1/2}}{[J^2(J^2 - \tfrac{3}{4})]^{1/2}} \ (1 - p_{j=0})^{-1/2},$$

i.e.

$$\phi^{02\pi} = (\tfrac{15}{2})^{1/2} \ \frac{\overline{JJ}}{[J^2(J^2 - \tfrac{3}{4})]^{1/2}} \ (1 - p_{j=0})^{-1/2} \quad (11)$$

$(p_{j=0}$ is the fractional occupation number of the $j = 0$ ground state), corresponding to a production of tensor polarization that depends only on the orientation of J ("normalized"); and

$$P_\pi = 1,$$

i.e.

$$\phi^{02\pi} = \phi^{02} = (\tfrac{15}{2})^{1/2} \ \frac{\overline{JJ}}{\langle J^2(J^2 - \tfrac{3}{4})\rangle_0^{1/2}} \ , \quad (12)$$

corresponding to a situation where the production is roughly proportional to J^2 ("unnormalized"). From eq. (10) it can be calculated that for classical linear molecules (mainly high rotational states occupied) these choices would correspond to $a_\pi \approx 1$ and 0.70, respectively. Note that for such molecules both choices lead to temperature-independent values for a_π. The experimental results therefore strongly suggest that the "unnormalized" polarization given in eq. (12) is a good approximation to $\phi^{02\pi}$ for all "classical" linear molecules. Note, however, that this solution is non-unique.

For para-hydrogen at 293 K and for ortho-deuterium at $T < 200$ K (essentially only $j = 0$ and $j = 2$ occupied) the "single-level" case is approximately reached. The experimental results for these gases show that $a_\pi = \langle P_\pi \rangle_0 \approx 1$, thereby confirming the assumption that P_π does not depend on W^2. For HD at temperatures between 90 and 293 K a value for a_π is found ranging from 0.90 to 0.83, illustrating part of the transition from the single-level case to the classical case (not shown here).

Full details about the comparison between the viscomagnetic effect and flow birefringence, supplemented with information obtained from experiments on the collisional broadening of the depolarized Rayleigh line, will be published in due course [10].

Acknowledgement

Appendix. A summary of the kinetic theory of angular momentum alignment in viscous flow

The equilibrium state of a gas of linear molecules is described by the one-particle distribution function $f^{(0)}$ (Maxwell distribution). As $f^{(0)}$ is normalized to n, an equilibrium average of a quantity A is given by

$$\langle A \rangle_0 = (1/n)\mathrm{Tr} \int f^{(0)} A \, \mathrm{d}^3 c, \qquad (A1)$$

with Tr the trace over internal states (j, m).

Small deviations from equilibrium may be taken into account by writing $f = f^{(0)}(1 + \phi)$. A non-equilibrium average of A may be written in scalar product notation (when $\langle A \rangle_0 = 0$)

$$\langle A \rangle_{\mathrm{ne}} \equiv \langle A | \phi \rangle = (1/n)\mathrm{Tr} \int f^{(0)} A\phi \, \mathrm{d}^3 c, \qquad (A2)$$

with c the molecular velocity. The scalar function ϕ has to obey the linearized Waldmann–Snider equation (a quantum-mechanical version of the Boltzmann equation). In the special case of viscous flow this equation may be formally written

$$\mathcal{R}\phi = -(2/n)\overline{WW} : \overrightarrow{\nabla v}, \qquad (A3)$$

with $\frown$ denoting the symmetric traceless part of a tensor $(\overline{WW} = [W]^{(2)}$ with W the reduced peculiar velocity $W = (m/2kT)^{1/2}(c - v))$ and $\mathcal{R}$ the linearized collision operator. A formal solution to this equation is

$$\phi = -(2/n)\mathcal{R}^{-1}\overline{WW} : \overrightarrow{\nabla v}, \qquad (A4)$$

where $\mathcal{R}^{-1}$ is the inverse of the operator $\mathcal{R}$. It can be seen that ϕ, which describes deviations from equilibrium, is proportional to the driving force $\overrightarrow{\nabla v}$. In order to represent $\mathcal{R}$ we chose a complete orthonormal set of basis functions which consist of a product of normalized irreducible tensors in W and J and a normalized scalar factor P_s which may depend on J^2 and W^2:

$$\phi^{pqs} = (2^p/p!)^{1/2} [W]^{(p)}$$

$$\times \left\{ \frac{2q + 1}{\langle [J]^{(q)} \odot [J]^{(q)} \rangle_0} \right\}^{1/2} [J]^{(q)} P_s. \qquad (A5)$$

The index s may be omitted if $P_s = 1$. Here $\odot$ denotes a q-fold contraction. As an example,

$$\phi^{02} = (\tfrac{15}{2})^{1/2}\overline{JJ}/\langle J^2(J^2 - \tfrac{3}{4}) \rangle_0^{1/2}. \qquad (A6)$$

Because $\mathcal{R}$ is an isotropic operator, the matrix elements of $\mathcal{R}$ or $\mathcal{R}^{-1}$ may be written as a product of trivial isotropic tensors and a scalar (reduced) matrix element which will be denoted $S(^{p\ q\ s}_{p'q's'})$ and $S^{-1}(^{p\ q\ s}_{p'q's'})$ respectively. The matrix elements of $\mathcal{R}$ are related to effective cross sections according to $S(^{p\ q\ s}_{p'q's'}) = \langle v \rangle_0 \mathfrak{S}(^{p\ q\ s}_{p'q's'})$. When the two rows of indices are equal one will be omitted for simplicity.

We will limit the discussion to viscous flow. From experiments on the viscomagnetic effect it is known that in this case the basis set may be restricted to two functions: ϕ^{20} and $\phi^{02\pi}$, with P_π an unknown function of W^2 and J^2.

This restriction allows expression of matrix elements of $\mathcal{R}^{-1}$ into those of $\mathcal{R}$ in a simple way. Furthermore it follows that the only non-zero non-equilibrium averages of the basis functions are those of ϕ^{20} and $\phi^{02\pi}$. The shear viscosity coefficient is determined by momentum transport which is related to the average of the tensor $\overline{WW}$, and therefore to $\langle \phi^{20} \rangle_{\mathrm{ne}}$. From eqs. (A2) and (A4) it follows that this may be written as

$$\langle \phi^{20} \rangle_{\mathrm{ne}} = -(2^{1/2}/n)\langle \phi^{20} | \mathcal{R}^{-1}\phi^{20} \rangle : \overrightarrow{\nabla v}. \qquad (A7)$$

The shear viscosity coefficient is thus proportional to the diagonal inverse scalar matrix element $S^{-1}(20) = \tfrac{1}{5}\langle \phi^{20} : \mathcal{R}^{-1}\phi^{20} \rangle_0$. (A contraction over the trivial tensor indices accounts for the factor $\tfrac{1}{5}$.)

In a viscous flow field the molecules are partially aligned, as described by the alignment tensor $\phi^{02\pi}$. The non-equilibrium average of this tensor is proportional to the off-diagonal inverse matrix element $S^{-1}(^{02\pi}_{20}) \equiv \tfrac{1}{5}\langle \phi^{02\pi} : \mathcal{R}^{-1}\phi^{20} \rangle_0$. Off-diagonal matrix elements are in general much smaller than diagonal ones. Using this fact and simple matrix inversion, the following approximate relations between the inverse matrix elements and effective cross sections may be derived

$$S^{-1}(20) \approx \frac{1}{S(20)} = \frac{1}{\langle v \rangle_0 \mathfrak{S}(20)}, \qquad (A8)$$

$$S^{-1}(^{02\pi}_{20}) \approx -\frac{S(^{02\pi}_{20})}{S(20)S(02\pi)} = -\frac{\mathfrak{S}(^{02\pi}_{20})}{\langle v \rangle_0 \mathfrak{S}(20)\mathfrak{S}(02\pi)}. \qquad (A9)$$

From the shear viscosity $\mathfrak{S}(20)$ can thus be calculated, while from the viscomagnetic effect both $\mathfrak{S}(^{02\pi}_{20})$ and $\mathfrak{S}(02\pi)$ can be obtained. The value of the field to pressure ratio B/p yields the decay cross sections $\mathfrak{S}(02\pi)$, while the production cross section $\mathfrak{S}(^{02\pi}_{20})$ can be de-

rived from the saturation value of the effect.

The non-equilibrium average of ϕ^{02}, which is observed in flow birefringence experiments, is proportional to $S^{-1}\binom{02}{20}$. This matrix element cannot directly be expressed into effective cross sections, since in principle ϕ^{02} does not belong to the basis set ϕ^{pqs}. However, this tensor can be expressed in terms of this set, leading to the relation between the viscomagnetic effect and flow birefringence discussed in this Letter.

A more detailed treatment of the kinetic theory of alignment may be found in ref. [11]. Note, however, that in this paper a different definition is used for ϕ^{02}.

References

[1] H. Hulsman, E.J. van Waasdijk, A.L.J. Burgmans, H.F.P. Knaap and J.J.M. Beenakker, Physica 50 (1970) 53.

[2] A.L.J. Burgmans, P.G. van Ditzhuyzen, H.F.P. Knaap, and J.J.M. Beenakker, Z. Naturforsch. 28a (1973) 835.

[3] P.G. van Ditzhuyzen, L.J.F. Hermans and H.F.P. Knaap, Physica 88A (1977) 452.

[4] 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.

[5] F. Baas, Phys. Letters 36A (1971) 107.

[6] F. Baas, J.N. Breunese, H.F.P. Knaap and J.J.M. Beenakker, Physica 88A (1977) 1.

[7] S. Hess, Phys. Letters 30A (1969) 239; Springers Tracts Mod. Phys. 54 (1970) 136.

[8] S. Hess, Z. Naturforsch. 29a (1974) 1121.

[9] H. van Houten, J. Korving and J.J.M. Beenakker, to be published.

[10] H. van Houten, E. Mazur and J.J.M. Beenakker, to be published.

[11] E. Mazur, J.J.M. Beenakker and I. Kuščer, Physica 121A (1983) 430.