



Toward a simple molecular theory of hydrophobic hydration



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ABSTRACT

A perturbation theory of water is extended to mixtures, and its application to aqueous solutions of noble gases is presented. The present approach is based on the thermodynamic perturbation theory of the primitive models of associating fluids, substituting the reference pseudo-hard-body term by a hard-sphere/pseudo-hard-body mixture term and introducing appropriate corrections. The primitive models are constructed in a rigorous way from realistic parents. The procedure yields equations of state allowing for the determination of all residual properties. The residual chemical potential is expressed and subsequently the Henry's law constants of noble gases, from He to Xe, are evaluated as functions of temperature showing qualitative agreement with experimental data. Throughout the procedure, no experimental data are used to adjust the parameters or to fine-tune the results.

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1. Introduction

Water exhibits anomalous behavior as both a pure liquid and a solvent. Nonpolar solutes show extremely low solubility in water, moreover, nonpolar particles tend to minimize the interface with the aqueous phase regardless of scale. The phenomenon is known as the hydrophobic effect [1] and has been studied on a whole range of industrially or biologically important solutes, yet it is not properly understood by molecular thermodynamics.

The hydrophobic hydration is characterized by certain thermodynamic features, e. g., a pronounced temperature maximum of the Henry's law constant (or minimum of solubility) [2] or the temperature of convergence of hydration entropies for different solute sizes [3]. These features should be reproduced by any approach aiming at being sufficiently predictive for the mixtures of nonpolar substances with water. However, this is usually not the case of the empirical and semi-empirical expressions commonly used in chemical engineering practice [4]; as an exception one can mention a semi-empirical soft-SAFT equation of state, which reproduces solubility minima of n-alkanes in water [5].

In order to obtain more sophisticated and thermodynamically consistent expressions, one should consider a molecular theory based on a suitable model for molecular interactions. The model has to be simple enough to be amenable to a mathematical treatment and yet complex enough to preserve the traits necessary for a qualitatively

correct description. A number of simple molecular models have been proposed, based on different opinions on what is essential for the water-like behavior, each model qualitatively reproducing some of the desired features of pure water and aqueous solutions [6].

Several theoretical, molecular-based approaches to thermodynamic modeling of hydrophobic effect are available in the literature. For instance, Graziano used the scaled particle theory for hard spheres to reproduce hydration properties of noble gases and selected hydrocarbons at 298.15 K [7] and to obtain hydration entropy convergence [3]. Ashbaugh et al. proposed [8] a simple analytical theory of hydrophobic hydration using an expression for partition function incorporating hydrogen bonding; both the solubility minimum and the entropy convergence were obtained. Other approaches have been published based on the lattice theory [9], integral equations [10,11], or the informational theory [12–14].

In the present contribution, a model of associating fluid based on simplistic, 'primitive' models [15,16] and their reference system, pseudo-hard bodies [17], is introduced and its application to aqueous solutions implemented. The model has already been used by the group of the present authors to reproduce, qualitatively, anomalies of pure liquid water [18–21,6] and some properties of aqueous mixtures [22,6]. An attempt is made to move further along this path toward a concise molecular-level understanding of hydrophobic phenomena and aqueous solutions in general. It is worth noting that primitive models have already been employed to study hydrophobic hydration by Nezbeda [23], who reproduced temperature dependence of the Henry's law constant of methane and obtained the entropy convergence using a scaled-particle-like expression for chemical potential of the solute.

In order to obtain equations of state, the thermodynamic perturbation theory is employed with pseudo-hard bodies taken as a reference

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system. The construction of the pseudo-hard body consists in the assumption that not only the attractive but also the repulsive forces are needed to appropriately describe the structural effects of hydrogen bonding [6]. Simulation data on mixtures of hard spheres and pseudo-hard water are parametrized into a reference pressure function, which is then combined with attractive terms to form a molecular-based equation of state for the solution. The equation of state allows for a consistent calculation of all thermodynamic properties of the mixture.

The article is organized as follows. In the next section the theory and its extension to mixtures is introduced. In the third section, **Results and Discussion**, the parameters of the method are determined, the Henry's law constant maximum and the entropy convergence of spherical solutes are shown, and results for noble gases are presented. In **Conclusions**, a brief summary of the contribution is given and future development of the approach is outlined. Further details are provided in **Appendices A–C**.

2. Theory

Within the perturbation theory of fluids [24], the intermolecular potential, u , is split into reference (ref) and perturbation (pert) parts,

$$u(\mathbf{1}, \mathbf{2}) = u^{\text{ref}}(\mathbf{1}, \mathbf{2}) + u^{\text{pert}}(\mathbf{1}, \mathbf{2}), \quad (1)$$

where $\mathbf{1}$ and $\mathbf{2}$ denote the generalized coordinates of interacting molecules. The division (1) leads to analogous division of the Helmholtz energy,

$$A = A^{\text{ref}} + A^{\text{pert}},$$

and therefore of its derivatives, such as the internal energy, U , or compressibility factor, Z . The reference part should reproduce the molecular structure of the full-potential fluid in order to guarantee the convergence of the perturbation expansion. The reference model itself usually yields a dominant contribution to thermodynamic functions as well and can serve as a zeroth order model for the phase behavior of the system at hand.

Suitable reference models for realistic soft potentials are their short-ranged (SR) variants, which are then approximated by simple stepwise potentials to allow for an analytical treatment:

$$u(\mathbf{1}, \mathbf{2}) = u_{\text{SR}}(\mathbf{1}, \mathbf{2}) + u^{\text{pert}}(\mathbf{1}, \mathbf{2}) \approx u_{\text{simple}}(\mathbf{1}, \mathbf{2}) + u^{\text{pert}}(\mathbf{1}, \mathbf{2}).$$

Classical example is eliminating the medium- and long-range attractive component of the Lennard-Jones potential, leaving a soft repulsive short-range reference, which is then substituted by the hard-sphere model, properties of which are known [25]. In the case of associating fluids it has been found that both repulsive and attractive forces are indispensable for reproducing the correct fluid structure [6], so the soft short-range reference and the derived step-wise model, the primitive model (PM), maintains both the repulsive and the attractive components.

The primitive models consist only of hard-sphere and square-well interactions and are derived from their realistic counterparts interacting via soft potentials, such as TIP4P [26] or SPC/E [27]. For detailed procedure of construction of primitive models, the reader may consult, e. g., the work of Nezbeda and Vlček [15]. In the case of water, resulting models possess the following form of the intermolecular potential:

$$u_{\text{PM}}(\mathbf{1}, \mathbf{2}) = u_{\text{HS}}(r_{\text{OO}}; d_{\text{OO}}) + \sum_{\substack{ij \in \{\text{XX}\} \\ ij \in \{\text{YY}\}}} u_{\text{HS}}(r_{ij}; d_{ij}) + \sum_{ij \in \{\text{XY}\}} u_{\text{SW}}(r_{ij}; \lambda), \quad (2)$$

where d_{OO} is the diameter of an oxygen-centered hard sphere representing the “neutral” component of repulsive forces, r_{ij} is the distance between site i on molecule 1 and site j on molecule 2, and

X and Y symbolize “positive” and “negative” Coulombic-like sites, respectively. The summation in the second term on the right-hand side of Eq. (2) runs over the pairs of like sites, that in the third term over the pairs of unlike sites. Further, the hard-sphere potential, u_{HS} , and square-well potential, u_{SW} , are defined as

$$u_{\text{HS}}(r; d) = \begin{cases} +\infty & \text{for } r < d \\ 0 & \text{for } r \geq d \end{cases}$$

and

$$u_{\text{SW}}(r; \lambda) = \begin{cases} -\varepsilon_{\text{HB}} & \text{for } r < \lambda \\ 0 & \text{for } r \geq \lambda, \end{cases}$$

respectively. The first two repulsive terms on the right-hand side of Eq. (2) together define a pseudo-hard body (PHB) [17].

Diameters, d_{ij} , are determined as follows. First, the effective pair potential, u_{ij}^{eff} , is found, which is defined by

$$e^{-\beta u_{ij}^{\text{eff}}(r_{ij})} = \left\langle e^{-\beta u_{\text{SR}}(\mathbf{1}, \mathbf{2})} \right\rangle_{r_{ij}=\text{const.}}$$

In the above the angular brackets, $\langle \cdot \rangle$, denote an unweighted angular average, and $\beta = 1/(k_{\text{B}}T)$, where k_{B} is the Boltzmann constant, and T is the absolute temperature. For an appropriate definition of u_{SR} see Appendix A. Let r_{ij}^{min} be the distance at which the effective potential attains a minimum value. The repulsive branch of the effective potential is defined as

$$u_{ij}^{\text{rep}}(r_{ij}) = \begin{cases} u_{ij}^{\text{eff}}(r_{ij}) - u_{ij}^{\text{eff}}(r_{ij}^{\text{min}}) & \text{for } r_{ij} < r_{ij}^{\text{min}} \\ 0 & \text{for } r_{ij} \geq r_{ij}^{\text{min}} \end{cases}$$

and used to determine a temperature-dependent effective diameter

$$d_{ij}(T) = \int_0^{r_{ij}^{\text{min}}} [1 - e^{-\beta u_{ij}^{\text{rep}}(r_{ij})}] dr_{ij}. \quad (3)$$

The range of the square-well interaction, λ , is usually set to a maximum value allowed by the condition of steric incompatibility, i. e., that a hydrogen site cannot form more than one bond with negative sites on other molecules [15,16].

Theoretical description of the primitive models was made possible by thermodynamic perturbation theory of Wertheim [28–31] used here in the second-order variant (TPT2). In terms of TPT2, the residual¹ Helmholtz energy per particle, $a^{\text{res}} = A^{\text{res}}/N$, of primitive water can be expressed as a function of the reduced density, $\rho^* = \rho d_{\text{OO}}^3$, and the reduced inverse temperature, $\beta^* = \beta \varepsilon_{\text{HB}}$, as

$$a_{\text{PM}}^{\text{res}}(\rho^*, \beta^*) = a_{\text{PHB}}^{\text{res}}(\rho^*) + a_{\text{assoc}}(\rho^*, \beta^*), \quad (4)$$

where $a_{\text{PHB}}^{\text{res}}$ is the value for the underlying pseudo-hard-body reference, and the perturbation term,

$$a_{\text{assoc}} = \frac{1}{\beta} [m(1-\nu) + \ln x_0],$$

arises due to the attractive square-well interaction – association. The compressibility factor of a PM is thus given by

$$Z_{\text{PM}} = Z_{\text{PHB}} + \rho^* \left(\frac{\partial}{\partial \rho^*} [m(1-\nu) + \ln x_0] \right)_{\beta^*},$$

¹ The term ‘residual’ is used herein for the excess value over the ideal gas with the same number of particles, volume and temperature.

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