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Structural behavior of an anomalous fluid under hydrophobic, hydrophilic and heterogeneous confinement

Rafael de C. Barbosa¹, Leandro B. Krott² and Marcia C. Barbosa¹

¹ Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, 91501-970, Porto Alegre, RS, Brazil

² Centro Araranguá, Universidade Federal de Santa Catarina, Rua Pedro João Pereira, 150, 88900-000, Araranguá, SC, Brazil

Abstract.

We perform molecular dynamics simulations of an anomalous fluid confined between parallel plates. The effects of the confinement on the structural behavior of the fluid when the plates are hydrophobic, hydrophilic and amphiphilic were investigated. The anomalous fluid was modeled using a two length scales potential, that exhibits density, diffusion and structural anomalies like observed in liquid water. We show that this fluid at the contact layer exhibits the formation of a solid/amorphous phase for temperatures at which the bulk system is liquid.

1. Introduction

Anomalous fluids, like water [1] and silica [2], exhibit a region in the pressure-temperature phase diagram at which thermodynamic, dynamic and structural properties behave differently when compared with other fluids. One example is the density of water that has a maximum value at $T = 4^{\circ}\text{C}$ at room pressure. Another example is its diffusion increases as the density decreases in a certain range of temperatures. But not only bulk water shows anomalies. The behavior of confined water is also very intriguing. In principle, under confinement, the disorder imposed by the confined walls should simply shift to lower temperatures all the bulk properties. Such a simple picture is not valid for water. At the nano scale for instance the fluid-wall hydrophobic/hydrophilic interactions that in the bulk are irrelevant compete with the fluid-fluid interactions [3, 4, 5] and lead to layering [6], large increase in the diffusion coefficient [6] and superflow [7, 8]. At the confining surface the water forms new ordered phases not observed in the bulk [9, 10, 11, 12].

Experiments of confined fluids show additional properties not observed in bulk systems. NMR and X-ray diffraction studies show that the pore size affects the freezing and the melting temperatures [13, 14]. But these results depend on the type of interaction between fluid and confining media. For the hydrophobic confinement the fluid remains at the liquid state for temperatures lower than in the bulk or for the hydrophilic confinement [3, 4, 5]. The freezing in both cases is not uniform. The contact layer and the middle layer do not melt at the same temperatures [15]. Therefore, a simple picture of the mechanism for the behavior of anomalous liquids under confinement is still lacking.



In addition to the atomistic models, core-softened potentials have been employed to describe the anomalous behavior of water-like systems [16, 17, 18, 19] in the bulk and in planar surfaces [20, 21, 22, 23]. These models represent the van der Waals and the hydrogen bonds interactions of water by means of a two length scales potential. The competition between the two scales generates in the bulk the density, diffusion and structural anomalies present in water. Even though the effective potentials can not produce quantitative agreement with the experiments they provide a picture of the mechanism behind the anomalies.

In this work we study the behavior of an anomalous liquid under confinement in the framework of effective interaction potentials. The fluid is modeled by a two length scales potential [17, 24, 23, 25]. The plates are immersed in the fluid. Three systems are analyzed: hydrophobic, hydrophilic and heterogeneous plate-fluid interactions. These three cases are analyzed for the presence of freezing and melting.

The paper is organized as follows: in the section 2 the model is introduced, in the section 3 the methods and simulations details are described, in the section 4 the results are shown and in the section 5 conclusions are presented.

2. The Model

The system is composed of two parallel plates immersed in a fluid of N spherical particles of diameter σ . The plates are made of particles of diameter σ organized in a square lattice of area L^2 . The distance between the parallel plates is given by d . A schematic representation of the system is depicted in the figure 1.

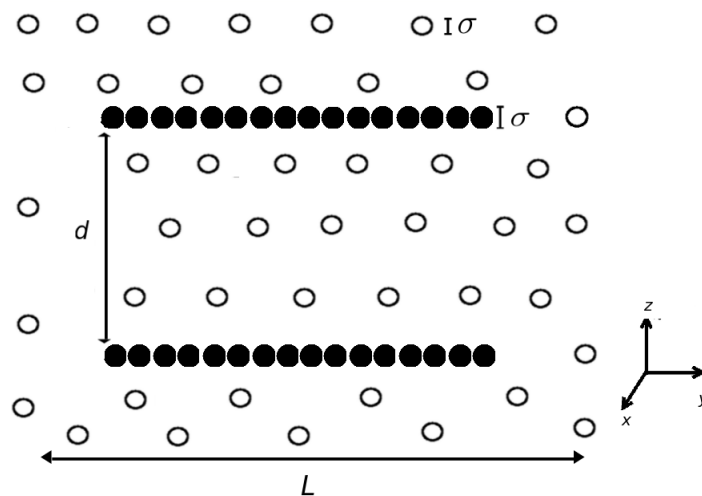


Figure 1. Schematic representation of the system formed by plates immersed in the fluid of spherical particles.

The particles of the fluid interact through a two length scales potential given by

$$\frac{U(r_{ij})}{\varepsilon} = 4 \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + a \exp \left[-\frac{1}{c^2} \left(\frac{r_{ij} - r_0}{\sigma} \right)^2 \right] \quad (1)$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the distance between two particles, i and j . The first term is a standard Lennard-Jones (LJ) 12-6 potential where ε is the depth, plus a gaussian centered on radius r_0 and width c . The chosen parameters are $a = 5$, $r_0/\sigma = 0.7$ and $c = 1$. Oliveira et. al [17, 24] studied the pressure versus temperature phase diagram of the bulk system interacting through

this potential and they found that the system exhibits a region in the pressure-temperature phase diagram where the density and the diffusion anomalous behavior are present. The presence of

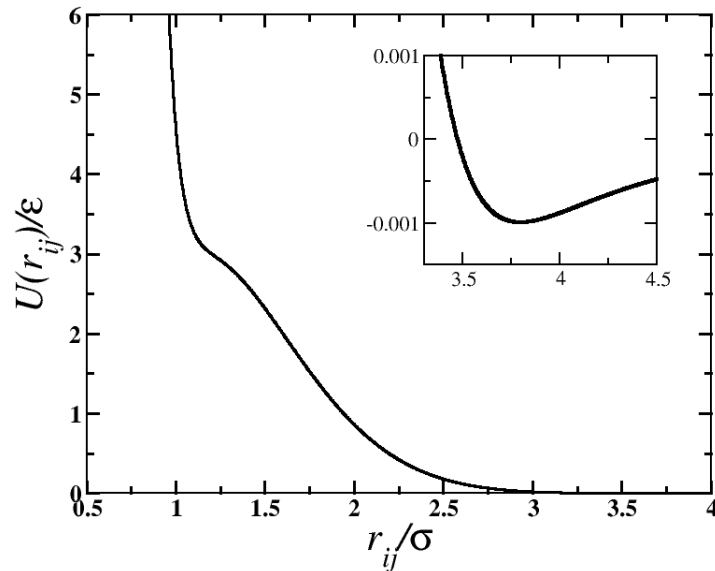


Figure 2. Effective potential of interaction between the water-like particles (Eq. 1). The potential parameters are $a = 5$, $r_0/\sigma = 0.7$ and $c = 1$. The inset shows a zoom of the small attractive part of the potential.

the anomalies is related with the two length scales: a repulsive shoulder at $r_{ij}/\sigma \approx 1$ and a very small attractive well at $r_{ij}/\sigma \approx 3.8$, as it can be seen in the figure 1. The same set of parameters is employed in this paper.

In order to check the effect of the particle-plates interaction potential in the behavior of the confined fluid three different types of walls are studied: hydrophobic, hydrophilic and heterogeneous fluid-wall interactions.

The hydrophobic interaction was simulated by the Weeks-Chandler-Andersen Lennard-Jones potential [26], given by

$$\frac{U_{WCA}}{\epsilon} = \begin{cases} U_{LJ}(r_{ij}) - U_{LJ}(r_{cw}), & r_{ij} \leq r_{cw} \\ 0, & r_{ij} > r_{cw} \end{cases} \quad (2)$$

where $U_{LJ}(r_{ij})$ is a standard 12-6 Lennard-Jones potential and $r_{cw} = 2^{1/6}\sigma$ is the cutoff distance.

The hydrophilic interaction of the plates was simulated by a strong attractive potential - SAT [25], given by

$$\frac{U_{SAT}}{\epsilon} = \begin{cases} D_1 [(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] + D_2 (r_{ij}/\sigma) - \epsilon_s, & r_{ij} \leq r_{cs} \\ 0, & r_{ij} > r_{cs} \end{cases} \quad (3)$$

where $r_{cs} = 2$, $\epsilon_s = D_1[(\sigma/r_{cs})^{12} - (\sigma/r_{cs})^6] + D_2(r_{cs}/\sigma)$. The parameters D_1 e D_2 are 1.2 and 0.545, respectively.

In the case of heterogeneous plates, around 20% random particles of the plates have hydrophobic wall-fluid interaction and the others, hydrophilic behavior.

The figure 3 illustrates the WCA and the SAT particle-plate interaction potentials.

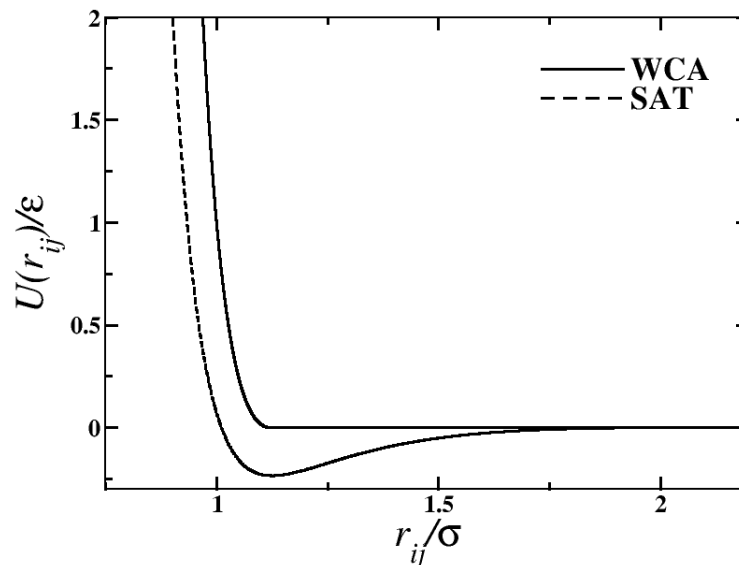


Figure 3. Particle-plate interaction potentials: hydrophobic, WCA (solid line), and hydrophilic, SAT (dashed-line).

3. The Methods and Simulation Details

The plates are composed by $N = 450$ spherical particles and they are immersed in the water-like fluid that is made by $N = 1700$ particles. The effective distance between the plates is fixed. Here the studied distances are $d = 3\sigma$, $d = 6.0\sigma$ and $d = 10\sigma$. The density of the systems was calculated considering just the water-like particles, excluding the particles of the wall. Due to the empty space near to each plate, the density needs to be corrected to an effective density, given by $\rho = N/(L^2L_e)$, where $L_e = L - 2$ and L is the size of simulation box.

Molecular dynamics (MD) simulations at NVT-constant ensemble were performed to study the different systems. In order to keep fixed the temperature, the Nosé-Hoover thermostat [27, 28] with coupling parameter $Q = 2$ was used. The particle-particle interaction potential has a cutoff radius of $r_c = 3.5$ and it was shifted in order to have $U = 0$ at r_c .

Several densities and temperatures were simulated. Initial configuration in the solid and the liquid phases were selected and in both cases the equilibrium states were reached after 2×10^6 steps of simulation, followed by 4×10^6 simulation run. The time step was 0.001 in reduced unit. The average of all physical quantities were obtained every 50 time step just after the systems to be equilibrated. The metastability was avoided analyzing the pressure versus density phases diagram and the energy after the equilibrium state.

The structure of the systems was analyzed by the lateral radial distribution function, $g_{\parallel}(r_{\parallel})$, for each layer between the plates. An usual definition for $g_{\parallel}(r_{\parallel})$ is

$$g_{\parallel}(r_{\parallel}) \equiv \frac{1}{\rho^2 V} \sum_{i \neq j} \delta(r_{\parallel} - r_{ij}) [\theta(|z_i - z_j|) - \theta(|z_i - z_j| - \delta z)]. \quad (4)$$

where r_{\parallel} is the parallel distance between the particles, considering just the x and y directions. The $\theta(x)$ is the Heaviside function and it restricts the sum of particle pairs in the same slab of thickness $\delta z = \sigma$.

The physical quantities in this paper are depict in LJ units [29],

$$r^* \equiv \frac{r}{\sigma}, \quad \rho^* \equiv \rho \sigma^3, \quad t^* \equiv t \left(\frac{\varepsilon}{m \sigma^2} \right)^{1/2} \quad \text{and} \quad T^* \equiv \frac{k_B T}{\varepsilon}, \quad (5)$$

for distance, density of particles, time and temperature, respectively.

Since we will use only reduced units in this paper, the * will be omitted in the results discussion.

4. Results

The effects of the temperature and density on the fluid structure around the immersed parallel plates were investigated for the three types of plates. The following temperatures were analyzed: $T = 0.100$, 0.200 and 0.300 . The densities studied correspond to sizes of simulation box in dimensionless units given by $L = 24$, 26 and 28 , what correspond to the densities $\rho = 0.134$, 0.105 and 0.083 , respectively also in dimensionless units.

4.1. Hydrophilic plates

In this subsection the distribution of the liquid under confinement with the hydrophilic plates is presented. The three densities analyzed show a very similar result and, for simplicity, we will show only results for $\rho = 0.134$. For this density, the transversal density profile is shown in the figure 4 for plates separated by (a) $d = 3$, (b) $d = 6.0$ and (c) $d = 10.0$. In all the cases layers are formed. We observed two, three and five layers for plates separated by (a) $d = 3$, (b) 6 and (c) 10 , respectively.

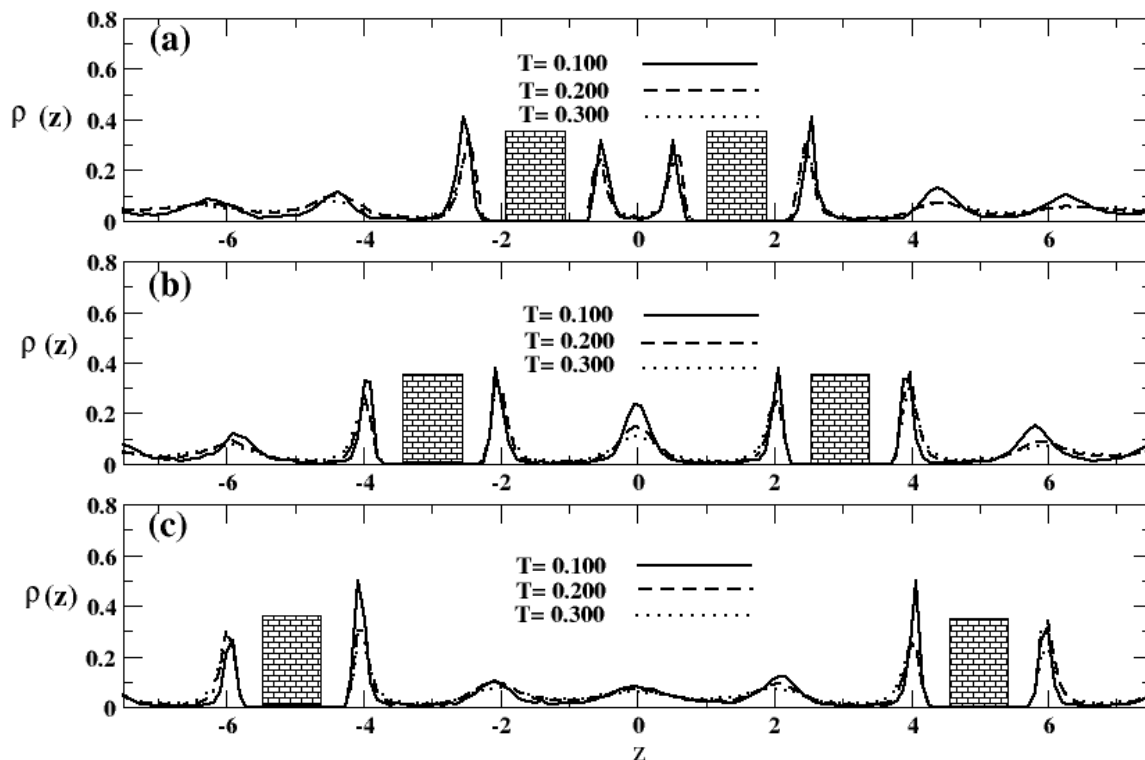


Figure 4. Transversal density profiles for $\rho = 0.134$ and three different distances of plates: (a) $d = 3.0$, (b) $d = 6.0$ and (c) $d = 10.0$. Solid, dashed and dotted lines represent $T = 0.100$, $T = 0.200$ and $T = 0.300$, respectively.

In order to analyze the different structures of the layers the radial distribution functions,

$g_{||}(r_{||})$, for the contact layers were computed. The structure of the contact layers inside and outside the plates for $d = 3$, shown in the figure 5 (a) and (b), respectively, are very similar. Both layers are in a liquid-like phase. As the temperature is decreased, the liquid is more structured, what can be seen by the increasing of the first peak of $g_{||}(r_{||})$.

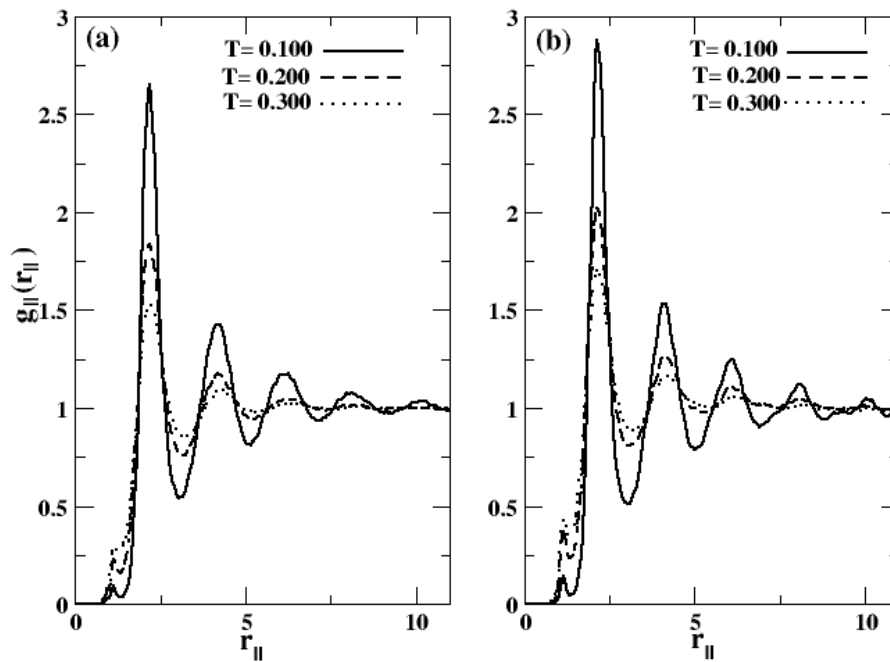


Figure 5. $g_{||}(r_{||})$ for contact layers (a) inside and (b) outside the hydrophilic plates separated by $d = 3$ for the indicated temperatures.

For the distance between the plates $d = 6$, the transversal density profile is shown in the figure 4 (b). In addition to the contact layers, there is the formation of a middle layer between the plates. As the temperature decreases, the density near the plates increases, what suggest that the fluid is more structured.

In figure 6 the radial distribution function $g_{||}(r_{||})$ for the contact and middle layers were computed. The middle layer for all the temperatures is liquid-like. The contact layer in region outside the plates is also liquid-like while the internal contact layer for low temperatures forms an amorphous phase, in agreement with previous results [23].

For plates separated by $d = 10$, the transversal density profiles are presented in figure 4 (c). The increases of density near the plates is similar to already observed for the other cases, $d = 3$ and $d = 6$. For these systems, all the layers present a liquid-like behavior and no amorphous phases was observed.

The presence of the amorphous phase at the contact layer for $d = 6$ and not for $d = 3$ and $d = 10$ is a consequence of the layering. The system with three layers exhibits a larger density at the contact layer leading to the formation of a solid-like phase.

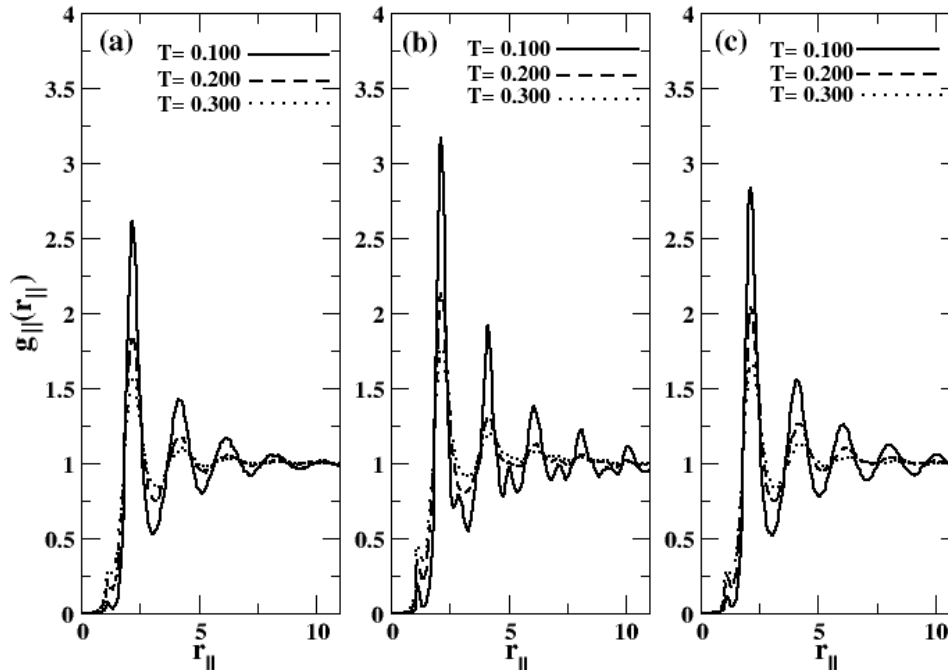


Figure 6. $g_{\parallel}(r_{\parallel})$ for a system with hydrophilic plates separated by $d = 6$ for (a) the contact layer outside of the plates, (b) the contact layer inside the plates and (c) the middle layer.

4.2. Hydrophobic plates

In this subsection the density profile of the liquid under confinement by the hydrophobic plates is shown. For simplicity, the analysis will be presented only for the density $\rho = 0.134$ and the distance between the plates $d = 6$. Figure 7 shows the layering structure observed for these systems, similar to observed for the hydrophilic confinement. It is possible to observe that for these systems, as the temperature decreases, the density of water-like particles increases near to each plate. These results are in agreement with observed for atomistic models of water confined in parallel plates [30] and hydrophobic surface of protein [31]. In order to investigate the structures of the particles of the layers, the radial distribution function, $g_{\parallel}(r_{\parallel})$, was computed for the contact and middle layers, as illustrated in the figure 8. The comparison between figure 8 and figure 6 shows differences between the fluid in the hydrophilic and hydrophobic confinement. While the hydrophilic confinement induces the formation of amorphous-like phases for low temperatures at $d = 6$, the hydrophobic system remain the fluid at low temperatures, what is in agreement with experimental results of Deschamps et al. [3] and Jelassi et al. [4].

4.3. Heterogeneous Parallel Plates

In the previous subsections, we studied the effects of the decrease in temperature in a homogeneous system of the fluid confined in hydrophobic or hydrophilic plates. However, in practical cases, immersed surfaces are expected to be chemically heterogeneous, that is, with hydrophilic and hydrophobic regions. First, we found a similar behavior to observed in the

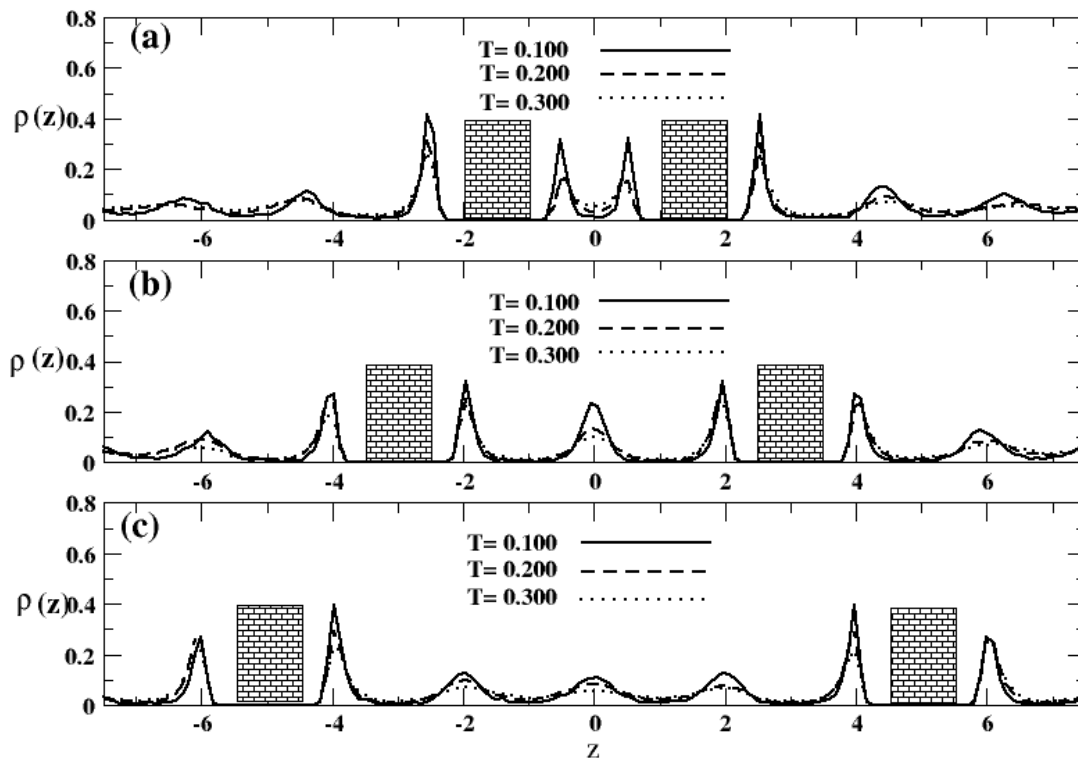


Figure 7. Density profiles for three different distances of hydrophobic plates. (a) $d = 3.0$, (b) $d = 6.0$ and (c) $d = 10.0$. Solid, dashed and dotted lines represent $T = 0.100$, 0.200 and 0.300 , respectively.

homogeneous plates, that is, the density increases upon cooling also near to heterogeneous surface. We also studied the structural properties of the confined and not confined water-like particles.

The transversal density profile presents a similar behavior to other cases and we will not present for simplicity. The structure was analyzed using the $g_{||}(r_{||})$, shown in the figure 9, for $d = 6$ and $\rho = 0.134$. The other cases were not shown for simplicity. As the temperature decreases, the density of particles near to plates increases and the systems becomes more structured. Again, as observed in the hydrophilic homogeneous system, the contact layer inside the plates presents an amorphous-like behavior, while the other layers present a liquid-like behavior. It happens because the heterogeneous plates have hydrophilic interaction predominating over the hydrophobic one.

5. Conclusions

In this work we studied the effect of temperatures on the interfacial properties of water immersed in a parallel plates using molecular dynamics simulations. Hydrophilic, hydrophobic and heterogeneous surfaces were studied. The formation of four layers, two in confined part and two in the not confined part of the system are observed for small values of d . As we increase the distance between the plates we observe other layers besides of the contact layers. These layers we call middle layers. Our results suggest that layers are formed in order to minimize the

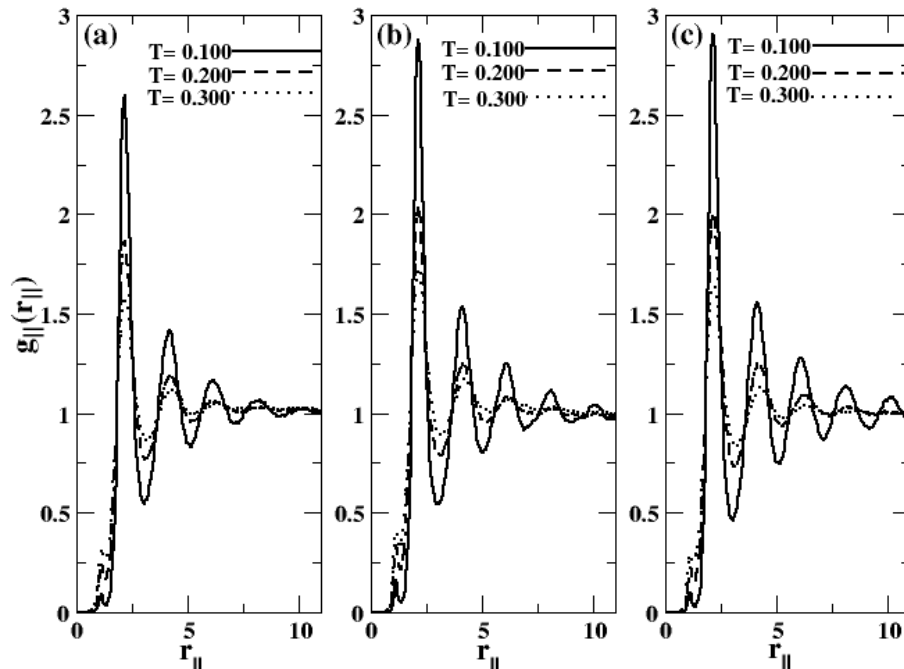


Figure 8. $g_{||}(r_{||})$ for water-like fluid in hydrophobic plates separated by $d = 6$, at $\rho = 0.134$, for (a) the contact layer outside of the plates, (b) the contact layer inside of the plates and (c) the middle layer.

particle-particle and the particle-plates interaction.

We also studied the structural properties of confined and not confined fluid. We calculate the lateral radial distribution function for each layer of the different regions of the system. The effects on the structure of water-like particles is better observed as the temperature decreases. The water-like particles in unconfined region has fluid characteristics in all cases analyzed. To the confined region we can observe that the contact layer to the hydrophilic plate has a liquid-like characteristic at $T = 0.300$ and $T = 0.200$, while at $T = 0.100$ the system presents an amorphous-like behavior. As the temperature is decreased the particles become more structured at the confined region. However, water-like particles confined by hydrophobic plates present a liquid-type characteristics.

In order to investigate the effects of plates type interaction with the fluid, we created a system with heterogeneous parallel plates, that is, plates with hydrophilic and hydrophobic interaction with fluid particles. These heterogeneous systems, that have around 80% of hydrophilic interaction, present results very similar to that observed for purely hydrophilic system. As the temperature decreases the system becomes more structured and at $T = 0.100$ the system presents an amorphous-type characteristic.

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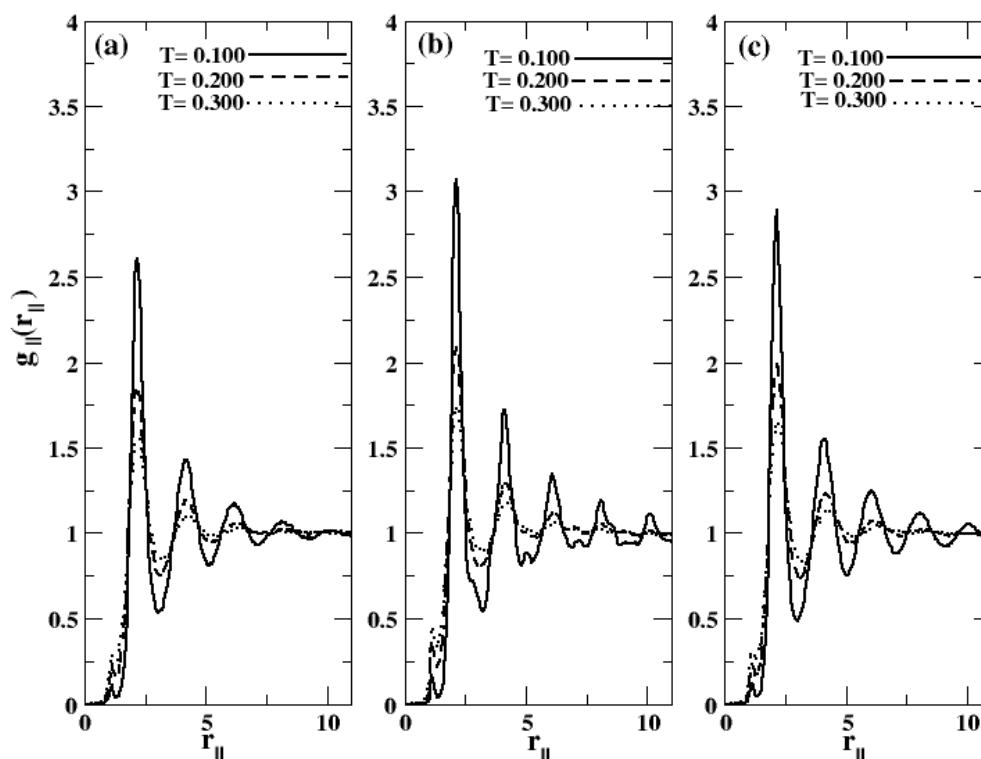


Figure 9. $g_{||}(r_{||})$ for water-like fluid in heterogeneous plates for $d = 6$ and $\rho = 0.134$. (a) is the contact layer outside of the plates, (b) is the contact layer inside the plates and (c) the middle layer.

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