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Orientation Polarization. III. Octopolar Systems

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Introduction

The orientation-dependent part of the molecular polarization of a multi-component system is given by the equation [1]

$$P_m^0 = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_\alpha^{(pi)} m_\alpha^{(qj)} \right\rangle, \tag{1}$$

in which N_i is the number of molecules of species i, and $m_\alpha^{(pi)}$ — the α-component of the total electric dipole moment of the molecule p of species i. The brackets $\langle\ \rangle$ in Eq. (1) denote the statistical average defined as follows:

$$\langle \Phi \rangle = \int_{(n)} \dots \int \Phi(\tau^N) P^{(n)}(\tau^n)\, d\tau^n, \tag{2}$$

where $\Phi(\tau^N)$ is an arbitrary function of the variables $\tau^N = (\tau_1, \tau_2, ..., \tau_N)$ describing the configuration of all N molecules of the system. The quantity $P^{(n)}(\tau^n)\, d\tau^n$ is the probability of finding a selected group of n molecules in the configurational element $d\tau^n$. By classical statistical mechanics we have in the case of a system of molecules of various kinds

$$\begin{gathered} x_i \varrho g_i^{(1)}(\tau_p) = N_i P_i^{(1)}(\tau_p), \\ x_i x_j \varrho^2 g_{ij}^{(2)}(\tau_p, \tau_q) = N_i (N_j - 1) P_{ij}^{(2)}(\tau_p, \tau_q), \\ x_i x_j x_k \varrho^3 g_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r) = N_i (N_j - 1)(N_k - 2) P_{ijk}^{(3)}(\tau_p, \tau_q, \tau_r), ..., \end{gathered} \tag{3}$$

wherein $x_i = N_i/N$ is the molar fraction of the i-th component of the system, $\varrho = N/V$ — the density of the system of volume V, and $g_i^{(1)}, g_{ij}^{(2)}, g_{ijk}^{(3)}, ...,$ are the correlation functions for singles, pairs, triples, etc. of unlike molecules, respectively.

In this paper we discuss the application of Eq. (1) to systems consisting of octopolar molecules of different species. The general result for dense systems is thereafter applied to imperfect gas mixtures. Numerical estimations of the second orientation polarization virial coefficient are given for methane.

Dense systems of octopolar molecules

We shall consider a system of unlike molecules which possess only an octopole electric moment defined in general by the tensor

$$\Omega^{(pi)}_{\alpha\beta\gamma} = \frac{1}{2} \sum_n e^{(pi)}_n \{5 r_{pn\alpha} r_{pn\beta} r_{pn\gamma} - r^2_{pn} (r_{pn\alpha} \delta_{\beta\gamma} + r_{pn\beta} \delta_{\gamma\alpha} + r_{pn\gamma} \delta_{\alpha\beta})\}, \tag{4}$$

with $e^{(pi)}_n$ denoting the n-th electric charge of the molecule p of species i, and $\mathbf{r}_{pn}$ — its radius vector.

The α-component of the induced dipole moment of the molecule p of species i due to the electric field of the octopoles of all the other molecules of the system is given by

$$m^{(pi)}_\alpha = -\frac{1}{15} \sum_k \sum_{r=1}^{N_K} a^{(pi)}_{\alpha\beta} T^{(pr)}_{\beta\gamma\delta\varepsilon} \Omega^{(rk)}_{\gamma\delta\varepsilon}, \tag{5}$$

where $a^{(pi)}_{\alpha\beta}$ is the electric polarizability tensor of molecule p of species i and the tensor characterizing the dipole-octopole interaction is of the form ($p \neq r$) [2]

$$\begin{aligned} T^{(pr)}_{\alpha\beta\gamma\delta} = -3 r^{-9}_{pr} \{35 r_{pr\alpha} r_{pr\beta} r_{pr\gamma} r_{pr\delta} - 5 r^2_{pr} (r_{pr\alpha} r_{pr\beta} \delta_{\gamma\delta} + \\ + r_{pr\alpha} r_{pr\gamma} \delta_{\beta\delta} + r_{pr\alpha} r_{pr\delta} \delta_{\beta\gamma} + r_{pr\beta} r_{pr\gamma} \delta_{\alpha\delta} + r_{pr\beta} r_{pr\delta} \delta_{\alpha\gamma} + \\ + r_{pr\gamma} r_{pr\delta} \delta_{\alpha\beta}) + r^4_{pr} (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma})\}, \end{aligned} \tag{6}$$

with r_{pr} denoting the distance between the centres of the p-th and r-th molecules.

By (5), for an octopolar system of arbitrary density, Eq. (1) becomes

$$P^0_m = \frac{4\pi}{2025\, kT} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} a^{(pi)}_{\alpha\beta} a^{(qj)}_{\alpha\gamma} \Omega^{(rk)}_{\delta\varepsilon\eta} \Omega^{(sl)}_{\lambda\mu\nu} T^{(pr)}_{\beta\delta\varepsilon\eta} T^{(qs)}_{\gamma\lambda\mu\nu} \right\rangle. \tag{7}$$

On expanding the right hand side of this equation in the sums relating, respectively, to interacting groups of two, three, ..., molecules (the first sum for $p = q = r = s$ vanishes) we obtain, by Eqs. (3) and averaging over all molecular orientations,

$$P^0_m = \sum_{ij} x_i x_j P^{(ij)}_m + \sum_{ijk} x_i x_j x_k P^{(ijk)}_m + \ldots \tag{8}$$

Here, the quantities $P^{(ij)}_m$ and $P^{(ijk)}_m$ are of the form

$$\begin{aligned} P^{(ij)}_m = \frac{2\pi\varrho^2}{42525\, kT} \{ a^{(i)}_{\alpha\beta} a^{(i)}_{\alpha\beta} \Omega^{(j)}_{\gamma\delta\varepsilon} \Omega^{(j)}_{\gamma\delta\varepsilon} + \\ + a^{(j)}_{\alpha\beta} a^{(j)}_{\alpha\beta} \Omega^{(i)}_{\gamma\delta\varepsilon} \Omega^{(i)}_{\gamma\delta\varepsilon} \} \int\int T^{(pq)}_{\eta\lambda\mu\nu} T^{(pq)}_{\eta\lambda\mu\nu} g^{(2)}_{ij} (\mathbf{r}_p, \mathbf{r}_q)\, d\mathbf{r}_p\, d\mathbf{r}_q, \end{aligned} \tag{9}$$

$$P^{(ijk)}_m = \frac{4\pi\varrho^3}{14175\, kT} a_i a_j \Omega^{(k)}_{\alpha\beta\gamma} \Omega^{(k)}_{\alpha\beta\gamma} \int\int\int T^{(pr)}_{\delta\varepsilon\eta\lambda} T^{(qr)}_{\delta\varepsilon\eta\lambda} g^{(3)}_{ijk} (\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)\, d\mathbf{r}_p\, d\mathbf{r}_q\, d\mathbf{r}_r, \tag{10}$$

where α_i is the mean electric polarizability of the molecule of species i, and by definition of (6) we have

$$(11)\quad T^{(pr)}_{\alpha\beta\delta\gamma} T^{(qs)}_{\alpha\beta\delta\gamma} = 45 r_{pr}^{-9} r_{qs}^{-9} \{245 (\mathbf{r}_{pr} \cdot \mathbf{r}_{qs})^4 - 180 r_{pr}^2 r_{qs}^2 (\mathbf{r}_{pr} \cdot \mathbf{r}_{qs})^2 - 9 r_{pr}^4 r_{qs}^4\}.$$

In particular, for tetrahedral molecules such as CH_4, having a single octopole moment $\Omega \equiv \Omega_{123}$, Eqs. (9) and (10) reduce to:

$$(12)\quad P_m^{(ij)} = \frac{32\pi\varrho^2}{15kT} (\alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2) \int\int r_{pq}^{-10} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q)\, d\mathbf{r}_p\, d\mathbf{r}_q,$$

$$(13)\quad P_m^{(ijk)} = \frac{8\pi\varrho^3}{105kT} \alpha_i \alpha_j \Omega_k^2 \int\int\int \{245 (\mathbf{r}_{pr} \cdot \mathbf{r}_{qr})^4 - 180 r_{pr}^2 r_{qr}^2 (\mathbf{r}_{pr} \cdot \mathbf{r}_{qr})^2 - 9 r_{pr}^4 r_{qr}^4\} r_{pr}^{-9} r_{qr}^{-9} g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)\, d\mathbf{r}_p\, d\mathbf{r}_q\, d\mathbf{r}_r.$$

Application to an imperfect gas mixture

In the case of a not too strongly compressed gas mixture we are justified in restricting ourselves to pairwise correlation for which [3]

$$(14)\quad g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) = e^{-\frac{u_{ij}(r_{pq})}{kT}} \{1 + O(\varrho)\},$$

and (9) yields

$$(15)\quad P_m^{(ij)} = \varrho \{B_P^{(ij)} + O(\varrho)\},$$

where *)

$$(16)\quad B_P^{(ij)} = \frac{16\pi N}{135\, kT} \{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(i)} \Omega_{\gamma\delta\varepsilon}^{(j)} \Omega_{\gamma\delta\varepsilon}^{(j)} + \alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\beta}^{(j)} \Omega_{\gamma\delta\varepsilon}^{(i)} \Omega_{\gamma\delta\varepsilon}^{(i)}\} \int r_{pq}^{-10} e^{-\frac{u_{ij}(r_{pq})}{kT}} d\mathbf{r}_{pq}$$

is the second orientation polarization virial coefficient describing the octopole-induced dipole effect. In Eqs. (14) and (16) $u_{ij}(r_{pq})$ is the central forces potential energy of interaction between molecules p and q of species i and j.

On using for $u_{ij}(r_{pq})$ the following special form of the Lennard-Jones potential [3]

$$(17)\quad u_{ij}(r_{pq}) = 4\varepsilon_{ij} \left\{\left(\frac{\sigma_{ij}}{r_{pq}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{pq}}\right)^6\right\},$$

we obtain from (16)

$$(18)\quad B_P^{(ij)} = \frac{16\pi^2 N}{405\, kT \sigma_{ij}^7 y_{ij}^4} \{\alpha_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(i)} \Omega_{\gamma\delta\varepsilon}^{(j)} \Omega_{\gamma\delta\varepsilon}^{(j)} + \alpha_{\alpha\beta}^{(j)} \alpha_{\alpha\beta}^{(j)} \Omega_{\gamma\delta\varepsilon}^{(i)} \Omega_{\gamma\delta\varepsilon}^{(i)}\} H_{10}(y_{ij}),$$

where ε_{ij} and σ_{ij} are force parameters having the dimension of an energy and length, respectively, H_{10} — a function known in tabulated form [4], and $y_{ij} = 2(\varepsilon_{ij}/kT)^{\frac{1}{2}}$. The force parameters for interactions between unlike and like molecules are related by the empirical combination rules [3]:

$$(19)\quad \sigma_{ij} = \tfrac{1}{2}(\sigma_{ii} + \sigma_{jj}), \qquad \varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}}.$$

*) Note added in Proof. From Eq. (16), in the case of a one-component gas consisting of tetrahedral molceules, we can obtain the result derived by Johnston, Oudemans and Cole (J. Chem. Phys., 33 (1960), 1310).

If the octopolar molecules are symmetric about the 3 principal axis, then $\Omega_3 \equiv \Omega_{333} = -2\Omega_{113} = -2\Omega_{223}$, and $\alpha_3 \equiv \alpha_{33}$, $\alpha_1 \equiv \alpha_{11} = \alpha_{22}$, and (18) assumes the form

$$B_P^{(ij)} = \frac{8\pi^2 N}{27kT\,\sigma_{ij}^7\,y_{ij}^4}\{\alpha_i^2(1+2\varkappa_i^2)\,\Omega_{3j}^2+\alpha_j^2(1+2\varkappa_j^2)\,\Omega_{3i}^2\}\,H_{10}(y_{ij}), \tag{20}$$

where $\varkappa_i = (\alpha_3^{(i)} - \alpha_1^{(i)})/3\alpha_i$ is the electric anisotropy of the molecule of species i.

For tetrahedral molecules Eq. (18) yields

$$B_P^{(ij)} = \frac{32\pi^2 N}{45kT\,\sigma_{ij}^7\,y_{ij}^4}\{\alpha_i^2\,\Omega_j^2+\Omega_i^2\,\alpha_j^2\}\,H_{10}(y_{ij}). \tag{21}$$

The second refractivity virial coefficient of tetrahedral molecules is in the same approximation given by [5]:

$$B_R^{(ij)} = \frac{4\pi^2 N}{9\sigma_{ij}^3\,y_{ij}^4}\left\{\alpha_i\,\alpha_j\left[(\alpha_i+\alpha_j)\,H_6(y_{ij})+2\frac{\alpha_i\,\alpha_j}{\sigma_{ij}^3}H_9(y_{ij})+\dots\right]+\frac{4}{3\sigma_{ij}^4}(\gamma_i\,\Omega_j^2+\Omega_i^2\,\gamma_j)\,H_{10}(y_{ij})+\dots\right\}, \tag{22}$$

where γ_i is the mean hyperpolarizability of the isolated molecule of species i.

In the case of a one-component gas, Eqs. (21) and (22) reduce to

$$B_P = \frac{64\pi^2\,\alpha^2\,\Omega^2\,N}{45kT\,\sigma^7\,y^4}H_{10}(y), \tag{23}$$

$$B_R = \frac{8\pi^2 N}{9\sigma^3\,y^4}\left\{\alpha^3\left[H_6(y)+\frac{\alpha}{\sigma^3}H_9(y)+\dots\right]+\frac{4\gamma\Omega^2}{3\sigma^4}H_{10}(y)+\dots\right\}. \tag{24}$$

For methane we have [2], [5]: $\varepsilon/k = 137°$K, $\sigma = 3.882$ Å, $\alpha = 2.6\times10^{-24}$ cm.^{3}, $\Omega = 12\times10^{-34}$ e.s.u. and $\gamma = 2.6\times10^{-36}$ e.s.u. Using these values and Eqs. (23) and (24) we obtain for $T = 298°$K:

$$B_P = 48\times10^{-24}\ \text{cm.}^6/\text{mol.},\quad B_R = 10\times10^{-24}\ \text{cm.}^6/\text{mol.}$$

Thus, it is seen that the contribution from the orientation octopole-induced dipole effect is about five times larger than that from distortion polarization.

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