Water Confined in Hydrophobic Environments

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Water: A Mysterious Material

- A water molecule is a chemical substance consisting of one oxygen atom and two hydrogen atoms.
- Water has 60+ anomalies. (http://www1.lsbu.ac.uk/water)

![Diagram of water molecule with bond angles and distances](http://www1.lsbu.ac.uk/water)

\[
\alpha = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p
\]

\[
< (\delta S \delta V) > = V k_B T \alpha
\]

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T
\]

\[
< (\delta V)^2 > = V k_B T \kappa_T
\]
Outline

1. Solid-liquid Phase Transitions in Confined Water Films

2. Diffusion Anomaly of Water

3. Hydrogen-bond Dynamics
1. Solid-liquid Phase Transitions in Confined Water Films
   (accepted for publication in Nature Physics)

2. Diffusion Anomaly of Water

3. Hydrogen-bond Dynamics
Three Phases of Water

Vapor

Solid

Liquid

more than 16 ice phases:
- hexagonal ice
- cubic ice
- ice II, III IV,V,VI, VII, VIII, IX, X, XI, XII, XIII, XIV, XV

low density amorphous ice

high density amorphous ice

low density liquid

high density liquid

Courtesy of Marcia Barbosa
Pressure-Temperature Phase Diagram

- Solid
- Liquid
- Vapor
- Fusion curve
- Vapor pressure curve
- Sublimation curve
- Triple point
- Liquid-vapor critical point
“It is widely believed that the fusion curve does not also terminate in a (second) critical point. However, thus far it has not been possible to prove the non-existence of a liquid-solid critical point.”

H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (1971)

People have thought a solid-liquid critical point might exist at high pressure, but could not find it. Instead, they found a variety of ice formation.

See http://www1.lsbu.ac.uk/water/
• “It is widely believed that the fusion curve does not also terminate in a (second) critical point. However, thus far it has not been possible to prove the non-existence of a liquid-solid critical point.” H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena (1971)

• (carbon nanotubes) “constraints on packing in the interior phase may generate subtlety in the phase diagram, and there is the intriguing possibility of a solid-liquid critical point, at which two phases lose their distinct identity. Symmetry arguments appear to rule out this possibility for bulk materials” P. Ball, Nature (1993)


How about (quasi-)two-dimensional systems?

People have thought a solid-liquid critical point might exist at high pressure, but could not find it. Instead, they found a variety of ice formation.

See http://www.l.lsbu.ac.uk/water/
Result: Possible Phase Diagram of Confined Bilayer Water

FIG. 5: Schematic phase diagram of confined water in the density–temperature ($\rho$–$T$) plane, estimated from behaviors of the potential energy, RDF, TDP, and MSD. While at low densities confined water undergoes a phase transition between solid (green circles) and liquid (yellow circles) phases by crossing a first-order line, the phase change is rather continuously for $\rho$ exceeding $\rho_c$. Accordingly, the first-order transition line (represented by the black solid line) terminates at the solid–liquid critical point (the red bullet), beyond which a continuous transition line (the blue dashed line) develops. Note the difference from a liquid–vapor critical point: Here the solid–liquid critical point is a tricritical point, which connects a first-order and a continuous transition line. The critical point is located in the ranges of density $1.30 < \rho_c < 1.33$ (g/cm$^3$) and of temperature $240 < T_c < 250$ (K). In the $\rho$–$T$ phase diagram, a first-order phase transition should be represented by a region of the two-phase coexistence. However, the finite size of the system and the choice of the $NVT$ ensemble apparently lead the coexistence region to be narrow, so that the coexistence region here appears as a line. Here $\rho$ in the $NVT$ ensemble plays almost the role of $P$ in the $NPT$ ensemble. Two ice phases have different symmetries and are thus separated by a phase boundary (denoted by a dotted line).
Simulation of Confined Bilayer Water

- Molecular dynamics simulations
- TIP5P model of water
- Two ensembles: NVT and NP_{xy} T
- Two infinitely-long hydrophobic unstructured plates
- The water-wall interaction: “Steele” potential

\[ U(z) = 4\varepsilon \left[ \left( \frac{\sigma}{z} \right)^9 - \left( \frac{\sigma}{z} \right)^3 \right] \]
Potential Energy for Below Critical Density: NVT Ensemble

$1.16 \text{ g/cm}^3$

$1.30 < \rho_c < 1.33 \text{ (g/cm}^3\text{)}$
Potential Energy for Below Critical Density: NVT Ensemble

$1.30 < \rho_c < 1.33 \text{ (g/cm}^3\text{)}$

1.16 g/cm$^3$

1.21 g/cm$^3$
Potential Energy for Below Critical Density: NVT Ensemble

1.16 g/cm³

1.21 g/cm³

1.28 g/cm³

1.30 < ρ_c < 1.33 (g/cm³)
Potential Energy for Below Critical Density: NVT Ensemble

1.16 g/cm$^3$  

1.30 < $\rho_c$ < 1.33 (g/cm$^3$)  

1.21 g/cm$^3$  

1.28 g/cm$^3$  

1.30 g/cm$^3$  

We find discontinuous changes and hysteresis loops.
Potential Energy for Above Critical Density: NVT Ensemble

$1.30 < \rho_c < 1.33 \text{ (g/cm}^3\text{)}$

FIG. 2: Absence of a hysteresis loop in potential energy $U$ during slow cooling and heating processes for $\rho > \rho_c$. The density for each panel is $\rho = a.1.33 \text{ g/cm}^3$, $b.1.39 \text{ g/cm}^3$, and $c.1.45 \text{ g/cm}^3$. Symbols are the same as those in Fig. 1.
Potential Energy for Above Critical Density: NVT Ensemble

FIG. 2: Absence of a hysteresis loop in potential energy $U$ during slow cooling and heating processes for $\rho > \rho_c$. The density for each panel is $\rho = a. 1.33 \text{ g/cm}^3$, $b. 1.39 \text{ g/cm}^3$, and $c. 1.45 \text{ g/cm}^3$. Symbols are the same as those in Fig. 1.
Potential Energy for Above Critical Density: NVT Ensemble

We find continuous changes and no hysteresis loops.

Three scenarios:
- No transition
- Weak first-order transition
- Continuous transition
Structure of Confined Bilayer Water I: **NVT Ensemble**

Lateral radial distribution function

**Below critical density**

**Above critical density**

MSG: discontinuous change with T

MSG: continuous change with T

parallel direction
Structure of Confined Bilayer Water II: NVT Ensemble

Transverse density profile

Below critical density

Above critical density

MSG: discontinuous change with T

MSG: continuous change with T

perpendicular direction
Potential Energy: \( \text{NP}_{xy}T \) Ensemble

Two Pressures:  \( P_{xy} = 540 \text{ MPa} < P_c \) and  \( P_{xy} = 1.5 \text{ GPa} > P_c \)

\[ U \text{ (kJ/mol)} \]

\[ T \text{ (K)} \]

\( P_{xy} = 540 \text{ MPa} < P_c \)
\( P_{xy} = 1.5 \text{ GPa} > P_c \)

\( \text{NP}_{xy}T \) ensemble calculations are consistent with \( \text{NVT} \) ensemble calculations.
Structure : $NP_{xy}T$ Ensemble

$P_{xy} = 540$ MPa ($< P_c$)

Discontinuous change with $T$

$P_{xy} = 1.5$ GPa ($> P_c$)

Continuous change with $T$

NPxyT ensemble calculations are consistent with NVT ensemble calculations.
Density of Confined Bilayer Water: $NP_{xy}T$ ensemble

**FIG. 6:** Density $\rho$ versus temperature $T$ for a. $P_{xy} < P_c$ and b. $P_{xy} > P_c$. When water freezes (designated by an arrow), $\rho$ changes discontinuously for $P_{xy} < P_c$ but continuously for $P_{xy} > P_c$. Discontinuous change with $T$ Continuous change with $T$
Distinction between Solid and Liquid?

Lateral mean square displacement for above critical density

FIG. 4: Log–log plot of the time evolution of the lateral mean square displacement (MSD) at several temperatures and density $\rho = 1.33$ g/cm$^3$ $(> \rho_c)$. At temperatures $T = 300$ K down to $250$ K, the MSD, starting from the ballistic regime ($\propto t^2$), eventually reaches the diffusive regime ($\propto t$) in the long time $t$. The plateau between the two regimes, observed at low temperatures, arises from the cage effect. We thus conclude that the MSD exhibits typical liquid behavior. At $T = 240$ K, in contrast, the evolution of the MSD appears almost flat and displays large fluctuations, indicating that water has turned into ice. The diffusion constant $D$, calculated from the MSD, takes the values $5.7 \times 10^{-6}$ cm$^2$/s, $1.3 \times 10^{-6}$ cm$^2$/s, and $2.2 \times 10^{-7}$ cm$^2$/s at $T = 300$ K, $270$ K, and $250$ K, respectively, while at $T = 240$ K it is given by $5.2 \times 10^{-9}$ cm$^2$/s.
Ice Formation

$\rho < \rho_c$ hexagonal

$\rho > \rho_c$ rhombic
Either first-order or continuous phase transitions can occur in bilayer water. It indicates a possible existence of a connection point between first-order and continuous phase transitions, which may be interpreted as a possible solid-liquid critical point in quasi-two dimensions.

$$1.30 < \rho_c < 1.33 \text{ (g/cm}^3\text{)} \quad 240 < T_c < 250 \text{ (K)}$$
Summary I

1. Solid-liquid Phase Transitions in Confined Water Films

- For bilayer water, a solid-liquid phase transition can be either first-order or continuous, depending on density and pressure. It indicates a possible existence of a connection point of first-order and continuous transition lines, which may be interpreted as a possible solid-liquid critical point in quasi-two dimensions.

2. Diffusion Anomaly of Water

3. Hydrogen-bond Dynamics
1. Solid-liquid Phase Transitions in Confined Water Films

2. Diffusion Anomaly of Water


3. Hydrogen-bond Dynamics
Diffusion Anomaly of Water

At low enough temperature, the self-diffusion of water increases when the density and pressure increase.

(See [http://www1.lsbu.ac.uk/water/](http://www1.lsbu.ac.uk/water/))
How to Calculate Diffusion Coefficient $D$

- From Einstein expression

$$D = \lim_{t \to \infty} \frac{1}{2dNt} \left\langle \sum_{i=1}^{N} [\vec{r}_i(t) - \vec{r}_i(0)]^2 \right\rangle$$

- From Green-Kubo formula

$$D = \frac{1}{dN} \int_0^\infty \left\langle \sum_{i=1}^{N} \vec{v}_i(t) \cdot \vec{v}_i(0) \right\rangle dt$$

$d$: dimension, $N$: the number of particles

How can we calculate the (effective) diffusion coefficient when the boundary conditions exist?
Effective Diffusion Coefficient in a Quasi-Two-Dimensional Slit

Separation = 1.1 nm
(maximally three layers of water)

Three residence regions

The characteristic residence time is the time required for a water molecule to diffuse the distance equal to the separation between two neighbor region. Hence the effective diffusion coefficient using the separation between two residence regions and the characteristic residence time can be calculated:

\[
D = \frac{\langle R_z^2 \rangle}{2 \langle \tau_{ch}^R \rangle}
\]

- \(R_z\): distance between two nearest regions
- \(\tau_{ch}^R\): characteristic residence time
Residence Region III
The First-Passage Time Method

A random walk of \( N+1 \) sites with one absorbing boundary at site 0 and one reflecting boundary at site \( N \)

\[ \begin{array}{ccccccccc}
0 & \rightarrow & 1 & \rightarrow & 2 & \rightarrow & 3 & \cdots & (N-2) & \rightarrow & (N-1) & \rightarrow & N \\
\end{array} \]

\( T_i \) : jumping rates to left  \hspace{1cm} \( R_i \) : jumping rates to right

Rate equations :
\[
\begin{align*}
\dot{p}_0(t) &= T_1 p_1(t) \\
\dot{p}_1(t) &= T_2 p_2(t) - (T_1 + R_1)p_1(t) \\
\dot{p}_i(t) &= T_{i+1} p_{i+1}(t) + R_{i-1} p_{i-1}(t) - (T_i + R_i)p_i(t) \quad \text{for} \quad 1 < i < N \\
\dot{p}_N(t) &= R_{N-1} p_{N-1}(t) - T_N p_N(t)
\end{align*}
\]

In a matrix representation : \( \dot{M}(t) = BM(t) \)

Residence time distribution \( P(\tau_R) \) shows an exponential behavior.

Characteristic time: \( \tau_{ch}^R(n) = -\sum_{m=1}^{N} B^{-1}(m, n) \)
Residence Time Distribution: Simulation Results

The residence time distribution function shows an exponential behavior for both outer and middle regions.

\[ P(\tau_R) \sim \exp \left( -\frac{\tau_R}{\tau_{ch}} \right) \]

From the residence time distribution function, we can find the characteristic time.
Absence of a diffusion anomaly of water

Maximum at characteristic residence time for the diffusion constant characterization.

In Fig. 4, we study diffusion coefficients in two directions.

Existence of a diffusion anomaly
An anomalous liquid

Absence of a diffusion anomaly
A normal liquid

Diffusion constant in the perpendicular direction rather than the hydrophobic property of the nanoconfinement.

The existence of a diffusion anomaly in the perpendicular direction might be the result of the shift found for thermodynamic and dynamic properties of confined water in the parallel direction.

Crossover down to the lowest temperature we simulated, suggesting that there is no diffusion anomaly of water is absent in the whole temperature range investigated. By comparing the results, we conclude that a diffusion anomaly of water is absent down to the lowest temperature we simulated.

Next we study diffusion constant in the perpendicular direction to the confining walls. We calculate the diffusion constant using a Vogel-Fulcher-Tammann VFT form for all the densities studied.

Anomalous diffusion constant in the perpendicular direction at very low temperatures.

Anomalous diffusion constant in the parallel direction at very low temperatures.

Existence of a diffusion anomaly of water.

An anomalous liquid.

Absence of a diffusion anomaly of water.

A normal liquid.

The diffusion constant in the perpendicular direction decreases as density increases over the entire temperature range investigated, suggesting that there is no diffusion anomaly of water.

Existence of a diffusion anomaly.

An anomalous liquid.

Absence of a diffusion anomaly.

A normal liquid.

In summary, we have performed MD simulations of water in various confining geometries. The results show that a diffusion anomaly does not exist in water confined between hydrophobic surfaces.

Existence of a diffusion anomaly.

An anomalous liquid.

Absence of a diffusion anomaly.

A normal liquid.
Summary II

1. Solid-liquid Phase Transitions in Confined Water Films

2. Diffusion Anomaly of Water
   - Nanoconfinement may induce the absence of a diffusion anomaly in the confining direction. Water behaves as a normal liquid in the confining direction, whereas it behaves as an anomalous liquid in the parallel direction to walls like bulk water.

3. Hydrogen-bond Dynamics
Conclusions: A Tiny Piece of Understanding Water

• For bilayer water, a solid-liquid phase transition can be either first-order or continuous, depending on density and pressure. It indicates a possible existence of a connection point between first-order and continuous transition lines, which may be interpreted as a possible solid-liquid critical point in quasi-two dimensions.

• Nanoconfinement may induce the absence of a diffusion anomaly in the confining direction. Water behaves as a normal liquid in the confining direction, whereas it behaves as an anomalous liquid in the parallel direction to walls like bulk water.

Extra piece:

• The temperature shift (40 K) in confined water compared to bulk water is attributed to the hydrogen-bond lifetime related to the fast dynamics.

Thank You