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Two dimensional fluid with one site-site associating point. Monte Carlo, integral equation and thermodynamic perturbation theory study

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Abstract

In this paper we propose a model for the two dimensional fluid with one site-site associating point. We studied its structural and thermodynamic properties by the Monte Carlo computer simulations, the site-site integral equation theory (RISM), the Wertheim's thermodynamic perturbation theory (TPT) and the Wertheim's integral equation theory (WIET) for associative liquids. The model can have arbitrary position of the associating point from the center of particles. All particles have Lennard-Jones core while interactions between associating points are modeled as Gaussian like potential where the interaction depends only on the distance between sites. The methods were used to study the thermodynamic and structural properties as a function of the position of associating point, temperature and density. The accuracy of the analytic theories were checked by comparing the theoretical results with the corresponding Monte Carlo ones. The theories are quite accurate for cases when the associating point is on the surface and only dimers can be formed. In this case, the theories correctly predict the pair correlation functions of the model, internal energy, ratios of free and bonded particles and chemical potential. This is no longer true when associating point is away from the surface of particles and the higher clusters are formed.

Keywords

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

1. Introduction

A major goal of physical chemistry is to develop models that capture the physics of different systems of interest. In recent years, the research of self-assembly of particles is very popular. The self-assembly is a phenomenon where the components of a system assemble themselves spontaneously via an interaction to form a larger functional unit. This spontaneous organization can be due to a direct specific interaction. Another reason might be indirect through their environment [1]. We have the spontaneous self association when there are

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strong forces present between the particles. These forces associate them into the dimers and other structures composed from more particles.

When we develop a model we have to study its properties to see if these properties and the model can be used to reliably predict properties of the real systems of interest. One way to do this is by means of the molecular simulations, either molecular dynamics or Monte Carlo [2] simulations. These simulations can take long time to yield one reliable single point on a phase diagram so we are always on the lookout of even faster methods or theories. Integral equations theories and thermodynamic perturbation theories are two faster options which provide us with a fast and easy-to-implement method for calculating the pair distribution function and thermodynamic properties for different models [2]. These quantities can be rather quickly calculated along the isotherms or isochores. One have to keep in mind that the IET and TPT are in principle approximations that can produce wrong results, so caution must therefore be exercised when using the IET with appropriate closures in regions where their use is justified.

Wertheim developed a theory for fluids comprised of molecules that associate into dimers and higher clusters due to the presence of highly directional attractive forces [3, 4], called Wertheim's associating theory. It has been successfully applied to a number of different three-dimensional fluid systems (see, for example [5, 6, 7] and references therein) and two-dimensional fluid systems like Mercedes-Benz model of water [8, 9, 10, 11, 12, 13, 14] in form of the thermodynamic perturbation theory (TPT) [3, 4, 15, 16], and the integral equation theory (WIET) [3, 17, 18]. The WIET provides both the structure and thermodynamics while the TPT can only give the thermodynamic properties.

In our study we also adopt the site-site integral equation theory, also known as the reference interaction site model (RISM) for molecular fluids, developed by Chandler and Andersen [19]. In the original formulation [19], a specific molecule was modeled as a superposition of hard spheres rigidly bonded together mimicking its atoms [20]. The integral equation theory based on the RISM formalism has been applied successfully to obtain the structural and thermodynamic properties of various chemical, biochemical and biological systems [21, 22, 23, 24, 25]. It was also successfully used in two dimensions to study Lennard Jones dimers [26, 27, 28]. In this work we allied the RISM to an associating fluid. In our work one site is the center of the molecule and the second site is the associating point. The associating point in our case has only an attraction and there is no repulsion between sites. Between the centers and sites there is no interaction.

In this study we investigate the properties of a fluid where particles have one associative site. The centers of the particles are soft Lennard-Jones and the associating potential depends only on the distance between sites. The potential is similar to the one used in Mercedes-Benz model of water [8], but without angle dependence. This work is in a way related to the model used in previous study [29, 30] where there was also angle dependence between sites. In this new model, the association depends only on distance [29, 30]. By not having any angle dependence, the particles form structures composed of more particles when the associating points are not on the surface or inside of soft core in comparison to the model used in [29] where only dimers can be formed independently of the distance of association

point from the center of particle. The new model can also be used to predict the properties of patch colloids with soft core and one attraction point and the assemblies they form. In case of strong association, the model can be also used to describe properties of dumbbell fluids, triangular particles or polygon-like particles like observed in experiment [31].

The paper is organized as follows. In Section 2, we present the model, and in Section 3, we discuss the details of computer simulations, which is followed by the description of RISM in Section 4 and TPT and WIET in Sections 5 and 6 respectively. In Section 7 we present, test and discuss the results of Monte Carlo simulation, theories and compare them. The paper is finished with concluding remarks in Section 8.

2. The model

The molecules of associating particles are represented as a two-dimensional (2D) Lennard–Jones (LJ) disks. Each disk has one associating point which can associate with the associating point of another molecule (see Figure 1) and form dimers and higher structures (see snapshots in Figures 3 and 5). The interaction potential between two particles is a sum of the Lennard–Jones term and the 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 potential has a standard form

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

The depth of potential is ϵ_{LJ} and σ_{LJ} is the distance where the potential is zero. The associative part of the interaction potential is calculated as

$$U_a(\vec{X}_i, \vec{X}_j) = \epsilon_a G(\vec{r}_{ij} - \vec{d}_i + \vec{d}_j). \quad (3)$$

$G(x)$ 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. $\vec{r}_{ij}$ is vector between the centers of particles. $\vec{d}_i$ and $\vec{d}_j$ are the vectors representing positions of associating points with respect

to the centers of the particles i and j . The orientation of molecule i is represented as angle θ_i between vector $\vec{d}_i$ and x axis (see Figure 2). The strongest association occurs when the associating points overlap. The LJ well-depth ϵ_{LJ} is one-tenth of associative interaction energy (ϵ_a). The width of Gaussian is $\sigma = 0.12 \sigma_{LJ}$.

3. Monte Carlo computer simulation

To analyze the properties of the system we performed the Monte Carlo simulations in the grand canonical ensemble (constant μ , V , and T). The periodic boundary conditions and the minimum image convention were used to mimic an infinite size of the system of particles. All simulations were started from a random configuration with different number of initial particles. In each step we randomly tried to translate or rotate a particle or insert new into or remove a particle from the box with same probability. On average we tried to translate and rotate each particle in one cycle and to make as many insertions or removals as were averaged number of particles in the system. The simulations were allowed to equilibrate for 50000 cycles and the averages were taken for 20 series each consisted of another 50000 cycles to obtain well converged results. In the system we had from 50 to 200 particles depending on the density of the system. The thermodynamic quantities such as the internal energy were calculated as statistical averages over the course of the simulations [32].

4. Integral Equation Theory

The site-site integral equation theory by Chandler and Andersen [19] provides an equation to relate the direct site-site correlation functions, $c_{\alpha\beta}(r)$, the intramolecular site-site correlation functions, $\omega_{\alpha\beta}(r)$, and the intermolecular site-site correlation functions, $h_{\alpha\beta}(r)$, between sites α and β . The site-site Ornstein-Zernike-like matrix equation in Fourier space has the form

$$H(k) = \Omega(k)C(k)\Omega(k) + \rho\Omega(k)C(k)H(k). \quad (5)$$

$H(k)$, $C(k)$ and $\Omega(k)$ are matrices with the Fourier transforms of site-site correlation functions as elements

$$H(k) = \begin{bmatrix} h_{11}(k) & h_{12}(k) \\ h_{21}(k) & h_{22}(k) \end{bmatrix}, C(k) = \begin{bmatrix} c_{11}(k) & c_{12}(k) \\ c_{21}(k) & c_{22}(k) \end{bmatrix}, \Omega(k) = \begin{bmatrix} \omega_{11}(k) & \omega_{12}(k) \\ \omega_{21}(k) & \omega_{22}(k) \end{bmatrix}. \quad (6)$$

The elements $\omega_{\alpha\beta}(k)$ are written explicitly as [33]

$$\omega_{\alpha\beta}(k) = J_0(kl_{\alpha\beta}), \omega_{\alpha\alpha}(k) = 1. \quad (7)$$

$l_{\alpha\beta}$ is distance between sites α and β . $l_{\alpha\beta}=0$ if $\beta = \alpha$ and $l_{\alpha\beta} = d$ if β is different from α and $J_0(x)$ is Bessel function of 0th order. In our case the site 1 is the center of LJ disk and the site 2 is the associating point. In order to solve the site-site OZ, we need the closure relation between $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$. Morita wrote it in the general form as [34]

$$g_{\alpha\beta}(r) = \exp(-\beta U_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) + B_{\alpha\beta}(r)). \quad (8)$$

Where the relationship $g_{\alpha\beta}(r) = h_{\alpha\beta}(r) + 1$ holds, $\beta = \frac{1}{kT}$ is the reverse temperature, $U_{\alpha\beta}(r)$ is the site-site interaction potential and $B_{\alpha\beta}(r)$ the bridge function, which is not known and must be approximated. In the hypernetted chain (HNC) approximation is neglected ($B_{\alpha\beta}(r) = 0$), and the closure relation simplifies to [34]

$$g_{\alpha\beta}(r) = \exp(-\beta U_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)). \quad (9)$$

Jerome K. Percus and George J. Yevick (PY) proposed a different approximation [35, 36] in which the closure is written as

$$g_{\alpha\beta}(r) = \exp(-\beta U_{\alpha\beta}(r))(1 + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)). \quad (10)$$

The HNC and PY closures have a narrow region of convergence and inherent thermodynamic inconsistency, this is why several other closures have been proposed. The Kovalenko-Hirata closure (KH) [37] expands the convergence region and is written as

$$h(r) = \begin{cases} \exp(d_{\alpha\beta}(r)) - 1, & d_{\alpha\beta}(r) \leq 0 \\ d_{\alpha\beta}(r), & d_{\alpha\beta}(r) > 0 \end{cases}$$

where $d_{\alpha\beta}(r) = -\beta U_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r)$. In the work we also implemented the soft mean-spherical approximation (SMSA). In this closure we divide the LJ part of potential into a short-range reference part $U_{\alpha\beta}^0(r)$ and a longer-range perturbation part $U_{\alpha\beta}^1(r)$ as suggested elsewhere [38],

$$U_{LJ}^{\alpha\beta}(r) = U_{\alpha\beta}^0(r) + U_{\alpha\beta}^1(r), \quad (11)$$

where

$$U_{\alpha\beta}^0(r) = \begin{cases} U_{LJ}^{\alpha\beta}(r) + \varepsilon_{\alpha\beta} & r \leq r_{\alpha\beta}^m \\ 0 & r > r_{\alpha\beta}^m \end{cases}$$

and

$$U_{\alpha\beta}^1(r) = \begin{cases} -\varepsilon_{\alpha\beta} & r \leq r_{\alpha\beta}^m \\ U_{LJ}^{\alpha\beta}(r) & r > r_{\alpha\beta}^m \end{cases}.$$

The distance $r_{\alpha\beta}^m$ that separates these two components is chosen to be at the position of the minimum of the LJ part of the potential function, i.e. $r_{\alpha\beta}^m = 2^{1/6}\sigma_{\alpha\beta}$. The SMSA closure relation is then written in the following form

$$g_{\alpha\beta}(r) = \exp(-\beta U_{\alpha\beta}^0(r))(1 + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - \beta U_{\alpha\beta}^1(r)). \quad (12)$$

5. Wertheim's thermodynamic perturbation theory

The Helmholtz free energy of the system is the starting point in TPT [3]. Here, it is written for a system consisting of N molecules at the temperature T as

$$\frac{A}{Nk_B T} = \frac{A_{LJ}}{Nk_B T} + \frac{A_a}{Nk_B T} \quad (13)$$

A_{LJ} is the Helmholtz free energy of Lennard–Jones reference system, A_a is the contribution of association to the free energy. A_{LJ} is calculated using the Barker–Henderson perturbation theory [2] with hard disks (HD) as a reference system.

$$\frac{A_{LJ}}{Nk_B T} = \frac{A_{HD}}{Nk_B T} + \frac{\rho}{2k_B T} \int_{\sigma_{LJ}}^{\infty} g_{HD}(r, \eta) U_{LJ}(r) d\vec{r}. \quad (14)$$

Here, A_{HD} is 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 is calculated with the approximation provided by Scalise et al [40]

$$\frac{A_{HD} - A_{ideal}}{Nk_B T} = -1.10865 - 0.8678 \log(1 - \eta) - 0.0157(1 - \eta) + \frac{1.1322}{1 - \eta} - \frac{0.00785}{(1 - \eta)^2}. \quad (15)$$

$\eta = \frac{1}{4}\pi d^2 \rho$ is the packing fraction and d the diameter of hard–disks. For $g_{HD}(r)$ we used the expression of Gonzalez et al [41]. The contribution of association to the Helmholtz free energy was calculated by the approximation proposed by Jackson et al [42], originally derived by Wertheim [3], in the following form

$$\frac{A_a}{Nk_B T} = \left(\log x - \frac{x}{2} + \frac{1}{2} \right) \quad (16)$$

where x is the fraction of molecules not bonded and is obtained from the mass–action law [3] written as

$$x = \frac{1}{1 + \rho x \Delta} \quad (17)$$

is calculated as an integral of orientationally averaged Mayer function for the associative part of potential, $\bar{f}_a(r)$, and correlation function of the reference system [3, 42]

$$\Delta = 2\pi \int g_{LJ}(r) \bar{f}_{HB}(r) r dr \quad (18)$$

The pair distribution function of reference system $g_{LJ}(r)$ is obtained by solving the Percus–Yevick equation for Lennard–Jones disks. Note that this theory permits only one bond per associating site so it is expected that it will perform worse in cases where the higher clusters are formed. Once the Helmholtz free energy is known, other thermodynamic quantities may be calculated from the standard thermodynamic relations [2].

6. Wertheim's Integral equation theory

With Wertheim's TPT we can only obtain information about the thermodynamics and nothing about the structural properties. Wertheim's integral equation theory can provide details about both, the structural and thermodynamics properties. We applied the orientationally averaged version of the multidensity Ornstein–Zernike (OZ) equation with the polymer Percus–Yevick (PPY) closure [3, 17, 18, 9] which allows one bond per site. The multidensity OZ equation in k -space is written as

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{c}}(k) + \hat{\mathbf{c}}(k) \boldsymbol{\rho} \hat{\mathbf{h}}(k), \quad (19)$$

where $\hat{\mathbf{h}}(k)$ and $\hat{\mathbf{c}}(k)$ are the matrices whose elements are the Fourier transforms of the partial correlation functions $h_{ij}(r)$, $c_{ij}(r)$ and $\boldsymbol{\rho}$ 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 have the form

$$\hat{\mathbf{w}}(k) = \begin{bmatrix} \hat{w}_{00}(k) & \hat{w}_{01}(k) \\ \hat{w}_{10}(k) & \hat{w}_{11}(k) \end{bmatrix} \quad (20)$$

where w represents the h or c function. $\boldsymbol{\rho}$ has the form [9, 29]

$$\boldsymbol{\rho} = \begin{bmatrix} \rho & \rho \\ \rho & 0 \end{bmatrix} \quad (21)$$

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 [3, 17, 18]

$$c_{ij}(r) = f_{LJ}(r)y_{ij}(r) + \delta_{i1}\delta_{j1}\bar{f}_a(r)y_{00}x^2e_{LJ}(r), \quad (22)$$

where $y_{ij}(r) = t_{ij}(r) + \delta_{0i}\delta_{0j}$, $t_{ij}(r) = h_{ij}(r) - c_{ij}(r)$, x is the fraction of not bonded particles, $f_{LJ}(r) = e_{LJ}(r) - 1$ and $e_{LJ} = \exp\left(-\frac{U_{LJ}}{k_B T}\right)$. We did not observe any convergence problems so we did not try any other closure, like polymer soft mean spherical approximation for example [9, 11]. As before $\bar{f}_a(r)$ is the orientationally averaged Mayer function for the associating part of the potential and x follows from mass action law. The total pair distribution function $g(r)$ is obtained by summing up the partial distribution functions

$$g(r) = g_{00}(r) + g_{01}(r) + g_{10}(r) + g_{11}(r), \quad (23)$$

where $g_{ij}(r) = h_{ij}(r) + \delta_{0i}\delta_{0j}$. Once partial pair distribution functions are known the thermodynamic properties can be calculated.

We solved the OZ equation together with different closures 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 [43]. 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, $n = 1024$.

7. 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 $\varepsilon_a\left(U^* = \frac{U}{\varepsilon_a}, T^* = \frac{k_B^* T}{\varepsilon_a}\right)$ and all the distances are scaled to the Lennard-Jones characteristic length $\sigma_{LJ}(r^* = \frac{r}{\sigma_{LJ}})$.

First, we determined the structural and thermodynamic properties of the model by the Monte Carlo computer simulations. We observed that there are different structures present in the system depending on the position of the associating point with respect to the LJ center of the particle. With simple geometry calculations we can determine the maximum distance for particular n -mer (See Table 1). When the association point is on the surface of the particles they form mainly dimers. As this distance increases we first observe trimers and upon further increase of the distance quartremers start to form and then higher clusters. Figure 3 shows snapshots with the characteristic structures present in the system for three different positions of the association point from the center. Green lines connects centers of the particles interacting through associating potential. When associating point is on the surface

we have mainly dimers in the system. Figure 4 shows probability that a randomly selected particle is bonded to the cluster of size n . We should point out that selected temperatures are low enough so that in the system we have strong association. In Figure 5 we are showing the density dependence of the cluster size distributions for two different sizes at two selected temperatures. We can see that increase of density makes clusters bigger and more defined. In the inserts we plotted also two additional snapshots for the bigger distance showing different kind of clusters.

As next, we checked the structure by means of the pair correlation functions. They were calculated by the Monte Carlo simulations and tested how well they can be reproduced by both integral equation theories (RISM and WIET). In Figures 6, 7 and 8 we plotted the pair correlation functions between the centers of molecules for the series of temperatures and densities for three different positions of the associating points from the center of molecules. The WIET has no problem obtaining results for all studied temperatures while for RISM we could obtain PY and HNC results only for high temperatures while at lower we had convergence only for SMSA and KH which is consistent with our previous studies [27, 28]. The PY and HNC have convergence problems at low temperatures. In all three figures, the Monte Carlo results are represented by red solid line and the Wertheim's IET results by green dashed line and RISM results by pink dotted line (for $T^* = 0.50$ we plotted HNC results and for $T^* = 0.25$ KH because HNC did not converge). When associating point is on the surface of the particle (Figure 6) we have quite good agreement for both IETs, but we could see that WIET is doing slightly better job in all cases because it takes properly into account association between dimers. For the distance of the associating point $\rho^* = 0.725$, when the preferred size of the clusters is four (Figure 7), we can see that the theories are still doing rather well, but they could not longer predicts proper structures of four particles at low temperatures and high densities (Insert 7d). The RISM can not predict the proper association of particles since all predicted peaks, although at the right positions, are lower. When the distance is even bigger (Figure 8) IETs are reproducing MC results well only for high temperatures while they completely fail at low temperatures. The reasons are for RISM problems with predicting association and for WIET inability for this version to predict multiple bonds per associating site. With the RISM theory we can also calculate the correlation functions between the associating points. This is plotted in Figure 9 for the case where the associating points are on the surface. We can see that RISM is constant underestimating association for low temperatures while it gives wrong structure for high temperatures and low densities due to approximations present in the RISM. For bigger distances the agreement is even worse and because of this we didn't plot those correlation functions.

We continued our study by calculating the thermodynamics properties. First, we calculated the internal energy U^* and the comparison is shown in Figure 10. The theories agree with the MC data rather well for high values of the temperatures and small values of the distances. Although we can see that WIET is doing slightly better job in comparison to TPT and RISM at small distances. At high distances and low temperatures no theory is able to predict the correct structure of the system. The TPT and WIET have reason for failure due to inability to take into account multiple bonds per associating site while RISM can not take into account the strong association between sites. At the high distance and high temperatures

RISM is doing very good job, the reason is low association and good approximation of the site's location and interaction between sites. Second, we checked how the Wertheim's theories are doing in predicting the fraction of particles that are not associated (x_0). Comparisons between the computer simulations and theories are plotted in Figure 11. The predictions for the fraction are rather good at small distances of association point from the center, but is becoming worse with increase of this distance. We can see that both theories give similar results since they are based on similar assumptions. Both theories predict more free particles than observed in the computer simulations. The reason is the fact that the structures beyond dimers are neglected. Third, we tested how the TPT is doing in predicting the chemical potential of the particles. The chemical potential can easily be calculated in the TPT while for the IETs there is no simple general formula and one has to do the thermodynamic integration in order to obtain it. This is the reason for comparing only results by the TPT. The results are presented in Figure 12. We can see surprisingly very good agreement for all temperatures, densities and small distances between the theoretical results and the results obtained by computer simulations. When the distance of the associating site increases the disagreement starts at high density and low temperatures and becomes worse when this distance increases. The reason is the fact that the TPT lacks terms to describe multiple bonds per associating point.

8. Conclusions

We have proposed the model for the two dimensional fluid with one associating site. Its structural and thermodynamic properties were studied by the Monte Carlo computer simulations, site-site (RISM) integral equation theory [19], Wertheim's thermodynamic perturbation theory [3, 4] and Wertheim's integral equation theory for associative liquids [3, 4]. In the Wertheim's theories we used version where molecules can form only one bond per associating site. The model can form different structures depending on the location of the associating site. When the position of the site is on the surface mainly monomers and dimers are present in the system. For bigger distances, the particles start to form trimers, tetramers and higher clusters. Regarding the theories, the IETs are somewhat more demanding from a computational point of view than the TPT, but all are the orders of magnitude more efficient than the Monte Carlo simulations. All theories reproduce the thermodynamics and structural properties quite well for all temperature and density ranges studied when the associating point is on the surface while they fail for bigger distances. Wertheim's theories can be corrected by including terms for the formation of multiple bonds per patchy site and it is expected that results will be in better agreement also for these state points.

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Highlights

- Site-site two dimensional dimerizing fluid with one associating site
- 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 associating fluid with one site on the surface of disk.

Figure 2.
The molecule of two dimensional associating fluid with one site away from the surface of disk.

Figure 3. Snapshots of the system for (a) $d = 0.5$ at $T^* = 0.15$, $\rho^* = 0.725$; (b) $d = 0.714$ at $T^* = 0.20$, $\rho^* = 0.734$; (c) $d = 1.071$ at $T^* = 0.30$, $\rho^* = 0.398$. Green lines are connecting centers of associated particles.

Figure 4. Probability $p(n)$ of finding molecule in cluster of size n for (a) $d=0.5$ at $T^*=0.2$, $\rho^*=0.725$; (b) $d=0.714$ at $T^*=0.20$, $\rho^*=0.734$; (c) $d=1.071$ at $T^*=0.30$, $\rho^*=0.398$.

Figure 5.

Probability $p(n)$ of finding molecule in a cluster of size n for (a) $d = 0.5$ at $T^* = 0.2$ and densities from left to right 0.25, 0.45, 0.59, 0.69, 0.75, 0.82 (b) $d = 0.714$ at $T^* = 0.25$, and densities from left to right 0.30, 0.48, 0.62, 0.70, 0.77, 0.82 and snapshots for (c) $d = 0.714$ at $T^* = 0.25$, $\rho^* = 0.30$, (d) $d = 0.714$ at $T^* = 0.25$, $\rho^* = 0.82$.

Figure 6.

The pair correlation functions between centers of molecules for association point at the surface of molecule, $d=0.5$, for (a) $T^* = 0.5$, $\rho^* = 0.136$; (b) $T^* = 0.5$, $\rho^* = 0.536$; (c) $T^* = 0.25$, $\rho^* = 0.062$; and (d) $T^* = 0.25$, $\rho^* = 0.502$. The results from MC are plotted by red solid lines and from WIET by green dashed lines and from RISM by pink dotted lines.

Figure 7.

The pair correlation functions between centers of molecules for association point at $d^* = 0.725$ for (a) $T^* = 0.5$, $\rho^* = 0.137$; (b) $T^* = 0.5$, $\rho^* = 0.542$; (c) $T^* = 0.25$, $\rho^* = 0.148$; and (d) $T^* = 0.25$, $\rho^* = 0.617$. Legend same as in Figure 6.

Figure 8.

The pair correlation functions between centers of molecules for association point at $d = 1.071$ for (a) $T^* = 0.5, \rho^* = 0.138$; (b) $T^* = 0.5, \rho^* = 0.544$; (c) $T^* = 0.25, \rho^* = 0.223$; and (d) $T^* = 0.25, \rho^* = 0.587$. Legend same as in Figure 6.

Figure 9.

The pair correlation functions between association points of molecules for association point at the surface of molecule, $d = 0.5$, for (a) $T^* = 0.5$, $\rho^* = 0.136$; (b) $T^* = 0.5$, $\rho^* = 0.536$; (c) $T^* = 0.25$, $\rho^* = 0.062$; and (d) $T^* = 0.25$, $\rho^* = 0.502$. Results from MC are plotted by red solid line and from RISM by pink dotted line.

Figure 10.

The density dependence of the internal energy for different temperatures and associative point distances from the center (a) $d = 0.5$ and $T^* = 0.25$; (b) $d = 0.5$ and $T^* = 0.5$; (c) $d = 0.714$ and $T^* = 0.25$; (d) $d = 0.714$ and $T^* = 0.5$; (e) $d = 1.071$ and $T^* = 0.25$; (f) $d = 1.071$ and $T^* = 0.5$. The results from MC are plotted by green symbols, from WIET by blue dashed line, from TPT by red solid line and from RISM by pink dotted line.

Figure 11.

The density dependence of the ratio of free particles for different temperatures and associative point distances from the center for (a) $d^* = 0.5$ and $T^* = 0.25$; (b) $d^* = 0.5$ and $T^* = 0.5$; (c) $d^* = 0.714$ and $T^* = 0.25$; (d) $d^* = 0.714$ and $T^* = 0.5$; (e) $d^* = 1.071$ and $T^* = 0.25$; (f) $d^* = 1.071$ and $T^* = 0.5$. The results from MC are plotted by symbols, from WIET by dashed line and from TPT by solid line.

(a)

(b)

(c)

Figure 12.

The density dependence of the chemical potential for different temperatures and associative point distances from the center (a) $d = 0.5$; (b) $d = 0.714$; (c) $d = 1.071$. The results from computer simulations are plotted by symbols, from the TPT results by lines. Red color is for low temperature $T^* = 0.25$ and green for high temperature $T^* = 0.5$.

Table 1

Maximum distance of associating point from the center of particles, d_{max} for the size of clusters, n ,

d_{max}	n
0.577	2
0.706	3
0.840	4
1.000	5
1.153	6
1.307	7
1.461	8
1.618	9