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

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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.

Keywords

Integral equation theory; association; thermodynamic perturbation theory; dimerising fluid

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

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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, 5, 6] and references therein) and two-dimensional fluid systems like Mercedes-Benz model of water [7, 8, 9, 10, 11, 12, 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 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 Figure 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 particle. The Lennard–Jones part of the potential is defined as

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

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

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

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

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

Further, $\varepsilon_a = -1$ 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 particle. 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]

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

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

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

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

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

The pair distribution function of reference system $g_{LJ}(r)$ is obtained by solving the Percus–Yevick equation for Lennard–Jones disks. Once the Helmholtz free energy is known, other thermodynamic quantities may be calculated from standard thermodynamic relations [1].

3.2. Integral equation theory

With thermodynamic perturbation theory we can only obtain information about thermodynamics of the system and we can not determine anything about the structural properties. Integral equation theory on the other hand can provide details about both, structural and thermodynamics properties of the studied system. In the present calculation we apply the orientationally averaged version of the multidensity Ornstein–Zernike (OZ) equation with the polymer Percus–Yevick (PPY) closure [2, 16, 17, 8]. The multidensity OZ equation in k -space is written as

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{c}}(k) + \hat{\mathbf{c}}(k) \boldsymbol{\rho} \hat{\mathbf{h}}(k), \quad (11)$$

where $\hat{\mathbf{h}}(k)$ and $\hat{\mathbf{c}}(k)$ are the matrices whose elements are the Fourier transforms of the partial correlation functions $h_{ij}(r)$ and $c_{ij}(r)$, respectively. Furthermore, $\boldsymbol{\rho}$ is the matrix containing the partial densities. The indices i and j denote the bonding states of the corresponding particles and assume the values 0 for non-bonded particle or 1 for bonded (h_{00} is correlation between two non-bonded particles, h_{11} between two bonded and h_{01} between non-bonded and bonded particles). Matrices can be explicitly written as

$$\hat{w}(k) = \begin{bmatrix} \hat{w}_{00}(k) & \hat{w}_{01}(k) \\ \hat{w}_{10}(k) & \hat{w}_{11}(k) \end{bmatrix} \quad (12)$$

where w stands for either the h or c correlation function, and $\boldsymbol{\rho}$ is the matrix containing the partial densities [8]

$$\boldsymbol{\rho} = \begin{bmatrix} \rho & \rho \\ \rho & 0 \end{bmatrix} \quad (13)$$

In order to solve the multidensity Ornstein–Zernike an appropriate additional (closure) relation between h and c correlation functions is needed. In present study we applied the polymer Percus–Yevick closure [2, 16, 17]

$$c_{ij}(r) = f_{LJ}(r)y_{ij}(r) + \delta_{i1}\delta_{j1}\bar{f}_a(r)y_{00}x^2e_{LJ}(r), \quad (14)$$

where $y_{ij}(r) = t_{ij}(r) + \delta_{i0}\delta_{j0}$, $t_{ij}(r) = h_{ij}(r) - c_{ij}(r)$, x is the fraction of not bonded particles,

$$f_{LJ}(r) = e_{LJ}(r) - 1 \text{ and } e_{LJ} = \exp\left(-\frac{U_{LJ}}{k_B T}\right).$$

As before $\bar{f}_a(r)$ is the orientationally averaged Mayer function for the hydrogen bonding potential and x follows from mass action law. The total pair distribution function $g(r)$ is obtained by summing up the partial distribution functions

$$g(r) = g_{00}(r) + g_{01}(r) + g_{10}(r) + g_{11}(r), \quad (15)$$

where $g_{ij}(r) = h_{ij}(r) + \delta_{i0}\delta_{j0}$. Once partial pair distribution functions are known the thermodynamic properties can be calculated.

We solved the OZ equation together with the polymer PY closure conditions using a direct iteration method. The forward and inverse Bessel–Fourier transforms, needed to couple the correlation functions in real and Fourier spaces, have been carried out using the method developed by Talman [23]. This method allows us to sample efficiently both the rapidly varying part of the correlation functions at small distances and the long ranged part using a relatively small number of the grid points, $n = 1024$.

4. Monte Carlo computer simulation

To test the theories we performed Monte Carlo simulations in grand canonical ensemble (constant μ , V , and T). We used periodic boundary conditions and the minimum image convention to mimic an infinite system of particles. Starting configurations were selected at random. In each move we randomly tried to translate or rotate random particle or insert new or remove random particle. Probability for translation, rotation and exchange of particles was the same. In one cycle we tried to translate and rotate each particle and to make as many insertions or removals as were averaged number of particles in system on average. The simulations were allowed to equilibrate for 50000 cycles and averages were taken for 20 series each consisted for another 50000 cycles to obtain well converged results. In the system we had from 50 to 200 particles depending on density of the system. Thermodynamic quantities such as energy were calculated as statistical averages over the course of the simulations [27]. Increasing the number of particles had no significant effect on the calculated quantities.

5. Results and Discussion

All the results are given in reduced units; the excess internal energy and temperature are normalized to the association energy interaction parameter ε_a ($U^* = \frac{U}{|\varepsilon_a|}$, $T^* = \frac{k_B T}{|\varepsilon_a|}$) and all the distances are scaled to the Lennard-Jones characteristic length σ_{LJ} ($r^* = \frac{r}{\sigma_{LJ}}$).

First, we consider how well IET predicts the structure of the dimerising fluid. Shown in Figures 2 and 3 are the pair distribution functions for two different temperatures at different distances of associative points from center of particles and different densities. The Monte Carlo results are represented by red solid line and the IET results by green dashed line. Figure 2 shows the pair distribution functions at high reduced temperature, $T^* = 0.3$ and Figure 3 for low temperature, $T^* = 0.12$. For all temperatures, distances and densities, the IET and the Monte Carlo simulation pair distribution functions are in very good agreement which is different as in case of MB model [8] where good agreement is at high temperatures while at low it is only quantitative. There is only small discrepancy at higher distances of associative point from center and high densities when packing of dimers is important. In this cases LJ peak predicted by IET is to high which is most probably due to approximation in IET and to get better agreement correct bridge graph function should be included in closure. similar was observed also for MB model [8]. But nevertheless since agreement was good for most of distances we checked what happens with correlation function at fixed temperature ($T^* = 0.1$) and density ($\rho = 0.49$) upon varying position of associative part of molecules from center and this is presented in Figure 4. If associative points are at distances below 0.6 then there is no association due to LJ repulsion and pair correlation functions are same as in case of LJ fluid. For distances above 0.6 we can see associative peak at distance of the associative point. Pair correlation also changes since part of molecules is now forming dimers. Total correlation function is as we would have it in case of mixture of dimers and single particles.

After checking structural properties we compared thermodynamics. Here, we could make comparison for both theories with computer simulations. First we checked how the theories are doing in case of internal energy U^* . Results of comparison are shown on Figure 5. Here agreement between theory and simulation for thermodynamical properties is very good for both values of the temperature and all values of the distances. Although we can see that IET is doing slightly better job comparing to TPT. As the density increases internal energy decreases because there are more particles forming dimers. As next we checked how good are theories in predicting the fraction of particles that are not associated. Results are plotted in Figure 6. Predictions for the fraction of the free particles x_0 are also very accurate. Chemical potential can easily be calculated in TPT while by IET there is no simple formula and one has to do thermodynamic integration to obtain it, this is why we showed only comparison of computer simulation data and TPT in Figure 7. Also here we can see very good agreement at all temperature, densities and distances between theoretical results and results obtained by computer simulations. We can expect same kind of agreement also in case of IET.

6. Conclusions

We have applied two statistical–mechanical theories developed for associated fluids by Wertheim [2, 3] to the two dimensional model of associating fluid. We also generated a set computer simulation data for thermodynamical and structural properties of the model and compare theoretical and simulation results. The IET is somewhat more demanding from a computational point of view than the TPT, but both are orders of magnitude more efficient than the Monte Carlo simulations. Both theories reproduce thermodynamics and structural properties of the model for all temperature and density ranges studied.

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Highlights

- TPT and IET for two dimensional dimerizing fluid is applied
- Thermodynamics and structural properties of the model are studied
- Predictions of the theory and simulation appears to be in a reasonably good agreement

Figure 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 .

Figure 2.

Pair correlation functions for high temperature $T^* = 0.3$ for different densities and at associative point distance (a) $r_a = 1.43$ and $\rho^* = 0.085$; (b) $r_a = 1.0$ and $\rho^* = 0.084$; (c) $r_a = 1.43$ and $\rho^* = 0.537$; (d) $r_a = 1.0$ and $\rho^* = 0.512$. Results from computers simulations are plotted by red solid line and from IET by green dashed line.

Figure 3. Pair correlation functions for low temperature $T^* = 0.12$ for (a) $r_a = 1.43$ and $\rho^* = 0.122$; (b) $r_a = 1.0$ and $\rho^* = 0.088$; (c) $r_a = 1.43$ and $\rho^* = 0.540$; (d) $r_a = 1.0$ and $\rho^* = 0.589$; legend as for Figure 2.

Figure 4. Pair correlation functions different distance of patch from center of particle for temperature $T^* = 0.1$ and density $\rho^* = 0.49$. Correlations functions from bottom up (each shifted for 1) are for distances 0.714, 1.0, 1.143, 1.286, 1.429, 1.714 and 2.142.

Figure 5.

Density dependence of internal energy for different temperatures and associative point distances from center (a) $r_a = 1.43$ and $T^* = 0.2$; (b) $r_a = 1.0$ and $T^* = 0.2$; (c) $r_a = 1.43$ and $T^* = 0.1$; (d) $r_a = 1.0$ and $T^* = 0.1$. Results from computer simulations are plotted by red symbols, from IET by blue dashed line and from TPT by green long dashed line.

Figure 6.

Density dependence of ratio of free particles for different temperatures and associative point distances from center. Details are same as in Figure 5.

(a)

(b)

Figure 7.

Density dependence of chemical potential energy for different temperatures and associative point distances from center (a) $r_a = 1.43$; (b) $r_a = 1.0$. Results from computers simulations are plotted by symbols, from TPT by line. Red color is for low temperature $T^* = 0.1$ and green for high temperature $T^* = 0.2$.