EFFECTS OF THE STRUCTURE OF THE CONFINEMENT MATRIX ON LIQUID-LIQUID PHASE TRANSITION

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It is contained in water.

If there is magic on this planet,

-- Loren Eiseley, The Immense Journey, 1957
Outline

1 Background
   - Liquid-Liquid Critical Point Hypothesis
   - Spherically-Symmetric Jagla Ramp Potential

2 Simulations
   - Geometry of the confinement
   - Effects on Liquid-Liquid Phase Transition
   - Spherically-Symmetric Jagla Ramp Potential
   - Liquid-Liquid Critical Point Hypothesis

3 Discussion
   - Summary
P.G. Debenedetti & H.E. Stanley


Outline
- Background
- Simulations
- Discussion

C and C', critical points

Crystalization curve

Homogeneous nucleation curve

Melting curve

LDL low-density liquid

HDL high-density liquid

LDA low-density amorphous ice

HDA high-density amorphous ice

Tc crystallization curve

Tm melting curve

Tc homogenous nucleation curve
Idealized system characterized by a pair interaction potential whose attractive well has two sub-wells, the outer of which is deeper and narrower.

Two idealized interaction configurations that correspond to the two sub-wells above.

Outlining background simulations.

Discussion

Outline

Background
Simulations
Discussion

Spherically-Symmetric Jagla Ramp Potential

\[ r/a = 3.56 \]
\[ b/a = 1.72 \]
\[ c/a = 3 \]
\[ U_0/U^R = 3.56 \]

\[ U^R \]
Spheircally-Symmetric Jagla Ramp Potential

Equation of State for

Physical Question: How does the structure of confinement affect liquid-liquid phase transition?

Why: Confined water is important in biological and technological applications.

We want to understand the disparity of previous experiments and simulations for water in different kinds of confinement and technological applications.

We need: a simple model to permit fast simulations to equilibrate to very low T.

Outline:

- Background
- Simulations
- Discussion
Liquid-Liquid Critical Point

Temperature $k_B T / U_0$

Pressure $Pa^3 / U_0$

Density $p_a$
Nanoparticle-liquid particle radial distribution function

$T > T_{\text{c}}$

$g(r)_{\text{NP-LP}}(r)$

$\rho_a = 0.280$

$\rho_a = 0.589$

$T_{\text{bulk}} < T$

Outline

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Outline
Number of liquid particles around a Nanoparticle in the first coordination shell.
Density of each Delaunay tetrahedral

$\rho_a$ = 0.34

$\rho_a$ at T

Density of Delaunay tetrahedral

$V$ is Total Volume

$V$ of volume $V$

$^+$ Density of $V$
Density of each Delaunay tetrahedral

\[ \text{Density of each Delaunay tetrahedral} \]

\[ \rho^a \text{ of each Delaunay tetrahedral} \]

Total volume \( V \)

Volume of Delaunay tetrahedral \( v \)
Density $\rho^\gamma$ of each Delaunay tetrahedral

Counts of $\rho_a^3$

RND

ORD

$\rho_R$
1. Liquid-Liquid Coexistence Region Shrinks
2. Liquid-Liquid Critical Point Shift Down In
   - Pressure
   - Temperature
   - Density

Why?

- High Vicinal Density of Liquid
- Formation of Clusters of Various Densities

Order → Disorder in Confinement
Conclusion

Confinement introduces significant changes in the phase diagram:

- Weakening of the LLPT,
- Narrowing of the coexistence region,
- Shifts in $T$, $P$ of the LLPT and LLCP,
- Weakening of density anomalies (more about it at Thesis Defense).

Our results clarify the disparity of previous experiments and simulations for water in different kinds of confinements due to the different amount of disorder in the confining geometries. Our results can be generalized to any confined anomalous liquid.

Disorder in confinement introduces significant changes in the phase diagram.


Thank you!