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

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The theory of the electric polarization of a multi-component system is developed on the basis of the existing statistical theories. It is assumed that a molecule $p$ has in general a $2^n$-pole permanent electric moment $M_p^{(n)}$ and the $2^n$-pole moment $P_p^{(n)}$ induced by the total electric field of order $n$ (external $E^{(n)}$ plus molecular $F_p^{(n)}$). A general expression for the $n$-th order molecular field $F_p^{(n)}$ at the molecule $p$ is obtained in terms of the permanent multipole moments $M_p^{(n)}$, $2^n$-pole — $2^m$-pole interactions tensor ${}^{(n)}T_{pq}^{(m)}$ between molecules $p$ and $q$, and $n+m$ rank polarizability tensor ${}^{(n)}A_p^{(m)}$ characterizing the polarization of the $2^n$-pole moment of a molecule $p$ due to the electric field of order $m$. The fundamental equation thus obtained for the dipole distortion polarizability $P_D$ of the medium is discussed in some orders of approximations. In the zeroth-approximation, when multipole interactions between permanent moments of the molecules are absent in the system, the calculation of $P_D$ is performed to the third power in the dipole polarizability and first power of the field gradient quadrupole polarizability, of the molecule. In this case $P_D$ is formally expressed as a power series in molar fractions, whose first term represents the additivity rule, while the subsequent terms account for deviations therefrom. By appropriate simplifying assumptions these results reduce to the known formulas. In further approximations the temperature-dependent contributions to $P_D$ resulting from the non-zero multipole interaction potential energy are calculated in the case of dipolar systems, quadrupolar systems or systems of molecules possessing both dipole and quadrupole moments. The effect of anisotropy in the dipole polarizability of the individual molecules is also taken into account. These calculations are performed for simplicity in the pairs correlation approximation only.

## 1. Introduction

The effect of molecular interactions on the electric permittivity $\varepsilon$ of a dense medium has been the subject of many experimental and theoretical investigations, and continues to present considerable scientific interest. It is well-known that molecular interactions of

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various kinds lead to deviations from the Clausius-Mossotti equation

$$\frac{\varepsilon-1}{\varepsilon+2} V = \frac{4\pi}{3} N\alpha \tag{1.1}$$

of a substance of volume $V$ (per mole) containing $N$ (Avogadro number) identical nondipolar molecules possessing the constant electric polaryzability $\alpha$ (polarizability of an isolated molecule independent of interactions with its neighbours).

In the case of nonpolar substances the deviations from (1.1) are small, whereas in dipolar substances the deviations from the Debye-Langevin equation,

$$\frac{\varepsilon-1}{\varepsilon+2} V = \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT}\right) \tag{1.2}$$

are particularly large ($\mu$ is the permanent dipole moment of an isolated molecule and $T$ — the temperature).

By Eq. (1.1), the Clausius-Mossotti function is independent of the temperature and density of the medium. This holds strictly only in the ideal case of a system of noninteracting molecules, e. g. a perfect gas. In dense systems of interacting molecules the $C$—$M$ function is not a constant but is density — or temperature — dependent.

The deviations from Eq. (1.1) can be satisfactorily explained on the basis of the classical statistical theories initiated by Kirkwood (1936) and Yvon (1937). In those theories, the effect of fluctuations in the induced dipole moment of molecules with constant polarizabilities gave rise to a small increase of the $C$—$M$ function proportional in a first approximation to the density. The Kirkwood-Yvon theoreis were modified and further developed by Van Vleck (1937), Brown (1950), De Boer, Maessen and Seldam (1953), Mandel and Mazur (1958), and others. Jansen and Mazur (1955) using a perturbation method calculated the variation of the molecular polarizability due to pairwise interactions of molecules and obtained in this way a further increase of the $C$—$M$ function with the density.

Another effect which contributes to the $C$—$M$ function of nondipolar substances and depends directly on the temperature arises from the statistical mean square of the dipole moments induced in the molecules by permanent multipole moments of neighbouring molecules in the absence of an external electric field. Buckingham and Pople (1955), Zwanzig (1956), Jansen (1958) and Johnston and Cole (1962) calculated this effect from permanent quadrupole moments by using a method of expansion of the $C$—$M$ function in a virial type series. Earlier, a virial theory of dielectric polarization in dipolar imperfect gases, analogous to Mayer's cluster expansion, was proposed and discussed by Harris and Alder (1953 b), and extended by Harris (1955) to include the effect of fluctuations in the dipole moments. In the case of quadrupolar gases we shall take into account the additional temperature-dependent effect resulting from the presence of the quadrupole-quadrupole and incluced dipole-induced dipole interactions between molecules, which cannot be neglected in comparison with the above-mentioned quadrupole-induced dipole effect alone (Kielich 1962a). The effect from higher permanent multipole moments was calculated by Johnston, Oudemans and Cole (1960) for the octopole moment of like tetrahedral molecules such as methane as well as by the present author for the case of unlike

molecules of arbitrary symmetry presenting an octopole moment (Kielich 1962b, 1963) or a hexadecapole moment (Kielich 1964). The general and systematic discussion of the virial expansion method of the dielectric constant of imperfect gases is due to Hill (1958) and, along different paths, to Kaufman and Watson (1961) and Isihara and Hanks (1962). Recently, Isihara (1963) formulated an interesting theory in which the Clausius-Mossotti function of a nonpolar fluid is expressed in terms of quantum-mechanical cluster integrals.

Other original treatments of the dielectric problem have been proposed by Onsager (1936) and Kirkwood (1939). Kirkwood in his statistical theory of the dielectric polarization of dipolar liquids considers the interaction of a spherical specimen of the dielectric of macroscopic size, surrounded by vacuum, with an applied electric field, and uses the Onsager model to derive his final formula. This semi-macroscopic treatment was subsequently modified and developed in various ways by Fröhlich (1949), Harris and Alder (1953a), Brown (1953), Harris (1955), Buckingham (1956) and Cole (1957) (see also Kielich 1958).

Fowler (1935) and Debye (1935) introduced rotational coupling of a dipolar molecule in the internal field of a surrouding medium of quasi-crystalline type. This method, which bases on a concrete molecular coupling model and the local field of Lorentz or Onsager type, has been used and further developed by Piekara (1937, 1950), Anselm (1943), Frenkel (1946), Piekara and Kielich (1958) and others.

The statistical theories mentioned above refer only to one-component systems of identical molecules. The virial theory of the $C-M$ function of a compressed gas mixtures has been given by Buckingham and Raab (1958) (see also Kielich 1962 a, b), and an analogous theory of the Lorentz-Lorenz function has been evolved by the present author (Kielich 1962 c, d). We should also mention that Bullough (1962) examined in general higher-order fluctuation effects and higher induced multipole contributions to the refractive index of two--component systems.

In the present paper, the foregoing statistical theories of electric polarization of fluids are extended to the case of an arbitrary system consisting of molecules of various species, where interactions of permanent multipole moments as well as anisotropy in the polarizability of molecules are considered. This theory leads to a formal expression for the total electric polarization of a multi-component system in the form

$$P_T \equiv \frac{\varepsilon-1}{\varepsilon+2} \, V = \sum_i x_i P_T^{(i)} + \sum_{ij} x_i x_j P_T^{(ij)} + \sum_{ijk} x_i x_j x_k P_T^{(ijk)} + \ldots , \qquad (1.3)$$

where $x_i$ is the mole fraction of the $i$-th component of the system of volume $V$.

Since $P_T^{(i)}$, the total polarization of the $i$-th component of noninteracting molecules, depends neither on the concentration nor on the density of the system as will be shown from Eqs (1.1) or (1.2), the first term in (1.3) expresses the well-known additivity of $P_T$. The remaining quantities $P_T^{(ij)}$ and $P_T^{(ijk)}$ are expressed, respectively, by the binary and ternary distribution functions $n_{ij}^{(2)}$, $n_{ijk}^{(3)}$ and are non-zero only for a system presenting non--zero interactions between pairs, triples, etc. of molecules of various species. In this way if $P_T^{(ij)}$ and $P_T^{(ijk)}$ depend on the density, on the temperature as well as on the concentration, then the second, third and higher terms in Eq. (1.3) constitute a measure of the deviation from the additivity rule of $P_T$.

It is well-known, that the total electric polarization $P_T$ is composed of the distortion (or deformation) polarization $P_D$, which represented the direct effect of the applied electric field polarizing the molecules of the system, and of the orientational (or directional) polarization $P_O$ arising from the statistical effect of alignment of the molecules in the direction of the external electric field. In the first part of our paper we are interested only in the distortion polarisation $P_D$. The explicit expressions obtained for $P_D^{(ij)}$ and $P_D^{(ijk)}$ by tensorial formalism, contain in the zeroth-approximation of our theory, besides the Kirkwood-Yvon effect of fluctuations in the induced dipole moments a similar effect from quadrupole moments induced in the molecules by the molecular field gradient. In this approximation the quantities $P_D^{(ij)}$ and $P_D^{(ijk)}$ are functions of the density but not dependent directly on the temperature (obviously in this case there is indirect dependence on the temperature through the distribution functions $n_{ij}^{(2)}$ and $n_{ijk}^{(3)}$). The additional contributions to $P_D^{(ij)}$ which depends diretly on the temperature is obtained if in the calculations of $P_D$ the multipole interaction potential energy and the anisotropy of dipole polarizability is taken into account. These calculations are performed for the case of systems consisting respectively of dipolar molecules, quadrupolar molecules or of molecules with dipole and quadrupole moments. To simplify the problem, however, the effect of molecular interaction on the polarizability of the molecules will not be considered in explicit form.

## 2. General theory

Let us consider a homogeneous medium of volume $V$, macroscopically isotropic in the absence of external forces. The relationship between the electric displacement vector $\boldsymbol{D}$ and the mean macroscopic electric field $\boldsymbol{E}_m$ existing within the medium is expressed by means of the electric permittivity $\varepsilon$ through the well-known expression

$$\boldsymbol{D} = \varepsilon \boldsymbol{E}_m. \tag{2.1}$$

On the other hand, since in a external electric field the medium undergoes polarization, the electric displacement vector can be formally expressed in the following general form (for comparison, see Jansen 1958)

$$\boldsymbol{D} = \boldsymbol{E}_m + 4\pi \sum_{n=0}^{\infty} (-1)^n \frac{2^{n+1}(n+1)!}{(2n+2)!} \, \nabla^n[n] \, \boldsymbol{P}^{(n+1)}, \tag{2.2}$$

where $\boldsymbol{P}^{(n+1)}$ is the electric polarization operator of order $n+1$ of the medium, $\nabla$ is the differential operator, and the symbol $[n]$ denotes in Jansen's notation that the product of the two $n$-th rank tensors $\nabla^n$ and $\boldsymbol{P}^{(n)}$ is contracted $n$ times.

By (2.1) and (2.2) we may write the electric permittivity of an isotropic medium as the following general equation:

$$(\varepsilon - 1)\boldsymbol{E}_m = 4\pi \sum_{n=0}^{\infty} (-1)^n \frac{2^{n+1}(n+1)!}{(2n+2)!} \, \nabla^n[n] \, \boldsymbol{P}^{(n+1)}, \tag{2.3}$$

from which we have in approximation

$$(\varepsilon-1)\boldsymbol{E}_m = 4\pi \left\{ \boldsymbol{P}^{(1)} - \frac{1}{3}\, \nabla \cdot \boldsymbol{P}^{(2)} + \frac{1}{15}\, \nabla\nabla : \boldsymbol{P}^{(3)} - \ldots \right\}. \tag{2.4}$$

Here, $\boldsymbol{P}^{(1)} \equiv \boldsymbol{P}$ is the first order polarization, or dipole polarization vector, $\boldsymbol{P}^{(2)} \equiv \boldsymbol{Q}$ is the second order polarization, or quadrupole polarization tensor, $\boldsymbol{P}^{(3)} \equiv \boldsymbol{O}$ is the third order polarization, or octopole polarization tensor, *etc.*

In the case when the applied electric field $\boldsymbol{E}$ is homogeneous, and when for convenience the medium is represented as a macroscopic spherical sample, in vacuum, for which $\boldsymbol{E} = (\varepsilon+2)\, \boldsymbol{E}_m/3$, Eq. (2.4) yields by statistical mechanics in the dipole polarization approximation

$$\frac{\varepsilon-1}{\varepsilon+2}\, E = \frac{4\pi}{3V}\, \langle \boldsymbol{M} \cdot \boldsymbol{e} \rangle_E = \frac{4\pi}{3V}\, \langle M_E \rangle_E. \tag{2.5}$$

Here, $M_E = \boldsymbol{M} \cdot \boldsymbol{e} = V\boldsymbol{P} \cdot \boldsymbol{e}$ is the component of the total dipole moment of the spherical sample in the direction $\boldsymbol{e}$ of the applied electric field, and $\langle M_E \rangle_E$ denotes the statistical mean value of $M_E$ in the presence of an external electric field defined as follows:

$$\langle M_E \rangle_E = \frac{\displaystyle\int M_E \exp\left\{ -\frac{U(\tau, \boldsymbol{E})}{kT} \right\} d\tau}{\displaystyle\int \exp\left\{ -\frac{U(\tau, \boldsymbol{E})}{kT} \right\} d\tau}, \tag{2.6}$$

with $U(\tau, \boldsymbol{E})$ denoting the total potential energy of the system when the configuration is $\tau$ and the external field $\boldsymbol{E}$.

In the case of a weak electric field we can restrict ourselves to the linear approximation in $E$ when expanding $\langle M_E \rangle_E$ in power of $E$, and Eq. (2.6) yields ($M_E = 0$ at $E = 0$)

$$\langle M_E \rangle_E = \left\{ \frac{\partial}{\partial E}\, \langle M_E \rangle_E \right\}_{E=0} E = \left\{ \left\langle \frac{\partial M_E}{\partial E} \right\rangle - \frac{1}{kT} \left\langle M_E\, \frac{\partial U}{\partial E} \right\rangle \right\} E, \tag{2.7}$$

where the brackets $\langle \; \rangle$ without lower index denote the statistical average at zero external field

$$\langle \Phi \rangle = \frac{\displaystyle\int \Phi \exp\left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}{\displaystyle\int \exp\left\{ -\frac{U(\tau, 0)}{kT} \right\} d\tau}, \tag{2.8}$$

with $U(\tau, 0)$ denoting the total potential energy of the system at configuration $\tau$ in the absence of an external electric field.

By (2.7), Eq. (2.5) yields for the total electric dipole polarizability of a medium, or Clausius-Mossotti function,

$$P_T \equiv \frac{\varepsilon-1}{\varepsilon+2}\, V = P_D + P_O, \tag{2.9}$$

where

$$P_D^{\cdot} = \frac{4\pi}{3} \left\langle \frac{\partial M_E}{\partial E} \right\rangle, \tag{2.10}$$

is the distortion polarizability of the medium, and

$$P_O = -\frac{4\pi}{3kT} \left\langle M_E \frac{\partial U}{\partial E} \right\rangle = \frac{4\pi}{9kT} \langle M^2 \rangle, \tag{2.11}$$

is its orientational polarizability.

We assume that in Eq. (2.8) the total potential energy of the system $U(\tau, 0)$ can be split into the central-force part $U^{(0)}, (r^N)$, which is a function of the set of $N$ position vectors $r^N = r_1, r_2, \dots r_N$ of the molecules contained in the volume $V$ only, and the tensorial-force part $V_t(r^N, \omega^N)$ dependent both on $r^N$ and on the angular coordinates $\omega^N$ determining the orientations of all $N$ molecules. Considering $V_t$ to represent a perturbation to the unpertubed energy $U^{(0)}$, the statistical mean values (2.8) can be put in the form

$$\langle \Phi \rangle = \frac{\displaystyle\sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{1}{kT} \right)^n \langle \Phi V_t^n \rangle_0}{\displaystyle\sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{1}{kT} \right)^n \langle V_t^n \rangle_0}, \tag{2.12}$$

where

$$\langle \Phi \rangle_0 = \frac{(N-h)!}{N!} \int \dots_{(h)} \int \overline{\Phi(r^N)} n^{(h)}(r^h) dr^h, \tag{2.13}$$

is the statistical average evaluated with the distributions functions of the $h$ molecules of the unperturbed system

$$n^{(h)}(r^h) = \frac{N! \int \dots_{(N-h)} \int \exp\left\{ -\frac{U^{(0)}(r^N)}{kT} \right\} dr^{N-h}}{(N-h)! \int \dots_{(N)} \int \exp\left\{ -\frac{U^{(0)}(r^N)}{kT} \right\} dr^N}. \tag{2.14}$$

Here, the unveighted average of the function $\Phi$ over all orientations of the molecules is defined as

$$\overline{\Phi(r^N)} = \frac{1}{\Omega^N} \int \dots_{(N)} \int \Phi(r^N, \omega^N) d\omega^N \text{ with } \Omega^N = \int \dots_{(N)} \int d\omega^N. \tag{2.15}$$

From (2.12) we obtain, to the desired approximation,

$$\langle \Phi \rangle = \langle \Phi \rangle_0 - \frac{1}{kT} \{ \langle \Phi V_t \rangle_0 - \langle \Phi \rangle_0 \langle V_t \rangle_0 \} +$$

$$+ \frac{1}{2k^2 T^2} \{\langle \Phi V_t^2 \rangle_0 - 2\langle \Phi V_t \rangle_0 \langle V_t \rangle_0 + \langle \Phi \rangle_0 (2\langle V_t \rangle_0^2 - \langle V_t^2 \rangle_0)\} -$$

$$- \frac{1}{6k^3 T^3} \{\langle \Phi V_t^3 \rangle_0 + ...\} + \frac{1}{24k^4 T^4} \{\langle \Phi V_t^4 \rangle_0 + ...\} - ... \qquad (2.16)$$

Assuming $N = \sum_i N_i$ molecules of various species to be present within the sphere of volume $V$, we can write in general

$$\boldsymbol{M} = \boldsymbol{M_0} + \sum_i \sum_{p=1}^{N_i} \sum_{n_1=1}^{\infty} \frac{2^{n_1} n_1!}{(2n_1)!} {}^{(1)}A_{pi}^{(n_1)}[n_1] (\boldsymbol{E}^{(n_1)} + \boldsymbol{F}_{pi}^{(n_1)}), \qquad (2.17)$$

where $\boldsymbol{M_0}$ is the electric dipole moment of the sphere at zero external field, $N_i$ is the number of molecules of species $i$, ${}^{(1)}A_{pi}^{(n_1)}$ is the tensor of rank $1+n_1$ characterizing the polarization of the dipole moment of the molecule $p$ of species $i$ due to the total electric field $\boldsymbol{E}^{(n_1)} + \boldsymbol{F}_{pi}^{(n_1)}$ of order $n_1$.

The molecular electric field $\boldsymbol{F}_{pi}^{(n_1)}$ of order $n_1$ at the centre of the $p$-th molecule of species $i$ due to all the other molecules of the system in the presence of an external electric field is of the form (Kielich 1965)

$$\boldsymbol{F}_{pi}^{(n_1)} = \sum_j \sum_{q=1}^{N_j} \sum_{n_2=1}^{\infty} (-1)^{n_2} \frac{2^{n_2} n_2!}{(2n_2)!} {}^{(n_1)}T_{pq}^{(n_2)}[n_2] (\boldsymbol{M}_{qj}^{(n_2)} + \boldsymbol{P}_{qj}^{(n_2)}), \qquad (2.18)$$

wherein

$${}^{(n_1)}T_{pq}^{(n_2)} = - \nabla^{n_1} \nabla^{n_2} \left(\frac{1}{r_{pq}}\right), \quad p \neq q \qquad (2.19)$$

is the tensor of rank $n_1 + n_2$ describing the $2^{n_1}$-pole — $2^{n_2}$-pole interactions between the molecules $p$ and $q$ separated by a distance $r_{pq}$; the differential operator $\nabla$ is directed from molecule $q$ to $p$. $\boldsymbol{M}_{qj}^{(n_2)}$ is the $n_2$-th rank tensor of the $2^{n_2}$-pole permanent moment of the molecule $p$ of species $i$ and

$$\boldsymbol{P}_{qj}^{(n_2)} = \sum_{n_3=1}^{\infty} \frac{2^{n_3} n_3!}{(2n_3)!} {}^{(n_2)}A_{qj}^{(n_3)}[n_3] (\boldsymbol{E}^{(n_3)} + \boldsymbol{F}_{qj}^{(n_3)}) \qquad (2.20)$$

is the tensor of its $2^{n_2}$-pole induced moment of order $n_2$.

In particular, we obtain from (2.20) for a first-order induced moment ($n_2 = 1$), or induced dipole moment,

$$\boldsymbol{P}_{qj}^{(1)} = {}^{(1)}A_{qj}^{(1)} \cdot (\boldsymbol{E}^{(1)} + \boldsymbol{F}_{qj}^{(1)}) + \frac{1}{3} {}^{(1)}A_{qj}^{(2)} : (\boldsymbol{E}^{(2)} + \boldsymbol{F}_{qj}^{(2)}) + \frac{1}{15} {}^{(1)}A_{qj}^{(3)} \vdots (\boldsymbol{E}^{(3)} + \boldsymbol{F}_{qj}^{(3)}) + ...,$$

$$(2.21)$$

where ${}^{(1)}A^{(1)}$, ${}^{(1)}A^{(2)}$ and ${}^{(1)}A^{(3)}$ are the tensors of dipole electric polarization caused by the first-order electric field $\boldsymbol{E}^{(1)}$ or — in brief — electric field, the second-order field

$E^{(2)}$ (or field gradient) and third-order field $E^{(3)}$ (or gradient of field gradient), respectively.

Similarly, for $n_2 = 2$ we obtain from (2.20) the second-order induced moment, or quadrupole induced moment,

$$P_{qj}^{(2)} = {}^{(2)}A_{qj}^{(1)} \cdot (E^{(1)} + F_{qj}^{(1)}) + \frac{1}{3} {}^{(2)}A_{qj}^{(2)} : (E^{(2)} + F_{qj}^{(2)}) + ..., \tag{2.22}$$

where ${}^{(2)}A^{(1)}$, ${}^{(2)}A^{(2)}$, ... are the tensors of quadrupole electric polarization due, respectively, to the electric field, field gradient *etc.*

From Eqs (2.18) and (2.20) it follows that the total molecular field is of the form

$$F_{pi}^{(n_1)} = F_{0pi}^{(n_1)} + \sum_j \sum_{q=1}^{N_j} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} (-1)^{n_2} \frac{2^{n_2+n_3} n_2! \, n_3!}{(2n_2)!(2n_3)!} {}^{(n_1)}T_{pq}^{(n_2)}[n_2]^{(n_2)}A_{qj}^{(n_3)}[n_3]E^{(n_3)} +$$

$$+ \sum_{jk} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \sum_{n_4=1}^{\infty} \sum_{n_5=1}^{\infty} (-1)^{n_3+n_4} \frac{2^{n_2+n_3+n_4+n_5} n_2! \, n_3! \, n_4! \, n_5!}{(2n_2)! \, (2n_3)! \, (2n_4)! \, (2n_5)!} \times$$

$$\times {}^{(n_1)}T_{pq}^{(n_2)}[n_2]^{(n_2)}A_{qj}^{(n_3)}[n_3]^{(n_3)}T_{qr}^{(n_4)}[n_4]^{(n_4)}A_{rk}^{(n_5)}[n_5]E^{(n_5)} + ..., \tag{2.23}$$

with

$$F_{0pi}^{(n_1)} = \sum_j \sum_{q=1}^{N_j} \sum_{n_2=1}^{\infty} (-1)^{n_2} \frac{2^{n_2} n_2!}{(2n_2)!} {}^{(n_1)}T_{pq}^{(n_2)}[n_2]M_{qj}^{(n_2)} +$$

$$+ \sum_{jk} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \sum_{n_4=1}^{\infty} (-1)^{n_3+n_4} \frac{2^{n_2+n_3+n_4} n_2! \, n_3! \, n_4!}{(2n_2)! \, (2n_3)! \, (2n_4)!} \times$$

$$\times {}^{(n_1)}T_{pq}^{(n_2)}[n_2]^{(n_2)}A_{qj}^{(n_3)}[n_3]^{(n_3)}T_{qr}^{(n_4)}[n_4]M_{rk}^{(n_4)}, \tag{2.24}$$

denoting the molecular field existing at the centre of the $p$-th molecule of species $i$ immersed in the medium when the external electric field is absent.

In this part of our paper we intend to discuss only the distortion polarizability of (2.10) which for a multi-component system is now given by Eqs (2.17) and (2.23) as

$$P_D = \frac{4\pi}{3} \left\langle \frac{\partial}{\partial E} (M \cdot e) \right\rangle = \frac{4\pi}{3} \left\{ \sum_i \sum_{p=1}^{N_i} \langle e \cdot {}^{(1)}A_{pi}^{(1)} \cdot e \rangle + \right.$$

$$+ \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} (-1)^{n_2} \frac{2^{n_1+n_2} n_1! \, n_2!}{(2n_1)! \, (2n_2)!} \langle e \cdot {}^{(1)}A_{pi}^{(n_1)}[n_1]^{(n_1)}T_{pq}^{(n_2)}[n_2]^{(n_2)}A_{qj}^{(1)} \cdot e \rangle +$$

$$+ \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \sum_{n_3=1}^{\infty} \sum_{n_4=1}^{\infty} (-1)^{n_2+n_4} \frac{2^{n_1+n_2+n_3+n_4} n_1! \, n_2! \, n_3! \, n_4!}{(2n_1)! \, (2n_2)! \, (2n_3)! \, (2n_4)!} \times$$

$$\left. \times \langle e \cdot {}^{(1)}A_{pi}^{(n_1)}[n_1]^{(n_1)}T_{pq}^{(n_2)}[n_2]^{(n_2)}A_{qj}^{(n_3)}[n_3]^{(n_3)}T_{qr}^{(n_4)}[n_4]^{(n_4)}A_{rk}^{(1)} \cdot e \rangle + ... \right\}. \tag{2.25}$$

This is a general equation for $P_D$ containing the effects due to the induced multipole interactions of unlike molecules. In the subsequent sections, Eq. (2.25) will be discussed for some special cases.

### 3. The contributions to $P_D$ for $V_t = 0$

Let us first calculate the contribution to $P_D$ for the case when the tensorial potential energy $V_t$ is absent.

If the molecules of all components of the system have a centre of inversion, we obtain from Eq. (2.25) up to the term linear in the field gradient quadrupole polarizability

$$P_D = \frac{4\pi}{3}\left\{\sum_i \sum_{p=1}^{N_i} \langle e \cdot {}^{(1)}A_{pi}^{(1)} \cdot e\rangle - \sum_{ij}\sum_{p=1}^{N_i}\sum_{q=1}^{N_j} \langle e \cdot {}^{(1)}A_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(1)} \cdot {}^{(1)}A_{qj}^{(1)} \cdot e\rangle + \right.$$

$$+ \sum_{ijk}\sum_{p=1}^{N_i}\sum_{q=1}^{N_j}\sum_{r=1}^{N_k} (\langle e \cdot {}^{(1)}A_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(1)} \cdot {}^{(1)}A_{qj}^{(1)} \cdot {}^{(1)}T_{qr}^{(1)} \cdot {}^{(1)}A_{rk}^{(1} \cdot e\rangle -$$

$$\left. - \frac{1}{9}\langle e \cdot {}^{(1)}A_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(2)} : {}^{(2)}A_{qj}^{(2)} : {}^{(2)}T_{qr}^{(1)} \cdot {}^{(1)}A_{rk}^{(1)} \cdot e\rangle + ...) + ...\right\}. \tag{3.1}$$

Here, the second and third terms represent the contribution to $P_D$ from the Kirkwood-Yvon induced dipole-induced dipole interaction effect, whereas the fourth term is due to the additional effect of the induced dipole-induced quadrupole interactions. In the last case the quadrupole moments are induced in the molecules by the field gradient of induced dipoles of all the other molecules of the system.

For $V_t = 0$ we have only the radial molecular correlation in the system and Eq. (3.1) yields by (2.13) and (2.16) for isotropically polarizable molecules of various species

$$P_D = \sum_i x_i P_D^{(i)} + \sum_{ij} x_i x_j P_D^{(ij)} + \sum_{ijk} x_i x_j x_k P_D^{(ijk)} + ..., \tag{3.2}$$

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

$$P_D^{(i)} = \frac{4\pi}{3}\int \alpha_i n_i^{(1)}(r_p) \, dr_p, \tag{3.3}$$

$$P_D^{(ij)} = \frac{4\pi}{3}\int\int \{\alpha_i\alpha_j(\alpha_i + \alpha_j) \, r_{pq}^{-6} + 5 \, (q_i\alpha_i^2 + \alpha_i^2 q_j) \, r_{pq}^{-8}\} \, n_{ij}^{(2)}(r_p, r_q) \, dr_p dr_q, \tag{3.4}$$

$$P_D^{(ijk)} = \frac{4\pi}{3}\int\int\int \{\alpha_i\alpha_j\alpha_k[3(r_{pq} \cdot r_{qr})^2 - r_{pq}^2 r_{qr}^2] \, r_{pq}^{-5}r_{qr}^{-5} - 5 \, \alpha_i q_j \alpha_k[5(r_{pq} \cdot r_{qr})^2 -$$

$$- 3r_{pq}^2 r_{qr}^2] \, (r_{pq} \cdot r_{qr}) \, r_{pq}^{-7}r_{qr}^{-7}\} \, n_{ijk}^{(3)}(r_p, r_q, r_r) \, dr_p dr_q dr_r. \tag{3.5}$$

Here, $\alpha_i$ is the scalar dipole polarizability of the molecule of species $i$ and $q_i$ is its scalar quadrupole polarizability. $n_i^{(1)}(r_p)$ is the ordinary distribution function of single molecules $p$

of species $i$, $n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)$ is the binary distribution function for pairs of molecules $p$ and $q$ of species $i$ and $j$, and $n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r)$ is the ternary distribution function for triples of molecules $p$, $q$ and $r$ of species $i$, $j$ and $k$, respectively.

For fluids consisting of molecules possessing constant polarizability Eq. (3.3) reduces to the well-known result

$$P_D^{(i)} = \frac{4\pi}{3} N\alpha_i. \tag{3.6}$$

In this case the first term in Eq. (3.2) expressing additivity of $P_D$ was already derived by Lorentz for refraction, $R$. The second, third and further terms of (3.2) responsible for the deviations from the additivity rule of $P_D$ result from interaction both between molecules of the same species and between those of the various components in condensed systems.

If the molecules of all components are in general anisotropically polarizable, we obtain instead of (3.4) (according to the definitions of (2.13) and (2.15) averageing is peformed first over the orientations of the molecules and then over their relative positions),

$$P_D^{(ij)} = \frac{4\pi}{9} \int \int \{ [\alpha_i(\alpha_j : \alpha_j) + (\alpha_i : \alpha_i) \alpha_j] r_{pq}^{-6} +$$

$$+ 5 [q_i(\alpha_j : \alpha_j) + (\alpha_i : \alpha_i) q_j] r_{pq}^{-8} \} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{3.7}$$

where $\boldsymbol{\alpha}_i \equiv {}^{(1)}\boldsymbol{A}_i^{(1)}$ is the electric dipole polarizability tensor of a molecule of species $i$.

For molecules possessing the axial symmetry, we can express the polarizability tensor $\boldsymbol{\alpha}_i$ in the following form:

$$\boldsymbol{\alpha}_i = \alpha_i \boldsymbol{U} + \alpha_i \varkappa_i (3\boldsymbol{ss} - \boldsymbol{U}), \tag{3.8}$$

where $\boldsymbol{U}$ is a unit tensor, $\boldsymbol{s}$ is a unit vector along the axis of symmetry, and

$$\varkappa_i = \frac{\alpha_{||}^{(i)} - \alpha_{\perp}^{(i)}}{3\alpha_i} = \frac{\alpha_{||}^{(i)} - \alpha_{\perp}^{(i)}}{\alpha_{||}^{(i)} + 2\alpha_{\perp}^{(i)}} \tag{3.9}$$

is a parameter describing the anisotropy of dipole polarizability of an axially symmetric molecule of species $i$ with $\alpha_{||}^{(i)}$ and $\alpha_{\perp}^{(i)}$ denoting, respectively, the polarizabilities parallel and perpendicular to molecular symmetry axis.

By Eq. (3.8)

$$\boldsymbol{\alpha}_i : \boldsymbol{\alpha}_i = 3\alpha_i^2(1 + 2\varkappa_i^2), \tag{3.10}$$

and Eq. (3.7) yields for axially symmetric molecules

$$P_D^{(ij)} = \frac{4\pi}{3} \int \int \{ \alpha_i \alpha_j [\alpha_i(1 + 2\varkappa_i^2) + \alpha_j(1 + 2\varkappa_j^2)] r_{pq}^{-6} +$$

$$+ 5 [q_i \alpha_j^2(1 + 2\varkappa_j^2) + \alpha_i^2(1 + 2\varkappa_i^2) \, q_j] r_{pq}^{-8} \} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{3.11}$$

In the case of a one-component system consisting of molecules possessing the axial symmetry but no quadrupole polarizability ($q = 0$), Eq. (3.11) yields a result similar to the one derived by Mazur and Postma (1959) for the Lorentz-Lorent function, whereas for isotropically polarizable and identical molecules ($\varkappa = 0$) — the result of De Boer *et al.* (1953).

## 4. Contribution of permanent multipole interaction to $P_D$

We now proceed to the problem of calculating the distortional polarization when multipole interaction between the permanent moments of the molecules are present. The total electrostatic potential energy of the multi-compoment system resulting from interaction of the $2^n$-pole permanent moment of one molecule with the $2^m$-pole permanent moment of an other is of the form (Kielich 1965)

$$V_{\text{el}} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (-1)^{m+1} \frac{2^{n+m} n! \, m!}{(2n)! \, (2m)!} \, M_{pi}^{(n)}[n]^{(n)} T_{pq}^{(m)}[m] \, M_{qj}^{(m)}. \quad (4.1)$$

From Eqs (2.17) and (2.23) we have approximately, to within the third power of the dipole polarizability $\alpha$,

$$\frac{\partial}{\partial E}(M' \cdot e) \equiv \frac{\partial}{\partial E}(M \cdot e) - \sum_i \sum_{p=1}^{N_i} e \cdot {}^{(1)}A_{pi}^{(1)} \cdot e$$

$$= - \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} e \cdot \alpha_{pi} \cdot {}^{(1)}T_{pq}^{(1)} \cdot \alpha_{qj} \cdot e +$$

$$+ \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} e \cdot \alpha_{pi} \cdot {}^{(1)}T_{pq}^{(1)} \cdot \alpha_{qj} \cdot {}^{(1)}T_{qr}^{(1)} \cdot \alpha_{rk} \cdot e - \dots \quad (4.2)$$

We shall restrict our further calculations of $P_D$ to the approximation of pairs correlations only.

### 4.1 Isotropically polarizable multipolar molecules

We assume as the first step in evaluating $P_D$ that the multipolar molecules of the system are isotropically polarizable. It is seen that $V_{\text{el}}$ of (4.1) vanishes on averaging over orientations of the molecules, whereas for the average of the square of (4.1) we obtain by Eq. (2.13) (Kielich 1965)

$$\langle V_{\text{el}}^2 \rangle = \frac{1}{2} \sum_{ij} x_i x_j \iint Q_{ij}^{\text{el}}(r_{pq}) \, n_{ij}^{(2)}(r_p, r_q) \, dr_p dr_q, \quad (4.3)$$

with $Q_i^{\text{el}}$ of the form

$$Q_{ij}^{\text{el}}(r_{pq}) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{2^{n+m}(2n+2m)! \, (n! \, m!)^2}{(2n)! \, (2m)! \, (2n+1)! \, (2m+1)!} \times$$

$$\times (M_i^{(n)}[n] M_i^{(n)}) \, (M_j^{(m)}[m] M_j^{(m)}) \, r_{pq}^{-2(n+m+1)}. \quad (4.4)$$

From (2.13), (4.1) and (4.2) we obtain for isotropically polarizable molecules

$$\left\langle \frac{\partial}{\partial E}\left(M'\cdot e\right)\right\rangle_0 = \sum_{ij} x_i x_j \alpha_i \alpha_j (\alpha_i + \alpha_j) \iint r_{pq}^{-6} n_{ij}^{(2)}(r_p, r_q) dr_p dr_q,$$

$$\left\langle \frac{\partial}{\partial E}\left(M'\cdot e\right)V_{el}^2\right\rangle_0 = \sum_{ij} x_i x_j \alpha_i \alpha_j (\alpha_i + \alpha_j) \iint r_{pq}^{-6} Q_{ij}^{el}(r_{pq}) n_{ij}^{(2)}(r_p, r_q) dr_p dr_q, \quad (4.5)$$

so that with respect to Eqs (2.10) and (2.16) $P_D$ is of the form of Eq. (3.2) with $P_D^{(ij)}$ given by

$$P_D^{(ij)} = \frac{4\pi}{3} \alpha_i \alpha_j (\alpha_i + \alpha_j) \iint \left\{ 1 + \frac{1}{2k^2 T^2} Q_{ij}^{el}(r_{pq}) \right\} r_{pq}^{-6} n_{ij}^{(2)}(r_p, r_q) \, dr_p dr_q. \quad (4.6)$$

For molecules exhibiting the axial symmetry

$$M_i^{(n)}[n] M_i^{(n)} = \frac{(2n)!}{2^n (n!)^2} \{M_i^{(n)}\}^2, \quad (4.7)$$

and Eq. (4.4) assumes the simpler form of

$$Q_{ij}^{el}(r_{pq}) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(2n+2m)!}{(2n+1)!\,(2m+1)!} \{M_i^{(n)}\}^2 \{M_j^{(m)}\}^2 r_{pq}^{-2(n+m+1)}, \quad (4.8)$$

where $M_i^{(n)}$ is the scalar multipole moment of order $n$.

By (4.8), Eq. (4.6) yields up to the quadrupole-quadrupole term

$$P_0^{(ij)} = \frac{4\pi}{3} \alpha_i \alpha_j (\alpha_i + \alpha_j) \iint \left\{ r_{pq}^{-6} + \frac{1}{3k^2 T^2} \left[ \mu_i^2 \mu_j^2 r_{pq}^{-12} + \frac{3}{2} (\mu_i^2 \Theta_j^2 + \right.\right.$$

$$\left.\left. + \Theta_i^2 \mu_j^2) r_{pq}^{-14} + \frac{21}{5} \Theta_i^2 \Theta_j^2 r_{pq}^{-16} + ... \right] \right\} n_{ij}^{(2)}(r_p, r_q) dr_p dr_q, \quad (4.9)$$

where $\mu_i \equiv M_i^{(1)}$ is the permanent dipole moment of the axially symmetric molecule of species $i$ and $\Theta_i \equiv M_i^{(2)}$ is its quadrupole moment. The temperature dependent terms in Eq. (4.9) correspond, respectively, to the contributions to $P_D^{(ij)}$ from dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.

For molecules possessing the tetrahedral symmetry (*e.g.* CH₄), the first electric moment they are able to present is octopolar, $M_i^{(3)} \equiv \Omega_i$, and Eq. (4.6) becomes

$$P_D^{(ij)} = \frac{4\pi}{3} \alpha_i \alpha_j (\alpha_i + \alpha_j) \iint \left\{ r_{pq}^{-6} + \frac{9504}{175 k^2 T^2} \Omega_i^2 \Omega_j^2 r_{pq}^{-20} \right\} n_{ij}^{(2)}(r_p, r_q) dr_p dr_q. \quad (4.10)$$

The second term of (4.10) is the contribution to $P_D^{(ij)}$ coming directly from the octopole--octopole interaction of two tetrahedral molecules.

## 4.2 Dipole molecules with anisotropic polarizability

By the general Eq. (4.1), the electrostatic potential energy of dipolar systems is of the form

$$V_{\mathrm{el}} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{\mu}_{pi} \cdot {}^{(1)}\boldsymbol{T}_{pq}^{(1)} \cdot \boldsymbol{\mu}_{qj}; \tag{4.11}$$

thus, up to the second order in $\alpha$ and pair correlations, Eq. (4.2) becomes

$$\left\langle \frac{\partial}{\partial E} (\boldsymbol{M}' \cdot \boldsymbol{e}) V_{\mathrm{el}}^2 \right\rangle_0 = \frac{1}{75} \sum_{ij} x_i x_j \{ 10\alpha_i \mu_i^2 (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) - (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) +$$

$$+ 10(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \alpha_j \mu_j^2 \} \iint r_{pq}^{-9} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{4.12}$$

$$\left\langle \frac{\partial}{\partial E} (\boldsymbol{M}' \cdot \boldsymbol{e}) V_{\mathrm{el}}^4 \right\rangle_0 = \frac{32}{1225} \sum_{ij} x_i x_j \mu_i^2 \mu_j^2 \{ 14\alpha_i \mu_i^2 (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) +$$

$$+ (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + 14(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \alpha_j \mu_j^2 \} \iint r_{pq}^{-15} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{4.13}$$

where we have introduced the anisotropic polarizability tensor

$$\boldsymbol{\alpha}_i^a = \boldsymbol{\alpha}_i - \alpha_i \boldsymbol{U}. \tag{4.14}$$

With respect to the foregoing result, Eqs (2.10) and (2.16) yield

$$P_D^{(ij)} = \frac{2\pi}{225 k^2 T^2} \iint \left\{ [10\alpha_i \mu_i^2 (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) - (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + \right.$$

$$+ 10(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \alpha_j \mu_j^2 ] r_{pq}^{-9} + \frac{8\mu_i^2 \mu_j^2}{49 k^2 T^2} [14\alpha_i \mu_i^2 (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) +$$

$$+ (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + 14(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) \alpha_j \mu_j^2 ] r_{pq}^{-15} + \dots \left. \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.15}$$

In the case of molecules exhibiting the axial symmetry, we have

$$\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i = 2\alpha_i \varkappa_i \mu_i^2, \tag{4.16}$$

and Eq. (4.15) reduces to

$$P_D^{(ij)} = \frac{8\pi \mu_i^2 \mu_j^2}{225 k^2 T^2} \alpha_i \alpha_j \iint \left\{ (5\varkappa_i - \varkappa_i \varkappa_j + 5\varkappa_j) r_{pq}^{-9} + \right.$$

$$+ \frac{8\mu_i^2 \mu_j^2}{49 k^2 T^2} (7\varkappa_i + \varkappa_i \varkappa_j + 7\varkappa_j) r_{pq}^{-15} + \dots \left. \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.17}$$

The further contributions to $P_D$ are of the third order in $\alpha$. In this case we should consider the additional energy of induction arising from interactions between the permanent

dipole moment of one molecule and the dipole moment induced in the other molecule. For a multicomponent system of anisotropically polarizable dipolar molecules we have, to linear term in $\alpha$,

$$V_{\text{ind}} = -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \boldsymbol{\mu}_{pi} \cdot {}^{(1)}\boldsymbol{T}_{pr}^{(1)} \cdot \boldsymbol{\alpha}_{rk} \cdot {}^{(1)}\boldsymbol{T}_{rq}^{(1)} \cdot \boldsymbol{\mu}_{qj} - \ldots \tag{4.18}$$

We obtain by Eqs (4.2), (4.11) and (4.18) for the contributions to $P_D$ in $\alpha^3$,

$$\left\langle \frac{\partial}{\partial E}(\boldsymbol{M}' \cdot \boldsymbol{e}) \right\rangle_0 = \frac{1}{3} \sum_{ij} x_i x_j \{\alpha_i(\boldsymbol{\alpha}_j:\boldsymbol{\alpha}_j^a) + (\boldsymbol{\alpha}_i:\boldsymbol{\alpha}_i)\alpha_j\} \iint r_{pq}^{-6} n_{ij}^{(2)}(\boldsymbol{r}_p,\boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{4.19}$$

$$\left\langle \frac{\partial}{\partial E}(\boldsymbol{M}' \cdot \boldsymbol{e}) V_{\text{ind}} \right\rangle = -\frac{1}{150} \sum_{ij} x_i x_j \{30\alpha_i^2(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + 10(\boldsymbol{\alpha}_i^a:\boldsymbol{\alpha}_i^a)\alpha_j\mu_j^2 -$$

$$-(\boldsymbol{\alpha}_i^a:\boldsymbol{\alpha}_i^a)(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) - (\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)(\boldsymbol{\alpha}_j^a:\boldsymbol{\alpha}_j^a) + 10\alpha_i\mu_i^2(\boldsymbol{\alpha}_j^a:\boldsymbol{\alpha}_j^a) +$$

$$+30(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)\alpha_j^2\} \iint r_{pq}^{-9} n_{ij}^{(2)}(\boldsymbol{r}_p,\boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{4.20}$$

$$\left\langle \frac{\partial}{\partial E}(\boldsymbol{M}' \cdot \boldsymbol{e}) V_{el}^2 \right\rangle_0 = \frac{1}{150} \sum_{ij} x_i x_j \{[(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\mu}_i) + 3(\boldsymbol{\alpha}_i:\boldsymbol{\alpha}_i)\mu_i^2] \times$$

$$\times [(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + 10\alpha_j\mu_j^2] + 6[3(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\mu}_i) - (\boldsymbol{\alpha}_i:\boldsymbol{\alpha}_i)\mu_i^2](\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) +$$

$$+6(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)[3(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j \cdot \boldsymbol{\alpha}_j \cdot \boldsymbol{\mu}_j) - (\boldsymbol{\alpha}_j:\boldsymbol{\alpha}_j)\mu_j^2] + [(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) +$$

$$+10\alpha_i\mu_i^2][(\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j \cdot \boldsymbol{\alpha}_j \cdot \boldsymbol{\mu}_j) + 3(\boldsymbol{\alpha}_j:\boldsymbol{\alpha}_j)\mu_j^2]\} \iint r_{pq}^{-12} n_{ij}^{(2)}(\boldsymbol{r}_p,\boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.21}$$

For axially symmetric molecules we have, besides Eqs (3.10) and (4.16),

$$\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a = 6\alpha_i^2\varkappa_i^2, \quad \boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_i \cdot \boldsymbol{\mu}_i = \alpha_i^2(1+4\varkappa_i+4\varkappa_i^2)\mu_i^2, \tag{4.22}$$

and Eqs (2.10) and (2.16) yield finally with respect to Eqs (4.19) — (4.21)

$$P_D^{(ij)} = \frac{4\pi}{3}\alpha_i\alpha_j \iint \left\{ [\alpha_i(1+2\varkappa_i^2) + \alpha_j(1+2\varkappa_j^2)]\, r_{pq}^{-6} + \right.$$

$$+ \frac{2}{25kT}[\alpha_i\mu_j^2(5\varkappa_j + 5\varkappa_i^2 - \varkappa_i^2\varkappa_j) + \mu_i^2\alpha_j(5\varkappa_i + 5\varkappa_j^2 - \varkappa_i\varkappa_j^2)]\, r_{pq}^{-9} +$$

$$+ \frac{\mu_i^2\mu_j^2}{75k^2T^2}[\alpha_i(5+2\varkappa_i+11\varkappa_i^2)(5+\varkappa_j) + 18\varkappa_i\varkappa_j(2\alpha_i + 2\alpha_j + \alpha_i\varkappa_i + \alpha_j\varkappa_j) +$$

$$\left. + (5+\varkappa_i)(5+2\varkappa_j+11\varkappa_j^2)\alpha_j]\, r_{pq}^{-12} + \ldots \right\} n_{ij}^{(2)}(\boldsymbol{r}_p,\boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.23}$$

If, in particular, the dipolar molecules are isotropically polarizable, $\varkappa = 0$, eq. (4.23) reduces to Eq. (4.9) up to the dipole-dipole term.

### 4.3 Quadrupole molecules with anisotropic polarizability

In the case of a multi-component system consisting of non-dipolar components having quadrupolar molecules, the general Eq. (4.1) becomes for quadrupole-quadrupol interaction

$$V_{\mathrm{el}} = -\frac{1}{18} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{M}_{pi}^{(2)} : {}^{(2)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{M}_{qj}^{(2)} = -\frac{1}{18} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{\Theta}_{pi} : {}^{(2)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{\Theta}_{qj}, \quad (4.24)$$

whereas for the induction energy of quadrupole-induced dipole-quadrupole interaction we have

$$V_{\mathrm{ind}} = \frac{1}{18} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \boldsymbol{\Theta}_{pi} : {}^{(2)}\boldsymbol{T}_{pr}^{(1)} \cdot \boldsymbol{\alpha}_{rk} \cdot {}^{(1)}\boldsymbol{T}_{rq}^{(2)} : \boldsymbol{\Theta}_{qj}. \quad (4.25)$$

From (2.13), (4.2), (4.24) and (4.25) it follows that the contributions to $P_D^{(ij)}$ are of the form

$$\left\langle \frac{\partial}{\partial E} \boldsymbol{M}' \cdot \boldsymbol{e}) V_{\mathrm{el}} \right\rangle_0 = \frac{4}{25} \sum_{ij} x_i x_j \{ (\boldsymbol{\alpha}_i : \boldsymbol{\Theta}_i) [\boldsymbol{\alpha}_j : (\boldsymbol{\alpha}_j \cdot \boldsymbol{\Theta}_j)] +$$

$$+ [\boldsymbol{\alpha}_i : (\boldsymbol{\alpha}_i \cdot \boldsymbol{\Theta}_i)] (\boldsymbol{\alpha}_j : \boldsymbol{\Theta}_j) \} \int\int r_{pq}^{-11} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \quad (4.26)$$

$$\left\langle \frac{\partial}{\partial E} (\boldsymbol{M}' \cdot \boldsymbol{e}) V_{\mathrm{ind}} \right\rangle_0 = -\frac{4}{525} \sum_{ij} x_i x_j \{ 7(\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a) (\boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) \alpha_j + 2[30\alpha_i^2 -$$

$$- (\boldsymbol{\alpha}_i^a : \boldsymbol{\alpha}_i^a)] [\boldsymbol{\Theta}_j : (\boldsymbol{\Theta}_j \cdot \boldsymbol{\alpha}_j^a)] + 2[\boldsymbol{\Theta}_i : (\boldsymbol{\Theta}_i \cdot \boldsymbol{\alpha}_i^a)] [30\alpha_j^2 - (\boldsymbol{\alpha}_j^a : \boldsymbol{\alpha}_j^a)] +$$

$$+ 7\alpha_i (\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i) (\boldsymbol{\alpha}_j^a : \boldsymbol{\alpha}_j^a) \} \int\int r_{pq}^{-11} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \quad (4.27)$$

$$\left\langle \frac{\partial}{\partial E} (\boldsymbol{M}' \cdot \boldsymbol{e}) V_{\mathrm{el}}^2 \right\rangle_0 = \frac{32}{441} \sum_{ij} x_i x_j \{ 7\alpha_i (\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i) [\boldsymbol{\Theta}_j : (\boldsymbol{\Theta}_j \cdot \boldsymbol{\alpha}_j^a)] - 2[(\boldsymbol{\alpha}_i^a \cdot \boldsymbol{\Theta}_i) : \boldsymbol{\Theta}_i] \times$$

$$\times [(\boldsymbol{\alpha}_j^a \cdot \boldsymbol{\Theta}_j) : \boldsymbol{\Theta}_j] + 7[\boldsymbol{\Theta}_i : (\boldsymbol{\Theta}_i \cdot \boldsymbol{\alpha}_i^a)] (\boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) \alpha_j \} \int\int r_{pq}^{-13} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \quad (4.28)$$

The foregoing contributions to $P_D^{(ij)}$ can be simplified by using the following identities:

$$\boldsymbol{\alpha}_i : \boldsymbol{\Theta}_i = 3\alpha_i \varkappa_i \Theta_i, \quad \boldsymbol{\alpha}_i : (\boldsymbol{\alpha}_i \cdot \boldsymbol{\Theta}_i) = 3\alpha_i^2 \varkappa_i (2 + \varkappa_i) \Theta_i,$$

$$\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i = \frac{3}{2} \Theta_i^2, \quad (\boldsymbol{\alpha}_i^a \cdot \boldsymbol{\Theta}_i) : \boldsymbol{\Theta}_i = \frac{3}{2} \alpha_i \varkappa_i \Theta_i^2, \quad (4.29)$$

which hold for quadrupolar molecules possessing the axial symmetry; namely, we have by (2.10)

$$P_D^{(ij)} = \frac{16\pi}{175kT} \alpha_i \alpha_j \int\int \left\{ [\alpha_i \Theta_j^2 (10\varkappa_j + 7\varkappa_i^2 - 2\varkappa_i^2 \varkappa_j) - \right.$$

$$- 21\varkappa_i \varkappa_j \Theta_i \Theta_j (2\alpha_i + 2\alpha_j + \alpha_i \varkappa_i + \alpha_j \varkappa_j) + \Theta_i^2 \alpha_j (10\varkappa_i + 7\varkappa_j^2 - 2\varkappa_i \varkappa_j^2)] r_{pq}^{-11} +$$

$$\left. + \frac{25}{21kT} \Theta_i^2 \Theta_j^2 (7\varkappa_i - 2\varkappa_i \varkappa_j + 7\varkappa_j) r_{pq}^{-13} + \ldots \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \quad (4.30)$$

## 4.4 Molecules with dipole and quadrupole moments

Let us now consider the case of a multicomponent system of molecules exhibiting both a dipole and quadrupole moment for which the electrostatic potential energy of dipole-quadrupole interaction is of the form, resulting from Eq. (4.1),

$$V_{\mathrm{el}} = -\frac{1}{6} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \{\boldsymbol{\mu}_{pi} \cdot {}^{(1)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{\Theta}_{qj} - \boldsymbol{\Theta}_{pi} : {}^{(2)}\boldsymbol{T}_{pq}^{(1)} \cdot \boldsymbol{\mu}_{qj}.\}. \tag{4.31}$$

With respect to Eqs (2.10), (4.2) and (4.31), the contribution to $P_D^{(ij)}$ from dipole — quadrupole interaction is given by the expression

$$P_D^{(ij)} = \frac{16\pi}{1575k^2T^2} \int\int \{2[(\boldsymbol{\alpha}_i^a \cdot \boldsymbol{\Theta}_i) : \boldsymbol{\Theta}_i] [10\alpha_j\mu_j^2 - (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j)] +$$

$$+7\alpha_i(\boldsymbol{\Theta}_i : \boldsymbol{\Theta}_i) (\boldsymbol{\mu}_j \cdot \boldsymbol{\alpha}_j^a \cdot \boldsymbol{\mu}_j) + 7(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i) (\boldsymbol{\Theta}_j : \boldsymbol{\Theta}_j) \alpha_j + 2[10\alpha_i\mu_i^2 -$$

$$-(\boldsymbol{\mu}_i \cdot \boldsymbol{\alpha}_i^a \cdot \boldsymbol{\mu}_i)] [(\boldsymbol{\alpha}_j^a \cdot \boldsymbol{\Theta}_j) : \boldsymbol{\Theta}_j]\} \int\int r_{pq}^{-11} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.32}$$

If, in particular, the molecules are axially symmetric, by Eqs (4.16) and (4.29), Eq. (4.32) reduces to

$$P_D^{(ij)} = \frac{16\pi\alpha_i\alpha_j}{525k^2T^2} \int\int \{\mu_i^2\Theta_j^2(7\varkappa_i + 10\varkappa_j - 2\varkappa_i\varkappa_j) +$$

$$+\Theta_i^2\mu_j^2(7\varkappa_j + 10\varkappa_i - 2\varkappa_i\varkappa_j)\} \int\int r_{pq}^{-11} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{4.33}$$

It is interesting to observe that the contributions to $P_D^{(ij)}$ given by Eqs (4.17), (4.30) and (4.33) are non-zero only if the anisotropy of dipole polarizability of the molecules is taken into account.

## 5. Applications of the theory to two-component systems

We now consider a two-component system of $N_1$ molecules of species 1 and $N_2$ molecules of species 2, with $N_1 + N_2 = N$. In this case Eq. (3.2) assumes the form

$$P_D = x_1 P_D^{(1)} + x_2 P_D^{(2)} + x_1^2 P_D^{(11)} + 2x_1 x_2 P_D^{(12)} + x_2^2 P_D^{(22)} + \ldots, \tag{5.1}$$

where $x_1$ and $x_2$ are the molar fractions of the components 1 and 2, respectively.

We first consider a binary system, the one component of which is monatomic with atoms possessing the dipole and quadrupole polarizabilities $\alpha_1$ and $q_1$ and the other quadrupolar consisting of axially symmetric molecules with dipole and quadrupole polarizabilities $\alpha_2$ and $q_2$ and permanent quadrupole moment $\Theta_2$. In this case Eqs (3.6), (3.11) and (4.30) yield

$$P_D^{(1)} = \frac{4\pi}{3} N\alpha_1, \qquad P_D^{(2)} = \frac{4\pi}{3} N\alpha_2, \tag{5.2}$$

$$P_D^{(11)} = \frac{8\pi}{3} \alpha_1^2 \int\int \{\alpha_1 r_{pq}^{-6} + 5 \, q_1 r_{pq}^{-8}\} n_{11}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{5.3}$$

$$P_D^{(12)} = \frac{4\pi}{3} \int\int \left\{ \alpha_1^2 \left[ \alpha_2 r_{pq}^{-6} + 5\, q_2 r_{pq}^{-8} + \frac{24}{35kT}\, \alpha_2 \varkappa_2 \Theta_2^2 r_{pq}^{-11} \right] \right. +$$

$$\left. + \alpha_2^2 (1+2\varkappa_2^2)\, (\alpha_1 r_{pq}^{-6} + 5\, q_1 r_{pq}^{-8}) \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{5.4}$$

$$P_D^{(22)} = \frac{8\pi}{3}\, \alpha_2^2 \int\int \left\{ (1+2\varkappa_2^2)(\alpha_2 r_{pq}^{-6} + 5\, q_2 r_{pq}^{-8}) \right. +$$

$$+ \frac{12\varkappa_2 \Theta_2^2}{175kT} \left[ \alpha_2(10-35\varkappa_2-23\varkappa_2^2)r_{pq}^{-11} + \frac{25\Theta_2^2}{21kT}\,(7-\varkappa_2)r_{pq}^{-13} \right] \right\} n_{22}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{5.5}$$

If the one component of the binary system is monatomic as before, but if the other is dipolar with axially symmetric molecules having the dipole polarizability $\alpha_2$ and permanent dipole moment $\mu_2$, we obtain by Eqs (4.17) and (4.23) in addition to Eqs (5.2) and (5.3)

$$P_D^{(12)} = \frac{4\pi}{3}\, \alpha_2 \int\int \left\{ \alpha_1^2 \left( r_{pq}^{-6} + \frac{2}{5kT}\, \varkappa_2 \mu_2 r_{pq}^{-9} \right) \right. +$$

$$\left. + \alpha_2(1+2\varkappa_2^2)\, (\alpha_1 r_{pq}^{-6} + 5\, q_1 r_{pq}^{-8}) \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{5.6}$$

$$P_D^{(22)} = \frac{8\pi}{3}\, \alpha_2^2 \int\int \left\{ \alpha_2 \left[ (1+2\varkappa_2^2)\, r_{pq}^{-6} + \frac{2\varkappa_2\mu_2^2}{25kT}\,(5+5\varkappa_2-\varkappa_2^2)\, r_{pq}^{-9} \right. \right. +$$

$$+ \frac{\mu_2^4}{75k^2T^2}\,(25+15\varkappa_2+93\varkappa_2^2+29\varkappa_2^3)\, r_{pq}^{-12} \Big] + \frac{\varkappa_2\mu_2^4}{75k^2T^2} \left[ (10-\varkappa_2)\, r_{pq}^{-9} \right. +$$

$$\left. \left. + \frac{8\mu_2^4}{49k^2T^2}\,(14+\varkappa_2)\, r_{pq}^{-15} \right] \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{5.7}$$

In the case of a mixture of a quadrupolar component with a dipolar component, the $P_D^{(12)}$ accounting for the interaction between quadrupolar and dipolar molecules, on the basis of Eqs (4.23), (4.30) and (4.33), is of the form

$$P_D^{(12)} = \frac{4\pi}{3}\, \alpha_1\alpha_2 \int\int \left\{ [\alpha_1(1+2\varkappa_1^2)+\alpha_2(1+2\varkappa_2^2)]\, r_{pq}^{-6} \right. +$$

$$+ \frac{2\alpha_1\mu_2^2}{25kT}\,(5\varkappa_2+5\varkappa_1^2-\varkappa_1^2\varkappa_2)\, r_{pq}^{-9} + \frac{12\Theta_1^2}{175kT} \left[ 10\varkappa_1 \left( \alpha_2 + \frac{\mu_2^2}{3kT} \right) \right. +$$

$$\left. \left. + \varkappa_2(7-2\varkappa_1) \left( \alpha_2\varkappa_2 + \frac{\mu_2^2}{3kT} \right) \right] r_{pq}^{-11} \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{5.8}$$

The numerical evaluations establishing the role of the respective multipole contributions to $P_D^{(ij)}$ will be given in the third part of this paper.

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