Core-softened fluids as a model for water and the hydrophobic effect

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An interaction model with core-softened potential in three dimensions was studied by Monte Carlo computer simulations and integral equation theory. We investigated the possibility that a fluid with a core-softened potential can reproduce anomalies found experimentally in 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 provided additional arguments that the old notion, postulating that only angular-dependent interactions result in density anomaly, is incorrect. We showed that potential with two characteristic distances is sufficient for the system to exhibit water-like behavior and anomalies, including the famous density maximum. We also found that this model can properly describe the hydrophobic effect. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821226>]

I. INTRODUCTION

Studies of fluids with anomalous properties (density maximum, heat capacity extrema, diffusion coefficient maxima, presence of low density fluid (LDL)-high density fluid (HDL) critical point, etc.) have garnered considerable attention recently. The leading reason for increasing interest therein is undoubtedly the liquid water, which is known to possess many of these anomalies.^{1–3} For water represents the central substance in analyzing and simulating chemical reactions and physical phenomena in living organisms as well as industrial processes, its complete understanding is viewed as the ultimate goal.

There are two very distinct mechanisms that give rise to the anomalous properties. Angular-dependent interactions, such as oriented hydrogen bonding in water, tetrahedral bonding in silica,^{4–6} and oriented bonds in BeF₂,⁷ can result in density maximum or LDL-HDL phase transition^{4,8–10} because of the competition between tetrahedral order (low density) and translational order (high density). It must be noted, however, that not all anomalies always appear and that detailed understanding of their origin and their hierarchy remain elusive.^{11,12}

LDL-HDL phase transition has a special case among water anomalies. It has been first postulated by computer simulations¹³ and only recently hinted at, but not proven, experimentally.¹⁴ It is the hallmark of two (singularity-free hypothesis,^{15,16} liquid-liquid critical point hypothesis¹³) of the three leading hypotheses (the other one being stability limit¹⁷) that account for anomalous water behavior in the supercooled region. It is believed to occur below homogenous nucleation temperature, making it difficult to study experimentally. Instead of this, a phase transition between high-density amorphous (HDA) and low-density amorphous (LDA) ice has been studied extensively as an analogue for

HDL-LDL phase transition.¹⁸ Whether the HDL-LDL phase transition actually exists in water and whether it accounts for the appearance of other anomalies above the supercooled region, has been a matter of debate ever since.^{19–23}

Somewhat surprisingly, the anomalous properties listed above can also arise in fluids, consisting of isotropically interacting particles with suitable pair-wise potentials. This has first been shown with computer simulations of isotropic Gaussian core model,²⁴ and heavily investigated since.^{9,12,25–28} Prominent examples of the latter group include (repulsive) shoulder potentials,¹⁰ ramp potentials,^{29,30} Jagla potential,^{31–35} honeycomb potential,³⁶ and continuous shouldered well (CSW) potential.³⁷ Such fluids exhibit LDL-HDL phase transition and often the other anomalies, as well.

Core-softened potentials were originally used to account for the isostructural solid-solid phase transition in a lattice gas system.^{38,39} Soon after, the suitability of these potentials to describe liquid systems became apparent. Many liquid metals that exhibit anomalies and complex phase behavior can be modeled using such potentials.^{40–47} Furthermore, when one averages the interaction over all angles between the water-like particles with angular interactions, core-softened potential is a first-order approximation,^{48,49} neatly bridging the two fundamentally different approaches.

A particular choice of the core-softened potential, the CSW potential was originally proposed by Franzese³⁷ to describe a system with a phase diagram with three fluid phases (gas, LDL, and HDL) and subsequently shown to reproduce the density anomaly. Studies were also extended to variants of the potential with varying steepness of repulsive shoulder. It has been studied quite extensively using molecular dynamic (MD) simulations^{11,37,50,51} that produced the entire phase diagram, revealing two critical points and a region of hierarchically occurring anomalies (structural parameter, diffusion coefficient, temperature of maximum density). Analytical treatment of the potential remains scarce, however. Egorov⁵² studied this potential with integral equations (IE) but limited

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his investigation to the supercritical region of the phase diagram, presumably due to convergence limitations. As our previous work has shown,⁵³ different closures of Ornstein-Zernike (OZ) IE yield slightly different convergence domains, but generally fail in subcritical portion of the phase diagram. So far critical points and the subcritical behavior have not yet been studied using analytical approach.

This paper is organized as follows. First, we set out to use OZ integral equation to obtain gas-low density liquid critical point and the part of subcritical portion of phase diagram. We employ the robust Kovalenko-Hirata (KH) closure and for the first time calculate the gas-liquid critical point using IE approach. Since IE can produce erroneous results near phase transitions, we verified the results with Monte Carlo (MC) simulations. Furthermore, we provide some comparison of the thermodynamic properties calculated from IE and those obtained from MC simulations. In the second part of this paper, we study the liquid portion of the phase diagram with MC simulation. We show that the CSW model captures the anomalous trends present in liquid water. Any useful model for describing anomalous properties in water-like fluids should also properly describe the hydrophobic effect. Accordingly, our next step was to study the hydration of hydrophobic particles. We present the results for the pair solute-solvent correlation function and the transfer thermodynamics.

II. THE MODEL

CSW particles interact by pair-wise potential function

$$U(r) = \frac{U_R}{1 + \exp(\Delta(r - R_R)/a)} - U_A \exp\left(-\frac{(r - R_A)^2}{2\delta_A^2}\right) + \left(\frac{a}{r}\right)^{24}. \quad (1)$$

The potential is composed of three parts: a soft repulsive shoulder of height U_R , an attractive Gaussian well of depth U_A , and width $2\delta_A\sqrt{2\ln 2}$, and a steep repulsive wall. R_R and R_A are the repulsive average radius and the distance of the attractive minimum, respectively, while a denotes the diameter of particles. Steepness of the repulsive shoulder is determined by the parameter Δ (see Figure 1).¹² With varying the parameters, the potential can assume quite distinct forms, ranging from the repulsive shoulder to the double well shape. In numerical work, we used the parameters as proposed in the original version of the potential:^{37,50,51} $U_R/U_A = 2$, $R_R/a = 1.6$, $R_A/a = 2$, $(\delta_A/a)^2 = 0.1$ while varying $\Delta = 15, 30, 100, 300$. As Δ increases, the steepness of the repulsive shoulder at R_R also increases. For $\Delta = 300$, the difference between finite values of Δ and $\Delta_\infty = \lim_{\Delta \rightarrow \infty} \Delta$ is negligibly small. One should take note that varying Δ only influences the steepness of the repulsive shoulder, while repulsive wall and attractive well remain unchanged.

To describe interaction of the hydrophobe with CSW particles, we proposed the Lennard-Jones-like potential. We used modified Lennard-Jones potential to get the same steepness ($U \propto r^{-24}$) of repulsive wall as in CSW. Thus, the interaction

FIG. 1. Comparison of CSW potential for various values of parameter Δ , which determines the steepness of the repulsive shoulder.

between hydrophobic particles becomes

$$U_{LJ} = \frac{4}{3} \cdot 2^{\frac{2}{3}} \epsilon_{LJ} \left[\left(\frac{\sigma_{LJ}}{r} \right)^{24} - \left(\frac{\sigma_{LJ}}{r} \right)^6 \right]. \quad (2)$$

The size of particles and the strength of attraction were chosen to be $\sigma_{LJ} = 2.0$, and $\epsilon_{LJ} = 0.10$ to approximate a typical small non-polar solute. For example, the van der Waals radius for argon equals $1.9 \text{ \AA}$, while water molecule features a bond length of $0.96 \text{ \AA}$. Interaction between the hydrophobe and solvent particles was approximated using Lorentz-Berthelot rules^{54,55}

$$\epsilon = \sqrt{\epsilon_{LJ} \cdot U_A}, \quad (3)$$

$$\sigma = \frac{\sigma_{LJ} + a}{2}. \quad (4)$$

Note that we set $\epsilon = U_A$ and $\sigma = a$ for CSW in these mixing rules.

III. THEORETICAL METHODS

A. Monte Carlo simulation

Monte Carlo simulations were carried out in *NVT* and *NPT* ensembles.⁵⁶ We put 1000 particles in a cubic box using the minimum image convention. To check for artifacts introduced by the box size, we ran a few simulations with 2000 particles; a complete overlap of pair correlation functions and an agreement in thermodynamic properties was found. The system was equilibrated in 100 000 cycles and then sampled in six runs. One cycle corresponded to the attempted move of every particle and one attempted change of volume for *NPT* ensemble. Each run consisted of 100 000 cycles. Near critical points, equilibration and run lengths were increased to 1 000 000 cycles to ensure that the system is properly equilibrated. This was ascertained with comparison of internal energy across runs, which showed consistent average without drifts. Additionally, we checked that pair distribution function in equilibrated systems matched regardless of the initial configuration of particles.

Volume and enthalpy were computed as the averages over the simulation run and averaged over all independent runs to calculate the standard deviation. Thermal expansion coefficient, α^* , isothermal compressibility, κ^* , and heat capacity,

c_p^* , were computed from the fluctuations, as follows:

$$\alpha^* = \frac{\langle V^* H^* \rangle - \langle V^* \rangle \langle H^* \rangle}{T^* \langle V^* \rangle}, \quad (5)$$

$$\kappa^* = \frac{\langle V^{*2} \rangle - \langle V^* \rangle^2}{T^* \langle V^* \rangle}, \quad (6)$$

$$c_p^* = \frac{\langle H^{*2} \rangle - \langle H^* \rangle^2}{N T^*}, \quad (7)$$

where N stands for number of particles, V^* for volume, T^* for temperature, and H^* for enthalpy. Asterisks denote that variables are dimensionless (see Sec. IV).

Thermodynamic properties of a solvation process were computed with Widom's particle insertion method. At each cycle, a ghost solute particle is placed randomly into the box and not allowed to interact with the solvent particles. We then calculate hypothetical interaction of the ghost particle with the solvent, and its weighted average. Thermodynamic quantities describing the solvation (free energy ΔG , enthalpy ΔH , entropy ΔS , and heat capacity Δc_p) and change in volume (ΔV) follow from⁵⁷

$$\Delta G = -\beta^{-1} \ln[\langle V \rangle_N^{-1} \langle V \exp(-\beta U) \rangle_N], \quad (8)$$

$$\Delta H = \frac{\langle H_{N+1} \exp(-\beta U) \rangle_N}{\langle \exp(-\beta U) \rangle_N} - \langle H_N \rangle_N, \quad (9)$$

$$T \Delta S = \Delta H - \Delta G, \quad (10)$$

$$k_b T^2 \Delta c_p = \frac{\langle H_{N+1}^2 \exp(-\beta U) \rangle_N}{\langle \exp(-\beta U) \rangle_N} - \frac{\langle H_{N+1} \exp(-\beta U) \rangle_N^2}{\langle \exp(-\beta U) \rangle_N^2} - \langle H_N^2 \rangle_N + \langle H_N \rangle_N^2, \quad (11)$$

$$\Delta V = \frac{\langle V \exp(-\beta U) \rangle_N}{\langle \exp(-\beta U) \rangle_N} - \langle V \rangle_N, \quad (12)$$

where $\beta = (k_b T)^{-1}$. Angle brackets $\langle \dots \rangle_N$ denote averages throughout the run over all insertions. U is the interaction of ghost particle with the system and H_{N+1} represents enthalpy of the system with ghost particles. $\langle H_N \rangle_N$ and $\langle H_N^2 \rangle_N$ stand for average enthalpy and average of squared enthalpy, respectively, of a system without a ghost particle.

B. Integral equations theory

We used the integral equation theory to calculate structure, pressure, and other thermodynamic quantities.⁵⁸ OZ equation relates the total correlation function, $h(r)$, with direct correlation function $c(r)$

$$h(r) = c(r) + \rho \int h(r') c(|r - r'|) dr', \quad (13)$$

where ρ is the bulk density. To solve for $h(r)$, from which $g(r)$ and subsequently other quantities can be calculated, we need an additional relation (closure). Based on our previous work,⁵³ we opted for KH closure⁵⁹ because of its robustness,

i.e., broad convergence domain. KH closure can be written as

$$h(r) = \begin{cases} \exp[d(r)] - 1; & \text{for } d(r) \leq 0, \\ d(r); & \text{for } d(r) > 0, \end{cases} \quad (14)$$

where $d(r) = -\beta U(r) + h(r) - c(r)$.

OZ equation was solved with direct iterative method. For greater numerical stability of the algorithm, we defined function $t(r) = h(r) - c(r)$ and employed Fast Fourier transform (FFT), simplifying OZ equation into an algebraic equation. Initially, setting $t(r) = 0$, system of equations is solved iteratively.⁵³ Pressure was calculated via the virial route.

To validate the results, we compared the calculated pair distribution functions with those obtained by MC simulations. Even at the highest density attained in our work ($\rho = 0.3$), agreement between the IE and MC methods for all variants of the CSW potential, is quantitative (see Figure 2). Varying Δ has a predictable effect on the pair distribution function. As shown in Figure 2, the discontinuity in pair distribution function becomes more pronounced as the parameter Δ , and thus the steepness of the repulsive shoulder increases.

IV. RESULTS AND DISCUSSION

The results are presented in dimensionless reduced units in terms of the particle diameter and the depth of the attractive well $T^* = k_b T/U_A$, $\rho^* = \rho a^3$, and $p^* = p a^3/U_A$.

A. Phase diagram and critical points

We set to determine the gas-LDL critical point for five variants of the CSW potential ($\Delta = 15, 30, 100, 300$, and 500). As shown in Figure 3, we calculated the pressure as a function of density along several isotherms. Below critical temperature, the isotherms display typical oscillating middle part where pressure decreases as density increases. This unstable portion of the phase diagram is compensated for using the Maxwell construction. Plotted coexistence curve connects the vertices of Maxwell lines. Critical point by definition is the saddle on the critical isotherm, where $(\frac{\partial p}{\partial T})_V = (\frac{\partial^2 p}{\partial T^2})_V = 0$.

IE typically exhibit convergence and accuracy problems near the critical points, therefore we benchmarked these results against the MC simulations. Data from IE were found to be in good agreement with MC simulations (see Figure 4). Critical points were determined from MC data as well, using the same Maxwell construction on the interpolated polynomial curves fitted to data. Margins of error for individual quantity were estimated as the standard deviation of that quantity across all simulation runs. Critical points obtained via different methods are in good agreement (see Table I for detailed information). We also compared these results with literature data from MD simulations by Vilaseca.⁵⁰

For $\Delta = 15$, critical point occurs at $T = 1.13$. As Δ increases, the critical temperature increases as well, reaching the maximum for $\Delta = 100$ around $T = 1.25$ and then slowly decreasing. The same non-monotonous behavior is encountered for density and pressure at the critical point, both reaching the maximum around $\Delta = 100$. Interestingly, MD

FIG. 2. Pair distribution functions from integral equation with KH closure (solid lines) and NVT ensemble MC simulations (full circles) for various values of Δ . (a) $\Delta = 15$; (b) $\Delta = 30$; (c) $\Delta = 100$; (d) $\Delta = 300$ (all for $T^* = 1.6$, $\rho^* = 0.3$).

FIG. 3. Subcritical portion of phase diagram for CSW fluid ($\Delta = 15$) around gas-liquid critical point (black full circle) as calculated with KH closure. Coexistence curve is displayed as dotted line.

FIG. 4. Comparison of isotherms calculated isotherms from KH closure (solid, dotted, and dashed-dotted lines) with MC simulation results (full circles).

data from Vilaseca⁵⁰ are consistently skewed towards lower temperatures and lower pressures. They also show monotonic increase of temperature, pressure, and density of the critical point with increasing parameter Δ , just in contrary to our findings. Our MC data are supported by good correspondence between IE and MC methods in the subcritical (gas-LDL critical point determination) and supercritical region of the phase diagram.⁵³

To the best of our knowledge, no integral equation closure was found to allow for the convergence near the second critical point. Since IE generally fail to exhibit convergence as temperature decreases, this was expected behavior. The determination of the second critical point, and the whole phase diagram, was therefore accomplished from MC simulations. For $\Delta = 15$, we found the LDL-HDL critical point at $T^* = 0.61 \pm 0.01$, $\rho^* = 0.257 \pm 0.003$, and $p^* = 0.130 \pm 0.004$ (see Figure 5 for a complete phase diagram). This is again in disagreement with Vilaseca and Franzese's estimate of $T^* = 0.49 \pm 0.01$, $\rho^* = 0.247 \pm 0.008$, and $p^* = 0.285 \pm 0.007$.^{37,50}

TABLE I. Gas-liquid critical point for different CSW potentials. Integral equation theory (KH), our Monte Carlo simulations, and molecular dynamics results from Vilaseca.⁵⁰

Δ	KH			MC			MD		
	T	ρ	p	T	ρ	p	T	ρ	p
15	1.13	0.0696	0.0264	1.13	0.085	0.0255	0.95	0.08	0.019
30	1.19	0.0718	0.0286	1.19	0.084	0.0290	1.01	0.08	0.022
100	1.23	0.0734	0.0305	1.25	0.085	0.0310	1.06	0.08	0.025
300	1.21	0.0710	0.0298	1.24	0.086	0.0291	1.06	0.09	0.027
500	1.20	0.0718	0.0290	1.24	0.085	0.0304	1.08	0.09	0.027

FIG. 5. Phase diagram for CSW fluid ($\Delta = 15$). Symbols are results from MC simulations and the connecting lines are a guide-for-eye. Numerical error is smaller than the size of the symbols. Black full circles represent vapor-liquid and LDL-HDL critical points.

We determined the second critical point for other versions of the potential, as well (see Table II for detailed comparison).

Additional thermodynamic properties were calculated by IE and MC techniques. First, we inspected density dependence to check for the density anomaly. IE showed LDL-gas phase transition below critical pressure ($p^* = 0.0255$) as shown in Figure 6. Density maximum occurs just above the melting temperature and moves towards lower temperatures as the pressure is decreased. Below $p^* = 0.02$, density maximum moves into the metastable supercooled region. When pressure is increased, the density maximum disappears due to spontaneous nucleation and freezing of the fluid at these temperatures.

Coefficients of thermal expansion, α^* , (Figure 7), isothermal compressibility, κ^* , (Figure 8), and heat capacity at constant pressure, c_p^* , (Figure 9), were also calculated. At the phase transition point, these quantities display typical non-continuous behavior. As pressure increases above the critical point, maxima are slowly shifted towards higher temperatures. We show that KH closure adequately describes this phase transition, and accurately predicts the maxima. At extreme pressures ($p^* > 0.5$), the extrema vanish. Unfortunately, IE loses its convergence below the critical temperature. Due to this limitation, we can only obtain these quantities by the MC method. Comparison of the results for liquid range with experimental data for water at 1 atm shows

TABLE II. LDL-HDL critical point for different CSW potentials. Our Monte Carlo simulation results and molecular dynamics results from Vilaseca.⁵⁰

Δ	MC			MD		
	T	ρ	p	T	ρ	p
15	0.61	0.257	0.130	0.49	0.247	0.285
30	0.64	0.261	0.111	0.50	0.255	0.267
100	0.66	0.267	0.085	0.53	0.262	0.243
300	0.64	0.267	0.077	0.51	0.271	0.231
500	0.64	0.271	0.081	0.52	0.272	0.204

FIG. 6. Density dependence upon pressure for CSW fluid ($\Delta = 15$) for different temperatures indicated in the figure.

FIG. 7. Thermal expansion coefficient dependence upon pressure for CSW fluid ($\Delta = 15$) for different temperatures indicated in the figure.

FIG. 8. Isothermal compressibility dependence upon pressure for CSW fluid ($\Delta = 15$) for different temperatures indicated in the figure.

FIG. 9. Heat capacity dependence upon pressure for CSW fluid ($\Delta = 15$) for different temperatures indicated in the figure.

FIG. 10. Calculated temperature trends for CSW fluid (left) display good agreement with experimental data⁶⁵ for pure water (right). Blue squares represent supercooled liquid.

similar trends (see Figure 10). For pressure $p^* = 0.024$, which is below critical point, the density maximum appears at $T^* = 0.52 \pm 0.01$, slightly above the melting temperature $T^* = 0.50 \pm 0.01$. Also, c_p^* and α^* show pronounced minima in the liquid range. Agreement of κ^* with experimental data is somewhat worse, but is notably improved at higher pressures (Figure 8). At $p^* = 0.1$, a very distinct minimum is visible.

B. Thermodynamics of solvation

Hydrophobic effect is an important peculiarity of water as solvent. We studied the transfer thermodynamics for introducing small non-polar solutes into the solvent.

Experimental data for such hydration are usually limited to high pressure regime, because of negligible solubility at room conditions. To compare the data, we had to use rather high pressure (above $p^* = 0.1$) for the simulations, as well.

Solute-solvent correlation functions at infinite dilution (see Figure 11) were calculated with Widom's method. On each cycle, one solvent particle and a direction are randomly selected. A ghost solute particle is then inserted at increasing distances from the selected solvent particle in increments of $\Delta r = 0.01$. From local excess chemical potential, $\mu^{ex}(r)$, at r and average excess chemical potential in system, $\overline{\mu^{ex}}$, both determined as ΔG from Eq. (8), a pair correlation function

FIG. 11. Solute-water pair correlation functions at $p^* = 0.2$ for the temperatures indicated in the figure.

can be computed as

$$g_{\text{solute-solvent}}(r) = \exp(\beta\bar{\mu}^{ex} - \beta\mu^{ex}(r)). \quad (15)$$

At lower temperatures, greater translational order is present, and correlation functions display sharper peaks. As temperature increases, the functions flatten out. Two effects contribute towards this phenomenon. With increasing temperature, bulk solvent structure breaks down naturally. Additionally, the solute is believed to induce some structural change in the solvent by solvent-solute interactions.

FIG. 12. Calculated temperature trends in the transfer thermodynamics of a modified LJ solute in CSW fluid at $p^* = 0.1$ (left) in comparison with the experimental data for the transfer of gaseous argon into water (right).^{60–62}

Transfer thermodynamics were studied using Widom's test-particle method. We found that CSW fluid behaves in many aspects like real water. In Figure 12, we show a comparison of the model thermodynamics with experimental values for the transfer of argon into water at 300 bars.^{60–62} The CSW model predicts correct non-monotonic temperature trends for the enthalpy, entropy, and free energy of solvation. Calculated molar volumes of transfer follow closely the experimental data. Heat capacity of transfer is a very useful measure for the magnitude of the hydrophobic effect. A large positive change in heat capacity is typical for solvation of hydrophobic particles in a polar solvent. Our model indicates a rather large positive change in heat capacity that declines with increasing temperature as found for other samples.

V. CONCLUSION

In this work, we presented several important results. First, we demonstrated that it is possible to capture the phase transition in CSW model with the integral equation approach. Kovalenko-Hirata closure was found to offer a suitable blend of robustness and exactness to yield a critical point. Thus, we were able to determine the critical points for five variants of the CSW potential, differing in the steepness of the repulsive shoulder. Interestingly, the critical temperature, pressure, and

density change non-monotonically with the steepness, reaching a maximum near $T = 1.24$ for $\Delta = 100$.

We showed that CSW model reproduces thermal anomalies of non-polar solvation that are typical of hydrophobic effect. At low temperatures, solvent molecules are ordered around the solute. As the temperature increases, more degrees of freedom become available, and entropic contribution becomes more important. Conversely, solvation at high temperature is energetically disfavored. This creates a typical competition between entropy and enthalpy. Similarly, the heat capacity change upon solvation is large and declines with the temperature increase. Volume of transfer increases with temperature, as cavities around the solute become larger with rising temperature. The results show that simple isotropic models with two characteristic lengths are equally efficient in describing water-like anomalies as more complicated models with angular-dependent interactions.^{63,64}

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