

Multipolar theory of dielectric polarization in dense mixtures

by S. KIELICH

Department of Physics, A. Mickiewicz University, Poznan, Poland

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By statistical mechanics and a multipole tensor formalism, an expression for the dielectric polarization of dense mixtures is derived, of such generality as to account for certain new factors of a molecular nature not taken into account in hitherto-existing theories. The general results are discussed in some special cases of dipolar, quadrupolar, octopolar, etc. systems and applied to moderately dense gases, in which the second dielectric virial coefficient provides the basis for determining molecular multipole moments or multipole polarizabilities of order higher than dipolar. This indirect method yields a quadrupole moment of 5×10^{-26} e.s.u. cm² for the CO₂ molecule and an octopole moment of 4×10^{-34} e.s.u. cm³ for the CH₄ molecule.

1. INTRODUCTION

The statistical theory of isotropic dielectrics initiated by Kirkwood [1] and Yvon [2] has been modified and further developed in various ways by several authors [3–18]. Most theoretical work on dielectric polarization dealt with one-component systems of identical non-polar spherical molecules [1–7], dipolar molecules [8–14] and quadrupolar molecules [15–19]. Brown [3], Harris and Brush [20] and Buckingham [21] discussed the application of the statistical mechanical theory of dielectric polarization [8–12] to dilute solutions of dipolar molecules in a non-polar solvent. A virial theory of dielectric polarization of compressed gas mixtures has been given by Buckingham and Raab [22] (see also ref. [23]).

The importance of investigating the dielectric polarization in various substances resides primarily in the possibility of obtaining information not only on the molecular dipole moments themselves, as already shown by Debye, but moreover on the higher order molecular moments such as quadrupolar [15–19], octopolar [23–25] or hexadecapolar [26]. Obviously, such information on the molecular multipole moments of order higher than dipolar can be obtained only when, in the medium under investigation, molecular interactions are sufficiently apparent. These interactions will lead to an effect consisting in the induction, in any given molecule of the dense medium, of a dipole moment by the electric field of the permanent quadrupoles [15–19], octopoles [23–25], etc. of its neighbours. Clearly, such data on molecular multipole moments will be of a rather orientational character. Nevertheless, this indirect method deserves further study.

The present investigation is aimed at deriving a statistical-molecular theory of dielectric polarization for multi-component systems on the basis of the existing theories. A consistent and general tensor formalism will be developed which

enables us to obtain a general expression for the dielectric polarization in terms of multipole permanent moments and multipole polarizability tensors of molecules of arbitrary symmetry as well as of statistical averages of inverse powers of the mutual distances between molecules interacting in pairs, triplets, etc. The theory thus generally formulated can be applied to a wide range of vastly varying special cases beyond the one-component systems mostly discussed hitherto, comprising two-, three-component systems, etc., consisting of quadrupolar, octopolar or hexadecapolar unlike molecules.

In the Appendices we give in explicit form the first, second- and third-order multipole moments induced in a molecule by a strong inhomogeneous electric field as well as the higher-order energies of interactions between multipolar molecules. Various aspects of intermolecular energies have been discussed and developed in suitable approaches by several authors (see refs. [27-31] and the papers cited there); a tensor formalism for the multipole expansion of intermolecular energy was given by Frenkel [27], Carlson and Rushbrooke [28] and later by Jansen [31], whose general and concise tensor notation we use in the present paper.

2. GENERAL THEORY

We shall consider a medium of volume V placed in an external, in general inhomogeneous electric field with the potential ϕ . The tensor of the electric permittivity of such a medium is given in general by the equation [17, 32]:

$$(\epsilon - \mathbf{U}) \cdot \mathbf{E} = 4\pi \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2^n n!}{(2n)!} \nabla^{n-1} [n-1] \mathbf{P}^{(n)}, \quad (1)$$

in which $\mathbf{P}^{(n)}$ is the 2^n -pole electric polarization operator of the medium and \mathbf{E} the homogeneous electric field in the medium; \mathbf{U} is the second-rank unit tensor, ∇ the differential operator and the symbol $[n]$ denotes n -fold contraction of the product of two tensors of rank n .

In the presence of the electric field at thermodynamical equilibrium of the system we have by classical statistical mechanics

$$\mathbf{P}^{(n)} = \frac{\int \frac{\mathbf{M}_T^{(n)}}{V} \exp \left\{ -\frac{U(\tau, \phi)}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau, \phi)}{kT} \right\} d\tau}, \quad (2)$$

wherein $\mathbf{M}_T^{(n)}(\tau, \phi)$ and $U(\tau, \phi)$ are respectively the 2^n -pole total electric moment and potential energy of the system at configuration τ in the electric field with potential ϕ .

In the case here considered we have:

$$U(\tau, \phi) = U(\tau, 0) - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \int_0^{E_0^{(n)}} \mathbf{M}_T^{(n)} [n] d\mathbf{E}^{(n)}, \quad (3)$$

where $U(\tau, 0)$ is the potential energy of the system in the absence of an external electric field ($\phi=0$) and $\mathbf{E}^{(n)} = -\{\nabla^n \phi\}_0$ is the strength of the external electric field of ∇ -degree n within the medium and $\mathbf{E}_0^{(n)}$ —at a large distance from the medium or in the absence of the medium (*in vacuo*).

If the medium contains N_1 molecules of the first species, N_2 of the second, . . . , and N_i of the i th species, its multipole electric moment is given by:

$$\mathbf{M}_T^{(n)} = \sum_i \sum_{p=1}^{N_i} \mathbf{T} \mathbf{M}_{pi}^{(n)}, \quad (4)$$

where $\mathbf{T} \mathbf{M}_{pi}^{(n)}$ is the total 2^n -pole electric moment of the p th molecule of species i . Generally, when the electric field is present, $\mathbf{T} \mathbf{M}_{pi}^{(n)}$ can be expanded in the form:

$$\mathbf{T} \mathbf{M}_{pi}^{(n)} = \mathbf{M}_{pi}^{(n)(0)} + \mathbf{M}_{pi}^{(n)(1)} + \mathbf{M}_{pi}^{(n)(2)} + \mathbf{M}_{pi}^{(n)(3)} + \dots = \sum_{s=0}^{\infty} \mathbf{M}_{pi}^{(n)(s)} \quad (5)$$

with $\mathbf{M}_{pi}^{(n)(0)} \equiv \mathbf{M}_{pi}^{(n)}$ denoting the 2^n -pole electric moment of the isolated molecule in the zeroth approximation, i.e. the permanent multipole moment in the absence of electric fields (see Appendix A).

In the case when the molecule of a medium is acted on by the total electric field $\mathbf{E}_0^{(n)} + \mathbf{F}_{pi}^{(n)}$ of degree n the multipole moment of order $s \geq 1$ induced in the p th molecule of species i is of the form:

$$\mathbf{M}_{pi}^{(n)(s)} = \frac{1}{s!} \sum_{n_1=1}^{\infty} \dots \sum_{n_s=1}^{\infty} \frac{2^{n_1+\dots+n_s} n_1! \dots n_s!}{(2n_1)! \dots (2n_s)!} \times {}^{(n)} \mathbf{A}_{pi}^{(n_1+\dots+n_s)} [n_1 + \dots + n_s] (\mathbf{E}_0^{(n_1)} + \mathbf{F}_{pi}^{(n_1)}) \dots (\mathbf{E}_0^{(n_s)} + \mathbf{F}_{pi}^{(n_s)}) \quad (6)$$

with $\mathbf{A}_{pi}^{(n_1+\dots+n_s)}$ denoting the s th-order multipole polarizability tensor of a molecule p of species i . This tensor describes the s th-order polarization of the 2^n -pole moment caused by the s th power of the electric field of degree n_s (see Appendix A).

The molecular electric field $\mathbf{F}_{pi}^{(n)}$ of degree n at the centre of the p th molecule of species i due to the other $N-1$ molecules of the system in the presence of an external electric field is defined in general as [32]:

$$\mathbf{F}_{pi}^{(n)} = \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{m=1}^{\infty} (-1)^m \frac{2^m m!}{(2m)!} {}^{(n)} \mathbf{T}_{pq}^{(m)} [m] \mathbf{T} \mathbf{M}_{qj}^{(m)}, \quad (7)$$

wherein

$${}^{(n)} \mathbf{T}_{pq}^{(m)} = -\nabla^{n+m} \left(\frac{1}{r_{pq}} \right)$$

is the tensor of rank $n+m$ describing the $(2^n$ -pole)- $(2^m$ -pole) interactions between the molecules p and q separated by a distance r_{pq} (see Appendix B); here, the differential operator ∇^{n+m} is directed from molecule q to p .

Equation (1) with the expressions (2)–(7) provide the basis for the general theory of the electric permittivity of a multi-component system whose components consist of molecules possessing multipole permanent electric moments as well as induced multipole moments of the first, second, third, etc. orders given by (6) for $s=1, 2, 3, \dots$. The multipole polarization operator (2) can, in general, be expanded in powers of the applied field \mathbf{E}_0 and its derivatives. Thus, the theory as formulated above is applicable not only to the case of a weak electric field but to the cases of non-linear variations of the electric permittivity tensor as produced by the square of a homogeneous electric field ($\mathbf{E} \equiv \mathbf{E}^{(1)} = -\nabla\phi$), by the gradient of an electric field ($\mathbf{E}^{(2)} = \nabla\mathbf{E}$), or by electric fields of higher degrees,

such as the gradient of a field gradient ($\mathbf{E}^{(3)} = \nabla \nabla \mathbf{E}$), and so forth. 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—are discussed in detail in this paper.

In the case when the applied electric field is weak and homogeneous, and when for convenience the isotropic medium is represented as a macroscopic spherical sample in vacuum for which $(\epsilon + 2)\mathbf{E} = 3\mathbf{E}_0$, equation (1) yields by (2) and (3) for the Clausius–Mossotti function:

$$\frac{\epsilon - 1}{\epsilon + 2} V = P_D + P_0, \quad (8)$$

where

$$P_D = \frac{4\pi}{3} \left\langle \frac{\partial}{\partial E_0} (\mathbf{M}_T^{(1)} \cdot \mathbf{e}) \right\rangle \quad (9a)$$

is the distortional or deformational polarizability of the medium and

$$P_0 = -\frac{4\pi}{3kT} \left\langle (\mathbf{M}_T^{(1)} \cdot \mathbf{e}) \frac{\partial U}{\partial E_0} \right\rangle = \frac{4\pi}{3kT} \langle (\mathbf{M}_T^{(1)} \cdot \mathbf{e})^2 \rangle \quad (9b)$$

is its orientational polarizability; \mathbf{e} is a unit vector in the direction of the applied electric field \mathbf{E}_0 .

The brackets in (9) denote the statistical average at zero external electric field:

$$\langle X \rangle = \frac{\int X(\tau, 0) \exp \left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}. \quad (10)$$

3. DISTORTIONAL POLARIZATION

We now discuss the distortional polarizability of (9a) which in the approximation of the first-order dipole moment given by (6) for $s=1$ and $n=1$ is of the form:

$$P_D = \frac{4\pi}{3} \sum_i \sum_{p=1}^{N_i} \left\{ \langle \mathbf{e} \cdot {}^{(1)}\mathbf{A}_{pi}^{(1)} \cdot \mathbf{e} \rangle + \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \left\langle \mathbf{e} \cdot {}^{(1)}\mathbf{A}_{pi}^{(n)} [n] \frac{\partial \mathbf{F}_{pi}^{(n)}}{\partial E_0} \right\rangle \right\}. \quad (11)$$

This is a general equation for P_D containing the effects due to induced multipole interactions of unlike molecules of the system; beyond the Kirkwood–Yvon effect from fluctuations in the induced dipole moments ($n=1$), equation (11) contains similar effects from quadrupole ($n=2$), octopole ($n=3$), etc. moments induced in the molecules by the molecular field gradient $\mathbf{F}_{pi}^{(2)}$, gradient of field gradient $\mathbf{F}_{pi}^{(3)}$, etc. of the other molecules.

By methods of statistical mechanics, equation (11) with (7) can be expressed formally as follows:

$$P_D = \sum_i x_i P_D^{(i)} + \sum_{ij} x_i x_j P_D^{(ij)} + \sum_{ijk} x_i x_j x_k P_D^{(ijk)} + \dots, \quad (12)$$

where $x_i = N_i/N$ is the mole fraction of the i th component of the system.

The first term in (12) expresses the well-known additivity of distortional polarizability:

$$P_D^{(i)} = \frac{4\pi}{3} N a_i \tag{13}$$

of the individual components consisting of non-interacting molecules possessing the mean dipole polarizabilities $a_i = {}^{(1)}\mathbf{A}_i^{(1)} : \mathbf{U}/3$.

The second, third and further terms of (12) responsible for the derivations from additivity of P_D arise from the interactions between unlike molecules in a dense medium. The quantities $P_D^{(ij)}$ and $P_D^{(ijk)}$ are in general of a very complicated form and, in the special case when the correlation functions do not depend on the mutual orientations of the molecules, are given as follows:

$$P_D^{(ij)} = \frac{2\pi}{9} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^n (n!)^2 m! (2n+2m)!}{(2n)! (2n+1)! (2m)!} \times \{ a_i^{(2m)} ({}^{(1)}\mathbf{A}_j^{(n)} [n+1] {}^{(n)}\mathbf{A}_j^{(1)}) + ({}^{(1)}\mathbf{A}_i^{(n)} [n+1] {}^{(n)}\mathbf{A}_i^{(1)}) a_j^{(2m)} \} \times \int \int r_{pq}^{-2(n+m+1)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \tag{14}$$

$$P_D^{(ijk)} = \frac{4\pi}{27} \sum_{n=1}^{\infty} (n+1)(2n+1) \{ a_i a_j a_k^{(2n)} + a_i a_j^{(2n)} a_k + a_i^{(2n)} a_j a_k \} \times \int \int \int (r_{pq} r_{qr})^{-(n+2)} P_{n+1} \left(\frac{r_{pq} \cdot r_{qr}}{r_{pq} r_{qr}} \right) n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r \tag{15}$$

Here,

$$a_i^{(2n)} = \frac{2^n n!}{(2n+1)!} {}^{(n)}\mathbf{A}_i^{(n)} [2n] \mathbf{U}^n \tag{16}$$

is the mean value of the 2^n -pole electric polarizability of a molecule of species i due to an electric field of degree n and P_{n+1} is the Legendre polynomial of degree $n+1$. In (14), $n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q)$ is the binary distribution function for a pair of molecules p and q of species i and j at positions \mathbf{r}_p and \mathbf{r}_q , whereas in (15) $n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r)$ is the ternary distribution function for triples of molecules p, q and r of species i, j and k at positions $\mathbf{r}_p, \mathbf{r}_q$ and \mathbf{r}_r .

If the higher-order terms are neglected, we obtain from (14) :

$$P_D^{(ij)} = \frac{4\pi}{9} \int \int \{ [a_i(\mathbf{a}_j : \mathbf{a}_j) + (\mathbf{a}_i : \mathbf{a}_i) a_j] r_{pq}^{-6} + [a_i ({}^{(1)}\mathbf{A}_j^{(2)} :: {}^{(2)}\mathbf{A}_j^{(1)}) + ({}^{(1)}\mathbf{A}_i^{(2)} :: {}^{(2)}\mathbf{A}_i^{(1)}) a_j] r_{pq}^{-8} + \frac{4}{5} [a_i ({}^{(1)}\mathbf{A}_j^{(3)} :: {}^{(3)}\mathbf{A}_j^{(1)}) + ({}^{(1)}\mathbf{A}_i^{(3)} :: {}^{(3)}\mathbf{A}_i^{(1)}) a_j] r_{pq}^{-10} + 5 [q_i(\mathbf{a}_j : \mathbf{a}_j) + (\mathbf{a}_i : \mathbf{a}_i) q_j] r_{pq}^{-8} + \frac{28}{3} [q_i ({}^{(1)}\mathbf{A}_j^{(2)} :: {}^{(2)}\mathbf{A}_j^{(1)}) + ({}^{(1)}\mathbf{A}_i^{(2)} :: {}^{(2)}\mathbf{A}_i^{(1)}) q_j] r_{pq}^{-10} + 12 [q_i ({}^{(1)}\mathbf{A}_j^{(3)} :: {}^{(3)}\mathbf{A}_j^{(1)}) + ({}^{(1)}\mathbf{A}_i^{(3)} :: {}^{(3)}\mathbf{A}_i^{(1)}) q_j] r_{pq}^{-12} + \dots \} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \tag{17}$$

where, by (16), $q_i \equiv a_i^{(4)} = \mathbf{U} : {}^{(2)}\mathbf{A}_i^{(2)} : \mathbf{U}/15$ is the mean quadrupole polarizability describing the quadrupole moment ${}^{(2)}\mathbf{A}_i^{(2)} : \mathbf{F}_i^{(2)}$ induced in the molecule of species i by the molecular electric field gradient $\mathbf{F}_i^{(2)}$. In (17), ${}^{(1)}\mathbf{A}_i^{(2)}, {}^{(1)}\mathbf{A}_i^{(3)}, \dots$ are the

tensors of dipole polarizabilities describing the dipole moments ${}^{(1)}\mathbf{A}_i^{(2)}: \mathbf{F}_i^{(2)}$ and ${}^{(1)}\mathbf{A}_i^{(3)}: \mathbf{F}_i^{(3)}$ induced in the molecule by the field gradient $\mathbf{F}_i^{(2)}$ and gradient of field gradient $\mathbf{F}_i^{(3)}$. Alternatively, the quadrupole polarizability tensor ${}^{(2)}\mathbf{A}_i^{(1)}$ and octopole polarizability tensor ${}^{(3)}\mathbf{A}_i^{(1)}: \mathbf{F}_i^{(1)}$ define the quadrupole moment ${}^{(2)}\mathbf{A}_i^{(1)}$ and octopole moment ${}^{(3)}\mathbf{A}_i^{(1)}: \mathbf{F}_i^{(1)}$ induced in the molecule by the field $\mathbf{F}_i^{(1)}$.

The successive terms in equation (17) with (A5) correspond to the term discussed strictly in explicit form by Jansen and Solem [17] on the basis of quantum-mechanical perturbation theory.

As a particular case of interest, we shall consider that of molecules with centres of inversion for which (17) yields in a good approximation:

$$P_D^{(ij)} = \frac{4\pi}{9} \int \int \{ [a_i(\mathbf{a}_j: \mathbf{a}_j) + (\mathbf{a}_i: \mathbf{a}_i)a_j] r_{pq}^{-6} + 5[q_i(\mathbf{a}_j: \mathbf{a}_j) + (\mathbf{a}_i: \mathbf{a}_i)q_j] r_{pq}^{-8} \} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (18)$$

or, if the molecules possess moreover the axial symmetry:

$$P_D^{(ij)} = \frac{4\pi}{3} \int \int \{ a_i a_j [a_i(1 + 2\kappa_i^2) + a_j(1 + 2\kappa_j^2)] r_{pq}^{-6} + 5[q_i a_j^2(1 + 2\kappa_j^2) + a_i^2(1 + 2\kappa_i^2)q_j] r_{pq}^{-8} \} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (19)$$

where $\kappa_i = (a_{zz}^{(i)} - a_{xx}^{(i)})/3a_i$ is a parameter determining the anisotropy of dipole polarizability.

For a one-component system with molecules possessing the isotropic dipole polarizability ($a_i \neq 0, \kappa_i = 0$) but no quadrupole polarizability ($q_i = 0$), equation (19) yields the result of De Boer *et al.* [4].

We now consider the further contributions to P_D from induced dipole moments of the second and third orders given by (6) for $n = 1$ and respectively for $s = 2$ and $s = 3$. In the zeroth approximation by unweighted averaging over all possible orientations of molecules $\partial \mathbf{M}_{pi}^{(2)}/\partial E_0$ vanishes, whereas $\partial \mathbf{M}_{pi}^{(3)}/\partial E_0$ is non-zero and yields the following contribution to distortional polarization:

$$P_D^{(ij)} = \frac{\pi}{9} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^{n+m}(n!m!)^2(2n+2m)!}{(2n)!(2n+1)!(2m)!(2m+1)!} \times \{ (\mathbf{U}: {}^{(1)}\mathbf{C}_i^{(1+2n)}[2n]\mathbf{U}^n)(\mathbf{M}_j^{(m)}[m]\mathbf{M}_j^{(m)}) + (\mathbf{M}_i^{(n)}[n]\mathbf{M}_i^{(n)})(\mathbf{U}: {}^{(1)}\mathbf{C}_j^{(1+2m)}[2m]\mathbf{U}^m) \} \times \int \int r_{pq}^{-2(n+m+1)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (20)$$

where ${}^{(1)}\mathbf{C}_i^{(1+2n)}$ is the third-order dipole polarizability tensor of the molecule of species i due to the second power of the electric field of degree n .

In the case of molecules possessing only the third-order mean dipole polarizability $c_i = \mathbf{U}: {}^{(1)}\mathbf{C}_i^{(2)}: \mathbf{U}/5$, the expression (20) becomes:

$$P_D^{(ij)} = \frac{5\pi}{27} \sum_{n=1}^{\infty} \frac{2^n(n+1)!n!}{(2n)!} \{ c_i(\mathbf{M}_j^{(n)}[n]\mathbf{M}_j^{(n)}) + (\mathbf{M}_i^{(n)}[n]\mathbf{M}_i^{(n)})c_j \} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (21)$$

Hitherto, in the foregoing calculations we have considered the simpler cases when in the definition (10) the potential energy $U(\tau, 0) = U(\mathbf{r})$ depended only on the positional variables \mathbf{r} of the molecules. If in general $U(\tau, 0)$ consists besides $U(\mathbf{r})$ also of that part of $V(\mathbf{r}, \boldsymbol{\omega})$ which depends both on the positional and orientational variables \mathbf{r} and $\boldsymbol{\omega}$ of the molecules, we can obtain some further contributions to P_D . However, we shall restrict these supplementary calculations to the contribution resulting from the second-order dipole moment $\mathbf{M}_{pi}^{(2)}$. By (6) for $s=2$ and $n=1$ we have:

$$\left\{ \frac{\partial \mathbf{M}_{pi}^{(2)}}{\partial E_0} \right\}_{E=0} = \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} {}^{(1)}\mathbf{B}_{pi}^{(1+n)} [1+n] \mathbf{e} \mathbf{F}_{0pi}^{(n)} + \dots, \quad (22)$$

where ${}^{(1)}\mathbf{B}^{(1+n)}$ is the second-order dipole polarizability tensor due to the molecular electric field $\mathbf{F}_0^{(n)}$ of ∇ -degree n at $\mathbf{E}_0=0$.

In the case when $V(\mathbf{r}, \boldsymbol{\omega})$ arises from electrostatic interaction between the 2^n -pole permanent electric moment of one molecule and the 2^m -pole permanent electric moment of another, i.e. when (see Appendix B)

$$V(\mathbf{r}, \boldsymbol{\omega}) = -\frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} (-1)^m \frac{2^{n+m} n! m!}{(2n)!(2m)!} \mathbf{M}_{pi}^{(n)} [n] {}^{(n)}\mathbf{T}_{pq}^{(m)} [m] \mathbf{M}_{qj}^{(m)} \quad (23)$$

is non-zero, we obtain by (9a) and (22) the following contribution:

$$P_D^{(ij)} = \frac{2\pi}{9kT} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^{n+m} (2n+2m)! (n! m!)^2}{(2n)!(2n+1)!(2m)!(2m+1)!} \{ (\mathbf{U} : {}^{(1)}\mathbf{B}_i^{(1+n)} [n] \mathbf{M}_i^{(n)}) \times (\mathbf{M}_j^{(m)} [m] \mathbf{M}_j^{(m)}) + (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) (\mathbf{U} : {}^{(1)}\mathbf{B}_j^{(1+m)} [m] \mathbf{M}_j^{(m)}) \} \times \int \int r_{pq}^{-2(n+m+1)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (24)$$

which, as we see, in contradistinction to the preceding contributions (14) and (20), depends directly on the temperature.

If, in particular, the molecules possess only the permanent dipole moment $\mathbf{M}_i^{(1)} = \mu_i \mathbf{k}$, expressions (21) and (24) yield:

$$P_D^{(ij)} = \frac{10\pi}{27} \left\{ c_i \mu_j^2 + \mu_i^2 c_j + \frac{6\mu_i \mu_j}{5kT} (b_i \mu_j + \mu_i b_j) \right\} \int \int r_{pq}^{-6} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (25)$$

where $b_i = \mathbf{U} : {}^{(1)}\mathbf{B}_i^{(2)} \cdot \mathbf{k}/3$ is the mean second-order dipole polarizability.

Analogously in the case of molecules with permanent quadrupole moments $\mathbf{M}_i^{(2)} = \Theta_i$ expressions (21) and (24) reduce to:

$$P_D^{(ij)} = \frac{10\pi}{27} \int \int \left\{ [c_i(\Theta_j : \Theta_j) + (\Theta_i : \Theta_i) c_j] r_{pq}^{-8} + \frac{56}{25kT} [(\mathbf{U} : {}^{(1)}\mathbf{B}_i^{(3)} : \Theta_i) \times (\Theta_j : \Theta_j) + (\Theta_i : \Theta_i) (\mathbf{U} : {}^{(1)}\mathbf{B}_j^{(3)} : \Theta_j)] r_{pq}^{-10} \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (26)$$

In a similar way we can calculate some other contributions to P_D dependent on T^{-1} and T^{-2} (see refs. [22, 23, 32]).

4. ORIENTATIONAL POLARIZATION

In the absence of an external electric field ($\mathbf{E}_0=0$) all directions of $\mathbf{M}^{(l)}$ with respect to \mathbf{e} have the same probability, so that $(\mathbf{M}^{(l)} \cdot \mathbf{e})^2$ appearing in (9b) can

be averaged over all directions and we obtain for the orientational polarizability of multi-component systems:

$$P_0 = \frac{4\pi}{9kT} \langle \mathbf{M}_T^{(1)} \cdot \mathbf{M}_T^{(1)} \rangle = \frac{4\pi}{9kT} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \mathbf{T} \mathbf{M}_{pi}^{(1)} \cdot \mathbf{T} \mathbf{M}_{qj}^{(1)} \right\rangle. \quad (27)$$

We shall discuss this equation only for the case when the system consists of molecules presenting no permanent electric dipoles ($\mathbf{M}_{pi}^{(1)} = 0$) but possessing permanent electric moments of higher orders $n \geq 2$. Up to the first-order induced dipole moment resulting from (6) for $s = 1$ and $n = 1$ at $\mathbf{E}_0 = 0$,

$$\mathbf{M}_{pi}^{(1)} = \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} {}^{(1)}\mathbf{A}_{pi}^{(n)} [n] \mathbf{F}_{0pi}^{(n)}, \quad (28)$$

equation (27) yields:

$$P_0 = \frac{4\pi}{9kT} \sum_{ij} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{n! 2^{n+m} m!}{(2n)! (2m)!} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} ({}^{(1)}\mathbf{A}_{pi}^{(n)} [n] \mathbf{F}_{pi}^{(n)}) \cdot ({}^{(1)}\mathbf{A}_{qj}^{(m)} [m] \mathbf{F}_{qj}^{(m)}) \right\rangle. \quad (29)$$

With the molecular electric field of (7) this equation can be represented in the form:

$$P_0 = \sum_{ij} x_i x_j P_0^{(ij)} + \sum_{ijk} x_i x_j x_k P_0^{(ijk)} + \dots, \quad (30)$$

where in the special case when $V(\mathbf{r}, \omega) = 0$ we have:

$$\begin{aligned} P_0^{(ij)} = & \frac{4\pi}{9kT} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^{n+m} (2n+2m+2)! [n! (m+1)!]^2}{(2n)! (2n+1)! (2m+2)! (2m+3)!} \\ & \times \left\{ ({}^{(1)}\mathbf{A}_i^{(n)} [1+n] ({}^{(1)}\mathbf{A}_i^{(n)}) (\mathbf{M}_j^{(1+m)} [1+m] \mathbf{M}_j^{(1+m)}) \right. \\ & - \frac{4m+2}{2n+3} ({}^{(1)}\mathbf{A}_i^{(n)} [1+n] \mathbf{M}_i^{(1+n)}) ({}^{(1)}\mathbf{A}_j^{(m)} [1+m] \mathbf{M}_j^{(1+m)}) \\ & \left. + (\mathbf{M}_i^{(1+m)} [1+m] \mathbf{M}_i^{(1+m)}) ({}^{(1)}\mathbf{A}_j^{(n)} [1+n] \mathbf{A}_j^{(n)}) \right\} \\ & \times \int \int r_{pq}^{-2(n+m+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (31) \end{aligned}$$

$$\begin{aligned} P_0^{(ijk)} = & \frac{4\pi}{27kT} \sum_{n=1}^{\infty} \frac{2^n (n+1)! n!}{(2n)!} \{ a_i a_j (\mathbf{M}_k^{(n)} [n] \mathbf{M}_k^{(n)}) \\ & + a_i (\mathbf{M}_j^{(n)} [n] \mathbf{M}_j^{(n)}) a_k + (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) a_j a_k \} \\ & \times \int \int \int (r_{pq} r_{qr})^{-(n+2)} P_{n+1} \left(\frac{\mathbf{r}_{pq} \cdot \mathbf{r}_{qr}}{r_{pq} r_{qr}} \right) n_{ijk}^{(3)}(\mathbf{r}_p, \mathbf{r}_q, \mathbf{r}_r) d\mathbf{r}_p d\mathbf{r}_q d\mathbf{r}_r. \quad (32) \end{aligned}$$

For molecules possessing only the permanent quadrupole moment expression (31) yields the formula [23]:

$$\begin{aligned} P_0^{(ij)} = & \frac{4\pi}{135kT} \{ 5(\mathbf{a}_i : \mathbf{a}_i)(\Theta_j : \Theta_j) - 6(\mathbf{a}_i : \Theta_i)(\mathbf{a}_j : \Theta_j) \\ & + 5(\Theta_i : \Theta_i)(\mathbf{a}_j : \mathbf{a}_j) \} \int \int r_{pq}^{-2} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (33) \end{aligned}$$

which in the case of axial symmetry assumes the simpler form:

$$P_0^{(ij)} = \frac{2\pi}{15kT} \{5a_i^2(1+2\kappa_i^2)\Theta_j^2 - 12a_i\kappa_i\Theta_i a_j\kappa_j\Theta_j + 5\Theta_i^2 a_j^2(1+2\kappa_j^2)\} \int \int r_{pq}^{-8} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (34)$$

Formula (33) or (34) determines the contribution to P_0 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 [15, 16]. This formula, when applied to a single-component system, yields immediately the result derived by Jansen [17].

In the case of molecules having only isotropic dipole polarizability of the first-order the general expression (31) can be simplified to:

$$P_0^{(ij)} = \frac{2\pi}{9kT} \sum_{n=2}^{\infty} \frac{2^n(n+1)!n!}{(2n)!} \{a_i^2(\mathbf{M}_j^{(n)}[n]\mathbf{M}_j^{(n)}) + (\mathbf{M}_i^{(n)}[n]\mathbf{M}_i^{(n)})a_j^2\} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (35)$$

or to the still simpler form:

$$P_0^{(ij)} = \frac{2\pi}{9kT} \sum_{n=2}^{\infty} (n+1) \{a_i^2(M_j^{(n)})^2 + (M_i^{(n)})^2 a_j^2\} \int \int r_{pq}^{-2(n+2)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (36)$$

if the molecules possess moreover the axial symmetry, i.e. when

$$\mathbf{M}_i^{(n)}[n]\mathbf{M}_i^{(n)} = \frac{(2n)!}{2^n(n!)^2} \{M_i^{(n)}\}^2, \quad (37)$$

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

Formula (35) can be used, *i. a.*, in the case of tetrahedrally symmetric molecules (e.g. CH_4) having the octopole, $M_{xyz}^{(3)} \equiv \Omega$, and hexadecapole, $M_{xxxx}^{(4)} \equiv \Phi$ electric moments; namely, we obtain in this case the formula:

$$P_0^{(ij)} = \frac{32\pi}{15kT} \int \int \left\{ (a_i^2\Omega_j^2 + \Omega_i^2 a_j^2) r_{pq}^{-10} + \frac{25}{7} (a_i^2\Phi_j^2 + \Phi_i^2 a_j^2) r_{pq}^{-12} \right\} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q, \quad (38)$$

which 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 and hexadecapoles of its neighbours. For $\Phi=0$ and a one-component system, this effect was first computed by Johnston *et al.* [24] and measured in methane.

For $\Omega=0$, formula (38), in turn, can be applied to octahedral molecules (e.g. SF_6), in which case the first non-zero permanent moment is hexadecapolar Φ .

We shall now calculate the contributions to P_0 arising from the potential energy $V(\mathbf{r}, \boldsymbol{\omega})$ given by (23). However, we assume for simplicity that the multipolar molecules of the system are isotropically polarizable and mutually

interacting in pairs only. Thus, by (10), (23) and (27) we obtain an additional contribution to $P_0^{(ij)}$ dependent directly on T^{-2} :

$$P_0^{(ij)} = \frac{4\pi}{9k^2T^2} \sum_{n=2}^{\infty} \sum_{m=2}^{\infty} \frac{2^{n+m} n! m! (n+m+1)!}{(2n+1)!(2m+1)!} a_i a_j (\mathbf{M}_i^{(n)} [n] \mathbf{M}_i^{(n)}) \times (\mathbf{M}_j^{(m)} [m] \mathbf{M}_j^{(m)}) \iint r_{pq}^{-(2n+2m+5)} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q. \quad (39)$$

This expression yields for axially symmetric quadrupolar molecules:

$$P_0^{(ij)} = \frac{8\pi}{15k^2T^2} a_i a_j \Theta_i^2 \Theta_j^2 \iint r_{pq}^{-13} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (40)$$

or, for molecules possessing the tetrahedral symmetry:

$$P_0^{(ij)} = \frac{256\pi}{35k^2T^2} a_i a_j \Omega_i^2 \Omega_j^2 \iint r_{pq}^{-17} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (41)$$

if the term with hexadecapole moment can be neglected.

Quite similarly, expressions (31), (35) and (39) can be applied for other kinds of molecular symmetry, but we shall refrain here from writing the results obtained in the various special cases [32].

5. APPLICATION TO GASEOUS SYSTEMS AND DISCUSSION

In the case of very dense systems, $P^{(ij)}$ and $P^{(ijk)}$ cannot in general be reduced to a form suitable for numerical calculations and for subsequent comparison of equations (8), (12) and (30) with the 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 $P^{(ij)}$ can be reduced in general to a form adapted to numerical evaluations. In this case of moderately dense gases, the binary distribution function can be expressed as follows [4]:

$$n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) = \rho^2 \exp \left\{ -\frac{u_{ij}(r_{pq})}{kT} \right\} \{1 + O(\rho)\}, \quad (42)$$

with $\rho = N/V$ denoting the average number of molecules of the system and $u_{ij}(r_{pq})$ the potential energy of radial interactions between molecules p and q of species i and j separated by a distance r_{pq} .

If u_{ij} in (42) is the Lennard-Jones potential of the form:

$$u_{ij}(r_{pq}) = 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{pq}} \right)^8 - \left(\frac{\sigma_{ij}}{r_{pq}} \right)^t \right\}, \quad (43)$$

we have:

$$\iint r_{pq}^{-n} n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q = \frac{6b_{ij}\rho}{s y_{ij}^2 \sigma_{ij}^n} H_n^{s-t}(y_{ij}), \quad (44)$$

wherein [33]

$$H_n^{s-t}(y_{ij}) = y_{ij}^{2(s+3-n)/s} \sum_{m=0}^{\infty} \frac{1}{m!} y_{ij}^{2m(s-t)/s} \Gamma \left(\frac{mt+n-3}{s} \right), \quad (45)$$

with ϵ_{ij} and σ_{ij} denoting the well-known central force parameters and $y_{ij} = 2(\epsilon_{ij}/kT)^{1/2}$ and $b_{ij} = \frac{2}{3}\pi N\sigma_{ij}^3$.

With the help of (44) the quantity $P^{(ij)}$ discussed in §§ 3 and 4 can be written as:

$$P^{(ij)} = V^{-1} \{ B_p^{(ij)} + O(\rho) \}, \quad (46)$$

where $B_p^{(ij)}$ is the second virial coefficient of dielectric polarization.

In cases when the values of the molecular parameters ϵ_{ij} and σ_{ij} are known, we can use expressions (44) and (46) for evaluating $B_p^{(ij)}$ numerically; obviously, according to the system dealt with, one will have to assume such values of the molecular quadrupole, octopole, etc. moments as to achieve satisfactory agreement with the experimental data available for the second dielectric virial coefficient. In this way we can obtain information concerning the values of the multipole electric moments of various molecules.

For the sake of simplicity we shall carry out the evaluation of B_p only for a one-component gas. In the case of a quadrupolar gas we obtain from equations (19), (34), (40), (44) and (46), if the anisotropy in polarizabilities are neglected,

$$B_D = \frac{24b^2}{sy^4} \left(\frac{a}{\sigma^3} \right)^2 \left\{ \left(\frac{a}{\sigma^3} \right) H_6^{s-t}(y) + 5 \left(\frac{q}{\sigma^5} \right) H_8^{s-t}(y) + \dots \right\}, \quad (47)$$

$$B_O = \frac{3b^2}{sy^2} \left(\frac{\Theta^2}{\sigma^5 \epsilon} \right) \left\{ \left(\frac{a}{\sigma^3} \right)^2 H_8^{s-t}(y) + 36 \left(\frac{q}{\sigma^5} \right)^2 H_{12}^{s-t}(y) + \frac{y^2}{10} \left(\frac{a}{\sigma^3} \right)^2 \left(\frac{\Theta^2}{\sigma^5 \epsilon} \right) H_{13}^{s-t}(y) \right\}. \quad (48)$$

Similarly we obtain for B_O in the case of tetrahedral molecules possessing only the octopole moment Ω ,

$$B_O = \frac{48b^2}{5sy^2} \left(\frac{a}{\sigma^3} \right)^2 \left(\frac{\Omega^2}{\sigma^7 \epsilon} \right) \left\{ H_{10}^{s-t}(y) + \frac{3y^2}{7} \left(\frac{\Omega^2}{\sigma^7 \epsilon} \right) H_{17}^{s-t}(y) \right\}. \quad (49)$$

The table compares the values of $B_p^{\text{calc}} = B_D + B_O$ calculated from equations (47) and (48) for N_2 and CO_2 and equations (47) and (49) for CH_4 with the experimental data [18, 24]. We have performed the theoretical calculation for simplicity for $s=12$ and $t=6$ (in this case the functions H_n^{12-6} are to be found tabulated in ref. [34]) with the help of the following molecular data [30, 35] for N_2 : $\epsilon/k = 91.5^\circ K$, $\sigma = 3.681 \text{ \AA}$, $a = 1.76 \times 10^{-24} \text{ cm}^3$, for CO_2 : $\epsilon/k = 190^\circ K$, $\sigma = 3.996 \text{ \AA}$, $a = 2.92 \times 10^{-24} \text{ cm}^3$, and for CH_4 : $\epsilon/k = 137^\circ K$, $\sigma = 3.882 \text{ \AA}$, $a = 2.60 \times 10^{-24} \text{ cm}^3$.

It is seen from the table that good agreement between the calculated and experimental values of the second dielectric virial coefficients is obtained if the quadrupole moment of the N_2 molecule is $\Theta = 1.5 \times 10^{-26} \text{ e.s.u. cm}^2$ and that of the CO_2 molecule is [18] $\Theta = 5 \times 10^{-26} \text{ e.s.u. cm}^2$ with the octopole moment of the CH_4 molecule amounting to $\Omega = 4 \times 10^{-34} \text{ e.s.u. cm}^3$. We note also that the second virial coefficient B of the equation of state yields $\Theta = 1.8 - 1.9 \times 10^{-26} \text{ e.s.u. cm}^2$ for the N_2 molecule, $\Theta = 4.59 - 5.0 \times 10^{-26} \text{ e.s.u. cm}^2$ for the CO_2 molecule [35, 36] and $\Omega = 5 \times 10^{-34} \text{ e.s.u. cm}^3$ for the CH_4 molecule [33].

It is evident that further research in this direction can be fruitful and will surely bring much interesting information on the electric multipole moments and multipole polarizabilities of molecules.

In concluding, it should be stressed that the total dielectric polarization P of a multi-component system can be expanded in a power series in the mole fraction,

$$P = \sum_i x_i P_i + \sum_{ij} x_i x_j P_{ij} + \sum_{ijk} x_i x_j x_k P_{ijk} + \dots, \quad (50)$$

where the first term represents the additivity rule, while the subsequent terms account for deviations therefrom. The quantities P_{ij} and P_{ijk} are non-zero only for systems in which interactions occur both between molecules of the same species and between those of various components in dense systems. The expressions obtained here for P_{ij} and P_{ijk} allow to state that investigation of deviations of P from additivity can be a source, *i.a.*, of information concerning the permanent and induced electric multipoles of molecules of various species as well as on the nature and magnitude of the forces with which they interact in the dense mixture.

Gas	$T^\circ\text{K}$	B_D	B_O	$B_P^{\text{calc}} = B_D + B_O$	B_P^{exper}
N ₂ $\Theta = 1.5 \times 10^{-24}$ e.s.u. cm ²	242	1.9	1.9	3.8	4.2 (± 1.0) [24]
	296	1.8	1.4	3.2	2.0 (± 1.0) [24]
CO ₂ $\Theta = 5 \times 10^{-26}$ e.s.u. cm ²	323	9.8	40.9	50.7	49.7 [18]
	348	9.6	37.3	46.9	46.4 [18]
CH ₄ $\Omega = 4 \times 10^{-34}$ e.s.u. cm ³	242	5.5	3.5	9.0	9.0 (± 0.4) [24]
	315	5.3	2.9	8.2	7.3 (± 1.8) [24]

Calculated and experimental values of the second polarization virial coefficient in cm⁶/mol².

APPENDIX A

Quantum mechanical form of first-, second- and third-order multipole moments

We now consider, for simplicity, a system of identical, non-interacting molecules subjected to an external inhomogeneous electric field. The Hamiltonian of a molecule is $H = H_0 + H'$, where H_0 is the Hamiltonian of the non-perturbed (isolated) molecule and

$$H' = - \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \mathbf{M}^{(n)}[n] \mathbf{E}_0^{(n)} \quad (\text{A1})$$

is the perturbation Hamiltonian resulting from interaction between the 2^n -pole moment operator of the molecule [33]

$$\mathbf{M}^{(n)} = \sum_{\nu} e_{\nu} r_{\nu}^n \mathbf{Y}^{(n)}(\mathbf{r}_{\nu}) \quad (\text{A2})$$

and an external electric field $\mathbf{E}_0^{(n)} = -\{\nabla^n \phi\}_0$ of ∇ -degree n †. In (A2), e_{ν} is the ν th electric charge of the molecule with radius vector \mathbf{r}_{ν} and the operator $\mathbf{Y}^{(n)}$ of order n is given by:

$$\begin{aligned} \mathbf{Y}^{(n)}(\mathbf{r}_{\nu}) &= \frac{(-1)^n}{n!} r_{\nu}^{n+1} \nabla^n \left(\frac{1}{r_{\nu}} \right) \\ &= \frac{1}{n! r_{\nu}^n} \{ (2n-1)!! \mathbf{r}_{\nu 1} \mathbf{r}_{\nu 2} \dots \mathbf{r}_{\nu n} - (2n-3)!! r_{\nu}^2 \sum \mathbf{U}_{12} \mathbf{r}_{\nu 3} \dots \mathbf{r}_{\nu n} + \dots \\ &\quad + (-1)^k (2n-2k-1)!! r_{\nu}^{2k} \sum \mathbf{U}_{12} \dots \mathbf{U}_{2k-1, 2k} \mathbf{r}_{\nu 2k+1} \dots \mathbf{r}_{\nu n} + \dots \}, \quad (\text{A3}) \end{aligned}$$

where \mathbf{U}_{12} is the unit second-rank tensor and $\sum \mathbf{U}_{12} \mathbf{r}_{\nu 3} \dots \mathbf{r}_{\nu n}$, etc. are sums of terms resulting from the one written out by interchanging the indices 1, 2, . . . n .

† By ∇ -degree n we mean n -fold application of the operator ∇ .

Using (A 1) and the quantal perturbation method we obtain in turn for the first-, second- and third-order multipole moments induced in the molecule by the external electric field :

$$\left. \begin{aligned}
 \mathbf{M}^{(n)} &= \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} {}^{(n)}\mathbf{A}^{(n_1)} [n_1] \mathbf{E}_0^{(n_1)}, \\
 \mathbf{M}^{(n)} &= \frac{1}{3} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{2^{n_1+n_2} n_1! n_2!}{(2n_1)!(2n_2)!} {}^{(n)}\mathbf{B}^{(n_1+n_2)} [n_1+n_2] \mathbf{E}_0^{(n_1)} \mathbf{E}_0^{(n_2)}, \\
 \mathbf{M}^{(n)} &= \frac{1}{6} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \frac{2^{n_1+n_2+n_3} n_1! n_2! n_3!}{(2n_1)!(2n_2)!(2n_3)!} \\
 &\quad \times {}^{(n)}\mathbf{C}^{(n_1+n_2+n_3)} [n_1+n_2+n_3] \mathbf{E}_0^{(n_1)} \mathbf{E}_0^{(n_2)} \mathbf{E}_0^{(n_3)}.
 \end{aligned} \right\} \quad (\text{A } 4)$$

Here, the first-order multipole polarizability tensor or, simply, the multipole polarizability tensor

$${}^{(n)}\mathbf{A}^{(n_1)} = \hbar^{-1} \sum_{k \neq g} \omega_{kg}^{-1} (\mathbf{M}_{gk}^{(n)} \mathbf{M}_{kg}^{(n_1)} + \mathbf{M}_{gk}^{(n_1)} \mathbf{M}_{kg}^{(n)}) \quad (\text{A } 5)$$

characterizes the linear or first-order polarization of the 2^n -pole electric moment of a molecule due to an electric field of degree n_1 ; $\mathbf{M}_{gk}^{(n)}$ is the matrix element for the transition from the ground state g to the excited state k with the frequency ω_{gk} in the absence of perturbation.

Similarly the quantum-mechanical expressions for the second- and third-order multipole polarizability tensors are of the form :

$$\begin{aligned}
 {}^{(n)}\mathbf{B}^{(n_1+n_2)} &= -\hbar^{-2} P(n, n_1, n_2) \left\{ \sum_{k \neq g} \omega_{kg}^{-2} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{gk}^{(n_1)} \mathbf{M}_{gk}^{(n_2)} \right. \\
 &\quad \left. - \sum_{k \neq g} \sum_{l \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{kl}^{(n_1)} \mathbf{M}_{lg}^{(n_2)} \right\}, \quad (\text{A } 6)
 \end{aligned}$$

$$\begin{aligned}
 {}^{(n)}\mathbf{C}^{(n_1+n_2+n_3)} &= \hbar^{-3} P(n, n_1, n_2, n_3) \left\{ \sum_{k \neq g} \omega_{kg}^{-3} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{gk}^{(n_1)} \mathbf{M}_{gk}^{(n_2)} \mathbf{M}_{gk}^{(n_3)} \right. \\
 &\quad - \sum_{k \neq g} \sum_{l \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} [\omega_{kg}^{-1} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{kg}^{(n_1)} \mathbf{M}_{gl}^{(n_2)} \mathbf{M}_{lg}^{(n_3)} + \omega_{lg}^{-1} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{kl}^{(n_1)} \mathbf{M}_{lg}^{(n_2)} \mathbf{M}_{gg}^{(n_3)} \\
 &\quad \left. + \omega_{kg}^{-1} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{gg}^{(n_1)} \mathbf{M}_{gk}^{(n_2)} \mathbf{M}_{kl}^{(n_3)} + \sum_{k \neq g} \sum_{l \neq g} \sum_{m \neq g} \omega_{kg}^{-1} \omega_{lg}^{-1} \omega_{mg}^{-1} \mathbf{M}_{gk}^{(n)} \mathbf{M}_{kl}^{(n_1)} \mathbf{M}_{lm}^{(n_2)} \mathbf{M}_{mg}^{(n_3)} \right\}, \quad (\text{A } 7)
 \end{aligned}$$

where $P(n, n_1, n_2, \dots)$ denotes a symmetrizing operation over all permutations of n, n_1, n_2, \dots .

The numerical values of diagonal matrix elements of the second- and third-order multipole polarizability tensors of (A 6) and (A 7) can be calculated directly by methods discussed in the paper of Dalgarno [37] for the case of first-order multipole polarizability.

The effect of molecular interactions on the multipole polarizability tensors (A 5)–(A 7) can be calculated, e.g., by a method analogical to that elaborated by Jansen *et al.* [5, 17].

APPENDIX B

Higher-order intermolecular energies

We consider two non-overlapping molecular systems p and q which have in general 2^n -pole and 2^m -pole electric moments, respectively. The vector connecting the centres of these interacting molecular systems is \mathbf{r}_{pq} , and $\mathbf{r}_{p'}$ and $\mathbf{r}_{q'}$

are radius vectors of their electric charges $e_{p\nu}$ and $e_{q\mu}$. The energy of electrostatic interaction between the two molecular systems

$$u_{pq} = \sum_{\nu} \sum_{\mu} \frac{e_{p\nu} e_{q\mu}}{|\mathbf{r}_{pq} - \mathbf{r}_{p\nu} + \mathbf{r}_{q\mu}|} \quad (\text{B1})$$

may be expanded in the following form [31, 33]:

$$u_{pq} = - \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^m \frac{2^{n+m} n! m!}{(2n)!(2m)!} \mathbf{M}_p^{(n)}[n]^{(n)} \mathbf{T}_{pq}^{(m)}[m] \mathbf{M}_q^{(m)}, \quad (\text{B2})$$

where the multipole interaction tensor is of the form:

$${}^{(n)}\mathbf{T}_{pq}^{(m)} = -\nabla^{n+m} \left(\frac{1}{r_{pq}} \right) = (-r_{pq})^{-(n+m+1)} \mathbf{Y}^{(n+m)}(\mathbf{r}_{pq}) \quad (\text{B3})$$

with ${}^{(n)}\mathbf{T}_{pq}^{(m)} = (-1)^{n+m} {}^{(m)}\mathbf{T}_{qp}^{(n)}$ and $\mathbf{Y}^{(n+m)}(\mathbf{r}_{pq})$ defined by (A3) if n is replaced by $n+m$ and \mathbf{r} by \mathbf{r}_{pq} .

We now generalize the equation (B2) to the case of a multi-component system containing $N_1, N_2, \dots, N_i, \dots$ molecular systems of the first, second, \dots i th species, and obtain for the total first-order (or electrostatic) energy of molecular interactions:

$$V^{(1)} = -\frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^m \frac{2^{n+m} n! m!}{(2n)!(2m)!} \mathbf{M}_{pi}^{(n)}[n]^{(n)} \mathbf{T}_{pq}^{(m)}[m] \mathbf{M}_{qj}^{(m)}, \quad (\text{B4})$$

or, in concise form:

$$V^{(1)} = -\frac{1}{2} \sum_i \sum_{p=1}^{N_i} \sum_{n=0}^{\infty} \frac{2^n n!}{(2n)!} \mathbf{M}_{pi}^{(n)}[n] \mathbf{F}_{0pi}^{(n)}, \quad (\text{B5})$$

where the molecular electric field of degree n at the centre of the molecular system p of species i due to the electric multipoles of all the other molecular systems is given by:

$$\mathbf{F}_{0pi}^{(n)} = \sum_j \sum_{q=1}^{N_j} \sum_{m=0}^{\infty} (-1)^m \frac{2^m m!}{(2m)!} {}^{(n)}\mathbf{T}_{pq}^{(m)}[m] \mathbf{M}_{qj}^{(m)}. \quad (\text{B6})$$

Similarly, the second-order intermolecular energy may be expanded in the following form:

$$V^{(2)} = -\frac{1}{2} \sum_i \sum_{p=1}^{N_i} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^{n+m} n! m!}{(2n)!(2m)!} \mathbf{F}_{0pi}^{(n)}[n]^{(n)} \mathbf{A}_{pi}^{(m)}[m] \mathbf{F}_{0pi}^{(m)}, \quad (\text{B7})$$

or by (B6) in explicit form:

$$V^{(2)} = -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sum_{n_1=0}^{\infty} \sum_{m_1=0}^{\infty} (-1)^{n+m} \frac{2^{n+m+n_1+m_1} n! m! n_1! m_1!}{(2n)!(2m)!(2n_1)!(2m_1)!} \\ \times \mathbf{M}_{qj}^{(n_1)}[n_1]^{(n_1)} \mathbf{T}_{qp}^{(n)}[n]^{(n)} \mathbf{A}_{pi}^{(m)}[m]^{(m)} \mathbf{T}_{pr}^{(m_1)}[m_1] \mathbf{M}_{rk}^{(m_1)}. \quad (\text{B8})$$

In general we have for the $(s + 1)$ -order energy of intermolecular interactions ($s = 1, 2, \dots$):

$$V^{(s+1)} = -\frac{1}{s+1} \sum_i \sum_{p=1}^{N_i} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \mathbf{M}_{pi}^{(n)} [n] \mathbf{F}_{0pi}^{(n)}, \tag{B 9}$$

where

$$\mathbf{M}_{pi}^{(s)} = \frac{1}{s!} \sum_{n_1=1}^{\infty} \dots \sum_{n_s=1}^{\infty} \frac{2^{n_1+\dots+n_s} n_1! \dots n_s!}{(2n_1)! \dots (2n_s)!} \times {}^{(n)}\mathbf{A}_{pi}^{(n_1+\dots+n_s)} [n_1 + \dots + n_s] \mathbf{F}_{0pi}^{(n_1)} \dots \mathbf{F}_{0pi}^{(n_s)} \tag{B 10}$$

is the s th-order multipole moment induced in a molecular system p of species i by molecular electric fields of (B 6).

It is clear that by appropriate simplifying assumptions we can obtain directly from the general expressions (B 4) and (B 8) the special results derived previously by Debye, Keesom and others (see e.g. [30]).

By (A 3) and (B 3), we obtain the following identity:

$${}^{(n)}\mathbf{T}_{pq}^{(m)} [n+m] {}^{(n)}\mathbf{T}_{rs}^{(m)} = \frac{(2n+2m)!}{2^{n+m}} (r_p q r_{rs})^{-(n+m+1)} P_{n+m} \left(\frac{r_p q \cdot r_{rs}}{r_p q r_{rs}} \right), \tag{B 11}$$

which has been recurred to in the course of the present investigation. If in particular $\vec{p} = r$ and $q = s$ we have $P_{n+m}(1) = 1$, and (B 11) yields the identity derived by Jansen [31].

The computations of the various contributions to P_D and P_0 were performed with the help of the following unweighted orientational average:

$$\langle \mathbf{M}_p^{(n)} \mathbf{M}_p^{(m)} \rangle_{\omega} = \begin{cases} \frac{1}{2n+1} (\mathbf{M}_p^{(n)} [n] \mathbf{M}_p^{(n)}) \mathbf{U}^n & \text{for } n=m, \\ 0 & \text{for } n+m \text{ odd.} \end{cases} \tag{B 12}$$

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