EXCESS FREE ENERGY OF MULTIPOLAR ASSEMBLIES

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Using a classical perturbation method, the contributions to the Helmholtz free energy from tensorial intermolecular forces are calculated up to two-body or three-body interactions. The calculations are carried out with the total tensorial potential energy of an assembly of unlike micro-systems composed of the electrostatic energy of interactions between permanent 2^n-pole and 2^n-pole charge distributions and the induction energy of interactions between permanent 2^m-pole charge distributions and the induced 2^m-pole moments of other charge distributions. The general results thus obtained are discussed for some simpler cases of axially symmetric molecules possessing dipole, quadrupole, octopole *etc.* moments, for tetrahedral molecules with octopole moment or for octahedral molecules with hexadecapole moment. The tensorial part of the free energy is applied to the case of two-component systems. Application to the equation of state of an imperfect gas mixture is also given.

1. Introduction

The macroscopic thermodynamic functions, such as the entropy S and the pressure p, can be obtained theoretically by differentiation of the Helmholtz free energy F with respect to the temperature T or volume V, namely

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}, \quad p = - \left(\frac{\partial F}{\partial V} \right)_{T, N}, \tag{1.1}$$

where N is the number of molecules contained in the volume V.

On the other hand, in equilibrium statistical mechanics, the free energy F is related to the partition function Z by the fundamental equation

$$F = - kT \ln Z_N, \tag{1.2}$$

which correlates the observed macroscopic properties of matter with its inferred microscopic properties.

In the present paper we are interested only in the part of F resulting from the fact that in the case of most molecular substances the intermolecular forces depend rather strongly on the relative orientation of the molecules. Investigation of this additional free energy of a substance in the absence of external fields can be used to obtain valuable informa-

tion about the nature and magnitude of the directional forces acting between its non-spherical molecules and on their electric multipole (*e.g* quadrupole, octopole *etc.*) moments and consequently, on the structure of the substance.

Pople [1, 2] proposed a general method for calculating the free energy of an assembly of axially symmetric molecules interacting not only according to a central-force law, but significantly with angularly dependent forces. He calculated the contribution to F from directional forces by treating the latter as a perturbation to the central intermolecular force. A similar approach has been used by Barker [3] for the case of an assembly of isotropically polarizable dipolar molecules. Recently, Parsonage and Scott [4] calculated the contribution to the free energy from octopole-octopole interaction of tetrahedral molecules. Earlier, a similar problem for the case of tetrahedral molecules in solids was discussed in detail by James and Keenan [5] in their theory of the phase transition in solid methane. We should also mention that recently Jepsen and Friedman [6] developed a general method for evaluating Mayer cluster diagrams for assemblies of molecules with pairwise orientation-dependent forces.

The first classical theories of angularly dependent intermolecular forces were given by Debye [7] and Keesom [8] and subsequently discussed in detail and developed by several authors (see *e.g* refs [1—3] and [9—12]). The tensor form of the multipole interaction forces was given by Frenkel [13] and more recently by Jansen [14], whose general and concise tensor notation we use in the present paper[1].

In addition to the electrostatic interaction of the 2^n-pole permanet charge distribution with another 2^m-pole, as discussed in general by Jansen, we take into account the interactions between a 2^n-pole permanent charge distribution with the 2^m-pole moments induced in another, and *vice versa*[2]. We generalize these electrostatic and inductive interactions to an assembly of micro-systems of various species and, by Pople's method, calculated the tensorial contributions to the excess free energy. The results obtained in this way hold in general for an assembly composed of 2^n-pole micro-systems of arbitrary symmetry, and are discussed for some special cases, namely for axially symmetric multipolar molecules, tetrahedral molecules and octohedral molecules. Applications to two-component systems are given as well as to the second virial coefficient of an imperfect gas of unlike multipolar molecules.

2. *Excess free energy and distribution functions*

We consider a classical assembly of N micro-systems (*e.g.* ions or molecules) occupying a volume V in equilibrium at the temperature T. According to the principle of classical statistical mechanics, the Helmholtz free energy (1.2) for the case considered can be expressed as follows:

$$F = F_{id} - kT \ln \left\{ \frac{Q_N}{V^N \Omega^N} \right\}. \qquad (2.1)$$

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[1] The tensor formalism used in our previous papers [15, 16] is less compact and not convenient for the definition of multipole moments of order n and the n-th rank interaction tensor as given by Jansen.

[2] However, we shall not consider here the anisotropic dispersion forces between the charge distributions as discussed previously by De Boer and Heller [17], London [18] and De Boer [19] (see also refs 2, 12, 15 and 20).

Here, F_{id} is the free energy of an ideal assembly of N non-interacting micro-systems, and

$$Q_N = \int \cdots_{(2N)} \int \exp\left\{ -\frac{U(\boldsymbol{r}^N, \boldsymbol{\omega}^N)}{kT} \right\} d\boldsymbol{r}_i^N d\boldsymbol{\omega}^N, \tag{2.2}$$

is the configurational integral of an assembly of N interacting micro-systems in which $U(\boldsymbol{r}^N, \boldsymbol{\omega}^N)$ is the total interaction potential energy. The $\boldsymbol{r}^N$ denote the set of N position vectors $\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_N$ of the micro-systems and $\boldsymbol{\omega}^N = \boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \dots \boldsymbol{\omega}_N$ — the angular coordinates determining their orientations; thus

$$V^N = \int \cdots_{(N)} \int d\boldsymbol{r}^N \text{ and } \Omega^N = \int \cdots_{(N)} \int d\boldsymbol{\omega}^N.$$

Following Pople, we write

$$U(\boldsymbol{r}^N, \boldsymbol{\omega}^N) = U^{(0)}(\boldsymbol{r}^N) + V_t(\boldsymbol{r}^N, \boldsymbol{\omega}^N), \tag{2.3}$$

where $U^{(0)}(\boldsymbol{r}^N)$ is the central-force part of the total potential energy, which is a function of $\boldsymbol{r}^N$ only, and $V_t(\boldsymbol{r}^N, \boldsymbol{\omega}^N)$ is the tensorial-force part — dependent both on $\boldsymbol{r}^N$ and on $\boldsymbol{\omega}^N$.

Considering V_t to represent a perturbation to the unperturbed energy $U^{(0)}$, the configurational integral (2.2) can be put in the form

$$Q_N = \Omega^N Q_N^{(0)} \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle V_t^n \rangle, \tag{2.4}$$

where

$$Q_N^{(0)} = \int \cdots_{(N)} \int \exp\left\{ -\frac{U^{(0)}(\boldsymbol{r}^N)}{kT} \right\} d\boldsymbol{r}^N, \tag{2.5}$$

denoting the configurational integral of an assembly of N micro-systems interacting with central forces only, and

$$\langle V_t^n \rangle = \{\Omega^N Q_N^{(0)}\}^{-1} \int \cdots_{(2N)} \int V_t^n(\boldsymbol{r}^N, \boldsymbol{\omega}^N) \exp\left\{ -\frac{U^{(0)}(\boldsymbol{r}^N)}{kT} \right\} d\boldsymbol{r}^N d\boldsymbol{\omega}^N \tag{2.6}$$

is the classical statistical average of V_t^n.

By (2.1) and (2.4), the excess free energy $F_{ex} = F - F_{id}$ (the difference between the free energy of the real assembly and that of an ideal assembly of the same structure and in the same thermodynamical state N, V, T) can now be expressed as follows:

$$F_{ex} = F_{central} + F_{tensorial}, \tag{2.7}$$

where

$$F_{central} = -kT \ln \left\{ \frac{Q_N^{(0)}}{V^N} \right\}, \tag{2.8}$$

is the contribution to F_{xe} from the central forces, and

$$F_{tensorial} = -kT \ln \left\{ 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle V_t^n \rangle \right\}, \tag{2.9}$$

is the contribution to F_{ex} from the tensorial forces.

For

$$-1 < \left\{ \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle V_t^n \rangle \right\} \leqslant 1,$$

which should be satisfied in most cases, we obtain from (2.9)

$$F_{\text{tensorial}} = kT \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \left\{ \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{1}{kT} \right)^n \langle V_t^n \rangle \right\}^m. \tag{2.10}$$

In a good approximation, this expression yields

$$F_{\text{tensorial}} = F_1 + F_2 + F_3 + F_4 + \ldots \tag{2.11}$$

where the successive terms are of the form

$$F_1 = \langle V_t \rangle,$$

$$F_2 = -\frac{1}{2kT} \langle (\Delta V_t)^2 \rangle = -\frac{1}{2kT} (\langle V_t^2 \rangle - \langle V_t \rangle^2),$$

$$F_3 = \frac{1}{6k^2 T^2} \langle (\Delta V_t)^3 \rangle = \frac{1}{6k^2 T^2} \{ \langle V_t^3 \rangle - 3 \langle V_t^2 \rangle \langle V_t \rangle + 2 \langle V_t \rangle^3 \},$$

$$F_4 = -\frac{1}{24k^3 T^3} \{ \langle (\Delta V_t)^4 \rangle - 3 \langle (\Delta V_t)^2 \rangle^2 \} = -\frac{1}{24k^3 T^3} \{ \langle V_t^4 \rangle -$$

$$- 3 \langle V_t^2 \rangle^2 - 4 \langle V_t^3 \rangle \langle V_t \rangle + 12 \langle V_t^2 \rangle \langle V_t \rangle^2 - 6 \langle V_t \rangle^4 \}, \tag{2.12}$$

with $\Delta V_t = V_t - \langle V_t \rangle$ denoting the fluctuation of V_t.

We see that the first-order perturbation to F_t is expressed directly by the statistical average of V_t, the second-order perturbation — by the statistical average of the square of the fluctuation of V_t, the third-order perturbation — by $\langle (\Delta V_t)^3 \rangle$, etc.

We now introduce the probability $P^{(h)}(r^h) dr^h$ of finding a selected group of h micro-systems in the elementary volume dr^h centered about the point r^h, independently of the positions of the remaining $(N-h)$ micro-systems of the assembly. Since the probability densities $P^{(h)}$ are of the form

$$P^{(h)}(r^h) = \frac{1}{Q_N^{(0)}} \int \cdots_{(N-h)} \int \exp \left\{ -\frac{U^{(0)}(r^N)}{kT} \right\} dr^{N-h}, \tag{2.13}$$

the statistical average (2.6) can be expressed as follows:

$$\langle V_t^n \rangle = \int \cdots_{(h)} \int \overline{V_t^n(r^N)} P^{(h)}(r^h) dr^h, \tag{2.14}$$

where

$$\overline{V_t^n(r^N)} = \Omega^{-N} \int \cdots_{(N)} \int V_t^n(r^N, \omega^N) d\omega^N, \tag{2.15}$$

is the unweighted average of V_t^n over all orientations of the micro-systems.

The probability $P^{(h)}(\mathbf{r}^N)$ of (2.13) is related with the distribution function of the h micro-systems as follows [21]:

$$n^{(h)}(\mathbf{r}^h) = \frac{N!}{(N-h)!}\, P^{(h)}(\mathbf{r}^h).\tag{2.16}$$

In the case of an assembly of $N_1,\ N_2,\ \dots\ N_i,\ \dots$ micro-systems of the first, second, ...i-th species, the functions (2.16) have to be replaced by the following distribution functions:

$$x_i n_i^{(1)}(\mathbf{r}_p) = N_i P_i^{(1)}(\mathbf{r}_p),$$

$$x_i x_j n_{ij}^{(2)}(\mathbf{r}_p,\mathbf{r}_q) = N_i(N_j-\delta_{ij})\, P_{ij}^{(2)}(\mathbf{r}_p,\mathbf{r}_q),$$

$$x_i x_j x_k n_{ijk}^{(3)}(\mathbf{r}_p,\mathbf{r}_q,\mathbf{r}_r) = N_i(N_j-\delta_{ij})(N_k-\delta_{ik}-\delta_{jk})\, P_{ijk}^{(3)}(\mathbf{r}_p,\mathbf{r}_q,\mathbf{r}_r),\ \dots,\tag{2.17}$$

where $x_i = N_i/N$ is the mole fraction of the i-th component. Here, $n_i^{(1)}(\mathbf{r}_p)$ is the ordinary distribution function for single micro-systems p of species i, $n_{ij}^{(2)}(\mathbf{r}_p,\mathbf{r}_q)$ is the binary distribution function for pairs of micro-systems p and q of species i and j, and $n_{ijk}^{(3)}(\mathbf{r}_p,\mathbf{r}_q,\mathbf{r}_r)$ is the ternary distribution function for triples of micro-systems p, q and r of species i, j and k, respectively.

3. Classical theory of tensorial forces

Let us consider two arbitrary electric charge distributions p and q separated by a distance $\mathbf{r}_{pq}$. The potential energy of interaction between these charge distribution is given by

$$v_{pq} = \sum_\nu \sum_\mu \frac{e_{p\nu}\, e_{q\mu}}{|\mathbf{r}_{pq}-\mathbf{r}_{p\nu}+\mathbf{r}_{q\mu}|}\,,\tag{3.1}$$

where $e_{p\nu}$ is the ν-th electric charge of the p-th distribution and $\mathbf{r}_{p\nu}$ — its radius vector; summation in (3.1) extends over all charges in the distributions p and q.

In the case of nonoverlapping charge distributions when $r_{p\nu}+r_{q\mu}<r_{pq}$ we can evaluate (3.1) in the form of two Taylor expansions [14],

$$v_{pq} = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{n+1}}{n!\,m!}\, \mathbf{N}_p^{(n)}[n]\,{}^{(n)}\mathbf{T}_{pq}^{(m)}[m]\, \mathbf{N}_q^{(m)},\tag{3.2}$$

where in Jansen's tensor notation

$$\mathbf{N}_p^{(n)} = \sum_\nu e_{p\nu}\, \mathbf{r}_{p\nu}^n\tag{3.3}$$

denotes the multipole moment operator of order n, of the p-th charge distribution, and

$${}^{(n)}\mathbf{T}_{pq}^{(m)} = -\,\boldsymbol{\nabla}^{n+m}\left(\frac{1}{r_{pq}}\right),\qquad p\neq q\tag{3.4}$$

is the $n+m$-th rank interaction tensor between 2^n-pole distribution p and 2^m-pole distribution q; $\boldsymbol{\nabla}$ is the differential operator. In Eq. (3.2), $[n]$ denotes that the product of two n-th — rank tensors $\mathbf{N}_p^{(n)}$ and ${}^{(n)}\mathbf{T}_{pq}$ is contracted n times.

We now introduce here n-th rank electric multipole tensor defined as

$$M_p^{(n)} = \sum_\nu e_{p\nu} S_{p\nu}^{(n)}, \tag{3.5}$$

where the operator $S_{p\nu}^{(n)}$ of rank n is given (the explicite form is given by A.3 in the Appendix) by

$$S_{p\nu}^{(n)} = \frac{(-1)^n}{n!} \, r_{p\nu}^{2n+1} \, \nabla^n \left(\frac{1}{r_{p\nu}} \right) \tag{3.6}$$

$M_p^{(0)} \equiv e_p$ is the unipole or total charge of the distribution p, $M_p^{(1)}$ is its dipole moment, $M_p^{(2)}$ — its quadrupole moment, $M_p^{(3)}$ — its octopole moment, $M_p^{(4)}$ — its hexadecapole moment, $M_p^{(n)}$ — its 2^n-pole moment.

With the help of definitions (3.4) and (3.5), Eq. (3.1) can be expressed as follows:

$$v_{pq} = \sum_{n=0}^\infty \sum_{m=0}^\infty \frac{(-1)^{m+1} 2^{n+m} n! m!}{(2n)! (2m)!} M_p^{(n)} [n]^{(n)} T_{pq}^{(m)} [m] M_q^{(m)}. \tag{3.7}$$

This expression represents the general form of the electrostatic energy of interaction of the permanent 2^n-pole charge distributions of micro-system p with the permanent 2^m-pole charge distribution of micro-system q; here, T_{pq} is directed from molecule q to p.

Analogously to this expression we obtain the total electrostatic potential energy of an assembly of N micro-systems of various species,

$$V_{el} = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=0}^\infty \sum_{m=0}^\infty \frac{(-1)^{m+1} 2^{n+m} n! m!}{(2n)! (2m)!} M_{pi}^{(n)}[n]^{(n)} T_{pq}^{(m)} [m] M_{qj}^{(m)}, \tag{3.8}$$

where the multipole tensor $M_{pi}^{(n)}$ now refers to the p-th micro-system of species i. Eq. (3.8) can also be expressed in the following form:

$$V_{el} = -\frac{1}{2} \sum_i \sum_{p=1}^{Ni} \sum_{n=0}^\infty \frac{2^n n!}{(2n)!} M_{pi}^{(n)} [n] F_{pi}^{(n)}, \tag{3.9}$$

where we have introduced the total electric field of order n at the centre of the p-th micro-system of species i due to all the other micro-systems of the assembly,

$$F_{pi}^{(n)} = \sum_j \sum_{q=1}^{N_j} \sum_{m=0}^\infty \frac{(-1)^m 2^m m!}{(2m)!} {}^{(n)}T_{pq}^{(m)}[m] M_{qj}^{(m)}. \tag{3.10}$$

In particular, we obtain from (3.10) for a zero-order field, or potential

$$F_{pi}^{(0)} \equiv -\varphi_{pi} = \sum_j \sum_{q=1}^{N_j} \sum_{m=0}^\infty \frac{(-1)^m 2^m m!}{(2m)!} {}^{(0)}T_{pq}^{(m)}[m] M_{qj}^{(m)}, \tag{3.11}$$

and for a first-order field, or shortly electric field $\boldsymbol{F}$,

$$\boldsymbol{F}_{pi}^{(1)} \equiv \boldsymbol{F}_{pi} = \sum_{j} \sum_{q=1}^{N_j} \sum_{m=0}^{\infty} \frac{(-1)^m 2^m m!}{(2m)!} \, {}^{(1)}\boldsymbol{T}_{pq}^{(m)}[m] \, \boldsymbol{M}_{qj}^{(m)}. \tag{3.12}$$

Similarly, for $n = 2$ we obtain from (3.10) the second-order field (or field gradient) for $n = 3$ the third-order field (or gradient of field gradient) *etc.*

In general, beside the purely electrostatic interaction between the permanent charge distributions as discussed above, we should consider the additional energy of induction arising from interactions between the permanent charge distribution of one micro-system and the moments induced in the other micro-system. To within the induced-dipole approximation, the potential energy of induction is given by

$$V_{\text{ind}}^{(1)} = - \frac{1}{2} \sum_{k} \sum_{r=1}^{N_k} \boldsymbol{F}_{rk} \cdot \boldsymbol{\alpha}_{rk} \cdot \boldsymbol{F}_{rk}, \tag{3.13}$$

where $\boldsymbol{\alpha}_{rk}$ is the electric dipole polarizability tensor of an r-th micro-system of species k.

On substituting the electric field (3.12) in Eq. (3.13) we have

$$V_{\text{ind}}^{(1)} = - \frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{m+1} 2^{n+m} n! \, m!}{(2n)! \, (2m)!} \times$$

$$\times \boldsymbol{M}_{pi}^{(n)}[n] \, {}^{(n)}\boldsymbol{T}_{pr}^{(1)} \cdot \boldsymbol{\alpha}_{rk} \cdot {}^{(1)}\boldsymbol{T}_{rq}^{(m)}[m] \, \boldsymbol{M}_{qj}^{(m)}. \tag{3.14}$$

In the Appendix, the expression of Eqs (3.8) and (3.14) are applied to micro-systems possessing the axial symmetry.

We now generalize Eq. (3.13) to the case of higher order induced moments as already considered by Frenkel [13]. The total moment of order n induced in the 2^n-pole charge distributions of an r-th micro-system of species k by the electric field of the permanent 2^m-pole charge distributions of all the other micro-systems of an assembly will be defined here as follows:

$$\boldsymbol{P}_{rk}^{(n)} = \sum_{m=1}^{\infty} \frac{2^m m!}{(2m)!} \, {}^{(n)}\boldsymbol{A}_{rk}^{(m)}[m] \, \boldsymbol{F}_{rk}^{(m)}, \tag{3.15}$$

where ${}^{(n)}\boldsymbol{A}_{rk}^{(m)}$ is the tensor of rank $n+m$ characterizing the polarization of the 2^n-pole permanent moment due to the electric field of order m defined in general by Eq. (3.10).

In terms of the induced moments (3.15), the total potential energy of induction is then given by the following general expression:

$$V_{\text{ind}} = - \frac{1}{2} \sum_{k} \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} \frac{2^n n!}{(2n)!} \, \boldsymbol{F}_{rk}^{(n)}[n] \boldsymbol{P}_{rk}^{(n)}, \tag{3.16}$$

which, by Eq. (3.15), we can rewrite thus

$$V_{\text{ind}} = -\frac{1}{2} \sum_k \sum_{r=1}^{N_k} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{2^{n+m} n! \, m!}{(2n)! \, (2m)!} F_{rk}^{(n)} [n] \, {}^{(n)}A_{rk}^{(m)} [m] \, F_{rk}^{(m)}. \qquad (3.17)$$

On substituting herein the field of (3.10), we obtain in terms of multipole moments, polarizabilities and interactions tensors

$$V_{\text{ind}} = -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n'=1}^{\infty} \sum_{m'=1}^{\infty} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{n'+m} 2^{n'+n+m'+m} n'! \, n! \, m'! \, m!}{(2n')! \, (2n)! \, (2m')! \, (2m)!} \times$$

$$\times M_{pi}^{(n)}[n]^{(n)} T_{pr}^{(n')}[n']^{(n')} A_{rk}^{(m')}[m']^{(m')} T_{rq}^{(m)}[m] \, M_{qj}^{(m)}. \qquad (3.18)$$

Eq. (3.17) gives for the first four terms

$$V_{\text{ind}} = -\frac{1}{2} \sum_k \sum_{r=1}^{N_k} \left\{ F_{rk}^{(1)} \cdot {}^{(1)}A_{rk}^{(1)} \cdot F_{rk}^{(1)} + \frac{1}{3} \left(F_{rk}^{(1)} \cdot {}^{(1)}A_{rk}^{(2)} : F_{rk}^{(2)} + \right. \right.$$

$$\left. \left. + F_{rk}^{(2)} : {}^{(2)}A_{rk}^{(1)} \cdot F_{rk}^{(1)} \right) + \frac{1}{9} F_{rk}^{(2)} : {}^{(2)}A_{rk}^{(2)} : F_{rk}^{(2)} + \ldots \right\}, \qquad (3.19)$$

where ${}^{(1)}A^{(1)}$ and ${}^{(1)}A^{(2)}$ are the tensors of dipole polarization caused by the electric field $F^{(1)}$ and field gradient $F^{(2)}$, respectively, and similarly ${}^{(2)}A^{(1)}$ and ${}^{(2)}A^{(2)}$ are the tensors of quadrupole polarization due, respectively, to the field and field gradient.

In explicit form we obtain from (3.19), in the same approximation,

$$V_{\text{ind}} = -\frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{m+1} 2^{n+m} n! \, m!}{(2n)! \, (2m)!} \times$$

$$\times \left\{ M_{pi}^{(n)}[n]^{(n)} T_{pr}^{(1)} \cdot {}^{(1)}A_{rk}^{(1)} \cdot {}^{(1)}T_{rq}^{(m)}[m] \, M_{qj}^{(m)} + \frac{1}{3} \left(M_{pi}^{(n)}[n]^{(n)} T_{pr}^{(1)} \cdot {}^{(1)}A_{rk}^{(2)} : {}^{(2)}T_{rq}^{(m)}[m] \, M_{qj}^{(m)} - \right. \right.$$

$$\left. \left. - M_{pi}^{(n)}[n]^{(n)} T_{pr}^{(2)} : {}^{(2)}A_{rk}^{(1)} \cdot {}^{(1)}T_{rq}^{(m)}[m] \, M_{qj}^{(m)} \right) - \frac{1}{9} M_{pi}^{(n)}[n]^{(n)} T_{pr}^{(2)} : {}^{(2)}A_{rk}^{(2)} : {}^{(2)}T_{rq}^{(m)}[m] \, M_{qj}^{(m)} + \ldots \right\}. \qquad (3.20)$$

The first term of this expression yields again the first-order induction potential energy of (3.14), if we only denote ${}^{(1)}A_{rk}^{(1)} \equiv \alpha_{rk}$, whereas the remaining terms describe the high order energies.

4. First-order perturbation to F_t

As seen from (2.12), in the first approximation the tensor contribution to the free energy is given directly by V_t. We assume that the total tensorial potential energy V_t is the sum of the electrostatic potential energy V_{el} given by (3.8) and the potential energy of induction

V_{ind} given in general by (3.18). However, in the first approximation, electrostatic interactions of permanent moments do not contribute to F_t, as the first power of V_{el} vanishes on isotropic averageing *i.e.* on averageing over all possible orientations of micro-systems with equal probability given by (2.15). The only non-zero contributions to F_t in the first approximation come from interactions of multipoles of the induced type leading in general to induction energy of the form (3.18).

We shall first compute the contributions to F_t from the induction energy in the dipole approximation (3.14). Obviously, on isotropic averageing of the energy of Eq. (3.14), the only non-vanishing term is the one with $p = q \neq r$, $n = m$ and the factor

$$\overline{M_{pi}^{(n)}[n]^{(n)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rp}^{(n)}[n] M_{pi}^{(n)}} = \frac{(-1)^{n+1}}{2n+1} \alpha_{rk}(M_{pi}^{(n)}[n] M_{pi}^{(n)}) \, ({}^{(n)}T_{pr}^{(1)}[n+1]^{(n)}T_{pr}^{(1)}),$$

(4.1)

and we obtain from (3.14)

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

(4.2)

where α_{qj} is the scalar dipole polarizability of a micro-system q of species j.

Recurring to the definition of (2.14) with the binary distribution function defined in (2.17) and the fact that [14]

$${}^{(n)}T_{pq}^{(m)}\,[n+m]^{(n)}T_{pq}^{(m)} = (2n+2m)!\,2^{-(n+m)}r_{pq}^{-2(n+m+1)},$$

(4.3)

we have, by (4.2)

$$\langle V_{\text{ind}}^{(1)} \rangle = -\frac{1}{2} \sum_{ij} x_i x_j \iint Q_{ij}^{(1)}(r_{pq}) \, n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q.$$

(4.4)

Here, we have introduced the following symmetrical quantity

$$Q_{ij}^{(1)}(r_{pq}) = \frac{1}{4} \sum_{n=0}^{\infty} \frac{2^n(2n+2)!\,(n!)^2}{(2n)!\,(2n+1)!} \{\alpha_i(M_j^{(n)}[n] M_j^{(n)}) + (M_i^{(n)}[n] M_i^{(n)}) \, \alpha_j\} \, r_{pq}^{-2(n+2)}.$$

(4.5)

Further simplification of the foregoing quantity can be achieved by assuming a particular type of symmetry of the micro-systems. This will now be effected for the following cases most commonly occuring:

(i) Axial symmetry. If the micro-systems present, in particular, symmetry with respect to the z-axis of the molecular coordinate system,

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

(4.6)

and the quantity of (4.5) assumes the simpler form of

$$Q_{ij}^{(1)}(r_{pq}) = \frac{1}{2} \sum_{n=0}^{\infty} (n+1) \{\alpha_i (M_j^{(n)})^2 + (M_i^{(n)})^2 \alpha_j\} r_{pq}^{-2(n+2)}, \tag{4.7}$$

where $M_i^{(n)}$ is the scalar multipole moment of order n for the axially-symmetric micro-system of species i.

Denoting the scalar monopole, dipole, quandrupole, octopole and hexadecapole moments of the axially-symmetric micro-system as follows [14, 16]:

$$e_i \equiv M_i^{(0)} = \sum_{\nu} e_{i\nu} \qquad\qquad \mu_i \equiv M^{(1)} = \sum_{\nu} e_{i\nu} z_{\nu},$$

$$\Theta_i \equiv M_i^{(2)} = \sum_{\nu} e_{i\nu}(z_{\nu}^2 - x_{\nu}^2) \qquad\qquad \Omega_i \equiv M_i^{(3)} = \sum_{\nu} e_{i\nu}(z_{\nu}^3 - 3z_{\nu}x_{\nu}^2),$$

$$\Phi_i \equiv M_i^{(4)} = \sum_{\nu} e_{i\nu}(z_{\nu}^4 - 6z_{\nu}^2 x_{\nu}^2 + x_{\nu}^4), \tag{4.8}$$

we obtain from (4.5)

$$Q_{ij}^{(1)}(r_{pq}) = \frac{1}{2}(\alpha_i e_j^2 + e_i^2 \alpha_j) r_{pq}^{-4} + (\alpha_i \mu_j^2 + \mu_i^2 \alpha_j) r_{pq}^{-6} + \frac{3}{2}(\alpha_i \Theta_j^2 + \Theta_i^2 \alpha_j) r_{pq}^{-8} +$$

$$+ 2(\alpha_i \Omega_j^2 + \Omega_i^2 \alpha_j) r_{pq}^{-10} + \frac{5}{2}(\alpha_i \Phi_j^2 + \Phi_i^2 \alpha_j) r_{pq}^{-12} + \dots \tag{4.9}$$

Here, the consecutive terms determine the interaction between the permanent multipole moments (charge, dipole, quadrupole, octopole and hexadecapole) of one micro-system and the induced dipole moment of the other. The three first terms in Eq. (4.9) determine the well-known Debye—Falkenhagen induction effect.

(ii) Tetrahedral symmetry. In the case of micro-systems having the tetrahedral symmetry (e.g. the molecules CH_4, S_nCl_4, etc.), the first non-zero moment is the octopole moment defined by the scalar quantity

$$(\Omega_{xyz})_i = \frac{5}{2} \sum_{\nu} e_{i\nu} x_{\nu} y_{\nu} z_{\nu}. \tag{4.10}$$

With this definition [22], $M_i^{(3)} : M_i^{(3)} = 6 (\Omega_{xyz})_i^2$, and Eq. (4.5) reduces to (on retaining only the induced dipole-octopole interaction term)

$$Q_{ij}^{(1)}(r_{pq}) = \frac{24}{5} \{\alpha_i (\Omega_{xyz})_j^2 + (\Omega_{xyz})_i^2 \alpha_j\} r_{pq}^{-10}. \tag{4.11}$$

(iii) Octahedral symmetry. Micro-systems possessing the octahedral symmetry, as the molecules SF_6 and UF_6, will present a hexadecapole moment but none of the lower order moments. In this case [16]

$$M_i^{(4)} : M_i^{(4)} = 30 (\Phi_{xxzz})_i^2 \text{ with } (\Phi_{xxzz})_i = \frac{7}{8} \sum_{\nu} e_{i\nu}(3z_{\nu}^2 x_{\nu}^2 - x_{\nu}^4), \tag{4.12}$$

and Eq. (4.5) yields

$$Q_{ij}^{(1)}(r_p) = \frac{120}{7} \{\alpha_i(\Phi_{xxzz})_j^2 + (\Phi_{xxzz})_i^2\alpha_j\} r_{pq}^{-12}, \tag{4.13}$$

for the induced dipole-hexadecapole interaction between octahedral molecules.

If we take into account the total induction potential energy of (3.20), we obtain for its statistical average value instead of (4.4)

$$\langle V_{\text{ind}} \rangle = \langle V_{\text{ind}}^{(1)} \rangle + \langle V_{\text{ind}}^{(2)} \rangle + \dots = -\frac{1}{2} \sum x_i x_j \iint Q_{ij}^{\text{ind}}(r_{pq}) \, n_{ij}^{(2)}(\mathbf{r}_p, \mathbf{r}_q) \, d\mathbf{r}_p d\mathbf{r}_q, \tag{4.14}$$

where the second order energy $V_{\text{ind}}^{(2)}$ is given in the general Equation (3.20) by the last term, containing the field gradient quadrupole polarizability tensor $^{(2)}A^{(2)}$ and

$$Q_{ij}^{\text{ind}}(r_{pq}) = Q_{ij}^{(1)}(r_{pq}) + Q_{ij}^{(2)}(r_{pq}) + \dots \tag{4.15}$$

is the sum of (4.5) and

$$Q_{ij}^{(2)}(r_{pq}) = \frac{1}{24} \sum_{n=0}^{\infty} \frac{2^n(2n+4)!(n!)^2}{(2n)!(2n+1)!} \{q_i(M_j^{(n)}[n]M_j^{(n)}) + (M_i^{(n)}[n]M_i^{(n)})q_j\} r_{pq}^{-2(n+3)}, \tag{4.16}$$

with q_i denoting the field gradient quadrupole polarizability of the micro-system of species i.

From Eq. (4.16) we have for the special cases of micro-systems (i) axially-symmetric

$$Q_{ij}^{(2)}(r_{pq}) = \frac{1}{6} \sum_{n=0}^{\infty} (n+1)(n+2)(2n+3) \{q_i(M_j^{(n)})^2 + (M_i^{(n)})^2 q_j\} r_{pq}^{-2(n+3)}, \tag{4.17}$$

or up to the term with induced quadrupole-quadrupole interaction,

$$Q_{ij}^{(2)}(r_{pq}) = (q_i e_j^2 + e_i^2 q_j)r_{pq}^{-6} + 5(q_i\mu_j^2 + \mu_i^2 q_j)r_{pq}^{-8} + 14(q_i\Theta_j^2 + \Theta_i^2 q_j)r_{pq}^{-10}, \tag{4.18}$$

(ii) tetrahedral

$$Q_{ij}^{(2)}(r_{pq}) = 72 \{q_i(\Omega_{xyz})_j^2 + (\Omega_{xyz})_i^2 q_j\} r_{ij}^{-12}, \tag{4.19}$$

(iii) octahedral

$$Q_{ij}^{(2)}(r_{pq}) = \frac{2640}{7} \{q_i(\Phi_{xxzz})_j^2 + (\Phi_{xxzz})_i^2 q_j\} r_{pq}^{-14}. \tag{4.20}$$

5. Second-order perturbation to F

By (2.12), the second-order perturbation to F_t contains the term $\langle V_t^2 \rangle$, which now yields the first non-zero contribution also in the case of electrostatic $(2^n$-pole$) - (2^m$-pole$)$ interactions. The square of the electrostatic potential energy (3.8),

$$V_{\text{el}}^2 = \frac{1}{4} \sum_{ijkl} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{m'=0}^{\infty} \frac{(-1)^{m+n'} 2^{n+m+n'+m'} n!m!n'!m'!}{(2n)!(2m)!(2n')!(2m')!} \times$$

$$\times M_{pi}^{(n)}[n]^{(n)}T_{pq}^{(m)}[m]M_{qj}^{(m)}M_{rk}^{(n')}[n']^{(n')}T_{rs}^{(m')}[m']M_{sl}^{(m')}, \tag{5.1}$$

averaged over all orientations, presents two non-vanishing terms for $p = r \neq q = s$ and $p = s \neq q = r$, respectively, which contain the factor

$$\overline{(\boldsymbol{M}_{pi}^{(n)}[n]^{(n)}\boldsymbol{T}_{pq}^{(m)}[m]\,\boldsymbol{M}_{qj}^{(m)})^2} =$$

$$= \frac{1}{(2n+1)\,(2m+1)}\,(\boldsymbol{M}_{pi}^{(n)}[n]\,\boldsymbol{M}_{pi}^{(n)})(^{(n)}\boldsymbol{T}_{pq}^{(m)}[n+m]\,^{(n)}\boldsymbol{T}_{pq}^{(m)})(\boldsymbol{M}_{qj}^{(m)}[m]\,\boldsymbol{M}_{qj}^{(m)})\,, \qquad (5.2)$$

whence, by (4.3), we have

$$\overline{V_{\text{el}}^2} = \frac{1}{2}\,\sum_{ij}\,\sum_{p=1}^{N_i}\,\sum_{\substack{q=1\\p\neq q}}^{N_j}\,\sum_{n=0}^{\infty}\,\sum_{m=0}^{\infty}\,\frac{2^{n+m}(2n+2m)\,!\,(n\,!m\,!)^2}{(2n)\,!(2m)\,!\,(2n+1)\,!\,(2m+1)\,!}\,\times$$

$$\times\,(\boldsymbol{M}_{pi}^{(n)}[n]\,\boldsymbol{M}_{pi}^{(n)})(\boldsymbol{M}_{qj}^{(m)}[m]\boldsymbol{M}_{qj}^{(m)})r_{pq}^{-2(n+m+1)} \qquad (5.3)$$

Substituting (5.3) in (2.14) and recurring to the binary distribution function defined in (2.17) we have, in the second approximation, the following contribution to F_t:

$$\langle V_{\text{el}}^2\rangle = \frac{1}{2}\,\sum_{ij}\,x_i x_j \iint Q_{ij}^{\text{el}}(r_{pq})n_{ij}^{(2)}(\boldsymbol{r}_p,\boldsymbol{r}_q)d\boldsymbol{r}_p d\boldsymbol{r}_q \qquad (5.4)$$

from electrostatic interactions between permanent multipole moments; here, use has been made of the notation

$$Q_{ij}^{\text{el}}(r_{pq}) = \sum_{n=0}^{\infty}\,\sum_{m=0}^{\infty}\,\frac{2^{n+m}(2n+2m)\,!(n\,!m\,!)^2}{(2n)\,!\,(2m)\,!\,(2n+1)\,!\,(2m+1)\,!}\,(\boldsymbol{M}_i^{(n)}[n]\boldsymbol{M}_i^{(n)})(\boldsymbol{M}_j^{(m)}[m]\,\boldsymbol{M}_j^{(m)})r_{pq}^{-2(n+m+1)}\,.$$

$$(5.5)$$

On applying this expression to axially-symmetric micro-systems, we have by (4.6) the following simple formula:

$$Q_{ij}^{\text{el}}(r_{pq}) = \sum_{n=0}^{\infty}\,\sum_{m=0}^{\infty}\,\frac{(2n+2m)\,!}{(2n+1)\,!\,(2m+1)\,!}\,(M_i^{(n)})^2(M_j^{(m)})^2 r_{pq}^{-2(n+m+1)} \qquad (5.6)$$

rendering, to within the term describing hexadecapole-hexadecapole interaction,

$$Q_{ij}^{\text{el}}(r_{pq}) = e_i^2 e_j^2 r_{pq}^{-2} + \frac{1}{3}\,(e_i^2\mu_j^2 + \mu_i^2 e_j^2)r_{pq}^{-4} + \frac{1}{15}\,(3e_i^2\Theta_j^2 + 10\mu_i^2\mu_j^2 + 3\Theta_i^2 e_j^2)r_{pq}^{-6} +$$

$$+ \frac{1}{7}\,(e_i^2\Omega_j^2 + 7\mu_i^2\Theta_j^2 + 7\Theta_i^2\mu_j^2 + \Omega_i^2 e_j^2)r_{pq}^{-8} + \frac{1}{45}\,(5e_i^2\Phi_j^2 + 60\mu_i^2\Omega_j^2 + 126\,\Theta_i^2\Theta_j^2 +$$

$$+ 60\Omega_i^2\mu_j^2 + 5\Phi_i^2 e_j^2)r_{pq}^{-10} + \frac{1}{3}\,(5\mu_i^2\Phi_j^2 + 18\Theta_i^2\Omega_j^2 + 18\Omega_i^2\Theta_j^2 + 5\Phi_i^2\mu_j^2)r_{pq}^{-12} +$$

$$\frac{11}{7}\,(7\Theta_i^2\Phi_j^2 + 12\Omega_i^2\Omega_j^2 + 7\Phi_i^2\Theta_j^2)r_{pq}^{-14} + \frac{143}{3}\,(\Omega_i^2\Phi_j^2 + \Phi_i^2\Omega_j^2)r_{pq}^{-16} + \frac{1430}{9}\,\Phi_i^2\Phi_j^2 r_{pq}^{-18} + \cdots.$$

$$(5.7)$$

The above results determine the well-known Keesom orientation effect as generalized to the case of axially-symmetric micro-systems presenting higher-pole moments.

Similarly, Eq. (5.5) yields, for micro-systems possessing the tetrahedral symmetry,

$$Q_{ij}^{el}(r_{pq}) = \frac{19008}{175} (\Omega_{xyz})_i^2 (\Omega_{xyz})_j^2 r_{pq}^{-14}, \tag{5.8}$$

or octahedral symmetry

$$Q_{ij}^{el}(r_{pq}) = \frac{366080}{49} (\Phi_{xxzz})_i^2 (\Phi_{xxzz})_j^2 r_{pq}^{-18}. \tag{5.9}$$

Eq. (5.8) together with (5.4) determines the contribution to F_t from octopole-octopole interaction of tetrahedrally symmetric micro-systems, whereas Eq. (5.9) determines the contribution in the case of hexadecapole-hexadecapole interaction of octahedral micro-systems.

A further contribution to F_t within the framework of the second approximation results from the cross term $\langle V_{el} V_{ind} \rangle$. On restricting the problem, as above, to pairwise correlations, we obtain $\langle V_{el} V_{ind}^{(1)} \rangle = 0$ for the case when the dipole polarizability tensor $\boldsymbol{\alpha}$ is isotropic, and $\langle V_{el} V_{ind}^{(1)} \rangle \neq 0$ if the tensor $\boldsymbol{\alpha}$ is anisotropic and if, moreover, the micro-system spossess a non-zero quadrupole moment $\boldsymbol{M}^{(2)} = \boldsymbol{\Theta}$. In this latter case we have, by (3.8) and (3.14),

$$V_{el} = -\frac{1}{18} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{M}_{pi}^{(2)} : {}^{(2)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{M}_{qj}^{(2)}, \tag{5.10}$$

$$V_{ind}^{(1)} = \frac{1}{18} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \boldsymbol{M}_{pi}^{(2)} : {}^{(2)}\boldsymbol{T}_{pr}^{(1)} \cdot \boldsymbol{\alpha}_{rk} \cdot {}^{(1)}\boldsymbol{T}_{rq}^{(2)} : \boldsymbol{M}_{qj}^{(2)}, \tag{5.11}$$

and, on isotropic averageing,

$$\overline{V_{el} V_{ind}^{(1)}} = -\frac{2}{4725} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} [\boldsymbol{M}_{pi}^{(2)} : (\boldsymbol{M}_{pi}^{(2)} \cdot \boldsymbol{M}_{pi}^{(2)})] (\boldsymbol{\alpha}_{qj} : \boldsymbol{M}_{qj}^{(2)}) [({}^{(2)}\boldsymbol{T}_{pq}^{(1)} \cdot {}^{(1)}\boldsymbol{T}_{qp}^{(2)}) \vdots {}^{(2)}\boldsymbol{T}_{pq}^{(2)}]. \tag{5.12}$$

Considering that

$$({}^{(2)}\boldsymbol{T}_{pq}^{(1)} \cdot {}^{(1)}\boldsymbol{T}_{qp}^{(2)}) \vdots {}^{(2)}\boldsymbol{T}_{pq}^{(2)} = 1080 \, r_{pq}^{-13}, \tag{5.13}$$

we finally obtain by (5.12)

$$2\langle V_{el} V_{ind}^{(1)} \rangle = -\frac{16}{35} \sum_{ij} x_i x_j \{ (\boldsymbol{\alpha}_i : \boldsymbol{\Theta}_i) [\boldsymbol{\Theta}_j : (\boldsymbol{\Theta}_j \cdot \boldsymbol{\Theta}_j)] +$$

$$+ [\boldsymbol{\Theta}_i : (\boldsymbol{\Theta}_i \cdot \boldsymbol{\Theta}_i)] (\boldsymbol{\alpha}_j : \boldsymbol{\Theta}_j) \} \iint r_{pq}^{-13} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) \, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{5.14}$$

For micro-systems having the axial symmetry, this result reduces to

$$2\langle V_{el} V_{ind}^{(1)} \rangle = -\frac{36}{35} \sum_{ij} x_i x_j \Theta_i \Theta_j \{ \alpha_i \varkappa_i \Theta_j^2 + \Theta_i^2 \alpha_j \varkappa_j \} \iint r_{pq}^{-13} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{5.15}$$

wherein $\varkappa_i = (\alpha_{zz}^{(i)} - \alpha_{xx}^{(i)})3\alpha_i$ is the anisotropy of dipole polarizability of a micro-system of species i. It is immediately obvious that in the case of isotropic polarizability ($\varkappa_i = 0$) the contribution (5.15) vanishes.

If in averageing the term $\langle V_{el} V_{ind}^{(1)} \rangle$ we take into consideration also ternary correlations, a non-zero contribution to F_t is obtained in the present approximation even if the polarizability tensor $\boldsymbol{\alpha}$ is isotropic. Indeed, by (3.8), (3.14), integration over angular coordinates and on neglecting the anisotropy in $\boldsymbol{\alpha}$, we have a non-zero factor

$$\overline{(M_{pi}^{(n)}[n]\,{}^{(n)}T_{pq}^{(m)}[m]\,M_{qj}^{(m)})(M_{pi}^{(n)}[n]\,{}^{(n)}T_{pr}^{(1)}\cdot\boldsymbol{\alpha}_{rk}\cdot{}^{(1)}T_{rq}^{(m)}[m]\,M_{qj}^{(m)})} =$$

$$= \frac{1}{(2n+1)\,(2m+1)}\,(M_{pi}^{(n)}[n]\,M_{pi}^{(n)})\,(M_{qj}^{(m)}[m]\,M_{qj}^{(m)})\,\boldsymbol{\alpha}_{rk}\,\{{}^{(n)}T_{pq}^{(m)}[n+m]\,({}^{(n)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(m)})\}, \tag{5.16}$$

and we find finally

$$\overline{V_{el}V_{ind}^{(1)}} = \frac{1}{2}\sum_{ijk}\sum_{p=1}^{Ni}\sum_{\substack{q=1\\q\neq q}}^{Nj}\sum_{\substack{r=1\\r\neq p\\r\neq q}}^{Nk} Q_{ijk}^{cross}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r), \tag{5.17}$$

with

$$Q_{ijk}^{cross}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{(-1)^n 2^{2(n+m)}(n!\,m!)^2}{(2n)!\,(2m)!\,(2n+1)!\,(2m+1)!}\,(M_i^{(n)}[n]\,M_i^{(n)})\,(M_j^{(m)}[m]\,M_j^{(m)})\times$$

$$\times\,\alpha_k\,\{{}^{(n)}T_{pq}^{(m)}[n+m]\,({}^{(n)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(m)})\}. \tag{5.18}$$

Using the definition (2.14) and the ternary distribution function as given in Eqs (2.17), we have

$$\langle V_{el}V_{ind}^{(1)}\rangle = \frac{1}{2}\sum_{ijk}x_i x_j x_k\iiint Q_{ijk}^{cross}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r)\,n_{ijk}^{(3)}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r)\,d\boldsymbol{r}_p d\boldsymbol{r}_q d\boldsymbol{r}_r. \tag{5.19}$$

With respect to (4.6), (5.18) now assumes the form for axially-symmetric micro-systems

$$Q_{ijk}^{cross}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r) = \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{(-1)^n 2^{n+m}}{(2n+1)!\,(2m+1)!}\,(M_i^{(n)})^2(M_j^{(m)})^2\alpha_k\{{}^{(n)}T_{pq}^{(m)}[n+m]({}^{(n)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(m)})\}. \tag{5.20}$$

Restricting ourselves to the quadrupole-induced dipole-quadrupole interaction, we have from (5.20)

$$Q_{ijk}^{cross}(\boldsymbol{r}_p,\boldsymbol{r}_q,\boldsymbol{r}_r) = e_i^2 e_j^2 \alpha_k\,{}^{(0)}T_{pq}^{(0)}({}^{(0)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(0)}) + \frac{1}{3}\,\{e_i^2\mu_j^{2(0)}\,{}^{(0)}T_{pq}^{(1)}\cdot({}^{(0)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(1)}) -$$

$$-\,\mu_i^2 e_j^2({}^{(1)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(0)})\cdot{}^{(1)}T_{pq}^{(0)}\}\,\alpha_k + \frac{1}{30}\,\{e_i^2\Theta_j^{2(0)}\,{}^{(0)}T_{pq}^{(2)}:({}^{(0)}T_{pr}^{(1)}\cdot{}^{(1)}T_{rq}^{(1)}) +$$

$$+ \Theta_i^2 e_j^2 (^{(2)}\mathbf{T}_{pr}^{(1)} \cdot {}^{(1)}\mathbf{T}_{rq}^{(0)}) : {}^{(2)}\mathbf{T}_{pq}^{(0)}\} \alpha_k - \frac{1}{90} \mu_i^2 \mu_j^2 \alpha_k {}^{(1)}\mathbf{T}_{pq}^{(1)} : (^{(1)}\mathbf{T}_{pr}^{(1)} \cdot {}^{(1)}\mathbf{T}_{rq}^{(1)}) -$$

$$- \frac{1}{90} \{\mu_i^2 \Theta_j^2 {}^{(1)}\mathbf{T}_{pq}^{(2)} : (^{(1)}\mathbf{T}_{pr}^{(1)} \cdot {}^{(1)}\mathbf{T}_{rq}^{(2)}) - \Theta_i^2 \mu_j^2 (^{(2)}\mathbf{T}_{pr}^{(1)} \cdot {}^{(1)}\mathbf{T}_{rq}^{(1)}) : {}^{(2)}\mathbf{T}_{pq}^{(1)}\} \alpha_k +$$

$$+ \frac{1}{900} \Theta_i^2 \Theta_j^2 \alpha_k {}^{(2)}\mathbf{T}_{pq}^{(2)} : (^{(2)}\mathbf{T}_{pr}^{(1)} \cdot {}^{(1)}\mathbf{T}_{rq}^{(2)}) - \dots \tag{5.21}$$

The cross term $\langle V_{el} V_{ind} \rangle$ yields also further contributions to F_t from induced moments of higher order. However, we refrain from calculating them here. Similarly, within the framework of the second approximation to F_t one can calculate the contributions due to the term $\langle V^2_{ind} \rangle$. The latter, however, are of the second order in the dipole polarizability α or higher-order polarizabilities, and in general play but a smaller role as compared with the contributions calculated above.

6. Further approximation to F_t

We shall evaluate the higher approximations to F_t including the terms $\langle V_t^3 \rangle$ and $\langle V_t^4 \rangle$. To avoid complicating the final results, we restrict at first our further calculations to the case of an assembly of dipolar molecules for which Eqs (3.8) and (3.14) yield for the total tensorial potential energy,

$$V_t = \frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \boldsymbol{\mu}_{pi} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)} \cdot \boldsymbol{\mu}_{qj} - \frac{1}{2} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \boldsymbol{\mu}_{pi} \cdot {}^{(1)}\mathbf{T}_{pr}^{(1)} \cdot \boldsymbol{\alpha}_{rk} \cdot {}^{(1)}\mathbf{T}_{rq}^{(1)} \cdot \boldsymbol{\mu}_{qj} - \dots \tag{6.1}$$

If we assume for simplicity that the dipolar molecules are isotropically polarizable, we find from (6.1) by averageing over all molecular orientations

$$\overline{V_t^3} = -\frac{1}{60} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mu_i^2 \mu_j^2 (\alpha_i \mu_j^2 + \mu_i^2 \alpha_j) \{(^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)})^2 + 2(^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)}) : (^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)})\} +$$

$$- \frac{1}{27} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq p \\ r \neq q}}^{N_k} \mu_i^2 \mu_j^2 \mu_k^2 (^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{qr}^{(1)}) : {}^{(1)}\mathbf{T}_{rp}^{(1)}, \tag{6.2}$$

$$\overline{V_t^4} = \frac{1}{150} \sum_{ij} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \mu_i^4 \mu_j^4 \{(^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)})^2 + 2(^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)}) : (^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{pq}^{(1)})\} +$$

$$+ \frac{1}{90} \sum_{ijk} \sum_{p=1}^{N_i} \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \sum_{\substack{r=1 \\ r \neq q}}^{N_k} \mu_i^2 \mu_j^4 \mu_k^2 \{(^{(1)}\mathbf{T}_{pq}^{(1)} : {}^{(1)}\mathbf{T}_{pq}^{(1)})(^{(1)}\mathbf{T}_{qr}^{(1)} : {}^{(1)}\mathbf{T}_{qr}^{(1)}) + 2(^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{qr}^{(1)}) : (^{(1)}\mathbf{T}_{pq}^{(1)} \cdot {}^{(1)}\mathbf{T}_{qr}^{(1)})\}.$$

$$\tag{6.3}$$

On introducing herein the distribution functions (2.17) we find finally

$$\langle V_t^3 \rangle = -\frac{6}{5} \sum_{ij} x_i x_j \mu_i^2 \mu_j^2 (\alpha_i \mu_j^2 + \mu_i^2 \alpha_j) \iint r_{pq}^{-12} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q +$$

$$+ \frac{1}{9} \sum_{ijk} x_i x_j x_k \mu_i^2 \mu_j^2 \mu_k^2 \iiint r_{pq}^{-5} r_{qr}^{-5} r_{rp}^{-5} \{9(\boldsymbol{r}_{pq} \cdot \boldsymbol{r}_{qr})(\boldsymbol{r}_{qr} \cdot \boldsymbol{r}_{rp})(\boldsymbol{r}_{rp} \cdot \boldsymbol{r}_{pq}) -$$

$$- 3r_{pq}^2 (\boldsymbol{r}_{qr} \cdot \boldsymbol{r}_{rp})^2 - 3r_{qr}^2 (\boldsymbol{r}_{rp} \cdot \boldsymbol{r}_{pq})^2 - 3r_{rp}^2 (\boldsymbol{r}_{pq} \cdot \boldsymbol{r}_{qr})^2 + 2r_{pq}^2 r_{qr}^2 r_{rp}^2\} n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) d\boldsymbol{r}_p d\boldsymbol{r}_q d\boldsymbol{r}_r,$$

$$(6.4)$$

$$\langle V_t^4 \rangle = \frac{12}{25} \sum_{ij} x_i x_j \mu_i^4 \mu_j^4 \iint r_{pq}^{-12} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q +$$

$$+ \frac{1}{5} \sum_{ijk} x_i x_j x_k \mu_i^2 \mu_j^4 \mu_k^2 \iiint r_{pq}^{-8} r_{qr}^{-8} \{(\boldsymbol{r}_{pq} \cdot \boldsymbol{r}_{qr})^2 + 3r_{pq}^2 r_{qr}^2\} n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) d\boldsymbol{r}_p d\boldsymbol{r}_q d\boldsymbol{r}_r.$$

$$(6.5)$$

Thus, by (4.9), (5.7), (6.4) and (6.5), the tensorial part of the free energy of the assembly of dipolar molecules is given, on retaining only terms linear in the binary distribution function by

$$F_t = -\frac{1}{2} \sum_{ij} x_i x_j \iint \left\{ (\alpha_i \mu_j^2 + \mu_i^2 \alpha_j) \left(r_{pq}^{-6} + \frac{2\mu_i^2 \mu_j^2}{5k^2 T^2} r_{pq}^{-12} + \dots \right) + \right.$$

$$\left. + \frac{\mu_i^2 \mu_j^2}{3kT} \left(r_{pq}^{-6} + \frac{3\mu_i^2 \mu_j^2}{25k^2 T^2} r_{pq}^{-12} + \dots \right) \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \qquad (6.6)$$

We likewise calculate the higher-order contributions in the case of micro-systems having a quadrupole moment, *i.e.* when the total energy of tensor interaction is the sum of the energies (5.10) and (5.11). However, we shall restrict these supplementary calculations to the third-order approximation resulting from electrostatic interaction (5.10), for which we obtain with the accuracy of ternary correlation

$$\langle V_{el}^3 \rangle = -\frac{8}{99225} \sum_{ij} x_i x_j [M_i^{(2)} : (M_i^{(2)} \cdot M_i^{(2)})] [M_j^{(2)} : (M_j^{(2)} \cdot M_j^{(2)})] \times$$

$$\times \iint \{(^{(2)}T_{pq}^{(2)} : {}^{(2)}T_{pq}^{(2)}) \vdots {}^{(2)}T_{pq}^{(2)}\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q +$$

$$- \frac{1}{91125} \sum_{ijk} x_i x_j x_k (M_i^{(2)} : M_i^{(2)})(M_j^{(2)} : M_j^{(2)})(M_k^{(2)} : M_k^{(2)}) \times$$

$$\times \iiint \{(^{(2)}T_{pq}^{(2)} : {}^{(2)}T_{qr}^{(2)}) \vdots {}^{(2)}T_{rp}^{(2)}\} n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) d\boldsymbol{r}_p d\boldsymbol{r}_q d\boldsymbol{r}_r. \qquad (6.7)$$

Omitting the term with the ternary distribution function, and considering that

$$(^{(2)}\boldsymbol{T}_{pq}^{(2)} : {}^{(2)}\boldsymbol{T}_{pq}^{(2)}) \vdots {}^{(2)}\boldsymbol{T}_{pq}^{(2)} = -19440 r_{pq}^{-15}, \tag{6.8}$$

we have for axially-symmetric micro-systems

$$\langle V_{\text{el}}^3 \rangle = \frac{216}{245} \sum_{ij} x_i x_j \, \Theta_i^3 \Theta_j^3 \int\int r_{pq}^{-15} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{6.9}$$

By combining Eqs (4.9), (4.18), (5.7) (5.15) and (6.9), we obtain F_t for an assembly or quadrupolar molecules in the form of

$$F_t = -\frac{3}{4} \sum_{ij} x_i x_j \int\int \left\{ (\alpha_i \Theta_j^2 + \Theta_j^2 \alpha_j) r_{pq}^{-8} + \frac{28}{3} (q_i \Theta_j^2 + \Theta_j^2 q_j) r_{pq}^{-10} + \right.$$

$$- \frac{24}{35kT} \, \Theta_i \Theta_j (\alpha_i \varkappa_j \Theta_j^2 + \Theta_j^2 \alpha_i \varkappa_j) r_{pq}^{-13} + \frac{14}{15kT} \, \Theta_i^2 \Theta_j^2 \left(r_{pq}^{-10} - \right.$$

$$\left. \left. - \frac{72 \Theta_i \Theta_j}{343kT} \, r_{pq}^{-15} \right) \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{6.10}$$

7. Application of F_t to two-component systems

The tensorial part of the free energy evaluated in Sec. 4, 5 and 6 can be expresesd formally as

$$F_{\text{tensorial}} = \sum_{ij} x_i x_j F_{ij}^{(2)} + \sum_{ijk} x_i x_j x_k F_{ijk}^{(3)} + ..., \tag{7.1}$$

where

$$F_{ij}^{(2)} = -\frac{1}{2} \int\int \left\{ Q_{ij}^{\text{ind}}(r_{pq}) + \frac{1}{2kT} \, Q_{ij}^{\text{el}}(r_{pq}) + O(T^{-2}) \right\} n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q \tag{7.2}$$

determine the contributions to F_t arising from pairwise interactions of multipolar micro-systems as given in general by the quantities of (4.5), (4.15), (4.16) and (5.5), and

$$F_{ijk}^{(3)} = -\frac{1}{4kT} \int\int\int \left\{ Q_{ijk}^{\text{cross}}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) + O(T^{-1}) \right\} n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) d\boldsymbol{r}_p d\boldsymbol{r}_q d\boldsymbol{r}_r \tag{7.3}$$

— the contributions to F_t from triples interactions of multipolar micro-systems given by the quantity of (5.18).

The expression (7.1) with (7.2) and (7.3) yields in appropriate special cases the result derived previously by Pople [2] and by Barker [3].

If, in particular, a two-component system is considered, Eq. (7.1) yields, on retaining only contributions from pairs interaction,

$$F_{\text{tensorial}} = x_1^2 F_{11}^{(2)} + 2x_1 x_2 F_{12}^{(2)} + x_2^2 F_{22}^{(2)}, \tag{7.4}$$

where $F_{11}^{(2)}$ and $F_{22}^{(2)}$ account for the interactions of like pairs in the pure components 1 and 2, respectively, and $F_{12}^{(2)}$ corresponds to the pair interactions between unlike micro-systems of component 1 and component 2.

We shall now apply these expressions to some special cases.

Let us assume that the molecules of system 1 are dipolar and those of component 2 quadrupolar and axially-symmetric. In this case we obtain by Eqs (6.6) (6.10) and (7.2)

$$F_{11}^{(2)} = - \int\int \left\{ \alpha_1\mu_1^2 \left(r_{pq}^{-6} + \frac{2\mu_1^4}{5k^2T^2}\, r_{pq}^{-12} \right) + \right.$$
$$\left. + \frac{\mu_1^4}{6kT} \left(r_{pq}^{-6} + \frac{3\mu_1^4}{25k^2T^2}\, r_{pq}^{-12} \right) \right\} n_{11}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{7.5}$$

$$F_{12}^{(2)} = - \frac{1}{2} \int\int \left\{ \alpha_2\mu_1^2 r_{pq}^{-6} + \frac{3}{2}\left(\alpha_1 + \frac{\mu_1^2}{3kT} \right) \Theta_2^2 r_{pq}^{-8} \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{7.6}$$

$$F_{22}^{(2)} = - \frac{3}{2} \int\int \left\{ \alpha_2\Theta_2^2 r_{pq}^{-8} + \frac{7\Theta_2^4}{15kT}\, r_{pq}^{-10} + \frac{28}{3}\, q_2\Theta_2^2 r_{pq}^{-10} + \right.$$
$$\left. - \frac{24}{35kT}\, \alpha_2\varkappa_2\Theta_2^4 r_{pq}^{-13} - \frac{24\Theta_2^6}{245k^2T^2}\, r_{pq}^{-15} \right\} n_{22}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{7.7}$$

In particular, when $\mu_1 = 0$, the foregoing expressions conform to the mixture of a monatomic component with a quadrupolar component, whereas for $\Theta_2 = 0$ — to the mixture of a monatomic component with a dipolar component.

In the case of a two-component system, wherein the one component again consists of dipolar molecules and the other consists of tetrahedral molecules possessing the octopole moment Ω_2, Eq. (7.2) yields, in addition to $F_{11}^{(2)}$ given by (7.5),

$$F_{12}^{(2)} = - \frac{1}{2} \int\int \left\{ \alpha_2\mu_1^2 r_{pq}^{-6} + \frac{24}{5}\left(\alpha_1 + \frac{\mu_1^2}{3kT} \right) \Omega_2^2 r_{pq}^{-10} \right\} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q, \tag{7.8}$$

$$F_{22}^{(2)} = - \frac{24}{5} \int\int \left\{ \alpha_2\Omega_2^2 r_{pq}^{-8} + \frac{198\Omega_2^4}{35kT}\, r_{pq}^{-14} \right\} n_{22}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{7.9}$$

On putting in the above expressions $\mu_1 = 0$, we obtain formulas for the mixture of a monatomic component and of one consisting of tetrahedral molecules with octopole moment Ω_2.

Eq. (7.9) with only the temperature-dependent term accounts for the octopole-octopole interactions, and yields, the result derived by Parsonage and Scott [4].

For a mixture composed of quadrupolar and tetrahedral molecules, we have by (7.2) for the contribution to $F_{12}^{(2)}$ resulting from the interaction between the quadrupole Θ_1 of component 1 and the octopole Ω_2 of component 2,

$$F_{12}^{(2)} = - \frac{18}{5kT}\, \Theta_1^2\Omega_2^2 \int\int r_{pq}^{-12} n_{12}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q)\, d\boldsymbol{r}_p d\boldsymbol{r}_q. \tag{7.10}$$

In the same way, we can discuss the tensorial contributions to the free energy for other special cases.

8. Application to the equation of state of a gas mixture

From (1.1), the equation of state can be expressed, in terms of the free energy, as

$$\frac{pV}{NkT} = - \frac{1}{\varrho kT} \left(\frac{\partial F}{\partial V}\right)_{T,\,N} = \frac{1}{VkT} \left(\frac{\partial F}{\partial \varrho}\right)_{T,\,N}, \tag{8.1}$$

where $\varrho = N/V$ is the molecular number density.

In the case of a not too strongly compressed gas mixture, the binary and ternary distributions functions can be expanded in the form resulting from classical statistical mechanics,

$$n_{ij}^{(2)}(\boldsymbol{r}_p, \boldsymbol{r}_q) = \varrho^2 \exp\left\{-\frac{u_{ij}(r_{pq})}{kT}\right\} \left\{1 + \varrho \sum_k x_k \int f_{ik}(r_{pr}) f_{kj}(r_{rq}) \, d\boldsymbol{r}_r + O(\varrho^2)\right\}, \tag{8.2}$$

$$n_{ijk}^{(3)}(\boldsymbol{r}_p, \boldsymbol{r}_q, \boldsymbol{r}_r) = \varrho^3 \exp\left\{-\frac{u_{ijk}(r_{pq}, r_{qr}, r_{rp})}{kT}\right\} \{1 + O(\varrho)\}, \tag{8.3}$$

with the function

$$f_{ij}(r_{pq}) = \exp\left\{-\frac{u_{ij}(r_{pq})}{kT}\right\} - 1. \tag{8.4}$$

Here, $u_{ij}(r_{pq})$ is the central forces potential energy of interaction between molecules p and q of species i and j, and $u_{ijk}(r_{pq}, r_{qr}, r_{rp})$ — that between three molecules p, q and r of species i, j and k, respectively.

With regard to the expressions (2.7), (4.14), (5.4) and (5.19), Eq. (8.1) now assumes the form

$$\frac{pV}{NkT} = 1 + \frac{1}{V} \sum_{ij} x_i x_j B_{ij} + \frac{1}{V^2} \sum_{ijk} x_i x_j x_k C_{ijk} + \ldots, \tag{8.5}$$

where

$$B_{ij} = B_{ij}^{\text{central}} + B_{ij}^{\text{tensorial}} \tag{8.6}$$

is the second virial coefficient composed of a part describing pair central interaction between molecules of species i and j,

$$B_{ij}^{\text{central}} = -2\pi N \int_0^\infty f_{ij}(r_{pq}) \, r_{pq}^2 dr_{pq}, \tag{8.7}$$

and a part resulting from the tensorial intermolecular forces,

$$B_{ij}^{\text{tensorial}} = -\frac{2\pi N}{kT} \int_0^\infty \left\{Q_{ij}^{\text{ind}}(r_{pq}) + \frac{1}{2kT} Q_{ij}^{\text{el}}(r_{pq}) + O(T^{-2})\right\} \exp\left\{-\frac{u_{ij}(r_{pq})}{kT}\right\} r_{pq}^2 dr_{pq}. \tag{8.8}$$

From Eq. (8.8) we can obtain immediately the result derived in the previous papers for dipolar and quadrupolar unlike molecules [20, 23], octopolar molecules [22] and hexadecapolar molecules [16].

Similarly, one can obtain an explicite expression for the third virial coefficient C_{ijk} of Eq. (8.5).

In concluding we should like to draw attention to an interesting fact arising from Eq. (8.8). Namely, if we use on the one hand the values of the well-known central forces parameters from viscosity data and, on the other, the experimental data for B, we can estimate from (8.8) reasonable values of the quadrupole moment of axially-symmetric molecules [20] or octopole moment of tetrahedral molecules [22]. Lately, Orcutt [24] has solidly established this method and extended it to a wide range of temperatures and has evaluated reliable values of the molecular quadrupole moments of H_2, N_2, CO_2, and C_2H_4. Hence, investigation of the tensorial contributions to the second virial coefficients, constitutes a sure and unfailing method of determining the quadrupole, octopole, *etc.* moments of molecules. This method of determining molecular quadrupoles or octopoles, although indirect, is of great convenience in its applications and leads in a simple manner to results whose accuracy is in many cases satisfactory and reliable.

APPENDIX

The total tensorial potential energy of assemblies of axially-symmetric micro-system. With the accuracy to the hexadecapole-hexadecapole interaction, Eq. (3.8) yields

$$V_{\text{el}} = -\frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \{ M_{pi}^{(0)\,(0)}T_{pq}^{(0)} M_{qj}^{(0)} - M_{pi}^{(0)\,(0)}T_{pq}^{(1)} \cdot M_{qj}^{(1)} + M_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(0)} M_{qj}^{(0)} -$$

$$- M_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(1)} \cdot M_{qj}^{(1)} + \frac{1}{3} (M_{pi}^{(0)\,(0)}T_{pq}^{(2)} : M_{qj}^{(2)} + M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(0)} M_{qj}^{(0)}) +$$

$$+ \frac{1}{3} (M_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(2)} : M_{qj}^{(2)} - M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(1)} \cdot M_{qj}^{(1)}) - \frac{1}{15} (M_{pi}^{(0)\,(0)}T_{pq}^{(3)} \vdots M_{qj}^{(3)} - M_{pi}^{(3)} \vdots {}^{(3)}T_{pq}^{(0)} M_{qj}^{(0)}) +$$

$$+ \frac{1}{9} M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(2)} : M_{qj}^{(2)} - \frac{1}{15} (M_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(3)} \vdots M_{qj}^{(3)} + M_{pi}^{(3)} \vdots {}^{(3)}T_{pq}^{(1)} \cdot M_{qj}^{(1)}) +$$

$$+ \frac{1}{105} (M_{pi}^{(0)(0)}T_{pq}^{(4)} \vdots M_{qj}^{(4)} + M_{pi}^{(4)} \vdots {}^{(4)}T_{pq}^{(0)} M_{qj}^{(0)}) - \frac{1}{45} (M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(3)} \vdots M_{qj}^{(3)} - M_{pi}^{(3)} \vdots {}^{(3)}T_{pq}^{(2)} : M_{qj}^{(2)}) +$$

$$+ \frac{1}{105} (M_{pi}^{(1)} \cdot {}^{(1)}T_{pq}^{(4)} \vdots M_{qj}^{(4)} - M_{pi}^{(4)} \vdots {}^{(4)}T_{pq}^{(1)} \cdot M_{qj}^{(1)}) - \frac{1}{225} M_{pi}^{(3)} \vdots {}^{(3)}T_{pq}^{(3)} \vdots M_{qj}^{(3)} +$$

$$+ \frac{1}{315} (M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(4)} \vdots M_{qj}^{(4)} + M_{pi}^{(4)} \vdots {}^{(4)}T_{pq}^{(2)} : M_{qj}^{(2)}) +$$

$$+ \frac{1}{1575} (M_{pi}^{(3)} \vdots {}^{(3)}T_{pq}^{(4)} \vdots M_{qj}^{(4)} - M_{pi}^{(4)} \vdots {}^{(4)}T_{pq}^{(3)} \vdots M_{qj}^{(3)}) + \frac{1}{11025} M_{pi}^{(4)} \vdots {}^{(4)}T_{pq}^{(4)} \vdots M_{qj}^{(4)} - \ldots \}. \quad \text{(A.1)}$$

Here, the successive terms correspond to the charge-charge, charge-dipole, dipole-dipole, charge-quadrupole, dipole-quadrupole, charge-octopole, quadrupole-quadrupole, dipole-octopole, charge-hexadecapole, quadrupole-octopole, dipole-hexadecapole, octopole-

octopole, quadrupole-hexadecapole, octopole-hexadecapole and hexadecapole-hexadecapole interactions, respectively.

By squaring V_{el} given by (A.1) and then carrying out integration over all orientation coordinates we obtains Eq. (5.4) with

$$Q_{ij}^{el}(r_{pq}) = (M_i^{(0)})^2(M_j^{(0)})^2 r_{pq}^{-2} + \frac{1}{3}\{(M_i^{(0)})^2(M_j^{(1)}\cdot M_j^{(1)}) + (M_i^{(1)}\cdot M_i^{(1)})(M_j^{(0)})^2\}\, r_{pq}^{-4} +$$

$$+\frac{2}{15}\{(M_i^{(0)})^2(M_j^{(2)}:M_j^{(2)}) + 5(M_i^{(1)}\cdot M_i^{(1)})(M_j^{(1)}\cdot M_j^{(1)}) + (M_i^{(2)}:M_i^{(2)})(M_j^{(0)})^2\}\, r_{pq}^{-6} +$$

$$+\frac{2}{105}\{3(M_i^{(0)})^2(M_j^{(3)}\vdots M_j^{(3)}) + 35(M_i^{(1)}\cdot M_i^{(1)})(M_j^{(2)}:M_j^{(2)}) +$$

$$+35(M_i^{(2)}:M_i^{(2)})(M_j^{(1)}\cdot M_j^{(1)}) + 3(M_i^{(3)}\vdots M_i^{(3)})(M_j^{(0)})^2\}\, r_{pq}^{-8} +$$

$$+\frac{8}{315}\{(M_i^{(0)})^2(M_j^{(4)}\vdots M_j^{(4)}) + 21(M_i^{(1)}\cdot M_i^{(1)})(M_j^{(3)}\vdots M_j^{(3)}) + 49(M_i^{(2)}:M_i^{(2)})(M_j^{(2)}:M_j^{(2)}) +$$

$$+21(M_i^{(3)}\vdots M_i^{(3)})(M_j^{(1)}\cdot M_j^{(1)}) + (M_i^{(4)}\vdots M_i^{(4)})(M_j^{(0)})^2\} r_{pq}^{-10} +$$

$$+\frac{8}{105}\{5(M_i^{(1)}\cdot M_i^{(1)})(M_j^{(4)}\vdots M_j^{(4)}) + 21(M_i^{(2)}:M_i^{(2)})(M_j^{(3)}\vdots M_j^{(3)}) +$$

$$+21(M_i^{(3)}\vdots M_i^{(3)})(M_j^{(2)}:M_j^{(2)}) + 5(M_i^{(4)}\vdots M_i^{(4)})(M_j^{(1)}\cdot M_j^{(1)})\} r_{pq}^{-12} +$$

$$+\frac{176}{525}\{5(M_i^{(2)}:M_i^{(2)})(M_j^{(4)}\vdots M_j^{(4)}) + 9(M_i^{(3)}\vdots M_i^{(3)})(M_j^{(3)}\vdots M_j^{(3)}) +$$

$$+5(M_i^{(4)}\vdots M_i^{(4)})(M_j^{(2)}:M_j^{(2)})\} r_{pq}^{-14} + \frac{2288}{525}\{(M_i^{(3)}\vdots M_i^{(3)})(M_j^{(4)}\vdots M_j^{(4)}) +$$

$$+(M_i^{(4)}\vdots M_i^{(4)})(M_j^{(3)}\vdots M_j^{(3)})\} r_{pq}^{-16} + \frac{18304}{2205}(M_i^{(4)}\vdots M_i^{(4)})(M_j^{(4)}\vdots M_j^{(4)}) r_{pq}^{-18} + \ldots \qquad \text{(A.2)}$$

Using (4.6) and the definitions of (4.8), we obtain from these expressions the result of (5.7) for axially symmetric micro-systems. Analogously, by (4.10), Eq. (A.2) reduces to (5.8) for tetrahedral molecules and by (4.12) — to Eq. (5.9) for octahedral molecules.

Denoting in the definition of (3.6) for simplicity $r_{p\nu} = r$, we have for the multipole operators of successive orders (the properties of the operator $S^{(n)}$ are the same as those of the spherical harmonics functions discussed e.g. in ref. [13])

$$S^{(0)} = 1,$$

$$S^{(1)} = r_1,$$

$$S^{(2)} = \frac{1}{2}(3r_1 r_2 - r^2 U_{12}),$$

$$S^{(3)} = \frac{1}{6}\{15 r_1 r_2 r_3 - 3r^2(U_{12} r_3 + U_{23} r_1 + U_{31} r_2)\},$$

$$S^{(4)} = \frac{1}{24} \{105\,\boldsymbol{r}_1\boldsymbol{r}_2\boldsymbol{r}_3\boldsymbol{r}_4 - 15r^2(\boldsymbol{U}_{12}\boldsymbol{r}_3\boldsymbol{r}_4 + \boldsymbol{U}_{23}\boldsymbol{r}_4\boldsymbol{r}_1 + \boldsymbol{U}_{34}\boldsymbol{r}_1\boldsymbol{r}_2 + \boldsymbol{U}_{14}\boldsymbol{r}_2\boldsymbol{r}_3 +$$

$$+ \boldsymbol{U}_{13}\boldsymbol{r}_2\boldsymbol{r}_4 + \boldsymbol{U}_{24}\boldsymbol{r}_1\boldsymbol{r}_3) + 3r^4(\boldsymbol{U}_{12}\boldsymbol{U}_{34} + \boldsymbol{U}_{13}\boldsymbol{U}_{24} + \boldsymbol{U}_{14}\boldsymbol{U}_{23})\}, \dots,$$

and, generally,

$$S^{(n)} = \frac{1}{n!} \{(2n-1)!!\,\boldsymbol{r}_1\boldsymbol{r}_2 \dots \boldsymbol{r}_n - (2n-3)!!\,r^2 \sum \boldsymbol{U}_{12}\boldsymbol{r}_3 \dots \boldsymbol{r}_n +$$

$$+ (2n-5)!!\,r^4 \sum \boldsymbol{U}_{12}\boldsymbol{U}_{34}\boldsymbol{r}_5 \dots \boldsymbol{r}_n - (2n-7)!!\,r^6 \sum \boldsymbol{U}_{12}\boldsymbol{U}_{34}\boldsymbol{U}_{56}\boldsymbol{r}_7 \dots \boldsymbol{r}_n + \dots$$

$$+ (-1)^k\,(2n-2k-1)!!\,r^{2k} \sum \boldsymbol{U}_{12} \dots \boldsymbol{U}_{2k-1,\,2k}\boldsymbol{r}_{2k+1} \dots \boldsymbol{r}_n + \dots\}, \tag{A.3}$$

where $\boldsymbol{U}_{12}$ is a unit tensor, $(2n-1)!! = 1.3.5.7\dots(2n-1)$, and $\Sigma \boldsymbol{U}_{12}\,\boldsymbol{r}_3\dots\boldsymbol{r}_n$ *etc.* are sums of the terms obtained from the one written by interchanging the suffixes $1, 2,\dots n$. The number of terms in the last sum in (A.3) is equal to $n!/\{2^k(n-2k)!k!\}$.

In terms of the operators $\boldsymbol{S}^{(n)}$ defined above, the multipole interaction tensor of (3.4) is of the form

$$\boldsymbol{T}_{pq}^{(n)} = (-1)^{n+1}\,n!\,r_{pq}^{-(2n+1)}\boldsymbol{S}_{pq}^{(n)}, \tag{A.4}$$

where $\boldsymbol{S}_{pq}^{(n)}$ is given by Eq. (A.3) if $\boldsymbol{r}$ is replaced by $\boldsymbol{r}_{pq}$.

With Eqs (3.5), (4.8), (A.3) and (A.4), we obtain for the respective terms in Eq. (A.1) of axially symmetric micro-systems, up to the octopole-octopole term,

$$M_{pi}^{(0)\,(0)}T_{pq}^{(0)}M_{qj}^{(0)} = -e_i e_j r_{pq}^{-1},$$

$$M_{pi}^{(0)\,(0)}\boldsymbol{T}_{pq}^{(1)} \cdot \boldsymbol{M}_{qj}^{(1)} = e_i \mu_j r_{pq}^{-3}(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq}),$$

$$\boldsymbol{M}_{pi}^{(1)} \cdot {}^{(1)}\boldsymbol{T}_{pq}^{(1)} \cdot \boldsymbol{M}_{qj}^{(1)} = -\mu_i \mu_j r_{pq}^{-5} \{3(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq}) - r_{pq}^2(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)\},$$

$$M_{pi}^{(0)\,(0)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{M}_{qj}^{(2)} = -\frac{3}{2}\,e_i \Theta_j r_{pq}^{-5} \{3(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^2 - r_{pq}^2\},$$

$$\boldsymbol{M}_{pi}^{(1)} \cdot {}^{(1)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{M}_{qj}^{(2)} = \frac{9}{2}\,\mu_i \Theta_j r_{pq}^{-7} \{5(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^2 - r_{pq}^2[(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq}) + 2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)]\},$$

$$M_{pi}^{(0)\,(0)}\boldsymbol{T}_{pq}^{(3)} \vdots \boldsymbol{M}_{qj}^{(3)} = \frac{15}{2}\,e_i \Omega_j r_{pq}^{-7} \{5(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^3 - 3r_{pq}^2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})\},$$

$$\boldsymbol{M}_{pi}^{(2)} : {}^{(2)}\boldsymbol{T}_{pq}^{(2)} : \boldsymbol{M}_{qj}^{(2)} = -\frac{27}{4}\,\Theta_i \Theta_j r_{pq}^{-9} \{35(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})^2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^2 - 5r_{pq}^2[(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})^2 +$$

$$+ (\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^2 + 4(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)] + r_{pq}^4[1 + 2(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)^2]\},$$

$$\boldsymbol{M}_{pi}^{(1)} \cdot {}^{(1)}\boldsymbol{T}_{pq}^{(3)} \vdots \boldsymbol{M}_{qj}^{(3)} = -\frac{15}{2}\,\mu_i \Omega_j r_{pq}^{-9} \{35(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_q \cdot \boldsymbol{s}_{pq})^3 - 15r_{pq}^2[(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq}) +$$

$$+ (\boldsymbol{s}_q \cdot \boldsymbol{r}_{pq})^2(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)] + 3r_{pq}^4(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)\},$$

$$M_{pi}^{(2)} : {}^{(2)}T_{pq}^{(3)} : M_{qj}^{(3)} = \frac{225}{4}\,\Theta_i\Omega_j r_{pq}^{-11}\{63\,(s_p\cdot r_{pq})^2(s_q\cdot r_{pq})^3 - 7r_{pq}^2[(s_q\cdot r_{pq})^3 +$$

$$+3\,(s_p\cdot r_{pq})^2(s_q\cdot r_{pq}) + 6\,(s_p\cdot r_{pq})(s_q\cdot r_{pq})^2(s_p\cdot s_q)] +$$

$$+3r_{pq}^4[(s_q\cdot r_{pq}) + 2(s_q\cdot r_{pq})(s_p\cdot s_q) + 2(s_q\cdot r_{pq})(s_p\cdot s_q)^2]\},$$

$$M_{pi}^{(3)} : {}^{(3)}T_{pq}^{(3)} : M_{qj}^{(3)} = -\frac{1125}{4}\,\Omega_i\Omega_j r_{pq}^{-13}\{231(s_p\cdot r_{pq})^3(s_q\cdot r_{pq})^3 -$$

$$-63r_{pq}^2\,[(s_p\cdot r_{pq})^2 + (s_q\cdot r_{pq})^2 + 3(s_p\cdot r_{pq})(s_q\cdot r_{pq})(s_p\cdot s_q)](s_p\cdot r_{pq})(s_q\cdot r_{pq}) +$$

$$+21r_{pq}^4\,[(s_p\cdot r_{pq})^2(s_p\cdot s_q) + (s_p\cdot r_{pq})(s_q\cdot r_{pq}) + (s_q\cdot r_{pq})^2(s_p\cdot s_q) +$$

$$+2(s_p\cdot r_{pq})(s_q\cdot r_{pq})(s_p\cdot s_q)^2] - r_{pq}^6[3 + 2(s_p\cdot s_q)^2](s_p\cdot s_q)\},\ldots, \tag{A.5}$$

where s_p is the unit vector along the axis of symmetry of the micro-system p.

The potential energy of induction up to the octopole-octopole ineractions is given by Eq. (3.14) as follows,

$$V_{\text{ind}} = \frac{1}{2}\sum_{ijk}\sum_{p=1}^{N_i}\sum_{q=1}^{N_j}\sum_{r=1}^{N_k}\{M_{pi}^{(0)\,(0)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(0)}M_{qj}^{(0)} - (M_{pi}^{(0)\,(0)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(1)}\cdot M_{qj}^{(1)} -$$

$$-M_{pi}^{(1)}\cdot{}^{(1)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(0)}M_{qj}^{(0)}) - M_{pi}^{(1)}\cdot{}^{(1)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(1)}\cdot M_{qj}^{(1)} +$$

$$+\frac{1}{3}\,(M_{pi}^{(0)\,(0)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} + M_{pi}^{(2)} : {}^{(2)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(0)}M_{qj}^{(0)}) +$$

$$+\frac{1}{3}\,(M_{pi}^{(1)}\cdot{}^{(1)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} - M_{pi}^{(2)} : {}^{(2)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(1)}\cdot M_{qj}^{(1)}) +$$

$$-\frac{1}{15}\,(M_{pi}^{(0)\,(0)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(3)} : M_{qj}^{(3)} - M_{pi}^{(3)} \vdots {}^{(3)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(0)}M_{qj}^{(0)}) +$$

$$+\frac{1}{9}\,M_{pi}^{(2)} : {}^{(2)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} -$$

$$-\frac{1}{15}\,(M_{pi}^{(1)}\cdot{}^{(1)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(3)} : M_{qj}^{(3)} + M_{pi}^{(3)} \vdots {}^{(3)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(1)}\cdot M_{qj}^{(1)}) +$$

$$-\frac{1}{45}\,(M_{pi}^{(2)} : {}^{(2)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(3)} : M_{qj}^{(3)} - M_{pi}^{(3)} \vdots {}^{(3)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)}) +$$

$$-\frac{1}{225}\,M_{pi}^{(3)} \vdots {}^{(3)}T_{pr}^{(1)}\cdot\alpha_{rk}\cdot{}^{(1)}T_{cq}^{(3)} \vdots M_{qj}^{(3)} - \ldots \tag{A.6}$$

Hence we obtain again by averageing over all orientations Eq. (4.4) with

$$Q_{ij}^{(1)}(r_{pq}) = \frac{1}{2}\,\{\alpha_i(M_j^{(0)})^2 + (M_i^{(0)})^2\alpha_j\}\,r_{pq}^{-4} + \{\alpha_i(M_i^{(1)}\cdot M_j^{(1)}) + (M_i^{(1)}\cdot M_i^{(1)})\,\alpha_j\}\,r_{pq}^{-6} +$$

$$+\{\alpha_j(M_i^{(2)} : M_j^{(2)}) + (M_i^{(2)} : M_j^{(2)})\,\alpha_j\}\,r_{pq}^{-8} + \frac{4}{5}\,\{\alpha_i(M_j^{(3)} \vdots M_j^{(3)}) + (M_i^{(3)} \vdots M_i^{(3)})\,\alpha_j\}\,r_{pq}^{-10} + \ldots$$

$$\tag{A.7}$$

In the case of micro-systems possessing the axial symmetry, the successive terms in Eq. (A.6) are, up to the quadrupole-induced dipole-quadrupole term (the anisotropy in the polarizability tensor is neglected), of the form

$$M_{pi}^{(0)(0)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(0)}M_{qj}^{(0)} = e_i e_j \alpha_k r_{pr}^{-3} r_{rq}^{-3} (\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq}),$$

$$M_{pi}^{(0)(0)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(1)} \cdot M_{jq}^{(1)} = -e_i \mu_j \alpha_k r_{pr}^{-3} r_{rq}^{-5} \{3(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq}) - r_{rq}^2 (\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr})\},$$

$$M_{pi}^{(1)} \cdot {}^{(1)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(1)} \cdot M_{qj}^{(1)} = \mu_i \mu_j \alpha_k r_{pr}^{-5} r_{rq}^{-5} \{9(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rp}) -$$

$$-3r_{pr}^2 (\boldsymbol{s}_p \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq}) - 3r_{rq}^2 (\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr}) + r_{pr}^2 r_{rq}^2 (\boldsymbol{s}_p \cdot \boldsymbol{s}_q)\},$$

$$M_{pi}^{(0)(0)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} = \frac{9}{2} e_i \Theta_j \alpha_k r_{pr}^{-3} r_{rq}^{-7} \{5(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})^2 -$$

$$- r_{rq}^2 [(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq}) + 2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})]\},$$

$$M_{pi}^{(1)} \cdot {}^{(1)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} = -\frac{9}{2} \mu_i \Theta_j \alpha_k r_{pr}^{-5} r_{rq}^{-7} \{15(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})^2 -$$

$$-5r_{pr}^2 (\boldsymbol{s}_p \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})^2 - 3r_{rq}^2 [r_{rq}^2 (\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr}) +$$

$$+2(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})] + r_{pr}^2 r_{rq}^2 [(\boldsymbol{s}_p \cdot \boldsymbol{r}_{rq}) + 2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)]\},$$

$$M_{pi}^{(2)} : {}^{(2)}T_{pr}^{(1)} \cdot \alpha_{rk} \cdot {}^{(1)}T_{rq}^{(2)} : M_{qj}^{(2)} = \frac{81}{4} \Theta_i \Theta_j \alpha_k r_{pr}^{-7} r_{rq}^{-7} \{25(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})^2 (\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})^2 -$$

$$- 5r_{pr}^2 [(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq}) + 2(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{rq})](\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})^2 - 5r_{rq}^2 [(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq}) +$$

$$+ 2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})](\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})^2 + r_{pr}^2 r_{rq}^2 [(\boldsymbol{r}_{pr} \cdot \boldsymbol{r}_{rq}) + 2(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_p \cdot \boldsymbol{r}_{rq}) +$$

$$+ 2(\boldsymbol{s}_q \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq}) + 4(\boldsymbol{s}_p \cdot \boldsymbol{r}_{pr})(\boldsymbol{s}_q \cdot \boldsymbol{r}_{rq})(\boldsymbol{s}_p \cdot \boldsymbol{s}_q)]\}. \tag{A.8}$$

By appropriate simplifying assumptions we can obtain immediately from Eqs (A.1), (A.5), (A.6) and (A.8) the result derived previously by Debye [7], Keesom [8], Falkenhagen [9] and others (ref. 2. 3, 11, 12, 15).

The energies of Eqs (A.1) and (A.6) up to the terms corresponding, respectively, to charge-charge, charge-dipole, dipole-dipole, charge-induced dipole and dipole-induced dipole interaction, are discussed in detail by Bellemans and Stecki [25, 26] in their molecular theory of electrostatic interaction between ions in a solvent.

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