Polyamorphism and polymorphism of a confined water monolayer: liquid-liquid critical point, liquid-crystal and crystal-crystal phase transitions

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Water is an anomalous liquid because its properties are different from those of the majority of liquids. Here, we first review what is anomalous about water. Then we study a many-body model for a water monolayer confined between hydrophobic plates in order to answer fundamental questions related to the origin of its anomalies and to predict new testable futures. In particular, we study by Monte Carlo simulations the low temperature phase diagram of the model. By finite size scaling, we find a liquid-liquid first order phase transition ending in a critical point (LLCP) in the region in which bulk water would be supercooled. We show that the LLCP belongs to the universality class of the two-dimensional (2D) Ising model in the limit of infinite walls. Next, we study the limit of stability of the liquid phase with respect to the crystal phases. To this goal we modify the model in order to characterize the crystal formation and find that the model has a crystal-crystal phase transition and that the LLCP is stable with respect to the liquid-crystal phase transition depending on the relative strength of the three-body interaction with respect to the rest of many-body interactions.

1. An overview of water

A mono-component substance is called anomalous if it behaves differently with respect to argon-like liquids. A few liquids are found to show anomalous properties: silica (SiO₂), silicon (Si), selenium (Se), phosphorus (P), among others. However, the most famous example is water.

Water is undoubtedly the most important liquid for life as we know it. More than 60% of the human body is composed by water. Almost all biological processes need water to work correctly. Water is largely used in modern technologies and industries. Climate changes are strikingly related to water cycling. Among all substances in nature, it is the only one occurring in solid, liquid and vapor phases at ambient conditions.

Despite the fact that liquid water is so common in nature, it has many
anomalous properties—more than sixty—with respect to other liquids. A famous example is its maximum of density at approximately 4°C, leading to a crystal that is less dense than the liquid.

In the following we will review some anomalies properties of water. These anomalies are stronger in the metastable liquid phase below the melting temperature. Water is a strongly metastable liquid and can exist as a supercooled liquid at temperatures far below the melting temperature. The lowest measured temperature for supercooled liquid water is about -92 °C at 2 kbars.\textsuperscript{12}

1.1. Thermodynamic anomalies

As already mentioned, water displays a temperature of maximum density (TMD) in the liquid phase at approximately 4°C at the atmospheric pressure. As a consequence, the isobaric thermal expansion coefficient \( \alpha_P \equiv (1/V)(\partial V/\partial T)_P \), vanishes at \( T \sim 4°C \) and is negative below 4°C where the volume \( V \) expands upon cooling at constant pressure \( P \). The absolute value \(|\alpha_P|\) increases as a power law in the supercooled region.\textsuperscript{13} Thermodynamic relations show that \( \alpha_P \) is proportional to the cross-fluctuations of \( V \) and the entropy \( S \). Hence, below the TMD at any \( P \), water volume and entropy are anti-correlated. This is just the opposite of what happens for the majority of the liquids. A consequence of this anomaly is, for the Clausius-Clapeyron relation, the negative slope of the melting line of water, \( P_m(T) \).

Other anomalous thermodynamic functions of water are the isothermal compressibility \( K_T \equiv -(1/V)(\partial V/\partial P)_T \),\textsuperscript{14} and the isobaric specific heat \( C_P \equiv (\partial H/\partial T)_P \),\textsuperscript{15} where \( H \) is the enthalpy of the system, related to fluctuations in volume and entropy, respectively. For a normal liquid \( K_T \) and \( C_P \) tend to 0 upon cooling, while in the case of water they reach a minimum value at a certain temperature (\( T \sim 46 °C \) for \( K_T \) and \( T \sim 35 °C \) for \( C_P \), at atmospheric pressure) and then increase for decreasing \( T \). Hence, both fluctuations of \( V \) and \( S \) increase upon cooling, at variance with normal liquids.

We remind here that a TMD at constant pressure is revealed also in other substances: by experiments in Ga,\textsuperscript{16} Bi,\textsuperscript{17} Te,\textsuperscript{18} S,\textsuperscript{19,20} Be, Mg, Ca, Sr, Ba,\textsuperscript{21} SiO\textsubscript{2}, P, Se, Ce, Cs, Rb, Co, Ge\textsuperscript{11} and by simulations on SiO\textsubscript{2},\textsuperscript{22–24} S,\textsuperscript{6} BeF\textsubscript{2}.\textsuperscript{22} As for the case of water, also for these substances the TMD implies anomalies in thermodynamic response functions.
Fig. 1. Scheme of water confined between hydrophobic plates of size $L$. The distance between plates is $h \approx 0.5$ nm.

Fig. 2. Phase diagram for a mono-layer of liquid water ($N = 10^4$ molecules) nano-confined between hydrophobic walls separated by a distance $h \approx 0.5$ nm. The loci, described in the text, are marked by full lines for the maxima, dashed lines for minima, and symbols, with labels nearby or in the legend. The liquid-to-gas spinodal (the lowest continuous line) delimits the region of stability of the liquid with respect to the gas phase. The LLCP (large circle with label “A”) is at the end of the LLPT (thick black) line. The indices “m”, “wM” and “M” refer, respectively, to minima, weak maxima and strong maxima of the corresponding thermodynamic quantities. Error bars are of the order of the swaying of the lines or the size of the symbols.
1.2. Dynamic anomalies

A characteristic dynamic anomaly is the non-monotonic behavior of the diffusion constant $D$ as a function of $P$ along isotherms. In a normal liquid $D$ decreases when the density or the pressure are increased.

Anomalous liquids, instead, are characterized by a region of the phase diagram where $D$ increases upon increasing the pressure at constant temperature. In the case of water, experiments show that the normal behavior of $D$ is restored only at pressures higher than $P \sim 1.1$ kbar at 283 K.

1.3. Structural anomalies, polymorphism and polyamorphism

A typical structural anomaly is the non-monotonic behavior of structural order parameters of the system as a function of $P$. Normal liquids tend to become more structured when compressed. The molecules adopt preferential separation and a certain orientational order. This ordering can be described by two order parameters: a translational order parameter and an orientational order parameter. The higher is the value of these parameters, the higher is the order of the system. Therefore, for normal liquids these parameters increase with increasing pressure or density at constant temperature.

Anomalous liquids, instead, show a region where the system becomes more disordered as the pressure increases, leading to lower values of the structural order parameters. This is emphasized in molecular dynamics simulations for water and for silica.

Another anomalous structural property is the occurrence of more than one crystal phase, a property called “polymorphism”. Water, carbon (with graphite, graphene and diamond), phosphorous (with black and red phosphorous) and hydrogen are examples of polymorphic substances. In particular, water has at least sixteen crystalline phases some of them stable only at high pressure.

However, water has also with several amorphous (glassy) states, hence is called also “polyamorphic”. A glass is a frozen liquid state, metastable with respect to the crystal but possibly stable for time scales as long as the life-time of our civilizations. Indeed, we can still appreciate man-made glasses of ancient times, or amber stones preserving prehistorical insects.

Experimental evidences of polyamorphism have been reported in many substances, including hydrogen, phosphorous, triphenyl phos-
phite, yttrium oxide aluminum oxide melts and stannic iodide. In the case of water, it has been found in experiments at low temperature and low pressure a low-density amorphous (LDA) ice. Upon increasing the pressure LDA transforms to high-density amorphous (HDA) ice, and upon further increasing of pressure a similar transformation has been observed from HDA to very-high-density amorphous (VHDA). As we discuss later, the presence of several amorphous states could be related to the occurrence of a metastable liquid-liquid phase transition.

2. Origin of water anomalies

Different scenarios have been proposed to explain the origin of water anomalies. The stability limit scenario hypothesizes that the limit of stability of superheated liquid water merges with the limit of stretched and supercooled water, giving rise to a single locus in the $P-T$ plane, with positive slope at high $T$ and negative slope at low $T$, in the supercooled regime. The reentrant behavior of this locus would be consistent with the anomalies of water observed at higher $T$. As discussed by Debedetti, thermodynamic inconsistency challenges this scenario.

The liquid-liquid critical point (LLCP) scenario supposes a first order phase transition in the supercooled region between two metastable liquids at different densities: the low-density liquid (LDL) at low $P$ and $T$, and the high-density liquid (HDL) at high $P$ and $T$. The phase transition line has a negative slope in the $P-T$ plane and ends in a critical point. Numerical simulations for several models for water are consistent with this scenario. The scenario is consistent also with several experiments for water, see for example, and for other systems, including silicon, phosphorous, triphenyl phosphite, yttrium oxide aluminum oxide melts and stannic iodide. Nevertheless, objections to this scenario have been raised, although they seem to apply only to a specific category of models.

The singularity-free scenario focuses on the anti-correlation between entropy and volume as cause of the large increase of response functions at low $T$ and hypothesizes no hydrogen bond (HB) cooperativity. The scenario predicts lines of maxima in the $P-T$ for the response functions, similar to those observed in the LLCP scenario, but shows no singularity for $T > 0$. Recent calculations show that the singularity-free scenario is a limiting case of the LLCP scenario with the LLCP at $T = 0$. The critical-point-free scenario hypothesizes an order-disorder transition, with a possible weak discontinuity of density, that extends to $P < 0$.
and reaches the supercooled limit of stability of liquid water. This scenario would effectively predicts no critical point and a behavior for the limit of stability of liquid water as in the stability limit scenario.

Stokely et al. have shown recently that all these scenarios have a common physical mechanism and that two key physical quantities determine which of the four scenarios describes water: (i) the strength of the directional component of the hydrogen bond and (ii) the strength of the cooperative (many-body) component of the hydrogen bond. Furthermore, estimates from experimental data for these two parameters of the hydrogen bond lead to the conclusion that water should have a LLCP at positive pressure.

Nevertheless, to date experiments for bulk liquid water able to discriminate between various models are not conclusive yet: the experimental resolution time is still bigger with respect to the homogeneous nucleation time and the system inevitably crystallize. As we will see in the next section, the confinement in nano-structures or nano-pores is, in some cases, a way to prevent the crystal formation.

3. A many-body model for confined water

A variety of statistical models have been proposed in order to reproduce the main features of liquid water, including the anomalies. Water molecule are often treated as rigid and the water-water interaction is modeled combining Coulomb interactions of a finite number of point charges and Lennard-Jones potential between the centers of mass of different water molecules. These pair potentials reproduce water anomalies with fair agreement, but do not succeed in reproducing all the properties. For example, many of them fail in reproducing the crystal phases of water. However, the real problem with these models is that they are computationally expensive due to the long range Coulomb interaction.

This problem is particular relevant in simulations of biological processes where macromolecules are surrounded by millions of water molecules. To overcome this problem a possible way is to consider coarse-grained models for water. In particular, these models can be used to study nano-confined water in extreme conditions and to compare with experiments.

The study of nano-confined water is of great interest for applications in nanotechnology and nano-science. The confinement of water in quasi-one or two dimensions (2D) is leading to the discovery of new and controversial phenomena in experiments and simulations. Nano-confinement, both in hydrophilic and hydrophobic materials, can keep water in the liquid
phase at temperatures as low as 130 K at ambient pressure. At these temperatures $T$ and pressures $P$ experiments cannot probe liquid water in the bulk, because water freezes faster than the minimum observation time of usual techniques, resulting in an experimental “no man’s land”. Nevertheless, new kind of experiments and numerical simulations can access this region, revealing interesting phenomena in the metastable state.

Here, we will describe in detail the model proposed by Franzese and Stanley in 2002. The simplest approximation of nano-confined water is a monolayer of water confined between two plates (see Fig. 1). We coarse grain the spatial distribution of the molecules dividing the system into cells, each one occupied at most by one water molecule, and introduce a density field, neglecting the position of the water molecules inside the cell. For each cell $i$ we associate an occupation number $n_i = 1$ if the local (dimensionless) density $v_0/v > 0.5$ (liquid-like configuration), otherwise $n_i = 0$ (gas-like configuration). Here, $v$ is the cell volume and the minimum volume of a cell corresponds to the hard core volume $v_0$ of a water molecule. Isotropic and long-range interaction (van der Waals attraction and hard core repulsion) in the system are represented by the Lennard-Jones potential.

$$\mathcal{H}_{\text{LJ}} = -\sum_{i,j} \epsilon \left[ \left( \frac{r_0}{r_{ij}} \right)^{12} - \left( \frac{r_0}{r_{ij}} \right)^6 \right], \quad (1)$$

where $r_{ij}$ is the distance between molecules $i$ and $j$ and the sum is performed over all the neighboring molecules up to a cutoff distance at about twenty shells. This term depends only on the relative distance between two molecules and represents the isotropic part of the interaction.

In order to describe the HB interaction, which is directional, we introduce the variables $\sigma_{ij} = 1...6$ for each occupied site $i$ facing the cell $j$. Assuming that a water molecule can form up to four HBs, we fix to four the number of variables $\sigma_{ij}$ for each cell. Variables $\sigma_{ij}$ are introduced to account for the number of bonding configurations accessible to a water molecule. The state of a water molecule is completely determined by the values assumed by the four variables $\sigma_{ij}$. The condition for two first neighbor molecules to form a HB is $\sigma_{ij} = \sigma_{ji}$. To take into account correctly the entropy loss due to the formation of a new HB, we consider that HB is broken if the angle $\hat{HOO}$ deviates more than $30^\circ$ from the linear bond. Therefore, we consider $q = 180^\circ/30^\circ = 6$ states, where only $1/6$ corresponds to the formation of a HB. This covalent HB interaction is represented by
the Hamiltonian term
\[ \mathcal{H}_{\text{HB}} \equiv -J \sum_{<ij>} n_in_j \delta_{\sigma_{ij},\sigma_{ji}}, \] (2)
where \( J > 0 \) represents the energy gained per HB, the sum is over nearest neighbors cells, and \( \delta_{ab} = 1 \) if \( a = b \), 0 otherwise.

Experimental evidences show that the distribution of angles \( \overrightarrow{OOO} \) changes with \( T \) and becomes sharper and sharper with the decrease of \( T \), approaching the distribution corresponding to tetrahedral arrangement.\(^{88}\)

Therefore, there is a correlation among the HBs formed by the same molecule. Hence, we introduce a term representing the many-body interaction between the HBs of a single molecule,
\[ \mathcal{H}_{\text{Coop}} \equiv -J_\sigma \sum_i \sum_{(k,l)} \delta_{\sigma_{ik},\sigma_{il}}, \] (3)
where \( J_\sigma > 0 \) is the characteristic energy of this cooperative component.

The formation of a HB leads to an open structure that induces a local increase of volume per molecule. This effect is incorporated in the model by considering that the total volume of the system depends linearly on the number of HBs. So the volume change is
\[ V \equiv V_0 + N_{\text{HB}}v_{\text{HB}}, \] (4)
where \( v_{\text{HB}} \) is the increment due to the HB, and \( V_0 \equiv Nv_0 \) for \( N \) water molecules.

The total enthalpy of the system is
\[ H \equiv U + \mathcal{H}_{\text{HB}} + \mathcal{H}_{\text{Coop}} + PV = U - (J - Pv_{\text{HB}})N_{\text{HB}} - J_\sigma N_{\sigma} + PV_0, \] (5)
where the total number of HB is
\[ N_{\text{HB}} \equiv \sum_{<ij>} n_in_j \delta_{\sigma_{ij},\sigma_{ji}}, \] (6)
and
\[ N_{\sigma} \equiv \sum_i \sum_{(k,l)} \delta_{\sigma_{ik},\sigma_{il}}, \] (7)
is the total number of HBs optimizing the cooperative interaction.\(^{52,69,73–76,85,87,89}\) In the following we adopt the parameters \( J/\epsilon = 0.5 \), \( J_\sigma/\epsilon = 0.05 \) and \( v_{\text{HB}}/v_0 = 0.5 \), consistent with the values that can be deduced from experiments.\(^{69}\)
4. Simulation details

We simulate the model at constant $T$ and $P$ using an efficient cluster algorithm\textsuperscript{89,90} that allows us to equilibrate the system very fast in the supercooled region of the phase diagram, also for those combinations of $T$ and $P$ where water exhibits glassy dynamics. To equilibrate our simulations, we implement an annealing protocol starting at high temperature and slowly decreasing $T$ at constant $P$. The thermodynamic equilibrium is verified by checking that the calculation of the isothermal compressibility $K_T(T) \equiv -\left( \frac{\partial \ln \langle V \rangle}{\partial P} \right)_T$, where $\langle V \rangle$ is the average volume from Eq. (4), and the isobaric specific heat $C_P(P) \equiv \frac{\partial \langle H \rangle}{\partial T}$, where $\langle H \rangle$ is the average enthalpy from Eq. (5), converge to their calculations from the fluctuation-dissipation relation.

A Monte Carlo step is by definition the sequence of $4N + 1$ trials of updating the $4N$ variables $\sigma$ and the volume of the system, in a random sequence. The trial change modifies the volume of a small random amount $\delta V$. We adjust $\delta V$ to keep a constant acceptance ratio $\approx 40\%$\textsuperscript{91,92}

In order to characterize the phase diagram of liquid water we simulate $\sim 10^4$ different thermodynamic state-points for a wide range of $T$ and $P$ with statistics of $5 \times 10^6$ independent calculations for systems with $N = 2500, \ldots, 40000$ water molecules\textsuperscript{25,76,89,90,93–96}

In real units the simulated range includes temperatures as low as $T = 120\, K$ and pressures as high as $P = 0.4\, \text{GPa}$\textsuperscript{93}. Here, we adopt the following units: $4e/k_B$ for $T$ and $4e/v_0$ for $P$, with $k_B$ the Boltzmann constant.

5. Results about the polyamorphism and the thermodynamics

5.1. Phase diagram

The phase diagram is reported in Fig. 2. We find the liquid-to-gas spinodal at $P < 0$ and low $T$, identifying the stability limit of the liquid phase with respect to the gas phase. Within the liquid region we find along isobars the temperatures of maximum density (TMD). At high $P$ the TMD line is reentrant, while at low $P$ it approaches the spinodal, without crossing it. At its lowest pressure the TMD line merges with the line of temperatures of minimum density (TminD) along isobars. This is consistent with experiments\textsuperscript{97} and other models\textsuperscript{98,99}

We calculate the isothermal compressibility $K_T(T)$ the isobaric expansivity $\alpha_P(P) \equiv \frac{\partial \ln \langle V \rangle}{\partial T}$ along isotherms, and the isobaric specific heat $C_P(P)$ along isotherms. For each quantity we find two maxima along
isobars at low $P$. A broader and weaker maximum at higher $T$, and a sharper and stronger maximum at lower $T$.95

We find that the loci of weak maxima $\alpha_P^{\text{wM}}$ and minima $|\alpha_P^{\text{wM}}$ of thermal expansivity along isotherms are both reentrant in pressure at low $T$. At high $T$ they converge toward each other forming a single locus of extrema that changes from maxima to minima where $dP/dT = \infty$ along the locus. This locus coincides within the error bars with the extrema of compressibility along isobars, weak maxima $K_T^{\text{wM}}$ and minima $K_T^{\text{m}}$, with the locus of extrema of $K_T$ changing from maxima to minima where $dP/dT = 0$ along the locus.

All these results are consistent with the thermodynamic relations.$^{68,98,99}$ This consistency holds also for $|\alpha_P^{\text{wM}}$ intersecting the TMD line in its turning point at high $T$,$^{68}$ and for $C_P^{\text{wM}}$, locus of weak $C_P$ maxima along isotherms, bending toward the point where the TMD line and the TminD line merge.$^{99}$

Finally, we find that the locus of strong $C_P$ maxima $(C_P^{\text{M}})$ coincides with the loci of stronger maxima $|\alpha_P^{\text{M}}$ and stronger maxima $K_T^{\text{M}}$. This last relation among the loci of strong maxima has been found only within the framework of this model,$^{86,100}$ likely because for other models is very expensive the computational cost to explore the thermodynamics of the metastable states at such a low $T$, where the dynamics is glassy$^{57}$ at low $P$, while at high $P$ the strong and weak maxima merge into each other.

All the loci of the maxima of the response functions converge towards the point with the label “A” in Fig. 2. Moreover, all the maxima along these loci increase in their values by approaching the point “A”.

5.2. Polyamorphism and the liquid-liquid critical point

The point “A” is at the end of a line along which we observe (i) a sudden change in the density of the liquid and (ii) a decrease of the maxima of the response functions for increasing $P$. These observations are consistent with the identification of this line with a first-order phase transition line separating two liquids with different densities, the HDL at high $P$ and $T$ and the LDL at low $P$ and $T$, consistent with the presence of polyamorphism in water.

The first-order liquid-liquid phase transition (LLPT) line ends in the state-point “A” where all the response functions diverge, that we, therefore, interpret as a liquid-liquid critical point, as in the LLCP scenario described in section 2. Confirmations of this interpretation come from the study of the correlation length and the critical exponent, discussed in the next sections.
5.3. The correlation length and the Widom line

The increase of the response functions at the LLCP in “A” of Fig. 2 is related to the increase of fluctuations and this, in turn, is related to the increase of the correlation length $\xi$. It is, therefore, interesting to calculate the spatial correlation function $G(\mathbf{r}) \equiv \langle \sigma_{ij}(\mathbf{r}) \sigma_{lk}(\mathbf{r}) \rangle - \langle \sigma_{ij} \rangle^2$ to estimate $\xi$, defined as the characteristic length over which $G(\mathbf{r})$ decays to zero.

We find that for $P$ below the LLCP in “A”, $G(\mathbf{r})$ decays as an exponential with a characteristic correlation length $\xi$. For $P$ approaching the LLCP, $G(\mathbf{r})$ is better approximated by a power-law decay with an exponential prefactor from which $\xi$ can be extracted. At the LLCP, the exponential prefactor approaches a constant leaving the power-law as the dominant contribution for the decay, corresponding to $\xi$ becoming of the order of the system size. All these observations confirm that the state point in “A” is, indeed, a critical point.

Furthermore, the calculation of $\xi$ near the LLCP allows us to gain an extremely relevant insight. We observe that for $P < P_C$, the pressure of the LLCP, $\xi$ has a maximum $\xi_M$ along isobars. The locus of these maxima, $T_W(P) \equiv T[\xi_M(P)]$, is by definition the Widom line.

Our results show that the Widom line departs from the LLCP, as expected. Furthermore, we find that the Widom line coincides with the loci of strong maxima in $C_P$, $K_T$ and $|\alpha|_P$.

This finding, together with the previous observations, confirms our interpretation of the state point “A” as LLCP at the end of a first-order LLPT line in the $P-T$ phase diagram, as discussed in previous works. Along the LLPT line the density, the energy and the entropy of the liquid are discontinuous. Next, we analyze in detail the LLCP and find that the correct order parameter for the LLPT is not just the density and that the confinement has a strong effect on the universality class of the LLCP.

5.4. The critical region

For a liquid-gas critical point it has been shown that an order parameter (o.p.) defined based solely on the difference in density between the two coexisting phases is not able to give rise to an o.p. distribution that is symmetric with respect to the ordered and disordered phases, as required at the critical point. The mixed-field finite-size scaling theory solves the problem by adopting as o.p.

$$M \equiv \rho + su,$$
Fig. 3. The size-dependent probability distribution $P_N$ for the rescaled order parameter $x$, calculated for size-dependent critical temperature $T_c(N)$ and pressure $P_c(N)$, has a symmetric shape that approaches continuously (from $N = 2500$, symbols at the top at $x = 0$, to $N = 40000$, symbols at the bottom) the limiting form for the 2D Ising universality class (full line), maximizing the difference with the 3D Ising universality class (dashed line). Lines connecting the symbols are guides for the eye. Error bars are smaller than the symbols size.

where the density $\rho$ represents the leading term, $u$ is the energy density and $s$ is the field mixing parameter. Here, both $\rho$ and $u$ are expressed in internal units in such a way to be dimensionless.

Within this theory, the probability distribution $P_N(M) \propto \tilde{p}_d(x)$ of $M$ at the critical point scales as an universal function $\tilde{p}_d$ of $x \equiv B(M - M_c)$. The function $\tilde{p}_d$ is characteristic of the universality class of the Ising model in $d$ dimensions and is the same for all the models belonging to the same universality class. The quantities $B$ and $M_c$ are adjusted in such a way that $P_N(M)$ has zero mean and unit variance. In particular, it can be shown that $B \equiv a_M^{-1} N^{\beta/\nu}$, where $\beta > 0$ is the critical exponent of $M \sim (T_c - T)^\beta$, $\nu > 0$ is the critical exponent of $\xi \sim |T - T_c|^{-\nu}$, $T_c$ the critical temperature, and $a_M$ is a non-universal system-dependent parameter. Both exponents $\beta$
and $\nu$ are defined by the universality class.

As observed by other authors,\textsuperscript{106} the hypothesis of the mixed-field finite-size scaling theory hold in general for any fluid-fluid phase transition at a critical point. We, therefore, apply these theory also to the LLCP and the LLPT and adopt as o.p. the Eq. (8), where $s$ is found as explained in the following.

Fig. 4. The size-dependent critical temperature $T_c(N)$ (a) and pressure $P_c(N)$ (b) at the LLCP, agree with the power low function $N^{-\theta/\nu}d^\theta$ using critical exponents of Ising universality class in $d = 2$ dimensions: $\theta = 0$, $\nu = 1$ and $\beta = 1/8$. From these data we extract, by fitting in the thermodynamic limit $N \to \infty$, $T_c \simeq 0.0597$ and $P_c \simeq 0.554$. Continuous lines are best fits results. (c) We compare here the normalization factor $B(N)$ (symbols) with the power law function $\propto N^{\beta/\nu}$ predicted by the theory (dashed line), finding a good agreement for large sizes. No fit is performed in this case and a systematic deviation from the predicted behavior is observed for small sizes.

For each system size $N \in [2.5 \times 10^3, 40 \times 10^3]$, we simulate $\sim 300$ state points, each for $\sim 100$ independent runs of $10^6$ MC calculations, in a range of $T$ and $P$ with $0.033 \leq T \leq 0.065$ and $0.01 \leq P \leq 0.90$, and use the multiple histogram reweighting method\textsuperscript{107} to extrapolate the calculations for intermediate state points. By tuning $s$ for these state points, we find that, for each $N$, the distribution $P_N(x)$ has a symmetric shape with respect
to $x = 0$ when $s = 0.25 \pm 0.03$ and $T$ and $P$ are in the vicinity of the state point “A” (Fig. 3).

We find that the resulting size-dependent critical parameters $T_c(N)$, $P_c(N)$ and the size-dependent normalization factor $B(N)$ follow in fair agreement the expected finite-size behaviors with the 2D Ising critical exponents$^{102-105}$ (Fig. 4). From the finite-size analysis we extract the asymptotic values $T_c = 0.0597 \pm 0.0001$ and $P_c = 0.554 \pm 0.003$, consistent with the state point “A”.

However, the behavior of $B(N)$ (Fig. 4c) clearly displays a systematic deviation from the predicted values for small sizes. A systematic analysis of the finite size affects of our results has been performed in,$^{86}$ finding the surprising results that by decreasing the wall size with respect to the monolayer thickness $h$, the LLCP is better described by the 3D Ising model universality class. We ascribe this result to the strong cooperativity and the low coordination number of the hydrogen bond network.$^{86}$

6. Study of the structural properties

The many-body model described in section 3 successfully describes the thermodynamics of water under confinement and predicts the polymorphism at low $T$. However, it coarse-grains the coordinates of the molecules, precluding the possibility to reproduce the details of the structure of the system. In particular, it does not allows to define the crystal phase.

6.1. The many-body model for fluid and crystal phases

In this section we introduce a modification of the model that includes explicitly the particle coordinates. As a consequence, the new formulation allows the calculation of the radial distribution function and the occurrence of the crystal-fluid phase transition, in addition to the properties already described by the previous sections.

To this goal we add to the enthalpy in Eq.(5) a three-body repulsive interaction between a central molecule $i$ and its H-bonded nearest neighbors $k, l$,

$$\mathcal{H}_{\text{Ang}} \equiv J_\theta \sum_i \sum_{(k, l)_i} \delta_{\sigma_{ik}, \sigma_{il}} \delta_{\sigma_{ik}, \sigma_{il}} \Delta(\theta^i_{k,l}),$$

that is different from zero only if both the possible H-bonds are present. Here, $J_\theta > 0$ is a characteristic interaction energy, $\theta^i_{k,l}$ is the angle formed
by the centers of the three molecules and
\[
\Delta(\theta) \equiv \frac{1}{2} [1 + \cos(4\theta - \pi)]
\]  (10)
is a positive-defined function with minima \((\Delta = 0)\) at angles 90° and 180°. For these two specific values of the \(\theta\) it has been shown, by molecular dynamics simulations of an atomistic model,\(^{81,82}\) that a water monolayer can form crystalline phases at low \(T\). In the following we adopt the parameters \(J/\epsilon = 0.75\), \(J_{\sigma}/\epsilon = 0.1\), \(v_{\text{HB}}/v_0 = 0.5\) and \(J_{\theta}/\epsilon = 0.1\). Here, the values for \(J/\epsilon\) and \(J_{\sigma}/\epsilon\) are larger than those adopted in the previous sections. The modification of these parameters does not change qualitatively the phase diagram of the fluid phases, but allows us the better calculate the properties of the crystal phases.

6.2. Simulation details

We perform Monte Carlo simulations using the Metropolis algorithm. Here a Monte Carlo step is by definition the sequence of \(5N+1\) trials of updating the \(N\) molecule coordinates \(\vec{r}_i\), each free to move within a cell, the \(4N\) variables \(\sigma\) and the volume of the system, all chosen in a random sequence. Each cell can be at most occupied by one molecule.

To equilibrate the system we check the validity of the fluctuation-dissipation relations, as described for the model in the previous sections. Since we use periodic boundary conditions, in order to allow the equilibration of an arbitrary crystal, we allow the change of the volume aspect ratio. We choose randomly the \(X\) or \(Y\) direction and attempt a trial change of the box lateral sizes \(L_X\) or \(L_Y\) of a small random amount \(\delta L\). We adjust \(\delta L\) to keep a constant acceptance ratio \(\approx 40\%\).\(^{91,92}\)

7. Results about the polymorphism

7.1. Radial Distribution Function

In order to study structural properties of our system, we calculate the radial distribution function in two dimensions,
\[
g(r) \equiv \frac{1}{2\pi r} \frac{1}{N\rho} \sum_{i=0}^{N} \sum_{i \neq j} \delta(r - r_{ij}),
\]  (11)
where \(r_{ij} \equiv |\vec{r}_i - \vec{r}_j|\) is the distance between two molecules \(i\) and \(j\), and \(r\) is the distance in units of \(r_0 \equiv \sqrt{v_0/h}\), where \(h \approx 0.5\) nm is the distance between the confining hydrophobic walls.
Fig. 5. Radial distribution function $g(r)$ of the 2D projection of the coordinates of the confined water monolayer at different temperatures for $P = 0.1$ (upper panel), and for $P = 1.5$ (lower panel). In both panels the $g(r)$ changes from a low-structured function of a fluid phases at high $T = 0.30$ to a highly-structured function of a crystal phase at low $T = 0.09$. For the same values of $T$, the $g(r)$ at the two values of $P$ are quite different. In particular, the $g(r)$ of the crystal phases at $T = 0.09$ have peaks in different positions, emphasizing that the two crystals are different and that the system is polymorphous as discussed in the text.
We find that $g(r)$ calculated at different $T$ and $P$ (Fig. 5) emphasizes the occurrence of fluids and crystals with different symmetries. This observation is consistent with the occurrence of polyamorphism and polymorphism in the confined water monolayer. Next we characterize the symmetries of the different phases.

7.2. Structural Order Parameters

![Fig. 6. Configurations for the coarse-grained model defined in section 6.1 at different temperatures for $P = 0.1$ (panels a, b, c), and for $P = 1.5$ (panels d, e, f). The orientational and translational order are quantified using the corresponding order parameters $|\Phi_4|$ and $|\Psi_G|$. Two different solid phases at low temperature are found having square and triangular symmetry at low and high pressure, respectively. Here $T$ and $P$ are as in Fig. 5.

We adopt a local bond-orientational order parameter $\phi_4$, similar to that introduced by Nelson and Halperin, which is a function of the state of
the system,

\[ \phi_{4,i} \equiv \frac{1}{n_i} \sum_{j=1}^{n_i} e^{i \theta_{ij}}, \]  

(12)

and its global average

\[ \Phi_4 \equiv \left\langle \frac{1}{N} \sum_{i=1}^{N} \phi_{4,i} \right\rangle. \]  

(13)

The angle \( \theta_{ij} \) is the angle formed by the vector going from the molecule \( i \) to the molecule \( j \) with respect to an arbitrary reference axis and \( n_i \) is the number of nearest neighbors of the molecules \( i \). The quantity \( \Phi_4 \) gives information about the amount of orientational local order in the system, being \( |\Phi_4| \approx 0 \) for random (fluid) configurations, and \( |\Phi_4| \approx 1 \) for crystalline configurations with 90° symmetry.

Next, we define the translational order parameter considering

\[ \psi_{G,i} \equiv e^{i \bar{G} \cdot \bar{r}_i}, \]  

(14)

and its average

\[ \Psi_G \equiv \left\langle \frac{1}{N} \sum_{i=1}^{N} \psi_{G,i} \right\rangle, \]  

(15)

where, taking as a reference a crystal with square symmetry, we choose \( \bar{G} = \frac{2\pi}{a} \bar{e}_X \), where \( a = L_X/\sqrt{N} \) is the lattice spacing and \( \bar{e}_X \) the unit vector along the coordinate \( X \). The order parameter \( \Psi_G \) quantifies the average translational order in the system and is \( |\Psi_G| \approx 1 \) only when the system is highly structured.

We find\(^{110}\) that at low pressure and low \( T \) the systems crystallize with long range translational and orientational order with square symmetry due to the formation of a fully connected hydrogen-bond network (Fig.6,a). At the same pressure and higher \( T \) the systems loses its long-range translational order and is characterized by a short-range orientational order (Fig.6,b) as in a hexatic phase.\(^{111,112}\) At higher \( T \) the system is in a disordered (fluid) state (Fig.6,c).

By increasing the pressure, the system crystallizes at low \( T \) with a triangular symmetry due to the breaking of the hydrogen bonds (Fig.6,d). In this case the crystal is better characterized by order parameters with triangular symmetry \( \Phi_6 \) and \( \Psi_G \) with definitions similar to those given in Eqs. (13, 15). By increasing \( T \), also at this pressure the system looses its long-range order, keeping the short-range order (Fig.6,e) as in another
hexatic phase. At even higher $T$ the system melts into a disordered (fluid) state (Fig. 6,f) with a density that is larger than the density of the fluid at lower pressure.

All these structural transformations are well reflected by the behavior of $g(r)$ seen in Fig. 5. We, therefore, conclude that a confined water monolayer displays polymorphism at low $T$, and polyamorphism at higher $T$, as a function of the pressure. A more quantitative analysis, with the definition of the limit of stability of the different phases, is performed in Ref. 110.

8. Conclusions

Our results show that a water monolayer confined between hydrophobic parallel walls separated by $h \approx 0.5$ nm has qualitatively the same phase diagram of bulk water at high $T$. At low $T$, where bulk water freezes, confined water can still be enough fluid to allow the coexistence of two liquids phases, HDL and LDL, with different density, energy, entropy and structure. Under these conditions, confined water is a polyamorphous.

The two liquids are separated by a LLPT ending in a LLCP. This critical point belongs to the 2D Ising universality class for a monolayer in the thermodynamic limit, i.e. when the walls lateral size $L \gg h$. Our analysis, as shown in Ref. 86, show the intriguing result that for $L/h \leq 50$ the system is better described by the 3D Ising universality class. Surprisingly this suggests that water, under strong confinement, could be better described by bulk-like critical behavior. We ascribe this property to the high cooperativity and low coordination number of the hydrogen bond network.

By introducing the molecules coordinates within the coarse-graining cells of the model, we are able to describe also the crystal phases of confined water. We find that the system is polymorphous, reminiscent of the large number of crystal phases of bulk water.

Our analysis allows us to understand the possible origin of different interpretations of numerical results coming from different models. In particular, in Ref. 110 we show that the LLPT is hindered by inevitable crystallization when the three-body interaction among the water molecules is stronger than the interaction coming from the remaining many-body contributions to the water-water coupling. Therefore, a model where the three-body interaction is dominant, as in the mW-water case, would favor the crystallization over the liquid-liquid coexistence, while in other models the contributions to the water-water coupling coming from four-body interaction and higher order interaction would favor the liquid-liquid coexistence over the crystallization.
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