Electric Polarization Caused by a Diffusion Flow in a Polar Gas Mixture

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The kinetic theory of the diffusio-electric polarization is developed analogous to the previously treated thermo-electric polarization (Waldmann, Hess 1969). The relevant constitutive law is derived. The characteristic coefficient determining the magnitude of this effect is related to collision integrals obtained from the Waldmann-Snider equation. A simple model calculation shows that this coefficient will be nonzero, in general, and of measurable size, for polar symmetric top molecules.

A diffusion flow in a mixture of polar symmetric top molecules with another gas may give rise to a preferential orientation of the average electric dipole moment of the polar molecules. Such an alignment leads to an electric polarization proportional to the concentration gradient. This effect is similar to the thermoelectric polarization which has previously been studied theoretically [1]. It is the purpose of this note to state the relevant constitutive law and to present some theoretical results for the diffusio-electric polarization which can be obtained from the kinetic theory based on the Waldmann-Snider equation [2, 3]. The thermo- and diffusio-electric polarization effects are examples of nonequilibrium alignment phenomena [4, 5] which are related to the influence of magnetic and electric fields on the transport properties of molecular gases [6, 7] (Senftleben-Beenakker effect).

Constitutive Law

The constitutive law for the electric polarization $\boldsymbol{P}$ caused by a temperature gradient ∇T is

$$\boldsymbol{P} = \Gamma \, T^{-1} \nabla T \, . \tag{1}$$

Here Γ is a characteristic coefficient determining the sign and the magnitude of the thermoelectric polarization. The derivation of (1) and of a microscopic expression for Γ has been given in Reference 1. Analogous to (1), the constitutive law for the electric polarization induced by a concentration gradient in a binary mixture (molar fractions x_1, $x_2 = 1 - x_1$) can be written as

$$\boldsymbol{P} = \Gamma_{\mathrm{D}} \, (x_1 \, x_2)^{-1} \nabla x_1 = -\Gamma_{\mathrm{D}} \, (x_1 \, x_2)^{-1} \nabla x_2 \tag{2}$$

with another characteristic coefficient Γ_{D}.

In the following, the derivation of (2) and of a microscopic expression for Γ_{D} is indicated for a special mixture where the components labelled by "1" and "2" are polar symmetric top molecules (e. g. NH_3, CH_3F, CF_3H, ...), and nonpolar molecules (e. g. noble gases, N_2, CH_4, SF_6, ...), respectively. First, the connection between the electric polarization and the average orientation of the electric dipole moment has to be discussed.

Electric Polarization and Average Electric Dipole Moment

The nonresonant component of the molecular dipole moment, i. e. its component parallel to the rotational angular momentum $\hbar \boldsymbol{J}$ only can be oriented in a stationary transport situation. For the mixture of a polar and a nonpolar gas the nonresonant part of the electric polarization is [1]

$$\boldsymbol{P} = n_1 \, d \, \langle \boldsymbol{U} \rangle \tag{3}$$

with

$$\boldsymbol{U} = J^{-2} \, \boldsymbol{J} \cdot \boldsymbol{u} \, \boldsymbol{J} \, . \tag{4}$$

The magnitude of the dipole moment and the unit vector parallel to it are denoted by d and $\boldsymbol{u}$. The bracket $\langle \ldots \rangle$ indicates a nonequilibrium average. Notice that $\boldsymbol{J} \cdot \boldsymbol{u} = 0$ for linear ${}^1\Sigma$-molecules.

According to (3), the average orientation $d \langle \boldsymbol{U} \rangle$ of the nonresonant part of the electric dipole moment caused by a diffusion flow has to be calculated in order to derive Equation (2). This can be accomplished by deriving the relevant transport-relaxation equation from the Waldmann-Snider equation with the help of the moment method [8].

Transport-Relaxation Equation

Subject to the assumption that $\langle \boldsymbol{U} \rangle$, the number densities n_1, n_2, and the diffusion velocity $\boldsymbol{v}_{12}$ are

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the only macroscopic variables needed to specify the nonequilibrium state of the gas, the following equation is found for $\langle \boldsymbol{U} \rangle$:

$$\frac{\partial \langle \boldsymbol{U} \rangle}{\partial t} + \omega_{\mathrm{d}} \langle \boldsymbol{U} \rangle + \boldsymbol{U}_0 \, v_0{}^{-1} \omega_{\mathrm{dv}} \, \boldsymbol{v}_{12} = 0 \,, \tag{5}$$

with

$$U_0 = (\tfrac{1}{3} \langle \boldsymbol{U}^2 \rangle_0)^{1/2} \,, \; v_0 = (k T / m_{12})^{1/2} \,; \tag{6}$$

$m_{12} = m_1 \, m_2 (m_1 + m_2)^{-1}$ is the reduced mass of a pair a polar and a nonpolar molecule. The bracket $\langle \ldots \rangle_0$ indicates an equilibrium average. The relaxation frequency ω_{d} is the inverse relaxation time of the nonresonant part of the electric polarization. It occurs in connection with nonresonant microwave absorption [9]. The nondiagonal relaxation coefficient ω_{dv} is a measure for the collision induced coupling between $\langle \boldsymbol{U} \rangle$ and the diffusion velocity $\boldsymbol{v}_{12}$. The relaxation coefficient ω_{d} is positive, ω_{dv} may have both signs. Both ω_{d} and ω_{dv} can be expressed in terms of collision integrals obtained from the linearized Waldmann-Snider collision term. Before these collision integrals are discussed, it is noticed that effective cross sections $\sigma_{..}$ associated with the relaxation coefficients ω_{d} and ω_{dv} can be introduced by

$$\omega_{\mathrm{d}} = n_1 \, v_{\mathrm{th}}^{(11)} \, \sigma_{\mathrm{d}}^{(11)} + n_2 \, v_{\mathrm{th}}^{(12)} \, \sigma_{\mathrm{d}}^{(12)}, \tag{7}$$

$$\omega_{\mathrm{dv}} = n_2 \, v_{\mathrm{th}}^{(12)} \, \sigma_{\mathrm{dv}}^{(12)}, \tag{8}$$

where

$$v_{\mathrm{th}}^{(ij)} = (8 \, k \, T / \pi \, m_{ij})^{1/2} \quad \text{with}$$

$$m_{ij} = m_i \, m_j (m_i + m_j)^{-1} \tag{9}$$

is a thermal velocity. Eqs. (7, 8) show the dependence of the relaxation coefficients on the number densities n_1 and n_2 explicitly. The superscript of $\sigma_{..}{}^{(ij)}$ refers to a collision of a particle "i" with a particle "j".

Collision Integrals

The collision integrals for the effective cross section defined by (7, 8) are

$$\sigma_{\mathrm{d}}^{(11)} = 2 \langle U^2 \rangle_0{}^{-1} \{ \boldsymbol{U} \cdot a \;\; [a^\dagger, (\boldsymbol{U} + \boldsymbol{U}_{\mathrm{I}})] \}_{(11)} \,, \tag{10}$$

$$\sigma_{\mathrm{d}}^{(12)} = 2 \langle U^2 \rangle_0{}^{-1} \{ \boldsymbol{U} \cdot a \;\; [a^\dagger, \boldsymbol{U}] \}_{(12)} \,, \tag{11}$$

$$\sigma_{\mathrm{dv}}^{(12)} = 2 \sqrt{2}^{1} \, \tfrac{1}{3} \, U_0{}^{-1} \{ \boldsymbol{U} \cdot (\gamma \, \boldsymbol{e} - \gamma' \, \boldsymbol{e}') \, a \, a^\dagger \}_{(12)} \,. \tag{12}$$

The curly bracket stands for

$$\{ \ldots \}_{(ij)} = (\mathrm{Tr} \, e^{-\varepsilon})^{-1} \, (\mathrm{Tr}_{\mathrm{I}} \, e^{-\varepsilon_1})^{-1} \, \mathrm{Tr} \, \mathrm{Tr}_{\mathrm{I}} \, e^{-(\varepsilon + \varepsilon_{\mathrm{I}})} \; \pi^{-3/2} \int_0^\infty \mathrm{d} \gamma \, e^{-\gamma^2} \gamma^2 \, \gamma' \; \frac{1}{4 \pi} \, \mathrm{d}^2 e \, \mathrm{d}^2 e' \ldots \tag{13}$$

Here ε is the internal energy operator in units of $k \, T$, γ and γ' are the magnitudes of the relative velocities after and before a collision in units of $2 \, k \, T / m_{ij}$, $\boldsymbol{e}'$ and $\boldsymbol{e}$ are unit vectors parallel to the relative linear momentum before and after a collision. In (10) and (13), the subscript "I" refers to the variables of the colliding partner. The quantities a and $a^\dagger$ occurring in $\{ \ldots \}_{(ij)}$ are the scattering amplitude operator and its adjoint for the collision of a particle "i" with a particle "j". For further details on collision integrals e. g. see Reference [4, 8].

Notice that all effective cross sections (10 – 12) vanish for a purely spherical scattering amplitude $a = a_0 (\gamma, \boldsymbol{e} \cdot \boldsymbol{e}')$ where a_0 is a scalar quantity. Hence these cross sections depend on the nonsphericity of the scattering amplitude [10] (and of the molecular interaction potential) in a crucial way.

A Special Model

Next, it is demonstrated that the effective cross section $\sigma_{\mathrm{dv}}^{(12)}$ which is responsible for the coupling between $\langle \boldsymbol{U} \rangle$ and $\boldsymbol{v}_{12}$ can be expected to be nonzero, in general. To this purpose, the simple model scattering amplitude

$$a = a_0 + a_1 \, \boldsymbol{U} \cdot (\boldsymbol{e} - \boldsymbol{e}') \tag{14}$$

is invoked for the scattering of a polar molecule with a nonpolar one. The spherical scattering amplitude a_0 and the coefficient a_1 are scalars. A nonspherical term as in (14) always occurs when the center of mass of a symmetric top molecule does not coincide with its geometric center. In general, additional nonspherical terms, in particular those which induce transitions between the internal energy states of a molecule, have to be taken into account. The simple ansatz (14), however, suffices to show that $\sigma_{\mathrm{dv}}^{(12)} \neq 0$.

Insertion of (14) into (12) yields

$$\sigma_{\mathrm{dv}}^{(12)} = \tfrac{8}{3} \sqrt{2} \, U_0 \{ \gamma (1 - \boldsymbol{e} \cdot \boldsymbol{e}') \, \mathrm{Re} (a_0 \, a_1{}^*) \} \,. \tag{15}$$

A nonsphericity parameter β can be introduced by

$$\mathrm{Re} (a_0 \, a_1{}^*) = \beta \, | a_0 |^2 \,. \tag{16}$$

If β and $| a_0 |^2$ are assumed to be independent of the scattering angle and of γ, (15) reduces to

$$\sigma_{\mathrm{dv}}^{(12)} = \sqrt{2 \pi} \, U_0 \, \beta \, \sigma_0 \tag{17}$$

with the spherical cross section $\sigma_0 = 4 \pi \, | a_0 |^2$. Notice that $\sigma_{\mathrm{dv}}^{(12)}$ and consequently ω_{dv} are linearly proportional to the nonsphericity parameter β.

Diffusio-electric Polarization

After these remarks on collision integrals, the discussion of Eq. (5) is resumed. For a steady state situation the time derivative of $\langle \boldsymbol{U} \rangle$ vanishes. Then Eq. (5) yields $\langle \boldsymbol{U} \rangle \sim \boldsymbol{v}_{12}$. In the hydrodynamic regime, the diffusion velocity obeys the equation

$$\boldsymbol{v}_{12} = -D (x_1 x_2)^{-1} \nabla x_1, \tag{18}$$

where D is the diffusion coefficient. Thus, with the help of Equation (3), the relation (2) is obtained with Γ_{D} now given by

$$\begin{aligned} \Gamma_{\mathrm{D}} &= n_1 d\, U_0 v_0{}^{-1} D\, \omega_{\mathrm{dv}}/\omega_{\mathrm{d}} \\ \cdot &= U_0 d \sqrt{\frac{m_1}{kT}}\, n D x_1 x_2 \sigma_{\mathrm{dv}}^{(12)} \\ &\cdot \left[x_1 \sigma_{\mathrm{d}}^{(11)} + x_2 \sqrt{\frac{m_1+m_2}{m_2}}\ \sigma_{\mathrm{d}}^{(12)} \right]^{-1}. \end{aligned} \tag{19}$$

This is the desired microscopic expression for Γ_{D}. It is recalled that the effective scattering cross sections are linked with the binary scattering amplitude operator by the collision brackets (10 – 12). Notice that Γ_{D} as given by (19) is independent of the total number density $n = n_1 + n_2$ due to $D \sim n^{-1}$.

An estimate of the order of magnitude of the diffusio-electric polarization is of interest. For the magnitude of the nonsphericity parameter β values of 0.01 to 0.1 can certainly be expected. By order of magnitude, one has $\sigma_{\mathrm{d}}^{(11)} \approx \sigma_{\mathrm{d}}^{(12)} \approx \sigma_0$ for gases polar symmetric top molecules. Thus $x_1 \,|\, \omega_{\mathrm{dv}} \,|\, \omega_{\mathrm{d}}{}^{-1} \approx 10^{-3}$ is a reasonable guess for $x_1 \approx x_2 \approx 1/2$. Then, for $\sqrt{m_1/kT}\, n D \approx 10^{15}\,\mathrm{cm}^{-2}$, $U_0 d \approx 1$ Debye, $(x_1 x_2)^{-1} \,|\nabla x_1|\, \approx 1\,\mathrm{cm}^{-1}$,

$$|\boldsymbol{P}| \approx 10^{-6}\,\mathrm{e.s.u.} \mathrel{\hat{=}} 3 \cdot 10^{-4}\,\mathrm{Volt\,cm}^{-1} \tag{20}$$

is found. Hence, the diffusio-electric polarization is of measurable size. Measurements of this type could provide values for $\omega_{\mathrm{dv}}/\omega_{\mathrm{d}}$. In view of the crucial dependence of this quantity on the nonsphericity of the scattering amplitude, its knowledge is of great interest for intermolecular mechanics.

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