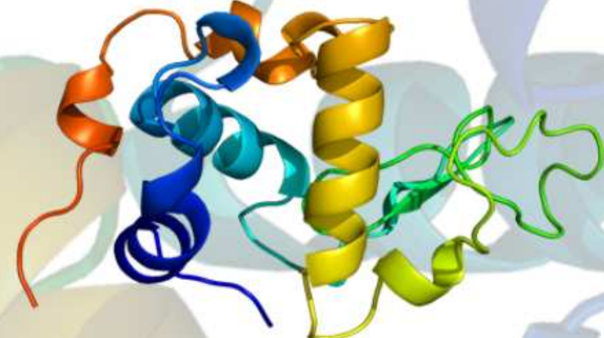
Effects of Confinement on Thermodynamics of Supercooled WATER



Elena G Strekalova

Boston University

April 12, 2012

Outline

1 Background
- Liquid-Liquid Critical Point Hypothesis

2 Discrete Molecular Dynamics (DMD) Simulations
- Spherically-Symmetric Jagla Ramp Potential

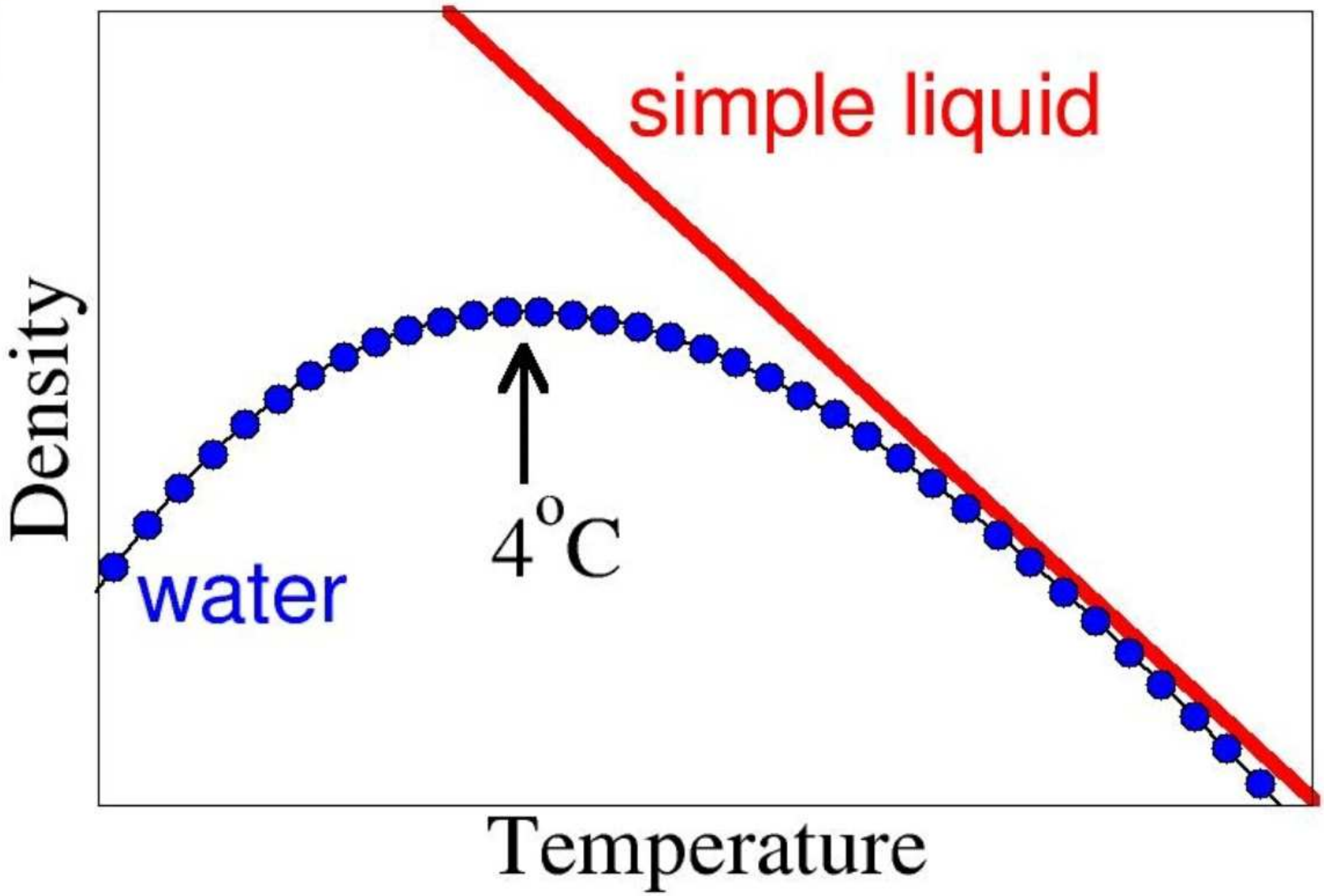
3 Monte Carlo (MC) Simulations
- Coarse-Grained Model for Water

4 All-Atom Molecular Dynamics (MD) Simulations
- Lysozyme In Aqueous Solution Of Trehalose

Why care about water?

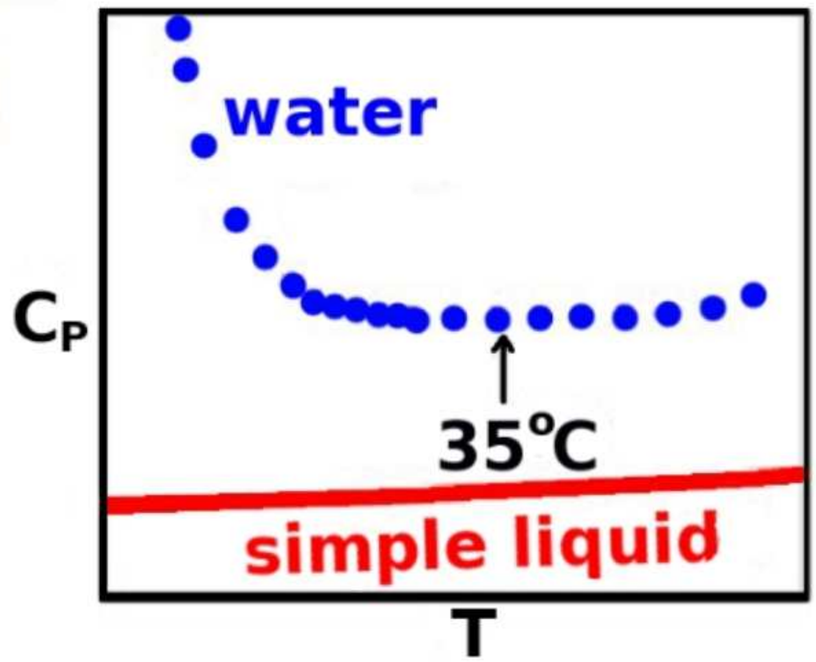
- Covers three-fourths of earth surface
- Constitutes ~70% of the living world
- Has great importance as a solvent
- The most anomalous liquid of all known

Density Anomaly of Water

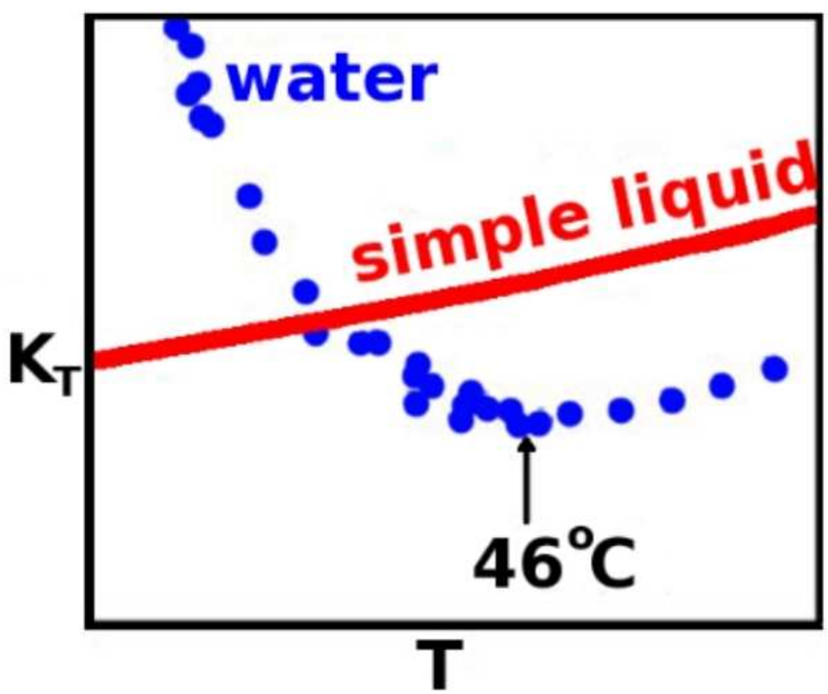


PG Debenedetti, *J. Phys.: Condens. Matter* **15**, R1669 (2003)

Large increase of the thermodynamic response functions



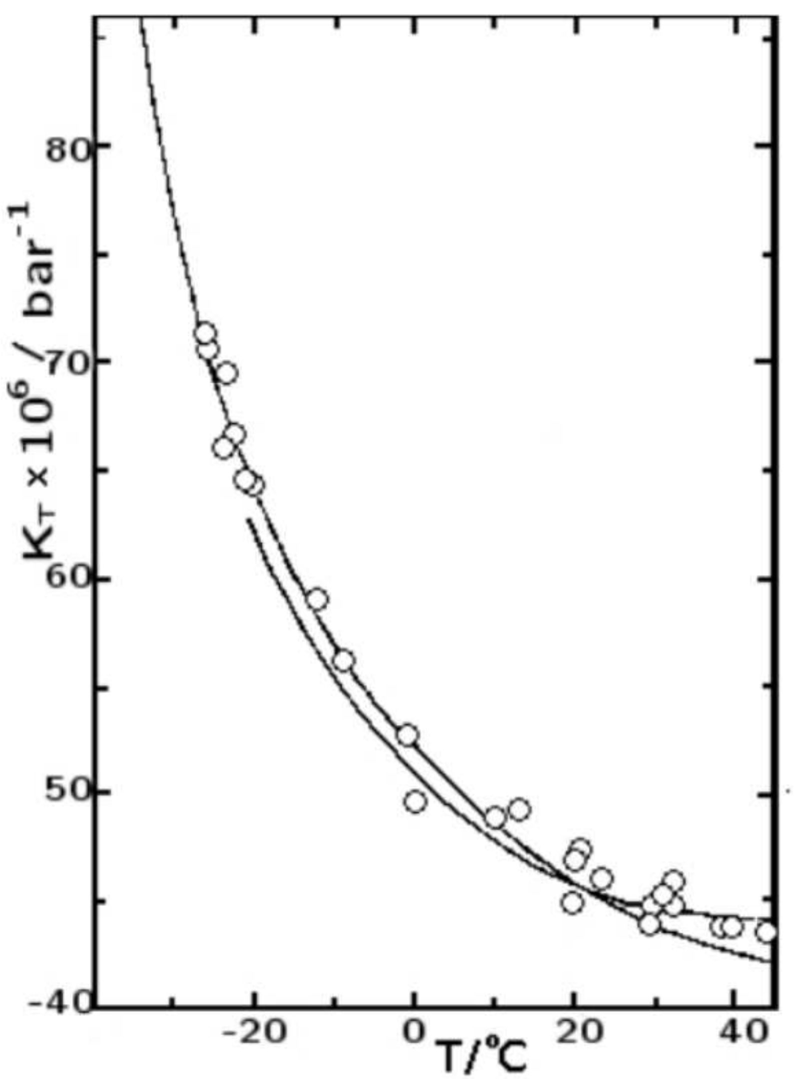
$$\langle(\delta S)^2\rangle = N k_B C_P$$



$$\langle(\delta V)^2\rangle = V k_B T K_T$$

PG Debenedetti,
J. Phys.: Condens. Matter
15, R1669 (2003)

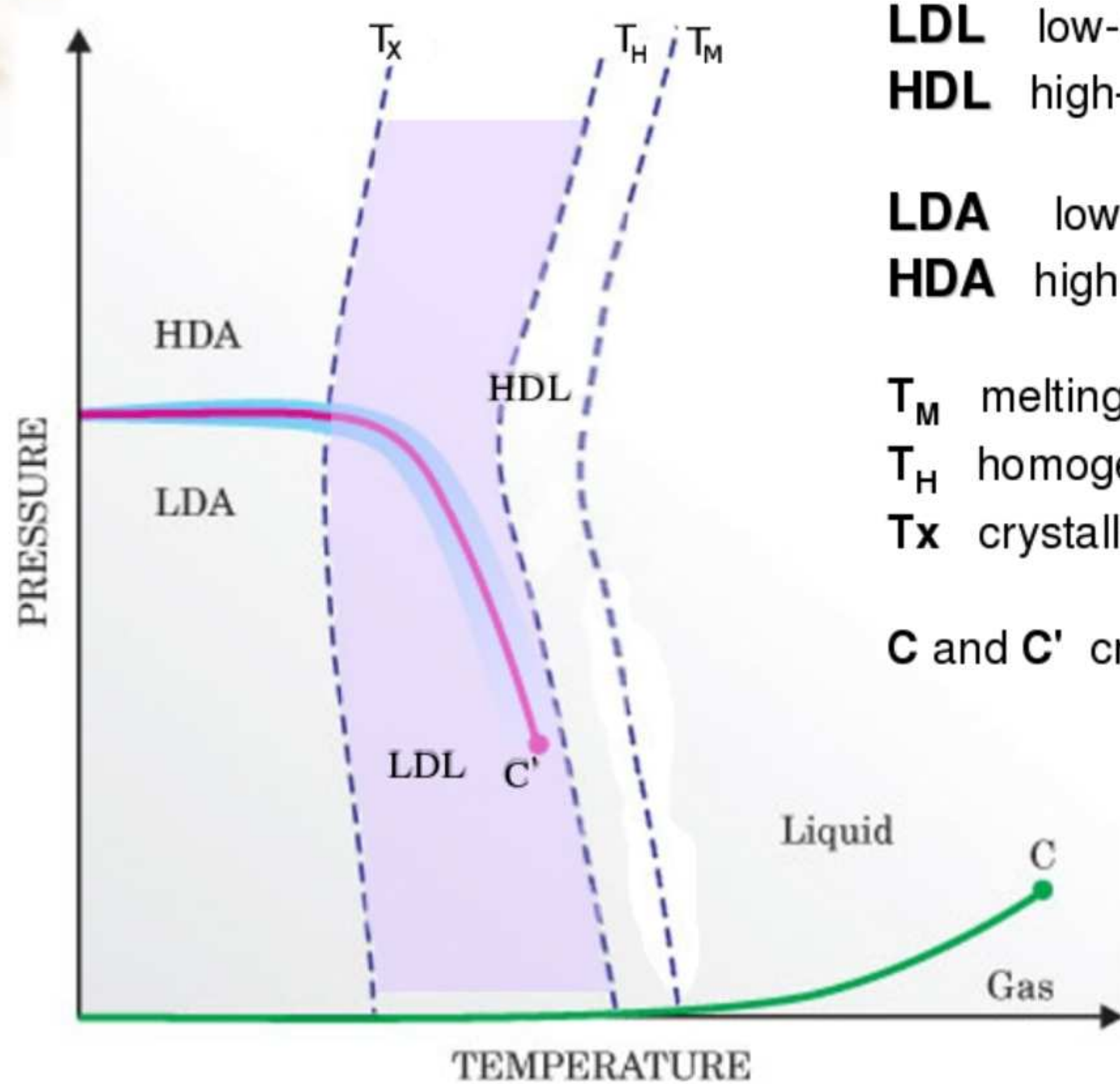
Anomalous Properties of Water are Enhanced in the Supercooled Region



Experimental data

R. J. Speedy and C. A. Angell,

J. Chem. Phys. **65**, 851 (1976)



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)

Outline

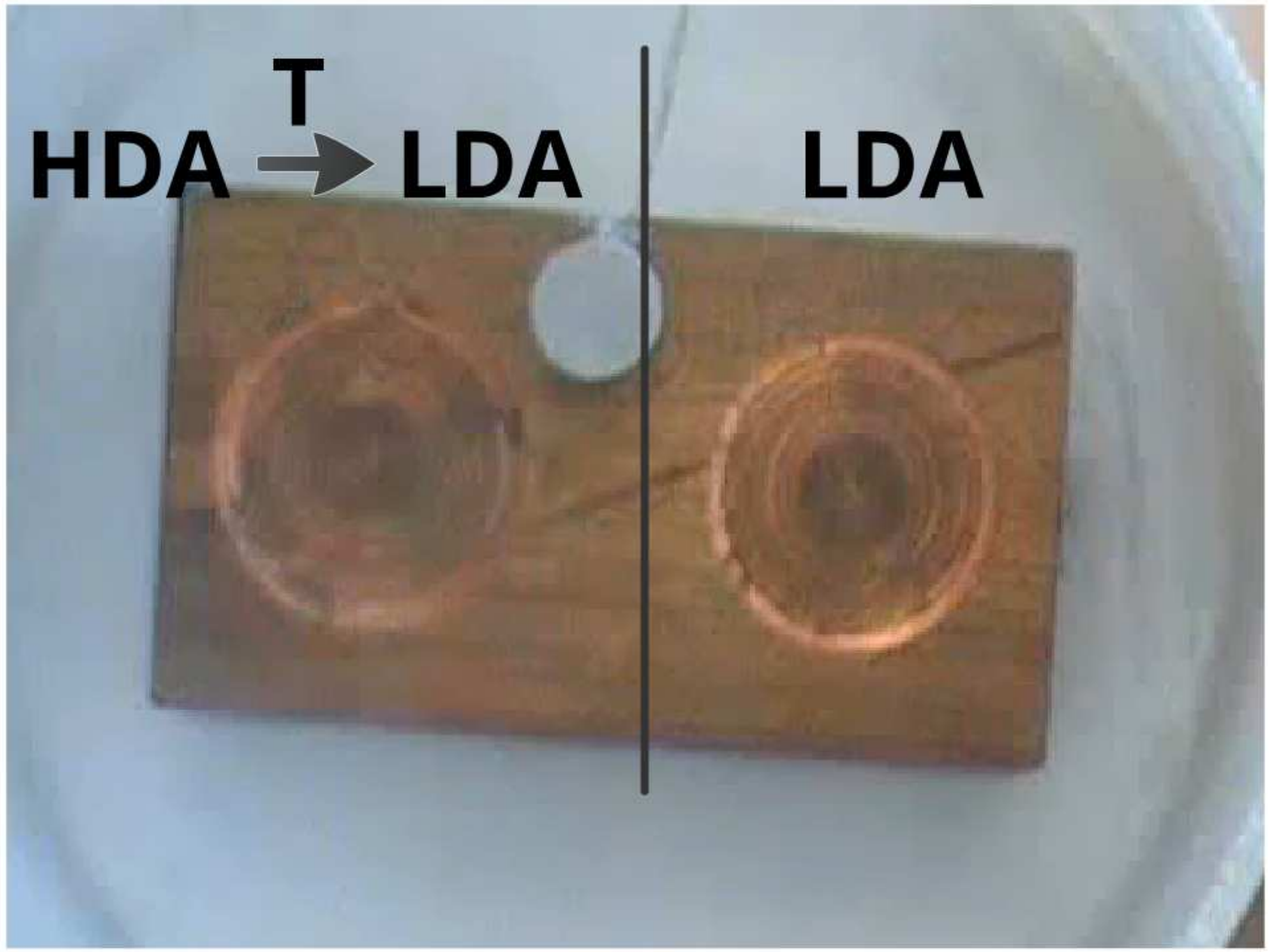
Background

Simulations

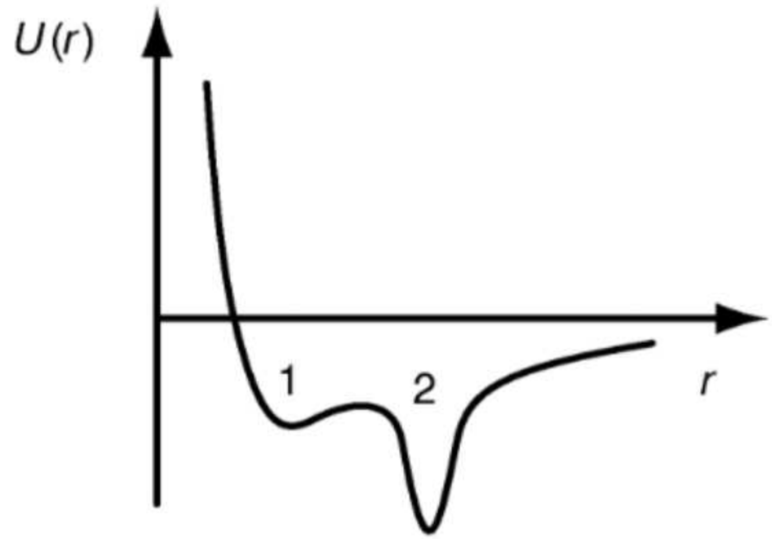
Discussion

From Thomas Loerting's lab

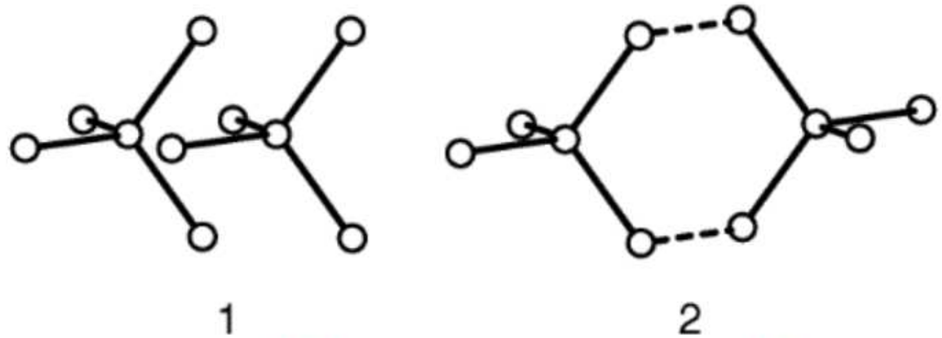
A sample of **HDA** glassy water at 77K, 1bar transforms into **LDA** glassy water



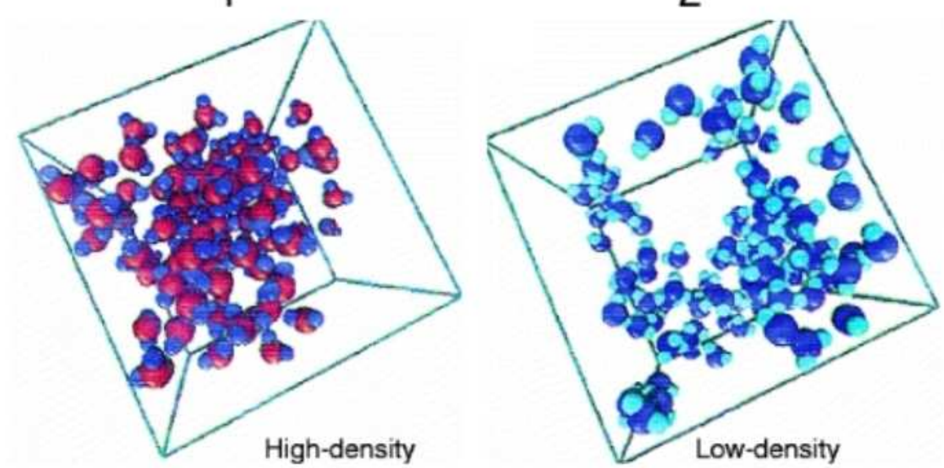
K. Winkel, E. Mayer, T. Loerting; J. Phys. Chem. B 115 14141–14148



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)

Question:

How does the confinement affect liquid-liquid phase transition ?

Why:

- biological and technological applications
- understanding the disparity of previous experiments and simulations for water in different kinds of confinements

We need:

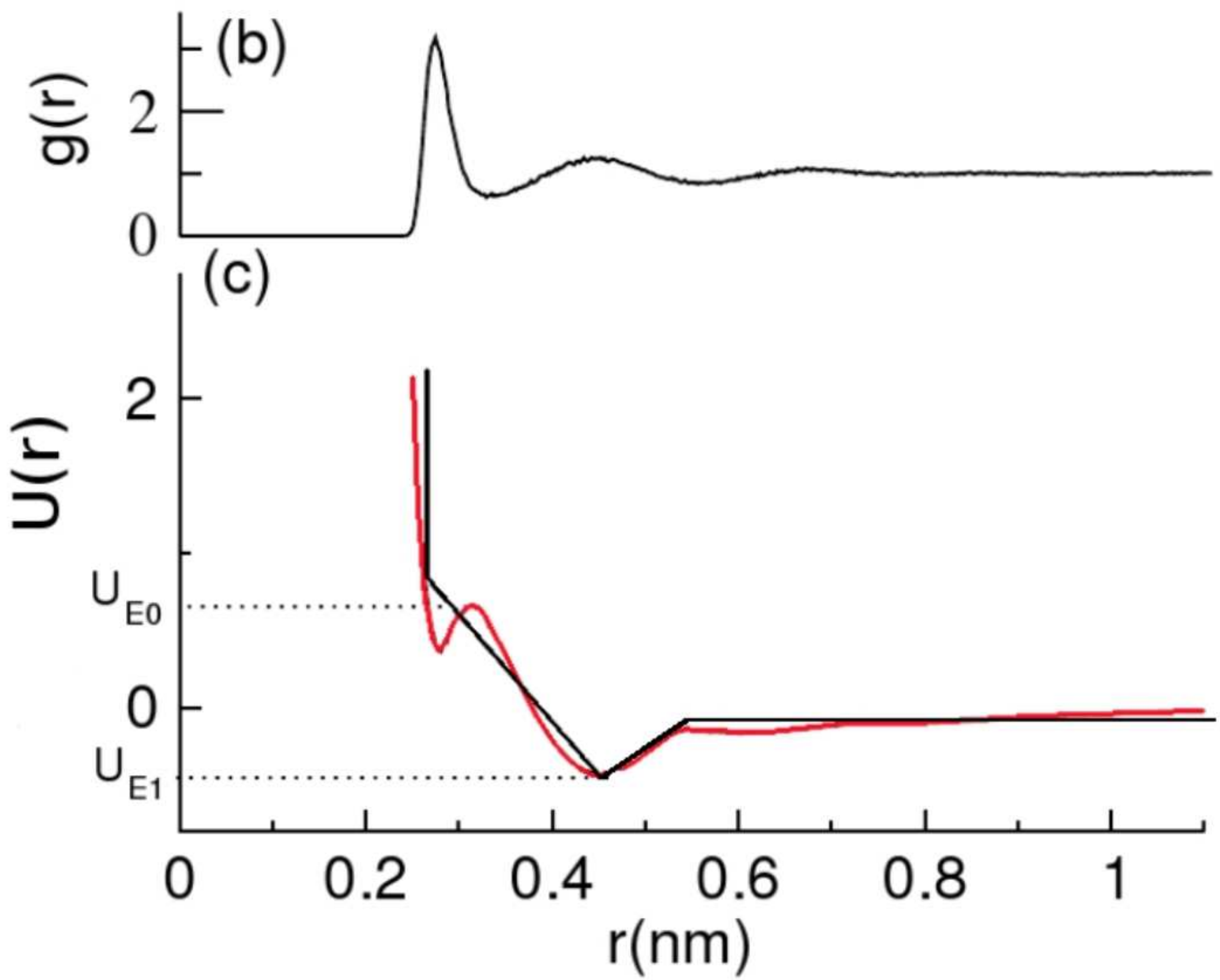
simple model: - to permit fast simulations
- to equilibrate to very low T

Discrete Molecular Dynamics (DMD)

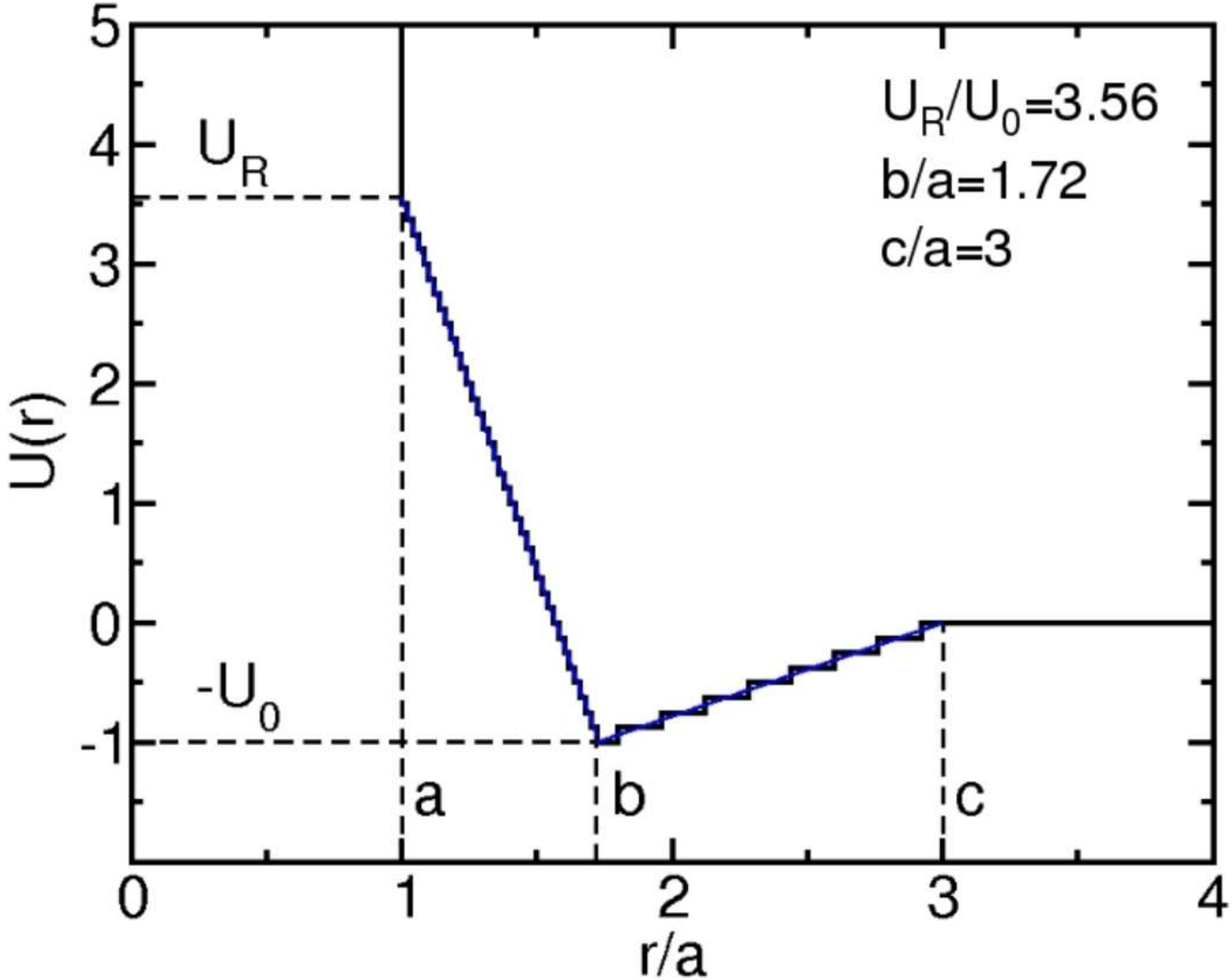
Spherically-Symmetric Jagla Ramp Potential

E. G. Strekalova, J. Luo, H. E. Stanley, G. Franzese, and S. V. Buldyrev, *Nanoparticle confinement in anomalous liquids* (under review 2012), arXiv:1107.1926

How to relate the ramp potential to water?
Hard core= water 1st coordination shell
Soft core = water 2nd coordination shell



Spherically-Symmetric Jagla Ramp Potential



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

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Simulations

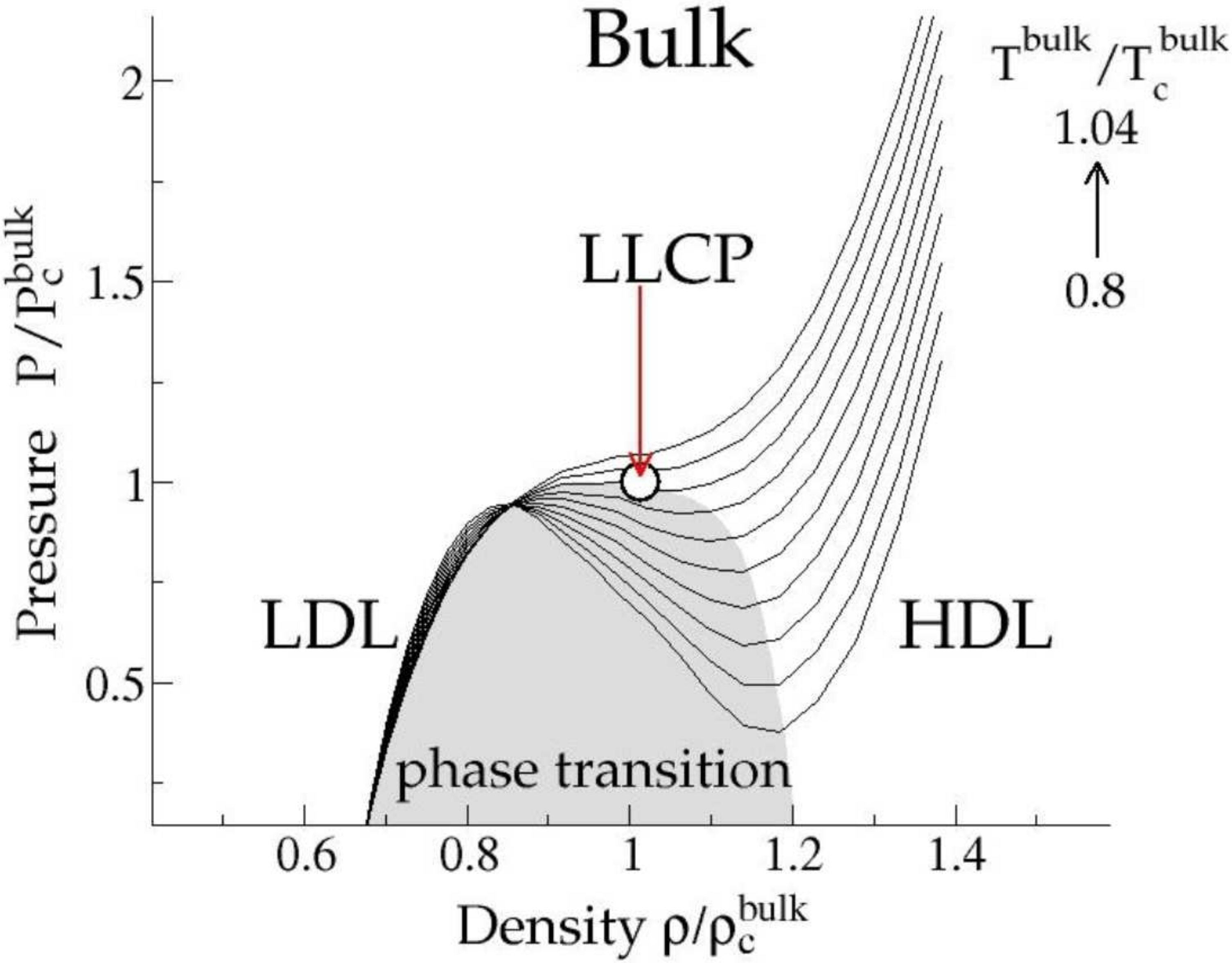
DMD

MC

MD

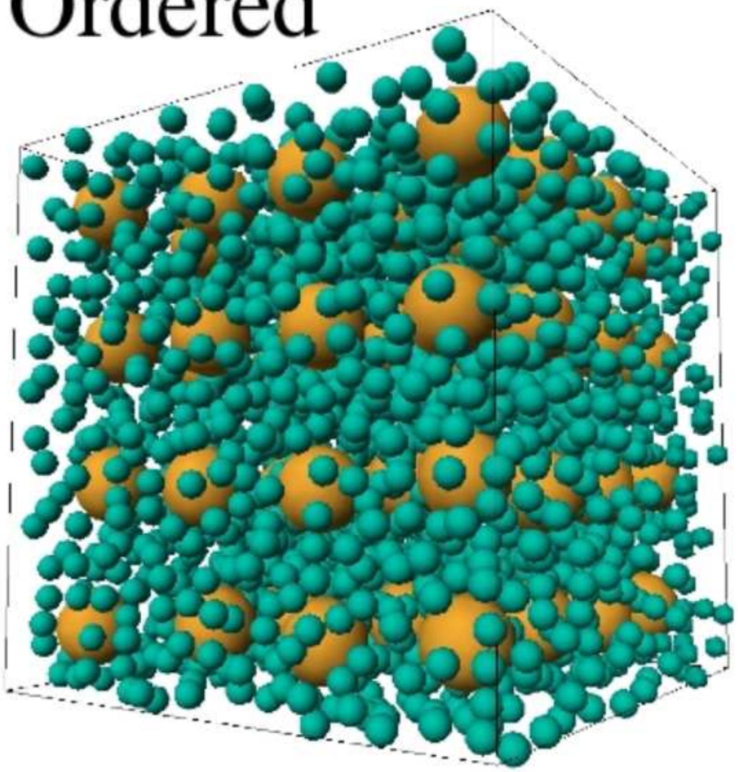
Discussion

Equation of State for Spherically-Symmetric Jagla Ramp Potential

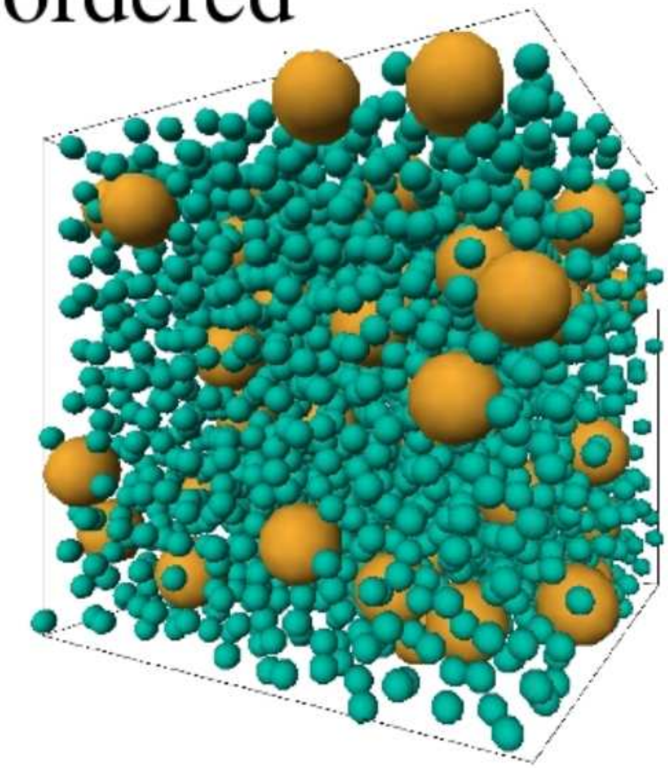


L. Xu, S. V. Buldyrev, C. A. Angell, and H. E. Stanley, *Phys. Rev. E* **74**, 031108 (2006)

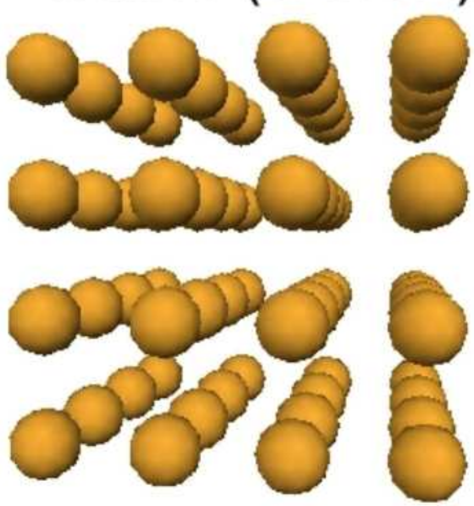
Ordered



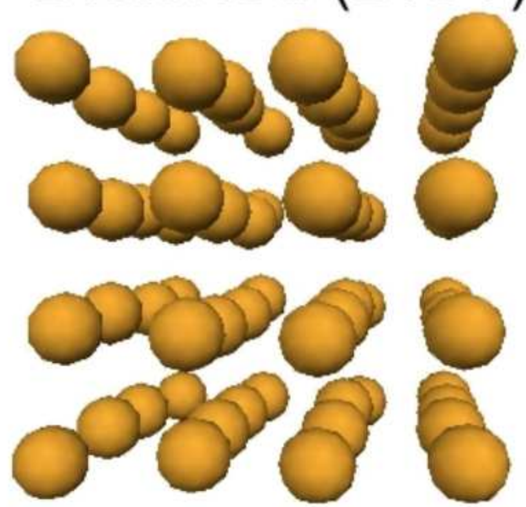
Disordered



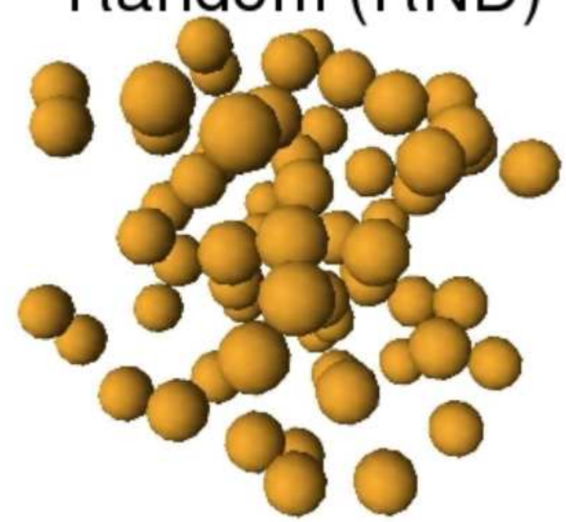
Cubic (CUBE)

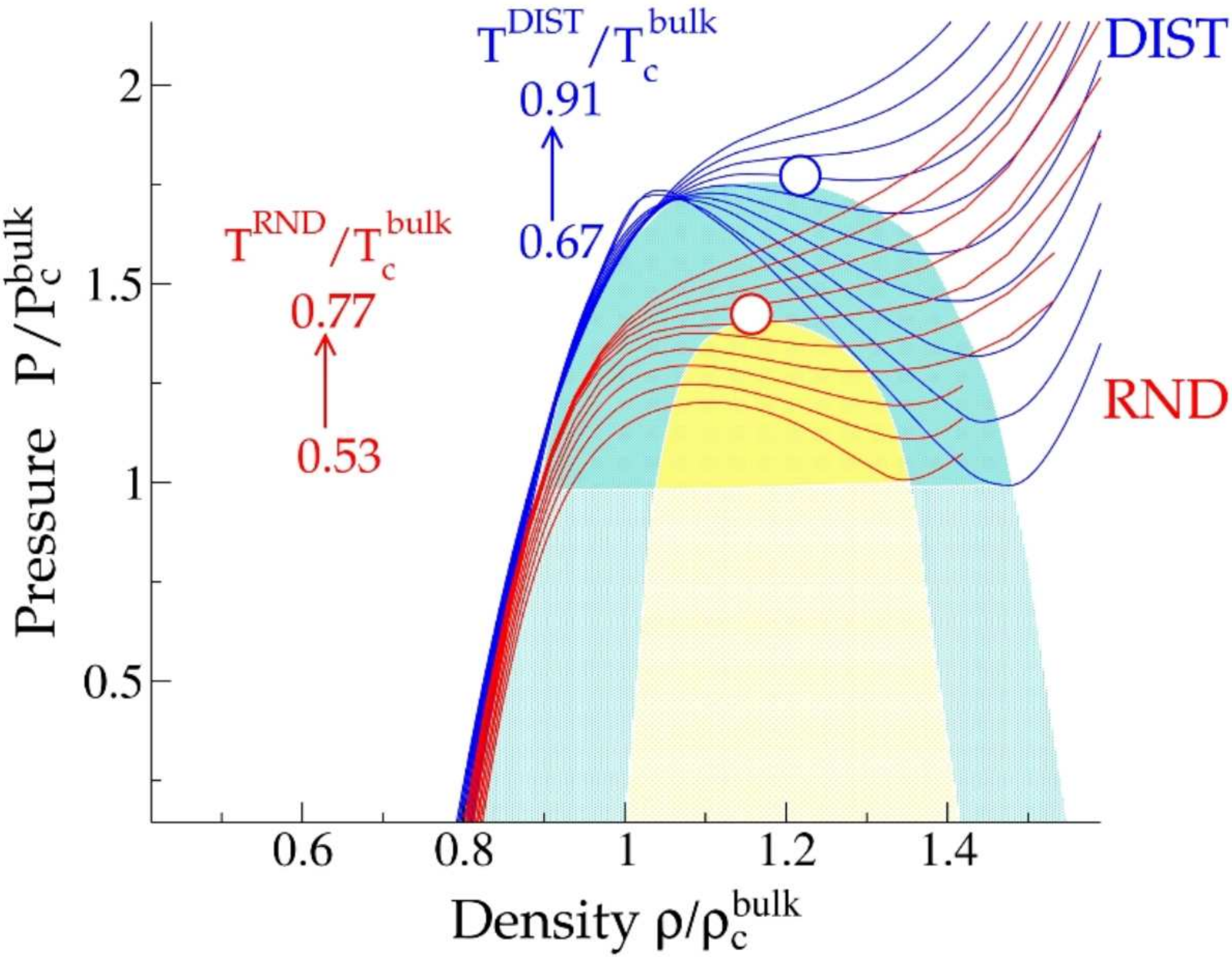


Distorted (DIST)



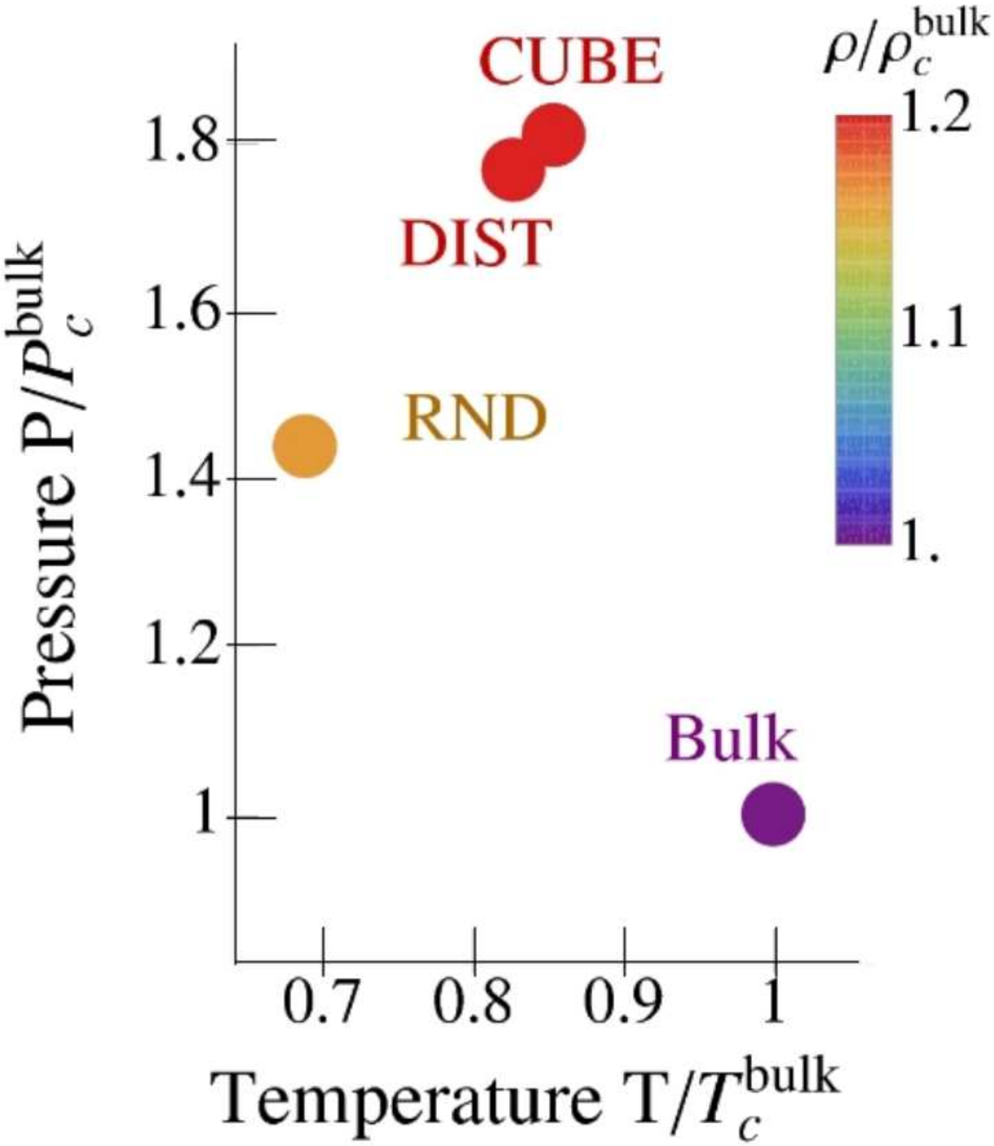
Random (RND)



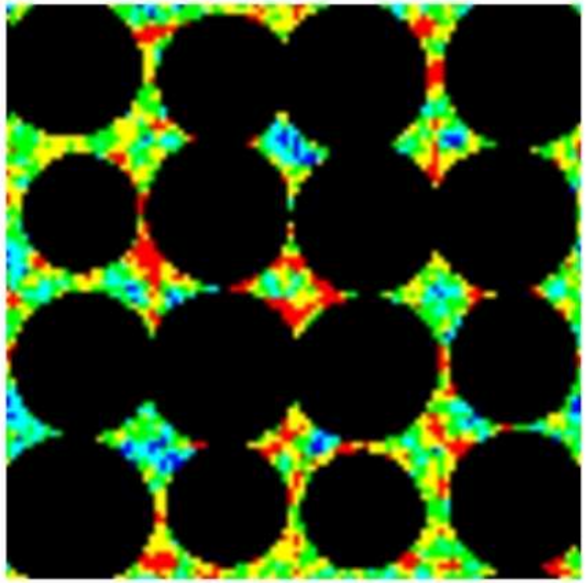


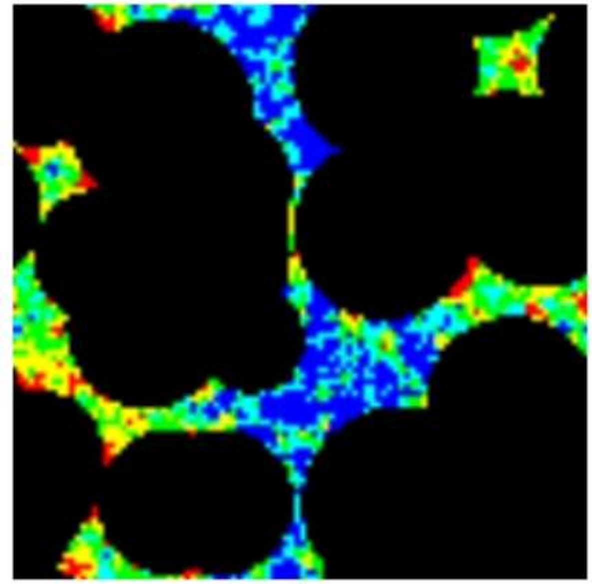
- Shrinks the region with anomalous density behavior
- Reduces *T* and *P* of the liquid-liquid critical point (*LLCP)*
- Reduces the separation between *HDL* and *LDL* spinodals.

Liquid-Liquid Critical Point

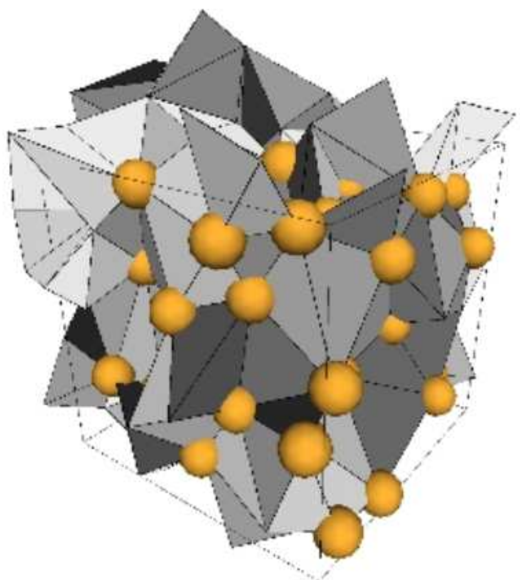


For increasing disorder in the confinement matrix **CUBE → DIST → RND**, *LLCP* shifts down in P, T, ρ.

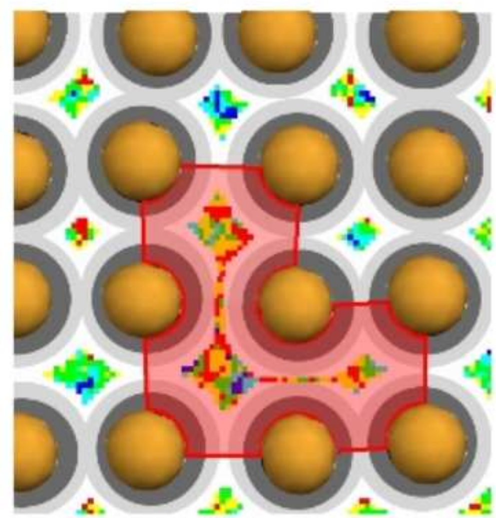




Local density of liquid (red = low density)
(blue = high density)

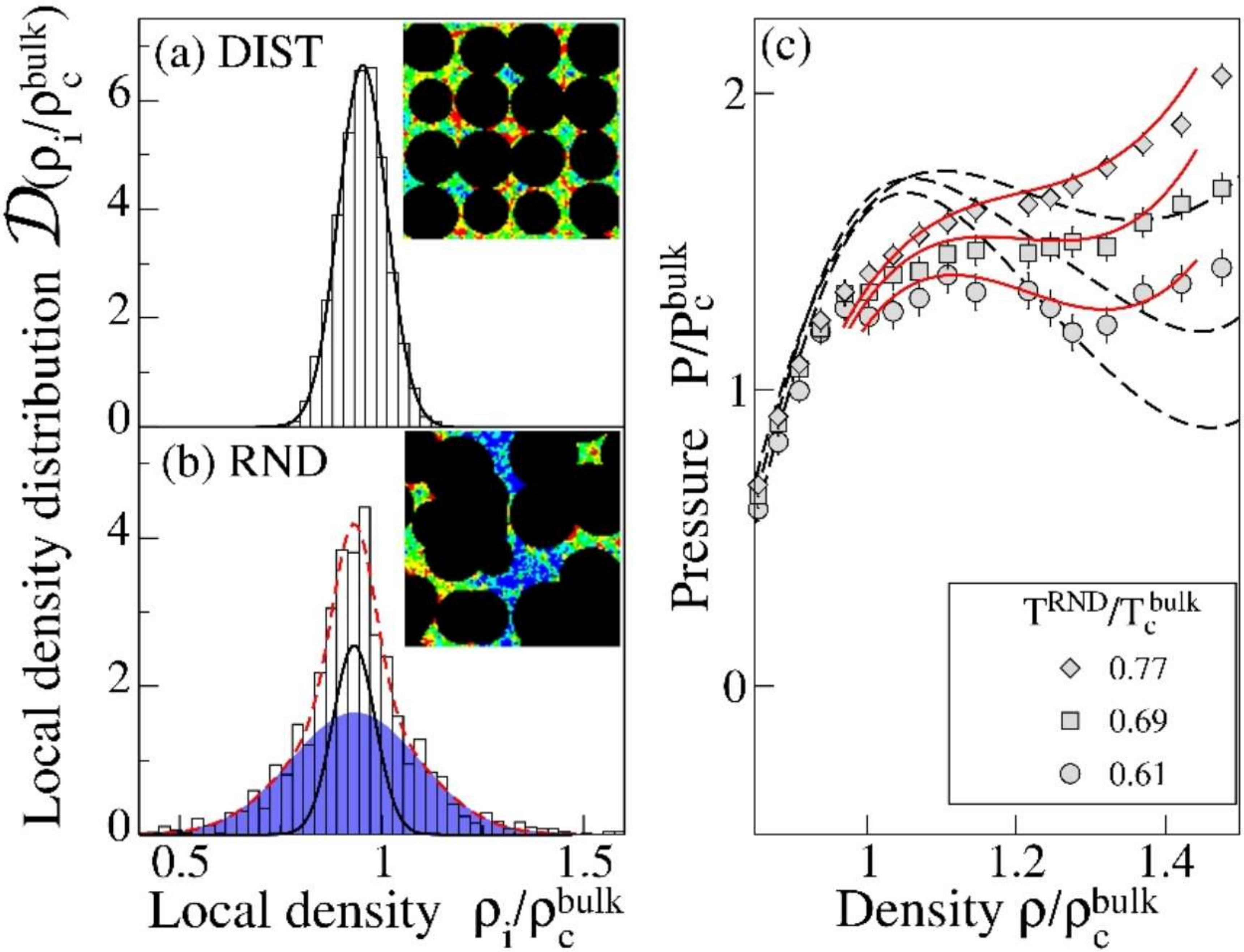


Delaunay Tessellation



Pockets with local density

Additional component of density distribution due to the heterogeneity in local volumes is responsible for shifts in T.



Order ⟶ Disorder in Confinement

1 Liquid-Liquid Coexistence Region Shrinks

2 Density Anomalies Region Shrinks

3 Liquid-Liquid Critical Point Shifts Down in
- Density
- Temperature
- Pressure

Why?
- Local Density Heterogeneity

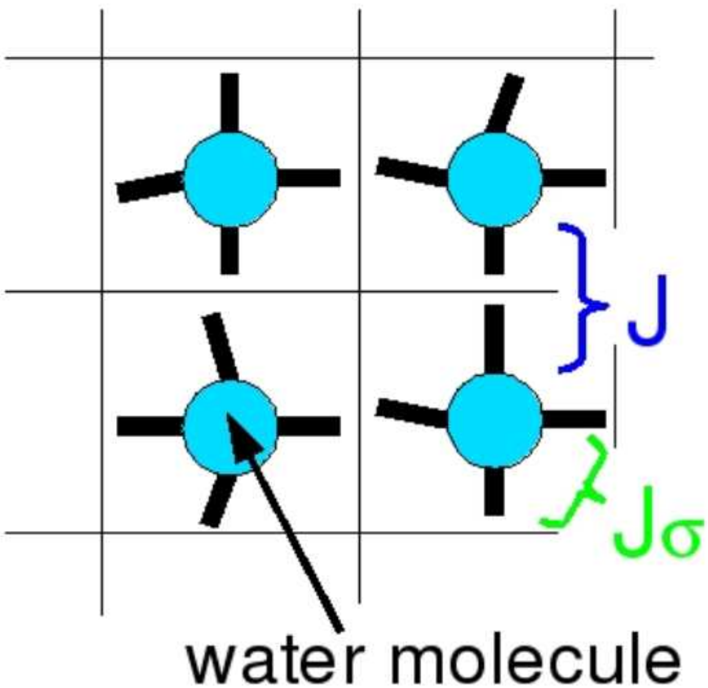
Monte Carlo (MC) simulations of a coarse-grained model

E. G. Strekalova, M. G. Mazza, H. E. Stanley, and G. Franzese
Large Decrease of Fluctuations for Supercooled Water in Hydrophobic Nanoconfinement,
Physical Review Letters **106**, 145701 (2011)

Monte Carlo (MC) simulations of a coarse-grained model

- Fluid is divided into cells of equal size.
- Each cell is occupied.
- Each cell has 4 nearest neighbors.

$$\mathscr{H} \equiv U - JN_{\mathrm{HB}} - J_\sigma N_\sigma$$



U

– 12-6 Lennard-Jones for water-water,

– repulsive for water-hydrophobe.

JN_{HB}

Hydrogen bond (HB) is formed with bond energy J ; N_{HB} is total number of HBs

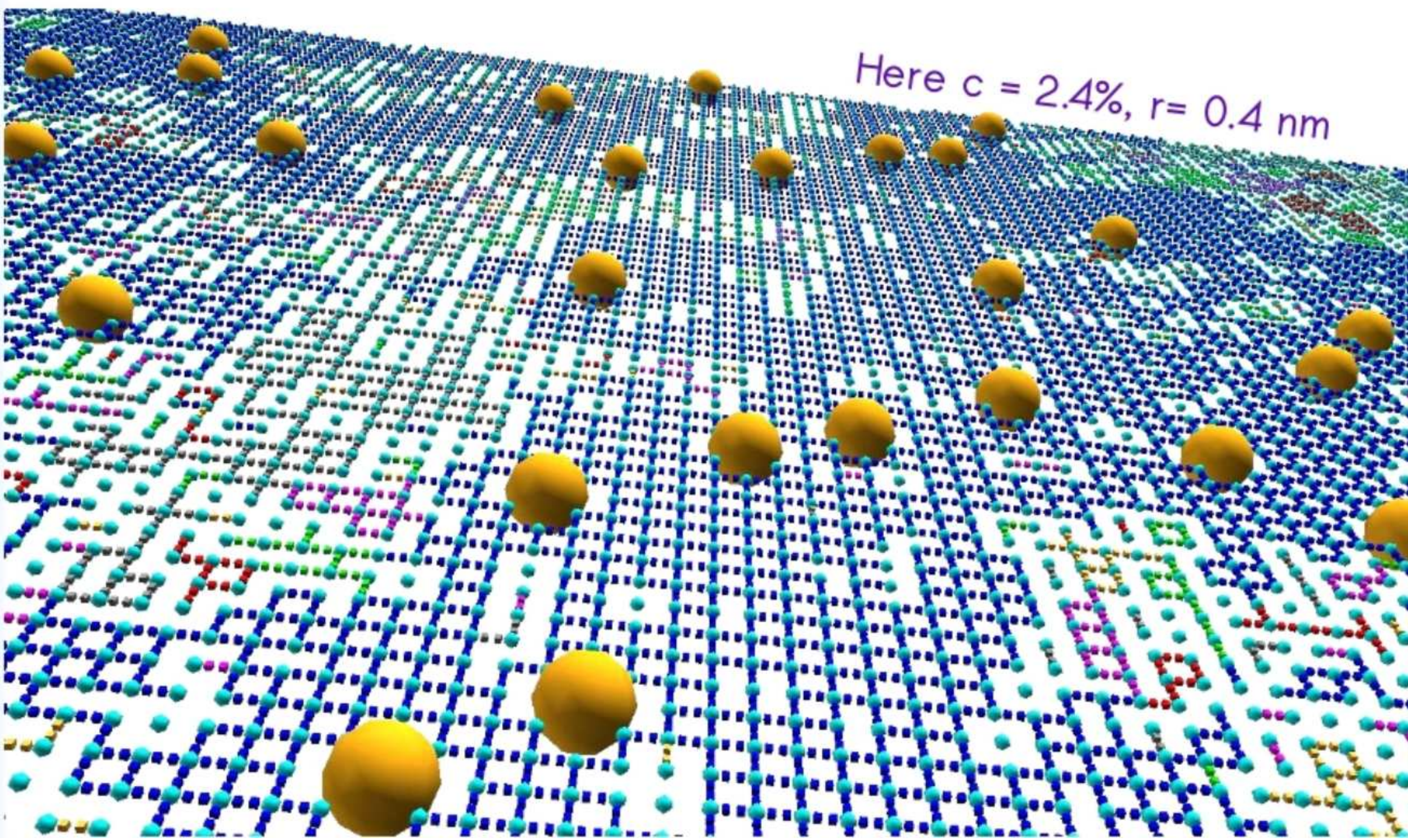
$J_\sigma N_\sigma$

Cooperative interaction J_σ among HBs models O-O-O correlation, locally driving molecules toward ordered configuration

Monte Carlo (MC) simulations in 2D in the NPT ensemble

Different hydrophobic particle concentrations: c = 0%, 2.4%, 25%

Different hydrophobic particle sizes: r = 0.4 nm, 1.6 nm



Confinement Introduces Significant Changes to the Phase Diagram

DMD simulations

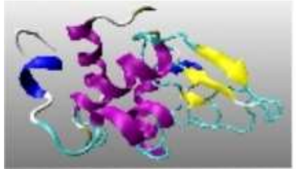
random confinement:

- Weakening of the the liquid-liquid phase transition
- Shifts in T, P, ρ

MC simulations

- Weakening of the the liquid-liquid phase transition
- Significant reduction in response functions

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.



Supercooled Confined Water
-Applications to Cryopreservation

freezing of cells, tissues, organisms

preservation of stem cells
- Lymphoma
- Leukemia
- Disease of liver & heart

Cryopreservation of embryos
- Surplus
- Transport
- Preserve valuable strains

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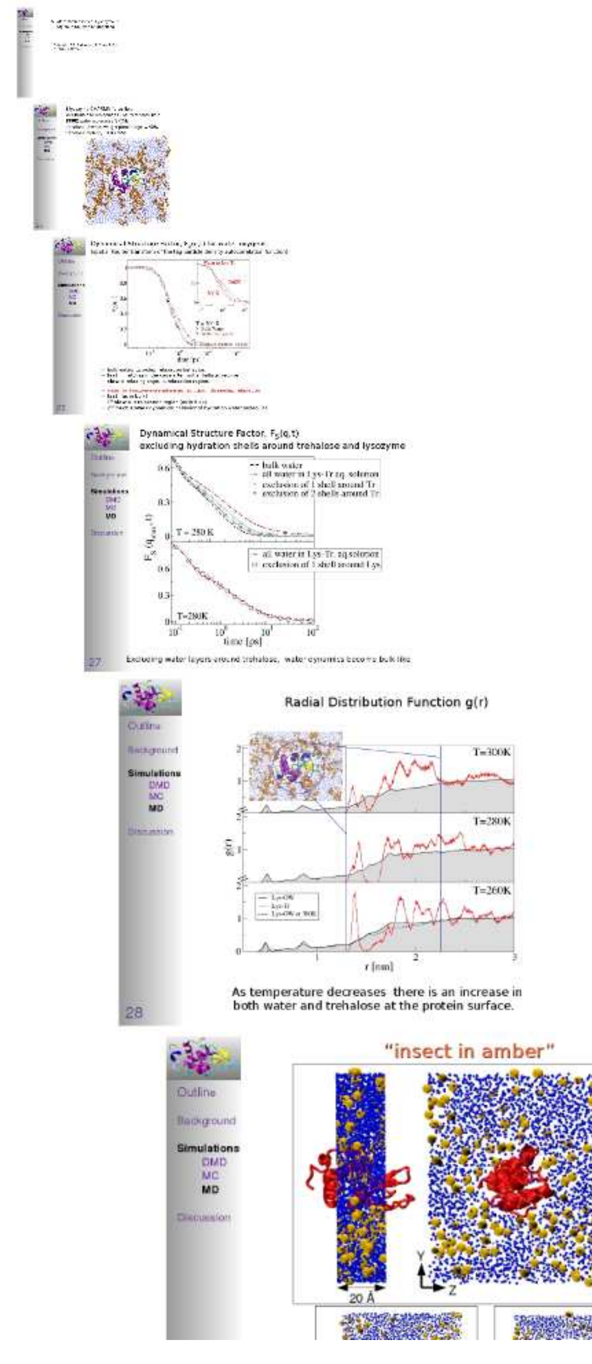
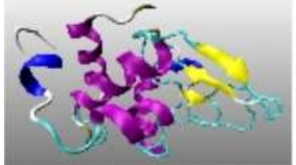
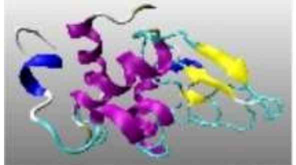




All-atom Simulations of Lysozyme in Aqueous Solution of Trehalose

D. Corradini, **E. G. Strekalova**, H. E. Stanley, P. Gallo

nice paper to come ...



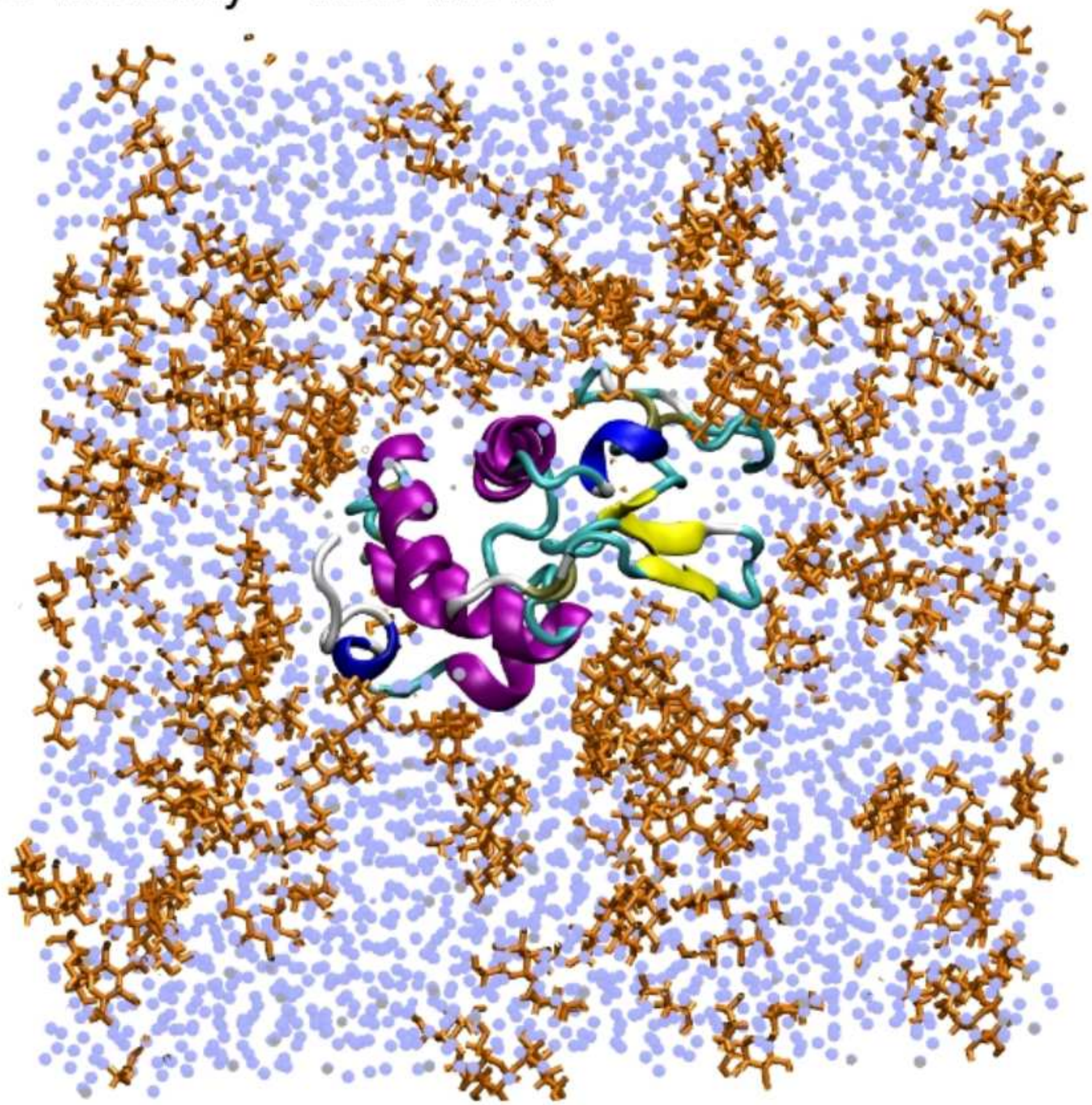
1 lysozyme CHARMM force-field,

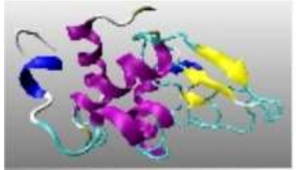
491 trehalose molecules CHARMM force-field,

13982 water molecules SPC/E

trehalose to water weight percentage = **40%**

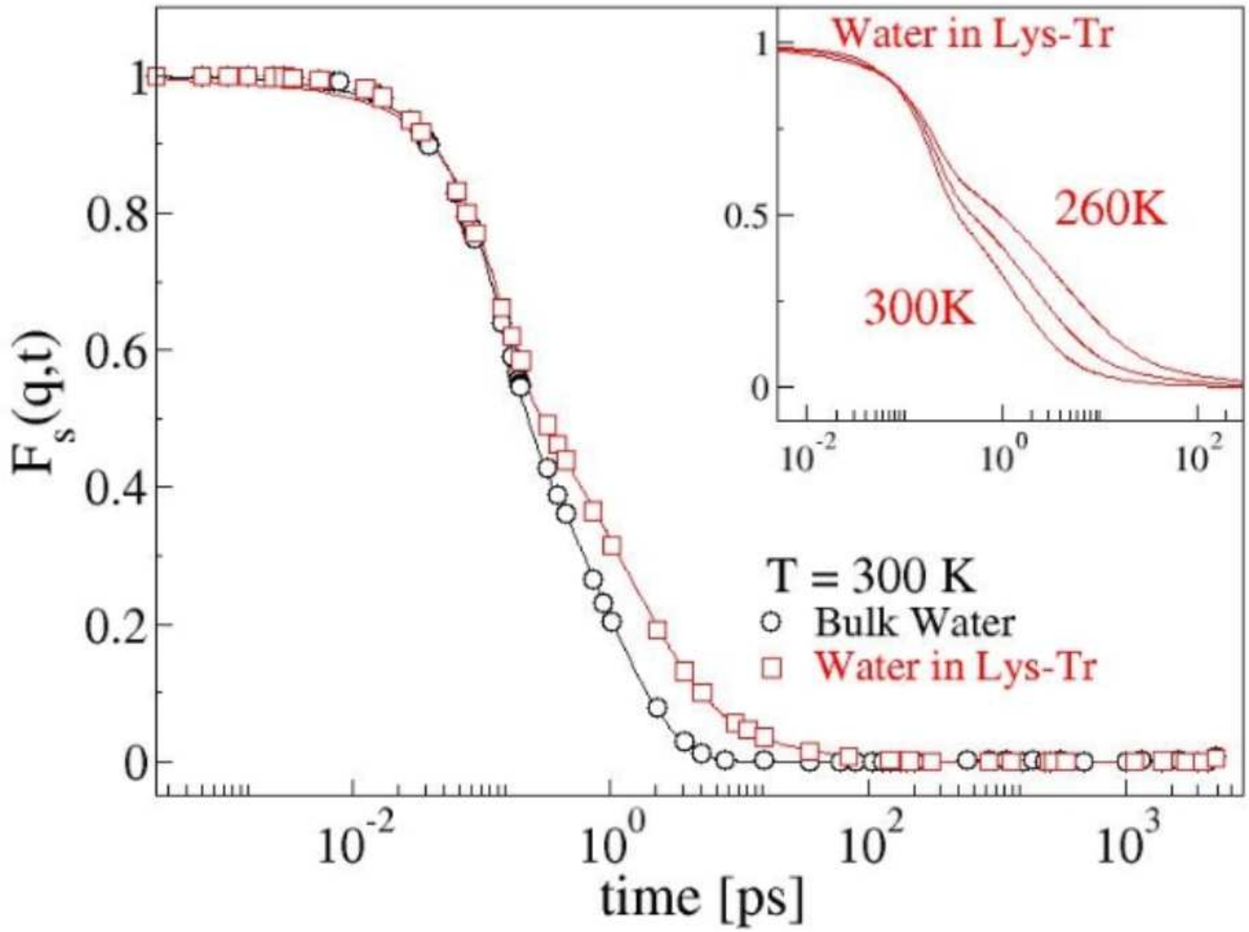
trehalose molarity ~**1.33 mol/l**





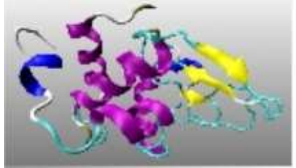
Dynamical Structure Factor, $F_S(q,t)$ for water oxygens

(spatial Fourier transform of the tag-particle density autocorrelation function)

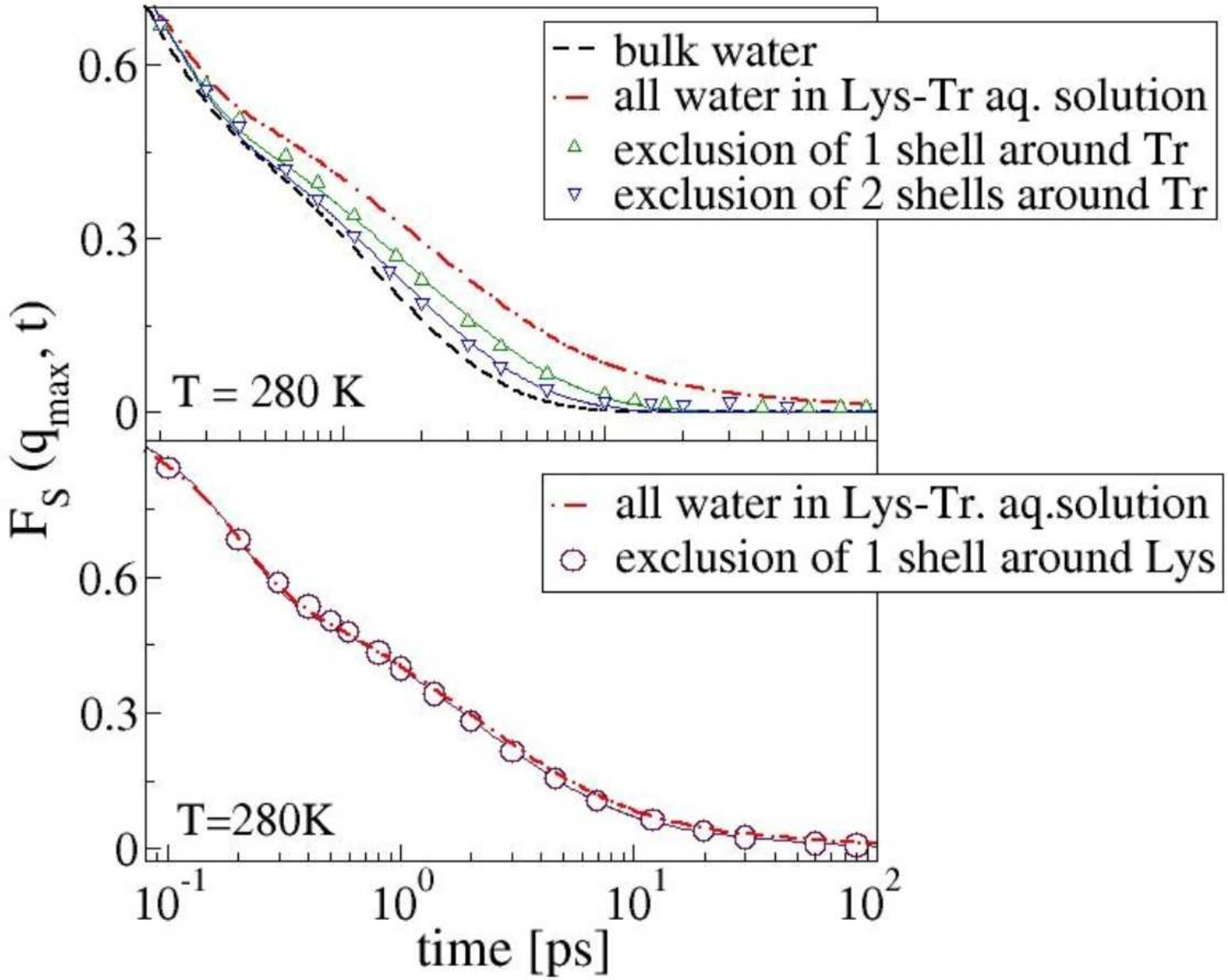


- bulk water: <u>two-step</u> relaxation behavior,
- **fast** = rattling in the cage after initial ballistic regime
- **slow** = relaxing cage, α relaxation region.

- water in lysozyme-trehalose aq. solution: <u>three-step relaxation</u>
- **fast** (as in bulk)
- 1st **slow** = α relaxation region (as in bulk).
- 2nd much **slower** dynamical behavior of hydration water molecules

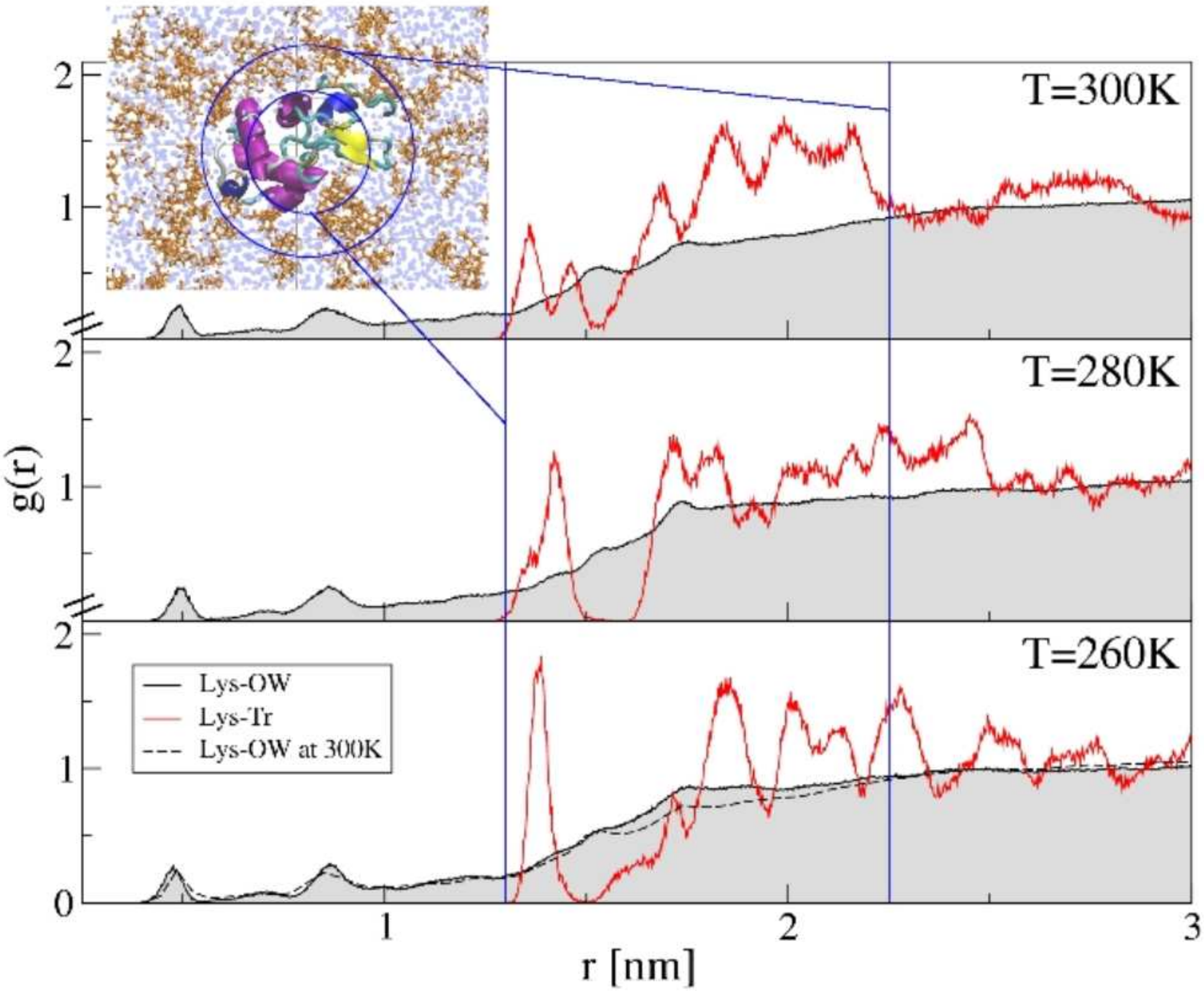


Dynamical Structure Factor, $F_S(q,t)$ excluding hydration shells around trehalose and lysozyme

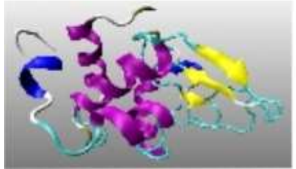


Excluding water layers around trehalose, water dynamics become bulk-like

Radial Distribution Function g(r)



As temperature decreases there is an increase in both water and trehalose at the protein surface.



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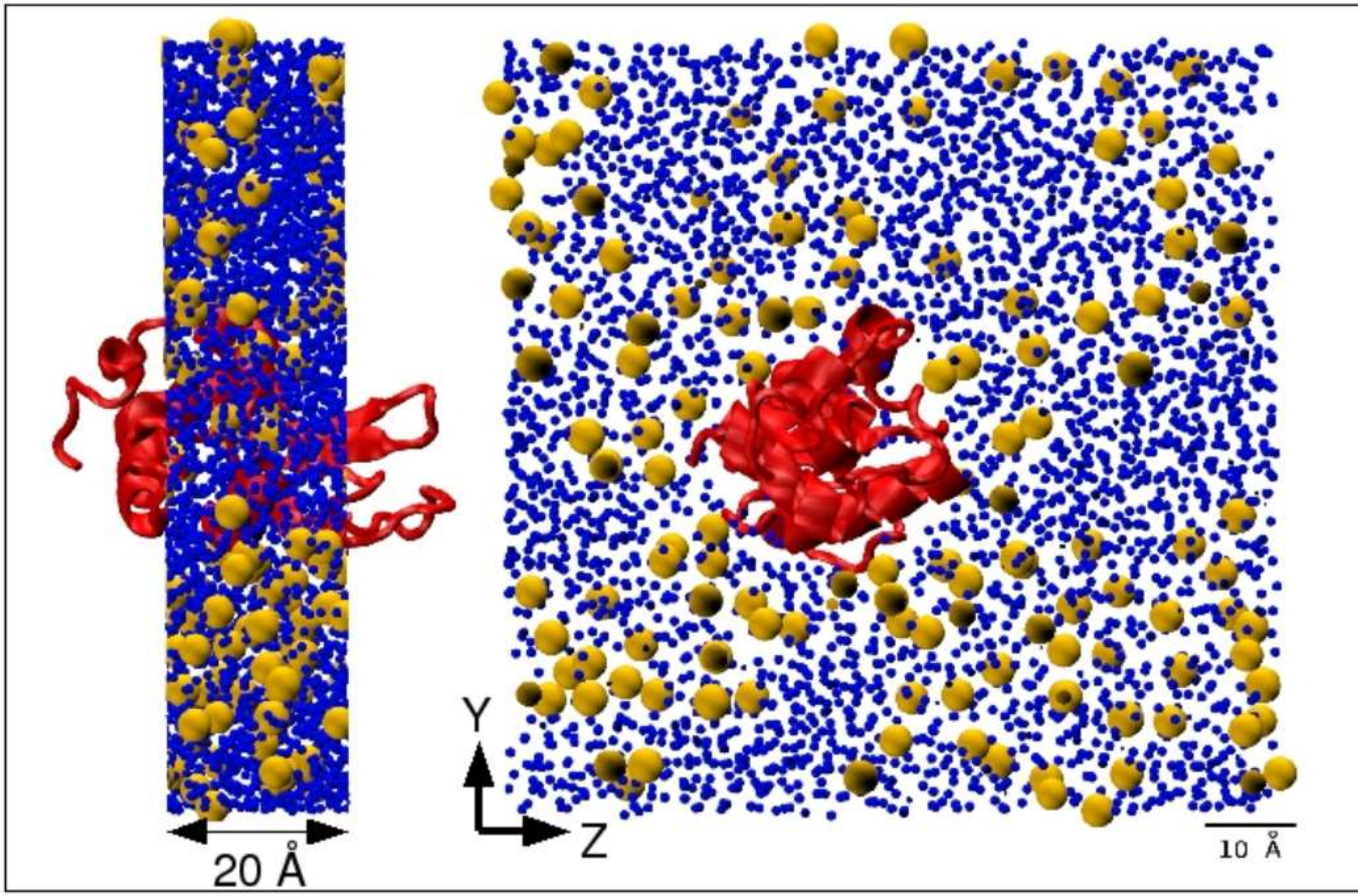
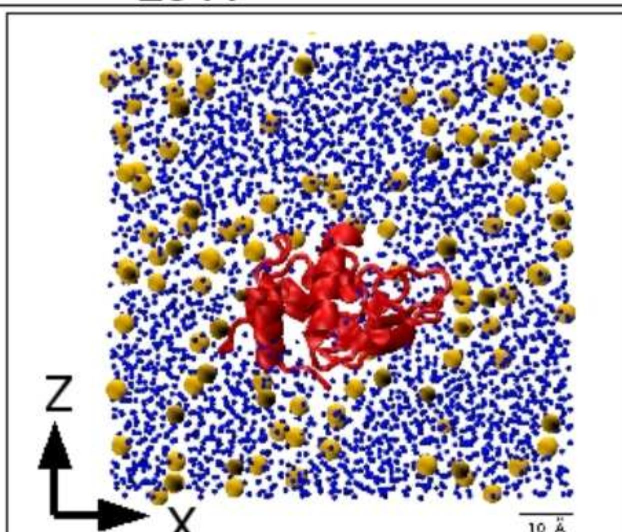
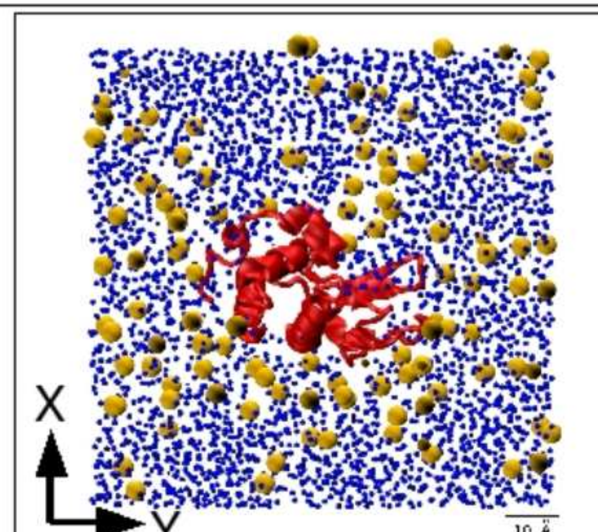
"insect in amber"







Insights into microscopic mechanism of cryopreservation

- Trehalose with very slow dynamics of water surrounds lysozyme.
- We support the hypotheses of the inhibition of protein motion due to the vitrification upon cooling.

Thank you!

Collaborators:

Paola Gallo,

Dario Corradini,

Marco G. Mazza,

Kevin Stokely,

Jiayuan Luo

Advisor: H. Eugene Stanley

Co-Advisors: Giancarlo Franzese and Sergey Buldyrev