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Abstract

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ON THE OSMOTIC THEORY OF SOLUTIONS

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As is known, the introduction of osmotic conditions makes it possible to present the theory of solutions in a form in which only the dissolved substances explicitly appear (^{1,2}). This, in turn, makes it possible to use convenient methods from the theory of the gaseous state (virial expansions, integral equations for distribution functions). In particular, if the osmotic pressure is found as a function of the temperature and of the chemical potentials of the solvent and of the dissolved substances, then the entire thermodynamics of the solution is thereby found as well. To carry out this program, however, it is necessary to know the activity coefficients $\gamma_\sigma = z_\sigma/\rho_\sigma$ and the potentials of mean force $W(\{n_\sigma\})$ for molecules of the dissolved substances at infinite dilution, i.e., for $z_\sigma \to 0$ and $z_\tau = \text{const}$ (z is the activity; ρ is the number of molecules per unit volume; the index τ refers to the solvent, the index σ characterizes the species of dissolved molecules; $\{n_\sigma\}$ denotes the configuration of the complex under consideration of molecules of the dissolved substances). The purpose of the present note is to show how γ_σ and $W(\{n_\sigma\})$ can be calculated if the distribution functions in the pure solvent are known. For simplicity of exposition, we shall assume all molecules to be monatomic.

Let us begin with γ_σ. Taking into account the known expression for ρ_σ, it is easy to show that

$$\gamma_\sigma^{-1} = \frac{\sum\limits_{N_\tau=0}^{\infty} \frac{z_\tau^{N_\tau}}{N_\tau!} \int \exp\left[-\beta V(\{N_\tau + 1_\sigma\})\right] d\{N_\tau\}}{\sum\limits_{N_\tau=0}^{\infty} \frac{z_\tau^{N_\tau}}{N_\tau!} \int \exp\left[-\beta V(\{N_\tau\})\right] d\{N_\tau\}}, \tag{1}$$

where $\{N_\tau\}$ denotes the configuration of a complex of N_τ solvent molecules; $\{N_\tau + 1_\sigma\}$ is the configuration of a complex of N_τ solvent molecules and one molecule of the dissolved substance of species σ; $V(\{N_\tau\})$ and $V(\{N_\tau + 1_\sigma\})$ are the potential energies of intermolecular interaction, respectively, in the first and second of these complexes; $\beta = (kT)^{-1}$, T is the absolute temperature, and k is Boltzmann’ s constant.

It is evident that the denominator on the right-hand side of (1) is the large statistical sum Ξ_0 for the pure solvent. It is further clear that*

$$V(\{N_\tau + 1_\sigma\}) = V(\{N_\tau\}) + \sum_{i_\tau=1}^{N_\tau} v_\sigma((1_\sigma), (i_\tau)),$$

where (1_σ) denotes the point at which the molecule of the dissolved substance is located in the configuration $\{N_\tau + 1_\sigma\}$; (i_τ) is the point at which the i-th solvent molecule is located in the configuration $\{N_\tau\}$; v_σ is the interaction energy of a molecule of the dissolved substance of species σ and a solvent molecule.

The numerator on the right-hand side of (1) therefore represents the large statistical sum Ξ for the pure solvent, which is in the potential field created by a molecule of the dissolved substance of species σ, fixed at the point (1_σ). Taking the logarithm of (1), we shall therefore have

$$-\ln \gamma_\sigma = \ln \Xi - \ln \Xi_0.$$

* The forces of interaction of the molecules are assumed to be pairwise.

But, as was shown in [3],

$$\ln \Xi - \ln \Xi_0 = \sum_{N_\tau=1}^{\infty} \frac{1}{N_\tau!} \int g^{(N_\tau)}(\{N_\tau\}) \times$$
$$\times \left[\prod_{i_\tau=1}^{N_\tau} [\exp[-\beta u((i_\tau))] - 1] \right] d\{N_\tau\}, \tag{2}$$

where $u((i_\tau))$ is the potential of the external field in which the solvent molecules are located, i.e., in the present case $u((i_\tau)) = v_\sigma((1_\sigma), (i_\tau))$, and $g^{(N_\tau)}(\{N_\tau\})$ are the Mayer-Ursell distribution functions for the pure solvent in the absence of an external field, related to the usual distribution functions by elementary relations*. The integration in relation (2) is in fact carried out only over a small three-dimensional neighborhood of the point (1_σ), where $v_\sigma((1_\sigma), (i_\tau)) \neq 0$. We thus see that the activity coefficient γ_σ can indeed be found if the distribution functions in the pure solvent are known.

Let us now turn to the potential of mean force $W(\{n_\sigma\})$. Starting from the relation

$$\exp[-\beta W(\{n_\sigma\})] = \lim_{z_\sigma \to 0} \rho(\{n_\sigma\}) / \prod_\sigma \rho_\sigma^{n_\sigma}, \tag{3}$$

where $\rho(\{n_\sigma\})$ is the distribution function for a complex of solute molecules with configuration $\{n_\sigma\}$, and taking into account the known expression for $\rho(\{n_\sigma\})$, it is easy to show that $W(\{n_\sigma\})$ can be represented in the form

$$W(\{n_\sigma\}) = V(\{n_\sigma\}) - kT\sum_\sigma n_\sigma \ln\gamma_\sigma - kT(\ln\Xi - \ln\Xi_0). \tag{4}$$

Here $V(\{n_\sigma\})$ is the potential energy of intermolecular interaction in the complex of solute molecules under consideration; Ξ_0 and Ξ are the grand statistical sums for the pure solvent, respectively in the absence and in the presence of an external field

$$u((i_\tau)) = \sum_\sigma \sum_{j_\sigma=1}^{n_\sigma} v_\sigma((j_\sigma),(i_\tau)). \tag{5}$$

Using relation (2) with the potential $u((i_\tau))$ defined by equality (5)**, one can therefore find $W(\{n_\sigma\})$, if the distribution functions in the pure solvent are known.

In practical calculations, it is, of course, sufficient to restrict oneself to taking into account only the first few terms of expansion (2), which give the main contribution. If, in addition, the validity of the superposition approximation is assumed, then it is enough to find the potentials of mean force $W(\{n_\sigma\})$ only for complexes of two solute molecules.

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* Thus, for example, $g^{(1)} = \rho_\tau$ and $g^{(2)} = \rho_\tau^2 G_\tau(r)$, where ρ_τ is the density of solvent molecules, and $G_\tau(r)$ is the correlation function for two solvent molecules (r is the distance between these molecules).

** The integration in relation (2) will then in fact be carried out only over a small three-dimensional neighborhood containing the configuration $\{n_\sigma\}$ within itself, in which the potential $u(i_\tau)$ is different from zero.

Note: Figure translations are in progress. See original paper for figures.

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