

Local Structure and Thermodynamics of a Core-Softened Potential Fluid: Theory and Simulation

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Phase behavior and structural properties of homogeneous and inhomogeneous core-softened (CS) fluid consisting of particles interacting via the potential, which combines the hard-core repulsion and double attractive well interaction, are investigated. The vapor-liquid coexistence curves and critical points for various interaction ranges of the potential are determined by discrete molecular dynamics simulation to provide guidance for the choice of the bulk density and potential parameters for the study of homogeneous and inhomogeneous structure. Spatial correlations in the homogeneous CS system are studied by the Ornstein-Zernike integral equation in combination with the modified hypernetted chain (MHNC) approximation. The local structure of CS fluid subjected to diverse external fields maintaining the equilibrium with the bulk CS fluid are studied on the basis of a recently proposed third order + second order perturbation density functional approximation (DFA). The accuracy of DFA predictions is tested against the results of a grand canonical ensemble Monte Carlo simulation. Reasonable agreement between the results of both methods proves the DFA theory applied in this work as a convenient theoretical tool for the investigation of the CS fluid, which is practically applicable for modeling of numerous real systems.

1. Introduction

Recently, behavior of single component systems comprised of particles interacting via

core-softened (CS) potentials has attracted a lot of attention ^[1] (see also Ref. 2 and references therein for a recent review). CS potentials exhibit a repulsive hard core plus a softening region, which can be a linear or non-linear repulsive ramp, a shoulder, a double (or multiple) attractive well, or a combination of all these features.^[3-12] These models were created with the purpose of constructing simple two-body isotropic potential capable of describing some aspects of anomalous behavior of water and some other fluids,^[13-15] like the maximum in density as a function of temperature, the increase of the isothermal compressibility upon cooling, and the increase of the molecular diffusivity upon compression. It has been proposed some time ago that these anomalies might be associated with a critical point at the terminus of a liquid-liquid line, in the unstable supercooled liquid region.^[16-18]

In the present work, we investigate a three-dimensional CS potential, which besides the hard-core repulsion incorporates a double square-well attractive interaction. On the contrary to the CS potentials exhibiting repulsive ramp or shoulder in a softening region, which gives rise to a second liquid-liquid critical point, the CS system comprising a fully attractive softening region of the potential function has only the gas-liquid critical point. However, a detailed phase behavior of this kind of CS model fluid has not been studied so far. For this reason, we have first determined the gas-liquid phase diagrams for various ranges of the individual square wells of the potential utilizing discrete molecular dynamics (DMD) simulation, which enables a treatment of the discontinuous step-wise potentials. From these diagrams, we could then read the range of parameters where the bulk CS fluid represents the one-phase system. They therefore served as a basis for the appropriate choice of bulk density and potential parameters, at which we studied the structural features of CS model fluid in

homogeneous phase and the inhomogeneous structure of the same fluid subjected to various external fields originating from the presence of various spatial constraints. For the latter, we have chosen a hard flat interface and a closed spherical surface mimicking a spherical cavity. For this purpose, we apply a recently proposed third order + second order perturbation density functional approximation (DFA), which has already proven successful in the structural studies of the systems of particles interacting via continuous potentials, i.e., the hard-core attractive Yukawa (HCAY),^[19] Lennard-Jones,^[20] and hard-core repulsive Yukawa^[21] systems. In the present work we extend these previous investigations on the applicability of this theory to a discontinuous (step-wise) type of interparticle potential. The quality of the performance of DFA theory is tested against the results of a grand canonical ensemble Monte Carlo (GCEMC) simulation.

The Section 2 contains a description of the models and the methods used in this study, i.e., the DMD and GCEMC simulation and the third order + second order perturbation DFT approach. Gas-liquid coexistence curve for various interaction ranges following from DMD simulations and numerical results for the bulk radial distribution function and for the inhomogeneous density profiles obtained by the DFT theory and GCEMC simulations are presented in the Section 3. Finally, some concluding remarks are summarized in the last Section 4.

2. Computational methods

2.1. Models

In this work, we study the system of particles interacting via a core-softened (CS) attractive pair potential

$$\begin{aligned}
 u(r) &= \infty, & r < \sigma \\
 &= -\delta\varepsilon, & \sigma < r < b \\
 &= -\varepsilon, & b < r < c \\
 &= 0, & r > c
 \end{aligned} \tag{1}$$

where σ is the hard-core diameter, while $\delta\varepsilon$ and ε are the depths of the two successive attractive wells of widths $b - \sigma$ and $c - b$, respectively. In our calculations δ is fixed at 0.5. Throughout this paper, we measure density, pressure, and temperature in units of σ^{-3} , $\varepsilon\sigma^{-3}$, and ε/k , respectively, where k is the Boltzmann constant. The corresponding reduced quantities are denoted as $\rho^* = \rho_b\sigma^3$, $P^* = P\sigma^3/\varepsilon$, and $T^* = kT/\varepsilon$.

Further, we investigate two cases of the source for the external potential $\varphi_{ext}(\mathbf{r})$. Besides the single hard wall we treat also a spherical cavity surrounded by the spherical hard wall. The external potentials due to the presence of these spatial constrains read:

$$\begin{aligned}
 \varphi_{ext}(z) &= \infty, & z < 0.5\sigma \\
 &= 0, & z > 0.5\sigma
 \end{aligned} \tag{2}$$

for a single hard wall, and

$$\begin{aligned}\varphi_{ext}(r) &= \infty, & r > R - 0.5\sigma \\ &= 0, & r < R - 0.5\sigma\end{aligned}\tag{3}$$

for a spherical cavity of radius R .

2.2. Discrete Molecular Dynamics (DMD)

As we mention in the introduction a system with the interparticle potential given by Equation (1) can have a second, liquid-liquid critical point, only if $\delta < 0$. In our case $\delta = 0.5$, thus the system has only the gas-liquid critical point. The simulation time is measured in units $\sigma(m/\varepsilon)^{1/2}$, where m is the mass of the particle.

The discontinuous step-wise potentials cannot be treated efficiently by a regular molecular dynamics based on the integration of the Newton's equations of motion with a fixed time step. These types of potentials including the simplest case, the hard spheres are usually simulated by the event driven molecular dynamics invented by Alder and Wainwright.^[22] This method was successfully used for simulations of polymers^[23] and proteins.^[24,25] It is presented in detail in Refs. [26] and [27]. The natural ensemble for the DMD simulations is the NVE ensemble, in which number of particles N , volume V , and total energy E are kept constant. We use a system of $N=1728$ particles in the cubical boxes of various volumes with periodic boundary conditions. To keep temperature T constant, we use a modified Berendsen method.^[28] We compute pressure P using the virial

theorem in the same way as in Refs. [10], [11], [29] and [30], averaging it over a certain period of time. The methods of the estimation of the critical point and the coexistence line from the constant volume molecular dynamics are discussed in Ref. [31].

2.3. Open Ensemble Simulation

For the core-softened (CS) model of Equation (1) we have carried out Grand Canonical Ensemble Monte Carlo (GCEMC) simulations at constant chemical potential μ , volume V , and temperature T . This set of independent parameters that define the thermodynamic state of the system made possible the study of equilibrium between the bulk CS fluid and that subjected to external fields originating from the presence of various spatial constrains. For the latter, we have chosen a hard flat interface and a closed spherical surface mimicking a spherical cavity. In this way we consider different geometries of confinement ranging from the simplest case of a single wall to the highest possible degree of confinement that fluid ‘feels’ in the spherical cavity. The general features of the GCEMC method are described elsewhere.^[26] Further, some details peculiar to this study are discussed in one of our previous works.^[19] In the present study we determined some thermodynamic properties following from the simulation of bulk CS fluid. The reduced excess Helmholtz free energy has been calculated from the general expression

$$\frac{A^{ex}}{\langle N \rangle kT} = \frac{\mu_b^{ex}}{kT} - Z - \ln \rho_b + 1 \quad (4)$$

where the reduced excess chemical potential of the bulk fluid μ_b^{ex}/kT is one of the input parameters, while the bulk density ρ_b and the compressibility factor $Z = P/\rho_b kT$ result from the open ensemble simulation, where the bulk pressure P has been calculated using virial equation. The final expression resembles that for the single square-well fluid with the only difference that we have to consider additional discontinuity at $r = c$. The final expression reads:

$$Z = \frac{P}{\rho_b kT} = 1 + \frac{2\pi \rho_b}{3} \left\{ \sigma^3 \cdot g(\sigma_+) + b^3 \cdot [g(b_+) - g(b_-)] + c^3 \cdot [g(c_+) - g(c_-)] \right\} \quad (5)$$

where $g(\sigma_+)$, $g(b_+)$, $g(b_-)$ etc. represent extrapolated values at the discontinuity points of the CS potential. Subscripts (+) and (-) denote extrapolation to these points from the right and from the left, respectively.

2.4. Third order + second order perturbation density functional theory

Spirit of the third order + second order perturbation DFT approach bases on the fact that the non-uniform quantities associated with the hard core part (denoted by subscript *hc*) of the interaction potential is treated by the third order functional perturbation expansion approximation (FPEA), while those associated with the tail part (denoted by subscript *tail*), whose dependence on the density argument is very weak, can be treated satisfactorily by the

second order FPEA.^[32,33] By direct application of the bulk hard sphere third order DCF^[34] to the hard core part of the bulk third order DCF of the fluid under consideration, one obtains the final expression for the non-uniform first order DCF,

$$C^{(1)}(\mathbf{r};[\rho]\cdots) = C_0^{(1)}(\rho_b \cdots) + \int d\mathbf{r}' [\rho(\mathbf{r}') - \rho_b] C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b \cdots) \\ + \frac{C_{0hc}^{(1)''}(\rho_b \cdots)}{2[C_{0hc}^{(1)}(\rho_b \cdots)]^3} \int C_{0hc}^{(2)}(\mathbf{r}, \mathbf{r}''; \rho_b \cdots) \left[\int C_{0hc}^{(2)}(\mathbf{r}', \mathbf{r}''; \rho_b \cdots) (\rho(\mathbf{r}') - \rho_b) d\mathbf{r}' \right]^2 d\mathbf{r}'' \quad (6)$$

Throughout the text, superscript (n) denotes the corresponding n -order quantities; absence of the subscript 0 refers to non-uniform case, while the presence of the subscript 0 refers to

the uniform case. The coefficient $\frac{C_{0hc}^{(1)''}(\rho_b \cdots)}{2[C_{0hc}^{(1)}(\rho_b \cdots)]^3}$ in the above Equation (6) is used as an

adjustable parameter denoted by λ . Then we finally have:

$$C^{(1)}(\mathbf{r};[\rho]\cdots) = C_0^{(1)}(\rho_b \cdots) + \int d\mathbf{r}' [\rho(\mathbf{r}') - \rho_b] C_0^{(2)}(|\mathbf{r} - \mathbf{r}'|; \rho_b \cdots) \\ + \lambda(\rho_b \cdots) \int C_{0hc}^{(2)}(\mathbf{r}, \mathbf{r}''; \rho_b \cdots) \left[\int C_{0hc}^{(2)}(\mathbf{r}', \mathbf{r}''; \rho_b \cdots) (\rho(\mathbf{r}') - \rho_b) d\mathbf{r}' \right]^2 d\mathbf{r}'' \quad (7)$$

Combination of Equation (7) with the DFT expression for the density profile of a single component fluid,

$$\rho(\mathbf{r}) = \rho_b \exp\{-\beta\varphi_{ext}(\mathbf{r}) + C^{(1)}(\mathbf{r};[\rho]\cdots) - C_0^{(1)}(\rho_b \cdots)\} \quad (8)$$

leads to the formalism enabling the calculation of the density profile $\rho(\mathbf{r})$ of the fluid subjected to diverse external fields. Here $\varphi_{ext}(\mathbf{r})$ is the external potential responsible for the generation of the inhomogeneous spatial density distribution $\rho(\mathbf{r})$, and β is the inverse thermal energy, $\beta=1/kT$. This DFT approach incorporates two externally imported parameters, i.e., the bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ and the pressure of the coexistence bulk fluid in the reservoir with which the inhomogeneous fluid under consideration is in equilibrium.

A convenient route for the determination of the bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ is numerical solution of the Ornstein-Zernike (OZ) integral equation (IE),^[35]

$$h(r) - C_0^{(2)}(r; \rho_b \dots) = \rho_b \int d\mathbf{r}_1 h(\mathbf{r}_1) C_0^{(2)}(|\mathbf{r} - \mathbf{r}_1|; \rho_b \dots), \quad (9)$$

along with a closure relation,

$$h(r) + 1 = \exp\{-\beta u(r) + \gamma + B(r)\}. \quad (10)$$

Above, $\gamma(r) = h - C_0^{(2)}(r; \rho_b \dots)$ is the indirect correlation function and $h(r) = g(r) - 1$ is the total correlation function with $g(r)$ being the radial distribution function (RDF). B is the so-called bridge function, which is the sum of “bridge” or “elementary” graphs in the diagrammatic analysis of the two-point functions. Although there exists a formal relationship between $B(r)$ and $g(r)$, it involves an infinite sum of highly connected diagrams, which render its utilization in practical calculation impossible. For this reason, an approximation

for $B(r)$ has to be made.^[35] After trying to use numerous bridge function approximations, we found the modified hypernetted chain (MHNC) approximation^[36,37] as the most appropriate for the calculation of the bulk RDF $g(r)$ for the core-softened model fluid considered in this work. Since $g(r)$ is connected with the bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ through the OZ IE, the MHNC approximation certainly performs well also for the prediction of the $C_0^{(2)}(r; \rho_b \dots)$. Therefore, throughout the present calculations, MHNC approximation is employed to provide the required bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$, which then enters the DFT calculations. Implementation of the MHNC approximation needs the hard sphere bridge function as an input. In the present investigation, we employ the following approximate hard sphere bridge function:

$$\begin{aligned}
 B_{hs}(r) &= \ln(y_{hs}(r)) + 1 + C_{0hs}^{(2)}(r) & r < \sigma_{hs} \\
 & \ln(g_{hs}(r)) + C_{0hs}^{(2)}(r) + 1 - g_{hs}(r) & r > \sigma_{hs}
 \end{aligned} \tag{11}$$

where $\ln(y_{hs}(r))$ is logarithm of the hard sphere cavity correlation function, $C_{0hs}^{(2)}(r)$ the bulk second order DCF of hard sphere fluid, and $g_{hs}(r)$ the RDF of the hard sphere fluid, given by the simulation data-fitting formulas of Ballance and Speedy,^[38] of Groot, van der Eerden, and Faber,^[39] and of Verlet and Weis,^[40] respectively. Therefore we call the Equation (11) as GvEF-BS-VW bridge function. In a recent paper,^[41] it has been shown that a combination of the GvEF-BS-VW hard sphere bridge function and the MHNC approximation performs very well for the Lennard-Jones fluid. The MHNC approximation is associated with an adjustable parameter, i.e. the effective hard sphere diameter d , whose value we specify by a local thermodynamic self-consistency condition. For the details about the numerical

procedure, we refer the reader to Ref. [41].

The other external parameter imported in the DFT calculations is the pressure of the coexistence bulk fluid, with which the inhomogeneous fluid under consideration is in equilibrium, needed for the determination of the adjustable parameter λ by a sum rule.^[19] In order to avoid small errors of the bulk pressure originating from the use of the approximate equation of state (EOS) or that calculated by OZ integral equation, which can then interfere the reliability of the judgment on the quality of the performance of the DFT approach, we utilize the simulation result for the pressure as an input. In practical cases, one can also employ the pressure based on the EOS or OZ integral equation, which, however, gives rise to small quantitative errors in the calculations, but does not affect the qualitative features of the results.

Concerning the division of the bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ into the hard-core part $C_{0hc}^{(2)}(r; \rho_b \dots)$ and the tail part $C_{0tail}^{(2)}(r; \rho_b \dots)$, the procedure described in a series of previous works^[19-21, 32, 33] can be followed:

$$C_0^{(2)}(r; \rho_b \dots) = C_{0hc}^{(2)}(r; \rho_b \dots) + C_{0tail}^{(2)}(r; \rho_b \dots) \quad (12)$$

where

$$C_{0hc}^{(2)}(r; \rho_b \dots) = \begin{cases} C_0^{(2)}(r; \rho_b \dots) & r < r_{cut} \\ = 0 & r > r_{cut} \end{cases} \quad (13)$$

and

$$\begin{aligned}
 C_{0tail}^{(2)}(r; \rho_b \dots) &= 0 & r < r_{cut} \\
 &= C_0^{(2)}(r; \rho_b \dots) & r > r_{cut}
 \end{aligned} \tag{14}$$

Here r_{cut} specifies the distance at which the bulk second order DCF is divided into a hard-core part and a tail part. For the core-softened potential of our present interest, the hard sphere diameter σ should obviously be chosen for r_{cut} as $g(r)=0$ for $r < \sigma$. This indicates a strong dependence of the bulk second order DCF on the density argument for the distances $r < \sigma$.

3. Results and discussion

3.1. Phase behavior

The discrete molecular dynamics (DMD) simulation method has been used to determine equilibrium densities and vapor pressures for CS fluid with reduced ranges (in units of σ) $b = 1.4, c = 2$, $b = 1.2, c = 1.5$, and $b = 1.1, c = 1.2$, at several temperatures. In all calculations the parameter δ in the potential function of Equation (1) was fixed at 0.5, which means that the depth of the intermediate attractive well of the width $b - \sigma$ is half of that in the range $c - b$. Some resulting values for the vapor-liquid coexistence densities ρ_V^* and ρ_L^* , pressures P^* and the corresponding critical values for the CS fluid of different ranges are gathered in Table I. These data are shown in full in the phase diagrams

depicted in Figure 1. The critical parameters for the individual ranges of the CS potential were assessed as $T_c^* = 2.237, \rho_c^* = 0.238$ ($b = 1.4, c = 2$), $T_c^* = 1.025, \rho_c^* = 0.29$ ($b = 1.2, c = 1.5$), and $T_c^* = 0.545, \rho_c^* = 0.410$ ($b = 1.1, c = 1.2$), respectively.

3.2. Homogeneous and inhomogeneous structure

The theoretical and simulation results for the structure of CS fluid in various physical situations are presented in Figures 2-13. Calculations were performed for the ranges of potential, for which the phase diagrams are known, i.e. for the same three sets of potential parameters as described in the preceding subsection. For $b = 1.4, c = 2$ and $b = 1.1, c = 1.2$ the calculations were carried out at the supercritical temperature $1.5 \cdot T_c^*$, while for $b = 1.2, c = 1.5$ the chosen supercritical temperature was closer to the critical value, i.e. $1.08 \cdot T_c^*$. Further, for the first set $b = 1.4, c = 2$ two subcritical temperatures, $0.98 \cdot T_c^*$ and $0.8 \cdot T_c^*$, were also considered. In turn, Figures 2a, 3a, 4a and 5 display the radial distribution function (RDF) of the bulk CS fluid for the individual sets of potential parameters and at different densities, whereas Figures 6-13 show the density profiles of the same fluid: (i) at a single hard wall (Figures 6-9), and (ii) in a hard spherical cavity of the radius $R = 4\sigma$ (Figures 10-13). For the sake of clarity, the majority of these figures are subdivided into two or three parts, which successively illustrate the effect of increase in the bulk density at constant values of potential parameters.

Bulk RDFs are computed by solving the OZ integral equation in combination with the

MHNC approximation for the bridge function. The shape of $g(r)$ resembles that for the usual single square-well fluid with the only difference that it exhibits two step discontinuities due to the double attractive well in the CS potential function. Rapid look at the resulting RDFs indicates very good agreement between the results obtained by the approximate integral equation theory and simulation data. For this reason, we can utilize the bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ based on the MHNC approximation for the bridge function as an input for our DFT formalism necessary for the determination of the inhomogeneous fluid structure. In Figures 2b, 3b, and 4b the bulk second order DCF as a function of the interparticle distance is plotted for individual sets of potential parameters and at different bulk densities. For the interparticle separations $r > \sigma$ we can observe very weak dependence on the density, the opposite is true for the separations $r < \sigma$. It is therefore natural to separate the function $C_0^{(2)}(r; \rho_b \dots)$ into the hard-core part $C_{0hc}^{(2)}(r; \rho_b \dots)$ and the tail part $C_{0tail}^{(2)}(r; \rho_b \dots)$ as described in the Section 2.4.

The present results for the inhomogeneous structure of the CS fluid displayed in Figures 6-13 show the characteristic structural features as reported by numerous articles in the literature dealing with the behavior of fluids at interfaces and in confined systems. In the vicinity of the wall(s) of the spatial constraints the interparticle interactions compete with steric effects leading to characteristic density profile, whose actual shape depends on the particular interactions among the fluid particles and in addition, on the temperature of the system. In any case, the interactions among the molecules gain in importance upon lowering temperature. In the case of CS attractive model fluid, the attractive molecules have a better chance for mutual attraction at sufficient distances from the wall(s) or outside the confined

system. For this reason, they are driven away from the hard obstacles or toward the center of the micro-objects with restricted geometry (spherical cavity). The stronger the attraction among the molecules, which is characterized by the range and the depth(s) of the potential well(s), and/or the lower the temperature, the more pronounced this effect. This can be clearly seen, for example, in Figures 9 and 13, which depict the density profiles for $b = 1.4, c = 2$ at an isolated wall (Figure 9) and in spherical cavity (Figure 13) at two rather low temperatures. In these cases the contact densities of the fluid are much lower than those for higher temperatures seen in Figures 6 and 10, when comparing the values that correspond to the same equilibrium (bulk) densities. Further discussion about the detailed structure is not necessary, as it would resemble those found in a series of studies reported in the literature. Namely, the main goal of the present study is an assessment of the quality of the performance of the perturbation DFT theory for the prediction of the inhomogeneous structure of the CS fluid.

A careful inspection of the results for the local structures of CS fluid in two different inhomogeneous systems displayed in Figures 6-13 indicates fair to very good agreement between the DFT predictions and simulation data. As expected, the accuracy of the pure theory depends on the expressiveness of the ‘inhomogeneity’ of the system. It therefore performs better in the case of a single hard wall (Figures 6-9) as a source of the external field, whereas slight to rather high discrepancies between the DFT and simulation results are observed in the case of much higher degree of confinement imposed in the spherical cavity (Figures 10-13). However, also in the latter case almost quantitative agreement between the results of both methods is observed in most cases, the exception being the DFT density

profiles referring to lower temperatures (Figures 11 and 13), which, nevertheless, still agree qualitatively with simulation data. We can therefore conclude that the third order + second order perturbation DFT approach represents an adequate theoretical tool for the investigations of the inhomogeneous structure of the CS fluid comprising a double attractive square well in the softening region of the potential function. As similar findings have been established for some purely repulsive fluids^[42] subjected to the same external fields, one can speculate that the present theory would be convenient also for other CS models incorporating repulsive part(s) in the softening region of the potential.

4. Conclusions

In this paper we report on the phase behavior and structural properties of homogeneous and inhomogeneous core-softened (CS) fluid consisting of particles interacting via the potential, which combines the hard-core repulsion and double attractive well interaction. First, the vapor-liquid coexistence curves and critical points for various interaction ranges of the potential were determined by discrete molecular dynamics simulation. On the basis of the corresponding phase diagrams we made appropriate choices for the values of potential and density parameters at which the calculations were performed. Spatial correlations in the homogeneous CS system were studied by the OZ integral equation along with the MHNC approximation. Inhomogeneous structure of the CS fluid subjected to various external fields was investigated by the third order + second order DFT approach. Theoretical DFT

predictions for the density profiles of the CS fluid are compared with the results of a grand canonical ensemble Monte Carlo simulation. Reasonable agreement between the theoretical results and simulation data for the inhomogeneous structure of the CS fluid indicates that the present theory can be successfully applied to the multiple discontinuous CS models. The CS model is known to reproduce anomalous thermal expansion and liquid-liquid phase transitions in some real fluids. As it is usually considered as a zero-th order approximation for the modeling of water, our DFT approach certainly settles a foundation of sophisticated theory for more practical model of water. Adsorption of water in porous materials is of great practical importance and finds applications in geophysics, pharmaceuticals and many other fields, where the evoked processes take advantage of the effect of confinement of water on nanometer scale.^[43,44] As the appropriate choice of the potential parameters links the CS model to the corresponding parameters of more practical model potentials for water, the present DFT approach can be applied to the theoretical investigation of the properties of water at confined conditions. Results of the works along this line will be reported in succeeding publications.

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Figure legends

Figure 1. Vapor-liquid coexistence curve $T^* = kT/\varepsilon$ versus $\rho^* = \rho_b \sigma^3$ for CS fluid of the range parameters: (a) $b = 1.4, c = 2$, (b) $b = 1.2, c = 1.5$, and (c) $b = 1.1, c = 1.2$.

Figure 2. (a) The theoretical (lines) and simulation (symbols) results for the bulk radial distribution function of the CS model fluid of the range parameters $b = 1.4, c = 2$ at the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 3.38$ and at different densities $\rho^* = \rho_b \sigma^3$. Theoretical predictions are obtained by the use of the OZ integral equation combined with the MHNC approximation. For the reason of clarity, the data corresponding to individual densities are shifted upwards by different factors (0.5, 1, 1.5, etc.). (b) Bulk second order DCF $C_0^{(2)}(r; \rho_b \dots)$ based on a combination of the OZ integral equation and MHNC closure relation as a function of interparticle distance at different bulk densities.

Figure 3. Same as Figure 2 but for the range parameters $b = 1.2, c = 1.5$ and the supercritical reduced temperature $T^* = 1.08 \cdot T_c^* = 1.1$.

Figure 4. Same as Figure 2 but for the range parameters $b = 1.1, c = 1.2$ and the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 0.83$.

Figure 5. The theoretical (lines) and simulation (symbols) results for the radial distribution function of the CS fluid of the range parameters $b = 1.4, c = 2$ at two subcritical reduced temperatures $T^* = 0.8 \cdot T_c^* = 1.8$ (a) and $T^* = 0.98 \cdot T_c^* = 2.18$ (b).

Figure 6. The theoretical (lines) and simulation (symbols) results for the density profiles of the CS fluid of the range parameters $b = 1.4, c = 2$ near a single hard wall at the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 3.38$ and at different values of the bulk density.

Figure 7. Same as Figure 6 but for the range parameters $b = 1.2, c = 1.5$ and the supercritical reduced temperature $T^* = 1.08 \cdot T_c^* = 1.1$.

Figure 8. Same as Figure 6 but for the range parameters $b = 1.1, c = 1.2$ and the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 0.83$.

Figure 9. The theoretical (lines) and simulation (symbols) results for the density profiles of the CS fluid of the range parameters $b = 1.4, c = 2$ near a single hard wall at two subcritical reduced temperatures $T^* = 0.8 \cdot T_c^* = 1.8$ and $T^* = 0.98 \cdot T_c^* = 2.18$.

Figure 10. The theoretical (lines) and simulation (symbols) results for the density profiles of the CS fluid of the range parameters $b = 1.4, c = 2$ in a spherical cavity of radius $R = 4\sigma$ at the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 3.38$ and at different values of the bulk density.

Figure 11. Same as Figure 10 but for the range parameters $b = 1.2, c = 1.5$ and the supercritical reduced temperature $T^* = 1.08 \cdot T_c^* = 1.1$.

Figure 12. Same as Figure 10 but for the range parameters $b = 1.1, c = 1.2$ and the supercritical reduced temperature $T^* = 1.5 \cdot T_c^* = 0.83$.

Figure 13. The theoretical (lines) and simulation (symbols) results for the density profiles of the CS fluid of the range parameters $b = 1.4, c = 2$ in a spherical cavity of radius $R = 4\sigma$ at two subcritical reduced temperatures $T^* = 0.8 \cdot T_c^* = 1.8$ and $T^* = 0.98 \cdot T_c^* = 2.18$.

Table 1. Vapor-liquid coexistence densities and equilibrium pressures of the CS fluid of various ranges. The last rows in individual parts correspond to the critical values.

b, c	T^*	ρ_V^*	ρ_L^*	P^*
1.4, 2.0	2.10	0.092	0.402	0.108
	2.15	0.114	0.369	0.123
	2.20	0.152	0.326	0.139
	2.21	0.163	0.313	0.143
	2.22	0.182	0.294	0.146
	2.225	0.187	0.287	0.148
	2.227	0.194	0.284	0.149
	2.232	0.205	0.268	0.151
	2.236	0.215	0.258	0.152
	2.237	0.238	0.238	0.153
1.2, 1.5	0.98	0.111	0.465	0.057
	0.99	0.125	0.448	0.061
	1.00	0.144	0.429	0.065
	1.01	0.169	0.403	0.070
	1.020	0.212	0.363	0.074
	1.021	0.219	0.356	0.075
	1.022	0.226	0.350	0.075
	1.023	0.236	0.343	0.076
	1.024	0.247	0.336	0.076
	1.025	0.29	0.29	0.077
1.1, 1.2	0.530	0.168	0.637	0.044
	0.532	0.181	0.624	0.046
	0.534	0.196	0.605	0.048

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0.536	0.214	0.588	0.049
0.538	0.235	0.566	0.051
0.540	0.266	0.538	0.053
0.541	0.289	0.517	0.054
0.542	0.308	0.493	0.055
0.543	0.406	0.420	0.056
0.545	0.410	0.410	0.058
