NOTIZEN

Electric Polarization Caused by a Temperature Gradient in a Polar Gas

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Transport processes in gases of particles with internal rotational degrees of freedom and nonspherical binary interaction give rise to a (partial) alignment of the internal angular momenta or to a correlation between linear and angular momenta of the particles. This fact has first been noticed by WALDMANN [1] in connection with the diffusion of particles with spin and by KAGAN and AFANASEV [2] who studied the heat conduction of a gas of classically rotating molecules.

The alignment set up in the nonequilibrium situation affects the transport coefficients. If the alignment is (partially) destroyed by the motion of the internal angular momenta due to an external magnetic (or electric) field, the transport coefficients are altered: SENFTLEBEN-BEENAKKER effect [3–6]. Hence the possibility to influence the transport properties of neutral gases of particles with magnetic or electric dipole moments by external magnetic or electric fields can be considered as an indirect evidence for the existence of the alignment.

As suggested by WALDMANN [7] direct evidence for two particular types of alignment could be obtained from measurements of the double refraction caused by a viscous flow (flow birefringence) and of the electric polarization caused by a heat flux in a polar gas. Flow birefringence of linear molecules which has recently been studied by HESS [8] as well as birefringence induced by sound waves and heat flow and diffusion flow birefringence in rarefied gases are associated with the second rank tensor polarization of the rotational angular momentum of the molecules. The macroscopic electric polarization, which could also be caused by a diffusion flow or, in a rarefied gas, by a viscous flow is simply associated with the average electric dipole moment of the molecules.

This note is concerned with the kinetic theory of the electric polarization induced by a temperature gradient. Symmetric top molecules (e. g. CH_3Cl) possessing a nonvanishing component of their electric dipole moment $\boldsymbol{d}$ parallel to their rotational angular momentum $\hbar\,\boldsymbol{I}$ are considered first. Then a few remarks are made on gases of linear polar molecules. Finally the order of magnitude of the electric potential difference associated with the electric polarization is discussed. Our theory is closely related to the theory of the electric Senftleben-Beenakker effect by LEVI, MCCOURT and TIP [9].

Relation between Electric Polarization and Molecular Dipole Moment

The electric polarization $\boldsymbol{P}$ of a gas is related to the molecular dipole moment $\boldsymbol{d} = d\,\boldsymbol{u}$ ($\boldsymbol{u}$ is a unit vector parallel to the figure axis of the molecule) by

$$\boldsymbol{P} = n\,d\langle \boldsymbol{u} \rangle\,. \tag{1}$$

In Eq. (1) n is the number density and the bracket $\langle \ldots \rangle$ denotes an average over the one-particle distribution function of the gas.

At densities where a symmetric top molecule undergoes many thermal rotations between two successive collisions only the component of $\boldsymbol{u}$ which is parallel to the internal angular momentum $\boldsymbol{I}$, viz.

$$\boldsymbol{u}\,(\boldsymbol{I}) = J^{-2}\,\boldsymbol{u}\cdot\boldsymbol{I}\;\boldsymbol{I} \tag{2}$$

is relevant in first approximation [9].

For linear $^1\Sigma$-molecules [9] one has $\boldsymbol{u}\,(\boldsymbol{I}) \equiv 0$. The effect vanishes in first approximation; the remaining second approximation will give much smaller values than in the symmetric-top case.

Transport-Relaxation Equation for $\langle \boldsymbol{u}\,(\boldsymbol{I}) \rangle$

The nonequilibrium average $\langle \boldsymbol{u}\,(\boldsymbol{I}) \rangle$ is obtained from a transport-relaxation equation for this quantity which again is derived from the appropriate kinetic

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equation [9, 10] (for particles with rotational degrees of freedom) by application of the moment method [11]. In the presence of a heat flux

$$\boldsymbol{q} = n\,k\,T\,\sqrt{2\,k\,T/m}\;\boldsymbol{Q} \tag{3}$$

(k, T, m are Boltzmann's constant, the temperature of the gas, the mass of a molecule and $\boldsymbol{Q}$ is a dimensionless heat flux) the said transport-relaxation equation reads

$$\frac{\partial}{\partial t}\langle \boldsymbol{u}(\boldsymbol{I})\rangle + \omega_{\mathrm{d}}\langle \boldsymbol{u}(\boldsymbol{I})\rangle + \omega_{\mathrm{dq}}\boldsymbol{Q} \approx 0\,. \tag{4}$$

The coefficient ω_{d} determines the dielectric relaxation and ω_{dq} is a measure for the coupling between $\langle \boldsymbol{u}(\boldsymbol{I})\rangle$ and the heat flux. In Eq. (4) the divergence of the flux of $\boldsymbol{u}(\boldsymbol{I})$ and the collisional coupling of $\langle \boldsymbol{u}(\boldsymbol{I})\rangle$ with other vectorial quantities have been negected. Both ω_{d} and ω_{dq} can be expressed in terms of collision brackets obtained from the linearized collision term $\omega(\ldots)$ (involving the binary scattering amplitude and its adjoint) of the kinetic equation [10, 11]. In particular one has

$$\omega_{\mathrm{d}} = \langle \boldsymbol{u}(\boldsymbol{I})\cdot\omega(\boldsymbol{u}\boldsymbol{I})\rangle_0\,(\langle \boldsymbol{u}(\boldsymbol{I})\cdot\boldsymbol{u}(\boldsymbol{I})\rangle_0)^{-1} \tag{5}$$

and

$$\omega_{\mathrm{dq}} = \tfrac{1}{3}\langle \boldsymbol{u}(\boldsymbol{I})\cdot\omega(\boldsymbol{\Phi})\rangle_0 = -\tfrac{1}{3}\langle \boldsymbol{\Phi}\cdot\omega(\boldsymbol{u}(\boldsymbol{I}))\rangle_0\,, \tag{6}$$

with

$$\boldsymbol{\Phi} = \left[\tfrac{2}{5}(V^2-\tfrac{5}{2}) + \frac{k}{c_{\mathrm{rot}}}(\varepsilon - \langle\varepsilon\rangle_0)\right]\boldsymbol{V} \tag{7}$$

where $\boldsymbol{V}$ is the particle velocity in units of $\sqrt{2\,k\,T/m}$, ε is the internal rotational energy of a molecule divided by $k\,T$ and c_{rot} is the internal specific heat per molecule. The bracket $\langle\ldots\rangle_0$ refers to an average weighted by the (one-particle) equilibrium distribution [12].

Electric Polarization Induced by a Temperature Gradient in a Polar Gas of Symmetric Top Molecules

In steady state Eq. (4) can be solved for $\langle \boldsymbol{u}(\boldsymbol{I})\rangle$. Use of Eqs. (1), (3), and of $\boldsymbol{q} = -\lambda\,\nabla T$ where λ is the heat conductivity leads to

$$\boldsymbol{P} = \gamma\,T^{-1}\,\nabla T \tag{8}$$

with

$$\gamma = (\omega_{\mathrm{dq}}/\omega_{\mathrm{d}})\;d(\lambda/k)\;\sqrt{m/2\,k\,T}\,. \tag{9}$$

For a dilute gas of symmetric top molecules γ as given by (9) does not depend on the number density [13]. Notice that, in general, γ may have both signs.

Linear Molecules

For most linear polar molecules the electric dipole moment is perpendicular to the internal angular momentum; the time average of its expectation value for the free linear Σ-molecule is zero. Thus it is only possible to obtain an electric polarization in the gas if the rotational motion of the molecules is frequently interrupted by collisions i. e. if, classically speaking, the thermal rotation frequency ω_{rot} of a molecule is comparable with the collision frequency ω_{coll}. The kinetic equation derived in Ref. [10], however, is only valid if the "condition of sufficient level spacing" [14], equivalent to the requirement $\omega_{\mathrm{coll}} \ll \omega_{\mathrm{rot}}$ is fulfilled. Despite the fact that the appropriate kinetic equation valid for $\omega_{\mathrm{coll}} \approx \omega_{\mathrm{rot}}$ is not known — then one is already in the dense gas regime — some qualitative remarks can be made on the electric polarization caused by a temperature gradient in a polar gas of linear molecules.

The unit vector operator $\boldsymbol{u}$ parallel to the molecular axis can be split into the parts $\boldsymbol{u}_+$ and $\boldsymbol{u}_-$ which induce up and down transitions between adjacent rotational levels. For simplicity a two-level system is treated i. e. only the molecules in the most frequently occupied rotational levels j and $j+1$ are taken into account. Then, a single ω_{rot} occurs and instead of Eq. (4) the two equations

$$\frac{\partial}{\partial t}\langle \boldsymbol{u}_+\rangle + i\,\omega_{\mathrm{rot}}\langle \boldsymbol{u}_+\rangle + \tilde{\omega}_{\mathrm{d}}\langle \boldsymbol{u}_+\rangle + \tfrac{1}{2}\,\tilde{\omega}_{\mathrm{dq}}\boldsymbol{Q} = 0\,, \tag{10}$$

$$\frac{\partial}{\partial t}\langle \boldsymbol{u}_-\rangle - i\,\omega_{\mathrm{rot}}\langle \boldsymbol{u}_-\rangle + \tilde{\omega}_{\mathrm{d}}\langle \boldsymbol{u}_-\rangle + \tfrac{1}{2}\,\tilde{\omega}_{\mathrm{dq}}\boldsymbol{Q} = 0 \tag{11}$$

have to be considered where $\tilde{\omega}_{\mathrm{d}}$ and $\tilde{\omega}_{\mathrm{dq}}$ are phenomenological relaxation coefficients.

In steady state Eqs. (10), (11) yield

$$\langle \boldsymbol{u}\rangle = \langle \boldsymbol{u}_+\rangle + \langle \boldsymbol{u}_-\rangle = -\,(\tilde{\omega}_{\mathrm{dq}}/\tilde{\omega}_{\mathrm{d}})\left(1+\frac{\omega_{\mathrm{rot}}^2}{\tilde{\omega}_{\mathrm{d}}^2}\right)^{-1}\boldsymbol{Q} \tag{12}$$

and thus for small values of $\tilde{\omega}_{\mathrm{d}}/\omega_{\mathrm{rot}}$ the coefficient γ as defined by Eq. (8) becomes

$$\gamma_{\mathrm{lin.\,mol.}} \approx (\tilde{\omega}_{\mathrm{dq}}\,\tilde{\omega}_{\mathrm{d}}/\omega_{\mathrm{rot}}^2)\;d(\lambda/k)\;\sqrt{m/2\,k\,T}\,. \tag{13}$$

Notice that $\gamma_{\mathrm{lin.\,mol.}}$ as given by (13) is proportional to n^2 whereas γ given by (9) is independent of the number density n.

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[12] The relaxation coefficent ω_{d} is related to the relaxation time τ occurring in the complex electric susceptibility $\chi(\omega) = \chi(0)\,(1 - i\,\omega\,\tau)^{-1}$ by $\tau = \omega_{\mathrm{d}}^{-1}$. Thus ω_{d} can be obtained experimentally from the dispersion and the nonresonant absorption of microwaves; cf. G. Boudouris, Riv. Nuovo Cimento **1**, 1 [1969]. — Collisions between molecules whose internal energies are equal, before collision and again after it, don't contribute to the bracket (6), pertaining to the cross coefficient ω_{dq}. All other collisions, energetically elastic or inelastic, may give non-vanishing contributions in principal.

[13] For molecules like NH_3 or ND_3 this statement is only true for sufficiently high pressures, i. e. if the time between two successive collisions is short compared with $\omega_{\mathrm{inv.}}^{-1}$ where $\omega_{\mathrm{inv.}}$ is the inversion frequency.

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Potential Difference Associated with the Electric Polarization

Consider heat conduction through a gas between two flat plates at temperatures T and $T+\delta T$ separated by the distance L. Then the potential difference $V=4\pi P L$ is, according to Eq. (8), given by

$$V=4\pi\gamma T^{-1}\delta T. \tag{14}$$

For $T^{-1}\delta T\approx 10^{-1}$, $d\approx 1$ Debye $=10^{-18}$ e. s. u. and $(\lambda/k)\sqrt{m/2kT}\approx 0.5\cdot 10^{15}$ cm^{-2} (NO at room temperature) one has

$$V_{\text{sym. top}}\approx 0.2\,\omega_{dq}/\omega_{d}\ \text{Volt} \tag{15}$$

and

$$V_{\text{lin. mol.}}\approx 0.2\,\tilde{\omega}_{dq}/\tilde{\omega}_{d}\ (\tilde{\omega}_{d}/\omega_{rot})^{2}\ \text{Volt}. \tag{16}$$

Ratios of "nondiagonal" and "diagonal" relaxation coefficients that are of importance for the Senftleben-Beenakker effect are of the order of 10^{-1} to 10^{-2}. The ratio ω_{dq}/ω_{d} can be expected to be smaller, but probably not more than by two orders of magnitude. Thus, at least the voltage (15) promises to be of detectable size.

Final Remarks

A measurement of the voltage due to electric polarization by a temperature gradient would be desirable. If measurable, one could obtain experimental values of the ratio ω_{dq}/ω_{d}. The relaxation coefficients ω_{dq} and ω_{d} are of particular interest with intermolecular mechanics since both vanish unless the binary interaction potential contains a nonspherical part.

Finally it seems worth mentioning that the electric polarization (8) could be influenced by an external magnetic field $\boldsymbol{H}$. In addition to the ratio ω_{dq}/ω_{d} measurements of this type would yield experimental values for the ratio ω_{H}/ω_{d} where ω_{H} is the precession frequency of the rotational angular momentum about the direction of the applied field.

Zur phänomenologischen Begründung nichtlinearer Casimir-Onsagerscher Reziprozitätsbeziehungen (Vereinfachung einer Voraussetzung)

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Kürzlich wurden hinreichende Bedingungen für eine phänomenologische Begründung von nichtlinearen Casimir-Onsagerschen Reziprozitätsbedingungen (CORB) angegeben und diskutiert [1]. Dabei zeigte es sich, daß neben einigen physikalisch evidenten Annahmen, wie die Taylor-Entwickelbarkeit der phänomenologischen Abbildungen um das enthemmte Gleichgewicht und die Einführung eines Satzes invertierbarer Parameter (z. B. Magnetfeld), die positive Semidefinitheit der Entropieerzeugungsdichte für eine phänomenologische Begründung der CORB nicht ausreicht (s. auch [2]). Zwei weitere Voraussetzungen waren nötig (VII und VIII [1]), nämlich die Möglichkeit, verschiedene thermodynamische Systeme im direkten Summenraum der Kräfte der Einzelsysteme gemeinsam beschreiben zu können und die Gültigkeit der sogen. Hall-Eigenschaft. Es wird nun gezeigt, daß sich diese beiden Voraussetzungen durch eine erheblich einfachere phänomenologische Annahme ersetzen lassen.

Die thermodynamischen Kräfte und Flüsse eines Systems lassen sich als Elemente von zueinander dualen Vektorräumen auffassen. Da die Basiswahl in diesen Vektorräumen beliebig ist, gibt es reguläre lineare Abbildungen T im Raum der Kräfte

$$\hat{\boldsymbol{x}}=T\boldsymbol{x} \tag{1}$$

und zugehörige kontragrediente im Raum der Flüsse

$$\hat{\boldsymbol{i}}=T^{-1\prime}\boldsymbol{i}, \tag{2}$$

die gleichberechtigte Koordinatendarstellungen des Systems unter Invarianz der Entropieerzeugungsdichte

$$\hat{\sigma}=\hat{\boldsymbol{i}}'\hat{\boldsymbol{x}}=\boldsymbol{i}'\,T^{-1}\,T\boldsymbol{x}=\sigma \tag{3}$$

ineinander überführen.

Unter den anderen noch möglichen Transformationen der Flüsse, die die Entropieerzeugungsdichte invariant lassen [3], sind keine Parameterinversionen. Dies folgt daraus, daß bei Parameterinversion ein zu einem Flußvektor senkrechter Unterraum aus Kraftvektoren senkrecht zum invertierten Flußvektor bleibt [4]. Es sei

$$\hat{\boldsymbol{x}}^{0}=T\boldsymbol{x}^{0},\ \hat{\boldsymbol{i}}=Q\boldsymbol{i}.$$

Dabei sei $\boldsymbol{i}$ ein fester Flußvektor und $\boldsymbol{x}^{0}$ die Gesamtheit aller zu $\boldsymbol{i}$ senkrechten Kräfte. Somit gilt

$$0=\hat{\boldsymbol{x}}^{0\prime}\,\hat{\boldsymbol{i}}=\boldsymbol{x}^{0\prime}\,T'\,Q\,\boldsymbol{i}=\boldsymbol{x}^{0\prime}\,\boldsymbol{i}.$$

Nach einem Satz von SYLVESTER [5] folgt daraus

$$T'\,Q\,\boldsymbol{i}=\lambda\,\boldsymbol{i}.$$

Invarianz der Entropieerzeugungsdichte [4] ergibt:

$$\sigma=\hat{\boldsymbol{x}}'\,\hat{\boldsymbol{i}}=\boldsymbol{x}'\,T'\,Q\,\boldsymbol{i}=\lambda\,\boldsymbol{x}'\,\boldsymbol{i}=\boldsymbol{x}'\,\boldsymbol{i},$$

woraus

$$\lambda=1,\qquad T'\,Q\,\boldsymbol{i}=\boldsymbol{i}$$

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