Kinetic Theory of Flow Birefringence in Dilute Gases of Symmetric Top Molecules

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Flow birefringence in dilute gases of symmetric top molecules is treated within the framework of the kinetic theory based on the Waldmann-Snider equation. A microscopic expression is derived for the characteristic flow birefringence coefficient. Its magnitude is related to the magnetic-field-induced change of the viscosity.

Flow birefringence in dilute gases of linear molecules has recently been studied [1, 2] within the framework of the kinetic theory based on the Waldmann-Snider equation [3]. The first measurements have been reported by Baas [4]. In this note, the theory is extended to gases of symmetric top molecules. Particular attention is paid to the relation between the magnitude of the flow birefringence and the magnetic-field-induced change of the viscosity [5, 6] (Senftleben-Beenakker effect). The previously made assumption that the same type of alignment which occurs in connection with flow birefringence is also of decisive importance for the Senftleben-Beenakker effect is abandoned. This point is also discussed for the special case of linear molecules.

Dielectric Tensor and Alignment

For a dilute gas of symmetric top molecules, the part of the dielectric tensor relevant for birefringence is

$$\overline{\boldsymbol{\epsilon}} = 4\pi n(\alpha_{\|}-\alpha_{\perp})\,\langle(\overline{\boldsymbol{u}\boldsymbol{u}})_{nr}\rangle\,. \tag{1}$$

Here n is the number density of the gas, $\boldsymbol{u}$ is a unit vector parallel to the figure axis of a molecule, $\alpha_{\|}$ and $\alpha_{\perp}$ are the polarizabilities for electric fields parallel and perpendicular to $\boldsymbol{u}$. The symbol $\overline{\ldots}$ indicats the symmetric traceless part of a tensor. The bracket $\langle\ldots\rangle$ refers to a nonequilibrium average. The nonresonant part $(\overline{\boldsymbol{u}\boldsymbol{u}})_{nr}$ of the tensor

$$\overline{\boldsymbol{u}\boldsymbol{u}} = \boldsymbol{u}\boldsymbol{u} - \tfrac{1}{3}\,\boldsymbol{\delta}$$

is proportional to $\overline{\boldsymbol{J}\boldsymbol{J}}$ where $\hbar\boldsymbol{J}$ is the rotational angular momentum of a molecule. More specifically, one has

$$(\overline{\boldsymbol{u}\boldsymbol{u}})_{nr} = -\tfrac{1}{2}(J^2-\tfrac{3}{4})^{-1}[1-3J^{-2}(\boldsymbol{J}\cdot\boldsymbol{u})^2]\,\overline{\boldsymbol{J}\boldsymbol{J}}\,. \tag{2}$$

To check the validity of Eq. (2), multiply both sides by $\overline{\boldsymbol{J}\boldsymbol{J}}$, contract and use

$$\overline{\boldsymbol{J}\boldsymbol{J}} : \overline{\boldsymbol{J}\boldsymbol{J}} = \tfrac{2}{3}J^2(J^2-\tfrac{3}{4})\,.$$

It is understood that the eigenvalues of J^2 and $\boldsymbol{J}\cdot\boldsymbol{u}$ are $j(j+1)$ and k with $-j \leqq k \leqq j$, where j is the rotational quantum number. For a linear $^1\Sigma$-molecule one has $\boldsymbol{J}\cdot\boldsymbol{u}=0$.

In connection with the kinetic theory it is more convenient to use the normalized tensor

$$\boldsymbol{\Phi}_{\mathrm{a}} = -\sqrt{30}\,c^{-1}(\overline{\boldsymbol{u}\boldsymbol{u}})_{nr} \tag{3}$$

with

$$c = \langle J^2(J^2-\tfrac{3}{4})^{-1}[1-3J^{-2}(\boldsymbol{J}\cdot\boldsymbol{u})^2]^2\rangle_0^{1/2}\,. \tag{4}$$

The bracket $\langle\ldots\rangle_0$ indicates an equilibrium average. The normalization coefficient has been chosen such that $\langle\boldsymbol{\Phi}_{\mathrm{a}}:\boldsymbol{\Phi}_{\mathrm{a}}\rangle_0 = 5$. The subscript "a" refers to alignment. For $\boldsymbol{J}\cdot\boldsymbol{u}=0$, (3) reduces to the tensor $\boldsymbol{\Phi}_{\mathrm{T}}$ ("T" refers to tensor polarization) used in References [1, 2]. The tensor

$$\mathbf{a} = \langle\boldsymbol{\Phi}_{\mathrm{a}}\rangle \tag{5}$$

characterizes the alignment of the particles which is of importance for birefringence. From (1, 2, 3) follows

$$\overline{\boldsymbol{\epsilon}} = -2\pi n(\alpha_{\|}-\alpha_{\perp})\sqrt{2/15}\,c\,\mathbf{a}\,. \tag{6}$$

For the theoretical treatment of flow birefringence, the alignment tensor $\mathbf{a}$ has to be related to the gradient $\overline{\nabla\boldsymbol{v}}$ of the flow velocity field $\boldsymbol{v}$. This is achieved by using standard techniques of kinetic theory.

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Flow Birefringence

An equation for the alignment tensor $\mathbf{a}$ can be derived from the Waldmann-Snider equation with the help of the moment method[7]. It is assumed that the velocity field $\boldsymbol{v}$ and the friction pressure tensor $\overline{\mathbf{p}}$ are the only macroscopic variables needed, in addition to $\mathbf{a}$, to characterize the nonequilibrium state of the gas. Then

$$\partial \mathbf{a}/\partial t + \omega_{\mathrm{a}}\, \mathbf{a} + (\sqrt{2}\, p_0)^{-1}\, \omega_{\mathrm{ap}}\, \overline{\mathbf{p}} = 0 \tag{7}$$

is obtained with $p_0 = n\, k_{\mathrm{B}}\, T$ (k_{B} is Boltzmann's constant and T is the temperature of the gas). The relaxation coefficients ω_{a} and ω_{ap} are related to the Waldmann-Snider collision operator $\omega(\dots)$ by

$$\omega_{\mathrm{a}} = \tfrac{1}{5}\, \langle \boldsymbol{\Phi}_{\mathrm{a}} : \omega(\Phi_{\mathrm{a}}) \rangle_{\mathbf{0}}\, , \quad \omega_{\mathrm{ap}} = \tfrac{1}{5} \langle \boldsymbol{\Phi}_{\mathrm{a}} : \omega(\boldsymbol{\Phi}_{\mathrm{p}}) \rangle_{\mathbf{0}}\, , \tag{8}$$

with $\boldsymbol{\Phi}_{\mathrm{p}} = \sqrt{2}\, \overline{\boldsymbol{V}\boldsymbol{V}}$ where $\boldsymbol{V}$ is the velocity of a particle in units of $(2\, k_{\mathrm{B}}\, T/m)^{1/2}$;m is the mass of a molecule. The subscript "p" refers to pressure. In Refs. [1, 2] the subscript "η" referring to viscosity has been used instead. The relaxation coefficient ω_{a} is positive, ω_{ap} may have either sign. They can be written as $\omega_{\,..} = n\, v_{\mathrm{th}}\, \sigma_{\,..}$ where

$$v_{\mathrm{th}} = 4\, (k_{\mathrm{B}}\, T/\pi\, m)^{1/2}$$

is a thermal velocity and $\sigma_{\,..}$ is an effective cross section. The collisional broadening of the depolarized Rayleigh line[8, 9] is determined by ω_{a}.

For $\partial \mathbf{a}/\partial t = 0$ (steady state), Eq. (7) yields

$$\mathbf{a} = -\,\omega_{\mathrm{ap}}\, (\omega_{\mathrm{a}} \sqrt{2}\, p_0)^{-1}\, \overline{\mathbf{p}}\, . \tag{9}$$

With $\overline{\mathbf{p}} = -2\, \eta\, \overline{\nabla \boldsymbol{v}}$ where η is the shear viscosity of the gas, Eqs (9) and (6) lead to

$$\overline{\boldsymbol{\epsilon}} = -2\, \beta\, \overline{\nabla \boldsymbol{v}}\, . \tag{9 a}$$

The flow birefringence coefficient β is given by

$$\beta = \frac{2\, \pi}{\sqrt{15}}\, (\alpha_{\parallel} - \alpha_{\perp})\, \frac{\eta}{k_{\mathrm{B}}\, T}\, c\, \frac{\omega_{\mathrm{ap}}}{\omega_{\mathrm{a}}}\, . \tag{10}$$

For the coefficient c see Eq. (4). Notice that β, much as the viscosity η, is independent of the number density n. Equation (10) is applicable in the hydrodynamic regime where Knudsen corrections[10] can be disregarded.

The Eq. (10) is the desired microscopic expression for the flow birefringence coefficient. The collision operator $\omega(..)$ needed for the evaluation of the relaxation coefficients contains the binary scattering amplitude operator and its adjoint which are related to the binary interaction potential[11]. Both ω_{a} and ω_{ap} vanish unless the potential contains a nonspherical part.

A careful analysis of the shape of the depolarized Rayleigh line[12] of some gases revealed that the quantity $\tilde{\omega}_{\mathrm{a}}$ defined by

$$\tilde{\omega}_{\mathrm{a}}^{\;-1} = \int_0^{\infty} C(t)\, \mathrm{d}t \tag{10 a}$$

differs (slightly) from the relaxation coefficient ω_{a}. In (10 a), $C(t)$ is the autocorrelation function of the alignment[2]. This fact can be accounted for by taking the collisional coupling between $\mathbf{a}$ and other types of alignment into consideration, cf. Reference[13]. Then ω_{a} occurring in Eqs. (9), (10) has to be replaced by $\tilde{\omega}_{\mathrm{a}}$. This conclusion has also been reached in Reference[14].

Next, the magnitude of ω_{ap} is related to data which can be inferred from the magnetic-field-induced change of the viscosity.

Flow Birefringence and the Senftleben-Beenakker Effect of the Viscosity

For all gases investigated so far[6] (except for NH_3, see[15]) the most important type of the collision-induced alignment associated with the influence of a magnetic field on the viscosity can be described by $\hat{\mathbf{a}} = \langle \hat{\boldsymbol{\Phi}}_{\mathrm{a}} \rangle$ with

$$\hat{\boldsymbol{\Phi}}_{\mathrm{a}} = \sqrt{15/2}\, S\, \overline{\mathbf{J}\mathbf{J}}\, . \tag{11}$$

It is assumed that $\hat{\boldsymbol{\Phi}}_{\mathrm{a}}$ is normalized according to $\langle \hat{\boldsymbol{\Phi}}_{\mathrm{a}} : \hat{\boldsymbol{\Phi}}_{\mathrm{a}} \rangle_0 = 5$. This implies $\langle S^2 J^2 (J^2 - \tfrac{3}{4}) \rangle_0 = 1$. In general, S depends on the scalar quantities V^2, J^2, $(\mathbf{J} \cdot \boldsymbol{u})^2$. This dependence, however, cannot be inferred from the Senftleben-Beenakker effect.

Within a single term description, the saturation value of the difference $\eta(H) - \eta$ between the viscosity $\eta(H)$ in the presence of a magnetic field with magnitude H and the field-free viscosity η is determined by[16, 17]

$$(\Delta\eta/\eta)_{\mathrm{sat}} = [\eta(H \to \infty) - \eta]/\eta = -\,\hat{\omega}_{\mathrm{ap}}\, \hat{\omega}_{\mathrm{pa}}/\omega_{\mathrm{p}}\, \hat{\omega}_{\mathrm{a}}\, . \tag{12}$$

Typically one has $|\Delta\eta|/\eta \lesssim 10^{-2}$. The relaxation coefficients occurring in Eq. (12) are related to the Waldmann-Snider collision operator $\omega(..)$ by expressions analogous to (8). Time reversal invariance implies $\hat{\omega}_{\mathrm{ap}} = \hat{\omega}_{\mathrm{pa}}$. The relaxation coefficient

$\hat{\omega}_a$ can be determined from the magnetic field value for which $\Delta\eta/\eta$ reaches half of its saturation value. In first approximation, ω_p is related to the viscosity η by $\eta = p_0\,\omega_p{}^{-1}$. Thus the magnitude of $\hat{\omega}_{ap}$ can be inferred from the Senftleben-Beenakker effect of the viscosity.

Next, a relation between ω_{ap} and $\hat{\omega}_{ap}$ is established. This allows to compare the magnitude of the flow birefringence with $(\Delta\eta/\eta)_{sat}$ (provided that the relaxation coefficient ω_a is known from other experiments, e. g. depolarized Rayleigh scattering). In general the collision operator $\omega(\Phi)$ can be written as

$$\omega(\Phi) = \omega'(\Phi) + \hat{\omega}_{ap}(\mathbf{\Phi}_p : \langle \hat{\mathbf{\Phi}}_a\, \Phi\rangle_0 + \hat{\mathbf{\Phi}}_a : \langle \mathbf{\Phi}_p\, \Phi\rangle_0) \quad (13)$$

with

$$\langle \hat{\mathbf{\Phi}}_a\, \omega'(\mathbf{\Phi}_p)\rangle_0 = 0\,. \quad (13\,a)$$

The part $\omega'(\Phi)$ of the collision operator is defined by (13), (13 a). Subject to the assumption made above that $\hat{\mathbf{\Phi}}_a$ is the only expansion tensor proportional to $\overline{\mathbf{J}\mathbf{J}}$ which has to be taken into consideration for the theory of the Senftleben-Beenakker effect of the viscosity, $\omega'(\Phi)$ has the property

$$\langle \mathbf{\Phi}_a\, \omega'(\mathbf{\Phi}_p)\rangle_0 = 0\,. \quad (14)$$

As a consequence of (13), (14), the evaluation of ω_{ap} (cf. 8) yields

$$\omega_{ap} = r\,\hat{\omega}_{ap} \quad \text{with} \quad r = \tfrac{1}{5}\,\langle \mathbf{\Phi}_a : \hat{\mathbf{\Phi}}_a\rangle_0\,. \quad (15)$$

The ratio between ω_{ap} and $\hat{\omega}_{ap}$ is determined by the overlap integral r. The magnitude of r is bounded according to $r^2 \leqq 1$. This follows from the fact that $\langle \mathbf{\Psi} : \mathbf{\Psi}\rangle_0 \geqq 0$, with $\mathbf{\Psi} = x\,\mathbf{\Phi}_a + y\,\hat{\mathbf{\Phi}}_a$, has to hold true for all values of the parameters x and y.

In Ref. [1] $\hat{\mathbf{\Phi}}_a = \mathbf{\Phi}_a$ had been assumed for simplicity. This yields the maximum value $r = 1$. In general, however, $\hat{\mathbf{\Phi}}_a \neq \mathbf{\Phi}_a$ can be expected.

In some papers on the kinetic theory of the Sentfleben-Beenakker effect of the viscosity [6, 16], S occurring in (11) had been assumed to be independent of V^2, J^2, $(\mathbf{J}\cdot\boldsymbol{u})^2$. This choice implies $S = \langle J^2(J^2 - \frac{3}{4})\rangle_0{}^{-1/2}$ and

$$r = \langle J^2 - 3\,(\mathbf{J}\cdot\boldsymbol{u})^2\rangle_0\, c^{-1}\, S\,. \quad (16)$$

For linear molecules which are predominantly in rotational states with $j > 2$, Eq. (16) reduces to $r = \langle J^2\rangle_0 \langle J^4\rangle_0{}^{-1/2}$. If the summation over the rotational quantum numbers is replaced by an integration, $r = 2^{-1/2} \approx 0.71$ is found for this special case [17a].

Concluding Remarks

An alternative description of flow birefringence in gases could be developed analogous to the theory presented in Ref. [18] for atomic vapors. In this picture, the gas is considered as a reacting mixture of particles labelled by the quantum numbers specifying the internal energy states (for symmetric tops these are j and $|k|$). In such a theory, $\frac{1}{2}N(N+1)$ relaxation coefficients for the alignment and N coupling coefficients between the alignment and the friction pressure tensor occur where N is the number of the components, i. e. of the internal energy states which have to be taken into consideration. Such an approach seems to be attractive if either few internal states have to be taken into account (small N) or if the scattering amplitude occurring in the collision operator is known (or, at least, assumed to be given by a certain model). An argument in favour of the simpler theory presented here is the fact that it involves just two characteristic relaxation coefficients, viz. ω_a and ω_{ap}.

Resently, the effect reciprocal to flow birefringence [19], the thermal [20] and the diffusion birefringence [21] in rarefied gases [22] have been treated theoretically for linear molecules. The extension of these theories to gases of symmetric tops along the lines indicated in this paper is straightforward.

An experimental determination of the overlap integral r defined by (15) as well as the comparison of ω_a and $\hat{\omega}_a$ would be of interest for gases of linear and symmetric top molecules. For linear molecules, ω_{ap} has been found to be positive [4]. A likely guess is that ω_{ap} is also positive for prolate symmetric tops. The test of this conjecture and the determination of the sign of ω_{ap} for oblate symmetric tops are further reasons why measurements of the flow birefringence in gases of symmetric top molecules are desirable.

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