THREE-BODY FREE-ENERGY TERMS AND EFFECTIVE POTENTIALS
IN POLAR FLUIDS AND IONIC SOLUTIONS

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Three-body free-energy terms and corresponding "effective" orientation-independent electrostatic potentials for polar fluids and ionic solutions are given.

1. Introduction

The purpose of this note is to give the dominant three-body contribution to the Helmholtz free energy of polar fluids and ionic solutions. As discussed elsewhere [1, 2] [**], these three-body terms have to be taken into account in any adequate treatment of the polar-fluid problem, and they are likely to be equally important in the ionic solution problem as well.

It is often convenient [6–8] [***] to consider the free energy of a system that contains orientation-dependent pair forces in terms of a thermodynamically equivalent system with orientational-independent forces. In the latter system there will be n-body potentials, $n \geqslant 2$, and our results here also give these potentials (to lowest order in the appropriate multipole moments) for $n = 3$ as well as the free energy itself. Because they

are equivalent (rather than actually equal) to the potentials among triplets of particles, we refer to these as *effective* electrostatic 3-body potentials. To the lowest orders considered here, they are just the electrostatic potentials themselves, integrated over orientations.

In the thermodynamic perturbation theory (TPT) developed by Pople [10], Zwanzig [11], and ourselves [1, 8, 9] the potential energy of interaction is written in the form

$$v(x_i, x_j) = v_0(r) + \sum_k \lambda_k w(x_i, x_j) ; \quad \lambda_k \geqslant 0 , \quad (1.1)$$

where following Pople we may expand $\lambda_k w(x_i, x_j)$ in terms of surface harmonics, provided the molecules have axial symmetry. Accordingly

$$\lambda_k w(x_i, x_j) = 4\pi \sum_{l_i} \sum_{l_j} \sum_m X^{l_i l_j m}(r)$$

$$\times S_{l_i m}(\theta_i^{ij}, \phi_i^{ij}) S_{l_j m}(\theta_j^{ji}, \phi_j^{ji}) , \quad (1.2)$$

where λ_k is *determined* by the integers (l_i, l_j), $m \leqslant \min(l_i, l_j)$ the sum over m extends over the integers from $-\min(l_i l_j)$ to $+\min(l_i l_j)$ and the pairs of

angles $(\theta_i^{ij}, \phi_i^{ij})$ and $(\theta_j^{ji}, \phi_j^{ji})$ determine the orientation of the molecular axes at i and j, respectively. For the molecule i the polar axis is assumed to be directed towards j and for molecule j it is directed towards i. The surface harmonics defined below follow the Darwin convention

$$S_{lm}(\theta,\phi) = \left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{1/2} P_l^{|m|}(\cos\theta)\, e^{im\phi},$$

(1.3)

where

$$P_l^{|m|}(x) = \frac{(1-x^2)^{|m|/2}}{2^l l!} \frac{d^{l+|m|}(x^2-1)^l}{dx^{l+|m|}}$$

(1.4)

(with $|m| \leqslant l$) in which we have written $\theta \equiv \theta_i^{ij}$ and $\phi \equiv \phi_i^{ij}$ for convenience. The coefficients $X^{l_i l_j m}(r)$ in (1.2) are related to the electric moments situated at (r_i, r_j) and follow the symmetric relation

$$X^{l_i l_j m}(r) = X^{l_i l_j -m}(r).$$

(1.5)

2. The three-body terms

The lowest order three-body contribution to the free energy in the perturbation theory for polar fluids and ionic solutions has the form [1, 8, 9]†

$$\iint g_{123}^0(r_{12}, r_{13}, r_{23})\, u(r_{12}, r_{23}, r_{13})\, dr_2\, dr_3\,,$$

(2.1)

where $g^0(r_{12}, r_{13}, r_{23})$ is the three-particle distribution function for the reference fluid, and $u(r_{12}, r_{23}, r_{13})$ is the "effective three-body potential" given by

$$u(r_{12}, r_{23}, r_{13}) = \lambda_1 \lambda_2 \lambda_3 \iiint w_{12}(x_1, x_2)$$

$$\times w_{13}(x_1, x_3)\, w_{23}(x_2, x_3)\, d\omega_1 d\omega_2 d\omega_3\,,$$

(2.2)

where $x_i \equiv (r_i, \omega_i)$, and w_{12}, w_{13} and w_{23} are determined by the electric moments of the molecules situated at (r_1, r_2, r_3) in the orientations $(\omega_1, \omega_2, \omega_3)$.

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† To be more precise, in the infinite volume limit, eq. (2.1) gives the free-energy contribution only when the w_{ij} of (2.2) are such that (2.1) remains finite. This will not be the case for the triplet of charges or for the charge–charge–dipole term. In the former case, part of the three-body term contributes to the "ring term" of $O(e^2/kT)^{3/2}$ while the rest is given with the Ursell function h_{123}^0 instead of g_{123}^0 in (2.1), as first discussed by Stell and Lebowitz [12]. A similar result holds in the mixed charge–dipole case.

In terms of Pople's expansion, $u(r_{12}, r_{13}, r_{23})$ may also be written as

$$\sum_m \sum_{m'} \sum_{m''} X^{l_1 l_2 m}(r_{12}) X^{l_1 l_3 m'}(r_{13}) X^{l_2 l_3 m''}(r_{23})$$

$$\times C_{mm'}^{l_1} C_{mm''}^{l_2} C_{m'm''}^{l_3},$$

(2.3)

where

$$C_{mm'}^{l_1} = \int S_{l_1 m}(\theta_1^{12}, \phi_1^{12})\, S_{l_1 m'}(\theta_1^{13}, \phi_1^{13})\, d\omega_1,$$

(2.4)

$$C_{mm''}^{l_2} = \int S_{l_2 m}(\theta_2^{21}, \phi_2^{21})\, S_{l_2 m''}(\theta_2^{23}, \phi_2^{23})\, d\omega_2$$

(2.5)

and

$$C_{m'm''}^{l_3} = \int S_{l_3 m'}(\theta_3^{31}, \phi_3^{31})\, S_{l_3 m''}(\theta_3^{32}, \phi_3^{32})\, d\omega_2.$$

(2.6)

The difficulty with the angular integrations in (2.4) to (2.6) is that in each of them the polar axes are pointing in different directions. However, by a well-known theorem of surface harmonics [13], we have, for example, in the case of (2.4), the relation

$$S_{l_1 m}(\theta_1^{12}, \phi_1^{12}) = \sum_{n=-l_1}^{l_1} D_{n,m}^{l_1}\, S_{l_1 n}(\theta_1^{13}, \phi_1^{13}),$$

(2.7)

where the coefficients $D_{n,m}^{l_1}$ are the coefficients of the rotation matrix which appear in the theory of angular momentum [13]. By using the orthogonality relation

$$\int S_{l_1 n}(\theta_1^{13}, \phi_1^{13}) S_{l_1 m}(\theta_1^{13}, \phi_1^{13})\, d\omega_1 = \delta_{n,-m'},$$

(2.8)

which applies to the product of surface harmonics defined with respect to the same polar axis (13), we have

$$C_{mm'}^{l_1} = \sum_{n=-l_1}^{l_1} D_{n,m}^{l_1}\, \delta_{n,-m'} = D_{-m',m}^{l_1}.$$

(2.9)

Since the elements $D_{n,m}^{l_1}$ are known (subject to minor differences in the conventions used in defining surface harmonics) the $C_{mm'}^{l_1}$, etc., are also known, which allows us to calculate the three-body potential $u(r_{12}, r_{23}, r_{13})$. In the case involving quadrupolar terms, the determination is greatly facilitated by making use of previous work of Bell [14] on three-body dispersion forces, and our problem is reduced to

the special case in which the molecular centers are placed in a straight line in the sequence 1−2−3, when

$$\vec{u}(r_{12}, r_{23}, r_{13}) = \sum_{m=-l}^{l} X^{l_1 l_2 m}(r_{12}) X^{l_1 l_3 m}(r_{13})$$

$$\times X^{l_2 l_3 m}(r_{23})(-1)^{l_2 + |m|}, \qquad (2.10)$$

where $l = \min(l_1, l_2, l_3)$. Using the various $X^{l_i l_j m}(r)$ for interactions between dipoles and/or quadrupoles [10] the following explicit relations for the linear configurations are easily obtained.

(a) For the triple-dipole term $l_1 = l_2 = l_3 = 1$

$$\vec{u}_{TD} = -\tfrac{2}{9}\mu^6\, r_{12}^{-3} r_{23}^{-3} r_{13}^{-3}. \qquad (2.11)$$

(b) For the dipole–dipole–quadrupole term, $l_1 = l_2 = 1$, $l_3 = 2$, when the dipole is placed between a dipole and quadrupole in a straight line,

$$\vec{u}_{DDQ} = -\tfrac{4}{15}\mu^4\theta^2\, r_{12}^{-3} r_{23}^{-4} r_{13}^{-4}. \qquad (2.12)$$

If the quadrupole is placed between the dipoles, the sign in (2.12) is reversed.

(c) For the dipole–quadrupole–quadrupole term, $l_1 = 1$, $l_2 = l_3 = 2$ when the quadrupole is in the center, and

$$\vec{u}_{DQQ} = \tfrac{2}{5}\mu^2\theta^4\, r_{12}^{-4} r_{23}^{-4} r_{13}^{-5}. \qquad (2.13)$$

The sign of $\vec{u}_{DQQ}$ is reversed if the dipole is placed between the two quadrupoles.

(d) For the triple-quadrupole term, $l_1 = l_2 = l_3 = 2$ and

$$\vec{u}_{TQ} = \tfrac{18}{25}\theta^6\, r_{12}^{-5} r_{13}^{-5} r_{23}^{-5}. \qquad (2.14)$$

From Bell's work on the three-body dispersion potentials we know that the three-body electrostatic potential for molecules in any configuration must have the form

$$u(r_{12}, r_{13}, r_{23}) = Z(\mu, \theta)\, W(r_{12}, r_{13}, r_{23}, \alpha_1, \alpha_2, \alpha_3), \qquad (2.15)$$

where $\alpha_1, \alpha_2, \alpha_3$ are the interior angles of a triangle with sides r_{12}, r_{13}, r_{23}. In (2.15) the geometrical factor W is known for TD, DDQ, DQQ and TQ interactions while the interaction constant $Z(\mu, \theta)$ has yet to be determined. According to Bell [14],

$$W_{TD} = [(1 + 3\cos\alpha_1 \cos\alpha_2 \cos\alpha_3)]\, r_{12}^{-3} r_{23}^{-3} r_{13}^{-3}, \qquad (2.16)$$

$$W_{DDQ} = [(9\cos\alpha_3 - 25\cos 3\alpha_3)$$

$$+ 6(3 + 5\cos 2\alpha_3)\cos(\alpha_1 - \alpha_2)]\, r_{12}^{-3} r_{23}^{-4} r_{13}^{-4}, \qquad (2.17)$$

$$W_{DQQ} = [3(\cos\alpha_1 + 5\cos 3\alpha_1)$$

$$+ 20(1 - 3\cos 2\alpha_1)\cos(\alpha_2 - \alpha_3)$$

$$+ 70\cos 2(\alpha_2 - \alpha_3)\cos\alpha_1]\, r_{12}^{-4} r_{23}^{-4} r_{13}^{-5}, \qquad (2.18)$$

$$W_{TQ} = [-27 + 220\cos\alpha_1 \cos\alpha_2 \cos\alpha_3$$

$$+ 490\cos 2\alpha_1 \cos 2\alpha_2 \cos 2\alpha_3$$

$$+ 175\{\cos 2(\alpha_1 - \alpha_2) + \cos 2(\alpha_2 - \alpha_3)$$

$$+ \cos 2(\alpha_3 - \alpha_1)\}]\, r_{12}^{-5} r_{23}^{-5} r_{13}^{-5}, \qquad (2.19)$$

where we have absorbed in the Z's all the numerical factors in Bell's equations for the W's.

Since the linear configuration 1−2−3 corresponds to $\alpha_1 = \alpha_3 = 0$, and $\alpha_2 = 180°$, it can be verified by comparison of (2.15) (containing the appropriate geometrical factors) with (2.11) to (2.14) that

$$Z_{TD} = \tfrac{1}{9}\mu^6, \qquad Z_{DDQ} = \tfrac{1}{240}\mu^4\theta^2,$$

$$Z_{DQQ} = \tfrac{1}{320}\mu^2\theta^4, \qquad Z_{TQ} = \tfrac{3}{3200}\theta^6. \qquad (2.20)$$

Combining (2.20) with the explicit forms for the geometrical factors in (2.16) to (2.19) we arrive at the complete expressions for the various electrostatic three-body potentials. For example the expression for the electrostatic tripole-dipole potential is

$$U_{TD} = \tfrac{1}{9}\mu^6(1 + 3\cos\alpha_1 \cos\alpha_2 \cos\alpha_3)r_{12}^{-3} r_{23}^{-3} r_{13}^{-3}, \qquad (2.21)$$

which agrees with an earlier derivation of this term by Linder [7] who used a reaction field technique. As far as we know, complete expressions for the other electrostatic three-body potentials have not been given before.

For an ionic solution in a solvent consisting of polar molecules (for a review, see ref. [15]) we have computed the various triplet terms involving charge (C), dipole (D) and quadrupole (Q). From elementary considerations the triple-charge term (u_{TC}) is [12]

$$u_{TC} = e_1^2 e_2^2 e_3^2 r_{12}^{-1} r_{13}^{-1} r_{23}^{-1}, \qquad (2.22)$$

where e_i is the charge on the ion at the ith vertex. The others can be derived from (2.3) if we recognize the charge–dipole ($X^{010}(r)$) and charge–quadrupole

$(X^{020}(r))$ interaction coefficients to be $e_1\mu/\sqrt{3}r^2$ and $e_1\theta/\sqrt{5}r^3$, respectively. Then using (2.9) and the relation

$$D^l_{m0}(\alpha) = [4\pi/(2l+1)]^{1/2} S_{l,-m}(\alpha, 0), \qquad (2.23)$$

we find, in obvious notation, that

$$u_{CCD} = \tfrac{1}{3}e_1^2 e_2^2 \mu^2 r_{12}^{-1} r_{13}^{-2} r_{23}^{-2} \cos\alpha_3, \qquad (2.24)$$

$$u_{CDD} = \tfrac{2}{3}e_1^2 \mu^4 r_{12}^{-2} r_{13}^{-2} r_{23}^{-3}$$
$$\times [\cos(\alpha_2 - \alpha_3) + \cos\alpha_2 \cos\alpha_3], \qquad (2.25)$$

$$u_{CCQ} = \tfrac{1}{20}e_1^2 e_2^2 \theta^2 r_{12}^{-1} r_{13}^{-3} r_{23}^{-3} [1 + 3\cos 2\alpha_3], \qquad (2.26)$$

$$u_{CDQ} = \tfrac{1}{20}e_1^2 \mu^2 \theta^2 r_{12}^{-2} r_{13}^{-3} r_{23}^{-4}$$
$$\times [\cos\alpha_2(1 + 3\cos 2\alpha_3) + 2\sin\alpha_2 \sin 2\alpha_3], \qquad (2.27)$$

$$u_{CQQ} = \tfrac{3}{400}e_1^2 \theta^4 r_{12}^{-3} r_{13}^{-3} r_{23}^{-5} [3(1 + \cos 2\alpha_2 \cos 2\alpha_3)$$
$$+ 16\cos 2(\alpha_2 - \alpha_3) + 5(\cos 2\alpha_2 + \cos 2\alpha_3)]. \qquad (2.28)$$

Eqs. (2.24) to (2.28) are consistent with the interaction energies which can be obtained directly from (2.10) for the different possible linear configurations. We have not found these expressions in the literature of ionic solution theory, although their fundamental nature makes it possible that some of them have already been derived in another connection.

The work reported here was motivated by recent progress in the perturbation theory of polar fluids [1, 2, 8, 9]. It has already been demonstrated that the electrostatic triple-dipole term makes a significant contribution to the free energy of a dipolar system [1, 2] and that for some molecules similar contributions involving quadrupolar interactions are likely [1]. We further anticipate that effective many-body interactions among ions, dipoles, and higher multipoles will make non-negligible contributions to the free energy of ionic solutions.

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