Notizen

The Effect Reciprocal to Flow Birefringence in Gases

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Flow birefringence in molecular gases is due to a collisional alignment (tensor polarization) of the rotational angular momentum of the molecules in the presence of a gradient of the flow velocity. The reciprocal phenomenon is an anisotropy of the velocity distribution caused by an externally maintained tensor polarization. The kinetic theory of this new effect is presented and methods for its experimental detection are indicated.

Flow birefrigence (Maxwell effect [1]) is a typical cross effect in the sense of irreversible thermodynamics [2]. Cross effects occur in reciprocal pairs (e. g. thermal diffusion and diffusion thermoeffect [2]). So, after 100 years of experimental and theoretical investigation of the flow birefringence it is appropriate to ask what is the phenomenon reciprocal to it. An ansver to this question is given for molecular gases by an amplification of the previously developed kinetic theory of flow birefringence [3]. The first measurements of flow birefringence in gases have been made recently [1].

Birefringence is associated with the anisotropic (symmetric traceless) part $\overline{\boldsymbol{\varepsilon}}$ of the dielectric tensor $\boldsymbol{\varepsilon}$. For gases of linear molecules with rotational angular momentum $\hbar \boldsymbol{J}$, $\overline{\boldsymbol{\varepsilon}} \neq 0$ is caused by an alignment of $\boldsymbol{J}$. More precisely, one has [3]

$$\overline{\boldsymbol{\varepsilon}} = \varepsilon' \, \mathbf{a}_{\mathrm{T}} \tag{1}$$

where the alignment or tensor polarization $\mathbf{a}_{\mathrm{T}}$ is defined by

$$\mathbf{a}_{\mathrm{T}} = \sqrt{\frac{15}{2}} \left(\left\langle \frac{J^2}{J^2 - 3/4} \right\rangle_0 \right)^{-1/2} \langle (J^2 - 3/4)^{-1} \, \overline{\boldsymbol{J}\boldsymbol{J}} \rangle \, . \tag{2}$$

The bracket $\langle \dots \rangle$ denotes a nonequilibrium average, $\langle \dots \rangle_0$ refers to an equilibrium average. The eigenvalues of J^2 are $j(j+1)$. The scalar quantity ε' is given by

$$\varepsilon' = -2 \pi n (\alpha_{\parallel} - \alpha_{\perp}) \sqrt{\frac{2}{15}} \left(\left\langle \frac{J^2}{J^2 - 3/4} \right\rangle_0 \right)^{1/2} \tag{3}$$

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where n is the number density of the gas and $\alpha_{\parallel}$, $\alpha_{\perp}$, are the molecular polarizabilities for electric fields parallel and perpendicular to the molecular axis.

According to (1), the tensor polarization set up by a viscous flow has to be calculated to treat the flow birefringence. For this problem and for the reciprocal phenomenon it is sufficient to characterize the nonequilibrium state of the gas by the flow velocity $\boldsymbol{v} = \langle \boldsymbol{c} \rangle$, the friction pressure tensor

$$\mathbf{p} = \sqrt{2} \, p_0 \, \mathbf{a}_{\eta} \, , \; \mathbf{a}_{\eta} = \frac{1}{\sqrt{2}} \frac{m}{k_{\mathrm{B}} T} \langle \, \overline{\boldsymbol{c}\boldsymbol{c}} \, \rangle \, , \tag{4}$$

and by $\mathbf{a}_{\mathrm{T}}$. Here $\boldsymbol{c}$ is the molecular velocity, m is the mass of a particle, T is the temperature of the gas and k_{B} is Boltzmann's constant. The equilibrium presure is $p_0 = n \, k_{\mathrm{B}} T$.

Coupled equations for the (dimensionless) macroscopic variables $\mathbf{a}_{\eta}$ and $\mathbf{a}_{\mathrm{T}}$ can be derived from the Waldmann-Snider equation [5], a generalized Boltzmann equation, by application of the moment method [6]. These equations are

$$\dot{\mathbf{a}}_{\eta} + \omega_{\eta} \, \mathbf{a}_{\eta} \; + \omega_{\eta\mathrm{T}} \, \mathbf{a}_{\mathrm{T}} = \mathbf{F}_{\eta} \, , \tag{5}$$

$$\dot{\mathbf{a}}_{\mathrm{T}} + \omega_{\mathrm{T}\eta} \, \mathbf{a}_{\eta} \; + \omega_{\mathrm{T}} \, \mathbf{a}_{\mathrm{T}} \; = \mathbf{F}_{\mathrm{T}} \, . \tag{6}$$

The relaxation coefficients $\omega_{..}$, in essence, are collision integrals [6] obtained from the Waldmann-Snider equation [5]. They can be written as $\omega_{..} = n \, v_{\mathrm{th}} \, \sigma_{..}$ where v_{th} is a thermal velocity and $\sigma_{..}$ is an effective cross section. The "diagonal" coefficients ω_{η}, ω_{T} are positive and one has

$$\omega_{\eta} \, \omega_{\mathrm{T}} > \omega_{\eta\mathrm{T}} \, \omega_{\mathrm{T}\eta} \, .$$

From time reversal invariance of the molecular interaction potential follows the Onsager symmetry relation [3, 6]

$$\omega_{\eta\mathrm{T}} = \omega_{\mathrm{T}\eta} \, . \tag{7}$$

The coefficients ω_{T} and $\omega_{\eta\mathrm{T}}$ are sensitive to the nonsphericity of the molecular interaction potential [7].

The "forces" occurring in Eqs. (5, 6) are, for the hydrodynamical regime

$$\mathbf{F}_{\eta} = -\sqrt{2} \, \overline{\boldsymbol{\nabla} \boldsymbol{v}} \, , \; \mathbf{F}_{\mathrm{T}} = (\dot{\mathbf{a}}_{\mathrm{T}})_{\mathrm{prod}} \, . \tag{8}$$

Here $(\dot{\mathbf{a}}_{\mathrm{T}})_{\mathrm{prod}}$ denotes the tensor polarization produced per unit time e. g. by an optical pumping technique (absorption of linearly polarized infrared radiation).

In a steady state situation, i. e. for $\dot{\mathbf{a}}_\eta = \dot{\mathbf{a}}_T = 0$, Eqs. (5, 6) lead to

$$\mathbf{a}_\eta = \tau_\eta \mathbf{F}_\eta + \tau_{\eta T} \mathbf{F}_T , \quad (9)$$

$$\mathbf{a}_T = \tau_{T\eta} \mathbf{F}_\eta + \tau_T \mathbf{F}_T , \quad (10)$$

with

$$\tau_\eta = \omega_\eta^{-1} \Delta^{-1}, \tau_T = \omega_T^{-1} \Delta^{-1}, \quad (11)$$

$$\tau_{\eta T} = -\omega_{\eta T} (\omega_\eta \omega_T \Delta)^{-1} = \tau_{T\eta} , \quad (12)$$

$$\Delta = 1 - \omega_{\eta T} \omega_{T\eta} (\omega_\eta \omega_T)^{-1}. \quad (13)$$

For $\mathbf{F}_T = 0$, i. e. if no tensor polarization is created by external means, Eq. (9) is equivalent to Newton's law $\mathbf{p} = -2 \eta \overline{\nabla \boldsymbol{v}}$ with the viscosity $\eta = p_0 \tau_\eta$, and Eq. (10) describes the collission-induced tensor polarization. With Eq. (1), Eq. (10) yields

$$\bar{\varepsilon} = -2 \beta \overline{\nabla \boldsymbol{v}} , \; \beta = \frac{1}{\sqrt{2}} \varepsilon' \tau_{T\eta} , \quad (14)$$

the basic equations describing flow birefringence. The relation between the characteristic coefficient β and the Senftleben-Beenakker effect [8] of the viscosity has been discussed previously [3].

Now, for the opposite case $\mathbf{F}_T \neq 0$, $\mathbf{F}_\eta = 0$, Eq. (10) reduces to $\mathbf{a}_T = \tau_\eta \mathbf{F}_T$, i. e. the tensor polarization is equal to the product of its lifetime τ_T and the rate $\mathbf{F}_T$ at which it is generated. The phenomenon reciprocal to flow birefringence is described by Eq. (9), viz. by

$$\mathbf{a}_\eta = \tau_{\eta T} \mathbf{F}_T = -\omega_{\eta T} \omega_\eta^{-1} \mathbf{a}_T . \quad (15)$$

In summary, in a flow birefringence experiment in gases, the tensor polarization $\mathbf{a}_T$ is detected which has been caused by an anisotropy in velocity space. According to Eq. (15), an externally maintained tensor polarization gives rise to an anisotropy in velocity space characterized by $\mathbf{a}_\eta$. This is the phenomenon reciprocal to flow birefringence.

Finally, 2 methods for the experimental detection of $\mathbf{a}_\eta \neq 0$ are indicated. i) The doppler width Γ_D of a spectral line (e. g. Raman line) is, for small anisotropy, given by

$$\Gamma_D = \Gamma_D^{iso} (1 + \boldsymbol{k} \cdot \mathbf{a}_\eta \cdot \boldsymbol{k} / \sqrt{2} k^2) \quad (16)$$

where $\Gamma_D{}^{iso} = (2 k_B T/m)^{1/2} k$ is the "isotropic" Doppler width and $\boldsymbol{k}$ is the relevant wave vector. Thus $\mathbf{a}_\eta \neq 0$ implies an anisotropy of Γ_D. A remark on the size of this anisotropy is in order. For most gases of linear molecules one has $\omega_{\eta T}/\omega_\eta \approx 0.1$. A tensor polarization $\mathbf{a}_T$ of the order of 1 can be achieved if the pump light induces a vibrational-rotational transition to an internal state which is not thermally occupied. Thus an anisotropy of the Doppler width of a few per cent can be expected. This applies to the spectral lines associated with Raman transitions orginating from the molecules which have first been optically pumped and have then undergone a collision. Notice, however, that the Doppler width can be observed only if a typical mean free path l of a molecule in the gas is very large compared with k^{-1}.

ii) If $\mathbf{F}_T$ and consequently $\mathbf{a}_\eta$ are spatially inhomogeneous a pressure gradient

$$\nabla p = -\sqrt{2} \; p_0 \nabla \cdot \mathbf{a}_\eta$$

is built up.

Measurements of the phenomenon reciprocal to flow birefringence are desirable not only in order to demonstrate the existence of the new effect but also to obtain experimental values of the coefficient $\omega_{\eta T}$ which contains information on the nonsphericity of the molecular interaction. Furthermore, such a measurement, together with data from flow birefringence, could provide an experimental verification of the Onsager symmetry relation (7).

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