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On the theoretical description of the liquid-vapor coexistence of water-like models with square-well attraction and site-site chemical association

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ABSTRACT

A liquid-vapor coexistence envelope for water-like models with square-well attraction between particles and with four attractive associating sites per particle has been investigated. The mean-field theory and the first-order mean spherical approximation for attractive interactions together with the first-order thermodynamic perturbation theory of Wertheim for association have been applied to construct the temperature - density and the temperature - chemical potential projections of the equation of state. In addition, the dependence of the fraction of non-bonded particles on the parameters of the models has been evaluated and analyzed. We explored a set of models with different square-well width and energy of associative interaction. In some cases a comparison with computer simulation data has been performed. For two specific parameter sets previously proposed to mimic water properties a comparison with experimental data for the vapor-liquid coexistence envelope and for vapor pressure has been performed. It is shown that the applied theoretical procedures are successful and can be used with confidence. On the other hand, they provide solid basis to apply in the theory of inhomogeneous associating fluids.

1. Introduction

Modelling of liquid water, aqueous mixtures and solutions, focused in adequate theoretical description of their thermodynamic, dynamic and dielectric properties still represents a challenging task [1–4]. A set of quite simple models that capture principal effects of excluded volume of molecules, of attraction and of intermolecular association has been proposed and applied with success to reproduce experimental observations concerning solely thermodynamic properties of this kind of systems. Widespread applications in the field of chemical engineering witness success of this area of academic research. To deal with the repulsive interactions, as well as with smoothly varying intermolecular attraction, all the machinery of the theory of simple liquids has been involved. Namely, the perturbation approaches by Weeks, Chandler and Andersen [5,6] as well as by Barker and Henderson [7,8] have been used. Usually, the attractive interactions have been taken into account in the framework of the mean field approximation, less frequently a more sophisticated, but also more computationally demanding procedures have been applied. On the other hand, description of variety of the association effects is exclusively based on the theory pioneered by Wertheim [9–12]. Chemical association between molecules results from a short-range strong attraction between sites assumed to be located on the molecule surface or in its interior in a specific arrangement. This theory permitted extensions for short-chain molecules, polymers and branched structures by using limit of complete association and yielded important applications for chemical engineering of complex fluids, see e.g. Refs. [13–16].

In the case of simple, non-associating fluids the first-order mean spherical approximation (FMSA) developed by Tang et al. [17–19] has been proved to be quite accurate for the description of structure, thermodynamics and phase behavior of square-well, Yukawa and of Lennard-Jones fluids. The method of the solution of the

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FMSA equation follows the same path as the solution of the full mean spherical approximation [20,21], but only the zero- and the first order terms in expansions of correlation functions in powers of inverse temperature are taken into account. Note that in the case of Lennard-Jones, as well as of Sutherland potential [22], the calculations are carried out by representing these potentials as a combination of Yukawa potentials. The analytic solutions of the FMSA equations for square-well systems have been presented by Tang and by Hlushak et al. [23–26].

The FMSA solution is explicit, simpler, and always secure if compared with the full MSA (mean spherical approximation) solution. A big advantage of the FMSA is its stable performance over the two-phase region, where the full MSA may go astray and breakdown. The above advantages determine that FMSA is more attractive in applications requiring the correlation functions. At present, the applications of FMSA prevail for Lennard-Jones fluid and chain molecules [27]. In addition to homogeneous fluids, FMSA has shown advantages for inhomogeneous applications, where explicit analytic direct correlation function is crucial for the success of density functional theory [28,29]. However, no extensive FMSA-based studies of neither uniform nor non-uniform system involving water molecules have been performed so far up to our best knowledge. This gap has stimulated our present study.

From the general theoretical thermodynamic perspective, the water molecules are conveniently modeled as hard-spheres (HS) interacting via an attractive square well (SW) pair potential with four associating sites [30–35]. The association between molecules is commonly described using the first order thermodynamic perturbation theory for association by Wertheim. The principal objective of the present work is to explore the vapor-liquid (VL) coexistence of associating model fluids with four sites per particle in very detail. To do that, we first apply theoretical approaches to the models with square well attraction in the absence of association. Next, the role of association is elucidated. Finally, we study two models that have been proposed previously and fitted to reproduce principal features of vapor - liquid coexistence of water [36]. Methodologically, we involve the mean field (MF) theory, the so-called SAFT-VR approach [37] and the first-order mean spherical approximation (FMSA) [18,29], to fill aspects of the problem that have been left unexplored so far.

The present report is organized into five sections as follows. In Sec.2, the pair potential model used to describe the intermolecular and association interactions is presented. In Sec.3, we briefly described the FMSA and SAFT-VR approaches for SW associating fluids. Phase coexistence, vapor pressure and chemical potential for these associating fluids are reported in Sec.4. Finally, in Sec.5, some conclusions are given.

2. Model

In the present work we consider one-component system of associating molecules. Each molecule has four associating sites, designated by A, B, C, and D placed at vertices of a tetrahedron inscribed into a spherical core [38]. The pair intermolecular potential between molecules i and j is assumed to consist of two terms. Namely,

$$u(r_{ij}) = u_{\text{non}}(r_{ij}) + \sum_{\alpha,\beta} u_{i\alpha,j\beta}\left(\mathbf{r}_{i\alpha,j\beta}\right), \tag{1}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the center-to-center vector between the molecules i and j, $r_{ij} = |\mathbf{r}_{ij}|$, α and β represent the sites on two interacting molecules. The second term is the contribution coming from the interaction between attractive sites belonging to the molecules i and j. The non-associative part of the pair potential, $u_{\text{non}}(r_{ij})$, is given as,

$$u_{\text{non}}(r_{ij}) = u_{\text{HS}}(r_{ij}) + u_{\text{att}}(r_{ij}), \tag{2}$$

where $u_{\text{HS}}(r)$ and $u_{\text{att}}(r)$ are the hard-sphere (HS) and attractive pair potential interaction, respectively. The HS pair potential is

$$u_{\text{HS}}(r_{ij}) = \begin{cases} \infty, \text{if } \; r_{ij} < \sigma \\ 0, \text{if } \; r_{ij} \geq \sigma \end{cases}, \tag{3}$$

where σ is the HS diameter. The attractive interaction is described by the SW pair potential,

$$u_{\text{att}}(r_{ij}) = \begin{cases} 0, \text{if } \; r_{ij} < \sigma \\ -\varepsilon, \text{if } \; \sigma \leq r_{ij} < \lambda\sigma \\ 0, \text{if } \; r_{ij} \geq \lambda\sigma \end{cases}, \tag{4}$$

where ε and λ are the depth and range of the potential, respectively.

The site-site interaction depends on $\mathbf{r}_{i\alpha,j\beta} = \mathbf{r}_{ij} + \mathbf{d}_\alpha(\omega_i) - \mathbf{d}_\beta(\omega_j)$, where $\mathbf{d}_\alpha$ and $\mathbf{d}_\beta$ denote the vectors from the center of the molecule i with orientation ω_i and from the center of j with orientation ω_j to the sites α and β, respectively.

Only AC, BC, AD, and BD site-site interaction are allowed in the model in question, similar to previous studies. Moreover, all the bonding energies are assumed to be identical. The association energy between the sites is described by a SW site-site interaction potential

$$u_{i\alpha,j\beta}\left(r_{i\alpha,j\beta}\right) = \begin{cases} -\varepsilon_{\text{ass}}, \text{if } \; 0 < r_{i\alpha,j\beta} \leq r_c, \\ 0, \text{if } \; r_{i\alpha,j\beta} > r_c, \end{cases} \tag{5}$$

where $r_{i\alpha,j\beta} = \left|\mathbf{r}_{i\alpha,j\beta}\right|$ and ε_{ass} is the depth of the association energy well, r_c is the cutoff range of the associative interaction.

3. Theory

3.1. Application of the first-order mean spherical approximation to associating fluids

The Helmholtz free energy per unit volume (the free energy density), f, can be expressed as the sum of an ideal contribution, f_{id}, and the excess contribution, f_{ex}, due to intermolecular interactions,

$$f = f_{\text{id}} + f_{\text{ex}}, \tag{6}$$

The ideal contribution is $f_{\text{id}} = kT\rho[\ln(\rho\Lambda^3) - 1]$, Λ is the de Broglie thermal wavelength, T is the temperature, k is the Boltzmann constant, and ρ is the fluid number density. According to perturbation treatment, the excess Helmholtz free energy can be written as,

$$f_{\text{ex}} = f_{\text{mono}} + f_{\text{ass}}, \tag{7}$$

where f_{ass} is the excess free energy density due to association and f_{mono} involves all the non-associative terms. Usually, f_{mono} is written as a sum of contributions resulting from HS, f_{HS}, and from attractive forces, f_{att},

$$f_{\text{mono}} = f_{\text{HS}} + f_{\text{att}}. \tag{8}$$

In this work the attractive force contribution, f_{att}, is evaluated employing the FMSA approach. For spherical particles, the Ornstein-Zernike equation in the Fourier space is given by