

Monte Carlo simulation of confined water

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Abstract: In living organisms and many applications water is nanoconfined. Here we study water confined between hydrophobic parallel walls as a function of the wall-wall separation L_z between 0.6 and 4.8 nm. We calculate response functions and density by Monte Carlo simulations at different temperatures and pressures of a many-body coarse-grained model of water that has been studied in previous works for the case of a single layer. For all the number of layers considered here we always find that water has density anomaly as in experimental bulk water and that it has a critical phase transition between two liquid phases with different structure, density and energy. We find that the phase diagram changes in a continuous way as the number of layers increases, suggesting that the liquid-liquid critical point should occur also in the bulk case. These results shed light onto the debated bulk-water phase diagram and could be relevant in nanotechnology applications and biological systems.

I. INTRODUCTION

The study of confined water in hydrophobic and hydrophilic materials has been of great interest in the recent years. Nanoconfinement in such materials allows the water to not freeze below the bulk homogeneous nucleation temperature (~ 150 K) remaining in a metastable (supercooled) liquid phase down to ~ 130 K at ambient pressure. Performing measures of temperature and pressure at these conditions is extremely difficult because crystal nucleation occurs at time scales that are faster than common experimental techniques. As a consequence, new kinds of experiments, such as resonant inelastic X-ray scattering [1, 2], and simulations have been developed in order to study the behavior of water under such conditions. In particular, simulations for water under extreme conditions were pioneered by Poole et al. [3] that speculated the occurrence of a liquid-liquid critical point (LLCP) between two metastable phases of water at different densities: a higher density phase at higher temperatures and pressures and a lower density phase at lower temperatures and pressures. These results have been recently confirmed [4] after years of debate [5].

Recent simulations [6] of a water monolayer under hydrophobic confinement show that the system has a liquid-liquid phase transition that leads to a LLCP in the universality class of the 2D Ising Model when the linear size of the layer, L , is at least 50 times bigger than the separation of the confinement walls, L_z . Ref. [6] shows also that the LLCP has a crossover to the 3D Ising universality class when $L/L_z < 50$. This is surprising because for simple (Lennard-Jones) liquids this crossover takes place for $L/L_z \cong 5$, i.e. the thickness of the layer is noticeably larger than in the water case. This peculiar behavior of water can be attributed to two properties of the water hydrogen bond network: a strong cooperativity and a low coordination number [6].

Here we study the behavior of water in nanoconfinement as a function of the distance between the walls. We fix the initial linear size of our system to $L = 15$ nm and vary the wall-to-wall distance $L_z = 0.6, 1.2, 2.4, 4.8$ nm. Because each monolayer has a thickness $h \cong 0.3$ nm [7], our simulations feature $N_z = 2, 4, 8, 16$ different layers. Our goal is to characterize how the phase diagram depends on the number of layers. At the end of this work we find that, for the range of wall-to-wall distance we consider, the phase diagram has a weak dependence on L_z . In particular, we always find the

LLCP and that its critical parameters are almost independent on L_z for between 0.6 and 4.8 nm. Because for all the cases considered here $L/L_z < 3.13 \ll 50$, although we do not check it directly, based on the results of Ref. [6] we expect that the LLCP belongs to the universality class of the 3D Ising Model. Hence, the main effect of changing L_z for our choice of L would consist in changing the universality class of the LLCP but not the other qualitative features of the phase diagram.

II. THE MODEL

We use a many-body coarse-grained model of water [8, 9], where each water molecule has four nearest neighbors. The molecule coordinates are coarse-grained into cell with an initial volume h^3 and with $N = 5 \cdot 10^3$ molecules, for $L_z = 0.6$ nm, up to $N = 4 \cdot 10^4$ molecules, for $L_z = 4.8$ nm, with each layer made of 2500 molecules. We fix N , the pressure P and the temperature T and calculate the density $\rho(P, T) \equiv \frac{N}{V}$, using a Monte Carlo algorithm that allows for changes of the volume V from its initial value Nh^3 [6, 9].

Here we consider that the system is homogeneous, hence each cell has a density $\rho_i(P, T) \equiv \rho(P, T) \leq \rho_0 \equiv 1/r_0^3$, $r_0 = 2.9$ Å is the water van der Waals diameter. We introduce a discretized density field n_i defined as $n_i = 0$ ($n_i = 1$) depending if $\frac{\rho_i}{\rho_0} \leq 0.5$ ($\frac{\rho_i}{\rho_0} > 0.5$) for each cell.

The interaction between water molecules is given by three terms: a Lennard-Jones potential, the directional component of the hydrogen bond and its cooperative component. The latter is due to quantum many-body effects [6]. The final Hamiltonian is

$$H \equiv \sum_{ij} U(r_{ij}) - JN_{HB} - J_{\sigma}N_{coop}, \quad (1)$$

The first term is the Lennard-Jones potential truncated at short and long distance, defined as

$$U(r) = \infty \text{ if } r < r_0, \\ U(r) = 4\epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \text{ if } r \geq r_0, \quad (2) \\ U(r) = 0 \text{ if } r > r_c \equiv 25 r_0,$$

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where r is the water-water distance, $\epsilon = 5.8 \text{ kJ/mol}$ is the depth of the potential well and r_c is the cut-off distance.

The second term is related to the directional component of the hydrogen bond with an interaction energy $J/4\epsilon \equiv 0.5$ and where the number of HBs, N_{HB} , is by definition

$$N_{HB} \equiv \sum_{\langle ij \rangle} n_i n_j \delta_{\sigma_{ij}} \delta_{\sigma_{ji'}} \quad (3)$$

where the sum is performed over all the nearest neighbors molecules, and $\sigma_{ij} = 1, \dots, q$ is the bonding index of the molecule i facing the nearest neighbor molecule j . The value $q = 6$ is chosen to take into account in the correct way the entropy variations associated to the formation and breaking of a HB.

The third term is due to the HB cooperativity, with an interaction energy $J_\sigma/4\epsilon \equiv 0.05$ and

$$N_{coop} \equiv \sum_i n_i \sum_{(l,k)_i} \delta_{\sigma_{il} \sigma_{ik}} \quad (4)$$

where $(l,k)_i$ denotes the six different pairs of the four indices σ_{ij} of the molecule i .

Finally, the formation of HBs leads to a tetrahedral structure made of four molecules HBonded to a central one. This structure propagates to the second hydration shell leading to the formation of a HB networks that is less dense than liquid water without HBs (and a coordination number larger than four). To take into account this effect the model has a volume that changes with N_{HB} as

$$V \equiv V_0 + N_{HB} v_{HB}, \quad (5)$$

where V_0 is the volume of the system without HBs and $v_{HB}/v_0^3 = 0.5$ is a parameter that takes into account the average variation of volume due to the HB formation [6].

III. METHOD

For each value of L_z , we perform Monte Carlo (MC) simulations at fixed N , P , T and allow the system to adjust the volume from the initial value Nh^3 to the equilibrium volume, V in Eq.(5). To reduce finite-size effects we adopt periodic boundary conditions along the two directions parallel to the plates. We use the following protocol: we equilibrate at near-zero T a random configuration for $\approx 10^5$ MC steps. Next we increase $k_B T/4\epsilon$ by 0.01 and equilibrate for 10^3 MC steps before averaging the results for other 10^3 MC steps and repeat until we reach $k_B T/4\epsilon = 0.8$. At any T we perform calculations starting from the last configuration obtained at the lower T along seven different isobars, at $Pv_0/4\epsilon = 0.0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8$. At any T and P we calculate the average enthalpy $\langle H \rangle$, and enthalpy fluctuation $\langle \Delta H^2 \rangle$, the average volume $\langle V \rangle$, and volume fluctuation $\langle \Delta V^2 \rangle$, the average number of HB and the average number of cooperative bonds. From these quantities we calculate the average density $\rho = N/\langle V \rangle$ and the thermodynamic response functions, isothermal compressibility K_T and isobaric specific heat C_p ,

$$K_T \equiv -\frac{1}{\langle V \rangle} \left(\frac{\partial \langle V \rangle}{\partial P} \right)_T = \frac{\langle \Delta V^2 \rangle}{k_B T \langle V \rangle}, \quad (6)$$

$$C_p \equiv \left(\frac{\partial \langle H \rangle}{\partial T} \right)_P = \frac{\langle \Delta H^2 \rangle}{k_B T}. \quad (7)$$

Taking these into account, it is possible to obtain the phase diagram with the response functions analysis and the density along the isobars.

IV. RESULTS

For $N_z=2$ (Fig.1) we find that the average density has a non-monotonic behavior along each isobar. In particular, at high T the density decreases for increasing T , as in normal liquids. However, for each P there is a temperature of maximum density (TMD) below which the density increases for increasing T , at variance with normal liquids. This is the famous density anomaly that occurs at $\sim 4^\circ\text{C}$ at ambient pressure in bulk water, guarantying that water at $\sim 4^\circ\text{C}$ sinks into colder water and that lakes freeze from the top.

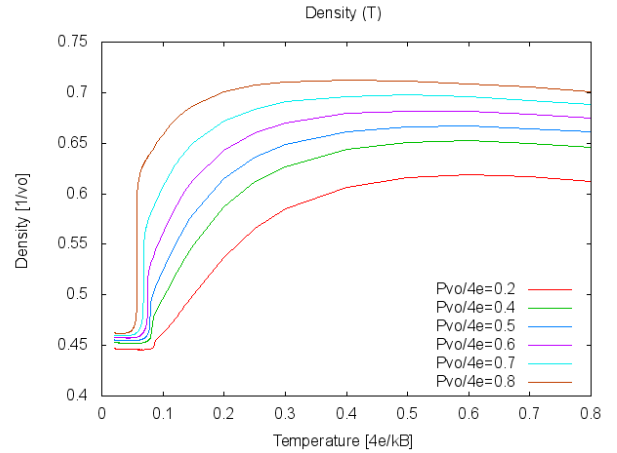


FIG. 1: Isobaric density for two water layers. Pressure is expressed in internal units $4\epsilon/v_0$.

Below the TMD we find that the density decreases toward a minimum for every isobar. The existence of this temperature of minimum density (TminD) has been predicted by simulations [10, 11] and measured in experiments with confined water [12].

The decrease of density toward the minimum is continuous at low P and abrupt at high P . As shown in Ref.s [6, 9] for a monolayer this is an evidence of the coexistence of two liquid phases with different densities in the low- T regime: a high-density liquid (HDL) at high P and higher T and a low-density liquid (LDL) at low P and lower T . The first-order phase transition between the LDL and the HDL ends in a LLCP when P decreases and the density change becomes more regular [6, 9]. However, from the analysis of the density it is difficult to estimate the critical parameters of the LLCP. For this reason we consider the response functions that are expected to diverge at a critical point.

We find that the isobaric specific heat at low pressure (Fig. 2) has a broad (weak) maximum at intermediate T and a

sharp (strong) maximum at low T . By increasing P (Figs 3,4) the strong maximum does not change in T , while the weak maximum converges toward the strong one. For example, for four layers of confined water at $Pv_0/4\varepsilon = 0$ the weak maxima is located around $k_B T/4\varepsilon = 0.3$, for $Pv_0/4\varepsilon = 0.4$ is around $k_B T/4\varepsilon = 0.14$ and for $Pv_0/4\varepsilon = 0.7$ it has almost completely merged with the strong maxima at $k_B T/4\varepsilon = 0.07$. We find that for all the number of layers considered here, as the pressure increases, the weak maxima value increases and gets nearer to the strong maxima, until it finally merges at $Pv_0/4\varepsilon = 0.7$ (Fig.5). This result is consistent with what has been found for the case of the monolayer [6, 13, 14] where it has been shown that the weak maxima denote a maxima in fluctuations of the number of HBs in the system, while the strong maxima is related to the largest fluctuations of the number of cooperative HBs. When the two fluctuations occur at the same thermodynamic state point, the liquid undergoes a critical phase transition in which the HBs form in a large number and in a cooperative way giving rise to the structural change between the LDA (with many cooperative HBs) and the HDA (with a few HBs). Therefore, we conclude that for all the number of layers considered here the critical point is located at $[P \cong 0.7, T \cong 0.07]$.

Having identified the critical point through heat capacity variation, and having studied the density behavior, it is interesting to observe how the phase diagram changes when the number of layers is increased from 2 to 16 (Figs 6, 7, 8 and 9).

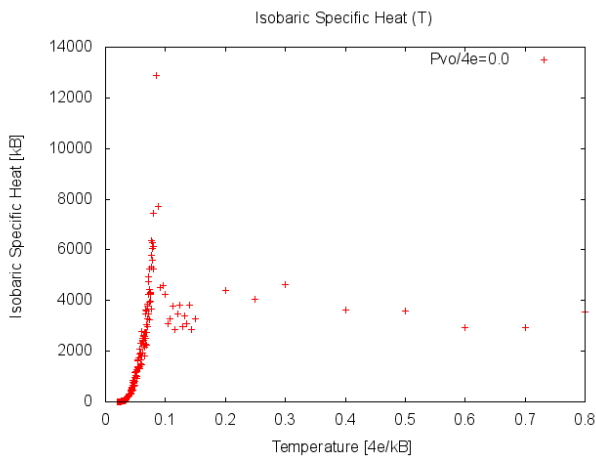


FIG. 2: Isobaric specific heat at $Pv_0/4\varepsilon = 0$ for four water monolayers.

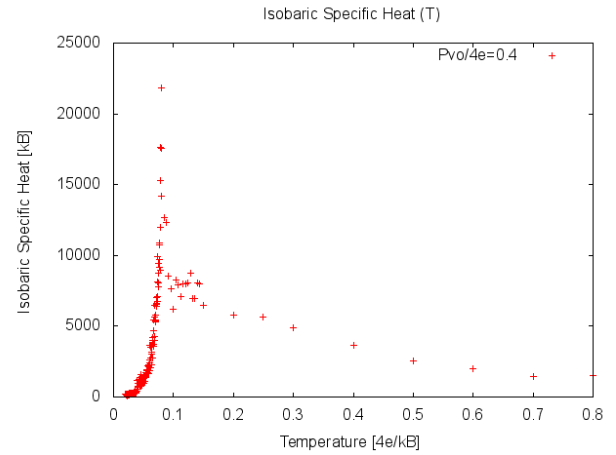


FIG. 3: Isobaric specific heat at $Pv_0/4\varepsilon = 0.4$ for four water monolayers.

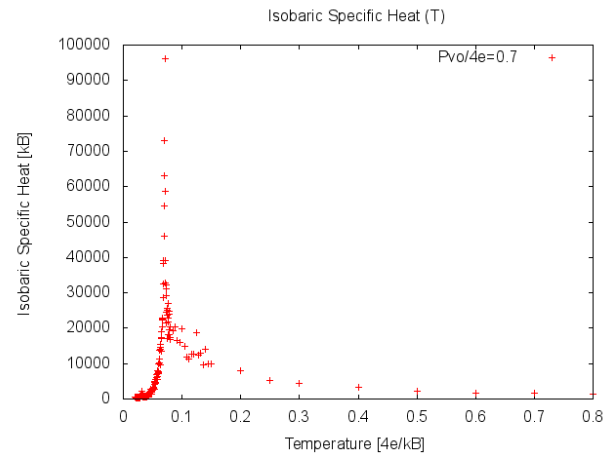


FIG. 4: Isobaric specific heat at $Pv_0/4\varepsilon = 0.7$ for four water monolayers.

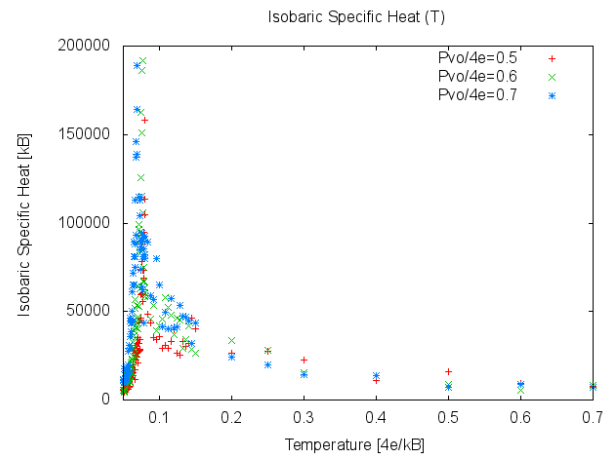


FIG. 5: Isobaric specific heat at $Pv_0/4\varepsilon = 0.5, 0.6, 0.7$ for sixteen water monolayers.

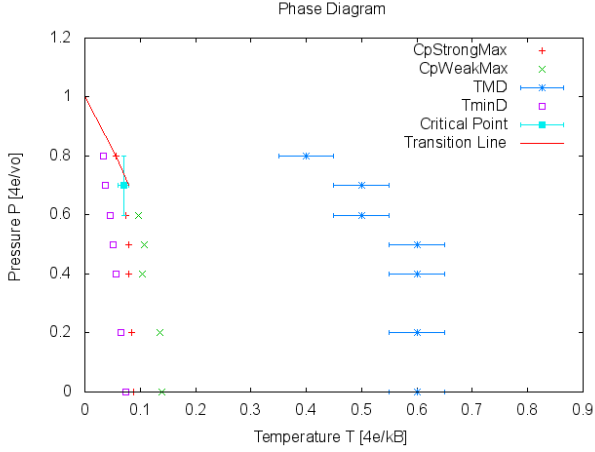


FIG. 6: Phase diagram for a nanoconfined water system with $N_z = 2$

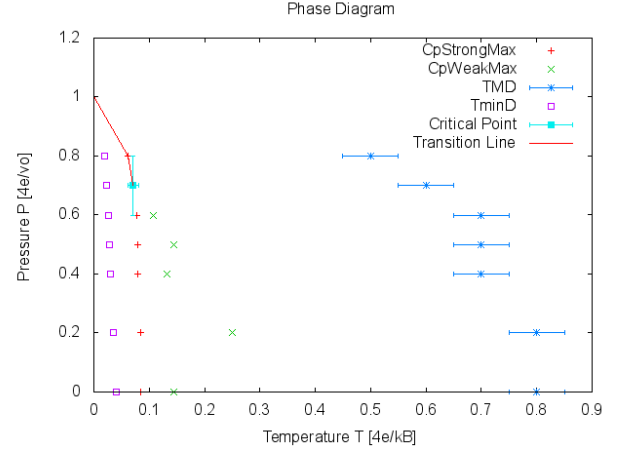


FIG. 9: Phase diagram for a nanoconfined water system with $N_z = 16$

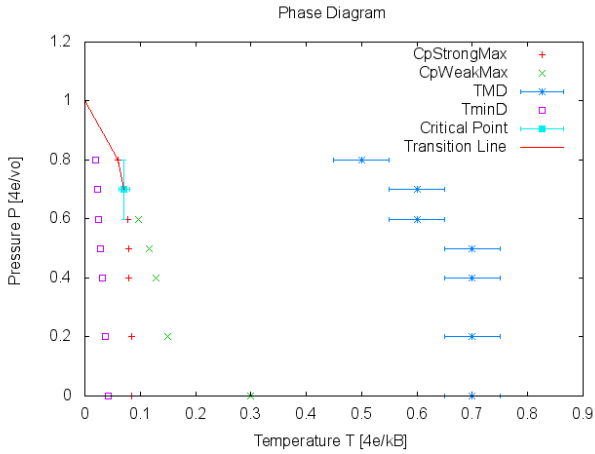


FIG. 7: Phase diagram for a nanoconfined water system with $N_z = 4$

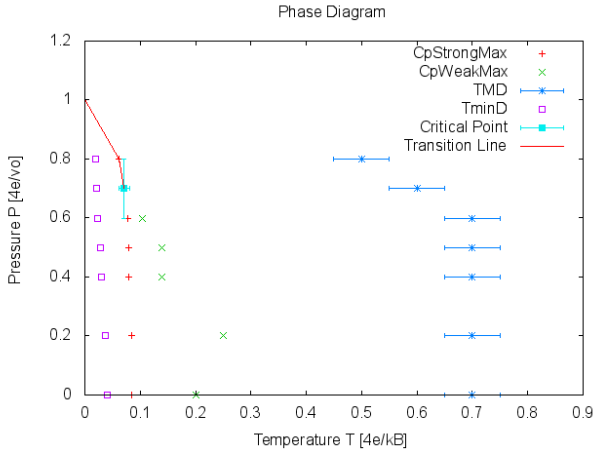


FIG. 8: Phase diagram for a nanoconfined water system with $N_z = 8$

The comparison emphasizes that by increasing the number of layers the high-temperature side of the phase diagram is more affected than the low-temperature region. In particular, the TMD line shifts toward higher T and the line of weak maxima for C_p extends toward slightly higher T at low P , but not at high P . On the other hand, all the loci calculated at approximately $k_B T / 4\epsilon < 0.15$ (line of strong maxima for C_p , TminD, LLCPP and first-order liquid-liquid phase transition line) are affected only in a very weak way within our resolution. This observation implies that the LLCPP and the liquid-liquid phase transition are substantially independent on the number of water layers within the range of values considered here, suggesting that the low-temperature phase diagram for the bulk case should be not very much different from the one found here. Considering that our choice is such that it is always $L/L_z < 3.13 \ll 50$, we hypothesize that the LLCPP belongs to the universality class of the 3D Ising Model, as in bulk water. We speculate that this behavior is due to the fact that the characteristic sizes of the system L and L_z are within the same order of magnitude and that (i) the cooperative nature and (ii) the low-coordination number of the HB network reduce the influence of the embedding dimensionality; hence the system has no longer a prevalent 2D symmetry and the results presented here could be relevant not only for confined water but also for bulk (supercooled) water. Further checks, beyond the scope of this work, will be necessary to test this hypothesis.

V. CONCLUSIONS

We have investigated by MC simulations of a coarse-grained model for water in hydrophobic nanoconfinement how increasing the number of water layers affects the low-temperature phase diagram. We compare our results for four to sixteen layers with the monolayer case [3] and find no qualitative differences with the case in which $L/L_z < 50$, being L_z the separation distance between the parallel walls and L the linear extension of each layer.

In particular, we find that the model reproduces the density anomaly of water along the line of temperature of maximum density (TMD) and displays a line of temperatures of minimum density (TminD) in the very-low-temperature region, as predicted by other models and verified by experiments with confined water. While the number of layers

does not affect the T_{minD} line, the TMD line shifts toward higher T for increasing the number of layers, suggesting that for bulk water the TMD should occur at T higher than those considered here.

We find that the isobaric specific heat at low P and low T has a weak maximum, and at lower T has a strong maximum, as found for the monolayer [6]. Here we find that the position of the loci of these two maxima does not change in a strong way by increasing the number of layers, suggesting that their position should be approximately the same as in bulk water.

In particular, strong and weak C_p maxima converge for all the cases considered here around the thermodynamic state point ($P \cong 0.7, T \cong 0.07$). As shown in previous works, this implies the existence of a LLCPP near the merging point, and located at the end of a high- P first order liquid-liquid phase transition separating two liquid phases that differs for density, structure and energy. Based on the conclusions of Ref. [6], we speculate that the LLCPP belongs to the 3D Ising model universality class, as it would be expected in bulk water.

We finally observe that all our conclusions could be affected by the approximations that we made about the confinement. Here we consider structureless walls that interact with the confined water only by volume exclusion. The presence of walls with atomistic structure and weak (van der Waals) interaction with water could modify our results. However, comparison with detailed atomistic simulations [7, 10] and experiments [12] suggests that the changes should be only quantitative and not qualitative.

Acknowledgments

I'd like to thank specially Giancarlo Franzese, Valentino Bianco and Artem Zantop for their dedication, guidance and patience, which I do really appreciate and I'm thankful for. Special thanks are given too for my friends and family, for always being there.

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