

# THE ROLE OF MOLECULAR MULTIPOLE INTERACTIONS IN THE ELECTRIC POLARIZATION OF MULTI-COMPONENT SYSTEMS

## II. ORIENTATION POLARIZATION

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Within the framework of the classical statistical theory of isotropic dielectrics, the effect of pairwise and triplet interactions between molecular electric multipoles on the orientational polarization  $P_O$  of a multi-component system is discussed. Applying an adequate tensor formalism, the general form of the contribution to  $P_O$  due to the induction of molecular dipoles by the electric fields deriving from permanent multipoles of neighbouring molecules of the medium is computed in the zeroth approximation of the theory, *i.e.* in the absence of potential energy of tensorial interaction of the electric multipoles. Analogously, as a first approximation of perturbation theory, the additional contributions to  $P_O$  accounting for the effect of the potential energy of tensorial interaction of permanent molecular multipoles on the permanent multipole-induced dipole effect resulting in the zeroth approximation of the theory are computed. Moreover, the effect on  $P_O$  of the anisotropy of the molecular dipolar polarization tensor is calculated. The general results are discussed in detail for systems whose components consist of (i) weakly dipolar molecules, (ii) quadrupolar axially-symmetric or arbitrarily-symmetric molecules, (iii) tetrahedrally-symmetric molecules presenting an octopole and hexadecapole moment, and (iiii) octahedral molecules presenting only a hexadecapole moment. The theory is applied to gaseous mixtures, for which the second virial coefficient of orientational polarization, providing the basis for determining molecular multipole moments of order higher than dipolar, is found.

### 1. Introduction

Part II of our paper is concerned with a detailed discussion of the influence of multipole molecular interactions on the orientational part of the electric polarization which, from Kirkwood's statistical theory (1939), is given by

$$P_O = \frac{4\pi}{9kT} \langle M^2 \rangle. \quad (1.1)$$

We shall concentrate on multi-component systems consisting of weakly dipolar molecules, or non-dipolar ones presenting higher order electric moments, thus a quadrupole, octopole

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or hexadecapole moment. The choice of these systems is linked with the restriction of the mean statistical average of the square of the system's dipole moment  $M^2$  to the zeroth or at the most to the first approximation of classical perturbation calculus

$$\langle M^2 \rangle = \langle M^2 \rangle_0 - \frac{1}{kT} \{ \langle M^2 V_t \rangle_0 - \langle M^2 \rangle_0 \langle V_t \rangle_0 \}, \quad (1.2)$$

wherein the total potential energy of tensorial interaction between the molecular electric multipoles,  $V_t$ , is the perturbing potential.

It is generally known that in dealing with a system of  $N$  identical permanent molecular dipoles  $\mu$  non-polarizable in the electric field of neighbouring molecules we obtain in the zeroth approximation *i.e.* in the absence of angular molecular correlations

$$\langle M^2 \rangle_0 = N\mu^2; \quad (1.3)$$

this result together with Eq. (1.1) yields the well-known formula derived by Debye for a dipolar gas. Debye's formula, which describes polarization in its dependence only on the square of the molecular dipole moments, their number and the temperature of the system  $T$ , has for many years provided the basis of a simple method of determining the values of molecular electric dipoles.

It can be asked whether the effect of electric orientational polarization of an isotropic medium can also provide information on molecular electric moments of higher orders. Several papers published in the course of the last ten years have answered this question in the affirmative.

However, since this case involves no direct orientation of molecular moments of order higher than dipoles under the influence of the externally applied electric field, the systems under investigation cannot be rarefied to such an extent as to preclude angular molecular correlations (which is the prerequisite for applicability of Debye's method of determining molecular dipoles); condensation of the molecules has rather to be such as to admit of the presence of interactions of the tensorial type between them. These interactions will then lead to an effect consisting in the fact that, in any given molecule of the medium, a dipole moment is induced by the electric field of the permanent electric multipoles of the neighbouring molecules in the medium. Thus, even in the case of molecules possessing no permanent dipolar moment we obtain in the zeroth approximation the corresponding contributions to  $P_0$ , since  $\langle M^2 \rangle_0 \neq 0$ . Accordingly, if the molecules present a permanent quadrupole moment  $\Theta$  and isotropic polarizability  $\alpha$  and are distant by  $r$ , we come to the formula

$$\langle M^2 \rangle_0 = 3\alpha^2\Theta^2 N \varrho \langle r^{-8} \rangle_R \quad (1.4)$$

containing the mean value

$$\langle r^{-n} \rangle_R = \int r^{-n} g(r) d\mathbf{r} \quad (1.5)$$

to be computed by means of the radial distribution function  $g(r)$ , with  $\varrho = N/V$  denoting the average number of molecules.

If the gas is condensed to the extent that only pairwise correlations appear, we have  $g(r) = \exp\left\{-\frac{u(r)}{kT}\right\}$ . Consequently, if the form of the energy  $u(r)$  of central interaction of a pair is known, we are able to compute the radial mean values of Eq. (1.5) and, if  $\alpha$  is known, we can determine numerically the quadrupole moment  $\Theta$  of the molecules from Eqs (1.1) and (1.4) and the appropriate experimental data for  $P_O$ . The effect in question, consisting in the induction of molecular dipoles by permanent molecular quadrupoles, was first discussed quantitatively in the theory of the dielectric permittivity of real gases by Buckingham and Pople (1955) as well as by Zwanzig (1956), who applied it for determining molecular quadrupoles (also, see Jansen 1958, Johnston and Cole 1962, Birnbaum and Maryott 1962).

Johnston, Oudemans and Cole (1960) showed that a similar effect takes place in gases such as methane, whose molecules possess a permanent octopole moment  $\Omega$  and are able to induce a dipole moment in neighbouring molecules leading, in the zeroth approximation, to the value (see also Kielich 1962)

$$\langle M^2 \rangle_0 = \frac{48}{5} \alpha^2 \Omega^2 N_Q \langle r^{-10} \rangle_R. \quad (1.6)$$

From this formula and appropriate measurements of  $P_O$ , we can determine the value of  $\Omega$  for tetrahedral molecules; thus, *e.g.* in the case of methane measurements by Johnston *et al.* (1960) yielded (Kielich 1963)  $\Omega_{\text{CH}_4} = 6 \times 10^{-34}$  e.s.u. cm<sup>3</sup>, which is a wholly reasonable figure.

Theoretically, analogous effects due to molecular moments of higher orders are possible. Numerically, however, they are negligible; we can hardly hope to detect any such effect, unless it be in a gas such as SF<sub>6</sub> whose octahedrally symmetric molecules possess a permanent hexadecapolar moment  $\Phi$  and induce dipoles in their neighbours, yielding the non-zero contribution (Kielich 1964)

$$\langle M^2 \rangle_0 = \frac{240}{7} \alpha^2 \Phi^2 N_Q \langle r^{-12} \rangle_R. \quad (1.7)$$

The above considerations show that the zeroth approximation of the theory of dielectric polarization provides a simple means of determining molecular electric multipoles of the respective order. The method loses much of its simplicity if we have to take into consideration other contributions to  $P_O$ , as *e.g.* the anisotropy of dipolar polarization of the molecules, or higher ones which appear in the first approximation of the theory *i.e.* when  $M^2$  in accordance with the expansions (1.2) contains contributions dependent on  $T^{-1}$ . Thus *e.g.* in the case of quadrupolar isotropically polarizable molecules we have by (1.2) to within the first approximation (see Johnston and Cole 1962, Kielich 1962)

$$\langle M^2 \rangle = 3\alpha^2 \Theta^2 N_Q \left\{ \langle r^{-8} \rangle_R + \frac{2\Theta^2}{5kT} \langle r^{-13} \rangle_R \right\}. \quad (1.8)$$

These complications mostly concern cases when the molecules are quadrupolar, since it is only in such cases that the first approximation yields a thus non-negligible contribution

to  $P_O$ . In dealing with higher order molecular moments (octopoles, *etc.*) there is generally no need to proceed beyond the zeroth approximation of the theory, and further approximations can be neglected.

In this paper, within the framework of classical statistical electric polarization theory, we will compute the above-mentioned effects for dense multi-component systems. The molecules of the systems will be considered to possess arbitrary symmetry as well as electric multipoles of arbitrary order (dipoles, quadrupoles, octopoles, hexadecapoles, and so forth), and multipolar interactions will be described by means of Jansen's tensor formalism. The theory thus generally formulated can be applied to a wide range of vastly differing special cases beyond the one-component systems mostly discussed hitherto, comprising two-, three-component systems and the like. The results applied to gaseous, not excessively condensed mixtures allow *i.a.* to glean information concerning interactions between the induced dipole of an atom or molecule of one kind and the permanent electric moments of various orders of molecules belonging to other components.

## 2. Fundamental equation for the orientation polarization

The statistical theory of electric polarization of an isotropic medium leads to the following equation for the orientational polarization

$$P_O = \frac{4\pi}{9kT} \langle \mathbf{M} \cdot \mathbf{M} \rangle, \quad (2.1)$$

where  $\mathbf{M}$  is the total electric dipole moment of a macroscopic spherical sample of the medium, and the symbol  $\langle \ \rangle$  stands for classical statistical averaging in the absence of an externally applied electric field.

In the general case, the total dipolar moment of a medium not subjected to an external electric field will consist of  $\mathbf{M}_{\text{perm}}$ , the sum of the permanent dipole moments of the molecules in the sphere, and  $\mathbf{M}_{\text{ind}}$ , the sum of the dipole moments induced in the various molecules by the electric fields of the remaining molecules of the sphere:

$$\mathbf{M} = \mathbf{M}_{\text{perm}} + \mathbf{M}_{\text{ind}}. \quad (2.2)$$

If, quite generally, the spherical sample contains  $N_1$  molecules of the first species,  $N_2$  of the second, ..., and  $N_i$  of the  $i$ -th species, we have

$$\mathbf{M}_{\text{perm}} = \sum_i \sum_{p=1}^{N_i} \boldsymbol{\mu}_{pi}, \quad (2.3)$$

where  $\boldsymbol{\mu}_{pi}$  is the permanent dipole moment of the  $p$ -th molecule of species  $i$  in the absence of intermolecular interactions within the sphere, thus representing the permanent moment of the isolated molecule.

Similarly to what has been done in (2.3), we can express the induced moment of the spherical sample which, in the first approximation, is of the form

$$\mathbf{M}_{\text{ind}} = \sum_i \sum_{p=1}^{N_i} \boldsymbol{\alpha}_{pi} \cdot \mathbf{F}_{pi} \quad (2.4)$$

with  $\alpha_{pi}$  denoting the tensor defining the dipolar electric polarizability of the  $p$ -th molecule of species  $i$  due to the electric field  $\mathbf{F}_{pi}$ , arising from the electric charges of the remaining molecules of the medium. In the general case, the molecular field  $\mathbf{F}_{pi}$  is of a complicated form; however, on restricting ourselves to the part due to the permanent molecular electric multipoles, it can be expressed by the following formula (Jansen 1958, Kielich 1965):

$$\mathbf{F}_{pi} = \sum_j \sum_{q=1}^{N_j} \sum_{m=1}^{\infty} (-1)^m \frac{2^m m!}{(2m)!} {}^{(1)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qj}^{(m)}, \quad (2.5)$$

wherein

$${}^{(1)}\mathbf{T}_{pq}^{(m)} = -\nabla^{m+1} \left( \frac{1}{r_{pq}} \right), \quad p \neq q \quad (2.6)$$

is the tensor of interaction between the electric dipole induced in the  $p$ -th molecule and the  $2^m$ -pole permanent electric moment  $\mathbf{M}_{qj}^{(m)}$  of the  $q$ -th molecule of species  $j$  distant by  $r_{pq}$  from the  $p$ -th molecule (the explicit definition is to be found in Appendix A);  $\nabla$  is a differential operator directed from molecule  $q$  to  $p$ ; while the symbol  $[m]$  in Eq. (2.5) denotes  $m$ -fold contraction of two tensors of order  $m$ .

If, in particular, the medium consists of molecules presenting no permanent electric dipoles but possessing permanent electric moments of higher orders (higher than 1), the fundamental Equation (2.1), by (2.2) and (2.4), assumes the form

$$P_O = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (\mathbf{F}_{pi} \cdot \alpha_{pi}) \cdot (\alpha_{qj} \cdot \mathbf{F}_{qj}) \right\rangle, \quad (2.7)$$

or explicitly, by (2.5),

$$P_O = \frac{4\pi}{9kT} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} (-1)^{m+1} \frac{2^{n+m} n! m!}{(2n)! (2m)!} \times \right. \\ \left. \times (\mathbf{M}_{rk}^{(n)} [n] {}^{(n)}\mathbf{T}_{qp}^{(1)} \cdot \alpha_{pi}) \cdot (\alpha_{qj} \cdot {}^{(1)}\mathbf{T}_{qs}^{(m)} [m] \mathbf{M}_{sl}^{(m)}) \right\rangle. \quad (2.8)$$

Thus, we have obtained a general formula determining the orientational polarization of systems consisting of molecules presenting permanent electric multipoles of order beyond the first, *i.e.* quadrupoles, octopoles, hexadecapoles, *etc.* We shall discuss this equation in detail later.

In writing Eq. (2.4) we assumed tacitly that the molecular fields acting within the medium are of the first order, *i.e.* that  $\mathbf{F}_{pi} \equiv \mathbf{F}_{pi}^{(1)}$ , and that these cause electric polarization of a molecule as given by its electric polarizability tensor  $\alpha$  of the second rank. In general, however, electric fields of higher orders arise between the polar molecules, thus a field of order two  $\mathbf{F}_{pi}^{(2)}$  or field gradient, one of order three  $\mathbf{F}_{pi}^{(3)}$  or gradient of field gradient, *etc.* and quite generally a field of the  $n$ -th order given by the equation

$$\mathbf{F}_{pi}^{(n)} = \sum_j \sum_{q=1}^{N_j} \sum_{m=1}^{\infty} (-1)^m \frac{2^m m!}{(2m)!} {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] \{ \mathbf{M}_{qj}^{(m)} + \mathbf{P}_{qj}^{(m)} \}, \quad (2.9)$$

wherein

$$\mathbf{P}_{qj}^{(m)} = \sum_{m'=1}^{\infty} \frac{2^{m'} m'!}{(2m')!} {}^{(m)}\mathbf{A}_{qj}^{(m')} [m'] \mathbf{F}_{qj}^{(m')} \quad (2.10)$$

is the  $2^m$ -pole electric moment induced in the  $q$ -th molecule of species  $j$  by the electric field of order  $m'$  of its neighbours,  ${}^{(m)}\mathbf{A}_{qj}^{(m')}$  denoting a tensor of rank  $m+m'$  describing the polarization of the  $2^m$ -pole permanent electric moment of the  $q$ -th molecule of species  $j$  due to the molecular electric field of order  $m'$ .

Taking this into consideration, Eq. (2.4) for the total induced dipole moment of the sphere has to be replaced by the equation

$$\mathbf{M}_{\text{ind}} = \sum_i \sum_{p=1}^{N_i} \mathbf{P}_{pi}^{(1)} = \sum_i \sum_{p=1}^{N_i} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} {}^{(1)}\mathbf{A}_{pi}^{(n)} [n] \mathbf{F}_{pi}^{(n)}, \quad (2.11)$$

which, with regard to (2.9) and (2.10) can be rewritten in a good approximation as follows:

$$\begin{aligned} \mathbf{M}_{\text{ind}} = & \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} (-1)^m \frac{2^{n+m} n! n!}{(2n)!(2m)!} {}^{(1)}\mathbf{A}_{pi}^{(n)} [n] {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qj}^{(m)} + \\ & + \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n'=1}^{\infty} \sum_{m'=1}^{\infty} (-1)^{m+m'} \frac{2^{n+m+n'} n! m! n'! m'!}{(2n)!(2m)!(2n')!(2m')!} \times \\ & \times {}^{(1)}\mathbf{A}_{pi}^{(n)} [n] {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] {}^{(m)}\mathbf{A}_{qj}^{(n')} [n'] {}^{(n')} \mathbf{T}_{qr}^{(m')} [m'] \mathbf{M}_{rk}^{(m')} + \dots \end{aligned} \quad (2.12)$$

Recurring to the expression already derived for the induced dipole moment of the sphere we can calculate, beside the contributions to the orientational polarization  $P_O$  from multipolar molecular interaction as taken into account to within dipolar polarizability  $\alpha \equiv {}^{(1)}\mathbf{A}^{(1)}$  (see Eq. (2.8)), further contributions resulting from the electric polarizabilities of higher orders taken into consideration in the present theory.

In addition to the already discussed direct influence of multipolar interactions upon the total dipole moment  $\mathbf{M}$  of the sphere and thus upon the orientational polarization  $P_O$ , we have to deal with the indirect influence of multipolar interactions arising through statistical averaging of  $M^2$  with the total potential energy  $U(\tau)$  of interaction between the molecules of the system at configuration  $\tau$  in the absence of an external electric field. Indeed, we have by a well-known formula of classical statistical mechanics

$$\langle M^2 \rangle = \frac{\int M^2 \exp \left\{ -\frac{U(\tau)}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau)}{kT} \right\} d\tau}. \quad (2.13)$$

In the general case, the configurational variables  $\tau$  are the set of positional variables of the molecules  $\mathbf{r}^N = \mathbf{r}_1 \dots \mathbf{r}_N$  and their orientational variables  $\omega^N = \omega_1 \dots \omega_N$ . In many cases it is convenient to resolve the total potential energy  $U(\tau) = U(\mathbf{r}, \omega)$ , which in general

is a function of the position and orientation of the  $N$  molecules of the system, into a term  $U^{(0)}(\mathbf{r}^N)$  due to interaction of central type and dependent only on the positional variables  $\mathbf{r}^N$ , and one  $V_t(\mathbf{r}^N, \boldsymbol{\omega}^N)$  due to interactions of non-central type and depending both on the positional and orientational variables of the molecules. Strictly,  $V_t$  is the potential energy of interaction between permanent or induced electric multipoles of molecules that cannot be dealt with as rigid spheres. Obviously, such interaction will in general be of a tensorial nature, leading to a mathematically highly involved form of the energy  $V_t$ . *E.g.* the potential energy of the system due to electrostatic interaction between the  $2^n$ -pole permanent electric moment of one molecule and the  $2^m$ -pole permanent electric moment of another is given as follows (Kielich 1965 a):

$$V_t^{el} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^{m+1} \frac{2^{n+m} n! m!}{(2n)! (2m)!} \mathbf{M}_{pi}^{(n)} [\mathbf{r}^{(n)}] \mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qj}^{(m)}. \quad (2.14)$$

Still more highly complicated mathematical expressions result for the case of the potential energy due to molecular interaction of the inductive type. Naturally, in these circumstances there can be no question of carrying out the calculations of Eq. (2.13) strictly, and we have to recur to approximations. Satisfactory success is achieved by treating the tensorial part of the potential energy  $V_t$  as a small perturbation to the central energy  $U^{(0)}$ , as this allows to replace the exact expression (2.13) by the following approximation:

$$\langle M^2 \rangle = \langle M^2 \rangle_0 - \frac{1}{kT} \{ \langle M^2 V_t \rangle_0 - \langle M^2 \rangle_0 \langle V_t \rangle_0 \} + O(T^{-2}), \quad (2.15)$$

where  $\langle \ \rangle_0$  denotes statistical averaging with the non-perturbed energy of the system  $U^{(0)}$ .

The approximation (2.15) is entirely satisfactory only in cases of systems consisting of molecules which are non-dipolar or weakly dipolar but present higher (quadrupole, octopole, *etc.*) electric moments. By this relatively simple approach, we are able to compute numerically the additional effect of multipole interactions on  $M^2$  as explicitly dependent on the temperature. Further approximations, more strongly dependent on the temperature, play an essential part only in the case of strongly dipolar molecules, and have been discussed in detail for gases by Harris and Alder (1953), Buckingham and Pople (1955), and this author (Kielich 1962) (see also Dymond and Smith 1964).

The statistical averaging on the right hand side of Eq. (2.15) can be put as follows:

$$\langle X \rangle_0 = \frac{(N-h)!}{N!} \int_{(h)} \dots \int \overline{X(\mathbf{r}^N)_{n^{(h)}}(\mathbf{r}^h)} d\mathbf{r}^h, \quad (2.16)$$

where

$$\overline{X(\mathbf{r}^N)} = \frac{1}{\Omega^N} \int_{(h)} \dots \int X(\mathbf{r}^N, \boldsymbol{\omega}^N) d\boldsymbol{\omega}^N \quad \text{with} \quad \Omega^N = \int_{(N)} \dots \int d\boldsymbol{\omega}^N \quad (2.17)$$

stands for averaging of the function  $X$  with equal probability over all possible orientations of the molecules.

Into the definition of Eq. (2.16) we have introduced the molecular distribution functions for  $h$  molecules defined as

$$n^{(h)}(\mathbf{r}^h) = \frac{N!}{(N-h)!} P^{(h)}(\mathbf{r}^h), \quad (2.18)$$

where

$$P_{\pm k}^{(h)}(\mathbf{r}^h) = \frac{\int \dots \int_{(N-h)} \exp \left\{ -\frac{U^{(0)}(\mathbf{r}^N)}{kT} \right\} d\mathbf{r}^{N-h}}{\int \dots \int_{(N)} \exp \left\{ -\frac{U^{(0)}(\mathbf{r}^N)}{kT} \right\} d\mathbf{r}^N} \quad (2.19)$$

is the probability of finding a chosen group of  $h$  molecules within the element  $d\mathbf{r}^h$  about the point  $\mathbf{r}^h$ . In the case of a multi-component system, the function (2.18) is replaced by the following molecular distribution functions:

$$\begin{aligned} x_i n_i^{(1)}(\mathbf{r}_p) &= N_i P_i^{(1)}(\mathbf{r}_p), \\ x_i x_j n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) &= N_i (N_j - \delta_{ij}) P_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q), \\ x_i x_j x_k n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) &= N_i (N_j - \delta_{ij}) (N_k - \delta_{ik} - \delta_{jk}) P_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r), \dots \end{aligned} \quad (2.10)$$

with  $x_i = N_i/N$  denoting the molar fraction of the  $i$ -th component. In (2.20),  $n_i^{(1)}$  is a single-molecular distribution function,  $n_{ij}^{(2)}$  a bi-molecular, and  $n_{ijk}^{(3)}$  — a tri-molecular distribution function.

### 3. Contributions to $P_0$ in the zeroth approximation of the theory

We will first compute  $\langle M^2 \rangle$  in the zeroth approximation *i.e.* when the potential energy of tensorial interaction vanishes ( $V_i = 0$ ) and by the expansion (2.15)  $\langle M^2 \rangle$  can be replaced by  $\langle M^2 \rangle_0$ . By the definition (2.16) we now perform the statistical averaging of  $\langle M^2 \rangle_0$  with a distribution function independent of the orientational variables, obviously subsequent to averaging  $M^2$  over all possible orientations with equal probability, as required by the definition (2.17). Thus, with regard to (2.2) we have to compute

$$\langle M^2 \rangle_0 = \langle M_{\text{perm}}^2 \rangle_0 + 2 \langle \mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}} \rangle_0 + \langle M_{\text{ind}}^2 \rangle_0. \quad (3.1)$$

The simplest case that we can consider here is that of molecules having only a permanent dipole moment  $\boldsymbol{\mu}$  non-polarizable in the electric field of neighbouring molecules. With  $\mathbf{M}_{\text{ind}} = 0$  we have the total permanent dipole moment  $\mathbf{M}_{\text{perm}}$  of the sphere given by Eq. (2.3), where by (2.16)

$$\begin{aligned} \langle M_{\text{perm}}^2 \rangle_0 &= \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{\mu}_{pi} \cdot \boldsymbol{\mu}_{qj} \right\rangle_0 = \sum_i x_i \int \mu_{pi}^2 n_i^{(1)}(\mathbf{r}_p) d\mathbf{r}_p + \\ &+ \sum_{ij} x_i x_j \int \int \overline{\boldsymbol{\mu}_{pi} \cdot \boldsymbol{\mu}_{qj}} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q = N \sum_i x_i \mu_i^2, \end{aligned} \quad (3.2)$$



as  $\overline{\boldsymbol{\mu}_{p_i} \cdot \boldsymbol{\mu}_{q_j}} = 0$  for  $p \neq q$ . Our fundamental Equation (2.1) in this special case yields the well-known result of Debye

$$P_O = \frac{4\pi N}{9kT} \sum_i x_i \mu_i^2 = \sum_i x_i P_O^{(i)}, \quad (3.3)$$

which states that the orientational polarization of a system (as a whole) of ideal dipolar components whose molecules do not interact tensorially and possess non-polarizable electric dipoles is an additive quantity of the orientational polarization  $P_O^{(i)}$  of the components.

In the present zeroth approximation of the theory, additional contributions to the foregoing result of Debye will appear only if we assume that the various components of the system undergo mutual polarization by the electric fields of their permanent electric dipoles. We will first take into account polarization of the molecules in the dipolar approximation, assuming for simplicity that, although they possess permanent electric multipoles, their tensor of dipolar polarization is isotropic

$$\boldsymbol{\alpha} = \alpha \mathbf{U}, \quad (3.4)$$

with  $\alpha$  denoting the scalar polarizability, and  $\mathbf{U}$  — the unit tensor. Here, also,  $\mathbf{M}_{\text{ind}} \neq 0$  and we have to compute, in addition to the term in (3.2), the cross term  $\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}}$  as well as  $M_{\text{ind}}^2$ . The general expression (2.12) yields to within the square of the dipolar polarizability of the molecules  $\boldsymbol{\alpha} = {}^{(1)}\mathbf{A}^{(1)}$ ,

$$\begin{aligned} \mathbf{M}_{\text{ind}} = & \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \boldsymbol{\alpha}_{p_i} \cdot {}^{(1)}\mathbf{T}_{pq}^{(n)} [n] \mathbf{M}_{q_j}^{(n)} + \\ & + \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} (-1)^n \frac{2^n n!}{(2n)!} \boldsymbol{\alpha}_{p_i} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)} \cdot \boldsymbol{\alpha}_{q_j} \cdot {}^{(1)}\mathbf{T}_{qr}^{(n)} [n] \mathbf{M}_{rk}^{(n)}. \end{aligned} \quad (3.5)$$

On taking the scalar product of the moments (2.3) and (3.5), and considering (3.4), averaging over all possible orientations of the molecules yields

$$\begin{aligned} \overline{(\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}})_{is}} = & \frac{1}{3} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \alpha_{p_i} \mu_{p_i}^2 \alpha_{q_j} {}^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)} + \\ & + \frac{1}{3} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} \mu_{p_i}^2 \alpha_{q_j} \alpha_{rk} {}^{(1)}\mathbf{T}_{pr}^{(1)} : {}^{(1)}\mathbf{T}_{rq}^{(1)}. \end{aligned} \quad (3.6)$$

As shown in Appendix A, we have

$${}^{(1)}\mathbf{T}_{pr}^{(1)} : {}^{(1)}\mathbf{T}_{rq}^{(1)} = 3r_{pr}^{-5} r_{rq}^{-5} \{3(\mathbf{r}_{pr} \cdot \mathbf{r}_{rq})^2 - r_{pr}^2 r_{rq}^2\}, \quad (3.7)$$

so that by the definition of Eq. (2.16) and considering the distribution functions (2.20), Eq. (3.6) goes over into

$$\begin{aligned} \langle \mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}} \rangle &= 2 \sum_{ij} x_i x_j \alpha_i \mu_i^2 \alpha_j \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q + \\ &+ \sum_{ijk} x_i x_j x_k \mu_i^2 \alpha_j \alpha_k \int \int \int r_{pr}^{-5} r_{rq}^{-5} \{3(\mathbf{r}_{pr} \cdot \mathbf{r}_{rq})^2 - r_{pr}^2 r_{rq}^2\} n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \end{aligned} \quad (3.8)$$

Taking the square of (3.5) and neglecting terms containing the dipolar polarizability in powers higher than the square, one obtains

$$\begin{aligned} M_{\text{ind}}^2 &= \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} (-1)^{m+1} \frac{2^{n+m} n! m!}{(2n)!(2m)!} \times \\ &\times (\mathbf{M}_{rk}^{(n)}[n]^{(n)} \mathbf{T}_{rp}^{(1)} \cdot \boldsymbol{\alpha}_{pi}) \cdot (\boldsymbol{\alpha}_{aj} \cdot {}^{(1)}\mathbf{T}_{qs}^{(n)}[m] \mathbf{M}_{sl}^{(m)}), \end{aligned} \quad (3.9)$$

whence, by isotropic averaging,

$$\begin{aligned} \overline{(M_{\text{ind}}^2)_{\text{is}}} &= \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=1}^{\infty} \sum_{\substack{q \neq p \\ q \neq p}} (-1)^{n+1} \frac{2^n (n!)^2}{(2n)!(2n+1)!} \alpha_{pi}^2 (\mathbf{M}_{aj}^{(n)}[n] \mathbf{M}_{qj}^{(n)}) ({}^{(n)}\mathbf{T}_{qp}^{(1)}[n+1] {}^{(1)}\mathbf{T}_{pq}^{(n)}) + \\ &+ \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} \sum_{\substack{q \neq p \\ r \neq p}} (-1)^{n+1} \frac{2^n (n!)^2}{(2n)!(2n+1)!} \alpha_{pi} \alpha_{qj} (\mathbf{M}_{rk}^{(n)}[n] \mathbf{M}_{rk}^{(n)}) ({}^{(n)}\mathbf{T}_{rp}^{(1)}[n+1] {}^{(1)}\mathbf{T}_{qr}^{(n)}). \end{aligned} \quad (3.10)$$

Applying statistical averaging (2.16) and the distribution functions (2.20), as well as the relation (see, Appendix A)

$${}^{(n)}\mathbf{T}_{rp}^{(1)}[n+1] {}^{(1)}\mathbf{T}_{qr}^{(n)} = \frac{(2n+2)!}{2^{n+1}} r_{rp}^{-(n+2)} r_{qr}^{-(n+2)} P_{n+1} \left( \frac{\mathbf{r}_{rp} \cdot \mathbf{r}_{qr}}{r_{rp} r_{qr}} \right), \quad (3.11)$$

we have finally

$$\begin{aligned} \langle M_{\text{ind}}^2 \rangle_0 &= \sum_{ij} x_i x_j \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \alpha_i^2 (\mathbf{M}_j^{(n)}[n] \mathbf{M}_j^{(n)}) \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q + \\ &+ \sum_{ijk} x_i x_j x_k \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \alpha_i \alpha_j (\mathbf{M}_k^{(n)}[n] \mathbf{M}_k^{(n)}) \times \\ &\times \int \int \int r_{pr}^{-(n+2)} r_{rq}^{-(n+2)} P_{n+1} \left( \frac{\mathbf{r}_{pr} \cdot \mathbf{r}_{rq}}{r_{pr} r_{rq}} \right) n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \end{aligned} \quad (3.12)$$

By substitution of (3.1) with the above contributions (3.2), (3.8) and (3.12) into the fundamental Equation (2.1), we can formally represent the orientational polarization of

a multi-component system in the form of a power series in the molar fractions

$$P_O = \sum_i x_i P_O^{(i)} + \sum_{ij} x_i x_j P_O^{(ij)} + \sum_{ijk} x_i x_j x_k P_O^{(ijk)} + \dots, \quad (3.13)$$

where we have introduced the notation

$$P_O^{(i)} = \frac{4\pi N}{9kT} \mu_i^2, \quad (3.14)$$

$$P_O^{(ij)} = \frac{4\pi}{9kT} \iint \left\{ 2\alpha_i \alpha_j (\mu_i^2 + \mu_j^2) r_{pq}^{-6} + \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{2(2n)!} [\alpha_i^2 (\mathbf{M}_j^{(n)}[n] \mathbf{M}_j^{(n)}) + (\mathbf{M}_i^{(n)}[n] \mathbf{M}_i^{(n)} \alpha_j^2) r_{pq}^{-2(n+2)}] n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \right\} \quad (3.15)$$

$$P_O^{(ijk)} = \frac{4\pi}{9kT} \iiint \left\{ 2(\mu_i^2 \alpha_j + \alpha_i \mu_j^2) \alpha_k r_{pr}^{-3} r_{rq}^{-3} P_2 \left( \frac{\mathbf{r}_{pr} \cdot \mathbf{r}_{rq}}{r_{pr} r_{rq}} \right) + \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \alpha_i \alpha_j (\mathbf{M}_k^{(n)}[n] \mathbf{M}_k^{(n)}) r_{pr}^{-(n+2)} r_{rq}^{-(n+2)} P_{n+1} \left( \frac{\mathbf{r}_{pr} \cdot \mathbf{r}_{rq}}{r_{pr} r_{rq}} \right) + \dots \right\} n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \quad (3.16)$$

From the above expressions, the orientational polarization is seen to behave additively in ideal systems only, *i.e.* only if molecular interaction is absent. Dense multi-component systems such as mixtures of real gases, or liquid mixtures, exhibit a deviation from additivity determined in the expansion of (3.13) by terms in the second or third power of the molar fractions. The coefficients  $P_O^{(ij)}$  and  $P_O^{(ijk)}$  of these terms depend respectively on the two-molecule and three-molecule distribution functions and are given in general by the expressions (3.15) and (3.16). The explicit form of these coefficients allows to state that investigation of deviations of  $P_O$  from additivity can be a source *i.a.* of information concerning the electric multipoles of various kinds of molecules.

If the various components of the system consist of molecules having only a permanent dipole moment, Eqs (3.15) and (3.16) reduce to

$$P_O^{(ij)} = \frac{4\pi}{9kT} \{ \alpha_i^2 \mu_j^2 + 2\alpha_i \alpha_j (\mu_i^2 + \mu_j^2) + \mu_i^2 \alpha_j^2 \} \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.17)$$

$$P_O^{(ijk)} = \frac{8\pi}{9kT} \{ \mu_i^2 \alpha_j \alpha_k + \alpha_i \alpha_j \mu_k^2 + \alpha_i \mu_j^2 \alpha_k \} \iiint r_{pr}^{-3} r_{rq}^{-3} P_2 \left( \frac{\mathbf{r}_{pr} \cdot \mathbf{r}_{rq}}{r_{pr} r_{rq}} \right) n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \quad (3.18)$$

Eqs (3.15) and (3.16), when applied to systems of components consisting of molecules having no permanent dipole moment but presenting higher order moments, such as quadrupoles, *etc.*, assume the form

$$P_O^{(ij)} = \frac{2\pi}{9kT} \sum_{n=2}^{\infty} \frac{2^n(n+1)! n!}{(2n)!} \{ \alpha_i^2 (M_j^{(n)}[n] M_j^{(n)}) + (M_i^{(n)}[n] M_i^{(n)}) \alpha_j^2 \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.19)$$

$$P_O^{(ijk)} = \frac{4\pi}{9kT} \sum_{n=2}^{\infty} \frac{2^n(n+1)! n!}{(2n)!} \alpha_i \alpha_j (M_k^{(n)}[n] M_k^{(n)}) \times \int \int \int r_{pr}^{-(n+2)} r_{rq}^{-(n+2)} P_{n+1} \left( \frac{\mathbf{r}_{pr} \cdot \mathbf{r}_{rq}}{r_{pr} r_{rq}} \right) n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \quad (3.20)$$

The expansion (3.13) and coefficients (3.19) and (3.20) indicate that deviations of  $P_O$  from additivity can be due to the presence of an effect consisting in the induction of electric dipoles in molecules of one species by the electric fields of quadrupoles, octopoles, *etc.*, of molecules of another species.

We now proceed to a fuller discussion of Eq. (3.19). Let us first consider the case of molecules of all components possessing the axial symmetry (*e.g.* along the  $z$ -axis of the molecule); we have now

$$M_i^{(n)}[n] M_i^{(n)} = \frac{(2n)!}{2^n (n!)^2} \{M_i^{(n)}\}^2, \quad (3.21)$$

and Eq. (3.19) reduces to

$$P_O^{(ij)} = \frac{2\pi}{9kT} \sum_{n=2}^{\infty} (n+1) \{ \alpha_i^2 (M_j^{(n)})^2 + (M_i^{(n)})^2 \alpha_j^2 \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.22)$$

where  $M_i^{(n)}$  is the  $2^n$ -pole scalar electric moment of an axially-symmetric molecule of species  $i$ .

If, in particular, the molecules possess only the quadrupole moment  $M_i^{(2)} = \Theta_i$ , Eq. (3.22) reduces to the simple formula (Kielich 1962)

$$P_O^{(ij)} = \frac{2\pi}{3kT} (\alpha_i^2 \Theta_j^2 + \Theta_i^2 \alpha_j^2) \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.23)$$

which determines the contribution to  $P_O$  from the effect consisting in the induction, in a given molecule of the medium, of a dipole moment by the electric field of the quadrupoles of its neighbours. This effect had originally been the object of calculations for the case of pure gases by Buckingham and Pople (1955) and by Zwanzig (1956).

The general formula (3.19) can also be applied to molecules whose symmetry is not axial. Indeed, it is applicable to ones of arbitrary symmetry having electric moment of

order  $n \geq 2$ . Expansion of (3.19) up to the term with hexadecapole moment yields

$$\begin{aligned}
 P_O^{(ij)} = & \frac{4\pi}{9kT} \int \int \left\{ [\alpha_i^2(\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)}) + (\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)})\alpha_j^2] r_{pq}^{-8} + \right. \\
 & + \frac{4}{5} [\alpha_i^2(\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) + (\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)})\alpha_j^2] r_{pq}^{-10} + \\
 & \left. + \frac{4}{7} [\alpha_i^2(\mathbf{M}_j^{(4)} : \mathbf{M}_j^{(4)}) + (\mathbf{M}_i^{(4)} : \mathbf{M}_i^{(4)})\alpha_j^2] r_{pq}^{-12} + \dots \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (3.24)
 \end{aligned}$$

This formula can be used *i.a.* in the case of tetrahedrally symmetric molecules (*e.g.*  $\text{CH}_4$ ). Their first non-zero electric moment is octopolar,  $M_{xyz}^{(3)} = \Omega$ , and their next moment is hexadecapolar with component  $M_{xxxx}^{(4)} = \Phi$ . Consequently, for tetrahedral molecules, we have to put

$$\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)} = 0, \quad \mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)} = 6\Omega^2, \quad \mathbf{M}_i^{(4)} : \mathbf{M}_i^{(4)} = 30\Phi^2 \quad (3.25)$$

in Eq. (3.24), leading to the simple formula

$$\begin{aligned}
 P_O^{(ij)} = & \frac{32\pi}{15kT} \int \int \left\{ (\alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2) r_{pq}^{-10} + \right. \\
 & \left. + \frac{25}{7} (\alpha_i^2 \Phi_j^2 + \Phi_i^2 \alpha_j^2) r_{pq}^{-12} \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.26)
 \end{aligned}$$

which, for  $\Phi_i = 0$ , reduces (*i.e.* if we can restrict the problem to the octopole moment only) to a formula derived earlier (Kielich 1962)

$$P_O^{(ij)} = \frac{32\pi}{15kT} \int \int \left\{ \alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2 \right\} r_{pq}^{-10} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (3.27)$$

Eq. (3.27) describes the effect arising in a dense medium owing to each molecule gaining a dipole moment under the influence of the electric fields of octopoles of its neighbours. For a real gas, this effect was first computed by Johnston, Oudemans and Cole (1960) and measured in methane.

Eq. (3.26) or (3.24), in turn, can be applied to molecules of higher symmetry, namely to octahedral molecules, in which case the first non-zero electric moment is hexadecapolar and is of the same form as for tetrahedrally symmetric molecules. Thus, on putting  $\Omega = 0$  in (3.26), we obtain for octahedral molecules such as *e.g.*  $\text{SF}_6$  the formula (*cf.*, Kielich 1964)

$$P_O^{(ij)} = \frac{160\pi}{21kT} \int \int \left\{ \alpha_i^2 \Phi_j^2 + \Phi_i^2 \alpha_j^2 \right\} r_{pq}^{-12} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (3.28)$$

which determines the permanent hexadecapole-induced dipole effect.

Quite similarly, Eq. (3.20) can be discussed for other kinds of molecular symmetry, but we shall refrain here from writing the results obtained in the various cases.

#### 4. Contributions to $P_O$ in the first approximation of the theory

As already mentioned, considering the potential energy of tensorial interaction between the molecules leads to the appearance of further contributions to  $P_O$  which depend explicitly on the temperature. Since we are primarily interested in systems whose components consist of molecules that are non-dipolar but possess higher non-zero electric moments, we may as well restrict our calculations to the first approximation taken into account in the expansion of Eq. (2.15). As now  $\mathbf{M}_{\text{perm}} = 0$  and, as readily seen,  $\langle V_i \rangle_0 = 0$ , we see from the expansion (2.15) that the only term to be computed is  $\langle M_{\text{ind}}^2 V_i \rangle_0$ . Assuming as before that the dipole polarizability tensor is isotropic and given by (3.4) we obtain, on taking the product of the energy (2.14) and the square of the induced moment (3.9) and on averaging over all possible molecular orientations,

$$\begin{aligned} \overline{M_{\text{ind}}^2 V_i} = & \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{n=2}^{\infty} \sum_{m=2}^{\infty} \frac{(-1)^{m+1} 2^{(n+m)} n! m!}{(2n)! (2m)! (2n+1)! (2m+1)!} \alpha_{pi} \alpha_{qj} \times \\ & \times (\mathbf{M}_{pi}^{(n)} [n] \mathbf{M}_{pi}^{(n)}) (\mathbf{M}_{aj}^{(m)} [m] \mathbf{M}_{aj}^{(m)}) \{({}^{(n)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{qp}^{(m)}) [n+m] {}^{(n)}\mathbf{T}_{pq}^{(m)}\} + \dots \end{aligned} \quad (4.1)$$

In the above computation, we have retained only the first non-vanishing term with double sums.

Introducing into (4.1) the definition (2.16) and the relation

$$({}^{(n)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{qp}^{(m)}) [n+m] {}^{(n)}\mathbf{T}_{pq}^{(m)} = \frac{(-1)^m (n+m+1)! (2n)! (2m)!}{2^{n+m} n! m!} r_{pq}^{-(2n+2m+5)}, \quad (4.2)$$

we obtain by (2.1) and (2.15) a new contribution to  $P_O^{(ij)}$  depending on  $T^{-2}$ :

$$\begin{aligned} P_O^{(ij)} = & \frac{4\pi}{9k^2 T^2} \sum_{n=2}^{\infty} \sum_{m=2}^{\infty} \frac{2^{n+m} (n+m+1)! n! m!}{(2n+1)! (2m+1)!} \alpha_i \alpha_j (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) \times \\ & \times (\mathbf{M}_j^{(m)} [m] \mathbf{M}_j^{(m)}) \int \int r_{pq}^{-(2n+2m+5)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \end{aligned} \quad (4.3)$$

On expanding this expression to within the term in octopole moments we have

$$\begin{aligned} P_O^{(ij)} = & \frac{32\pi\alpha_i\alpha_j}{135k^2 T^2} \int \int \left\{ (\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)}) r_{pq}^{-13} + \right. \\ & + \frac{6}{7} [(\mathbf{M}_i^{(2)} : \mathbf{M}_i^{(2)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) + (\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(2)} : \mathbf{M}_j^{(2)})] r_{pq}^{-15} + \\ & \left. + \frac{6}{7} (\mathbf{M}_i^{(3)} : \mathbf{M}_i^{(3)}) (\mathbf{M}_j^{(3)} : \mathbf{M}_j^{(3)}) r_{pq}^{-17} \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \end{aligned} \quad (4.4)$$

If the molecules of all components of the system are axially-symmetric, Eq. (4.3) with regard to the relation (3.21) reduces to

$$\begin{aligned} P_O^{(ij)} = & \frac{4\pi}{9k^2 T^2} \sum_{n=2}^{\infty} \sum_{m=2}^{\infty} \frac{(n+m+1)!}{n! m! (2n+1)! (2m+1)!} \alpha_i \alpha_j (M_i^{(n)})^2 (M_j^{(n)})^2 \times \\ & \times \int \int r_{pq}^{-(2n+2m+5)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \end{aligned} \quad (4.5)$$

which, for the case of molecules having only a permanent quadrupole moment, leads to the simple result

$$P_O^{(ij)} = \frac{8\pi}{15k^2T^2} \alpha_i \alpha_j \Theta_i^2 \Theta_j^2 \iint r_{pq}^{-13} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (4.6)$$

On substituting into (4.4) the relations (3.25) one obtains immediately a result that holds for a system of components with tetrahedrally-symmetric molecules:

$$P_O^{(ij)} = \frac{256\pi}{35k^2T^2} \alpha_i \alpha_j \Omega_i^2 \Omega_j^2 \iint r_{pq}^{-17} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (4.7)$$

In order to take into account here the higher contributions due to the hexadecapole moments possessed by tetrahedral molecules, we would have to apply the general expression (4.3). Also, for octahedral molecules, Eq. (4.3) yields a formula describing the contribution to  $P_O^{(ij)}$  due to the influence of hexadecapole-hexadecapole type interaction on the permanent hexadecapole-induced dipole effect.

### 5. Effect of anisotropy of dipolar polarizability on $P_O$

The calculations of Sections 3 and 4 were based on the assumption of an isotropic tensor  $\alpha$  of dipolar polarizability of the molecules. Obviously, if the latter present permanent electric multipoles, this assumption is valid as a first approximation only, and has to be replaced by one stating that  $\alpha$  is an anisotropic tensor which can be represented as the sum of the isotropic term (3.4) and an anisotropic term  $\alpha^a$

$$\alpha = \alpha U + \alpha^a, \quad (5.1)$$

wherein the tensor  $\alpha^a$  accounting for the anisotropy of dipolar polarizability has the property of vanishing on isotropic averaging; similarly, the trace of  $\alpha^a$  vanishes, *i.e.*  $\alpha^a : U = 0$ .

Our subsequent calculations both in the zeroth and first approximation will be restricted to terms which, ultimately, can be expressed by means of bi-molecular correlation functions. Thus, considering the dipole polarizability tensor in Eq. (3.5) as an anisotropic tensor, one obtains in place of (3.6) the following expression:

$$\overline{\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}}} = \frac{1}{3} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} (\boldsymbol{\mu}_{pi} \cdot \boldsymbol{\alpha}_{pi} \cdot \boldsymbol{\mu}_{pj}) \alpha_{qj}^{(1)} \mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)}, \quad (5.2)$$

which, by (5.1), can be resolved into two parts:

$$\overline{\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}}} = \overline{(\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}})_{\text{is}}} + \overline{(\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}})_{\text{anis}}}. \quad (5.3)$$

The first, which is purely isotropic, is given by the first term of (3.6). The other, purely anisotropic part is expressed as follows:

$$\overline{(\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}})_{\text{anis}}} = 2 \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} (\boldsymbol{\mu}_{pi} \cdot \boldsymbol{\alpha}_{pi}^a \cdot \boldsymbol{\mu}_{pj}) \alpha_{qj}^a r_{pq}^{-6}. \quad (5.4)$$

Similarly, by (3.9) one obtains instead of (3.10) the following result:

$$\begin{aligned} \overline{M_{\text{ind}}^2} &= \frac{1}{3} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \left\{ \frac{1}{75} (\mathbf{M}_{pi}^{(2)} : \boldsymbol{\alpha}_{pi}) (\mathbf{M}_{qj}^{(2)} : \boldsymbol{\alpha}_{qj}) ({}^{(2)}\mathbf{T}_{pq}^{(1)} : {}^{(2)}\mathbf{T}_{pq}^{(1)}) + \right. \\ &+ \left. \sum_{n=1}^{\infty} \frac{(-1)^{n+1} 2^{2n} (n!)^2}{(2n)! (2n+1)!} (\boldsymbol{\alpha}_{pi} : \boldsymbol{\alpha}_{pi}) (\mathbf{M}_{qj}^{(n)}[n] \mathbf{M}_{qj}^{(n)}) ({}^{(n)}\mathbf{T}_{pq}^{(1)}[n+1] ({}^{(1)}\mathbf{T}_{pq}^{(n)})) \right\}, \end{aligned} \quad (5.5)$$

or

$$\overline{M_{\text{ind}}^2} = (\overline{M_{\text{ind}}^2})_{\text{is}} + (\overline{M_{\text{ind}}^2})_{\text{anis}}, \quad (5.6)$$

wherein the first, isotropic term is given by the first term in (3.10) while the second, anisotropic term is given as follows:

$$\begin{aligned} (\overline{M_{\text{ind}}^2})_{\text{anis}} &= -\frac{1}{3} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \left\{ \frac{6}{5} (\mathbf{M}_{pi}^{(2)} : \boldsymbol{\alpha}_{pi}^a) (\mathbf{M}_{qj}^{(2)} : \boldsymbol{\alpha}_{qj}^a) r_{pq}^{-8} - \right. \\ &- \left. \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} (\boldsymbol{\alpha}_{pi}^a : \boldsymbol{\alpha}_{pi}^a) (\mathbf{M}_{qj}^{(n)}[n] \mathbf{M}_{qj}^{(n)}) r_{pq}^{-2(n+2)} \right\}, \end{aligned} \quad (5.7)$$

since  $\mathbf{M}_{pi}^{(2)} : \boldsymbol{\alpha}_{pi} = \mathbf{M}_{pi}^{(2)} : (\boldsymbol{\alpha} \mathbf{U} + \boldsymbol{\alpha}_i^a) = \mathbf{M}_{pi}^{(2)} : \boldsymbol{\alpha}_{pi}^a$  with regard to  $\mathbf{M}_i^{(2)} : \mathbf{U} = 0$ , and  $\boldsymbol{\alpha}_{pi} : \boldsymbol{\alpha}_{pi} = 3\boldsymbol{\alpha}_{pj}^2 + \boldsymbol{\alpha}_{pi}^a : \boldsymbol{\alpha}_{pi}^a$  with regard to  $\mathbf{U} : \mathbf{U} = 3$  and  $\boldsymbol{\alpha}^a : \mathbf{U} = 0$ .

On assembling the above results (5.4) and (5.7) we obtain the following contribution to  $P_O^{(ij)}$  from anisotropy of dipolar polarizability

$$\begin{aligned} \text{anis} P_O^{(ij)} &= \frac{8\pi}{9kT} \iint \left\{ [\boldsymbol{\alpha}_i : (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \boldsymbol{\alpha}_j] r_{pq}^{-6} + \right. \\ &- \frac{1}{5} (\boldsymbol{\alpha}_i^a : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j^a : \boldsymbol{\Theta}_j) r_{pq}^{-8} + \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{12(2n)!} [(\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a) (\mathbf{M}_j^{(n)}[n] \mathbf{M}_j^{(n)}) + \\ &+ (\mathbf{M}_i^{(n)}[n] \mathbf{M}_i^{(n)}) (\boldsymbol{\alpha}_j^a : \boldsymbol{\alpha}_j^a)] r_{pq}^{-2(n+2)} \left. \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \end{aligned} \quad (5.8)$$

wherein by  $\boldsymbol{\Theta}_i = \mathbf{M}_i^{(2)}$  we have denoted the tensor of the quadrupole moment of a molecule of species  $i$ .

If, in particular, the molecules of the various components present a dipole moment only, Eq. (5.8) becomes

$$\begin{aligned} \text{anis} P_O^{(ij)} &= \frac{4\pi}{27kT} \{ (\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a) \mu_j^2 + 6[\boldsymbol{\alpha}_i : (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \boldsymbol{\alpha}_j] + \\ &+ \mu_i^2 (\boldsymbol{\alpha}_j^a : \boldsymbol{\alpha}_j^a) \} \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \end{aligned} \quad (5.9)$$



or, in the case of the axial symmetry,

$$\begin{aligned} \text{anis}P_O^{(ij)} = & \frac{8\pi}{9kT} \{ \alpha_i^2 \mathcal{H}_i^2 \mu_j^2 + 2\alpha_i \alpha_j (\mathcal{H}_i \mu_i^2 + \mu_j^2 \mathcal{H}_j) + \\ & + \mu_i^2 \alpha_j^2 \mathcal{H}_j^2 \} \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \end{aligned} \quad (5.10)$$

since  $\alpha_i^a : \alpha_i^a = 6\alpha_i^2 \mathcal{H}_i^2$  and  $\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i = 2\alpha_i \mathcal{H}_i \mu_i^2$ , with  $\mathcal{H}_i = (\alpha_x^{(i)} - \alpha_x^{(j)})/3\alpha$  standing for the anisotropy of dipolar polarizability of an axially-symmetric molecule of species  $i$ .

By summation of the results (3.17) and (5.10) (see, Kielich 1962) we obtain finally

$$\begin{aligned} P_O^{(ij)} = & \frac{4\pi}{9kT} \{ \alpha_i^2 (1 + 2\mathcal{H}_i^2) \mu_j^2 + 2\alpha_i \alpha_j [(1 + 2\mathcal{H}_i) \mu_i^2 + \mu_j^2 (1 + 2\mathcal{H}_j)] + \\ & + \mu_i^2 \alpha_j^2 (1 + 2\mathcal{H}_j^2) \} \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \end{aligned} \quad (5.11)$$

For molecules presenting a quadrupole moment only, the general formula (5.8) yields

$$\begin{aligned} \text{anis}P_O^{(ij)} = & \frac{4\pi}{135kT} \{ 5(\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a) (\boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) - 6(\boldsymbol{\alpha}_i^a : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j^a : \boldsymbol{\Theta}_j) + \\ & + 5(\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j^a : \boldsymbol{\alpha}_j^a) \} \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \end{aligned} \quad (5.12)$$

whence for axially-symmetric molecules we have

$$\text{anis}P_O^{(ij)} = \frac{4\pi}{15kT} \{ 5\alpha_i^2 \mathcal{H}_i^2 \Theta_j^2 - 6\alpha_i \mathcal{H}_i \Theta_i \alpha_j \mathcal{H}_j \Theta_j + 5\Theta_i^2 \alpha_j^2 \mathcal{H}_j^2 \} \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (5.13)$$

On assembling the results (3.23) and (5.13), we have finally for quadrupolar axially-symmetric molecules<sup>1</sup>

$$\begin{aligned} P_O^{(ij)} = & \frac{2\pi}{15kT} \{ 5\alpha_i^2 (1 + 2\mathcal{H}_i^2) \Theta_j^2 - 12\alpha_i \mathcal{H}_i \Theta_i \alpha_j \mathcal{H}_j \Theta_j + \\ & + 5\Theta_i^2 \alpha_j^2 (1 + 2\mathcal{H}_j^2) \} \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \end{aligned} \quad (5.14)$$

Eq. (5.14) when applied to a single-component gas, yields immediately the result derived by Jansen (1958).

For the general case of quadrupolar molecules of arbitrary symmetry, Eqs (3.24) and (5.12) yield

$$\begin{aligned} P_O^{(ij)} = & \frac{4\pi}{135kT} \{ 5(\boldsymbol{\alpha}_i : \boldsymbol{\alpha}_i) (\boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) - 6(\boldsymbol{\alpha}_i : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j : \boldsymbol{\Theta}_j) + \\ & + 5(\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j : \boldsymbol{\alpha}_j) \} \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \end{aligned} \quad (5.15)$$

<sup>1</sup> In the second part of our previous paper (Kielich 1962), in Eqs (10) and (13) analogous to Eqs (5.14) and (5.15) of this paper as well as in Eqs (8), (16), (19), (21) and (22), the middle term containing the product  $\Theta_i \Theta_j$  was erroneously preceded by the sign + instead of the correct sign minus.

On referring the polarizability tensor  $\alpha$  and quadrupole moment tensor  $\Theta$  to the principle axes of the molecule, one has to put in Eq. (5.15)

$$\begin{aligned}\alpha: \alpha &= 3\alpha^2 + (2/3)(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - \alpha_x\alpha_y - \alpha_y\alpha_z - \alpha_z\alpha_x), \\ \alpha: \Theta &= \alpha_x\Theta_x + \alpha_y\Theta_y + \alpha_z\Theta_z, \quad \Theta: \Theta = \Theta_x^2 + \Theta_y^2 + \Theta_z^2.\end{aligned}\quad (5.16)$$

with  $\alpha_x, \alpha_y, \alpha_z$  and  $\Theta_x, \Theta_y, \Theta_z$  denoting the components of the tensors  $\alpha$  and  $\Theta$  in the directions of the three principle axes  $x, y$  and  $z$ , respectively.

Recurring to the expressions (5.16), we can apply Eq. (5.15) to a one-component gas and after some transformations obtain the result of Johnston and Cole (1962) for ethylene and similar molecules.

We will now calculate the effect of anisotropy upon  $P_O$  within the framework of the first approximation of the theory, restricting ourself for simplicity to the two special cases of 1) molecules presenting only a permanent dipole moment and 2) ones presenting only a permanent quadrupole moment. In the first case, we will carry out our calculations only to within the term linear in  $\alpha$  *i.e.* when by (3.5) we can write

$$\mathbf{M}_{\text{ind}} = - \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \alpha_{pi} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)} \cdot \boldsymbol{\mu}_{qj}.\quad (5.17)$$

Since for the same case Eq. (2.14) yields

$$V_t^{\text{el}} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{\mu}_{pi} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)} \cdot \boldsymbol{\mu}_{qj},\quad (5.18)$$

we obtain, on considering Eq. (2.3),

$$\overline{(\mathbf{M}_{\text{perm}} \cdot \mathbf{M}_{\text{ind}}) V_t^{\text{el}}} = - \frac{1}{9} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} (\boldsymbol{\mu}_{pi} \cdot \alpha_{pi} \cdot \boldsymbol{\mu}_{pi}) \mu_j^2 {}^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)}.\quad (5.19)$$

We thus obtain for  $P_O^{(ij)}$  in the first approximation, taking into account the anisotropy of the tensor  $\alpha$ ,

$$P_O^{(ij)} = \frac{8\pi}{27k^2T^2} \{(\boldsymbol{\mu}_i \cdot \alpha_i \cdot \boldsymbol{\mu}_i) \mu_j^2 + \mu_i^2 (\boldsymbol{\mu}_j \cdot \alpha_j \cdot \boldsymbol{\mu}_j)\} \iint r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q,\quad (5.20)$$

or on assuming axial symmetry of the tensor  $\alpha$ ,

$$P_O^{(ij)} = \frac{8\pi}{27k^2T^2} \{\alpha_i(1+2\mathcal{H}_i) + \alpha_j(1+2\mathcal{H}_j)\} \mu_i^2 \mu_j^2 \iint r_{pq}^{-6} n_{ii}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q\quad (5.21)$$

Similarly, we obtain from Eqs (2.14) and (3.5) for a system of quadrupolar components

$$V_t^{\text{el}} = - \frac{1}{18} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \Theta_{pi} : {}^{(2)}\mathbf{T}_{pq}^{(2)} : \Theta_{qj},\quad (5.22)$$

$$\mathbf{M}_{\text{ind}} = \frac{1}{3} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \alpha_{pi} \cdot {}^{(1)}\mathbf{T}_{pq}^{(2)} : \Theta_{qj},\quad (5.23)$$

so that isotropic averaging in the approximation of pairwise correlations leads to

$$\begin{aligned}
 \overline{M_{\text{ind}}^2 V_{\text{r}}^{\text{el}}} = & \frac{1}{99225} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \{42[(\alpha_{pi} \cdot \alpha_{pi} : \Theta_{pi})(\Theta_{qj} \cdot \Theta_{qj} : \Theta_{qj}) + \\
 & + (\Theta_{pi} \cdot \Theta_{pi} : \Theta_{pi})(\alpha_{qj} \cdot \alpha_{qj} : \Theta_{qj})](^{(2)}T_{qp}^{(1)} \cdot ^{(1)}T_{pq}^{(2)}) : ^{(2)}T_{pq}^{(2)} + \\
 & + [49\alpha_{pi}(\Theta_{pi} : \Theta_{pi})\alpha_{qj}(\Theta_{qj} : \Theta_{qj}) + 14\alpha_{pi}(\Theta_{pi} : \Theta_{pi})(\alpha_{qj}^a : \Theta_{qj} \cdot \Theta_{qj}) + \\
 & + 76(\alpha_{pi}^a : \Theta_{pi} \cdot \Theta_{pi})(\alpha_{qj}^a : \Theta_{qj} \cdot \Theta_{qj}) + 14(\alpha_{pi}^a : \Theta_{pi} \cdot \Theta_{pi})\alpha_{qj}(\Theta_{qj} : \Theta_{qj})] \times \\
 & \times ^{(2)}T_{pq}^{(1)} \cdot ^{(1)}T_{pq}^{(2)} : ^{(2)}T_{pq}^{(2)}\}. \tag{5.24}
 \end{aligned}$$

Now, considering that

$$^{(2)}T_{pq}^{(1)} \cdot ^{(1)}T_{pq}^{(2)} : ^{(2)}T_{pq}^{(2)} = -^{(2)}T_{qp}^{(1)} \cdot ^{(1)}T_{pq}^{(2)} : ^{(2)}T_{pq}^{(2)} = -1080 r_{pq}^{-13}, \tag{5.25}$$

we obtain by (2.1), (2.15) and (5.24)

$$\begin{aligned}
 P_O^{(ii)} = & -\frac{32\pi}{6615 k^2 T^2} \{42(\alpha_i \cdot \alpha_i : \Theta_i)(\Theta_j \cdot \Theta_j : \Theta_j) - 49\alpha_i(\Theta_i : \Theta_i)\alpha_j(\Theta_j : \Theta_j) - \\
 & - 14\alpha_i(\Theta_i : \Theta_i)(\alpha_j^a : \Theta_j \cdot \Theta_j) - 76(\alpha_i^a : \Theta_i \cdot \Theta_i)(\alpha_j^a : \Theta_j \cdot \Theta_j) - 14(\alpha_i^a : \Theta_i \cdot \Theta_i)\alpha_j(\Theta_j : \Theta_j) + \\
 & + 42(\Theta_i \cdot \Theta_i : \Theta_i)(\alpha_j \cdot \alpha_j : \Theta_j)\} \int \int r_{pq}^{-13} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \tag{5.26}
 \end{aligned}$$

On substituting herein the relations

$$(\Theta_i \cdot \Theta_i) : \Theta_i = \frac{3}{4} \Theta_i^3, \quad \alpha_i^a : (\Theta_i \cdot \Theta_i) = \frac{3}{2} \alpha_i \mathcal{H}_i \Theta_i^2, \quad (\alpha_i \cdot \alpha_i) : \Theta_i = 3\alpha_i^2 \mathcal{H}_i (2 + \mathcal{H}_i) \Theta_i, \tag{5.27}$$

one gets for quadrupolar axially-symmetric molecules

$$\begin{aligned}
 P_O^{(ij)} = & -\frac{8\pi \Theta_i \Theta_j^a}{735 k^2 T^2} \{42\alpha_i^2 \mathcal{H}_i (2 + \mathcal{H}_i) \Theta_j^2 - \alpha_i \Theta_i \alpha_j \Theta_j [49 + 14(\mathcal{H}_i + \mathcal{H}_j) + \\
 & + 76\mathcal{H}_i \mathcal{H}_j] + 42\Theta_i^2 \alpha_j^2 \mathcal{H}_j (2 + \mathcal{H}_j)\} \int \int r_{pq}^{-13} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \tag{5.28}
 \end{aligned}$$

With  $\mathcal{H}_i = \mathcal{H}_j = 0$ , this formula reduces to Eq. (4.6) which holds for quadrupolar isotropically polarizable molecules.

## 6. Application to gaseous systems

The formulas derived for  $P_O$  in Sections 3, 4 and 5 will now be applied to not excessively condensed gaseous systems *i.e.* to ones admitting of a binary distribution function  $n_{ij}^{(2)}$  in the form

$$n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) = \rho^2 \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} \{1 + o(\rho)\}, \tag{6.1}$$

in accordance with classical statistical mechanics, with  $\varrho = N/V$  denoting the average number of molecules of the gas and  $u_{ij}$  the potential energy of central interactions between molecules  $p$  and  $q$  of species  $i$  and  $j$ , respectively, distant from one another by  $r_{pq}$ .

By the approximation of Eq. (6.1), the quantities  $P_O^{(ij)}$  appearing in the expansion (3.13) can be represented as follows:

$$P_O^{(ij)} = \varrho \{B_O^{(ij)} + 0(\varrho)\}, \quad (6.2)$$

where  $B_O^{(ij)}$  is the second virial coefficient of orientational polarization describing the interaction of a pair of molecules of species  $i$  and  $j$ .

With regard to (3.13) and (6.2), the total orientational polarization of a mixture of real gases is given by the following expansion:

$$P_O = \sum_i x_i A_O^{(i)} + \varrho \sum_{ij} x_i x_j B_O^{(ij)} + 0(\varrho^2), \quad (6.3)$$

wherein  $A_O^{(i)} = P_O^{(i)}$  is the first virial coefficient of orientational polarization which, for dipolar gases, is determined by Eq. (3.14) and is always zero,  $A_O^{(i)} = 0$ , for non-dipolar gases.

In particular, if the various components of a gaseous mixture consist of weakly dipolar, axially-symmetric molecules, one obtains by (5.11), (5.21), (6.1) and (6.2)

$$B_O^{(ij)} = \frac{4\pi N}{9kT} \left\{ \alpha_i^2 (1 + 2\mathcal{H}_i^2) \mu_j^2 + 2\alpha_i \alpha_j [(1 + 2\mathcal{H}_i) \mu_i^2 + \mu_j^2 (1 + 2\mathcal{H}_j)] + \mu_i^2 \alpha_j^2 (1 + 2\mathcal{H}_j^2) + \frac{2\mu_i^2 \mu_j^2}{3kT} [\alpha_i (1 + 2\mathcal{H}_i) + \alpha_j (1 + 2\mathcal{H}_j)] \right\} \langle r_{ij}^{-6} \rangle_R, \quad (6.4)$$

where we have introduced the radial mean values

$$\langle r_{ij}^{-n} \rangle_R = \int r_{pq}^{-n} \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} d\mathbf{r}_{pq}. \quad (6.5)$$

Applying Eqs (5.14) and (5.28), we obtain the following expression for the second virial coefficient of quadrupolar, axially-symmetric molecules:

$$B_O^{(ij)} = \frac{2\pi N}{15kT} \left\{ [5\alpha_i^2 (1 + 2\mathcal{H}_i^2) \Theta_j^2 - 12\alpha_i \mathcal{H}_i \Theta_i \alpha_j \mathcal{H}_j \Theta_j + 5\Theta_i^2 \alpha_j^2 (1 + 2\mathcal{H}_j^2)] \langle r_{ij}^{-8} \rangle_R + \right. \\ \left. - \frac{4\Theta_i \Theta_j}{49kT} [42\alpha_i^2 \mathcal{H}_i (2 + \mathcal{H}_i) \Theta_j^2 - \alpha_i \Theta_i \alpha_j \Theta_j (49 + 14\mathcal{H}_i + 14\mathcal{H}_j + 76\mathcal{H}_i \mathcal{H}_j) + \right. \\ \left. + 42\Theta_i^2 \alpha_j^2 \mathcal{H}_j (2 + \mathcal{H}_j)] \langle r_{ij}^{-13} \rangle_R \right\}, \quad (6.6)$$

which, for  $\mathcal{H}_i = \mathcal{H}_j = 0$ , reduces to

$$B_O^{(ij)} = \frac{2\pi N}{3kT} \left\{ (\alpha_i^2 \Theta_j^2 + \Theta_i^2 \alpha_j^2) \langle r_{ij}^{-8} \rangle_R + \frac{4}{5kT} \alpha_i \alpha_j \Theta_i^2 \Theta_j^2 \langle r_{ij}^{-13} \rangle_R \right\}. \quad (6.7)$$

For gases having tetrahedral molecules, Eqs (3.26) and (4.7) on neglecting small contributions from hexadecapole moments yield

$$B_O^{(ij)} = \frac{32\pi N}{15kT} \left\{ (\alpha_i^2 \Omega_j^2 + \Omega_i^2 \alpha_j^2) \langle r_{ij}^{-10} \rangle_R + \frac{24}{7kT} \alpha_i \alpha_j \Omega_i^2 \Omega_j^2 \langle r_{ij}^{-17} \rangle_R \right\}. \quad (6.8)$$

Similarly, for octahedral molecules we have, by (3.28) and (4.3),

$$B_O^{(ij)} = \frac{160\pi N}{21kT} \left\{ (\alpha_i^2 \Phi_j^2 + \Phi_i^2 \alpha_j^2) \langle r_{ij}^{-12} \rangle_R + \frac{64}{3kT} \alpha_i \alpha_j \Phi_i^2 \Phi_j^2 \langle r_{ij}^{-21} \rangle_R \right\}. \quad (6.9)$$

In order to be able to test numerically the foregoing expressions for  $B_O^{(ij)}$ , we have to know the values of the radial averages (6.5). To compute the latter, one has to assume some form of the central forces potential  $u(r)$ . With

$$u_{ij}(r_{pq}) = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{pq}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{pq}} \right)^6 \right\}, \quad (6.10)$$

and applying the Lennard-Jones method (1924), the radial averages (6.5) reduce to

$$\langle r_{ij}^{-n} \rangle_R^{s-t} = \frac{4\pi}{s} y_{ij}^{-4} \sigma_{ij}^{3-n} H_n^{s-t}(y_{ij}), \quad (6.11)$$

where we have introduced the functions (Kielich 1965 b)

$$H_n^{s-t}(y_{ij}) = y_{ij}^{\frac{4s+6-2n}{s}} \sum_{m=0}^{\infty} \frac{1}{m!} y_{ij}^{\frac{2m(s-t)}{s}} \Gamma \left( \frac{tm+n-3}{s} \right) \quad (6.12)$$

of argument  $y_{ij} = 2(\varepsilon_{ij}/kT)^{1/2}$ , with  $\varepsilon_{ij}$  and  $\sigma_{ij}$  denoting central forces parameters having the dimensions of an energy and length, respectively.

If in particular  $s = 12$  and  $t = 6$  *i.e.* if using the 12—6 Lennard-Jones potential, the functions of Eq. (6.12) reduce to the functions  $H_n^{12-6}$  introduced by Pople (1954), whereas  $s = 18$  and  $t = 6$  as well as  $s = 28$  and  $t = 7$  involve the functions introduced by Saxena and Joshi (1962).

In cases when the values of the parameters  $\varepsilon_{ij}$  and  $\sigma_{ij}$  are known, we can use Eq. (6.11) for evaluating  $B_O^{(ij)}$  numerically; obviously, according to the system dealt with, one will have to assume such values of the molecular quadrupole, octopole or hexadecapole moment as to achieve satisfactory agreement with the experimental values available for the second dielectric virial coefficient. In this way we can obtain information concerning the values of the higher order electric moments of various molecules.

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## APPENDIX A

### *Explicite expressions for $M^{(n)}$ and $T_{pq}^{(n)}$*

In contradistinction to Jansen's definition (1958), we have been applying the following definition of the  $2^n$ -pole permanent moment of a system of electric charges (*e.g.* a molecule)

$$M^{(n)} = \sum_v e_v r_v^n Y^{(n)}(r_v) \quad (A.1)$$

wherein

$$\mathbf{Y}^{(n)}(\mathbf{r}_\nu) = \frac{(-1)^n}{n!} r_\nu^{n+1} \nabla^n \left( \frac{1}{r_\nu} \right), \quad (\text{A.2})$$

and  $e_\nu$  is the  $\nu$ -th electric charge distant by  $r_\nu$  from the centre of the system. The operator of order  $n$  determined by Eq. (A.2) can be expressed as follows (for simplicity, the index  $\nu$  is omitted):

$$\begin{aligned} \mathbf{Y}^{(n)}(\mathbf{r}) = & \left( \frac{1}{n! r^n} \right) \left\{ (2n-1)!! \mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_n - (2n-3)!! r^2 \sum \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n + \dots + \right. \\ & \left. + (-1)^k (2n-2k-1)!! r^{2k} \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{2k+1} \dots \mathbf{r}_n \right\}, \quad (\text{A.3}) \end{aligned}$$

$\Sigma \mathbf{U}_{12} \mathbf{r}_3 \dots \mathbf{r}_n$  etc. being sums of terms resulting from the one written out by interchanging the indices 1, 2, ...  $n$  and the number of such terms amounting to  $n! / \{2^k (n-2k)! k!\}$ . The properties of the operator  $\mathbf{Y}^{(n)}$  resemble those of spherical harmonic functions.

From (A.1) and (A.3) we derive the uni-pole, dipole, quadrupole, octopole and hexadecapole electric moment as follows:

$$\begin{aligned} M^{(0)} &= \sum_\nu e_\nu, \\ M^{(1)} &= \sum_\nu e_\nu \mathbf{r}_{\nu 1}, \\ M^{(2)} &= \frac{1}{2} \sum_\nu e_\nu (3\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} - r_\nu^2 \mathbf{U}_{12}), \\ M^{(3)} &= \frac{1}{2} \sum_\nu e_\nu \{5\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} - r_\nu^2 (\mathbf{U}_{12} \mathbf{r}_{\nu 3} + \mathbf{U}_{23} \mathbf{r}_{\nu 1} + \mathbf{U}_{31} \mathbf{r}_{\nu 2})\}, \\ M^{(4)} &= \frac{1}{8} \sum_\nu e_\nu \{35\mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} \mathbf{r}_{\nu 4} - 5r_\nu^2 (\mathbf{U}_{12} \mathbf{r}_{\nu 3} \mathbf{r}_{\nu 4} + \mathbf{U}_{23} \mathbf{r}_{\nu 4} \mathbf{r}_{\nu 1} + \mathbf{U}_{34} \mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} + \\ & + \mathbf{U}_{14} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 3} + \mathbf{U}_{13} \mathbf{r}_{\nu 2} \mathbf{r}_{\nu 4} + \mathbf{U}_{24} \mathbf{r}_{\nu 1} \mathbf{r}_{\nu 3}) + r_\nu^4 (\mathbf{U}_{12} \mathbf{U}_{34} + \mathbf{U}_{13} \mathbf{U}_{24} + \mathbf{U}_{14} \mathbf{U}_{23})\}. \quad (\text{A.4}) \end{aligned}$$

By means of the operator  $\mathbf{Y}^{(n)}$  we can express the interaction tensor  $\mathbf{T}_{pq}^{(n)}$  defined by (2.6) thus

$$\mathbf{T}_{pq}^{(n)} = (-1)^{n+1} n! r_{pq}^{-(n+1)} \mathbf{Y}^{(n)}(\mathbf{r}_{pq}) \quad (\text{A.5})$$

on replacing  $\mathbf{r}$  by  $\mathbf{r}_{pq}$  in (A.2) or (A.3), with  $\mathbf{T}_{pq}^{(n)} = (-1)^n \mathbf{T}_{qp}^{(n)}$ .

By the definition of (A.5) we have

$$\begin{aligned} T_{pq}^{(0)} T_{rs}^{(0)} &= r_{pq}^{-1} r_{rs}^{-1}, \\ \mathbf{T}_{pq}^{(1)} \cdot \mathbf{T}_{rs}^{(1)} &= r_{pq}^{-3} r_{rs}^{-3} (\mathbf{r}_{pq} \cdot \mathbf{r}_{rs}), \\ \mathbf{T}_{pq}^{(2)} : \mathbf{T}_{rs}^{(2)} &= 3r_{pq}^{-5} r_{rs}^{-5} \{3(\mathbf{r}_{pq} \cdot \mathbf{r}_{rs})^2 - r_{pq}^2 r_{rs}^2\}, \\ \mathbf{T}_{pq}^{(3)} : \mathbf{T}_{rs}^{(3)} &= 45r_{pq}^{-7} r_{rs}^{-7} \{5(\mathbf{r}_{pq} \cdot \mathbf{r}_{rs})^3 - 3r_{pq}^2 r_{rs}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{rs})\}, \\ \mathbf{T}_{pq}^{(4)} : \mathbf{T}_{rs}^{(4)} &= 315r_{pq}^{-9} r_{rs}^{-9} \{35(\mathbf{r}_{pq} \cdot \mathbf{r}_{rs})^4 - 30r_{pq}^2 r_{rs}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{rs})^2 + 3r_{pq}^4 r_{rs}^4\}, \quad (\text{A.6}) \end{aligned}$$

or, quite generally, recurring to the definition of Legendre polynomials  $P_n$ ,

$$\mathbf{T}_{pq}^{(n)}[\mathbf{T}_{rs}^{(n)}] = (2n)! 2^{-n} r_{pq}^{-(n+1)} r_{rs}^{-(n+1)} P_n \left( \frac{\mathbf{r}_{pq} \cdot \mathbf{r}_{rs}}{r_{pq} r_{rs}} \right). \quad (\text{A.7})$$

If in particular  $p = r$  and  $q = s$ , we have  $P(1) = 1$ , yielding the identity derived by Jansen (1958):

$$\mathbf{T}_{pq}^{(n)}[\mathbf{T}_{pq}^{(n)}] = (2n)! 2^{-n} r_{pq}^{-2(n+1)}. \quad (\text{A.8})$$

Similarly, one obtains the following identities recurred to in the course of the present investigation

$$\begin{aligned} \mathbf{T}_{pq}^{(0)}(\mathbf{T}_{qr}^{(1)} \cdot \mathbf{T}_{rp}^{(1)}) &= -r_{pq}^{-1} r_{qr}^{-3} r_{rp}^{-3} (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}), \\ \mathbf{T}_{pq}^{(1)} \cdot (\mathbf{T}_{qr}^{(2)} \cdot \mathbf{T}_{rp}^{(1)}) &= -r_{pq}^{-3} r_{qr}^{-5} r_{rp}^{-2} \{3(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})(\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}) - r_{qr}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{rp})\}, \\ \mathbf{T}_{pq}^{(2)} : (\mathbf{T}_{qr}^{(2)} \cdot \mathbf{T}_{rp}^{(2)}) &= -3r_{pq}^{-5} r_{qr}^{-5} r_{rp}^{-5} \{9(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})(\mathbf{r}_{qr} \cdot \mathbf{r}_{rp})(\mathbf{r}_{rp} \cdot \mathbf{r}_{pq}) - \\ &\quad - 3r_{pq}^2 (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp})^2 - 3r_{qr}^2 (\mathbf{r}_{rp} \cdot \mathbf{r}_{pq})^2 - 3r_{rp}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^2 + 2r_{pq}^2 r_{qr}^2 r_{rp}^2\}, \\ \mathbf{T}_{pq}^{(2)} : (\mathbf{T}_{qr}^{(3)} \cdot \mathbf{T}_{rp}^{(1)}) &= -9r_{pq}^{-5} r_{qr}^{-7} r_{rp}^{-3} \{5(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^2 (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}) - \\ &\quad - r_{qr}^2 [r_{pq}^2 (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}) + 2(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})(\mathbf{r}_{rp} \cdot \mathbf{r}_{pq})]\}, \\ \mathbf{T}_{pq}^{(3)} : (\mathbf{T}_{qr}^{(3)} \cdot \mathbf{T}_{rp}^{(2)}) &= -9r_{pq}^{-7} r_{qr}^{-7} r_{rp}^{-5} \{5(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr}) [15(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})(\mathbf{r}_{qr} \cdot \mathbf{r}_{rp})(\mathbf{r}_{rp} \cdot \mathbf{r}_{pq}) - \\ &\quad 5r_{rp}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^2 - 6r_{pq}^2 (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp})^2 - 6r_{qr}^2 (\mathbf{r}_{rp} \cdot \mathbf{r}_{pq})^2] - \\ &\quad - 3r_{pq}^2 r_{qr}^2 [(\mathbf{r}_{pq} \cdot \mathbf{r}_{rp})(\mathbf{r}_{rp} \cdot \mathbf{r}_{qr}) - 7r_{rp}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})]\}, \\ \mathbf{T}_{pq}^{(3)} : (\mathbf{T}_{qr}^{(4)} \cdot \mathbf{T}_{rp}^{(1)}) &= -45r_{pq}^{-7} r_{qr}^{-9} r_{rp}^{-3} \{35(\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})^3 (\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}) - \\ &\quad - 15r_{qr}^2 (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr}) [(\mathbf{r}_{qr} \cdot \mathbf{r}_{rp}) r_{pq}^2 + (\mathbf{r}_{pq} \cdot \mathbf{r}_{qr})(\mathbf{r}_{rp} \cdot \mathbf{r}_{pq})] + 3r_{pq}^2 r_{qr}^4 (\mathbf{r}_{pq} \cdot \mathbf{r}_{rp})\}, \dots \end{aligned} \quad (\text{A.9})$$

## APPENDIX B

### *Total multipole electric moment of a dense medium*

Both in Part I and in the present, second part of our paper we have taken into account explicitly only the multipole electric moments induced in a molecule by an electric field of order  $n$  in the first power. Generally, the total multipole electric moment will contain, in the higher approximations, moments induced by higher powers of the electric field, and can be written in the form

$$\mathbf{M}_I^{(n)} = \sum_i \sum_{p=1}^{N_i} \{ \mathbf{M}_{pi}^{(n)(0)} + \mathbf{M}_{pi}^{(n)(1)} + \mathbf{M}_{pi}^{(n)(2)} + \mathbf{M}_{pi}^{(n)(3)} + \dots \}, \quad (\text{B.1})$$

with  $\mathbf{M}_{pi}^{(n)} = \mathbf{M}_{pi}^{(n)}$  denoting the  $2^n$ -pole electric moment in the zeroth approximation *i.e.* when the molecule is not acted on by the external electric field.

In the first approximation, the total electric field  $\mathbf{E}^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}$  induces in the  $p$ -th molecule of species  $i$  the  $2^n$ -pole electric moment

$$\mathbf{M}_{pi}^{(n)} = \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} {}^{(n)}\mathbf{A}_{pi}^{(n_1)} [n_1] (\mathbf{E}^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}), \quad (\text{B.2})$$

(this moment has previously been denoted by  $\mathbf{P}_{pi}^{(n)}$ ). The molecular electric field of order  $n_1$  given rise to by the other molecules of the medium immersed in the electric field, and acting on the  $p$ -th molecule of species  $i$ , is given by the expression

$$\mathbf{F}_{pi}^{(n)} = \sum_j \sum_{q=1}^{N_j} \sum_{n_2=1}^{\infty} \frac{(-1)^{n_2} 2^{n_2} n_2!}{(2n_2)!} {}^{(n_1)}\mathbf{T}_{pq}^{(n_2)} [n_2] (\mathbf{M}_{qj}^{(0)} + \mathbf{M}_{qj}^{(1)} + \mathbf{M}_{qj}^{(2)} + \dots). \quad (\text{B.3})$$

The induced electric moments of the second and third approximations appearing in the expansion (B.1) are produced in molecule  $p$  of species  $i$  by electric fields in the second and third powers, respectively, and can be expressed thus

$$\mathbf{M}_{pi}^{(2)} = \frac{1}{2} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)! (2n_2)!} {}^{(n)}\mathbf{A}_{pi}^{(n_1+n_2)} [n_1+n_2] (\mathbf{E}^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}) (\mathbf{E}^{(n_2)} + \mathbf{F}_{pi}^{(n_2)}), \quad (\text{B.4})$$

$$\begin{aligned} \mathbf{M}_{pi}^{(3)} &= \frac{1}{6} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{2^{n_1+n_2+n_3} n_1! n_2! n_3!}{(2n_1)! (2n_2)! (2n_3)!} {}^{(n)}\mathbf{A}_{pi}^{(n_1+n_2+n_3)} \times \\ &\times [n_1+n_2+n_3] (\mathbf{E}^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}) (\mathbf{E}^{(n_2)} + \mathbf{F}_{pi}^{(n_2)}) (\mathbf{E}^{(n_3)} + \mathbf{F}_{pi}^{(n_3)}), \end{aligned} \quad (\text{B.5})$$

wherein  ${}^{(n)}\mathbf{A}_{pi}^{(n_1+n_2)}$  and  ${}^{(n)}\mathbf{A}_{pi}^{(n_1+n_2+n_3)}$  are tensors respectively of ranks  $n+n_1+n_2$  and  $n+n_1+n_2+n_3$  accounting for the electric deformation of, respectively, the second and third degree of the molecule under consideration as arising through the effect of the second and third power of the total electric field  $\mathbf{E}^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}$ .

The expansion of (B.1) together with the equation

$$(\boldsymbol{\epsilon} - \mathbf{U}) \cdot \mathbf{E} = \frac{4\pi}{V} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \langle \nabla^{n-1} [n-1] \mathbf{M}_T^{(n)} \rangle \quad (\text{B.6})$$

provides the basis for the general theory of the electric permittivity of a multicomponent system whose components consist of molecules possessing  $2^n$ -pole permanent electric moments  $\mathbf{M}^{(n)}$  as well as  $2^n$ -pole induced moments of the first, second and third orders given respectively by Eqs (B.2), (B.4) and (B.5). Obviously, a theory thus generally formulated is, in its explicit form, apt to present obstacles of a mathematical nature; this, however, is compensated by its wide range of applicability to various special cases, of which only some — and we might well say the simplest — have been discussed in detail in this paper. Moreover, the theory as formulated above is applicable to the case of variations of the electric permittivity tensor as induced by the square of a homogeneous electric field, by the gradient of an electric field, or by electric fields of higher orders, such as the gradient of a field gradient, and so forth.



## APPENDIX C

*Effect of second and third order moments on  $P_D$* 

In Part I of this paper, the distortional polarization was defined as

$$P_D = \frac{4\pi}{3} \left\langle \frac{\partial}{\partial E} (\mathbf{M} \cdot \mathbf{e}) \right\rangle; \quad (\text{C.1})$$

here, with regard to the expansion (B.1), it can be put in the form

$$P_D = P_D^{(1)} + P_D^{(2)} + P_D^{(3)} + \dots, \quad (\text{C.2})$$

where

$$P_D^{(n)} = \frac{4\pi}{3} \sum_i \left\langle \sum_{p=1}^{N_i} \frac{\partial}{\partial E} (\mathbf{e} \cdot \mathbf{M}_{pi}^{(n)}) \right\rangle \quad (\text{C.3})$$

is the distortional polarization due to a dipole moment of order  $n = 1, 2, 3, \dots$ .

The distortional polarization  $P_D^{(1)}$  given rise to by the induced moment of the first order (B.2) has been discussed in detail in Part I (Kielich 1965a). We shall now deal in brief with the polarizations  $P_D^{(2)}$  and  $P_D^{(3)}$  deriving from induced dipole moments of the second and third orders given, respectively, by (B.4) and (B.5) for  $n = 1$ . By (B.4) and (C.3), we have

$$P_D^{(2)} = \frac{4\pi}{3} \sum_i \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \left\langle \sum_{p=1}^{N_i} \mathbf{e} \cdot {}^{(1)}\mathbf{A}_{pi}^{(1+n)} [1+n] \left( \mathbf{e} + \frac{\partial \mathbf{F}_{pi}^{(1)}}{\partial E} \right) \mathbf{F}_{pi}^{(n)} \right\rangle_{E=0}, \quad (\text{C.4})$$

or, on substituting herein the molecular field (B.3) and neglecting higher order terms,

$$P_D^{(2)} = \frac{4\pi}{3} \sum_{ij} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_2} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)! (2n_2)!} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \mathbf{e} \cdot {}^{(1)}\mathbf{A}_{pi}^{(1+n_1)} \cdot \mathbf{e} [n_1]^{(n_1)} \mathbf{T}_{pq}^{(n_2)} [n_2] \mathbf{M}_{qj}^{(n_2)} \right\rangle. \quad (\text{C.5})$$

In the zeroth approximation, *i.e.*  $V_i = 0$ , this contribution vanishes, whereas in the first approximation by the expansion (3.13) we obtain to within pairwise correlations

$$P_D^{(2)} = \sum_{ij} x_i x_j P_D^{(ij)}, \quad (\text{C.6})$$

with

$$P_D^{(ij)} = \frac{2\pi}{27kT} \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \{ (\mathbf{U} : {}^{(1)}\mathbf{A}_i^{(2)} \cdot \boldsymbol{\mu}_i) (\mathbf{M}_j^{(n)} [n] \mathbf{M}_j^{(n)}) + (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) (\mathbf{U} : {}^{(1)}\mathbf{A}_j^{(2)} \cdot \boldsymbol{\mu}_j) \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (\text{C.7})$$

${}^{(1)}\mathbf{A}_i^{(2)}$  being a third rank tensor determining the non-linear polarization of the dipole moment of a molecule of species  $i$  as due to the square of a homogeneous electric field.

Quite similarly, we obtain by (B.5) and (C.3) in the zeroth approximation to within pairwise correlations

$$P_D^{(3)} = \sum_{ij} x_i x_j P_D^{(ij)(3)}, \quad (\text{C.8})$$

with

$$P_D^{(ij)(3)} = \frac{\pi}{27} \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \{(\mathbf{U} : {}^{(2)}\mathbf{A}_i^{(2)} : \mathbf{U})(M_j^{(n)} [n] M_j^{(n)}) + \\ + (M_i^{(n)} [n] M_i^{(n)})(\mathbf{U} : {}^{(2)}\mathbf{A}_j^{(2)} : \mathbf{U})\} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (\text{C.9})$$

where  ${}^{(1)}\mathbf{A}_i^{(3)} = {}^{(2)}\mathbf{A}_i^{(2)}$  is the tensor of non-linear dipole polarization of a molecule of species  $i$ .

If, in particular, the molecules of all the components of the system have the axial symmetry, Eqs (C.7) and (C.9) by (3.12) reduce to the form

$$P_D^{(ij)(2)} = \frac{2\pi}{9kT} \sum_{n=1}^{\infty} (n+1) \{ \beta_i \mu_i (M_j^{(n)})^2 + (M_i^{(n)})^2 \beta_j \mu_j \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (\text{C.10})$$

$$P_D^{(ij)(3)} = \frac{5\pi}{27} \sum_{n=1}^{\infty} (n+1) \{ \gamma_i (M_j^{(n)})^2 + (M_i^{(n)})^2 \gamma_j \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (\text{C.11})$$

where  $\beta_i$  and  $\gamma_j$  denote the mean values of the non-linear polarizability tensors  ${}^{(1)}\mathbf{A}_i^{(2)}$  and  ${}^{(2)}\mathbf{A}_j^{(2)}$ , i.e.  $\beta_i = (\mathbf{U} : {}^{(1)}\mathbf{A}^{(2)} \cdot \mathbf{k})/3$  and  $\gamma_i = (\mathbf{U} : {}^{(2)}\mathbf{A}^{(2)} : \mathbf{U})/5$ .

If we assume in (C.10) and (C.11) that all molecules are of a single species and on putting therein  $n = 1$  or, in (C.11),  $n = 2$  as well, results are obtained that are analogous to those derived by Buckingham (1956) in his theory of the molecular refraction of real gases.

In the case of tetrahedral molecules  $\mathbf{U} : {}^{(1)}\mathbf{A}^{(2)} \cdot \boldsymbol{\mu} = 0$ , and the contribution (C.7) vanishes whereas (C.9) becomes (Kielich 1963, 1964)

$$P_D^{(ij)(3)} = \frac{16\pi}{9} \int \int \left\{ (\gamma_i \Omega_j^2 + \Omega_i^2 \gamma_j) r_{pq}^{-10} + \frac{25}{7} (\gamma_i \Phi_j^2 + \Phi_i^2 \gamma_j) r_{pq}^{-12} \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (\text{C.12})$$

On putting herein  $\Omega_i = 0$  we obtain a formula valid for octahedral molecules.

Similarly, a discussion could be given of the effect of the induced moments (B.4) and (B.5) at  $\mathbf{E}^{(n)} = 0$  on the orientational polarization  $P_O$ . We refrain, however, from proceeding thereto in the present paper, but wish to draw attention to the curious fact that the effect on  $P_O$  of the second-order moment given by (B.4) yields in the zeroth approximation a result identical with that obtained above for  $P_D$  in the first approximation and given by (C.7). Consequently, certain contributions to  $P_O$  and  $P_D$  can be identical or of the same order.

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