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

Elena G. Strekalova

Collaborators:

Sergey Buldyrev ,

Dario Corradini,

Jiayuan Luo

Advisor: H. Eugene Stanley

Co-Advisor: Giancarlo Franzese

BOSTON UNIVERSITY

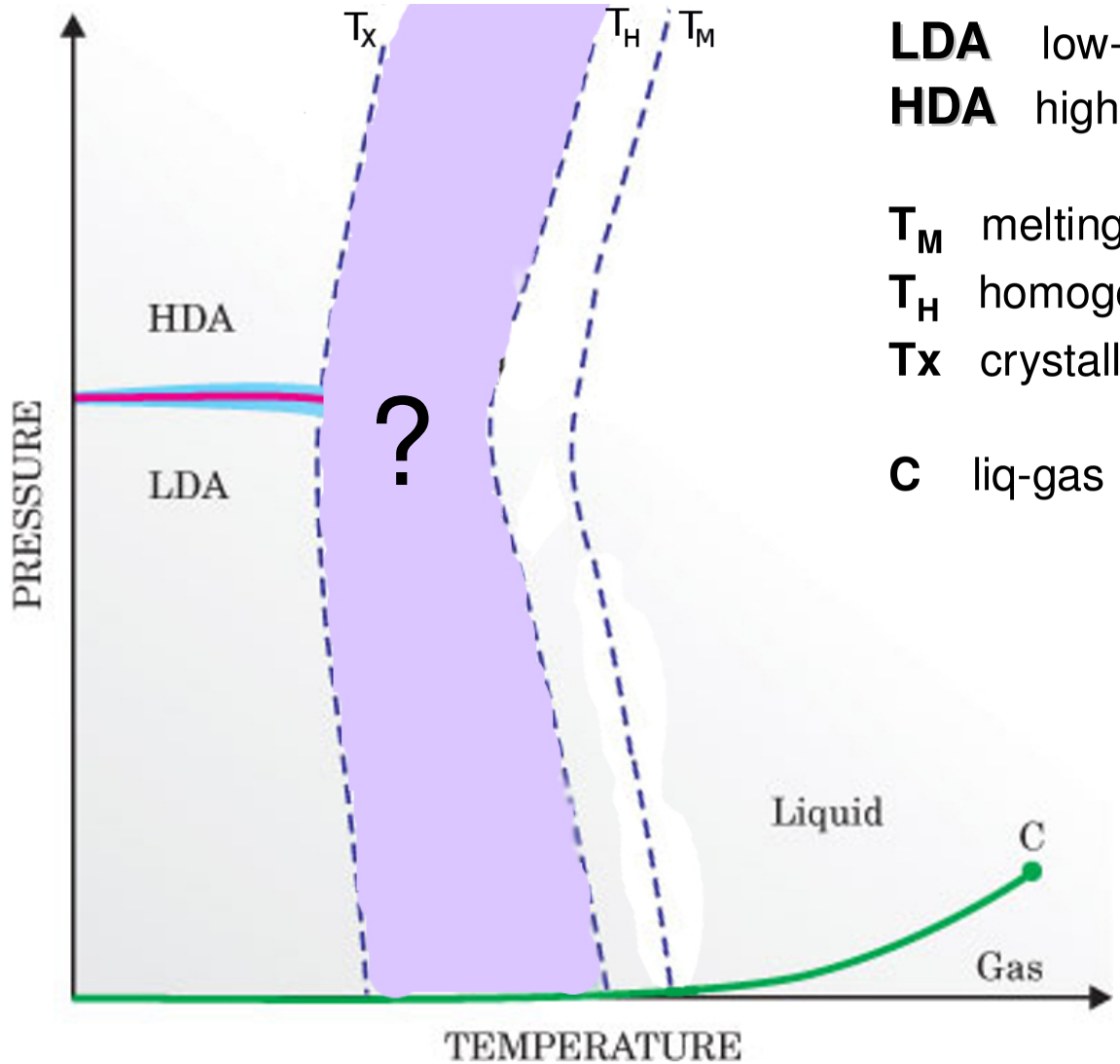
If there is magic on this planet,

it is contained in water.

-- Loren Eiseley, *The Immense Journey, 1957*

Outline

arXiv:1107.1926

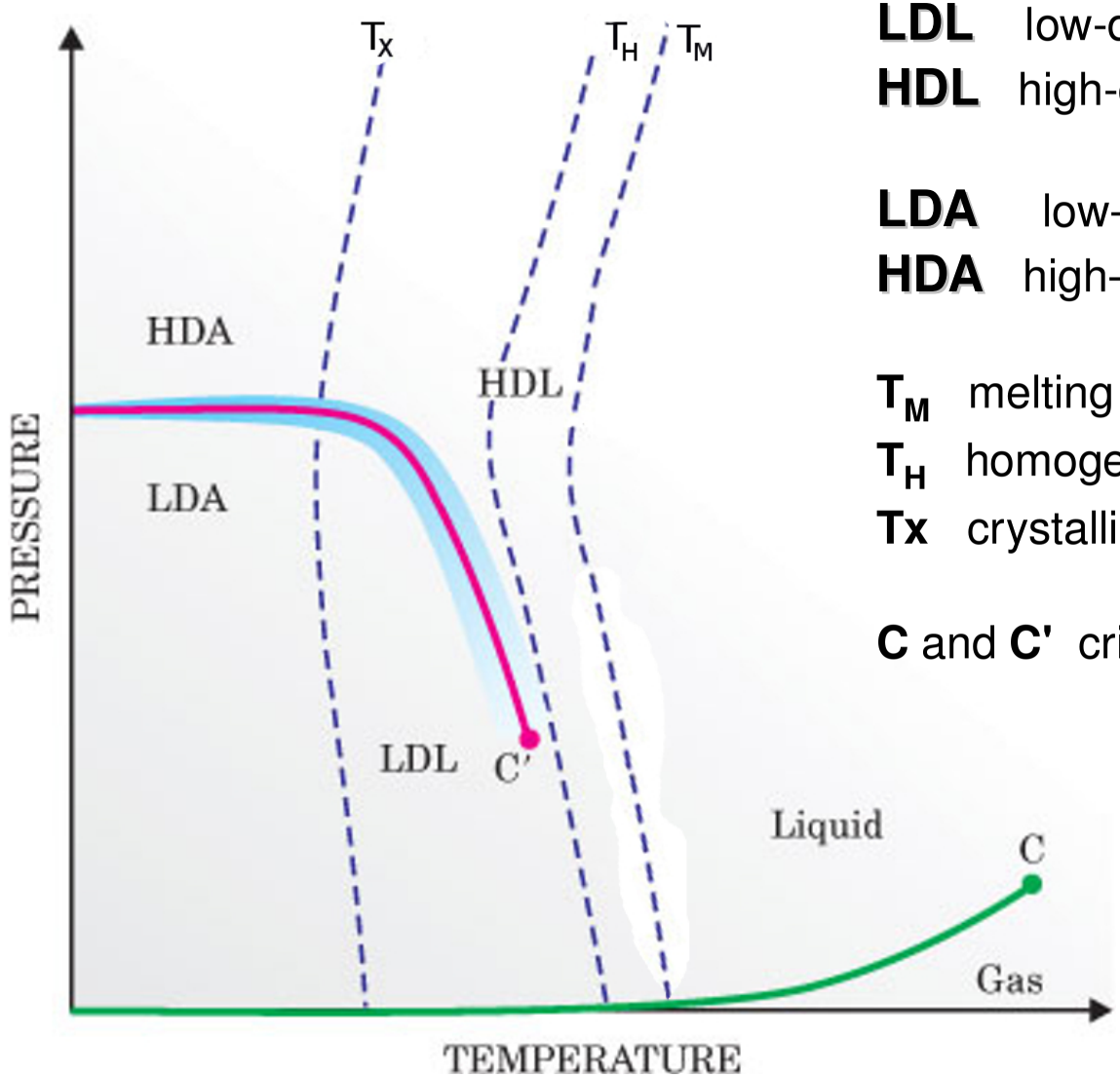


LDA low-density amorphous ice
HDA high-density amorphous ice

T_M melting curve
T_H homogeneous nucleation curve
Tx crystallization curve

C liq-gas critical point

P.G. Debenedetti & H.E. Stanley
Physics Today, *June*, 40 (2003)



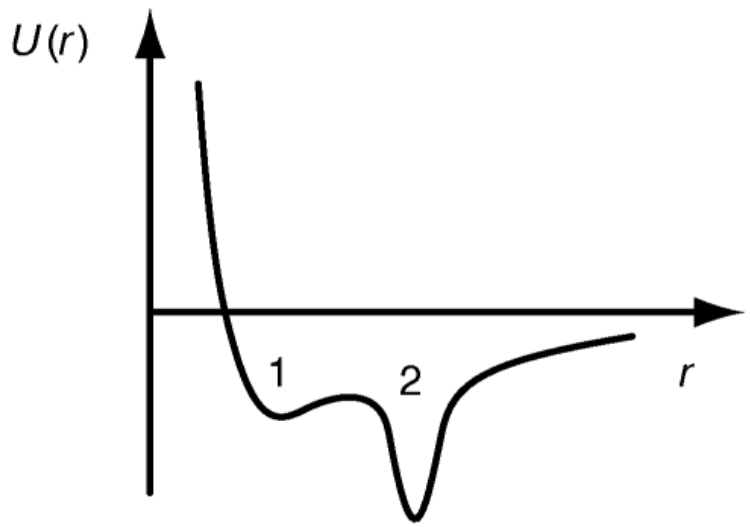
LDL low-density liquid
HDL high-density liquid

LDA low-density amorphous ice
HDA high-density amorphous ice

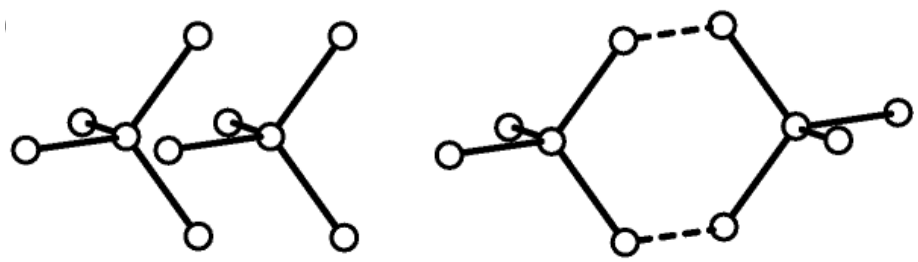
T_M melting curve
T_H homogeneous nucleation curve
Tx crystallization curve

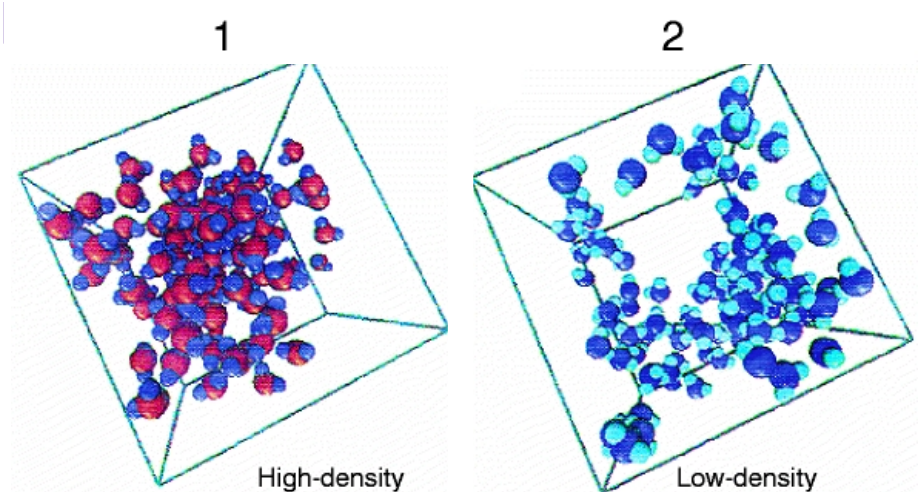
C and **C'** critical points

P.G. Debenedetti & H.E. Stanley
Physics Today, *June*, 40 (2003)



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

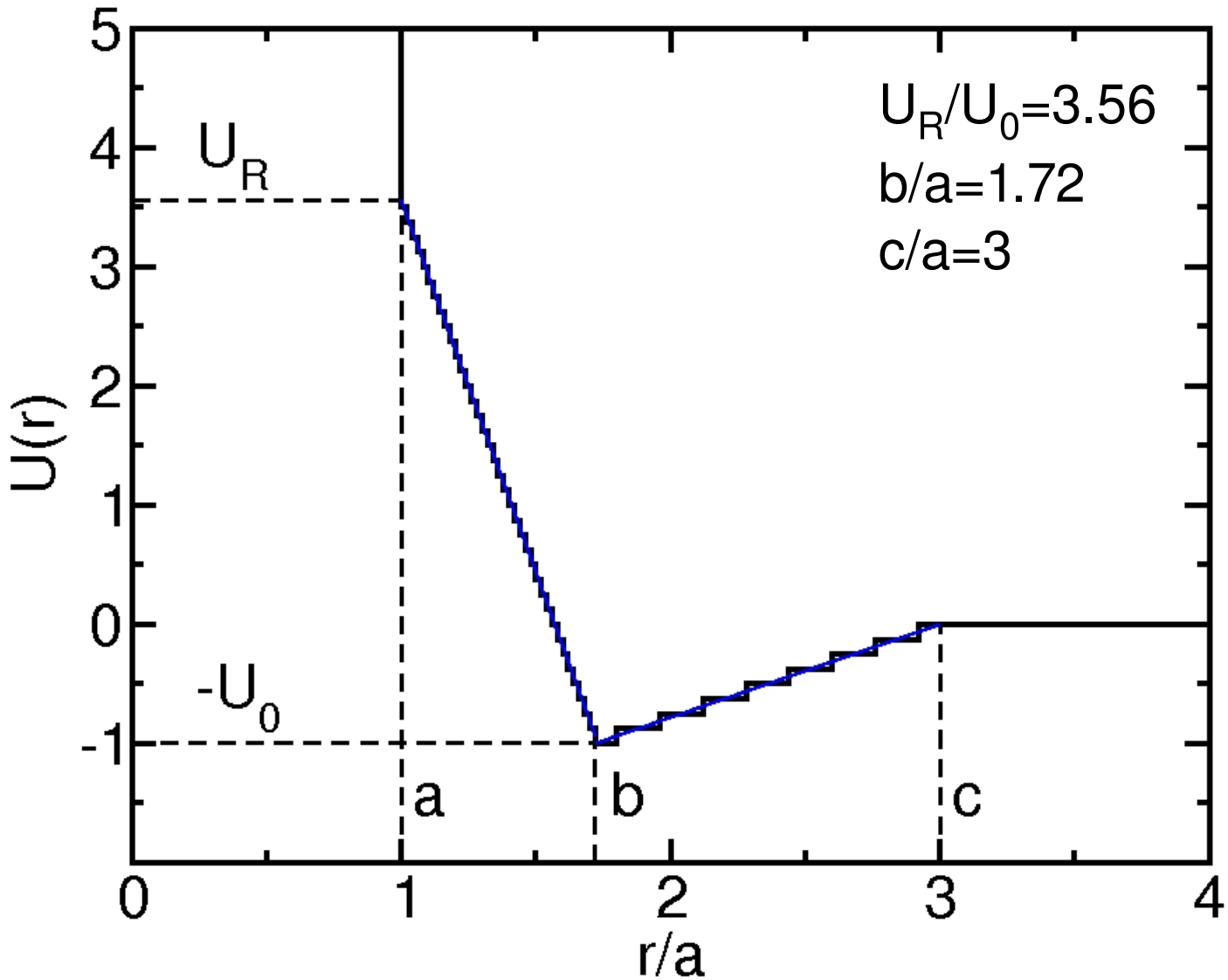




Two idealized interaction clusters of water molecules in configurations that correspond to the two sub-wells above

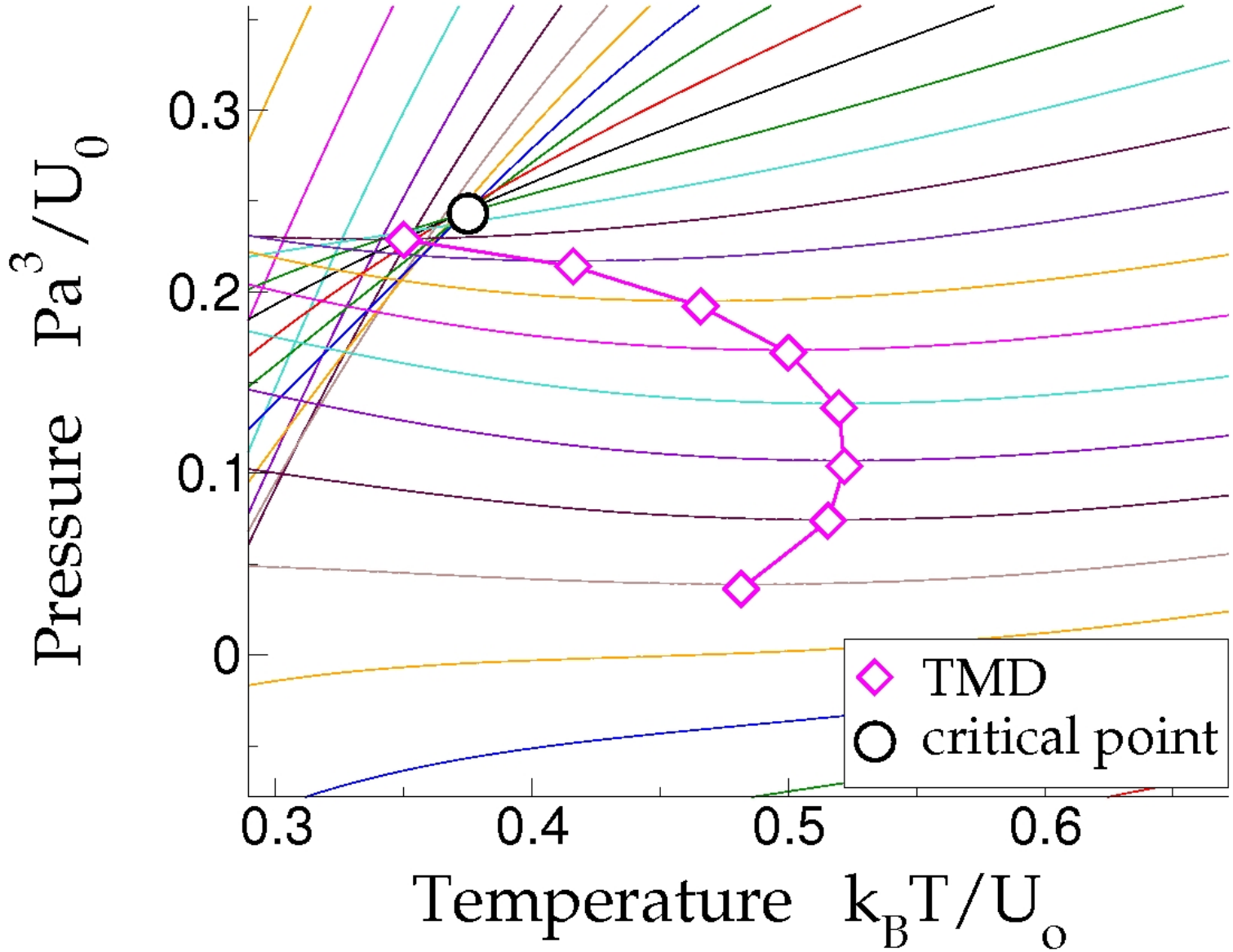
O. Mishima & H.E. Stanley
Nature, *396*, 329 (1998)
Nature, *392*, 164 (1998)

Spherically-Symmetric Jagla Ramp Potential



E. A. Jagla, *Phys. Rev. E* **58**, 1478 1998
E. A. Jagla, *J. Chem. Phys.* **111**, 8980 1999

Equation of State for Spherically-Symmetric Jagla Ramp Potential



L. Xu, S. V. Buldyrev, C. A. Angell, and H. E. Stanley, *Phys. Rev. E* **74**, 031108 (2006)

Physical Question:

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

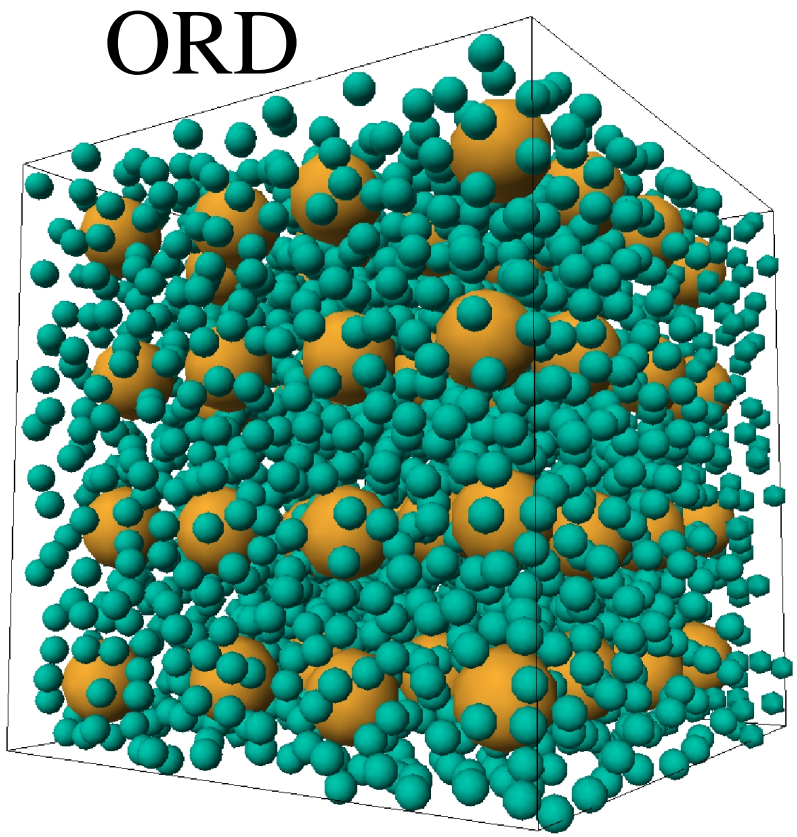
Why:

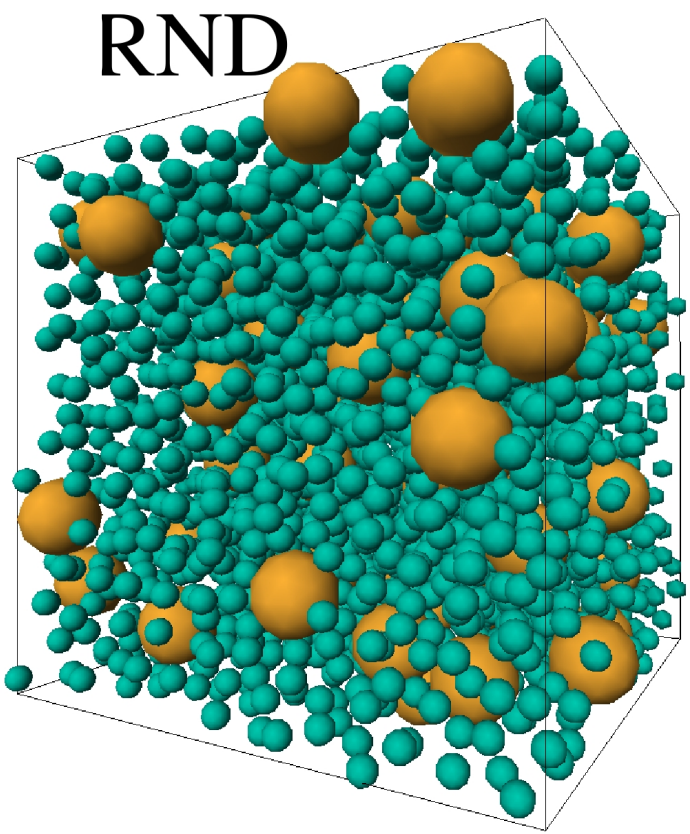
Confined water is important in biological and technological applications

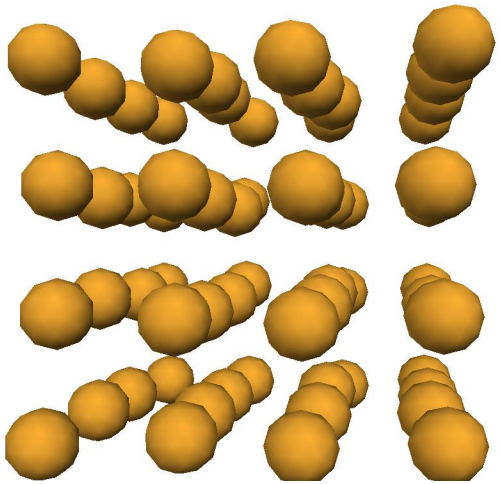
We want to understand the disparity of previous experiments and simulations for water in different kinds of confinements

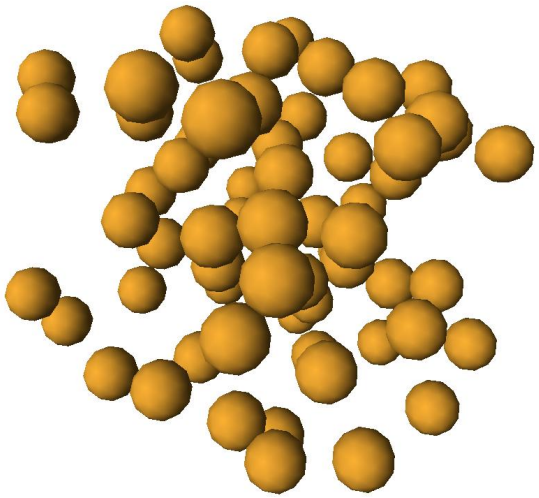
We need:

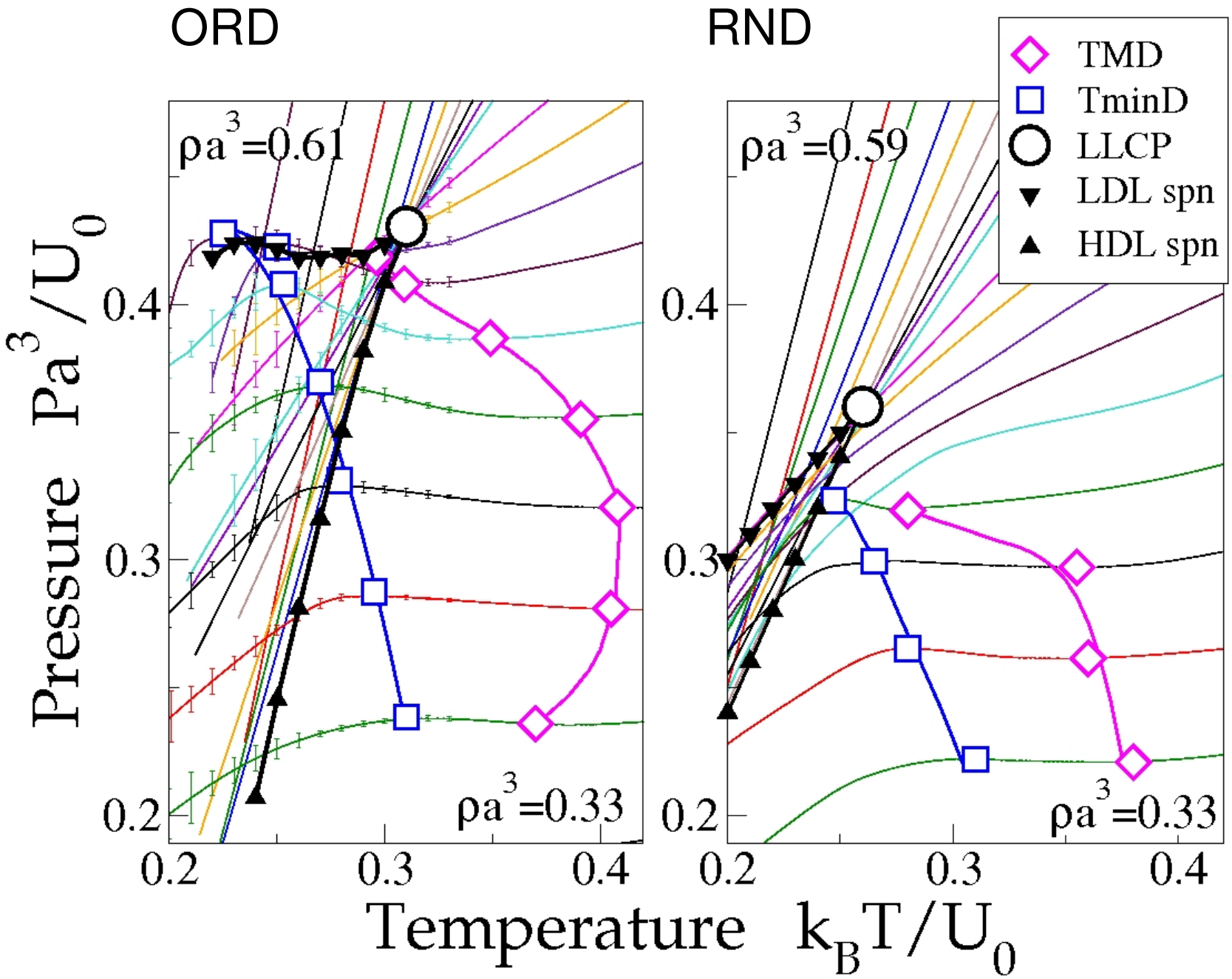
simple model to permit fast simulations
to equilibrate to very low T

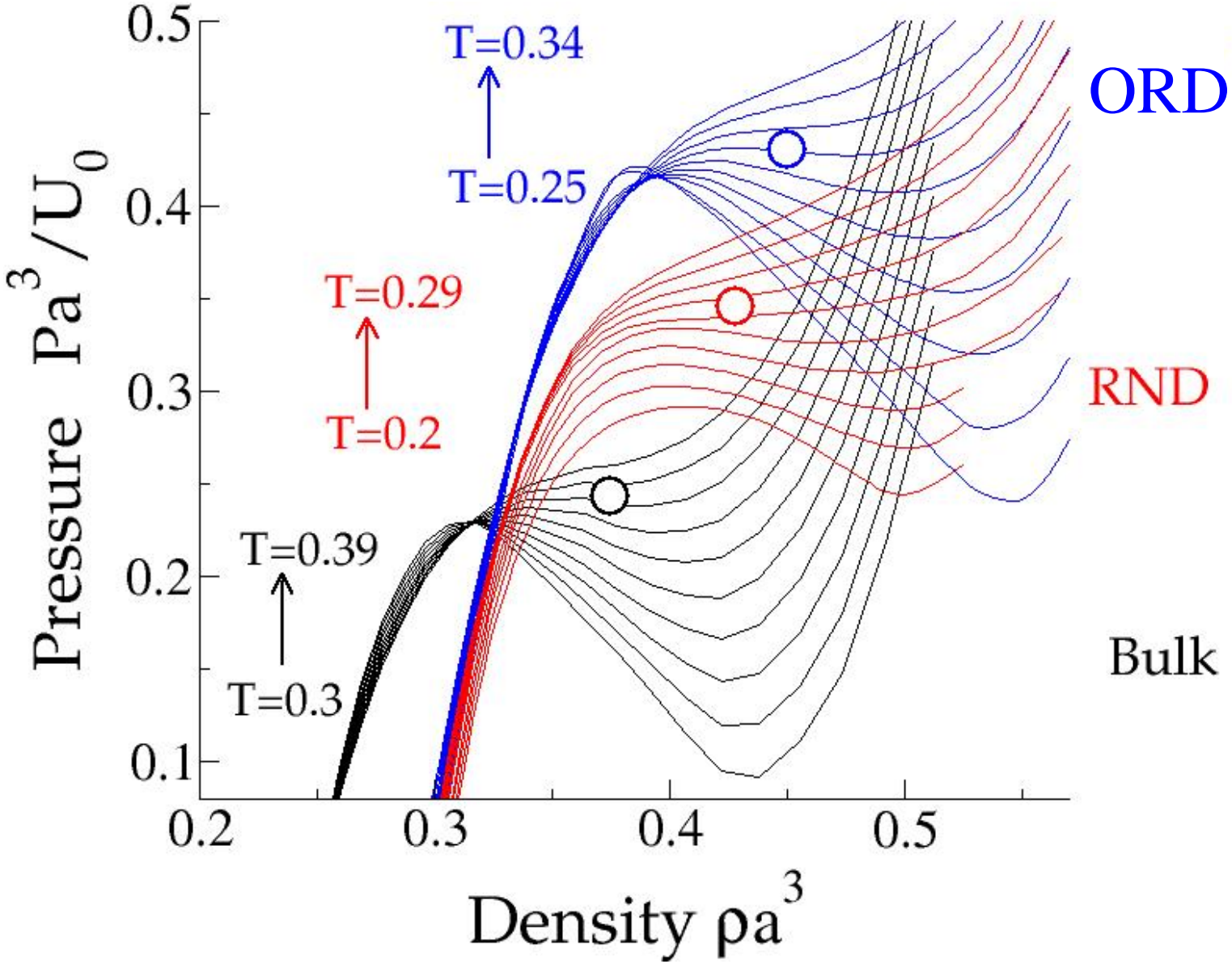

ORD


RND

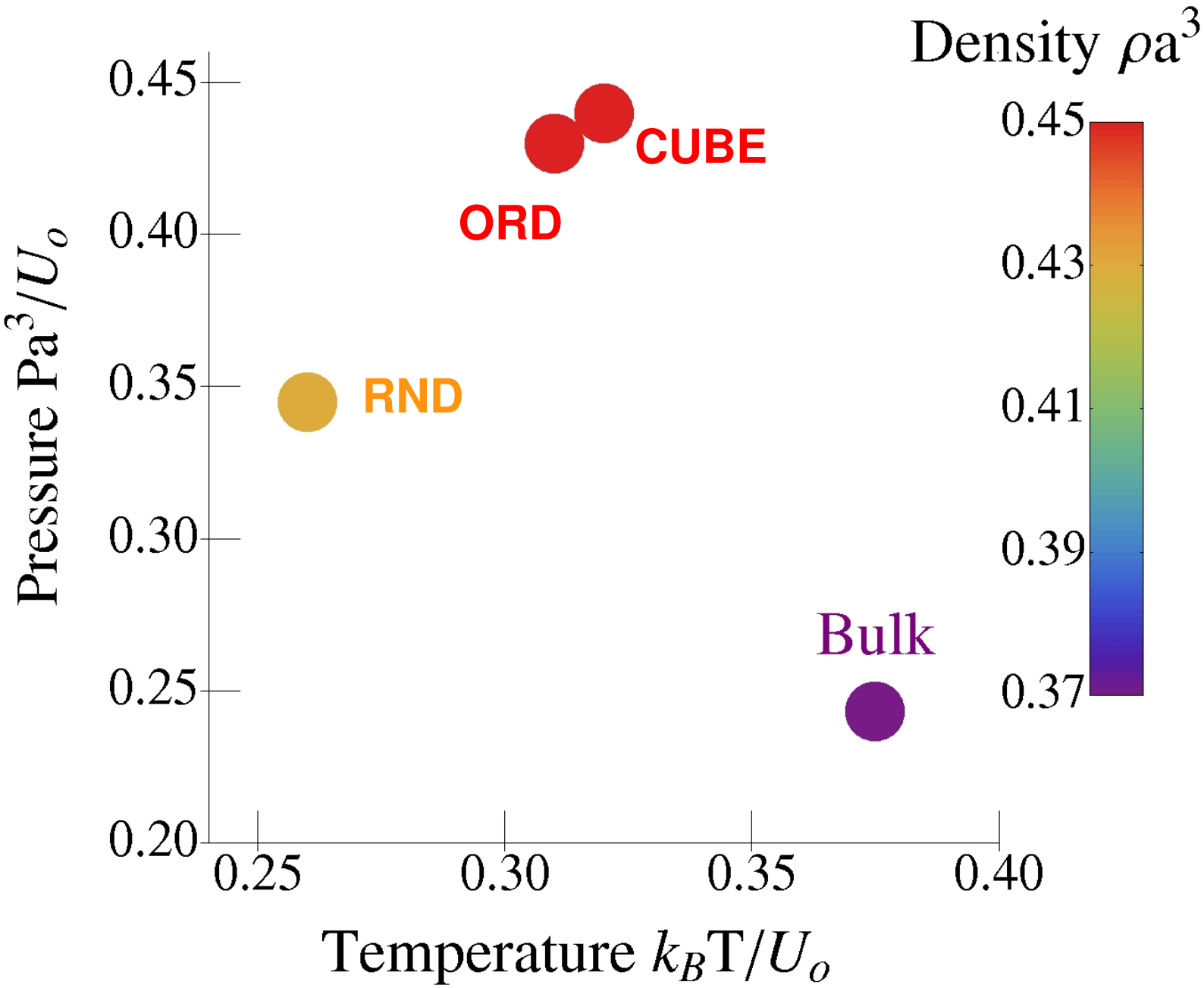





ORD
RND
TMD
TminD
LLCP
LDL spn
HDL spn
ρa³=0.61
ρa³=0.59
ρa³=0.33
ρa³=0.33
Pressure Pa³/U₀
Temperature k_BT/U₀
0.2
0.3
0.4

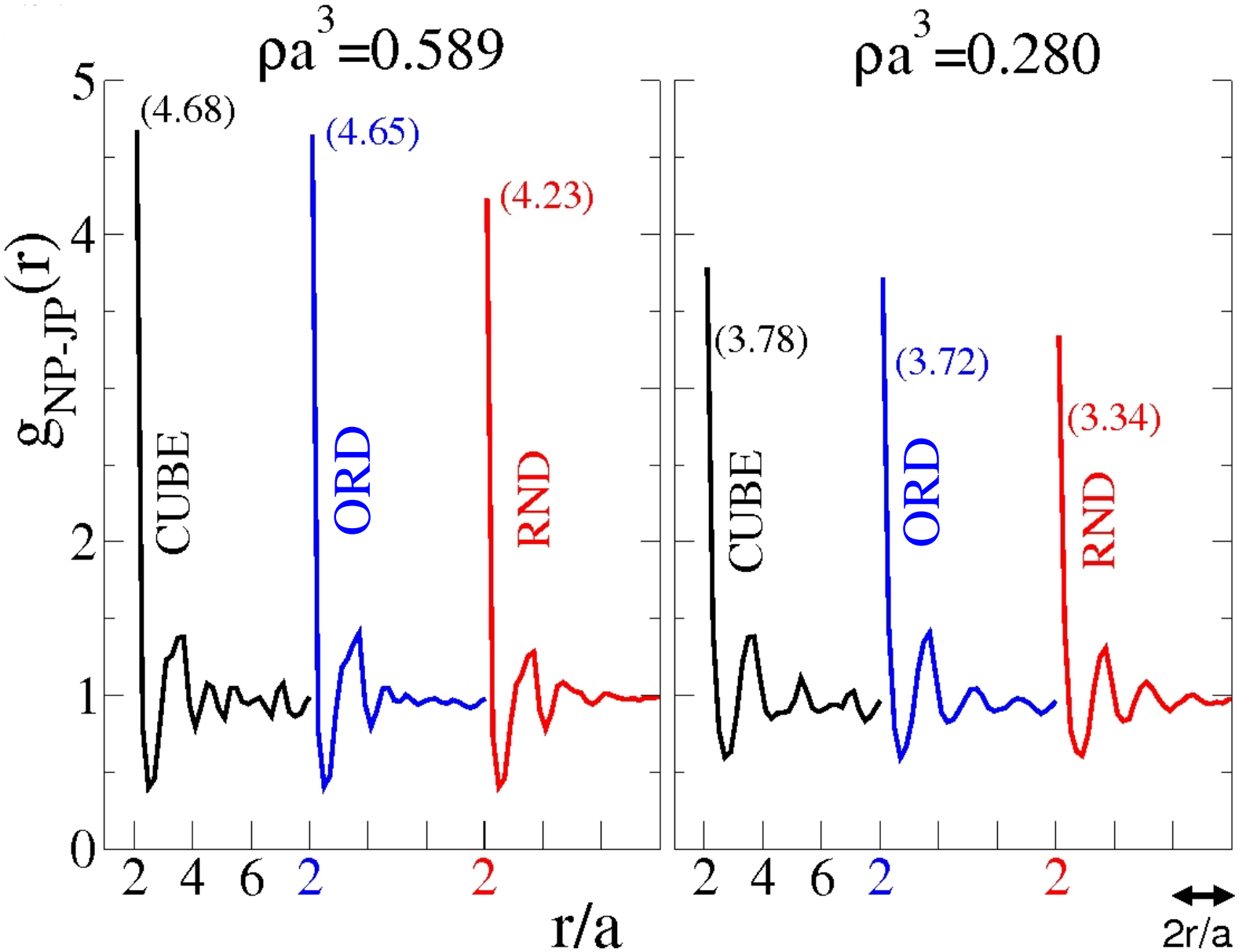

T=0.34
T=0.25
T=0.29
T=0.2
T=0.39
T=0.3
ORD
RND
Bulk
Pressure Pa^3/U_0
Density ρa^3
0.5
0.4
0.3
0.2
0.1
0.2
0.3
0.4
0.5

Liquid-Liquid Critical Point

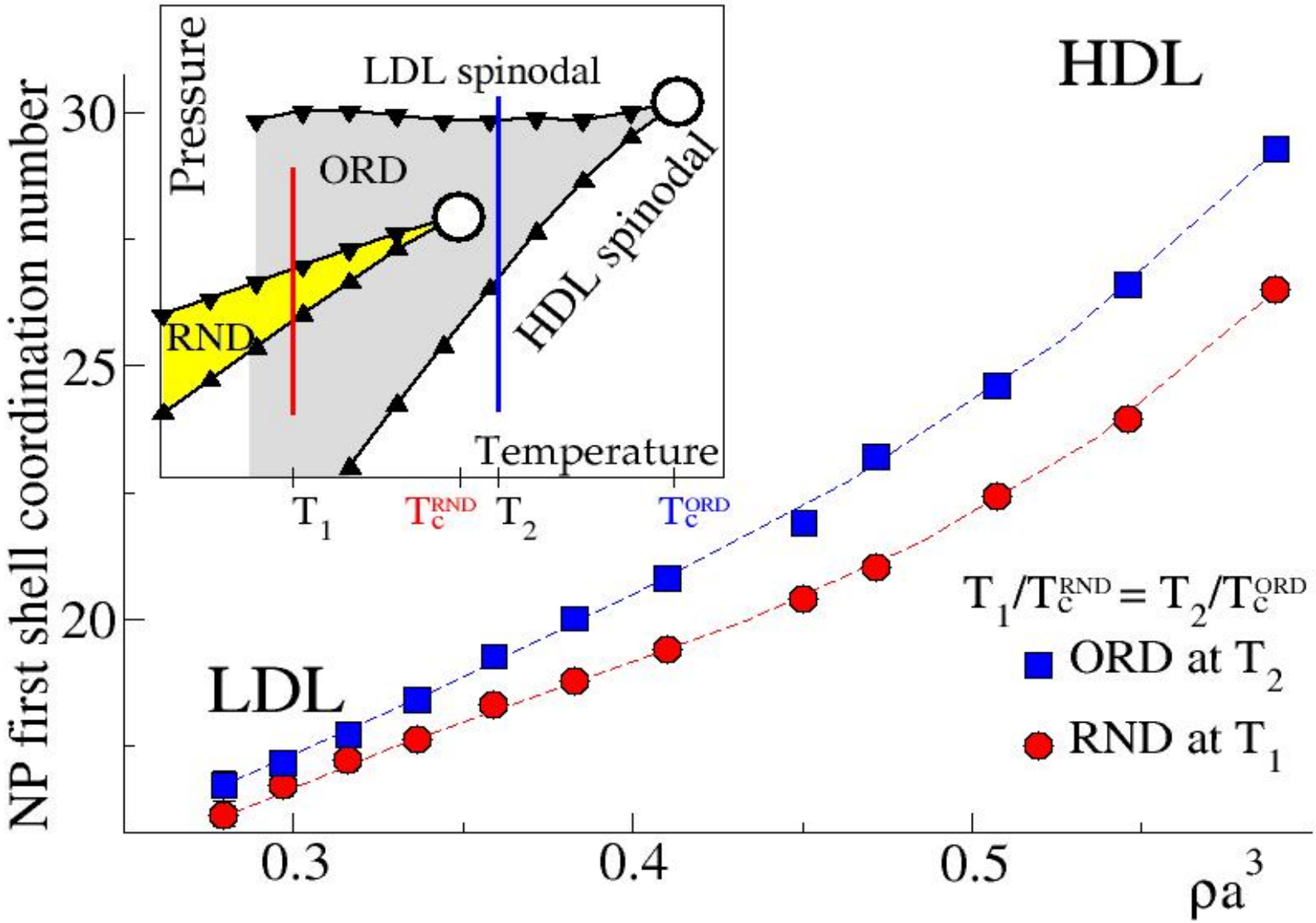


Nanoparticle-liquid particle radial distribution function

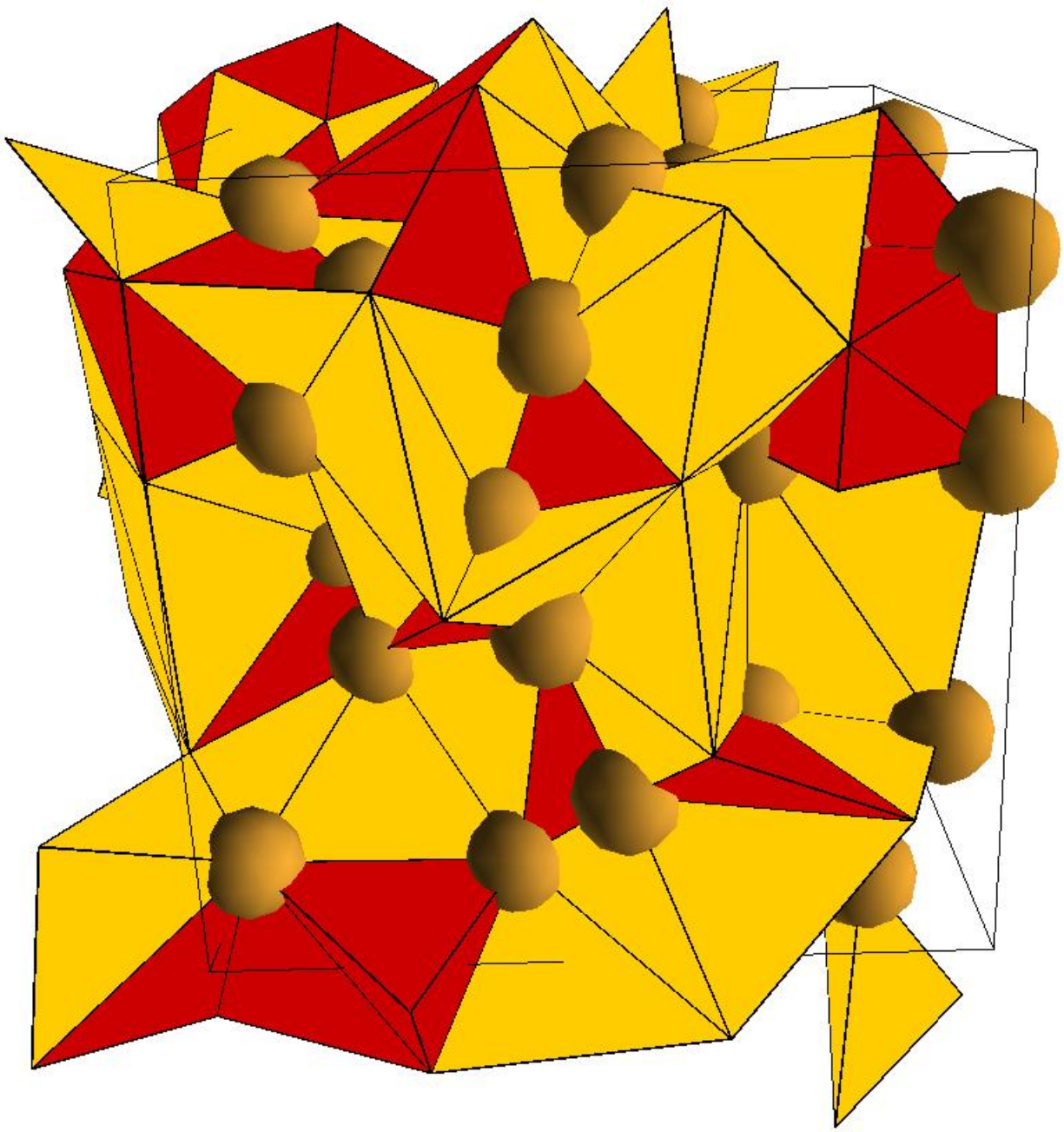
$T > T_c^{bulk}$



Number of liquid particles around Nanoparticle in the first coordination shell



Delaunay Tessellation

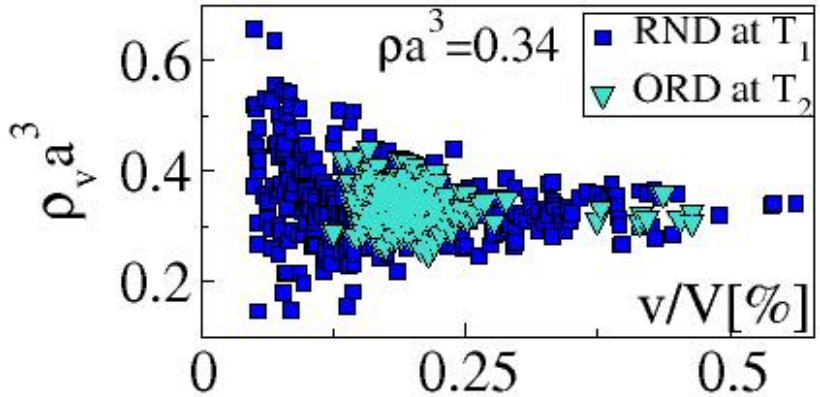


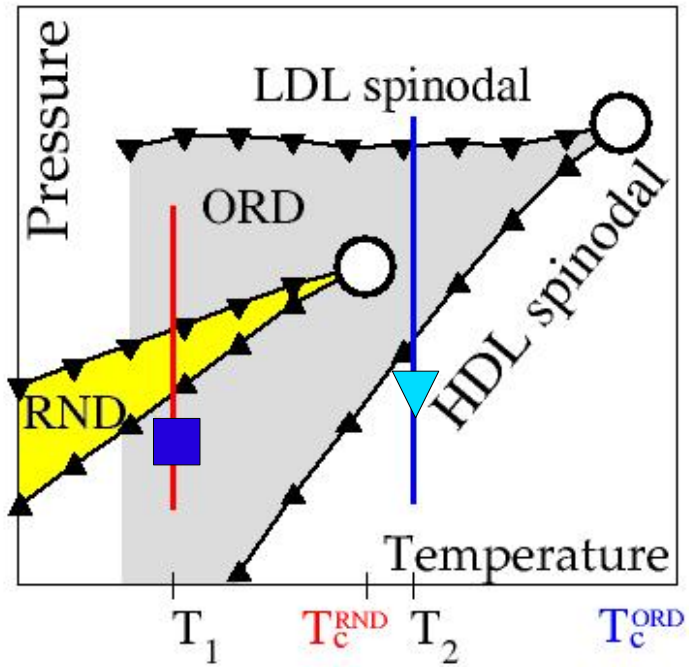
Density ρ_v of each Delaunay tetrahedral

yellow
$\rho_v > \rho_c$

red
$\rho_v < \rho_c$

Density ρ_v of each Delaunay tetrahedral



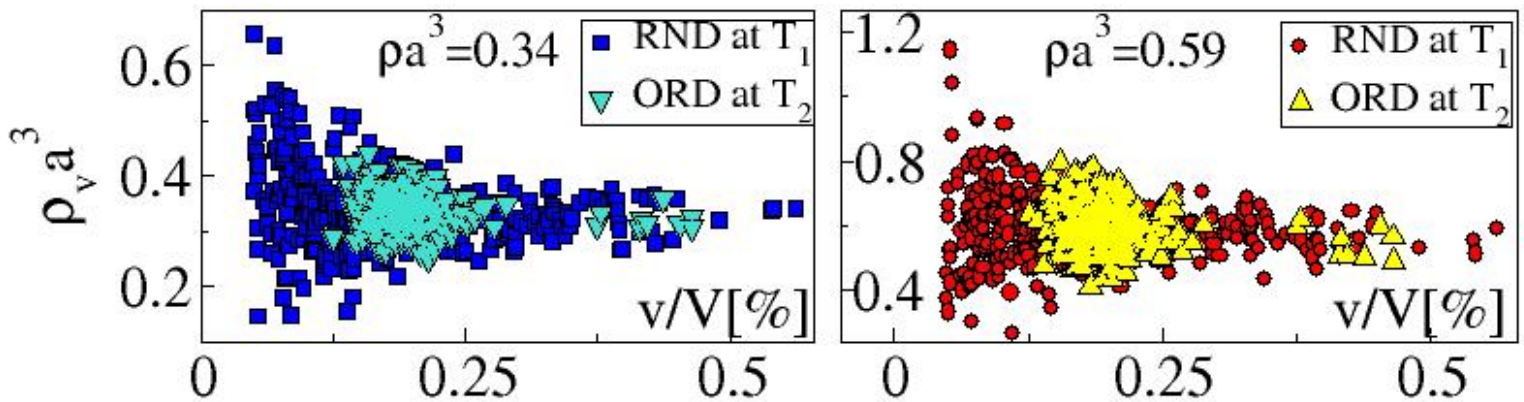


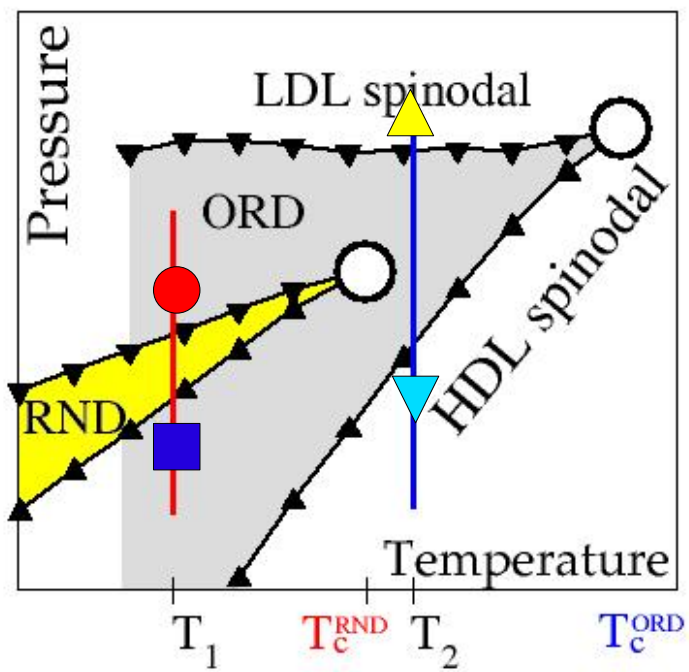
$T_1/T_c^{RND} = T_2/T_c^{ORD}$

ρ_v Density of Delaunay tatrahedral of volume **v**

V is Total volume

Density ρ_v of each Delaunay tetrahedral



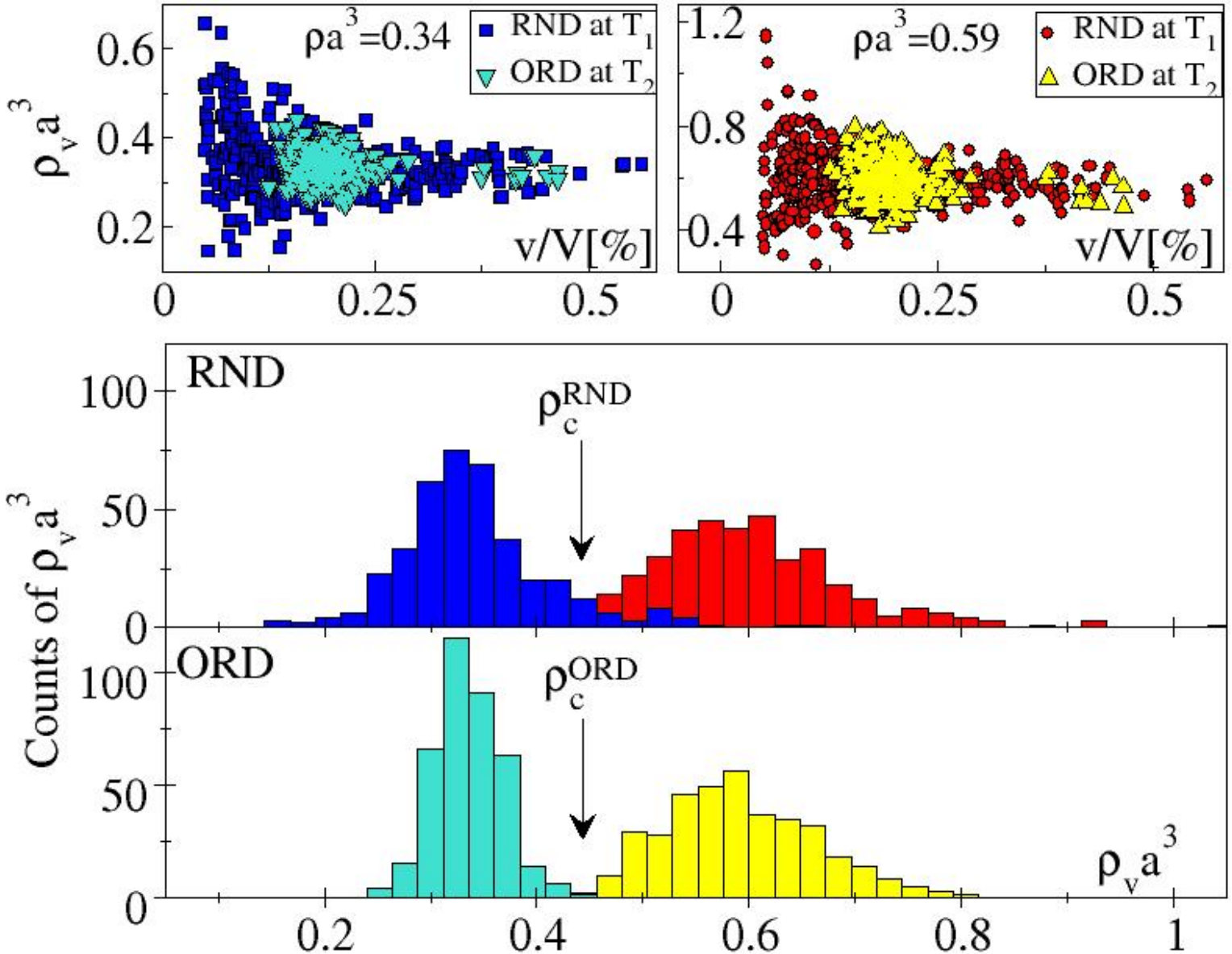


$T_1/T_c^{RND} = T_2/T_c^{ORD}$

ρ_v Density of Delaunay tatrahedral of volume **v**

V is Total volume

Density ρ_v of each Delaunay tetrahedral



Order $\longrightarrow$ Disorder in Confinement

1 Liquid-Liquid Coexistence region shrinks

2 Liquid-Liquid Critical Point shift down in
- Density
- Temperature
- Pressure

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

Conclusion

Confinement Introduces Significant Changes in the Phase Diagram

Disorder in confinement:

- weakening of the LLPT,
- narrowing of the coexistence region,
- shifts in T, P, ρ 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.

- Can be generalized to any confined anomalous liquid.

Thank you!

---

1. **E. G. Strekalova**, J. Luo, H. E. Stanley, S. V. Buldyrev, and G. Franzese *Effects of Topological Order in Confinement on Liquids with Anomalous Behavior* (arXiv:1107.1926)

2. **E. G. Strekalova**, D. Corradini, M. G. Mazza, S. V. Buldyrev, P. Gallo, G. Franzese, and H. E. Stanley, *Effect of Hydrophobic Environments on the Hypothesized Liquid-Liquid Critical Point of Water*, Journal of Biological Physics (accepted 2011)