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Elena G. Strekalova, Marco G. Mazza, H. Eugene Stanley, and Giancarlo Franzese
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Large decrease of fluctuations for supercooled water in hydrophobic nanoconfinement

Elena G. Strekalova,1 Marco G. Mazza,2 H. Eugene Stanley,1 and Giancarlo Franzese3

1Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA
2Stranski-Laboratorium für Physikalische und Theoretische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
3Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Using Monte Carlo simulations we study a coarse-grained model of a water layer confined in a fixed disordered matrix of hydrophobic nanoparticles at different particle concentrations c. For c = 0, we find a first-order liquid-liquid phase transition (LLPT) ending in one critical point at low pressure. For c > 0, our simulations are consistent with a LLPT line ending in two critical points at low and high pressure P. For c = 25%, at high P and low temperature T, we find a dramatic decrease of compressibility, thermal expansion coefficient, and specific heat. Surprisingly, the effect is present also for c as low as 2.4%. We conclude that even a small presence of nanoscopic hydrophobes can drastically suppress thermodynamic fluctuations, making the detection of the LLPT more difficult.

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Many recent experiments investigate the behavior of water in confined geometries [1] for its relevance to nanotechnology, e.g., filtering water in carbon nanotubes [2], and biophysics, e.g., intracellular water [3]. An interesting property of nanoconfined water is that it remains liquid at temperatures where bulk water freezes. The present technology allows us to observe bulk water in its liquid phase below 0°C if quenched very rapidly (supercooled), but ice formation cannot be avoided below \( T_H = -41°C \) (at 1 atm). Interestingly, a number of theories and models predict a peculiar thermodynamic behavior for bulk water below \( T_H \), with a liquid-liquid phase transition (LLPT) [4–6]. Although studying nanoconfined water could shed light on the phase diagram of water monolayer of thickness \( h \lesssim 1 \) nm in a volume \( V/N \) partitioned into \( N \) cells of a square section of size \( \sqrt{V/N} \). Each cell is occupied by either a water molecule or a hydrophobic particle. Particles can occupy more than one cell, depending on their size, are spherical and approximated by the set of cells with more than 50% of their volume inaccessible to water. Particles are randomly distributed and form a fixed matrix that mimics a porous system or a rough atomic interface. \( N \leq N \) is the total number of cells occupied by water molecules and \( V \leq V' \) is their total volume. The Hamiltonian for water-water interaction is [5]

\[
\mathcal{H} = \sum_{ij} U(r_{ij}) - J N_{HB} - J \sigma \sum_i n_i \sum_{(k,\ell)} \delta_{\sigma_{ik},\sigma_{\ell k}}. \tag{1}
\]

Here \( r_{ij} \) is the distance between water molecules \( i \) and \( j \), \( U(r) = \infty \) for \( r < r_0 = 2.9 \) Å, the water van der Waals diameter, \( U(r) = \epsilon_w [(r_0/r)^{12} - (r_0/r)^6] \), with \( r_0 = 0 \) with \( \epsilon_w = 5.8 \) kJ/mol, the van der Waals attraction energy, and \( U(r) = 0 \) for \( r > r_c = \sqrt{V/\pi}/4 \), the cut-off distance.

The second term of Eq. (1) describes the directional HB interaction, with \( J = 2.0 \) kJ/mol, and the total number of HBs \( N_{HB} = \sum_{(i,j)} n_i n_j \delta_{\sigma_{ij},\sigma_{ji}} \), where \( n_i = 1 \) for a water molecule when \( N v_0/\sqrt{\pi} \geq 0.5 \) (liquid density, with \( v_0 = h r_0^2 \)) and \( n_i = 0 \) for a hydrophobic particle. A HB breaks when the OH—O distance exceeds \( r_{max} - r_{OH} = 3.14 \) Å, because \( n_i n_j = 0 \) when the O—O distance \( r \geq r_{max} = 4.10 \) Å (\( r_{OH} = 0.96 \) Å). It also breaks if \( \hat{O}OH > 30° \). Therefore, only 1/6 of the orientation range \([0, 360°]\) in the OH—O plane is associated with a bonded state. By allowing \( q = 6 \) possible states for each index \( \sigma_{ij} \), we account for the entropy loss associated with the formation of a HB because, by definition, \( \delta_{\sigma_{ij},\sigma_{ji}} = 1 \) if \( \sigma_{ij} = \sigma_{ji} \), \( \delta_{\sigma_{ij},\sigma_{ji}} = 0 \) otherwise. The notation \( (i,j) \) denotes that the sum is performed over nearest–neighbors (n.n.) water molecules \( i \) and \( j \), so that each water molecule can form up to four HBs.

HB formation increases the volume per molecule, because it leads to an open network of molecules with reduced n.n. due to close molecular packing. We incorporate this effect by an enthalpy increase \( P v_{HB} \) for each HB, where \( v_{HB}/v_0 = 0.5 \) is the average density increase.
from low density ice Ih to high density ices VI and VIII.

The third term of Eq. (1) accounts for the HB cooperativity, with $J_p \equiv 0.29\text{ kJ/mol}$, where $(k, \ell)_i$ indicates each of the six different pairs of the four bond-indices $\sigma_{ij}$ of a molecule $i$. It gives rise to the O–O–O correlation, locally driving the molecules toward an ordered configuration [14].

The water-nanoparticle interaction is purely repulsive, $U_{wn}(r) \equiv \epsilon_h[(r_0/r)^{12}]$, with $\epsilon_h \equiv \epsilon_w \sqrt{\Delta T} = 1.8\text{ kJ/mol}$ [12], where $r < r_c$ is the distance between the water cell and each of the cells occupied by the nanoparticle. The restructuring effect of hydrophobic particles on water is incorporated by replacing $J$ and $J_p$ in the hydration shell with $J^W = 1.30 J$ and $J_p^W = 1.30 J_p$, following [20]. Because bonding indices facing the nanoparticle cannot form HBs, at intermediate $T$ they have a number of accessible states larger than those facing water molecules, inducing an increase of hydration entropy [18].

We perform Monte Carlo (MC) simulations for constant pressure $P$, $T$, and $N$, with variable water volume $V \equiv V_0 + N_{HB}V_{HB}$, where $V_0 \geq N_{HB}$ is a stochastic continuous variable that fluctuates following the MC acceptance rule [21]. We simulate systems with $N \leq 1.6 \times 10^5$ within a fixed matrix of spherical nanoparticles of radius $R = 1.6\text{ nm}$, with nanoparticle concentration $c \equiv (N - N_0)/N = 2.4\%$ and $25\%$. We repeat the analysis for $R = 0.4\text{ nm}$. For $c = 0$, the model has a phase diagram with a first-order LLPT, between a low density liquid and a high density liquid, starting at $P \approx 0.2\text{ GPa}$ for $T \to 0$ and ending in a critical point at $T \approx 174\text{ K}$ and $P \approx 0.13\text{ GPa}$ [5].

We find that for $c > 0$ the liquid-gas spinodal is shifted to lower $T$ and the line of temperature of maximum density (TMD) is shifted to lower $T$ at low $P$ and to higher $T$ at high $P$, with respect to the $c = 0$ case, reminiscent of results for other models of confined water [10, 12]. We find stronger changes for increasing $c$ (Fig. 1).

Further, we next find that confinement drastically reduces volume and entropy fluctuations at low $T$. To quantify this reduction, we calculate volume fluctuations, entropy fluctuations, and cross-fluctuations of volume and entropy, and analyze the associated measurable response function, respectively, isothermal compressibility $K_T$, isobaric specific heat $C_P$ and isobaric thermal expansion coefficient $\alpha_P$, e.g., see Figs. (2) and (3).

For a water monolayer with $N = 1.6 \times 10^5$ cells confined within nanoparticles with $R = 1.6\text{ nm}$ at $c = 25\%$, we find a maximum $K_T^{\text{max}}$ along the isobar at $P \approx 0.16\text{ GPa}$ that is 99.7% smaller than the $c = 0$ case. If we decrease $c$ to 2.4%, the reduction of $K_T^{\text{max}}$ is still remarkable: 92.3% (Fig. 3). We find similar reductions for $C_P^{\text{max}}$ and $\alpha_P^{\text{max}}$.

Such a dramatic $K_T^{\text{max}}$ reduction at low $T$ and high $P$ suggests a possible change in the region of the phase diagram where water at $c = 0$ has the LLPT. The general theory of finite size scaling tells us that at a first-order phase transition, $K_T^{\text{max}}, C_P^{\text{max}}$ and $\alpha_P^{\text{max}}$ linearly increase with the number of degrees of freedom, here equal to $4N$. We find a linear increase for $0.14\text{ GPa} \leq P \leq 0.20\text{ GPa}$ for $c = 0$, and only for $0.14\text{ GPa} \leq P < 0.16\text{ GPa}$ for $c = 25\%$ and 2.4%, consistent with the absence of a first-order LLPT outside these ranges.

To better understand this new feature, i.e., the effect of confinement on the LLPT at high $P$, we study the finite size scaling of the Binder cumulant [23] $U_{N'} \equiv 1 - \langle (V^4)_{N'} / 3 (V^2)_{N'}^2 \rangle$, where $\langle \cdot \rangle_{N'}$ stands for the thermodynamic average for a system with $N'$ cells. For $N' \to \infty$, at fixed $c$ and $P$, $U_{N'} = 2/3$ for any $T$ away from a first-order phase transition, while $U_{N'}^{\text{min}} < 2/3$ at a first-order phase transition [23].

For $c = 0$, we find that $U_{N'}^{\text{min}} < 2/3$ for $N' \to \infty$ at $0.14\text{ GPa} \leq P \leq 0.20\text{ GPa}$, while $U_{N'}^{\text{min}} = 2/3$, within the error bar, at $P = 0.12\text{ GPa}$ (Fig. 4a). Hence, this analysis confirms that for $c = 0$ there is a first-order LLPT in the range $0.14\text{ GPa} \leq P \leq 0.2\text{ GPa}$.

For $c = 2.4\%$ and 25%, we find that, for large $N'$, $U_{N'}^{\text{min}} < 2/3$ at 0.14 GPa, but not at 0.12 GPa or at
$P \geq 0.16 \text{ GPa (Fig. 4b,c). Hence, for } c = 2.4\% \text{ and } 25\% \text{ the first-order LLPT occurs only in a limited range of pressures around } 0.14 \text{ GPa, consistent with our results for } \langle (\delta V)^2 \rangle \text{ (Fig. 2) or } K^\text{max}_T \text{ (Fig. 3), with two end-points: one at } \approx 0.15 \text{ GPa, another at } \approx 0.13 \text{ GPa (Fig. 1).}

We interpret our findings as follows. As a consequence of the stronger HB in the solutes hydration shell, at low $T$ the hydration water is more ordered than the $c = 0$ case. However, shells around different nanoparticles have a different local orientational order. This generates competing domains, reminiscent of the locally structured regions proposed in Ref. [15], and exhibits no macroscopic order (Fig. 1 upper inset). The large decrease in fluctuations and response functions, e.g. $K_T$, is due to the many domain boundaries. Our results for $c$ as low as $2.4\%$ indicates that the decrease is due to the introduction of a characteristic length scale, inversely proportional to $c$, that limits the growth of the ordered structured regions. This is consistent also with the results for $K^\text{max}_T$ (Fig. 3), where the lower is $c$, the larger is $N$ beyond which the confined behavior deviates from the $c = 0$ case.

In previous theoretical analysis, with water confined by a fixed matrix of randomly distributed Lennard-Jones disks, the reduction of compressibility was observed only for large hydrophobic obstacle concentrations [11]. Here, instead, we find that $K_T$ is reduced for very low $c$, possibly because of the different water-nanoparticle interaction.

Our results are qualitatively consistent with recent experiments on $\text{H}_2\text{O}$ confined in the hydrophobic mesoporous material CMK-1-14 consisting of micrometer-sized grains, each with a 3-dimensional interconnected bicontinuous pore structure, with an average pore diameter 14 Å, at a hydration level of 99% at ambient pressure [19]. Zhang et al. find that the TMD is shifted down by 17 K with respect to the hydrophilic confinement in si-
therefore repeat our analysis for small nanoparticles with
$R = 0.4 \, \text{nm}$, and find that our results are robust if the
amount of hydrophobic interface in contact with water is kept
constant with respect to the case of $R = 1.6 \, \text{nm}$.

In conclusion, we predict that a water monolayer con-
lined in a fixed matrix of hydrophobic nanoparticles at
concentration $c$ displays changes in the thermodynamics
and a drastic reduction, $> 90\%$, in $K_T$, $C_P$, and $\alpha_P$ with
respect to the $c = 0$ case. At $c$ as small as $2.4\%$ the
first-order LLPT at high $P$ is no longer detected.

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FIG. 4: (a) At $c = 0$, for $N \rightarrow \infty$ is $U_{\alpha}^{min} = 2/3$, within
the error bar, for $P = 0.12 \, \text{GPa}$ and tends to a value
$\leq 2/3$ for $P \geq 0.14 \, \text{GPa}$, indicating a first-order LLPT for
$P \geq 0.14 \, \text{GPa}$. At nanoparticle concentrations $c = 2.4\%$
(b) and $25\%$ (c), for $N \rightarrow \infty$ we find $U_{\alpha}^{min} < 2/3$ only for
$P = 0.14 \, \text{GPa}$, indicating that the first-order LLPT is washed
out by the hydrophobic confinement at high $P$. For sake of
clarity, typical error bars are indicated only for a few points.
Lines through the points are fits, while other lines are linear
interpolations between fits at intermediate $P$. Black arrows
mark isobars crossing the first-order LLPT line.

ica mesopores and that $\alpha_P$ shows a much broader peak,
spanning from 240 to 180 K, in contrast to the sharp peak
at 230 K in hydrophilic confinement [19], reminiscent of
our results on the shift of TMD and the reduction of the
response functions with respect to the $c = 0$ case.

Recent results for small angle x-ray scattering for
aqueous solutions of amphiphilic tetraalkyl-ammonium
cations at ambient conditions suggest that the strengthen-
ing of the structure of hydration water is present only for
solutes with radius smaller than $\approx 0.44 \, \text{nm}$ [24]. We