Two-dimensional core-softened model with water like properties: Monte Carlo and integral equation study

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Monte Carlo simulations and integral equation theory were used to study the thermodynamics and structure of particles interacting through the smooth version of Stell-Hemmer interaction. We checked the possibility that a fluid with a core-softened potential reproduces anomalies of liquid water such as the density anomaly, the minimum in the isothermal compressibility as a function of temperature, and others. Critical points of the fluid were also determined. We showed that a potential with two characteristic distances is sufficient for the system to exhibit water-like behavior and anomalies, including the famous density maximum. We also showed that some versions of the integral equation theory completely fail to predict structure of such system, while others only predict it qualitatively. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4827862>]

I. INTRODUCTION

Water is the most important liquid on Earth. To understand the physical and chemical properties of water is important for understanding its role in chemical and biological processes. Water has many properties that are different from simpler liquids.^{1–3} The most known anomalies of pure water are the following: (i) an increase in the volume of water upon freezing, (ii) an increased density of liquid water in the range from 0 °C up to approximately 4 °C (depending on the pressure), (iii) high heat capacity and surface tension, and (iv) minimum in the compressibility vs. temperature. As a solvent, water also has some unusual properties: for nonpolar solutes, a large entropy that opposes the solvation at room temperature and a large heat capacity of transfer. Water's complexity is due to its strong orientation-dependent hydrogen bonding and strong intermolecular associations.

The anomalous properties can be explained by two different mechanisms. First, by interactions that are angular-dependent (oriented hydrogen bonding in water, tetrahedral bonding in silica).^{4–6} These interactions can result in density maximum or liquid-liquid phase transition⁴ because of the competition between tetrahedral order (low density) and translational order (high density). Second, the anomalous properties listed above can also arise in fluids, where particles interact with spherical symmetric potential with two characteristic lengths. An example are core-softened potentials, originally proposed by Stell and Hemmer in 1970.⁷ They proposed a possibility of a second critical point in addition to the standard liquid-gas critical point, when interaction potentials have region of negative curvature. It had been shown before that the core-softened and similar potentials can reproduce various fluid anomalies, typical of water,^{4,8} such as silica,⁴ silicon,⁹ BeF₂.¹⁰ Such potentials were also used to study the single-component liquid metal systems.^{11–15}

After the liquid-liquid phase transition was suggested as an explanation for water's anomalous properties by Poole *et al.*,¹⁶ there was an increase in the interest of studies of such transitions. Various studies have been done to understand the liquid-liquid phase transition and the associated properties.¹⁷ Franzese *et al.*¹⁹ showed that the reason for the liquid-liquid phase transition and its critical point might be due to the potential with two characteristic distances (hard core and soft core). In their work, they reported the existence of the low-density liquid phase and the high-density liquid phase in a 3D model, using molecular dynamics (MD) simulations. On the other hand, 2D MD calculation produced only density anomaly but no liquid-liquid phase transition.^{20,21} Scala *et al.*²² carried out MD simulations of 2D discrete and smoothed version of the potential to study liquid anomalies. These studies were continued by Buldyrev *et al.*¹⁷ to explore the liquid-liquid phase transition for 2D and 3D version of potentials, and by Almudallal *et al.*¹⁸ They both produced phase diagrams for the discrete version of potential with liquid anomalies, and no liquid-liquid critical point in stable liquid region was obtained.

The integral equation theory (IET) provides us with a fast and easy-to-implement method of calculating pair distribution functions and thermodynamic properties. IET also allows rather quick calculation of properties along the isotherms or isochores, but it also has drawbacks. It is based on approximations which can lead to convergence problems and even wrong results. Caution must therefore be exercised when using IET with a particular closure.

This paper is organized as follows. First, we present the core-softened model. In Sec. II, we present Monte Carlo (MC) simulation details and IET with different closure relations. In Sec. V, we first present the Monte Carlo calculations for thermodynamic and structural properties. In addition, we provide a comparison of pair correlation functions calculated from various IET approximations and those obtained from MC simulations.

II. MODEL

In this work, we use the smooth version of the core-softened potential proposed by Scala *et al.*²² The interaction potential $U(r)$ is calculated by adding a Gaussian well to the Lennard-Jones (LJ) part of the potential

$$U(r) = U_{LJ}(r) + U_G(r), \quad (1)$$

where $U_{LJ}(r)$ is the standard Lennard-Jones potential and is defined as

$$U_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right). \quad (2)$$

Here ϵ denotes the well-depth and σ the contact parameter of LJ potential. The Gaussian part of the interaction is

$$U_G(r) = -\lambda\epsilon \exp \left(-a \left(\frac{r-r_0}{\sigma} \right)^2 \right). \quad (3)$$

For the sake of comparison with the previous studies, we adopt the units and values of model parameters as used before by Scala *et al.*²² We use $\epsilon = 1.0$, $\sigma = 1.0$, $\lambda = 1.7$, $a = 25.0$, $r_0 = 1.5\sigma$. Figure 1 shows the shape of this smooth version of the core-softened potential.

III. MONTE CARLO SIMULATION DETAILS

To obtain thermodynamic and structural properties of the model water we applied the Monte Carlo simulation method in the isothermal-isobaric (N,p,T) and in the canonical (N,V,T) ensembles. At each step, displacements in the x , y coordinates were chosen randomly. We used the periodic boundary conditions and the minimum image convention to mimic an infinite system of particles. Starting configurations were selected at random. In N,p,T ensemble, after 10 moves of particles on average, an attempt is made to scale the dimensions of the box, and all of its component particles, to hold the pressure constant. Here are some of the simulation details: 5×10^4 moves per particle were needed to equilibrate the system. The statistics were gathered over the next 1×10^6 moves to obtain well converged results. All simulations were performed with $N = 200$ or 400 molecules. The maximum volume change was calibrated during equilibration simulations. Mechanical properties such as enthalpy and volume were calculated as the statistical averages of these quantities over the course of the simulations.²³ Heat capacity, C_p ,

FIG. 1. The core-softened potential $U(r)$ (solid line), the LJ contribution (long dashed line), and the Gaussian part (dashed line).

isothermal compressibility, κ , and thermal expansion coefficient, α are computed from the fluctuation formulas of enthalpy, H , and volume, V ,²⁴

$$\begin{aligned} c_p &= \frac{\langle H^2 \rangle - \langle H \rangle^2}{NT^2}, \\ \kappa &= \frac{\langle V^2 \rangle - \langle V \rangle^2}{T\langle V \rangle}, \\ \alpha &= \frac{\langle VH \rangle - \langle V \rangle \langle H \rangle}{T^2\langle V \rangle}. \end{aligned} \quad (4)$$

IV. INTEGRAL EQUATION THEORY

The integral equation theory is based on the Ornstein-Zernike (OZ) equation which was proposed by Leonard Salomon Ornstein and Frits Zernike in 1914.²⁵ The OZ equation relates the total correlation function, $h(r)$, with the direct correlation function $c(r)$ as

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})h(r_{32})d\mathbf{r}_3. \quad (5)$$

Here ρ is the density of particles. The total correlation function, $h(r)$ is related to the pair distribution function, $g(r)$, as $g(r) = h(r) + 1$. In order to solve the OZ, we need an additional relation between $h(r)$ and $c(r)$, called the closure relation, which assumes the general form²⁶

$$g(r) = \exp(-\beta U(r) + h(r) - c(r) + B(r)). \quad (6)$$

Here β is the reverse temperature, $\beta = \frac{1}{kT}$, $U(r)$ is the interaction potential between particles, and $B(r)$ is the bridge function, which is an infinite series of irreducible cluster diagrams and is not known. Various approximations are employed for the bridge function. The simplest option is the hypernetted chain (HNC) approximation, which neglects the bridge function ($B(r) = 0$), and simplifies the closure relation to²⁶

$$g(r) = \exp(-\beta U(r) + h(r) - c(r)). \quad (7)$$

Another simple approximation was proposed by Percus and Yevick.^{27,28} The Percus-Yevick (PY) closure is obtained as linearization of HNC closure and is written as

$$g(r) = \exp(-\beta U(r))(1 + h(r) - c(r)). \quad (8)$$

Several other closures have been developed to address the shortcomings of HNC and PY, especially a narrow region of convergence and inherent thermodynamic inconsistency. The Kovalenko-Hirata closure (KH),²⁹ constructed to expand the convergence region, takes the following form:

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

where $d(r) = -\beta U(r) + h(r) - c(r)$. The Rogers-Young closure (RY)³⁰ is constructed to obey the consistency between the compressibility and virial pressure. This is done by interpolating between the HNC and PY closures based on equating the isothermal compressibilities from virial and compressibility routes. The RY closure has the following

form:

$$h(r) = \exp(-\beta U(r)) \left(1 + \frac{\exp(f(r)(h(r) - c(r))) - 1}{f(r)} \right) - 1, \quad (9)$$

where $f(r) = 1 - \exp(-\eta r)$ and parameter η varies with temperature and density and is chosen on the self-consistency condition

$$(\rho k T \chi_T^v)^{-1} = \left(\frac{\partial \beta P^v}{\partial \rho} \right) = 1 - \rho \int c(r) 2\pi r dr = (\rho k T \chi_T^c)^{-1}, \quad (10)$$

where virial pressure is evaluated as

$$\beta P^v = \rho - \frac{\pi \beta \rho^2}{2} \int_0^\infty \frac{dU}{dr} g(r) r^2 dr. \quad (11)$$

We have also implemented the soft mean-spherical approximation (SMSA). In this closure, we divide the LJ part of potential into a short-range reference part $U_0(r)$ and a longer range perturbation part $U_1(r)$ as suggested in Ref. 31,

$$U_{LJ}(r) = U_0(r) + U_1(r), \quad (12)$$

where

$$U_0(r) = \begin{cases} U_{LJ}(r) + \varepsilon_{LJ} & r \leq r_m \\ 0 & r > r_m \end{cases}$$

and

$$U_1(r) = \begin{cases} -\varepsilon_{LJ} & r \leq r_m \\ U_{LJ}(r) & r > r_m \end{cases}.$$

The distance r_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., $r_m = 2^{1/6} \sigma_{LJ}$. The SMSA closure relation is then written in the following form:

$$g(r) = \exp(-\beta U_0(r)) (1 + h(r) - c(r) - \beta(U_1(r) + U_G(r))). \quad (13)$$

The OZ equation together with the closure condition was solved by a direct iteration. The forward and inverse Bessel-Fourier transforms, needed to couple the correlation functions in real and Fourier spaces, have been performed by the method of Talman.³²

V. RESULTS AND DISCUSSION

Results are given in reduced units; excess internal energy and temperature are normalized to the LJ interaction parameter ε ($E^* = \frac{E}{\varepsilon}$, $T^* = \frac{k_B T}{\varepsilon}$) and the distances are scaled to the characteristic length σ ($r^* = \frac{r}{\sigma}$).

In Figure 2(a), we present the temperature dependence of density for the high density liquid phase for different isobars obtained from the Monte Carlo simulations in the N,p,T ensemble. We observed density maxima for reduced pressures $p^* = 1.0$ or lower. Figure 2(b) shows the region with density maxima in more details. In addition to density of the high density fluid we also plotted temperature dependence of density for the low density liquid phase. We also present temperature of maximum density line. At low pressures high density liquid changes to low density liquid on decrease of temperature.

FIG. 2. (a) Temperature dependence of the density for different isobars for high density liquid. Results are for pressures 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2.0, and 3.0 from bottom up. Lines are plotted as guide for the eye. (b) Temperature dependence of the density for different isobars. Results are for pressures 0.25 (red solid line), 0.5 (green long dashed line), 0.6 (blue dashed line), 0.75 (pink dotted line), and 1.0 (orange dashed-dotted line). Lines are plotted as guide for the eye. Black points are maximum densities. (c) The density jumps along isobars for reduced pressure 1.0 (red solid line) and 0.75 (green dashed line).

At pressure 1.0 or higher, pressure is too high for observation of the low density liquid phase. Upon decrease of temperature high density liquid phase (snapshot in Figure 3(a)) freezes into dense solid phase (snapshot in Figure 3(d)). This is demonstrated in Figure 2(c), where we plotted temperature dependence of density including solid phases for pressure 1.0 and 0.75. Upon decrease of temperature at lower pressure, high density liquid first changes into low density liquid (snapshot in Figure 3(b)) and then freezes into the low density solid (snapshot in Figure 3(c)). From snapshots in Figure 3, we see that the system has a density hexagonal solid phase, a cubic solid phase; at very high pressures ($p^* > 10$) we also observed a high density hexagonal solid phase. Snapshots for high density liquid phase at different pressures and

FIG. 3. Snapshots of the system for: (a) $p^* = 1.0$, $T^* = 0.55$; (b) $p^* = 1.0$, $T^* = 0.575$; (c) $p^* = 0.75$, $T^* = 0.425$, and (d) $p^* = 1.0$, $T^* = 0.475$.

temperatures are topologically similar as the one plotted in Figure 3. From these MC results, we can conclude that model has water-like density anomalies. At low pressures, the model freezes in a low density solid phase which has lower density than a liquid phase. In the liquid range the model has density maxima which disappear at high pressures. The same behavior was also observed by molecular dynamics by Scala *et al.*²²

Next, we explored other thermodynamic properties, such as isothermal compressibility (Figure 4), thermal expansion coefficient (Figure 5) and heat capacity (Figure 6). Isothermal compressibility has minimum in temperature dependence like water has. At higher temperatures, compressibility decreases as pressure increases. The same behavior we observe also at low temperatures. When high density liquid changes to low density liquid, there is a divergence in isothermal compressibility which confirms phase transition. Thermal expansion coefficient is positive at high temperatures, this means that volume of the system increases with increase of temperature and decreases with the increase of pressure, at low temperature increase of pressure has the opposite effect. Thermal

FIG. 4. Temperature dependence of the isothermal compressibility for different isobars. Results are for pressures 0.25 (red solid line), 0.5 (green long dashed line), 0.6 (blue dashed line), 0.75 (pink dotted line), and 1.0 (orange dashed-dotted line). Lines are plotted as guide for the eye.

FIG. 5. Temperature dependence of the thermal expansion coefficient for different isobars. Results are for pressures 0.25 (red solid line), 0.5 (green long dashed line), 0.6 (blue dashed line), 0.75 (pink dotted line), and 1.0 (orange dashed-dotted line). Lines are plotted as guide for the eye.

expansion coefficient is negative at low temperatures. In this temperatures range, the liquid density decreases with increase of temperature. Heat capacity is almost constant at high temperatures and decreases with increase of pressure. When we are approaching the liquid-liquid phase transition heat capacity increases, showing divergence and phase transition. Heat capacity is also having minimum in the high density liquid phase.

We also calculated also liquid-gas and liquid-liquid critical points. Figure 7(a) shows isotherms around liquid-gas critical point. We calculated the pressure as a function of density for several isotherms. Below the critical temperature, isotherms display typical phase transition behavior where pressure decreases as density increases and the Maxwell construction can be done for determination of two phases in equilibrium. Critical point by definition is the saddle on the critical isotherm, where $(\frac{\partial p}{\partial T})_V = (\frac{\partial^2 p}{\partial T^2})_V = 0$. On the interpolated polynomial curves fitted to data, we estimated the liquid-gas critical point (C1) to be at $T_{C1}^* = 1.082 \pm 0.005$, $p_{C1}^* = 0.0614 \pm 0.0001$, and $\rho_{C1}^* = 0.33 \pm 0.01$. Figure 7(b) shows isotherms around liquid-liquid critical point. By extrapolation we estimated the liquid-liquid critical point (C2) to be at $T_{C2}^* = 0.628 \pm 0.005$, $p_{C2}^* = 0.48 \pm 0.01$, and $\rho_{C2}^* = 0.598 \pm 0.005$.

Pair distribution function $g(r)$ was calculated for several densities and temperatures by Monte Carlo simulation and

FIG. 6. Temperature dependence of the heat capacity for different isobars. Results are for pressures 0.25 (red solid line), 0.5 (green long dashed line), 0.6 (blue dashed line), 0.75 (pink dotted line), and 1.0 (orange dashed-dotted line). Lines are plotted as guide for the eye.

FIG. 7. (a) p - V isotherms in region of the liquid-gas critical point for $T^* = 1.05$ (red), for $T^* = 1.08$ (blue), and $T^* = 1.10$ (green). (b) p - V isotherms in region of the liquid-liquid critical point for $T^* = 0.62$ (red), $T^* = 0.63$ (green), and for $T^* = 0.64$ (blue).

FIG. 9. The pair distribution functions from MC simulations and IET at $T^* = 1.1$ and $\rho^* = 0.7$. Legend same as in Figure 8.

FIG. 8. The pair distribution functions from MC simulations (symbols) for $T^* = 1.1$ and $\rho^* = 0.5$ and from IET (a) PY (blue dashed line) and HNC (green long dashed line); (b) SMSA (blue dashed line) and KH (green long dashed line).

FIG. 10. The pair distribution functions from MC simulations (symbols) for $T^* = 0.6$ and $\rho^* = 0.6$ and from IET SMSA (blue dashed line), KH (green long dashed line), and HNC (pink dotted line).

FIG. 11. The pair distribution functions from MC simulations and IET at $T^* = 0.6$ and $\rho^* = 0.65$. Legend same as in Figure 10.

TABLE I. The comparison of pressure for different IET closures with Monte Carlo calculations.

T^*	ρ^*	P_{MC}^*	P_{HNC}^*	P_{PY}^*	P_{KH}^*	P_{RY}^*	P_{SMSA}^*
1.5	0.4	0.341	0.443	0.543	0.423	...	0.322
1.5	0.6	1.501	2.078	2.094	2.171	...	1.523
1.1	0.5	0.136	0.424	0.661	0.389	...	0.178
1.1	0.7	2.677	3.319	2.712	2.268	...	2.280
0.6	0.65	0.621	0.342	...	0.291	...	-0.082
0.6	0.6	1.073	0.929	...	0.975	...	0.379

the integral equation theory with different closures. We compared the results from integral equations with PY, HNC, KH, SMSA, RY closures and our Monte Carlo simulation results. Figures 8–11 show this comparison. The Monte Carlo results are represented by symbols and the IET results are shown by lines. The agreement between IETs and the Monte Carlo simulations is only semi-quantitative in all range. IETs correctly predict the positions of the pair distribution function peaks, but not their heights. In other words, the pair distribution function obtained by the approximate theory shows less structure than the corresponding function resulting from computer simulations. Somehow the best agreement is for the SMSA closure. PY closure lacks the convergence at temperatures lower than 1.0. The situation with the RY closure is completely different than other ones. There is no thermodynamically self-consistent solution to this closure and as such no solution for all temperatures and densities. The same kind of failure was also observed earlier in a different system by Lang *et al.*³³ RY closure is mixture of PY and HNC closure. For RY to work, the PY closure should typically predict too low pressures, and on the other hand, the HNC too high pressures. In our case both PY and HNC pressures are too high, which is the reason for the RY failure. In Table I, we printed the calculated pressure by MC and IET for different closures. SMSA pressure agrees quite well at higher temperatures, while other closures fail. At lower temperatures, all closures of integral equations fail to reproduce the simulation results.

VI. CONCLUSIONS

We have discussed the thermodynamics, structure, and phase transitions in 2D core-softened models, using Monte Carlo computer simulations and different variants of integral equation theories with various closures: PY, HNC, SMSA, Rogers-Young, and Kovalenko-Hirata. We have calculated the liquid-gas and the liquid-liquid phase transition and determined both critical points. The liquid-liquid transition state points inside the coexistence region separate into two phases characterized by different densities and structures. We find that the fluid with the core-softened potential exhibits the same kind of anomalies as water, including the volumetric and thermal anomalies: solid is less dense than liquid, has a temperature of maximum density in the liquid range, a large heat capacity, a minimum in the isothermal compressibility, and a thermal expansion coefficient that is negative in the low-temperature liquid range. The IET is somewhat less demanding from the computational point of view than the

Monte Carlo simulations; however, it reproduces the structure only qualitatively. We systematically examined several closures and the results are: the RY closure completely fails, the PY loses convergence at low temperatures. HNC, SMSA, and KH fail at predicting the proper height of the peak located at the minimum of the potential. This version of IET is not suitable for such systems due to the strong association of particles.

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