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The Onsager Approximation and Nonspecific Intermolecular Interactions in Polar Media

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Onsager's model for isotropic dielectric liquids greatly overestimates the molecular orientation correlations and the dipole–dipole interaction energy and cannot be used to estimate the solvation energy.

It has been shown by Solomonov *et al.*[1] that the solvation energy of polar molecules is practically independent of the molecular dipole moment and depends only on molecular refraction or essentially on molecular volume (in other words, solvation energy is defined primarily by dispersive interactions). This fact conflicts with the results obtained when Onsager's model[2] is applied for the theoretical estimation of the increment in solvation energy caused by dipole–dipole interaction. It should be noted that this model is widely used for such estimations. It is of interest to elucidate the reasons for such a conflict and to define the limits of the application of this 'popular' approximation.

In Onsager's model[2] a molecule is considered as a point dipole in the centre of a spherical cavity immersed in a homogeneous dielectric continuum. The dipole polarizes its environment through its electric field and generates a reaction field acting on the molecule, thus long range interactions are taken into account. In accordance with this, a molecular dipole moment μ, and static and optical molecular polarizabilities a and b in a dense fluid are defined as in eqns. (1), (2) and (3),

$$\mu = \mu^0 + a^0\boldsymbol{R} = \mu^0 \Bigg/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right] \qquad (1)$$

$$a = a^0 \Big/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right] \qquad (2)$$

$$b = b^0 \Big/ \left[1 - \frac{2(n^2 - 1)b^0}{(2n^2 + 1)r^3}\right], \qquad (3)$$

where μ^0, a^0, b^0, $\boldsymbol{R}$, ϵ, n and r are the vacuum dipole moment, average molecular static and optical polarizabilities, reaction field, the dielectric permittivity and refractive index of a medium and the cavity radius, respectively. Application of this model to a calculation of long range dipole–dipole interaction energy F_{dd} as component of the solvation energy of a polar molecule in a medium leads to eqn. (4).[3]

$$F_{dd} = -1/2\mu\boldsymbol{R} = -\frac{(\epsilon - 1)\mu^2}{(2\epsilon + 1)r^3} \qquad (4)$$

The cavity radius can be determined either by the simple

$$(4\pi r^3)/3 = M/(\rho N_A), \qquad (5)$$

Onsager relation [eqn. (5)], where M, ρ and N_A are the molecular weight, the density and Avogadro's number, respectively, or by other methods.[4]

In order to solve the above-mentioned problem and to evaluate which kinds of multiparticle dense systems obey the simple Onsager model we have used the Kirkwood–Fröhlich approach,[5] which considers a large number N of polar molecules in a macroscopic spherical cavity of radius l immersed in a homogeneous dielectric continuum, with dipole–dipole interactions being neglected inside the cavity. The dense fluid dipole moment $\mu^{(p)}$ of the p-th molecule of this spherical totality is

$$\mu_\sigma^{(p)} = \mu_\sigma^{0(p)} + a_{\sigma\tau}^{0(p)}[\boldsymbol{R}_\tau + \boldsymbol{F}_\tau^{(p)}] \qquad (6)$$

given by eqn. (6), where $\boldsymbol{R}$ is the reaction field of the total spontaneous moment $\boldsymbol{M}$

$$(\boldsymbol{M} = \sum_{q=1}^{N} \mu^{(q)}),$$

which is changing continuously due to thermal motion.

$$\boldsymbol{R} = [2(\epsilon - 1)\boldsymbol{M}]/[(2\epsilon + 1)l^3 = f\boldsymbol{M} \qquad (7)$$

$\boldsymbol{F}^{(p)}$ is the field of all molecules of the spherical totality, except molecule p, at the point of localization of molecule p. In further examinations we neglected $\boldsymbol{F}^{(p)}$ in accordance with the spirit of the Onsager approximation. Eqn. (7), for an extended moment $\boldsymbol{M}$ placed at any point inside the spherical cavity, is also true for point moment μ placed in the centre of a cavity.[6] Solution of eqn. (6) by a simple iteration method leads to eqn. (8).

$$\mu_\sigma^{(p)} = \mu_\sigma^{0(p)} + f\sum_{q=1}^{N} a_{\sigma\tau}^{0(p)}\mu_\tau^{0(q)} + f^2\sum_{q=1}^{N}\sum_{l=1}^{N} a_{\sigma\tau}^{0(p)}a_{\tau\gamma}^{0(q)}\mu_\gamma^{0(l)} + \ldots \qquad (8)$$

Using eqn. (8), it is easy to calculate the average quantity $\langle \boldsymbol{M}^2\rangle$. When the number N is large, the quantity $\langle \boldsymbol{M}^2\rangle$ is

$$\langle \boldsymbol{M}^2\rangle = N\langle \mu\mu\boldsymbol{M}\rangle \qquad (9)$$

determined from eqn. (9),[5] and an average must be obtained over all the molecules inside the spherical totality. By substituting eqn. (8) into eqn. (9), considering for simplicity that $a_{\sigma\tau}^0 = a^0\delta_{\sigma\tau}$, one can obtain eqn. (10),

$$\langle \mu\boldsymbol{M}\rangle = (\mu^0)^2 g[1 + 2fa^0N + 3f^2(a^0)^2N^2 + \ldots] \qquad (10)$$

where $g = 1 + (N - 1)\langle\cos\gamma\rangle$ (the Kirkwood factor[5]) and $\langle\cos\gamma\rangle$ is the average cosine of the angle γ between every pair of molecular dipole moments inside the spherical cavity. The sum is determined by eqn. (11), taking into account that $fa^0N < 1$ and $Nr^3 = l^3$, where r is determined by eqn. (5).

$$\langle \mu\boldsymbol{M}\rangle = (\mu^0)^2 g \Big/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right]^2 \qquad (11)$$

In eqn. (11) the g factor is multiplied by the square of the right-hand part of eqn. (1) and the left-hand part is effectively the average square of the dense fluid dipole moment $\langle\mu^2\rangle$ when correlations are neglected. By means of the same approximation one can calculate the average quantity $\langle\mu\rangle$ from eqn. (8).

$$\langle\mu_\sigma\rangle = \mu_\sigma^0\left\{1 + \left[\frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)l^3}\right]\Big/\left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)l^3}\right]\right\} \qquad (12)$$

The average $\langle\mu\rangle$ is equal to μ^0 because $a^0 \ll l^3$. If all the molecules inside the macroscopic cavity are aligned parallel, eqn. (8) is transformed into eqn. (13).

$$\mu_\sigma = \mu_\sigma^0 \Big/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right] \qquad (13)$$

Eqn. (13) is equivalent to eqn. (1), *i.e.* eqn. (1) for a dense fluid dipole moment μ (but not for μ^2) is valid for a model liquid, which closely approximates to a solid. However, the components of the dielectric permittivity theory expressions are actually $\langle\mu^2\rangle$ and $\langle\mu\boldsymbol{M}\rangle$ quantities; thus, the molecular orientations are not overestimated, as shown by eqn. (11).

An analogous examination of the static polarizability leads to eqn. (14) when correlations are neglected and to eqn. (15) when all molecules are aligned parallel.

$$\langle a_\sigma\rangle = a_\sigma^0 \Big/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right] \qquad (14)$$

$$\langle a_\sigma\rangle = a_\sigma^0 \Big/ \left[1 - \frac{2(\epsilon - 1)a_\sigma^0}{(2\epsilon + 1)r^3}\right] \qquad (15)$$

Eqns. (14) and (15) are equivalent to eqn. (2) if the molecular polarizability is isotropic. In contrast to the average $\langle\mu\rangle$, the average $\langle a_\sigma\rangle$ from eqn. (14) is quite close to that from eqn. (2). This is because induced dipole moments are approximately parallel, while permanent dipole moments are chaotically orientated. The results for optical polarizability are similar if one substitutes ϵ for n^2 and $a_{\sigma\tau}^0$ for $b_{\sigma\tau}^0$.

Let us calculate the spherical totality free energy to be connected with the spontaneous polarization. This quantity F will be equal to the sum of the spherical totality vacuum polarizability free energy, F_s, and the reaction field interaction free energy of this spontaneously polarized totality with the continuum medium, F_e [eqns. (16)].[5]

$$F_s = [2\pi(\epsilon + 2)\boldsymbol{M}^2/[3V(\epsilon - 1)];$$

$$F_e = -[4\pi(\epsilon - 1)\boldsymbol{M}^2/[3V(2\epsilon + 1)]$$

$$(V = 4\pi l^3/3) \qquad (16)$$

By considering eqn. (17) from the theory of dielectric permittivity, where k and T are Boltzmann's constant and absolute

$$[(\epsilon - 1)(2\epsilon + 1)]/3\epsilon = [4\pi\langle\boldsymbol{M}^2\rangle]/[3V3kT] \qquad (17)$$

temperature, respectively, eqn. (18) follows from eqn. (16).

$$\langle F\rangle = \langle F_s\rangle + \langle F_e\rangle = 3kT/2 \qquad (18)$$

Hence, the average free energy of spontaneous polarization of a macroscopic spherical totality is very small. The quantities $\langle F_s\rangle$ and $\langle F_e\rangle$ are also small. Eqn. (19) follows from eqns. (9), (11) and (16).

$$\langle F_e\rangle = -\left[\frac{(\epsilon - 1)}{(2\epsilon + 1)}\right](\mu^0)^2 g \Big/ \left[1 - \frac{2(\epsilon - 1)a^0}{(2\epsilon + 1)r^3}\right]^2 \qquad (19)$$

The difference between eqns. (19) and (4) is dramatic. The right-hand parts of these equations are equal if $g = 1$ (*i.e.*, the molecules are not correlated), except that eqn. (4) is for a single molecule while eqn. (19) is for a macroscopic totality. The same result can be obtained if one considers the interaction between a single molecule and the spherical totality reaction field. In connection with this conclusion it is not difficult to understand why solvation energy does not in fact depend on the molecular dipole moment, but depends solely on molecular refractivity,

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i.e., on molecular volume.[1] Eqn. (4) can be obtained when $\langle \cos\gamma \rangle = 1$, *i.e.*, when the medium is a solid rather than a liquid.

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