

## Orientation Polarization. I. Dipolar Systems

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*Presented by W. RUBINOWICZ on July 10, 1962*

### Introduction

The theory of molecular polarization of dipolar gas mixtures, vapours and infinitely dilute solutions is due to Debye [1]. The theory dealing with the solutions of polar liquids was given by Onsager [2] and developed and modified by Piekara [3], Brown [4], Work [5] and others. Harris and Brush [6] and Buckingham [7] discussed the application of the statistical mechanical theory of dielectric polarization to dilute solutions of polar molecules in a non-polar solvent

In the present paper, the theory of molecular polarization of multi-component systems is discussed on the basis of the statistical theory initiated by Kirkwood [8] and developed by others [9]—[12]. It will be shown that the molecular polarization of a multi-component system can be expressed as follows:

$$(1) \quad P_m = \sum_i x_i P_m^{(i)} + \sum_{ij} x_i x_j P_m^{(ij)} + \sum_{ijk} x_i x_j x_k P_m^{(ijk)} + \dots,$$

where  $x_i$  is the mole fraction of the  $i$ -th component of the system. Since  $P_m^{(i)}$  is the molecular polarization of the  $i$ -th component in the gaseous state, the first term in (1) expresses the additivity of  $P_m$ . The further terms of (1) responsible for the deviations from additivity of  $P_m$  arise from the interactions between the molecules in a dense system. The quantities  $P_m^{(ij)}$  and  $P_m^{(ijk)}$  are here expressed, respectively, by the correlation functions  $g_{ij}^{(2)}$  and  $g_{ijk}^{(3)}$  for pairs and triples of molecules of various species and discussed separately for the cases of: I. Dipolar systems, II. Quadrupolar systems and III. Octopolar systems.

In the case of dense systems,  $P_m^{(ij)}$  and  $P_m^{(ijk)}$  cannot be reduced in general to a form suitable for numerical calculations and for subsequent comparison of Eq. (1) with experimental data. Only in the exceptional case of imperfect but not too dense gases can we confine ourselves to pairwise interaction between the molecules for which, by using an easy though cumbersome procedure,  $P_m^{(ij)}$  can be reduced to a form adapted to numerical evaluations. For this case,  $P_m^{(ij)}$  is calculated for some molecular models of interacting pairs of unlike molecules by means of the tensor

formalism already applied by the author in other papers [13]. In particular, we shall take into account the influence on  $P_m^{(ij)}$  of anisotropy in the polarizability of the molecules as well as of London's anisotropic dispersion forces. It results that the anisotropic-dispersional interactions contribute to  $P_m^{(ij)}$  much more than the dipole-dipole interaction in the one case; albeit, they are still sufficiently strong in the other cases not to be negligible in comparison with the dipole-dipole contribution.

#### General formula for the molecular polarization

Let us consider a macroscopic spherical sample of the isotropic medium of volume  $V$  (molar volume), whose electric permittivity is  $\epsilon$ . The classical statistical mechanical theory yields for the molecular polarization

$$(2) \quad P_m = \frac{\epsilon - 1}{\epsilon + 2} V$$

the following general expression [11]:

$$(3) \quad P_m = \frac{4\pi}{9} \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} + \frac{M_\alpha M_\alpha}{kT} \right\rangle.$$

Here,  $M_\alpha$  is the  $\alpha$ -component of the total electric dipole moment of the sample in the presence of the applied electric field  $E$ , and the brackets  $\langle \rangle$  denote the statistical average at  $E = 0$ .

For a sample containing  $N = \sum_i N_i$  molecules of various species we have

$$(4) \quad M_\alpha = \sum_i \sum_{p=1}^{N_i} m_\alpha^{(pi)},$$

where  $N_i = x_i N$  is the number of molecules of species  $i$ , and  $m_\alpha^{(pi)}$  — the  $\alpha$ -component of the total electric dipole moment of molecule  $p$  of species  $i$  in the medium.

Substitution of (4) into Eq. (3) yields the molecular polarization of a multi-component system as follows:

$$(5) \quad P_m = \frac{4\pi}{9} \left\{ \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial m_\alpha^{(pi)}}{\partial E_\alpha} \right\rangle + \frac{1}{kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_\alpha^{(pi)} m_\alpha^{(qj)} \right\rangle \right\}.$$

The first term in this expression represents the distortion polarization  $P_m^D$ , and the second — the orientation polarization  $P_m^0$ . In certain cases, we are justified in neglecting the difference between the low and high frequency distortion polarizations. Making use of this, the first term in (5) can in good approximation be replaced by the molecular refraction  $R_m$ ,

$$(6) \quad P_m^D = \frac{4\pi}{9} \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial m_\alpha^{(pi)}}{\partial E_\alpha} \right\rangle = R_m.$$

By (6), Eq. (5) may be represented in the form

$$(7) \quad P_m = P_m^D + P_m^0,$$

where

$$(8) \quad P_m^0 = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} m_a^{(pi)} m_a^{(qj)} \right\rangle$$

is the orientational molecular polarization.

The molecular refraction  $R_m$  as given by (6) was discussed for dense mixtures [14] and for imperfect gas mixtures [15] elsewhere. In the present paper we intend to discuss only the orientational molecular polarization as given in general by Eq. (8).

#### Systems of non-polarizable dipolar molecules

For simplicity, we first suppose that the dipolar molecules of the system are non-polarizable,  $m_a^{(pi)} = \mu_a^{(pi)}$ , where  $\mu_a^{(pi)}$  is the  $\alpha$ -component of the permanent electric dipole moment of the isolated molecule  $p$  of species  $i$ . In this case, we obtain from (8) the quantities  $P_m^{(i)}$  and  $P_m^{(ij)}$  of Eq. (1) in the form

$$(9) \quad P_m^{(i)} = \frac{4\pi N}{9kT} \mu_i^2,$$

$$(10) \quad P_m^{(ij)} = \frac{4\pi \rho^2}{9kT} \int \int \mu_a^{(pi)} \mu_a^{(qj)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q,$$

where  $g_{ij}^{(2)}(\tau_p, \tau_q)$  is the correlation function for pairs of molecules of species  $i$  and  $j$ , and  $\rho = N/V$ . The configurational variable  $\tau_p$  consists of the variables  $\mathbf{r}_p$  and  $\omega_p$  determining the position and orientation of the  $p$ -th molecule, respectively.

In the case of systems the molecules of which are mutually independent (perfect gas),  $\Omega^2 g_{ij}^{(2)}(\tau_p, \tau_q) = 1$ , where  $\Omega = \int d\omega$ ; hence, by integration over all possible orientations of the molecules  $P_m^{(ij)} = 0$ , and Eq. (1) goes over into Debye's [1] well-known additive relation:

$$(11) \quad P_m^0 = \sum_i x_i P_m^{(i)} = \frac{4\pi N}{9kT} \sum_i x_i \mu_i^2.$$

For moderately dense systems, the binary correlation function can be expressed as follows:

$$(12) \quad \Omega^2 g_{ij}^{(2)}(\tau_p, \tau_q) = e^{-\frac{u_{ij}(r_{pq}, \omega_p, \omega_q)}{kT}} \{1 + O(\rho)\};$$

herein,  $u_{ij}(r_{pq}, \omega_p, \omega_q)$  is the total potential energy of interaction between a pair of molecules of species  $i$  and  $j$  separated by a distance  $r_{pq}$ .

By the foregoing expression,  $P_m^{(ij)}$  as given by Eq. (10) can be written

$$(13) \quad P_m^{(ij)} = \rho \{B_P^{(ij)} + O(\rho)\},$$

wherein

$$(14) \quad B_p^{(ij)} = \frac{4\pi N}{9kT\Omega^2} \int \int \int \mu_a^{(pt)} \mu_a^{(qt)} e^{-\frac{u_{ij}(r_{pq}, \omega_p, \omega_q)}{kT}} dr_{pq} d\omega_p d\omega_q$$

is the second polarization virial coefficient describing the interactions between two dipolar molecules of species  $i$  and  $j$ .

In the case under consideration here, the total potential energy  $u_{ij}$  is given by

$$(15) \quad u_{ij}(r_{pq}, \omega_p, \omega_q) = u_{ij}(r_{pq}) + \mu_a^{(pt)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(qt)} - \dots,$$

where  $u_{ij}(r_{pq})$  is the central force energy, and the last term — the dipole-dipole energy with the tensor characterizing these interactions of the form

$$(16) \quad T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta});$$

$\delta_{\alpha\beta}$  is the unit tensor (unity for  $\alpha = \beta$  and zero for  $\alpha \neq \beta$ ), and  $p \neq q$ .

If the dipole-dipole energy in (15) is regarded as a perturbation in  $u_{ij}(r_{pq})$ , we obtain from (14)

$$(17) \quad a-a B_p^{(ij)} = \frac{8\pi\mu_i^4 \mu_j^4 N}{675k^4 T^4} \left\{ \langle r_{pq}^{-9} \rangle_{ij} + \frac{8\mu_i^2 \mu_j^2}{49k^2 T^2} \langle r_{pq}^{-15} \rangle_{ij} + \frac{5\mu_i^4 \mu_j^4}{441k^4 T^4} \langle r_{pq}^{-21} \rangle_{ij} + \dots \right\},$$

where we have denoted

$$(18) \quad \langle r_{pq}^{-n} \rangle_{ij} = \int r_{pq}^{-n} e^{-\frac{u_{ij}(r_{pq})}{kT}} dr_{pq}.$$

#### Systems of anisotropically polarizable dipolar molecules

We now assume that the dipolar molecules of the system are anisotropically polarizable in the electric molecular field  $F$ . Let  $\alpha_{\alpha\beta}^{(pt)}$  be the electric polarizability tensor of the  $p$ -th molecule of species  $i$ , so that  $m_a^{(pt)}$  is, at  $E = 0$ ,

$$(19) \quad m_a^{(pt)} = \mu_a^{(pt)} + \alpha_{\alpha\beta}^{(pt)} F_\beta^{(pt)},$$

where

$$(20) \quad F_\beta^{(pt)} = - \sum_k \sum_{r=1}^{N_k} T_{\beta\gamma}^{(pr)} m_\gamma^{(rk)}$$

is the total electric molecular field at the centre of molecule  $p$  of species  $i$  as produced by all the other molecules of the system. From (19) and (20), we obtain

$$(21) \quad F_\beta^{(pt)} = - \sum_k \sum_{r=1}^{N_k} T_{\beta\gamma}^{(pr)} \mu_\gamma^{(rk)} + \sum_{kl} \sum_{r=1}^{N_r} \sum_{s=1}^{N_l} T_{\beta\gamma}^{(pr)} \alpha_{\gamma\delta}^{(rk)} T_{\delta\epsilon}^{(rs)} \mu_\epsilon^{(sl)} - \dots$$

By (19) and (21), Eq. (8) can be written in the form

$$(22) \quad P_m^0 = \frac{4\pi}{9kT} \left\{ \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \mu_a^{(pi)} \mu_a^{(qj)} \right\rangle - \right. \\ \left. - \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} (\mu_a^{(pi)} \alpha_{\alpha\beta}^{(qj)} T_{\beta\gamma}^{(qr)} \mu_\gamma^{(rk)} + \mu_a^{(qj)} \alpha_{\alpha\beta}^{(pi)} T_{\beta\gamma}^{(pr)} \mu_\gamma^{(rk)}) \right\rangle + \right. \\ \left. + \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} (\mu_a^{(pi)} \alpha_{\alpha\beta}^{(qj)} T_{\beta\gamma}^{(qr)} \alpha_{\gamma\delta}^{(rk)} T_{\delta\epsilon}^{(rs)} \mu_\epsilon^{(sl)} + \right. \right. \\ \left. \left. + \alpha_{\alpha\beta}^{(pi)} T_{\beta\gamma}^{(pr)} \mu_\gamma^{(rk)} \alpha_{\alpha\delta}^{(qj)} T_{\delta\epsilon}^{(qs)} \mu_\epsilon^{(sl)} + \mu_a^{(qj)} \alpha_{\alpha\beta}^{(pi)} T_{\beta\gamma}^{(pr)} \alpha_{\gamma\delta}^{(rk)} T_{\delta\epsilon}^{(rs)} \mu_\epsilon^{(sl)}) \right\rangle - \dots \right\}.$$

This expression may be represented in the form of Eq. (1) with  $P_m^{(i)}$  given by (9). The quantities  $P_m^{(ij)}$  and  $P_m^{(ijk)}$  are in general of a very complicated form and in the special case of correlation functions not dependent on the orientations of the molecules are given as follows:

$$(23) \quad P_m^{(ij)} = \frac{4\pi\varrho^2}{9kT} \{ \alpha_i^2 (1 + 2\kappa_i^2) \mu_j^2 + 2\alpha_i \alpha_j [(1 + 2\kappa_i) \mu_i^2 + (1 + 2\kappa_j) \mu_j^2] + \\ + \alpha_j^2 (1 + 2\kappa_j^2) \mu_i^2 \} \int \int r_{pq}^{-6} g_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q,$$

$$(24) \quad P_m^{(ijk)} = \frac{4\pi\varrho^3}{9kT} (\alpha_i \alpha_j \mu_k^2 + \alpha_j \alpha_k \mu_i^2 + \alpha_k \alpha_i \mu_j^2) \times \\ \times \int \int \int \{ 3(\mathbf{r}_{pr} \cdot \mathbf{r}_{qr})^2 - r_{pr}^2 r_{qr}^2 \} r_{pr}^{-5} r_{qr}^{-5} g_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r,$$

where  $g_{ij}^{(2)}$  and  $g_{ijk}^{(3)}$  are the binary and ternary correlation functions, and  $\alpha_i = (\alpha_{33}^{(i)} + 2\alpha_{11}^{(i)})/3$  and  $\kappa_i = (\alpha_{33}^{(i)} - \alpha_{11}^{(i)})/3\alpha_i$  are the mean polarizability and the anisotropy of polarizability of an axially symmetric molecule of species  $i$ .

In the case of an imperfect gas mixture, by (12), (13) and (22), the second polarization virial coefficient is given as follows (terms of order  $\alpha^2$  are omitted):

$$(25) \quad B_P^{(ij)} = \frac{4\pi N}{9kT\Omega^2} \int \int \int \{ \mu_a^{(pi)} \mu_a^{(qj)} - (\mu_a^{(pi)} \alpha_{\alpha\beta}^{(pi)} \mu_\gamma^{(qj)} + \mu_a^{(pi)} \alpha_{\alpha\beta}^{(qj)} \mu_\gamma^{(pi)} + \\ + \mu_a^{(qj)} \alpha_{\alpha\beta}^{(pi)} \mu_\gamma^{(qj)} + \mu_a^{(qj)} \alpha_{\alpha\beta}^{(qj)} \mu_\gamma^{(pi)}) T_{\beta\gamma}^{(pq)} + \dots \} e^{-\frac{u_{ij}(r_{pq}, \omega_p, \omega_q)}{kT}} d\mathbf{r}_{pq} d\omega_p d\omega_q.$$

The total potential energy  $u_{ij}$  is now given by [13]

$$(26) \quad u_{ij}(r_{pq}, \omega_p, \omega_q) = u_{ij}(r_{pq}) + \mu_a^{(pi)} T_{\alpha\beta}^{(pq)} \mu_\beta^{(qj)} - \frac{1}{2} (\alpha_{\alpha\beta}^{(pi)} \mu_\gamma^{(qj)} \mu_\delta^{(qj)} + \\ + \alpha_{\alpha\beta}^{(qj)} \mu_\gamma^{(pi)} \mu_\delta^{(pi)}) T_{\alpha\gamma}^{(pq)} T_{\beta\delta}^{(pq)} - \frac{h\nu_i \nu_j}{4(\nu_i + \nu_j)} (\alpha_{\alpha\beta}^{(pi)} \alpha_{\gamma\delta}^{(qj)} - \alpha_i \alpha_j \delta_{\alpha\beta} \delta_{\gamma\delta}) T_{\alpha\gamma}^{(pq)} T_{\beta\delta}^{(pq)} - \dots,$$

where the third term is the dipole-induced dipole energy and the last one — the anisotropic dispersion energy ( $\nu_i$  is the frequency of electron oscillations of a molecule of species  $i$ , and  $h$  — the Planck constant).

With (26) for  $u_{ij}$ , Eq. (25) can be written as follows:

$$(27) \quad B_P^{(ij)} = a_{-a} B_P^{(ij)} + a_{-ia} B_P^{(ij)} + a_{-ia}^{\text{anis}} B_P^{(ij)} + a_{\text{anis-disp}} B_P^{(ij)}.$$

Here, the first contribution to  $B_P^{(ij)}$  resulting from the dipole-dipole interaction is again given by (17), and the second one, deriving from the dipole-induced dipole interaction between isotropically polarizable dipolar molecules, by

$$(28) \quad a_{-ia} B_P^{(ij)} = \frac{8\pi\mu_i^2\mu_j^2N}{27k^2T^2} \left\{ (\alpha_i + \alpha_j) \left( \langle r_{pq}^{-6} \rangle_{ij} + \frac{6\mu_i^2\mu_j^2}{25k^2T^2} \langle r_{pq}^{-12} \rangle_{ij} + \dots \right) + \right. \\ \left. + \frac{2}{5kT} (\alpha_i\mu_j^2 + \mu_i^2\alpha_j) \left( \langle r_{pq}^{-9} \rangle_{ij} + \frac{12\mu_i^2\mu_j^2}{35k^2T^2} \langle r_{pq}^{-15} \rangle_{ij} + \dots \right) + \dots \right\}.$$

The last two terms in (27) appear only if we assume the dipolar molecules to be anisotropically polarizable. These terms originate from dipole-induced dipole and anisotropic dispersive interactions and, in the case of axially symmetric molecules, are determined by

$$(29) \quad a_{-ia}^{\text{anis}} B_P^{(ij)} = \frac{16\pi\mu_i^2\mu_j^2N}{27k^2T^2} \left\{ (\alpha_i\kappa_i + \alpha_j\kappa_j) \left( \langle r_{pq}^{-6} \rangle_{ij} + \frac{6\mu_i^2\mu_j^2}{25k^2T^2} \langle r_{pq}^{-12} \rangle_{ij} + \dots \right) + \right. \\ \left. + \frac{4}{25kT} (\alpha_i\kappa_i\mu_j^2 + \mu_i^2\alpha_j\kappa_j) \left( \langle r_{pq}^{-9} \rangle_{ij} + \frac{24\mu_i^2\mu_j^2}{49k^2T^2} \langle r_{pq}^{-15} \rangle_{ij} + \dots \right) + \dots \right\},$$

$$(30) \quad a_{\text{anis-disp}} B_P^{(ij)} = \frac{4\pi\alpha_i\alpha_j}{75k^2T^2} \left( \frac{h\nu_i\nu_j}{\nu_i + \nu_j} \right) \left\{ [\alpha_i\mu_j^2(5\kappa_i + 5\kappa_i^2 - \kappa_i^2\kappa_j) + \right. \\ \left. + \alpha_j\mu_i^2(5\kappa_i + 5\kappa_j^2 - \kappa_i\kappa_j^2)] \langle r_{pq}^{-9} \rangle_{ij} + \frac{\mu_i^2\mu_j^2}{3kT} \left[ (5\kappa_i - \kappa_i\kappa_j + 5\kappa_j) \langle r_{pq}^{-9} \rangle_{ij} + \right. \right. \\ \left. \left. + (\alpha_i + \alpha_j + 2\alpha_i\kappa_i + 2\alpha_j\kappa_j) (5\kappa_i + 19\kappa_i\kappa_j + 5\kappa_j) \langle r_{pq}^{-12} \rangle_{ij} + \right. \right. \\ \left. \left. + \frac{6\mu_i^2\mu_j^2}{49k^2T^2} (63\kappa_i + 65\kappa_i\kappa_j + 63\kappa_j) \langle r_{pq}^{-15} \rangle_{ij} + \dots \right] + \dots \right\}.$$

#### Numerical estimations and discussion

If  $u_{ij}(r_{pq})$  is the Lennard—Jones potential of the form:

$$(31) \quad u_{ij}(r_{pq}) = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{pq}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{pq}} \right)^6 \right\},$$

then

$$(32) \quad \langle r_{pq}^{-n} \rangle = \frac{\pi\sigma_{ij}^{3-n}}{3y_{ij}^4} H_n(y_{ij}),$$

where the functions  $H_n(y_{ij})$  are those tabulated by Buckingham and Pople [16], and  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are force parameters having the dimensions of an energy and length, respectively, and  $y_{ij} = 2(\varepsilon_{ij}/kT)^{1/2}$ .

With expression (32), we are able to evaluate the contributions to  $B_P^{(ij)}$  calculated above, provided we know the values of  $\varepsilon_{ij}$  and  $\sigma_{ij}$  and those of the remaining molecular parameters such as  $\alpha_i$  and  $\mu_i$  of the gas in question. For the sake of simplicity we shall carry out the evaluation for a one-component dipolar gas. In this case, on the basis of the formulae (17), (28)–(30) and (32), we get

$$(33) \quad a_{-d}B_P = \frac{\pi^2 \sigma^6 d^4 y^4 N}{64800} \left\{ H_9(y) + \frac{d^2 y^4}{98} H_{15}(y) + \frac{5d^4 y^8}{112896} H_{21}(y) + \dots \right\},$$

$$(34) \quad a_{-id}B_P = \frac{\pi^2 \sigma^3 ad^2 N}{81} \left\{ H_6(y) + \frac{dy^2}{10} H_9(y) + \right. \\ \left. + \frac{3d^2 y^4}{200} H_{12}(y) + \frac{3d^3 y^6}{1400} H_{15}(y) + \dots \right\},$$

$$(35) \quad a_{-id}^{anis}B_P = \frac{2\pi^2 \sigma^3 \alpha \kappa d^2 N}{81} \left\{ H_6(y) + \frac{dy^2}{25} H_9(y) + \right. \\ \left. + \frac{3d^2 y^4}{200} H_{12}(y) + \frac{3d^3 y^6}{2450} H_{15}(y) + \dots \right\},$$

$$(36) \quad a_{anis-disp}B_P = \frac{4\pi^2 \sigma^3 \kappa d N}{675} \left\{ a \left[ (5 + 5\kappa - \kappa^2) H_9(y) + \right. \right. \\ \left. \left. + \frac{dy^2}{12} (1 + 2\kappa) (10 + 19\kappa) H_{12}(y) \right] + \frac{\sigma^3 dy^2}{24} \left[ (10 - \kappa) H_9(y) + \right. \right. \\ \left. \left. + \frac{3d^2 y^4}{392} (126 + 65\kappa) H_{15}(y) \right] + \dots \right\},$$

where  $d = \mu^2/\varepsilon\sigma^3$ . The expressions (33) and (34) correspond to the result obtained by Buckingham and Pople [11] for isotropically polarizable dipolar molecules.

For chloroform, the following figures are valid [15]:  $\varepsilon/k = 327^\circ\text{K}$ ,  $\sigma = 5.43 \text{ \AA}$ ,  $\alpha = 8.23 \times 10^{-24} \text{ cm}^3$ ,  $\kappa = -0.09$ , and  $\mu = 1.05 \times 10^{-18} \text{ e.s.u.}$  Thus, on the basis of (33)–(36), we get for  $T = 298^\circ\text{K}$ :

$$a_{-d}B_P = 0.01 \times 10^{-24} \text{ cm}^6/\text{mol.}, \quad a_{-id}^{is}B_P = 353 \times 10^{-24} \text{ cm}^6/\text{mol.}, \\ a_{-id}^{anis}B_P = -63 \times 10^{-24} \text{ cm}^6/\text{mol.}, \quad a_{anis-disp}B_P = -318 \times 10^{-24} \text{ cm}^6/\text{mol.}$$

It follows from the foregoing evaluation that the contribution to  $B_P$  originating from dipole-dipole interaction is entirely negligible as compared with the contributions from dipole-induced dipole and anisotropic-dispersional interactions. The contribution from the anisotropy in polarizability amounts to about 18% of the value of  $a_{-id}^{is}B_P$ .

For  $\text{CH}_3\text{F}$ , using the values [15]  $\epsilon/k = 196^\circ\text{K}$ ,  $\sigma = 3.37 \text{ \AA}$ ,  $\alpha = 2.6 \times 10^{-24} \text{ cm}^3$ ,  $\kappa = 0.11$  and  $\mu = 1.82 \times 10^{-18} \text{ e.s.u.}$ , we get from (33)—(36):

$$\begin{aligned} \bar{a}-\bar{a}B_P &= 3270 \times 10^{-24} \text{ cm}^6/\text{mol}, & \bar{a}-\bar{a}^{is}B_P &= 5906 \times 10^{-24} \text{ cm}^6/\text{mol}, \\ \bar{a}-\bar{a}^{anis}B_P &= 1295 \times 10^{-24} \text{ cm}^6/\text{mol}, & \bar{a}-\bar{a}^{anis-disp}B_P &= 2408 \times 10^{-24} \text{ cm}^6/\text{mol}. \end{aligned}$$

In this case, the main contribution to  $B_P$  arises from dipole-dipole and dipole-induced dipole interactions; nevertheless, the contribution of the anisotropic-dispersional interactions is not negligible.

We conclude that the influence of the anisotropy in polarizability and, in particular, of the anisotropic-dispersional interactions on the second polarization virial coefficient can be quite large and cannot be neglected.

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