



Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Integral equation and thermodynamic perturbation theory for a two-dimensional model of dimerising fluid

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ARTICLE INFO

Article history:

Received 2 August 2016

Received in revised form 17 September 2016

Accepted 20 September 2016

Available online xxxxx

Keywords:

Integral equation theory

Association

Thermodynamic perturbation theory

Dimerising fluid

ABSTRACT

In this paper we applied an analytical theory for the two dimensional dimerising fluid. We applied Wertheims thermodynamic perturbation theory (TPT) and integral equation theory (IET) for associative liquids to the dimerising model with arbitrary position of dimerising points from center of the particles. The theory was used to study thermodynamical and structural properties. To check the accuracy of the theories we compared theoretical results with corresponding results obtained by Monte Carlo computer simulations. The theories are accurate for the different positions of patches of the model at all values of the temperature and density studied. IET correctly predicts the pair correlation function of the model. Both TPT and IET are in good agreement with the Monte Carlo values of the energy, pressure, chemical potential, compressibility and ratios of free and bonded particles.

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1. Introduction

A major goal of computational solution chemistry is to develop models that capture the physics of solvation and yet are computationally tractable. Molecular simulations can take long time to yield one reliable single point on a phase diagram. Integral equations theory (IET) and thermodynamic perturbation theory (TPT) provide us with a fast and easy-to-implement method of calculating pair distribution function and thermodynamic properties for these models [1] and allows a rather quick calculation of properties along the isotherms or isochores. Unfortunately, IET and TPT are in principle approximations that can produce wrong results. Caution must therefore be exercised to use IET with appropriate closures in regions where their use is justified.

A theory has been developed for fluids comprised of molecules that associate into dimers and higher clusters due to the presence of highly directional attractive forces [2,3]. This theory is so called Wertheim's associating theory and it has been successfully applied to a number of different three-dimensional fluid systems, including water and aqueous solutions (see, for example [4–6] and references therein) and two-dimensional fluid systems like Mercedes-Benz model of water [7–13]. In the present work, we tested two variants of the theory of associating fluids: the thermodynamic perturbation theory (TPT) [2,3,14,15], and the integral equation theory (IET) [2,16,17]. IET has advantage over TPT because it provides both the structure (in form of various pair correlation functions) and thermodynamics for studied model while the thermodynamic perturbation theory, on the other hand, is simpler to use but can only give the thermodynamic properties.

Water has a lot of anomalous properties that distinguish it from simpler liquids. The most important anomalies of pure water are: a temperature of maximum density in the liquid phase, a minimum in the isothermal compressibility, and large heat capacity. The anomalies appear to be related to the ability of water molecules to form tetrahedrally coordinated hydrogen bonds. Many theoretical and computational models have been developed to capture some of these properties. Among the simplest of these is the MB model, originally proposed by Ben-Naim in 1971 [18]. It captures two aspects of water physics in a simple way: Lennard-Jones interactions for long-ranged attractions and short-ranged repulsions, and an orientation dependent interaction to mimic hydrogen bonding effects. Water molecules are represented as two-dimensional Lennard-Jones disks, with three hydrogen-bonding arms, arranged as in the Mercedes-Benz (MB) logo. As a validation of the model, NPT Monte Carlo simulations have shown that it predicts qualitatively the density anomaly, the minimum in the isothermal compressibility as a function of temperature, the large heat capacity, and the experimental trends for the thermodynamic properties of solvation of nonpolar solutes [7]. Theoretical treatments of MB model was in agreement with simulation for high temperatures [8], but at low temperatures the agreement was not that good. There are multiple reasons possible for this. One possibility is omitting ring structures in theoretical treatment, another possibility is closure. In this study we investigate the properties fluid described by an associative potential with soft core. Potential is similar to the one used in Mercedes-Benz model of water [7,18], but we kept only one arm so that molecules can only form dimers. This model can no form ring structures and our study can show if this is possible reason for disagreement in case of MB

<http://dx.doi.org/10.1016/j.molliq.2016.09.061>

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model. For our one arm model we wanted to see if the in TPT and IET can perform well and from this conclude what might be problem for MB model. Meaning if disagreement is related to number of associative arms and their positions. Beside testing the affect of number of arms on correctness of theories studied model can be used as a model for chemical reaction of dimerising. Dimerising takes place due to site-site associative interactions. Model can be used to predict properties of patch colloids with soft core and one attraction point. In case of strong dimerization the model can be also used to describe properties of dumbbell fluids.

The paper is organized as follows. In Section 2, we present the model, continue with description of the TPT and IET specialized for the model at hand in Section 3 and in Section 4, we discuss details of the computer simulations. In Section 5 we tested, presented and discussed results of theories in comparison with Monte Carlo simulation data for potential like in MB, but with only one active arm. The paper is finished with concluding remarks in Section 6.

2. The model

Molecules of dimerising fluid are represented as two-dimensional (2D) Lennard-Jones (LJ) disks. Each disk has one arm which can associate with arm of another molecule (see Fig. 1) and form dimers. The interaction potential between two particles is a sum of a Lennard-Jones term and an associative term

$$U(\vec{X}_i, \vec{X}_j) = U_{LJ}(r_{ij}) + U_a(\vec{X}_i, \vec{X}_j). \quad (1)$$

r_{ij} is the distance between centers of particles i and j , \vec{X}_i and \vec{X}_j denotes the vector representing the coordinates and the orientation of the i th and j th particles. The Lennard-Jones part of the potential is defined as

$$U_{LJ}(r_{ij}) = 4\epsilon_{LJ} \left(\left(\frac{\sigma_{LJ}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{LJ}}{r_{ij}} \right)^6 \right), \quad (2)$$

where ϵ_{LJ} is the well-depth and σ_{LJ} is the contact parameter. The form of the associative part of the interaction potential is

$$U_a(\vec{X}_i, \vec{X}_j) = \epsilon_a G(r_{ij} - r_a) G(\vec{i} \cdot \vec{u}_{ij} - 1) G(\vec{j} \cdot \vec{u}_{ij} + 1) \quad (3)$$

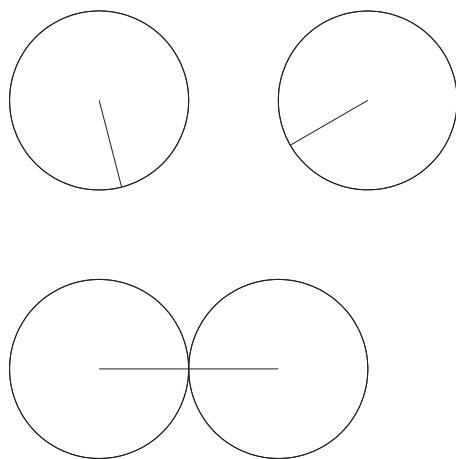


Fig. 1. The molecules of two dimensional dimerising fluid. Particles associate the strongest when arms are collinear and the distance between two particles is equal to r_a .

where $G(x)$ is an unnormalized Gaussian function

$$G(x) = \exp\left(-\frac{x^2}{2\sigma^2}\right). \quad (4)$$

Further, $\epsilon_a = -1$ is an associative energy parameter and r_a is a characteristic length of associative interaction. \vec{u}_{ij} is the unit vector along \vec{r}_{ij} , \vec{i} and \vec{j} are the unit vectors representing the arm of the i th and j th particles. The strongest association occurs when the arm of one particle is collinear with the arm of another particle and particles are on distance r_a from each other. The LJ well-depth ϵ_{LJ} is one-tenth of associative interaction energy (ϵ_a). The width of Gaussian ($\sigma = 0.085r_a$) is small enough that it is not possible to have more than one association per arm.

3. Theory

3.1. Thermodynamic perturbation theory

In TPT [2] we have to determine the Helmholtz free energy of the system. Here, it is written for a system consisting of N molecules with temperature T as

$$\frac{A}{Nk_B T} = \frac{A_{LJ}}{Nk_B T} + \frac{A_a}{Nk_B T}. \quad (5)$$

A_{LJ} is the Helmholtz free energy of Lennard-Jones reference system, A_a is contribution of association to free energy and k_B is Boltzmann's constant. One way to calculate A_{LJ} is using the Barker-Henderson perturbation theory [1] with hard disks (HD) as a reference system.

$$\frac{A_{LJ}}{Nk_B T} = \frac{A_{HD}}{Nk_B T} + \frac{\rho}{2k_B T} \int_{\sigma_{LJ}}^{\infty} g_{HD}(r, \eta) U_{LJ}(r) d\vec{r}. \quad (6)$$

A_{HD} is here the hard-disk part of the Helmholtz free energy, $g_{HD}(r)$ pair correlation function between hard disks and ρ the total number density of particles. The Helmholtz free energy of hard disks can be calculated with approximation provided by Scalise et al. [20]

$$\begin{aligned} \frac{A_{HD} - A_{ideal}}{Nk_B T} = & -1.10865 - 0.8678 \log(1 - \eta) - 0.0157(1 - \eta) \\ & + \frac{1.1322}{1 - \eta} - \frac{0.00785}{(1 - \eta)^2}. \end{aligned} \quad (7)$$

η is the packing fraction and is calculated as $\eta = \frac{1}{4}\pi d^2 \rho$. d is the diameter of hard-disks. For $g_{HD}(r)$ the expression of Gonzalez et al. [21] was used. The contribution of the association to the Helmholtz free energy was calculated using approximation proposed by Jackson et al. [22], originally derived by Wertheim [2], in the following form

$$\frac{A_a}{Nk_B T} = \left(\log x - \frac{x}{2} + \frac{1}{2} \right) \quad (8)$$

where x is the fraction of molecules not bonded and is obtained from the mass-action law [2] written as

$$x = \frac{1}{1 + \rho x \Delta}. \quad (9)$$

Δ is calculated as internal of an orientationally averaged Mayer function for the associative part of potential, $\tilde{f}_a(r)$, and correlation function of reference system [2,22]

$$\Delta = 2\pi \int g_{LJ}(r) \tilde{f}_{HB}(r) r dr. \quad (10)$$

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