Understand water-like anomalies with two-scale isotropic interactions

Limei Xu

Peking University, China

International School of Neutron Science and Instrumentation 3rd Course: Water and the water systems

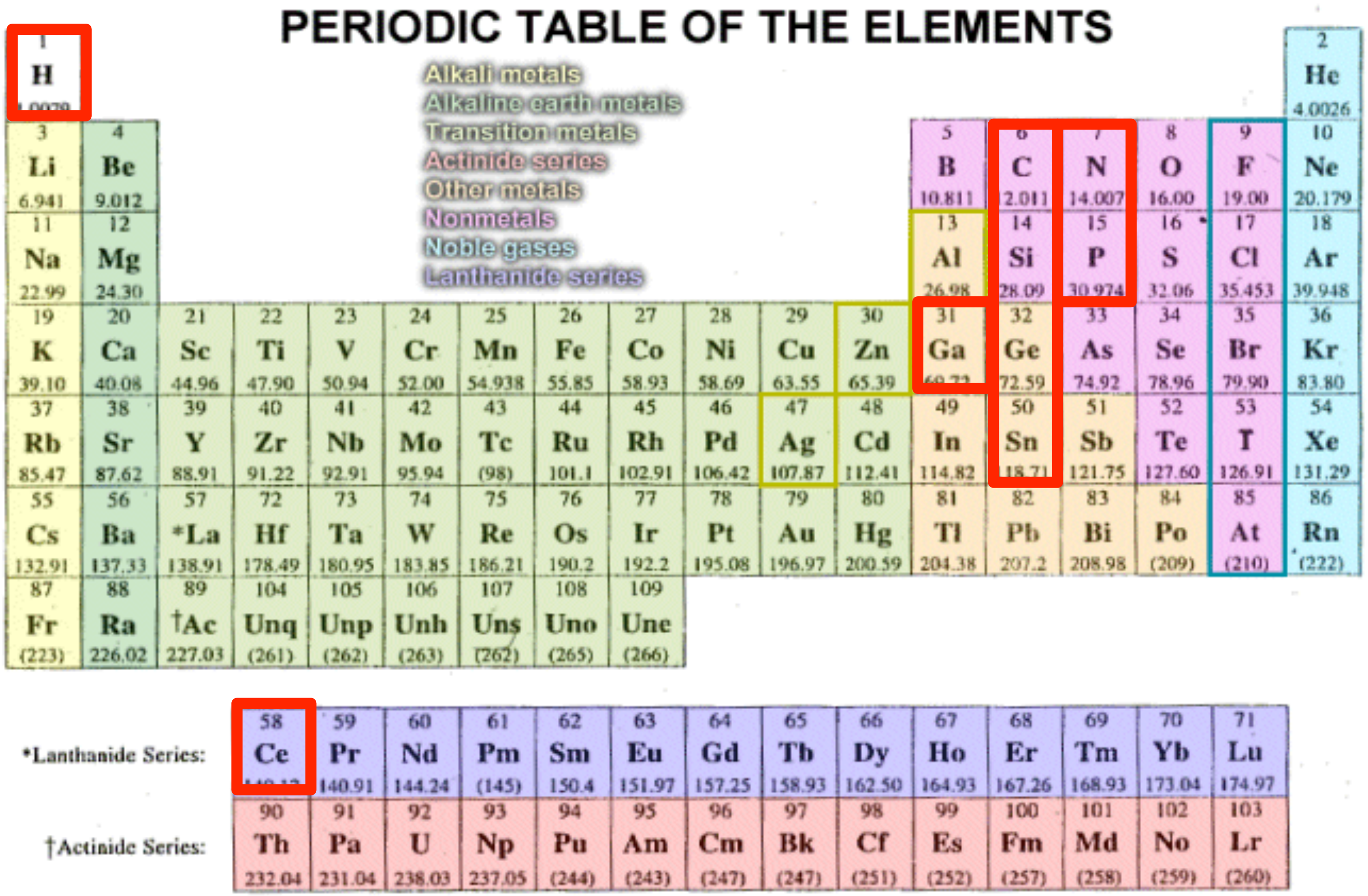
Erice-Sicily, July 2016

PERIODIC TABLE OF THE ELEMENTS

- Alkali metals
- Alkaline earth metals
- Transition metals
- Actinide series
- Other metals
- Nonmetals
- Noble gases
- Lanthanide series

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)									

*Lanthanide Series:	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series:	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)



Tetrahedral structured: H_2O, SiO_2, BeF_2, etc

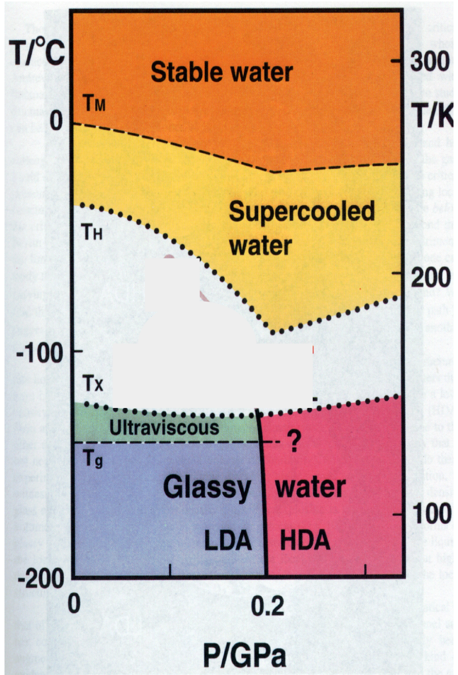
Compounds: Y_2O_3-Al_2O_3, Fe-Co, Ce-Al, etc

Poole, Nature 1992; Wilding, Science 2008; Debenedetti, Nature 2014; Wu Nature Comm 2015.

Materials share similar anomalous properties

- Negatively-sloped melting line

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T \Delta V}$$

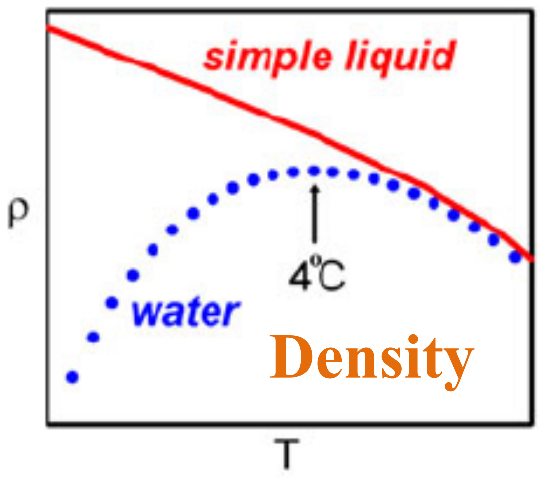


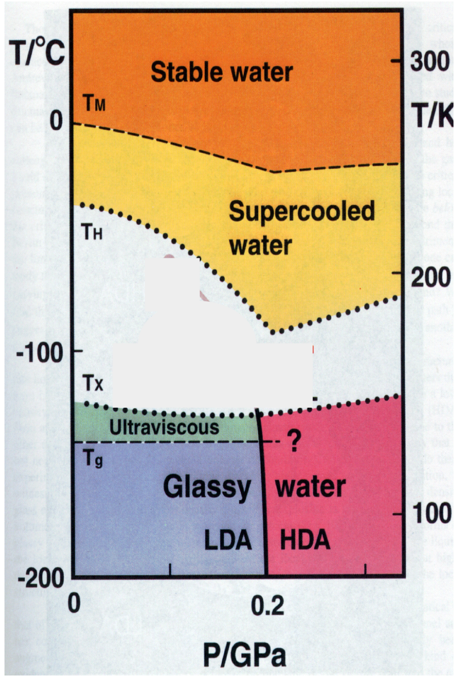
Poole et. al, Nature (1992)
Mishima and Stanley, Nature (1998)

Materials share similar anomalous properties

- Negatively-sloped melting line
- Density anomaly

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\,\Delta V}$$



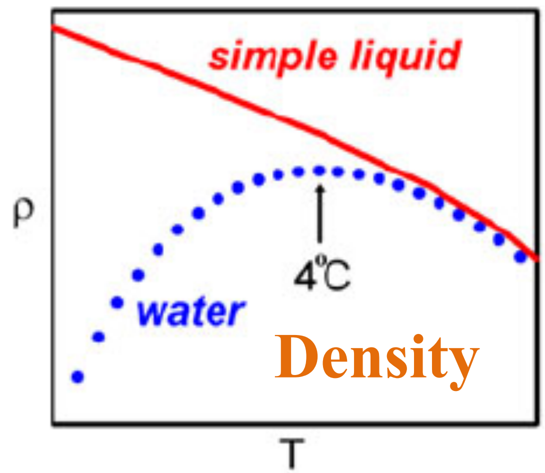


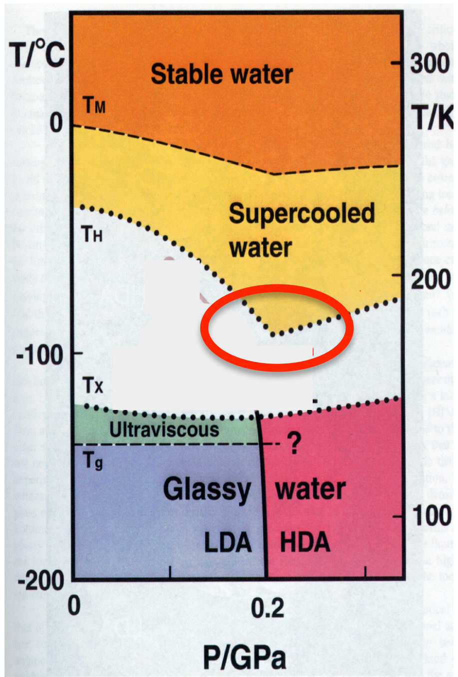
Poole et. al, Nature (1992)
Mishima and Stanley, Nature (1998)

Materials share similar anomalous properties

- Negatively-sloped melting line
- Density anomaly
- Extrema in melting curve

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$



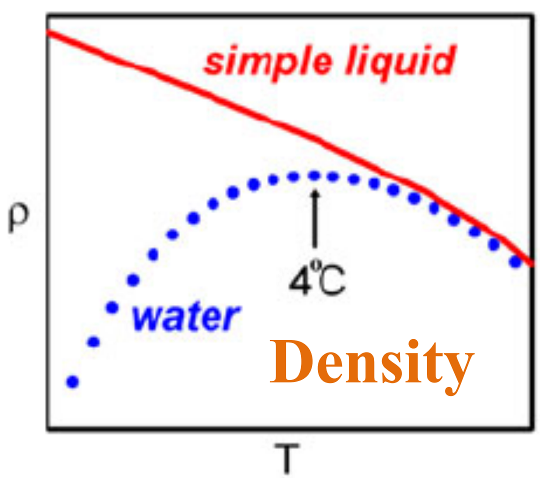


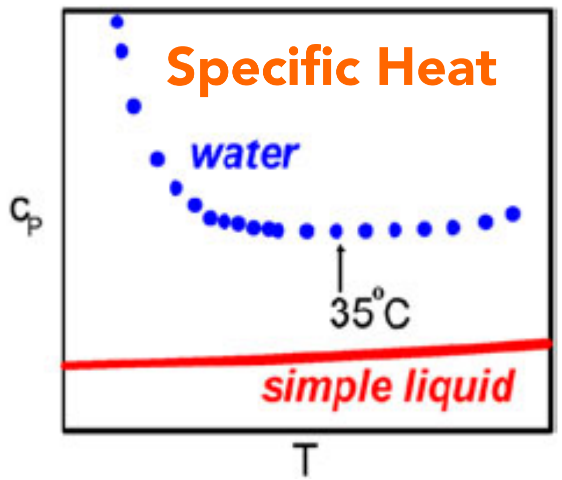
Poole et. al, Nature (1992)
Mishima and Stanley, Nature (1998)

Materials share similar anomalous properties

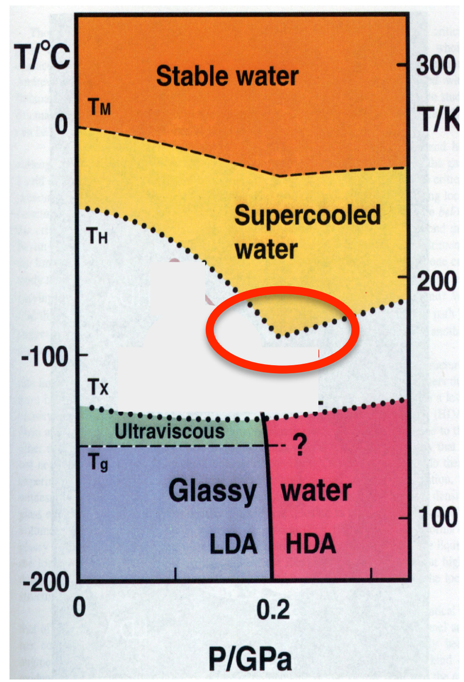
- Negatively-sloped melting line
- Density anomaly
- Extrema in melting curve
- Response function anomaly

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$





$<(\delta S)^2> \sim N k_B Cp$



Poole et. al, Nature (1992)
Mishima and Stanley, Nature (1998)

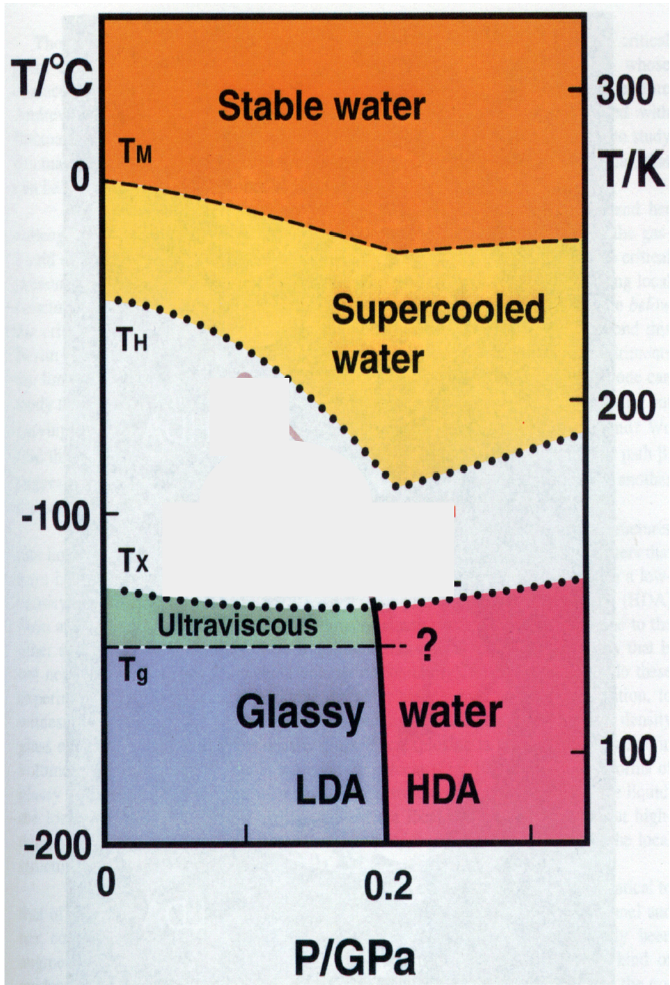
Understanding water anomalies

Scenarios and views
(with or without second critical point)

- Liquid-liquid critical point (Stanley)
- Two-state model (Anisimov)
- Two-order parameter model (Tanaka)
- Spinodal reentrant (Angell & Speedy)
- Singularity-free (Sastry & Debenedetti)

Challenges remains to detect experimentally

Liquid-liquid hypothesis



Poole et. al, Nature (1992)
Mishima and Stanley, Nature (1998)

Difficulty: not easily to testify the location of liquid phases in deep supercooled region due to crystallization

Anders Nilsson's & Thomas Loerting's group lowering the limit from above and pushing the limit up

- Can we construct a simple model that shows stable LLCP and captures water-like anomalies?

- How to understand properties of water in terms of isotropic two-scale interactions

- How confinement and surface chemistry affect the anomalous properties and phase behaviors?

- Can we construct a simple model that shows stable LLCP and captures water-like anomalies?

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Characteristics of model

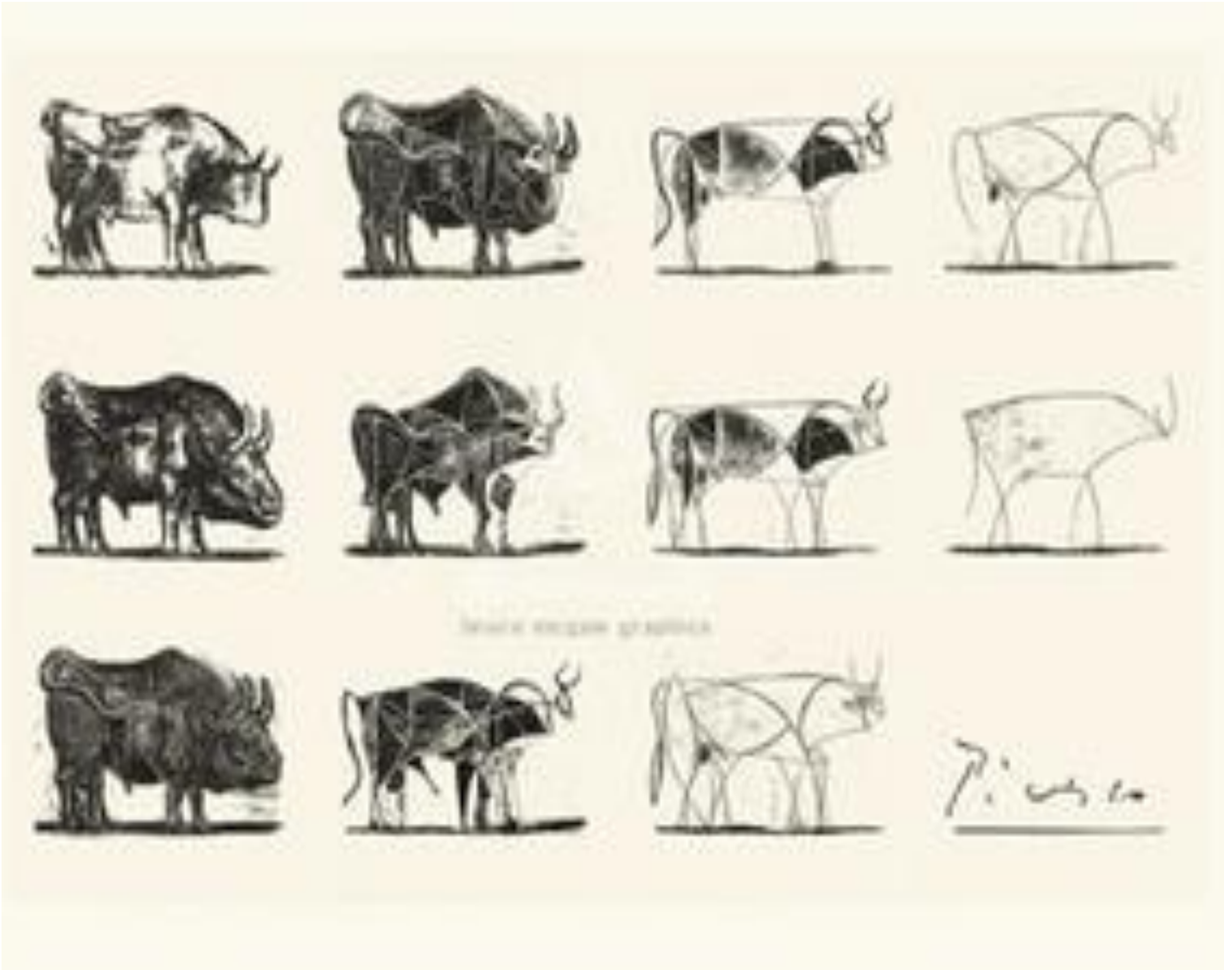
- Accessible liquid-liquid critical point

(Testify the liquid-liquid phase transition hypothesis)

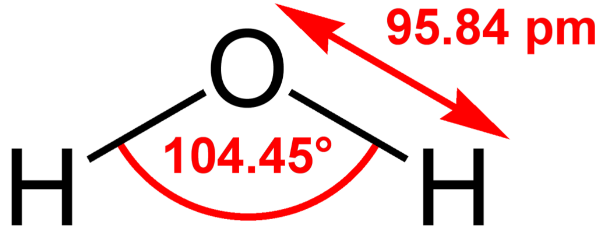
- Water-like anomalies

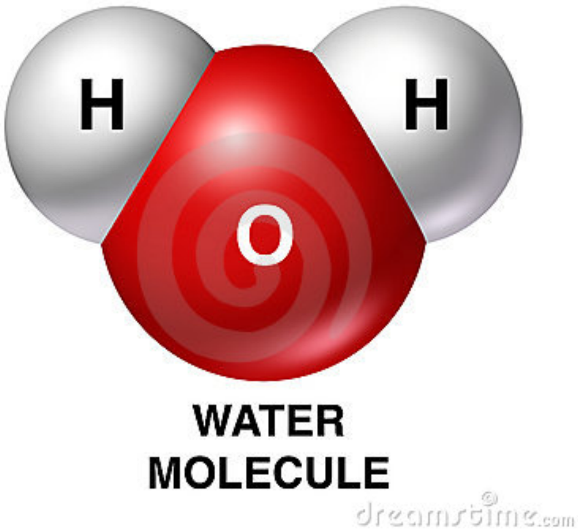
(Map simulation result to experimental results)

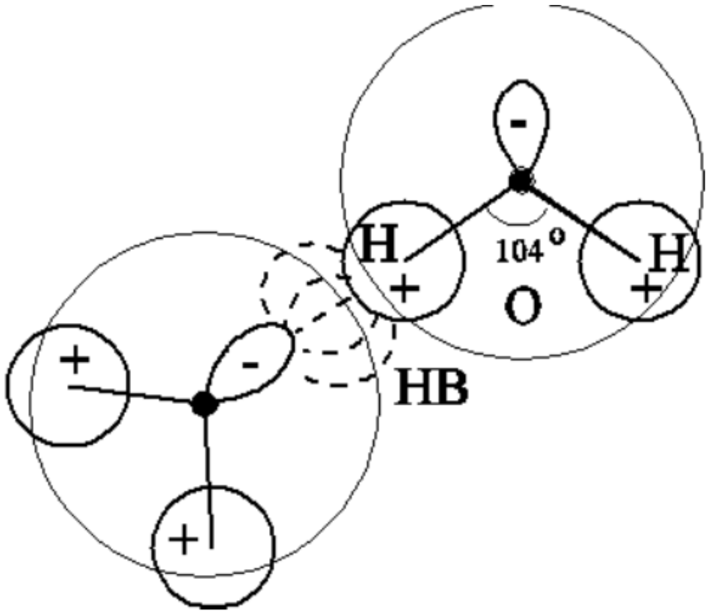
What makes water water



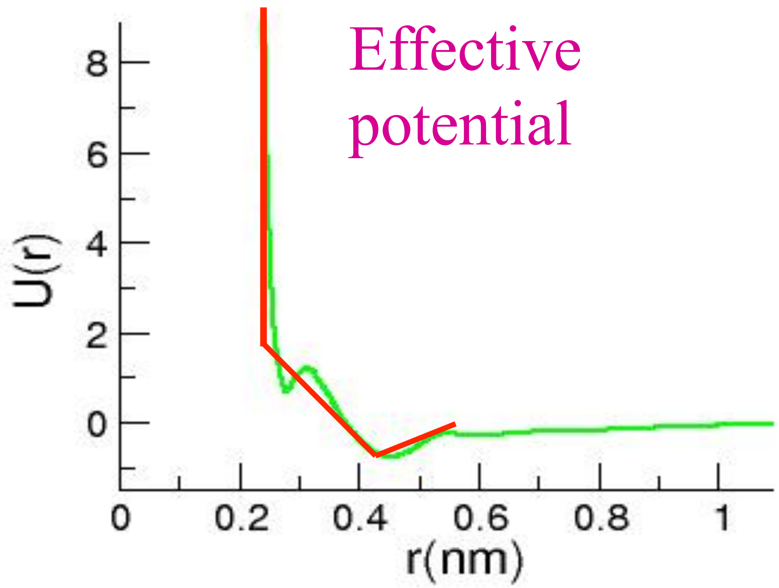
Simulation approach







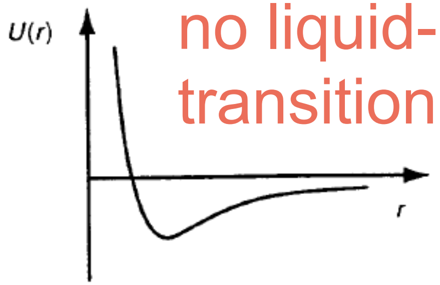
Spherically symmetric potentials



T. Head-Gordon and F. H. Stilinger.
J. Chem. Phys. 98, 3313 (1993)

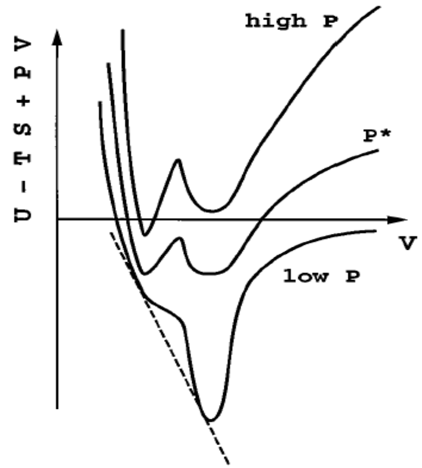
$U(r) \sim \ln g(r)$

no liquid-liquid transition



with liquid-liquid transition

$$G(P,T) \equiv \min_V \{U + PV - TS\}$$

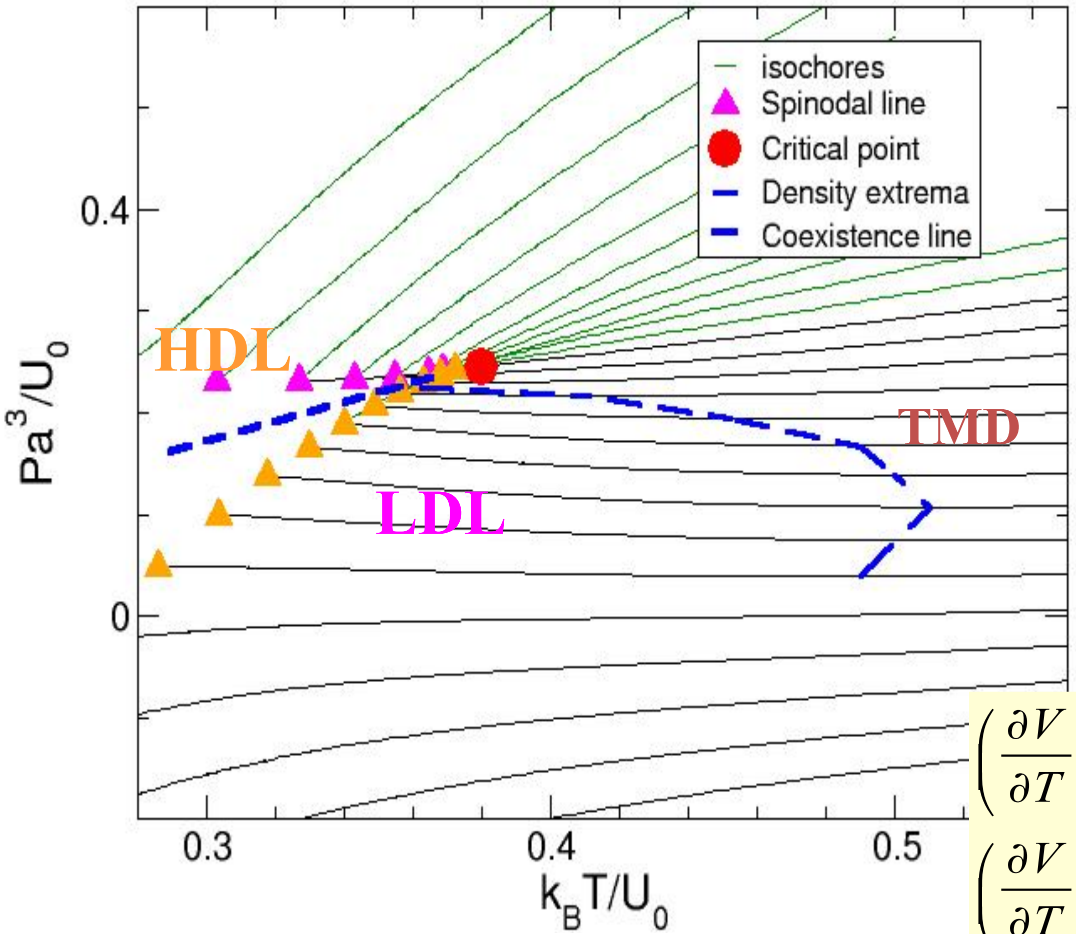


L. Xu et al., Phys. Rev. E 74, (2006)

Characteristics:

- Coarse-grained spherical symertrical potential
- Two-length scale: hardcore & softcore

Equation of State

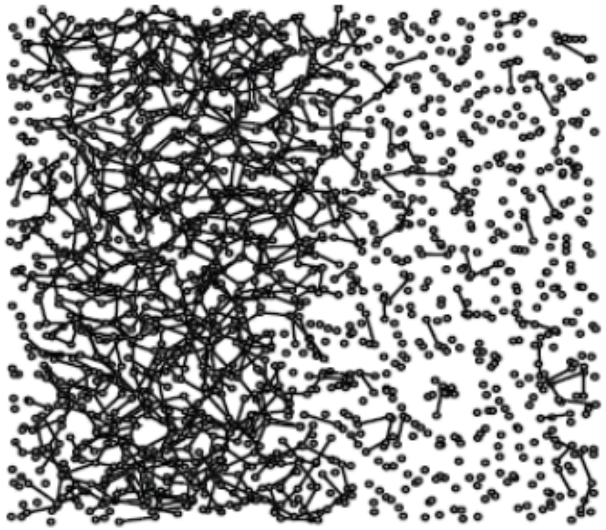


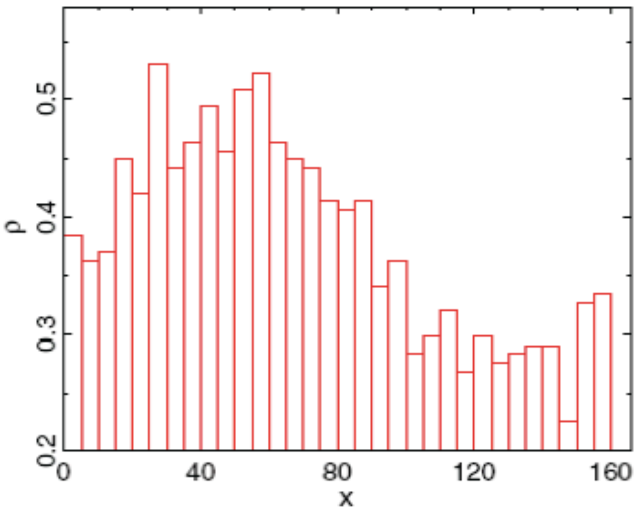
$$\left(\frac{\partial V}{\partial T}\right)_P = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1$$

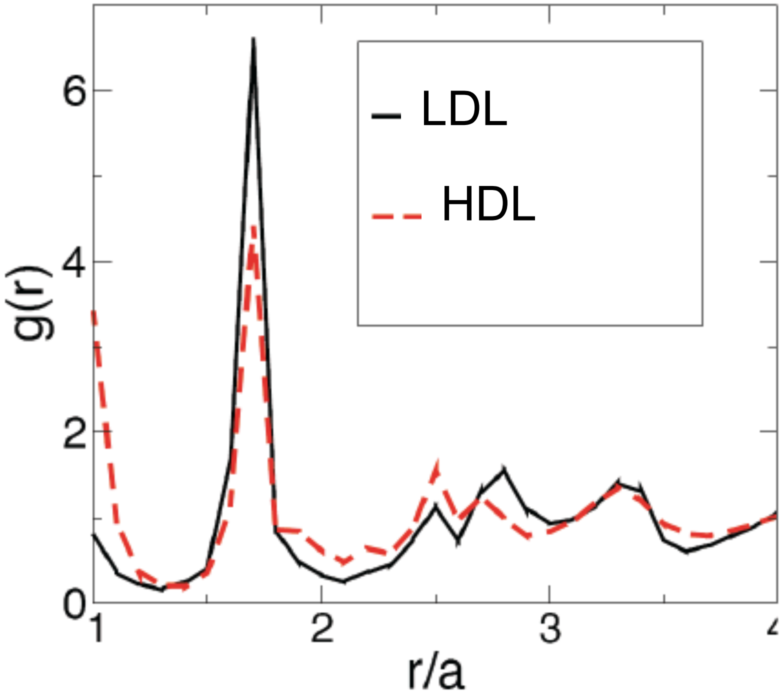
$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T = VK_T \left(\frac{\partial P}{\partial T}\right)_V$$

Liquid polyamorphism

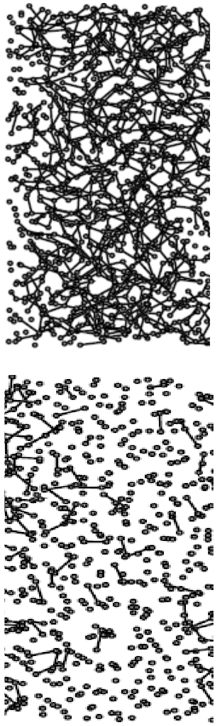


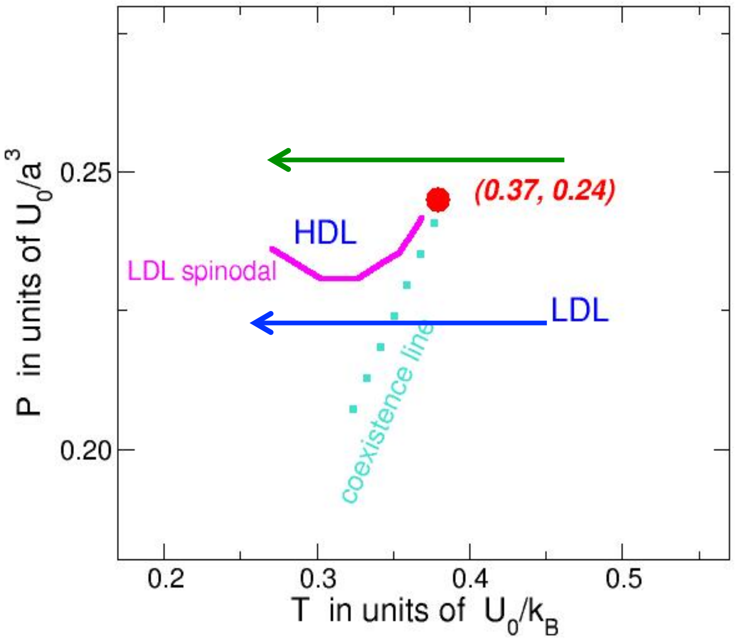


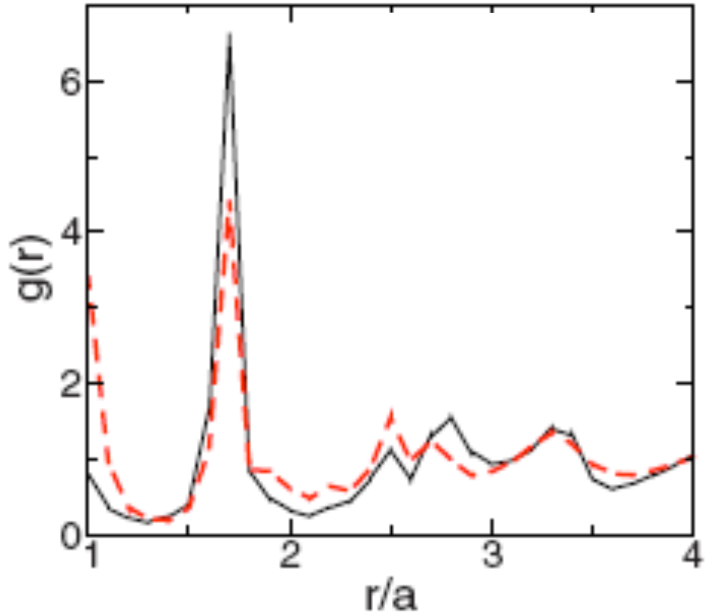
Phase Segregation
at coexistence line



Two glasses upon cooling







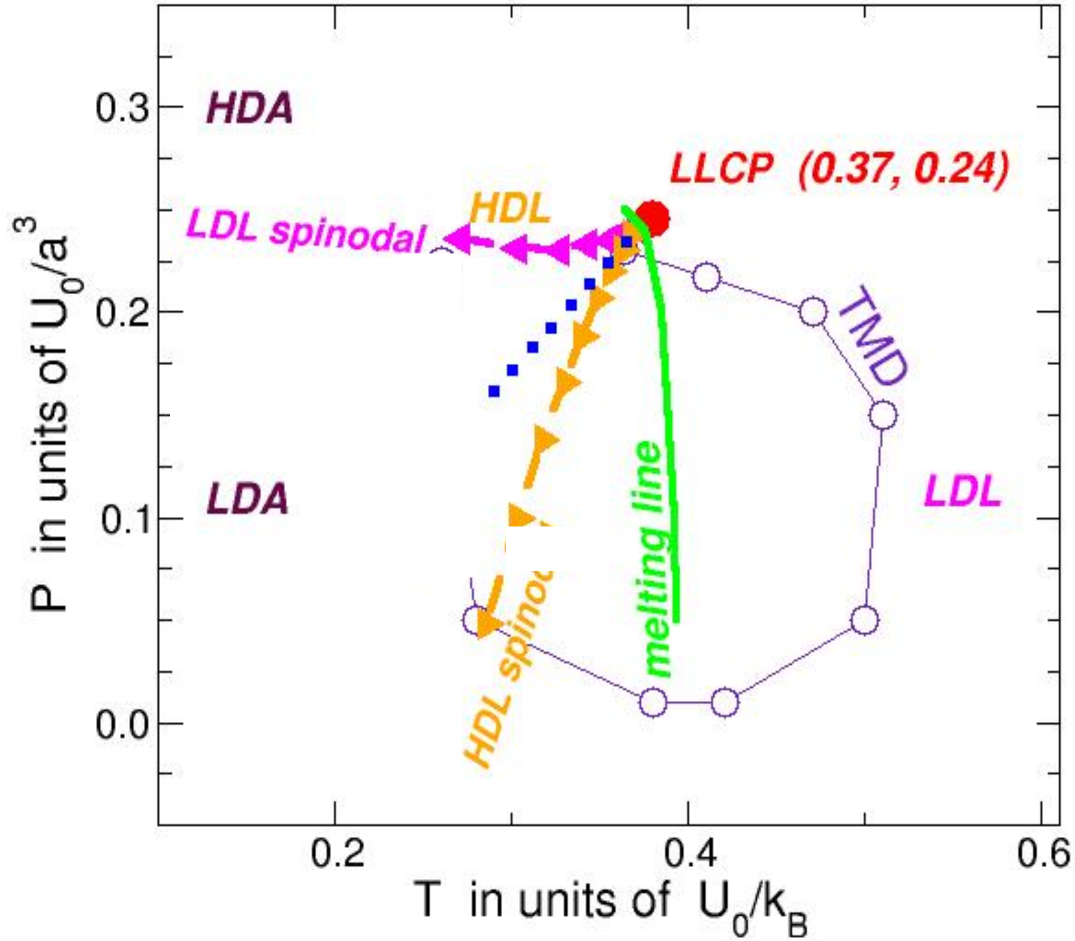
Two glass states obtained upon cooling

Low density liquid → Low density amorphous (LDA)

High density liquid → High density amorphous (HDA)

Xu et. al., JCP (2009)

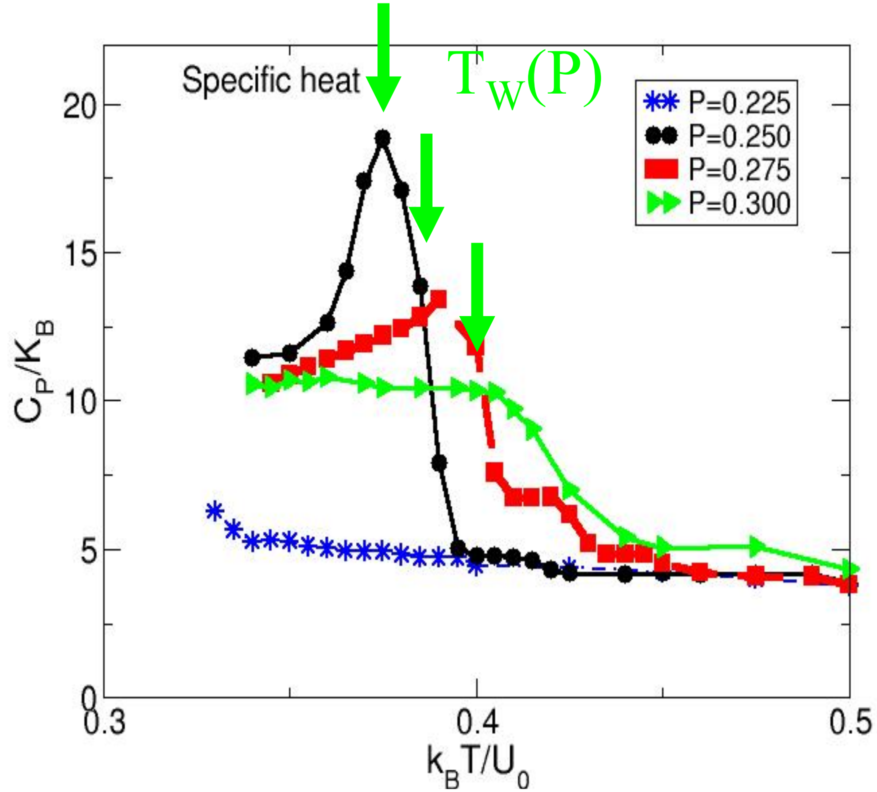
Phase diagram

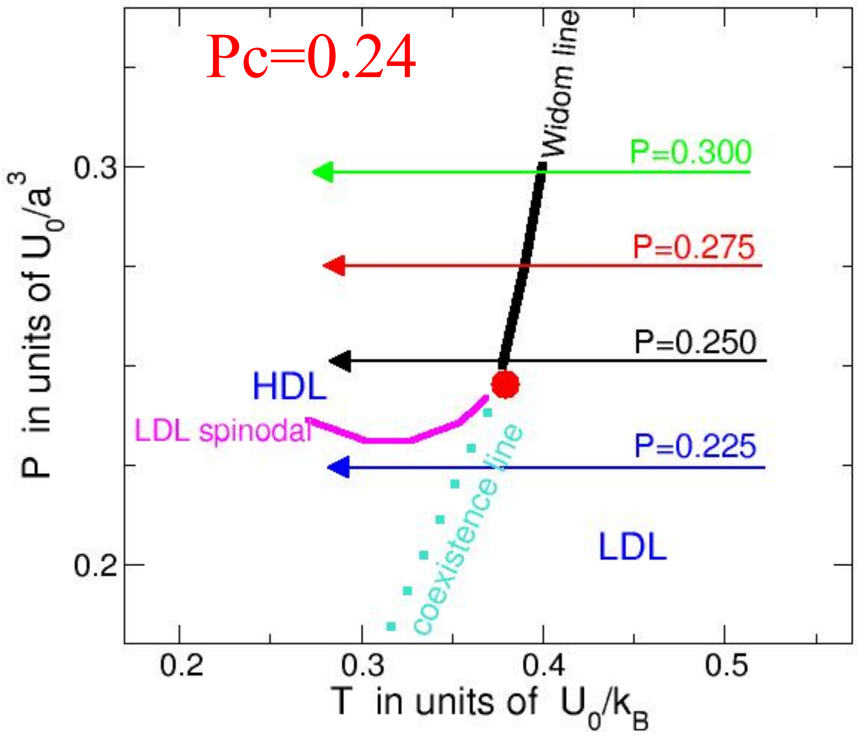


- Stable liquid-liquid critical point (LLCP)
- Density anomaly (TMD and TmD)
- LDA and HDA

Xu et al., J. Chem. Phys. , 2009; Xu et. al., J. Chem. Phys. 2011

Changes in thermal response functions



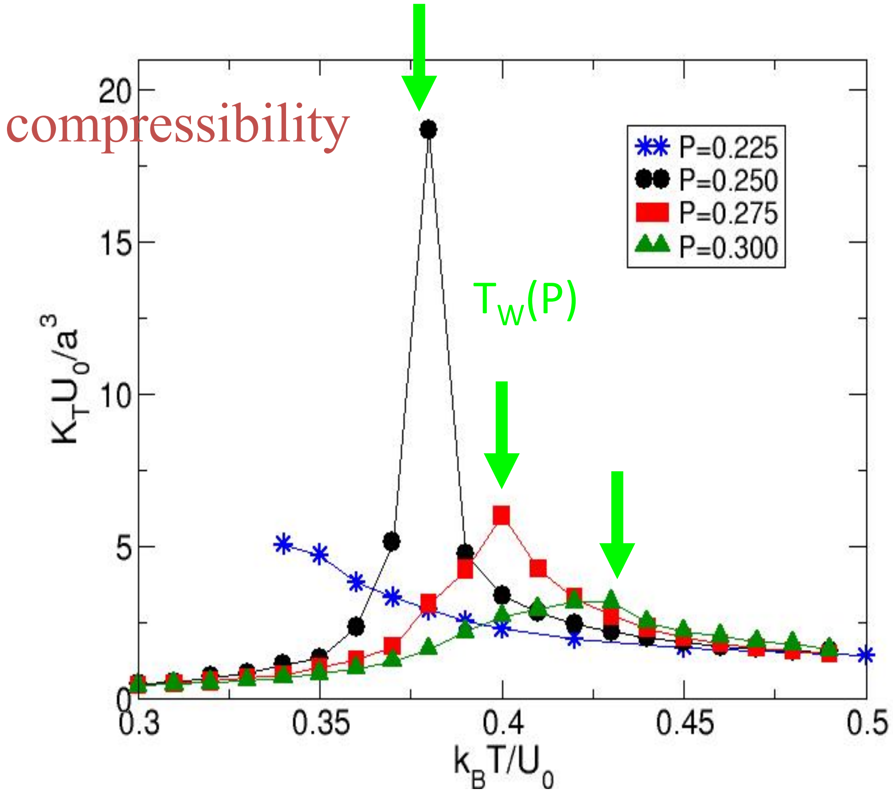


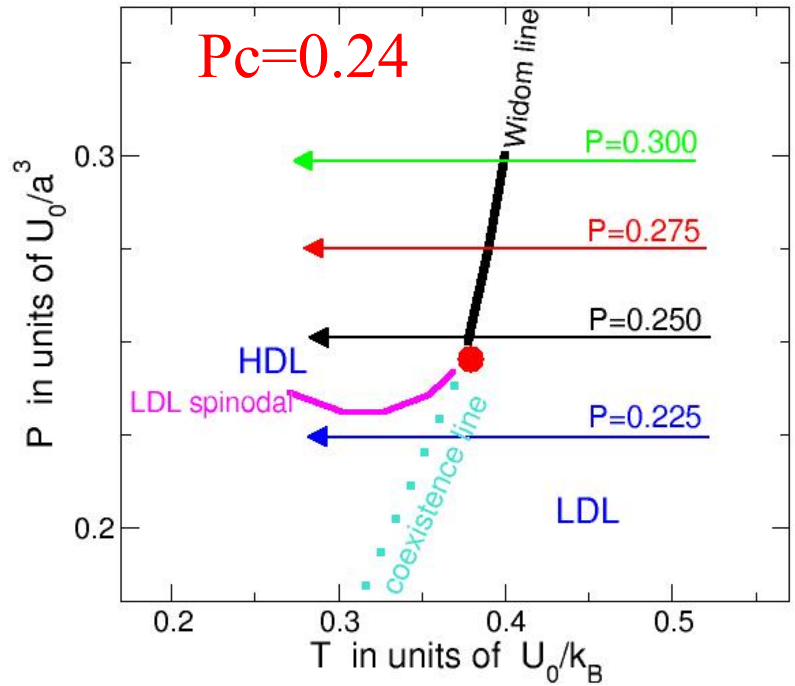
- $P<P_c$: No anomalous behaviour! (Metastability)
- $P>P_c$: Cp show peaks (Widom line –locus of the C_p^{max})

The Widom line terminates at the liquid-liquid critical point

Xu et al., PRE 74 (2006)

Changes in compressibility

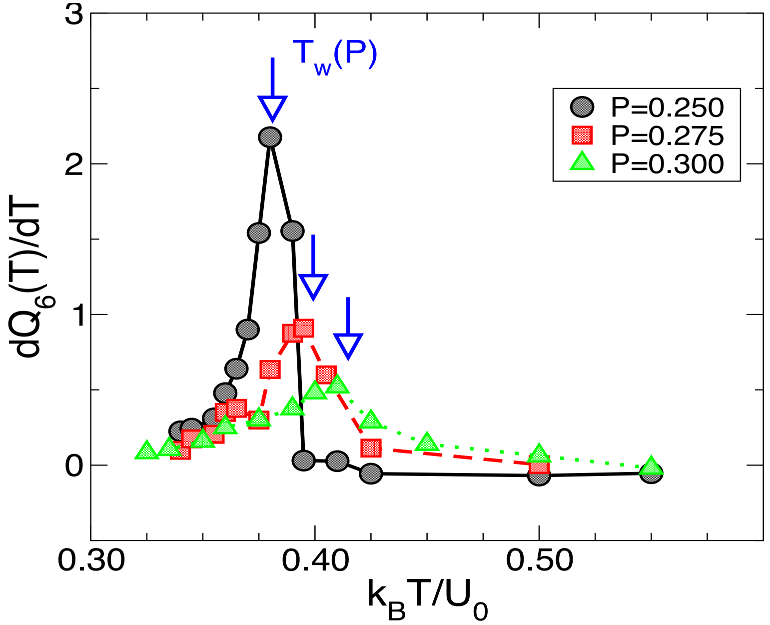


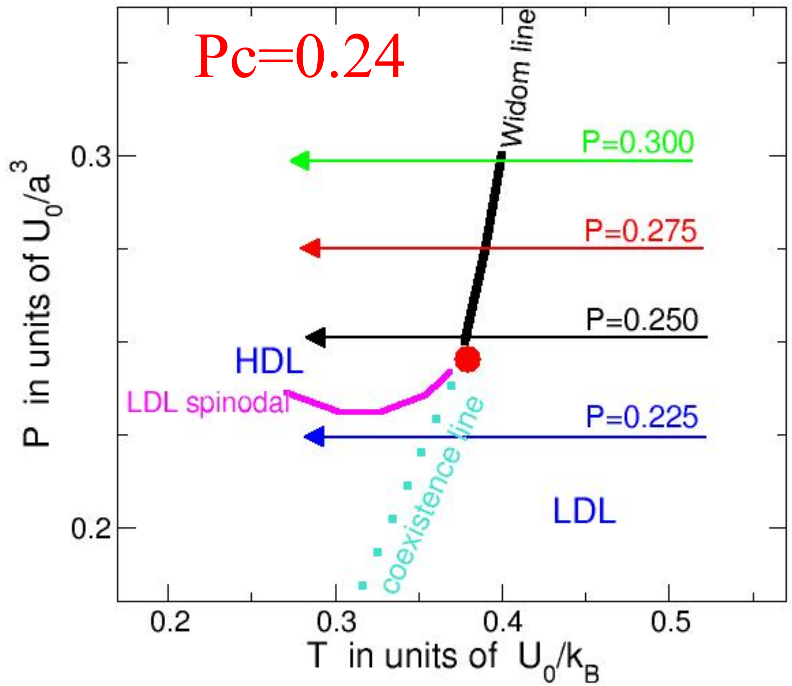


- $P<P_c$: No anomalous behaviour (Metastability)
- $P>P_c$: Response functions show peaks. The location of the peaks decreases approaching to the critical pressure

Xu et al. PRE 2006

Changes in structures: orientational order



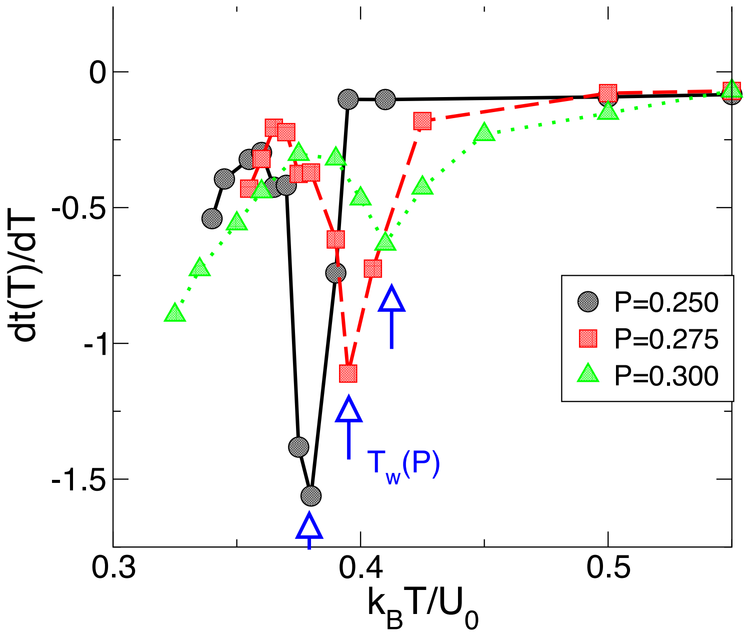


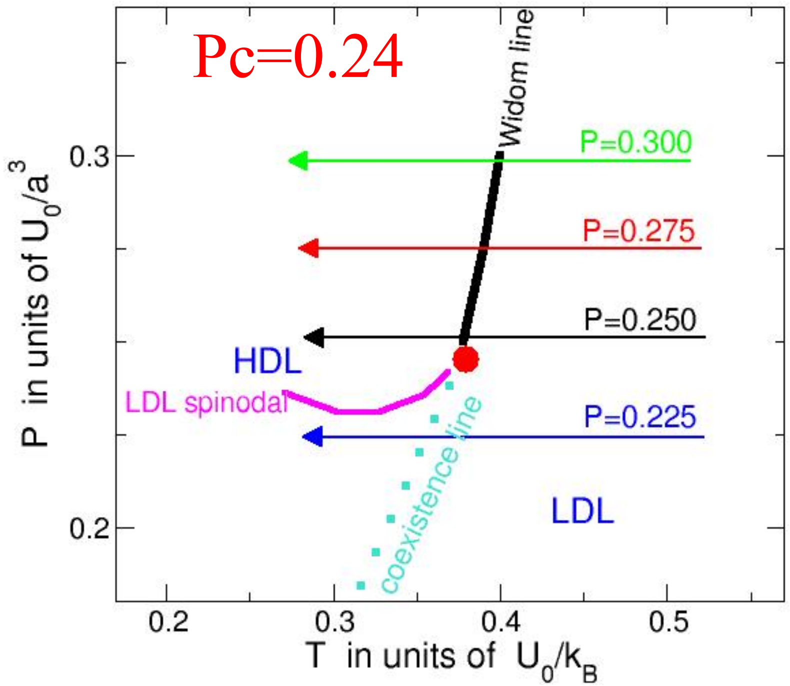
Orientational order:

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} | Y_{l,m}(\theta,\varphi) |^2 \right]^{1/2}$$

Xu et al., PRE 2006

Changes in structures: translational order



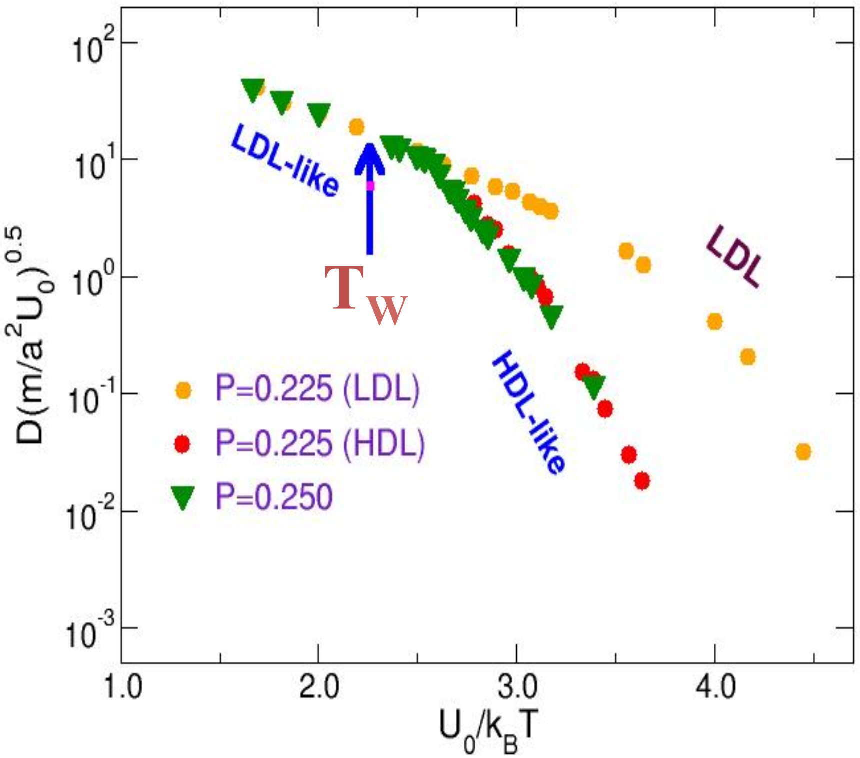


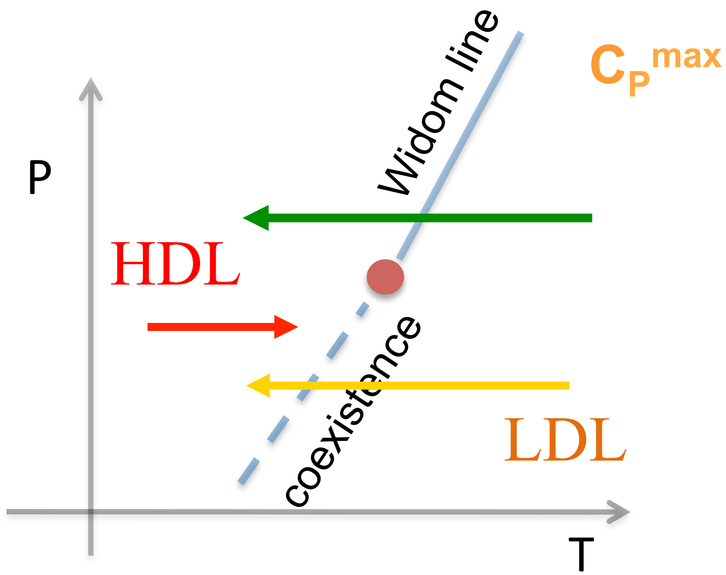
Translational order parameter: $$t \equiv \int_0^{r_c} |g(r) - 1| dr$$

Upon crossover the Widom line, structure change is a maximum

Xu et al., PRE 2006

Changes in dynamics





Upon crossover the Widom line, a kink in D occurs near T_W

Xu et al., J. Chem. Phys. , 2009; Xu et. al., J. Chem. Phys. 2011

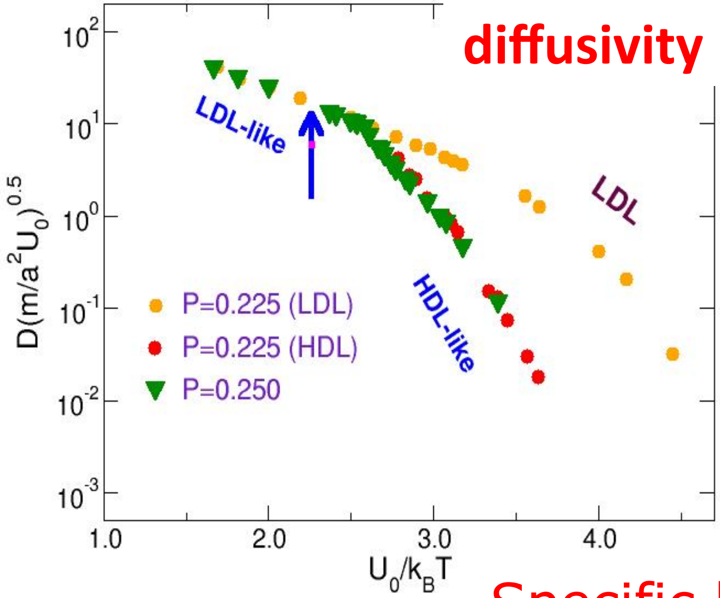
- Can we construct a simple model that shows stable LLCP and captures water-like anomalies?

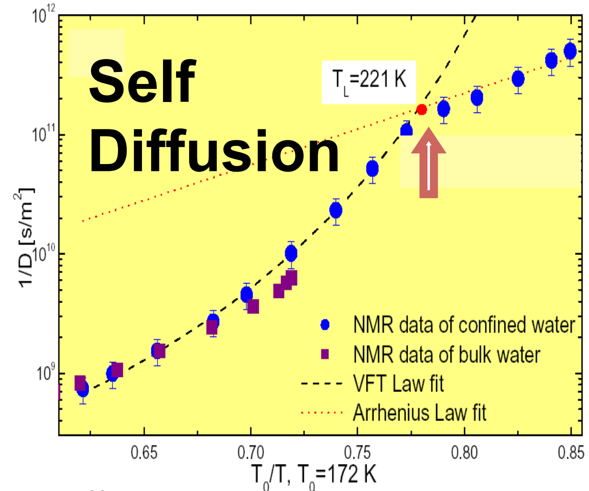
- How to understand properties of water in terms of isotropic two-scale interactions

- How confinement and surface chemistry affect the anomalous properties and phase behaviors?

Compare computation results with experiment

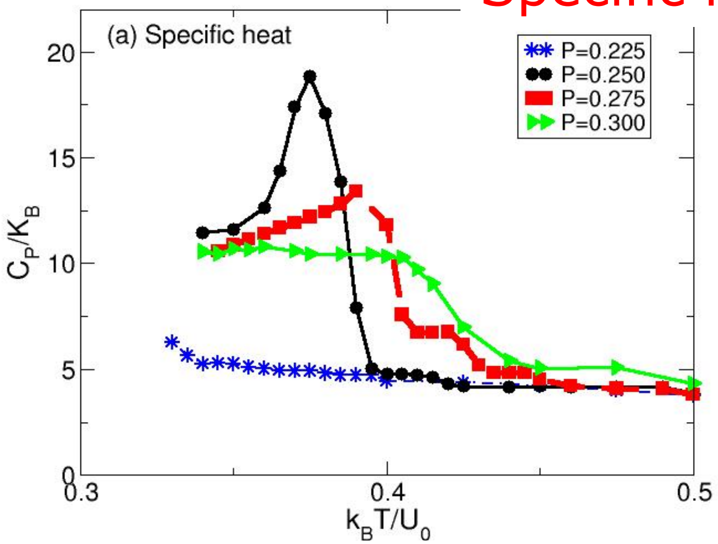
diffusivity



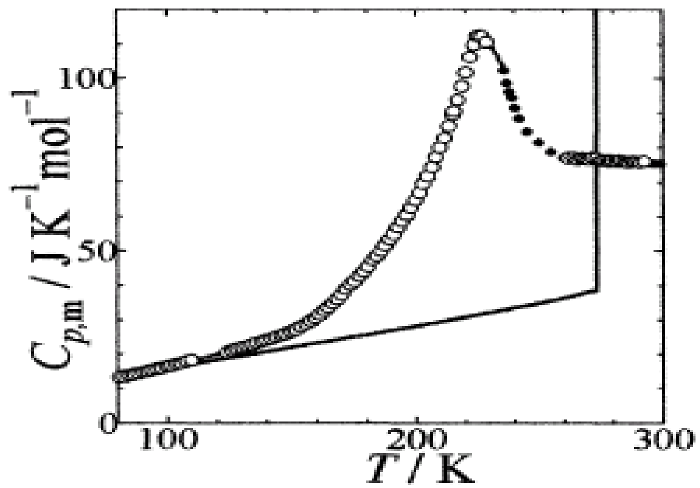


Mallamace et al, JCP 124, 161102 (2006)

Specific heat

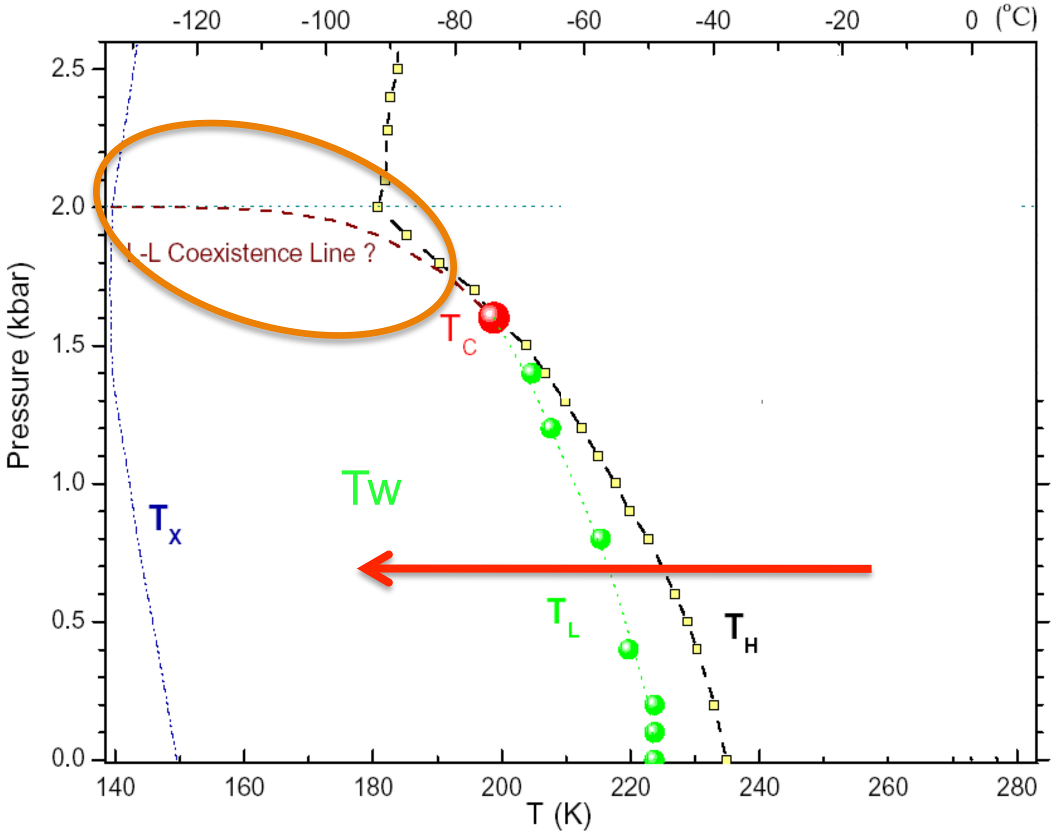


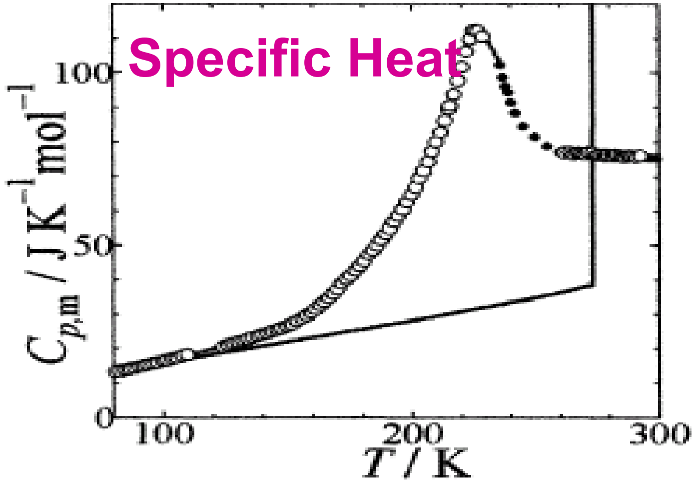
Specific Heat

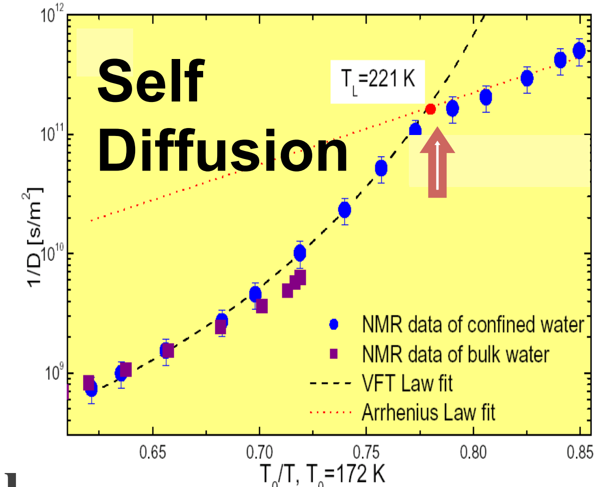


Maruyama et. al.,AIP conf. Proc. 708, 675 (2004)

Detection of second critical point in experiment





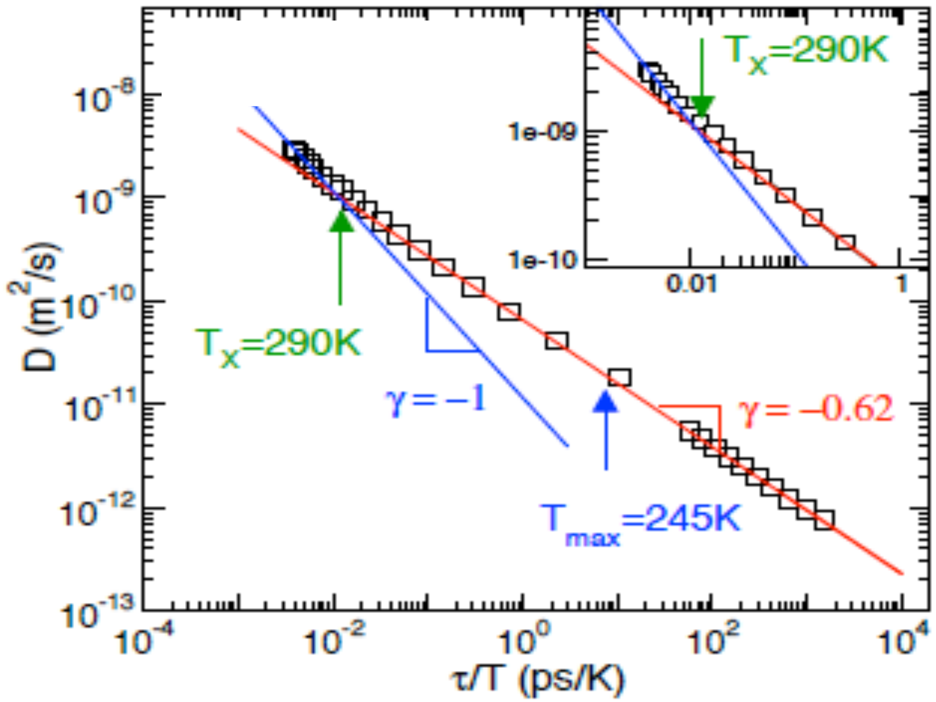


Region to detect: **high temperature and low pressure**

Criteria: **response function maxima**

L. Xu et. al, Proc. Natl. Acad. Sci. **102**, 16558-16562 (2005)   L. Liu et. at. PRL 95, 117802 (2005)

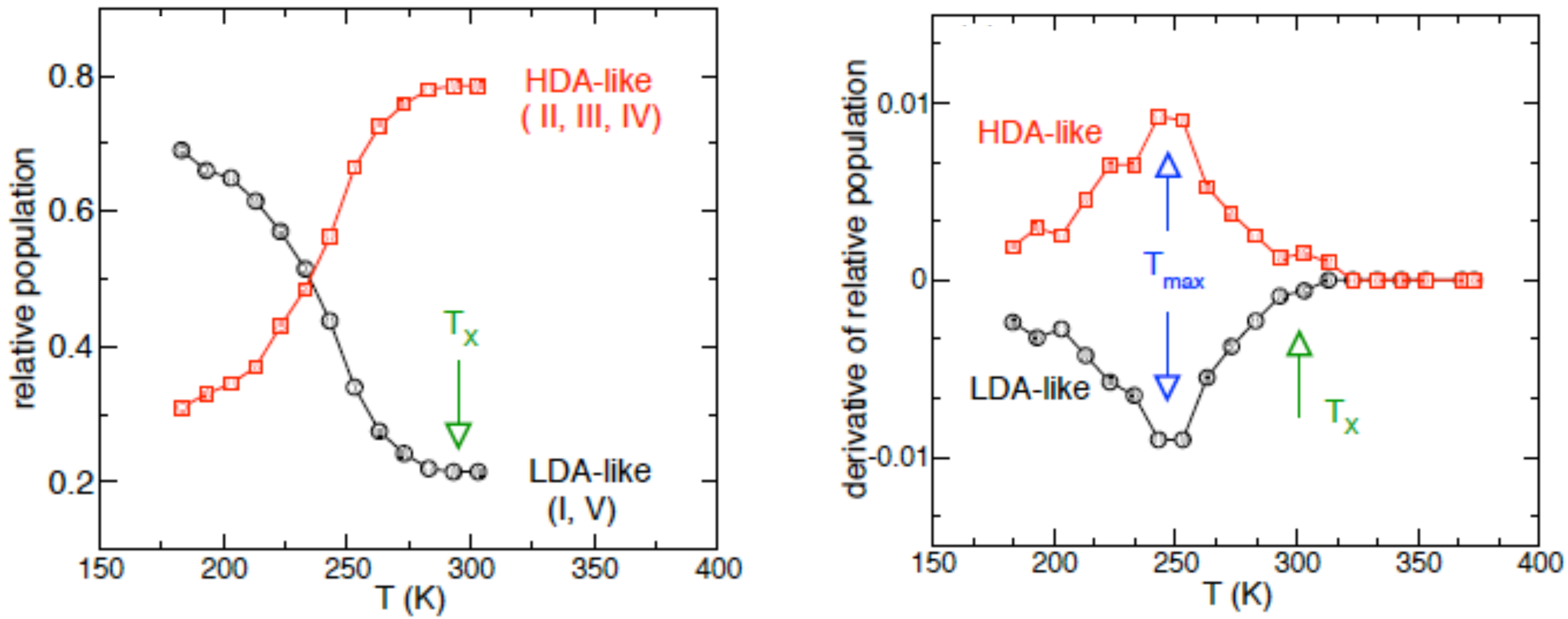
Fractional Stokes-Einstein relation and its breakdown



- There exists a fractional Stokes-Einstein relation，the breakdown temperature Tx～290K
- Breakdown of Stokes-Einstein relation Tx～290K > Tw > Tg, not directly associated with the Widom line

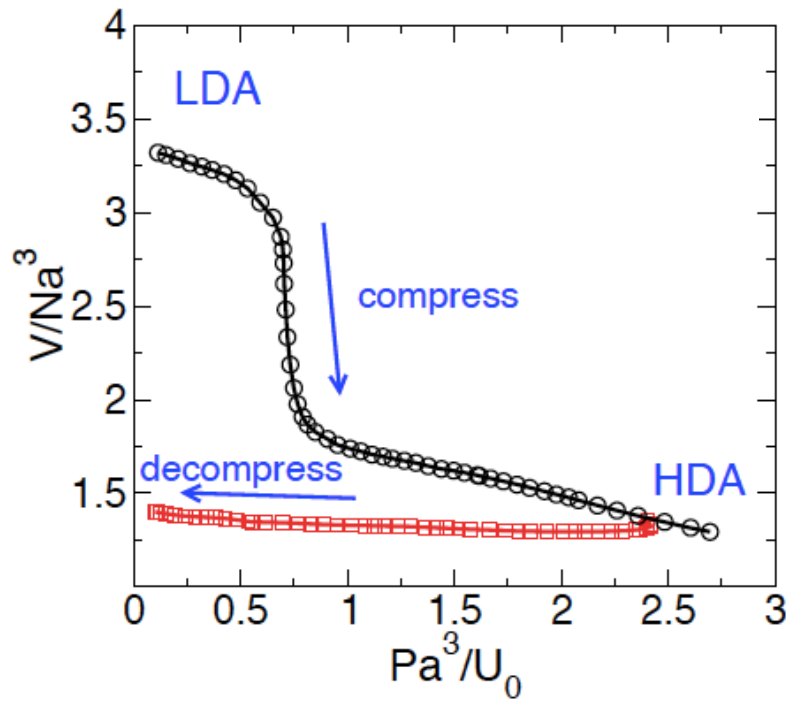
Xu et al., Nature Physics 2009

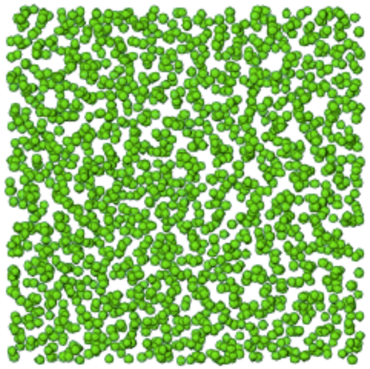
Changes in structure and breakdown of SER (EXP)



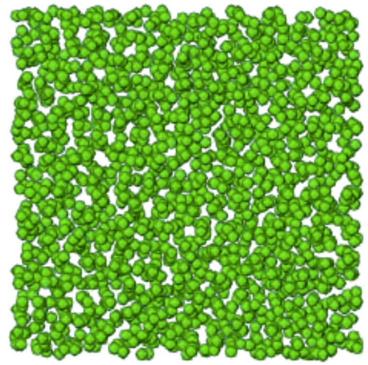
- SER breakdown occurs at temperature where the local structure of water changes
- Near the Widom line temperature, structure change is a maximum

Low density glass to high density glass transition





LDA

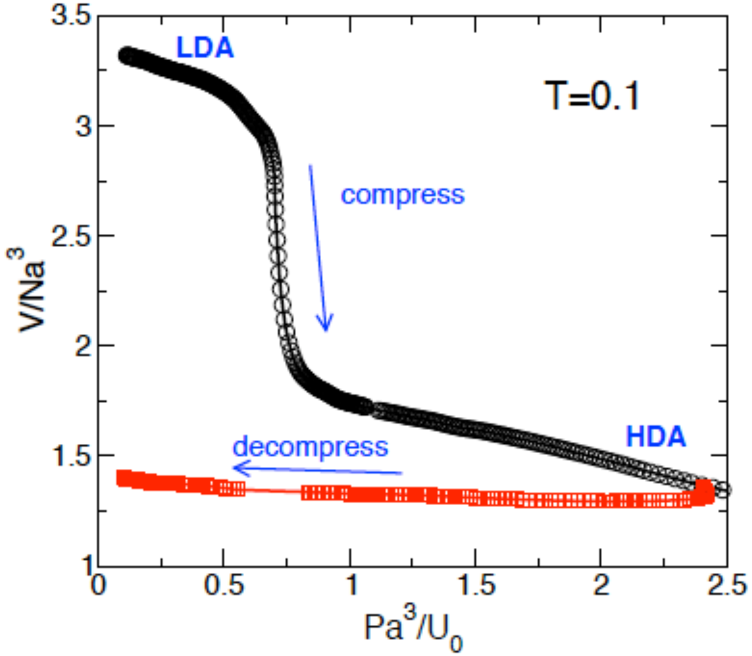


HDA

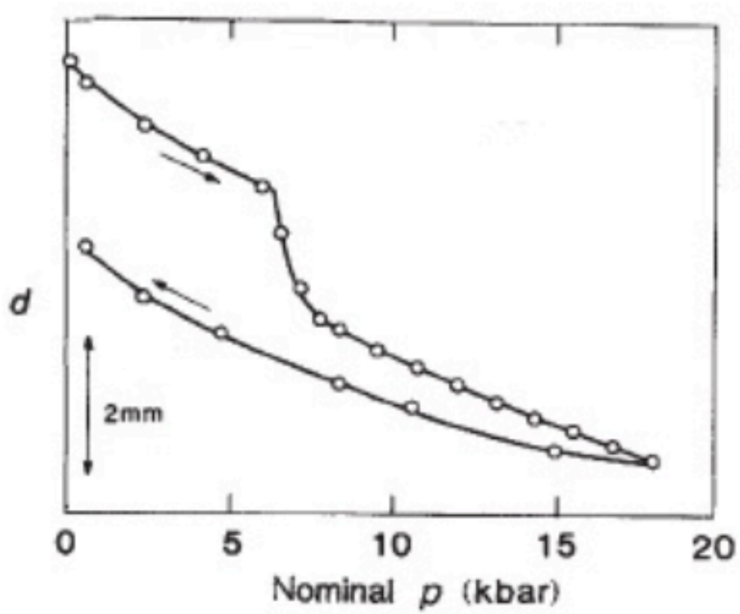
Formation of new high density glasses by compression and decompression along constant pressure

L. Xu et. al, J. Chem. Phys. 134, 064507 (2011)

Polyamorphism



EXP

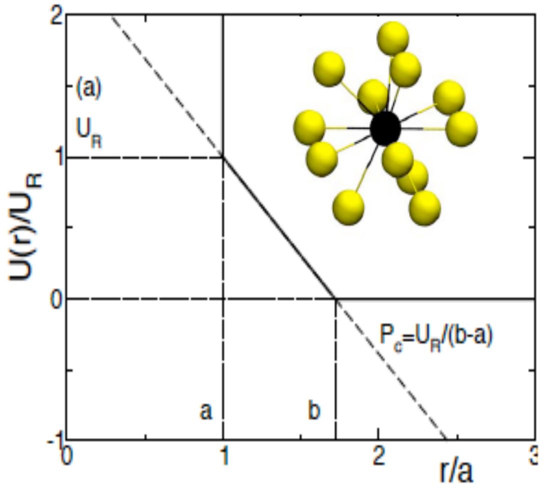


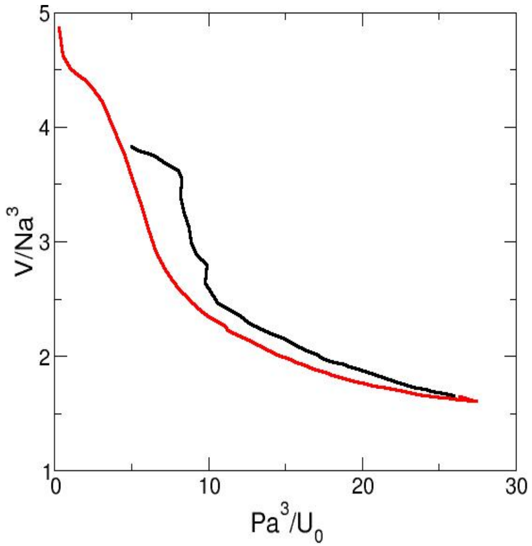
Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984)

HDA is stable at low pressure upon decompression

L. Xu, S. V. Buldyrev, N. Giovambattista, C. A. Angell, H. E. Stanley, JCP (2009)

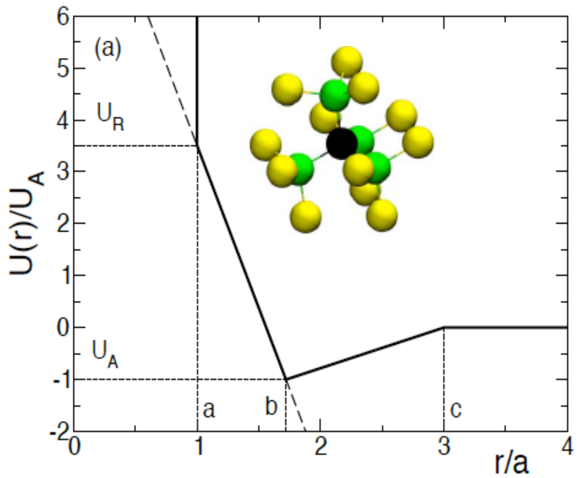
Stability of liquid-liquid critical point and polyamorphism

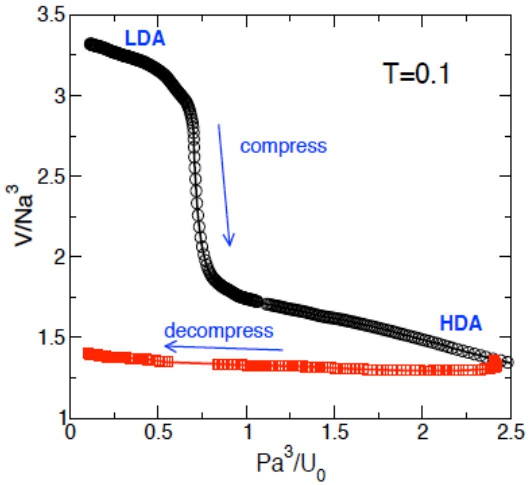




LLCP unaccessible

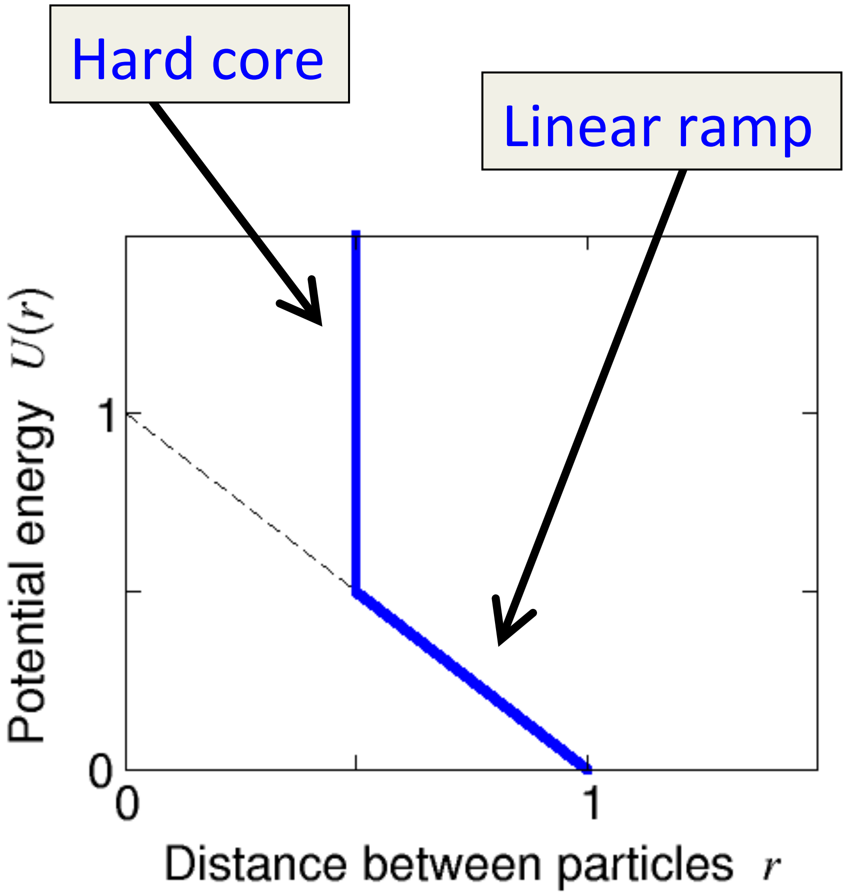
TMD, diffusivity, etc

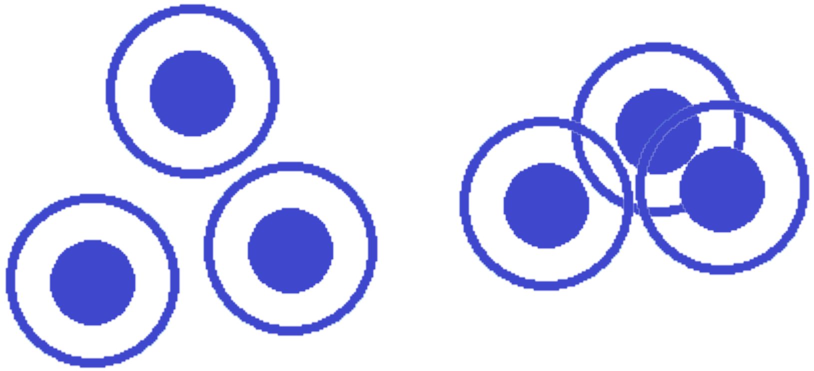




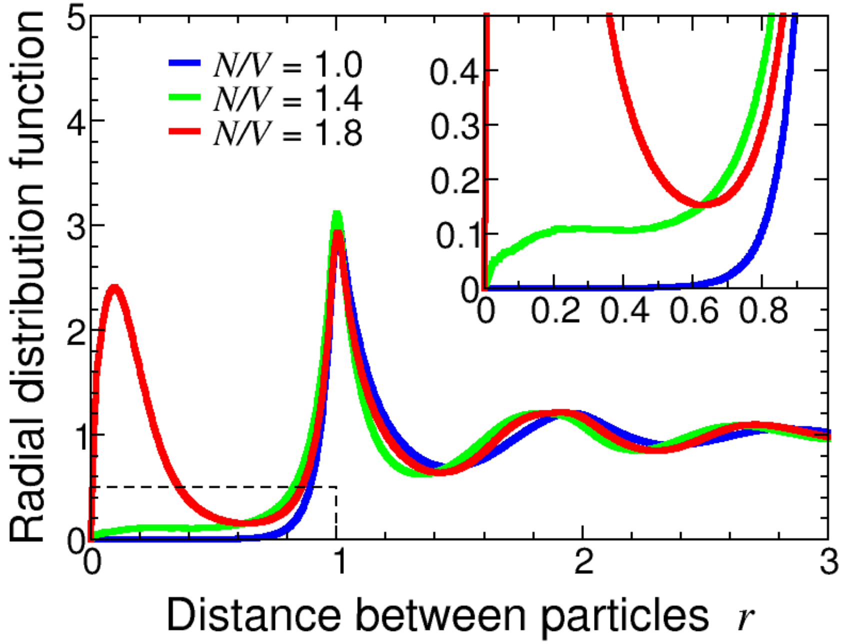
Stable LLCP

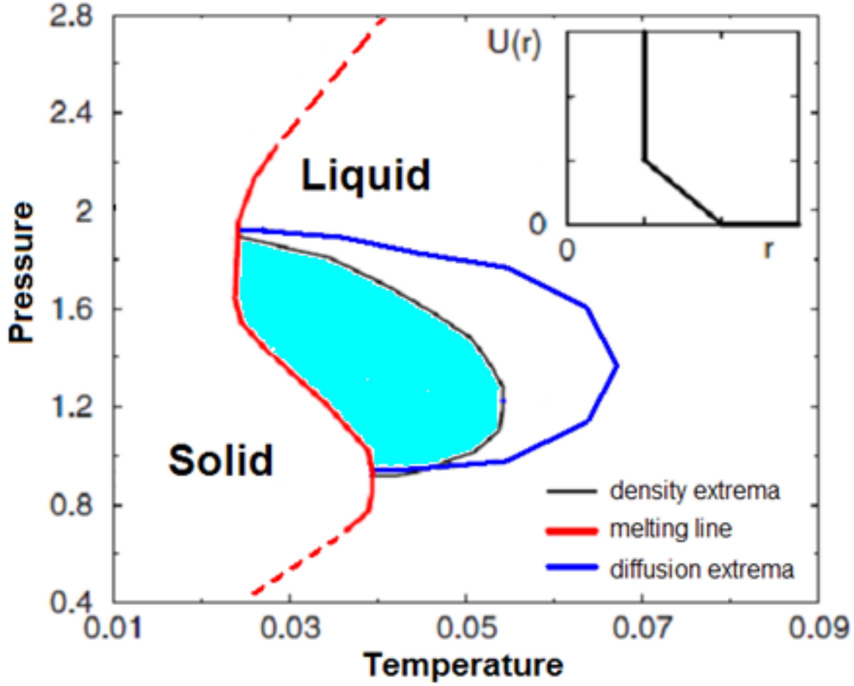
How to understand anomalies with two scales





Two "competing" length scales

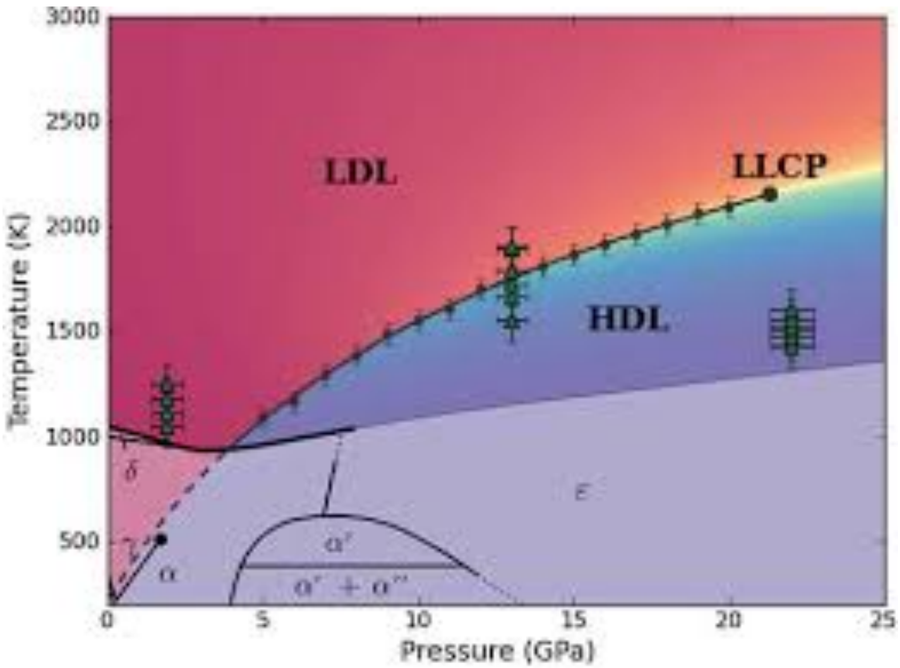




Within anomaly region, some particles are on the ramp

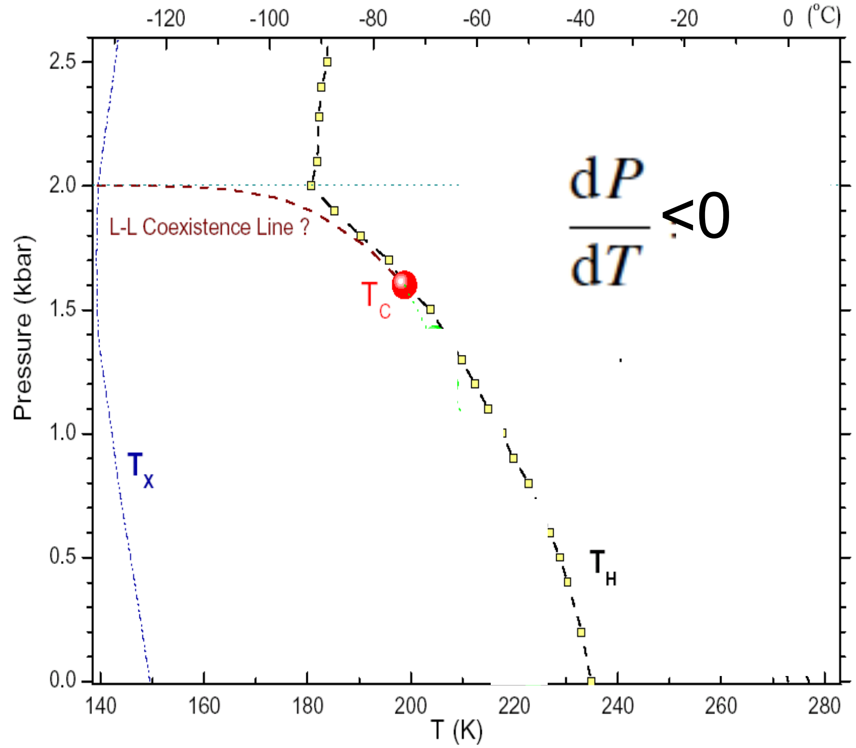
Materials with different types of coexistence line

Cerium



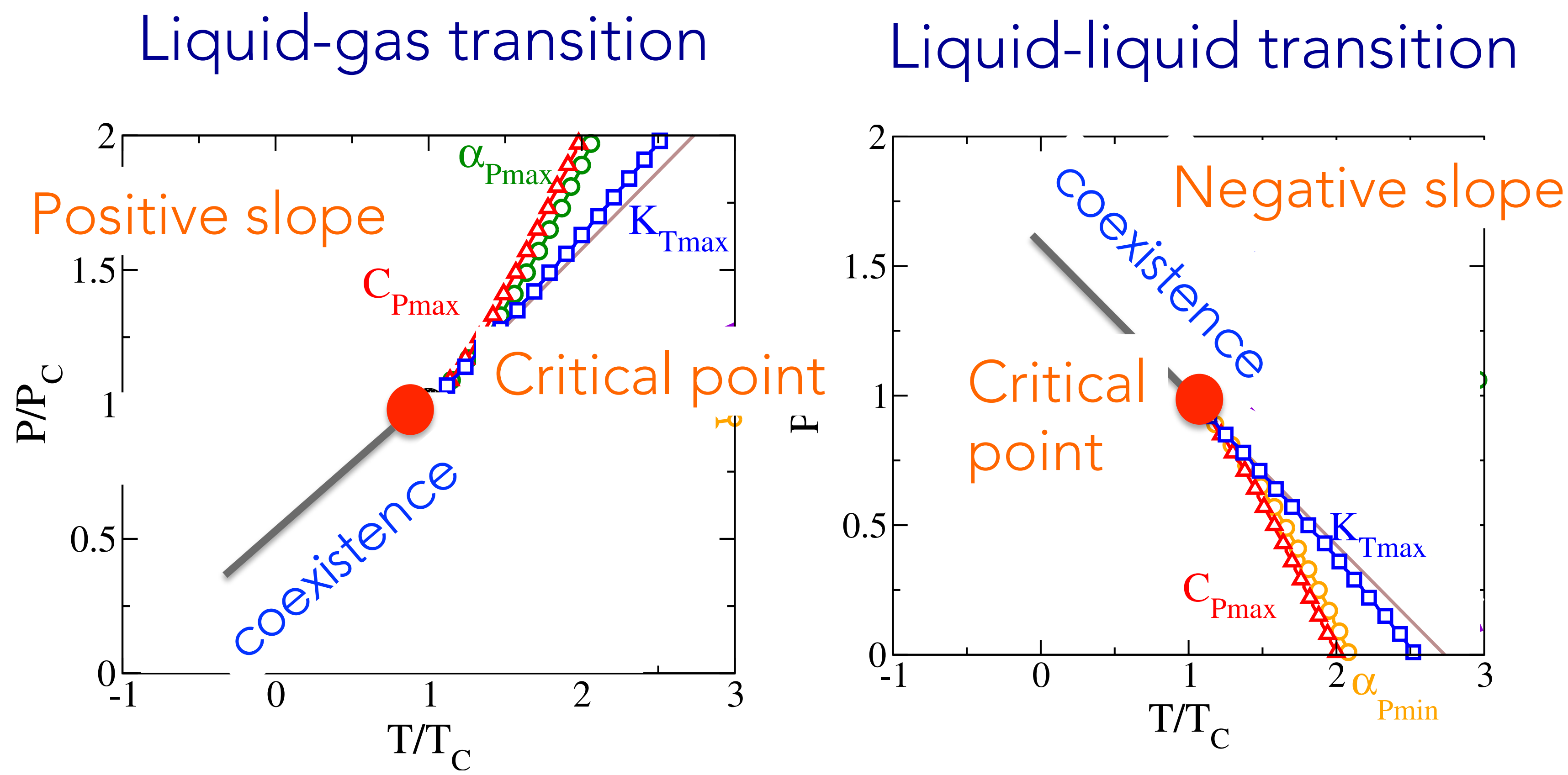
positively sloped liquid-liquid phase transition line

Water



negatively sloped liquid-liquid phase transition line

Supercritical phenomenon in different transitions



Tracing critical point from supercritical region along the Widom can be a rather general approach

Luo et. al., Phys. Rev. Lett. PRL 112, 135791(2014)

Conclusion I & II

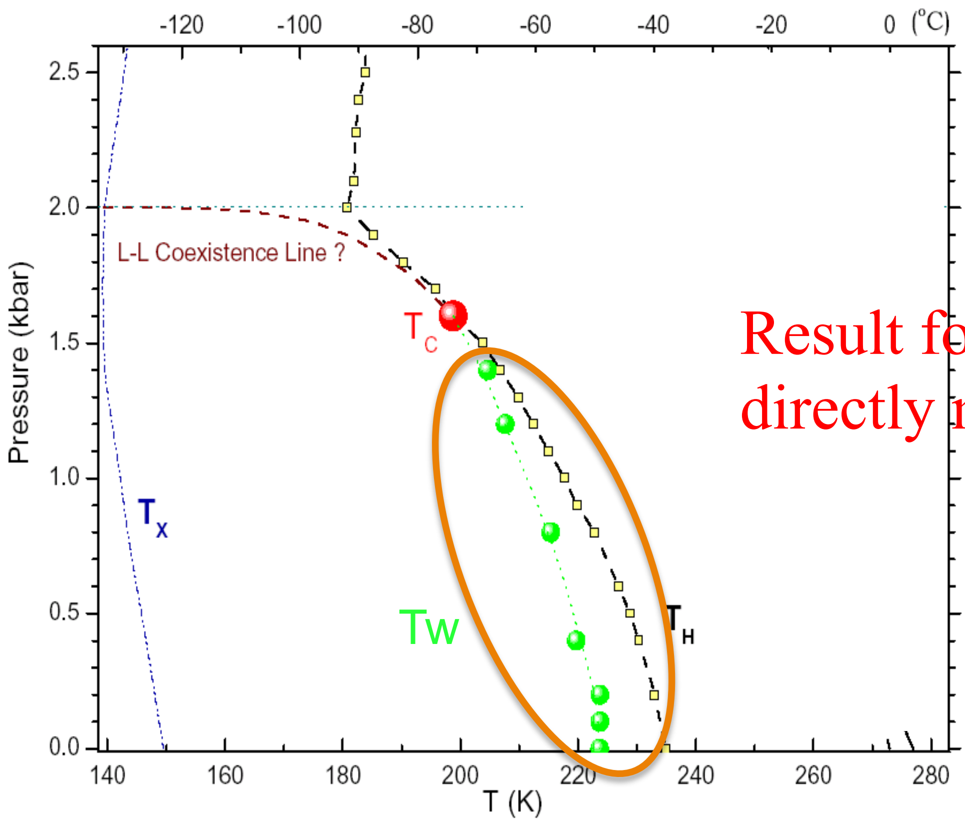
- The two-scale model can reproduce water-like anomalies
- Thermodynamic and dynamic quantities shows changes upon crossing the Widom line, not upon crossing the coexistence line
- Provide a way for experiments to locate the possible existence of liquid-liquid critical point
- Maybe not hydrogen bond, not tetrahedral local structure, but the two-scale matters for some of water-like anomalies?

- Can we construct a simple model that shows stable LLCP and captures water-like anomalies?

- How to understand properties of water in terms of isotropic two-scale interactions

- How confinement and surface chemistry affect the anomalous properties and phase behaviors?

Bulk and confined water



Result for confined system directly map to bulk system

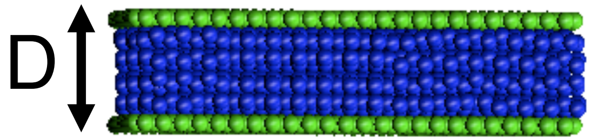
Question:

Is the phase diagram for confined system good to represent the phase diagram of bulk water?

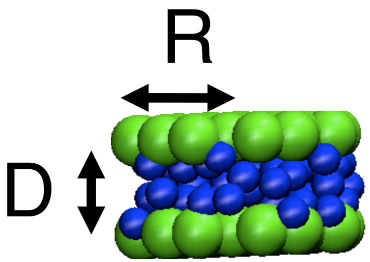
Difference between bulk and confined system

Bulk liquid: temperature T , pressure P

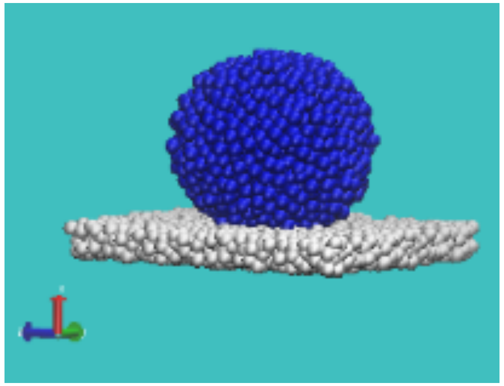
Confined liquid:

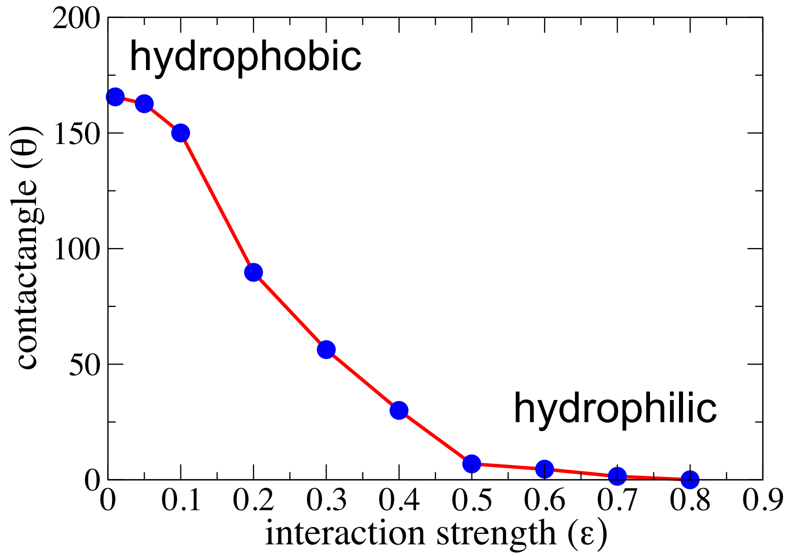


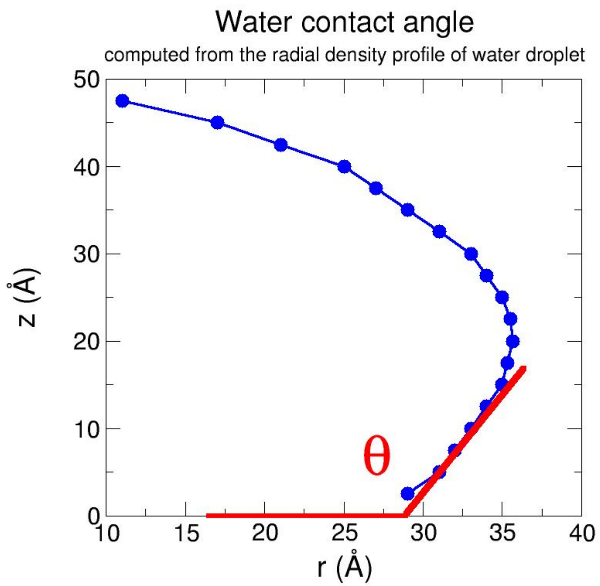
- Infinite plates: T, P, D
- Finite plates: T, P, D, R
- Confined effect and surface interaction effect



Surface chemistry: hydrophobic or hydrophilic





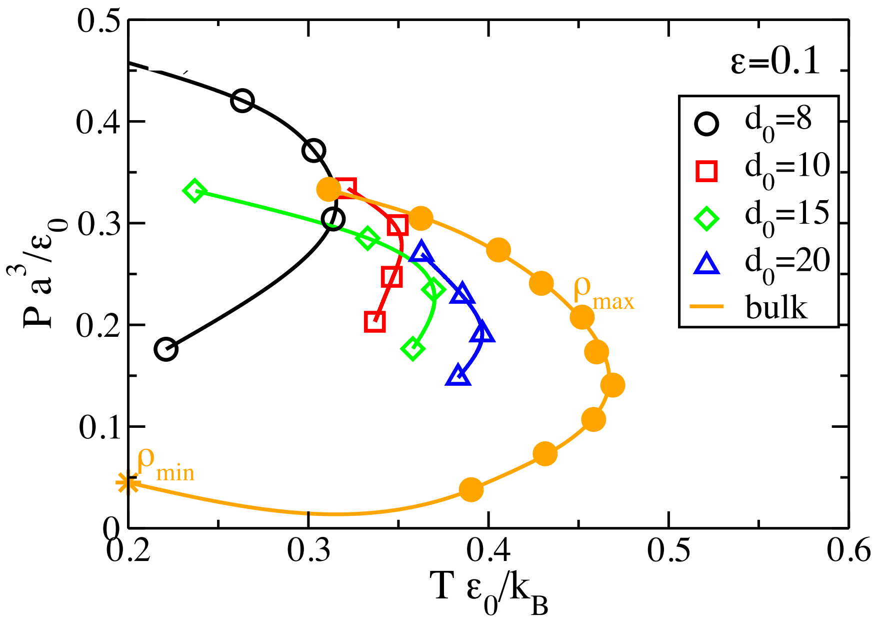


The surface is hydrophobic for interaction length $\varepsilon<0.2$, and hydrophilic for $\varepsilon>0.2$

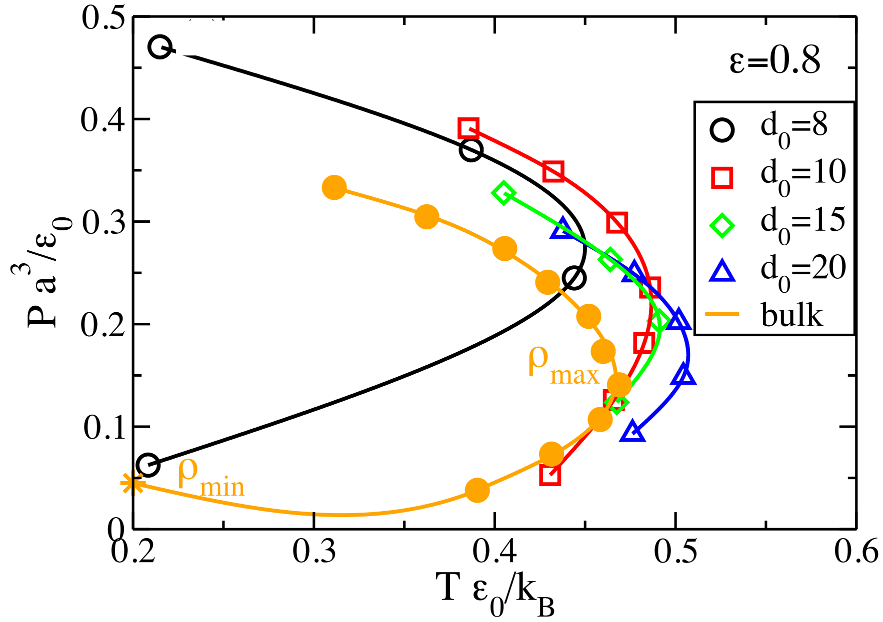
L. Xu, V. Molinero JPCB (2010); JPCB (2011)

Effect of confinement on density anomaly

Hydrophobic



Hydrophilic

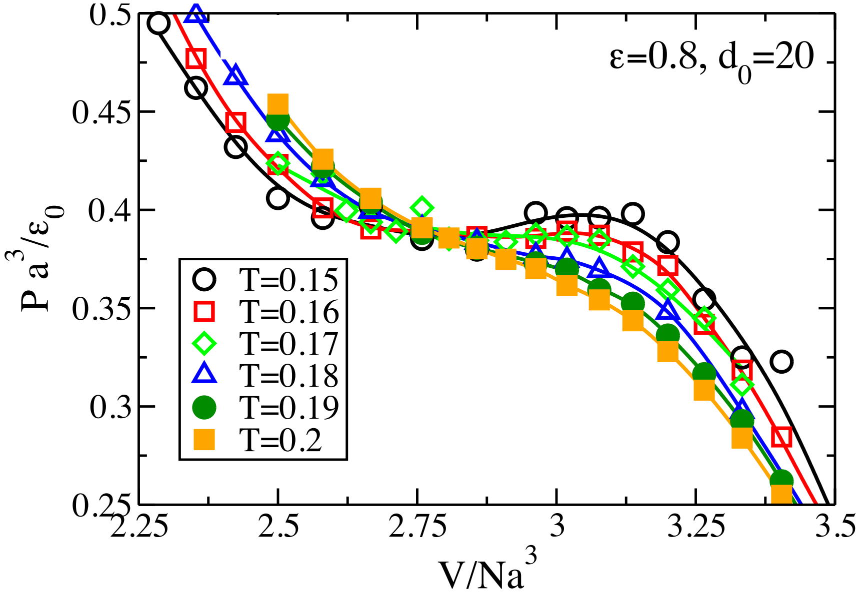


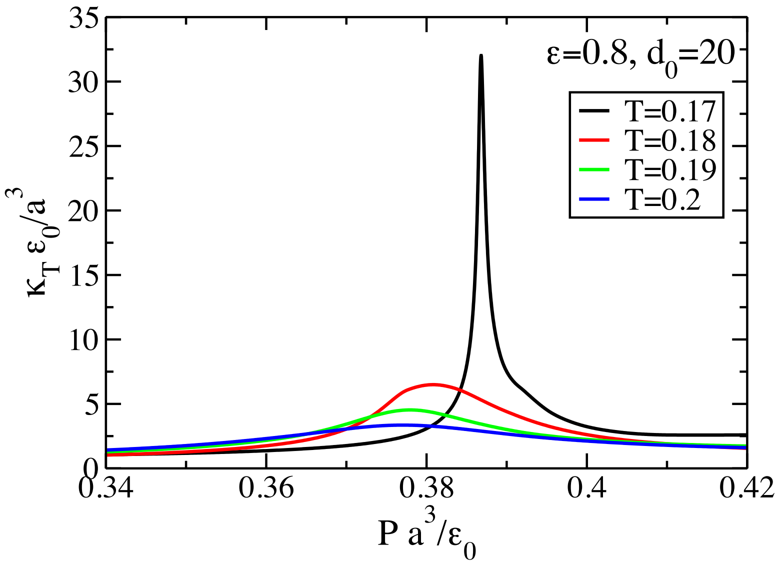
Hydrophobic surface： phase diagram shifts to low-temperature

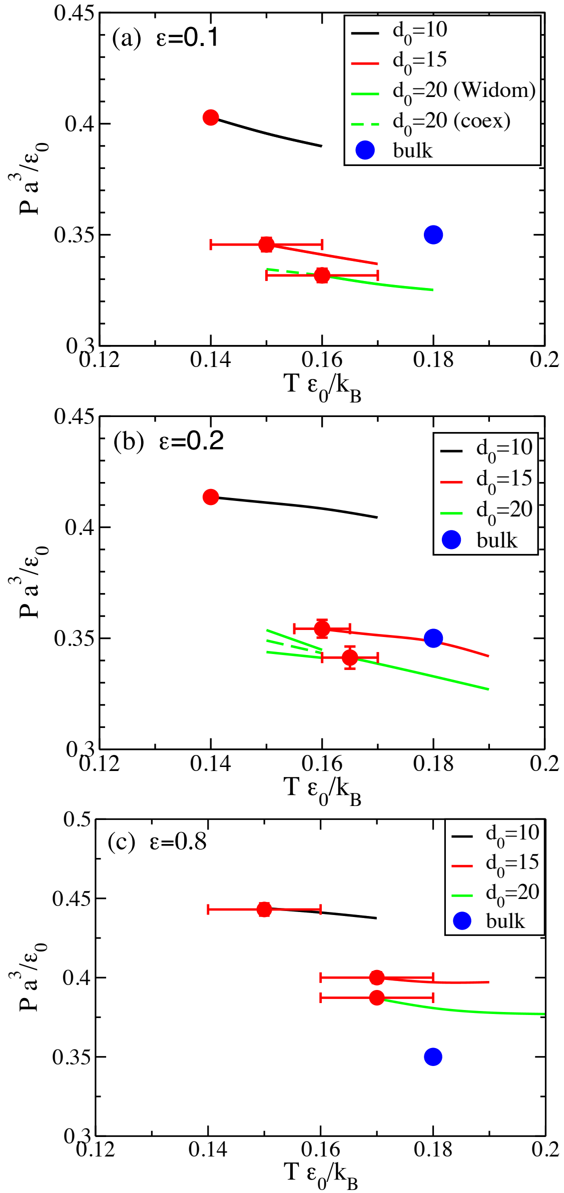
Hydrophilic surface： phase behavior is not significantly affected

G. Sun, N. Giovambattista, L. Xu, J. Chem. Phys. (2015)

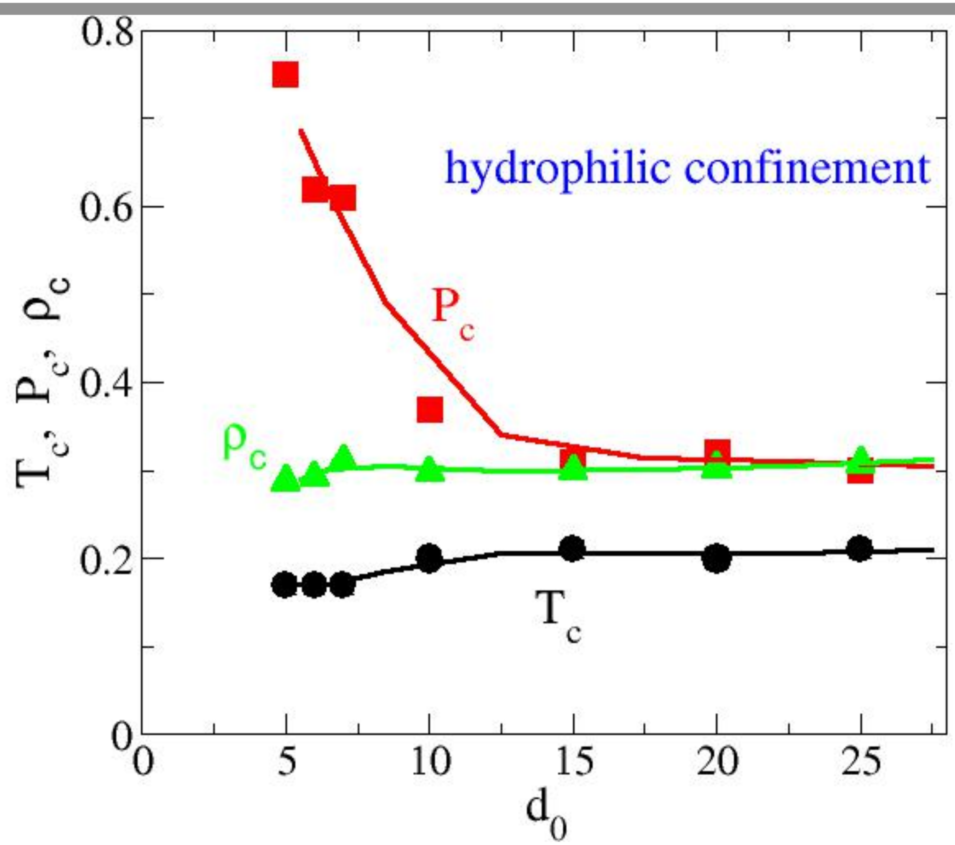
Equation of state for hydrophilic confinement

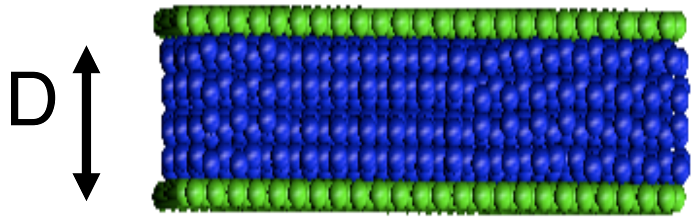






Confinement effect on liquid-liquid critical point



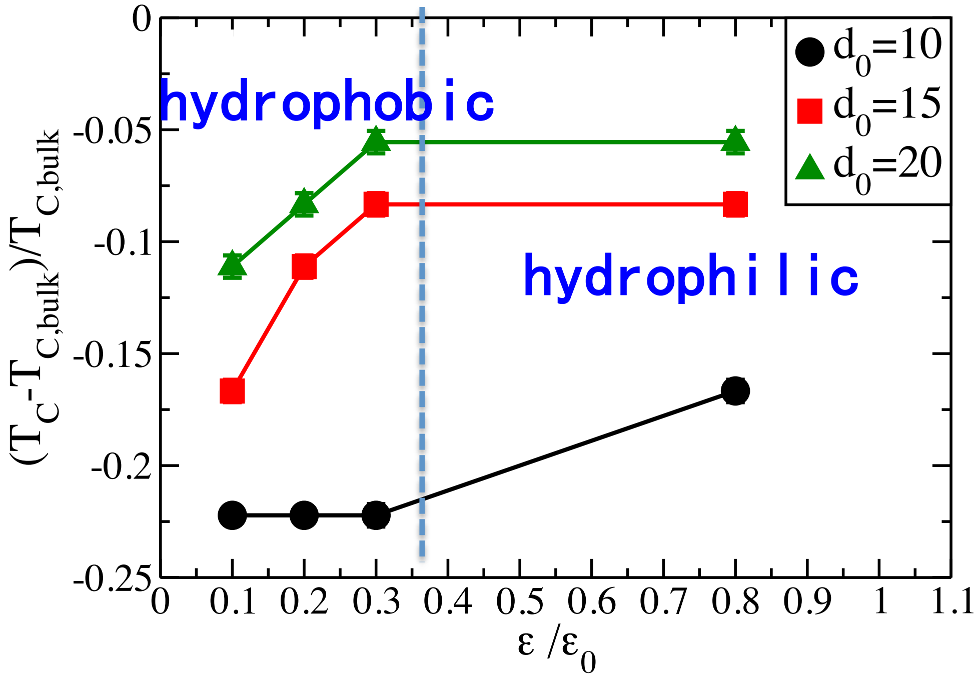


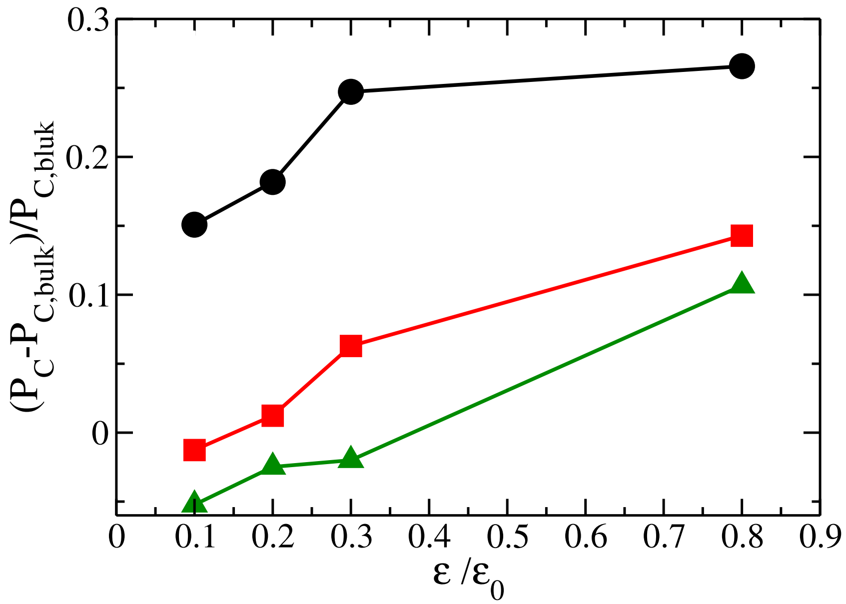
Confinement effect:

- **second critical point shifts to high pressure when strongly confined**
- **phase behavior approaches to that of bulk liquid at larger separation**

G. Sun, N. Giovambattista, L. Xu, J. Chem. Phys. (2015)

Surface chemistry effect on liquid-liquid critical point





Hydrophobic： Critcal point move to lower temperatures

Hydrophilic：

- Severe confinement， Tc lower than that of bulk
- Under not severe confinement, Tc is not much affected

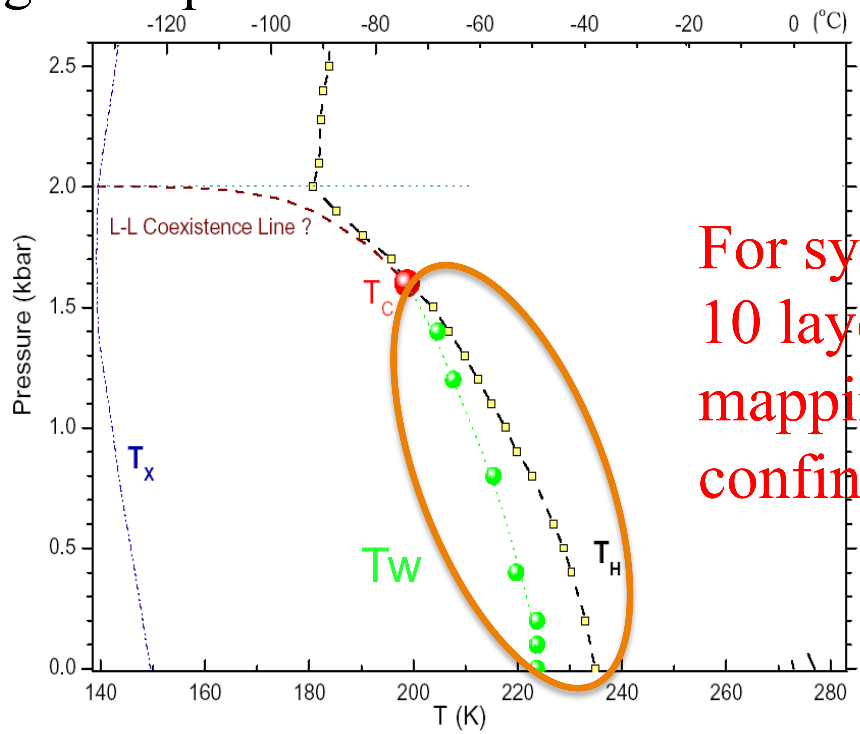
Summary

✓ **Phase behaviors depends on confinement and chemistry of surface**

✓**Hydrophilic confinement effect:**

◆ No significant effect on the phase diagram for systems with more than 10 layers of water molecules

◆ Drastically changes the phase behavior for severe confined systems



For system with more than 10 layers of liquids, the mapping between bulk and confined system is reliable

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Graduate students:

Gang Sun

Jiayuan Luo

Renzhong Li