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Statistical fluid theory for systems of variable range interacting via triangular-well pair potential

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ABSTRACT

The interest for describing the thermodynamic properties of fluids is growing in many fields from pure theoretical to those with technological applications. In this work, we have developed an analytical expression for the Helmholtz free energy of particles interacting via the triangular-well pair potential (TW), in the Barker-Henderson framework. This theoretical equation of state (EoS) uses the analytical radial distribution function of the hard-sphere (HS) fluid coupled with the Barker-Henderson perturbation theory. Thermodynamic properties as vapor-liquid coexistence, vapor pressures, internal energies and critical properties are obtained for attractive particles whose interaction potential range lies between $1.2 \leq \lambda \leq 2.6$. The performance of the TW equation of state is assessed by comparing with Monte Carlo (MC) simulation data. Finally, this theoretical approach is used to model real fluids as methane, oxygen, fluoromethane and hydrogen sulfide, in a wide range of temperature and pressures.

1. Introduction

In the context of the liquid theory, the hard sphere system is the simplest representation of particles in a real fluid at high temperature. The existence of an attraction among particles lets the HS system to present other phases, additional to the fluid and crystal ones. The attractive interaction makes possible the vapor-liquid coexistence or even a crystal-crystal coexistence [1]. The square-well (SW) pair potential is the simplest attractive potential, the thermodynamic properties and phase diagram of SW fluids have been extensively studied in the literature, through theoretical approaches [1–19] and simulations [20–24]. Even though the SW potential is an unphysical interaction, it has proved to be very useful due to its simple form and because other kind of potentials, with a more complex functional form, as the Yukawa, Lennard-Jones, Asakura-Oosawa or Morse potentials, can be represented by a suitable SW according to the extended law of corresponding states [25]. Besides, the SW potential could be a crude representation of the effective interaction in complex fluids, as colloids and protein suspensions. In those systems the attraction range is smaller that the molecular diameter [19,26]. But if the attraction range is longer than the molecular diameter, the system can be a representation of a simple fluid composed by neutral molecules.

Another attractive potential, with a slightly more complicated mathematical form than the SW, is the TW potential. A schematic representation of the TW potential with an attraction range of $\lambda = 1.5$ is represented in Fig. 1. Despite its simple form, it has not received the same attention as the SW potential. Some of earlier work about TW fluids has been focused on developing equations of state to predict the thermodynamic properties as well as the phase behavior, for different attraction ranges, and to compare the predictions with simulation data. Largo and Solana [27] obtained an analytical expression for the first and second order perturbation terms of the Barker-Henderson (BH) perturbation theory (PT) [2,28] based on the Chang-Sandler expression for the radial distribution function (RDF) [29]. The BH [2,28] theory has been successfully applied to model the thermodynamic properties of other kind of fluids, as for example square well (SW) and Lennard-Jones (LJ) fluids. In a more recently work, they analyzed the performance of several approximations for the second-order perturbation term [30]. Betancourt-Cárdenas et al. [31] developed an EoS based on the BH PT to calculate the properties of TW fluids and solids with a short-ranged potentials, $\lambda = 1.1$, to intermediate-range ones, $\lambda = 2.0$ and in the Ref. [32] they calculated thermodynamic properties as well as the phase diagram of TW fluids through perturbation theory, self-consistent Orstein-Zernike approach and Monte Carlo simulation. They focused

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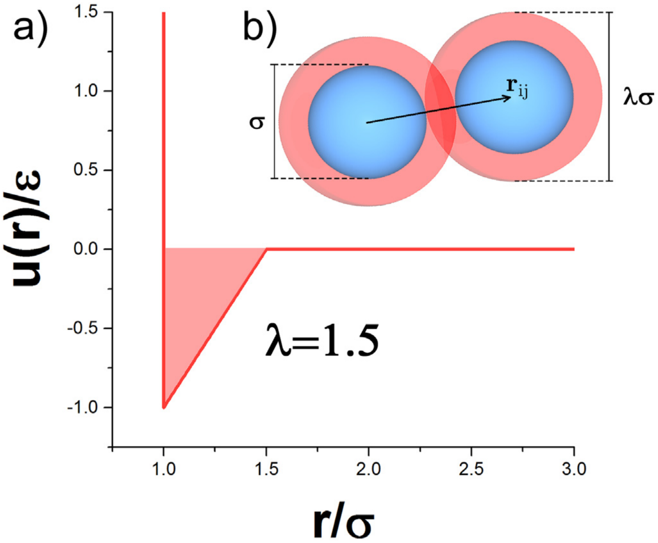

Fig. 1. a) Schematic representation of the triangular-well pair potential model for λ = 1.5. b) Particles separated by a distance smaller than σ exert an infinite repulsion, but if the distance is less than λ they attract each other, otherwise they have not interaction. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

in particles interacting through a long-ranged potential, $2 \leq \lambda \leq 4$. Adhikari and Kofke [33] obtained the vapor-liquid, fluid-solid and solid-solid coexistence boundaries using MC simulations for several attraction ranges, $1.05 \leq \lambda \leq 2.5$. Zhou [34] used his own thermodynamic perturbation theory to obtain a fifth-order EoS valid for ranges, $1.5 \leq \lambda \leq 3$. Rivera et al. [35] obtained an EoS based on perturbation theory using the macroscopic compressibility approximation, they obtained accurate results for ranges around $\lambda = 2.0$. Bárcenas et al. [36] obtained the binodal and interfacial properties for TW with $1.5 \leq \lambda \leq 3.0$ and in Ref. [37] they used MC simulations with the replica exchange technique to obtain the binodal of short-ranged TW fluids, they considered some values in the range: $1.15 \leq \lambda \leq 1.4$. Sengupta et al. [38,39] studied the properties of TW fluids in confinement. Guérin [40,41] developed a framework to predict the thermodynamic behavior of TW fluids, also useful to study other kind of fluids as the SW and Sutherland ones.

The TW potential has been used to model experimental systems in a pair of works, those are the following. In Ref. [42], it is shown that particles in a microemulsion can be modeled with a short-ranged attractive TW with $\lambda = 1.47$. In Ref. [31], the EoS developed is used to model methane and ethane, the range of the well of these fluids are 2.4925 and 2.1834, respectively. The previous works serve as our motivation to develop an EoS valid in the colloidal regime, for short-ranged potentials, as well as in the simple fluids regime, which correspond to long-ranged attractions.

The main purpose of this work is to present an analytic EoS for the description of thermodynamic properties of fluids in the framework of the Barker-Henderson perturbation theory [2,28] and compare its predictions with recent MC simulation data reported the literature [31,32,37]. In this framework, the Helmholtz free energy, A, is expressed as the sum of a reference term, obtained from a reference potential, and a perturbation. The perturbation contribution is obtained by following a standard procedure, in particular we follow the one developed for SW fluids [43,44].

This paper is organized as follows. In Section 2, the fundamentals of the BH PT [2,28] for TW pair potentials are revised. Additionally, an analytic parameterization for the first and the second order perturbation theory terms of the so-obtained EoS for TW potentials, is presented. Section 3 presents the Monte Carlo (MC) simulation scheme and some details about our implementation to calculate the free energy and the vapor-liquid equilibrium (VLE). In Section 4, the results of the TW-EoS against MC molecular simulation results are presented for different thermodynamic properties as VLE, vapor pressure, critical points and internal energy. Additionally, we have included the VLE and vapor pressure calculation of fluoromethane (R41), hydrogen sulfide (H_2S), methane (CH_4) and oxygen (O_2) by using the TW-EoS, the molecular parameters were obtained by fitting our results to the data from Ref. [45]. Finally, in Section 5, some conclusions and perspectives are provided.

2. Theoretical framework

2.1. Perturbation theory for TW fluids

In this work, the description of the fluids is given in the framework of the BH PT [2,28]. We consider a system of molecules interacting through the potential, $u(r)$, which can be split in two contributions

$$u(r) = u^{\mathrm{HS}}(r) + u^{\mathrm{att}}(r), \tag{1}$$

where $u^{\mathrm{HS}}(r)$ and $u^{\mathrm{att}}(r)$ are the repulsive HS potential and the attractive pair potential (which plays the role of the perturbation), respectively. The HS contribution is given by

$$u^{\mathrm{HS}}(r) = \begin{cases} \infty, & \text{if } r < \sigma, \\ 0, & \text{if } r \geq \sigma, \end{cases} \tag{2}$$

where r is the distance between the centers of two particles and σ is the particle diameter. For a system of particles interacting via TW pair potential, the attractive contribution is given by

$$u^{\mathrm{attr}}(r) = \begin{cases} 0, & \text{if } r < \sigma, \\ -\varepsilon(\lambda - r)/(\lambda - \sigma), & \text{if } \sigma \leq r < \lambda, \\ 0, & \text{if } r \geq \lambda, \end{cases} \tag{3}$$

where ε and λ are the energy-depth and range of the potential, respectively. Once the pair potential, $u(r)$, is split in two contributions the Helmholtz free energy, A, for a system of interacting particles can be written in the BH [2,28] approach as

$$\frac{A}{NkT} = \frac{A^{\mathrm{id}}}{NkT} + \frac{A^{\mathrm{exc}}}{NkT}, \tag{4}$$

where k is the Boltzmann's constant, N is the number of particles in the system, T is the absolute temperature and A^{id} and A^{exc} are the ideal and excess Helmholtz free energy. The ideal gas contribution to the free energy is given by [46]

$$\frac{A^{\mathrm{id}}}{NkT} = \ln\left(\rho\lambda_B^3\right) - 1, \tag{5}$$

where λ_B the de Broglie wavelength and ρ the density of the system. The excess energy is composed by different parts to take into account the different interactions among particles, then there is a contribution for the excluded volume, a second contribution due to the dispersion forces and another one that comes from the hydrogen bonds, etc. The excess free energy could be written as

$$\frac{A^{\mathrm{exc}}}{NkT} = \frac{A^{\mathrm{HS}}}{NkT} + \frac{A^{\mathrm{attr}}}{NkT} + \frac{A^{\mathrm{assoc}}}{NkT} + \cdots \tag{6}$$

to take into account the contribution of the reference, the perturbation and also the associating potentials, respectively. The free