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Large Decrease of Fluctuations for Supercooled Water in Hydrophobic Nanoconfinement

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Large decrease of fluctuations for supercooled water in hydrophobic nanoconfinement

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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 1st order liquid-liquid phase transition (LLPT) ending in one critical point at low pressure $P$. For $c > 0$ our simulations are consistent with a LLPT line ending in two critical points at low and high pressure. 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.

Abstract

Water monolayer is partitioned into cells of equal size. Each cell is occupied either by a water molecule or a hydrophobic unit. Each water cell has 4 bond indices with orientation represented by 6 Potts variables.

Interaction Hamiltonian: $\mathcal{H} = U - J N_{HB} - J_\sigma N_{\sigma}$

- $U$ is 12-6 Lennard-Jones potential for water-water interactions and repulsive potential for water-hydrophobe.
- Hydrogen bond (HB) is formed with bond energy $J$ with total number of HBs $N_{HB}$.
- Cooperative interaction $J_\sigma$ among HBs models O-O-O correlation, locally driving molecules toward ordered configuration.

Restructuring effect of hydrophobic particles on water is incorporated by making $J$ and $J_\sigma$ in the hydration shell 30% stronger.

We perform Monte Carlo simulations in 2D in the NPT ensemble using Wolff algorithm.

Results

(a) Volume fluctuations $<\Delta V^2>$ for $c = 25\%$ have maxima that follow a locus (The Widom line) in the $P - T$ plane.
(b) Projection of maxima of $<\Delta V^2>$ increase at $P = 0.132$ GPa and 0.156 Gpa, consistent with our estimate of two critical points

Conclusion

For nanoparticle concentration $c = 0$, we observe a 1st order liquid-liquid phase transition (LLPT) that terminates in a critical point at $P \approx 0.13$ Gpa. For $c > 0$, LLPT occurs only in a limited range of pressures with two end-points at $P \approx 0.15$ GPa and $\approx 0.13$ GPa.

Away from 1st order LLPT Binder parameter $U_n = 2/3$ as system size $N \to \infty$. By plotting minimum $U_n$ with $N^{-1/2}$ we see the absence of LLPT for $P \geq 0.16$ GPa with $c > 0$. Black arrows mark isobars crossing 1st order LLPT line, which is consistent with our findings of LLPT in a limited ranges of $P$ with $c > 0$.

For $c > 0$ at $P > 0.16$ GPa we see only locally ordered regions of HBs. This generates competing domains with no macroscopic order and the 1st order LLPT is no longer detected. The presence of many domain boundaries contributes to more then 99% reduction in response fluctuations, such as compressibility $K_T$. Even for a small particle concentration $c > 0$ there is a huge reduction in isothermal compressibility $K_T$ above 0.16 GPa!