Thank: many collaborators (Sastry, Ray, Gopikrishnan, Kumar, Viswanathan, ...) & Kanpur hosts

**QUESTION 1: "Understanding" the 64 anomalies of water?

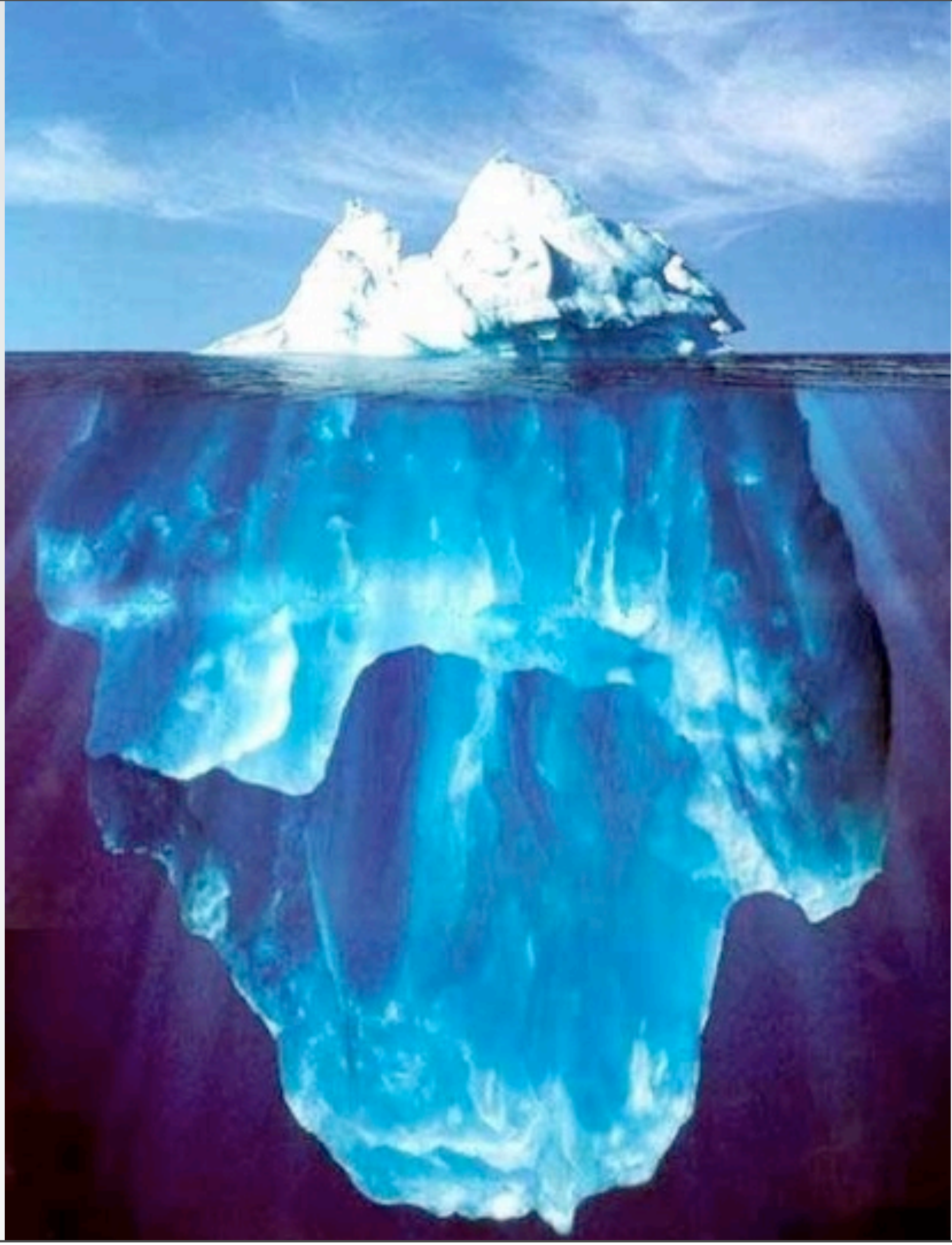
A: One anomaly is easy, and gives clues for many more: Why ice floats...?

**QUESTION 2: Why care about water?

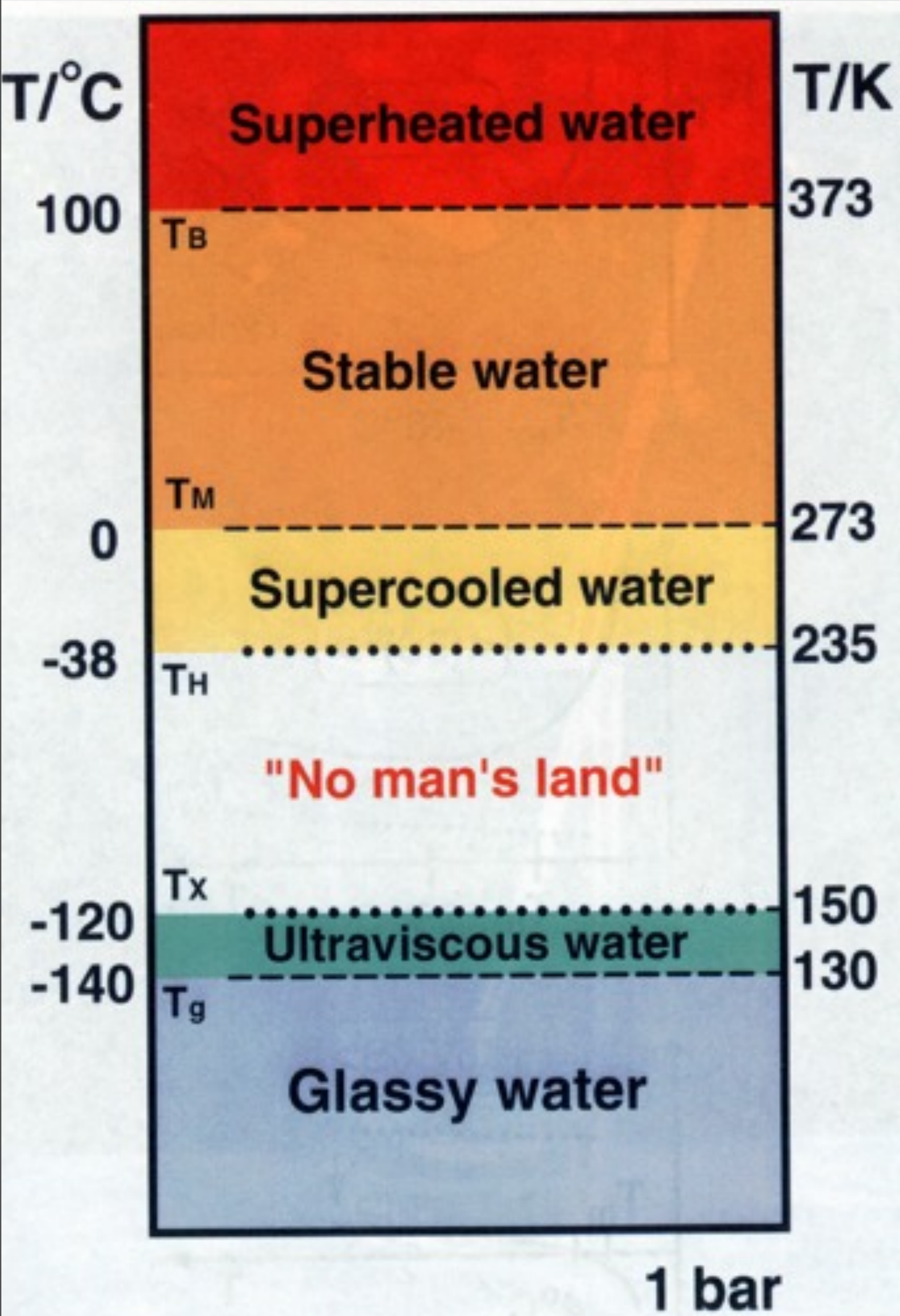
A. Practical

B. Scientific

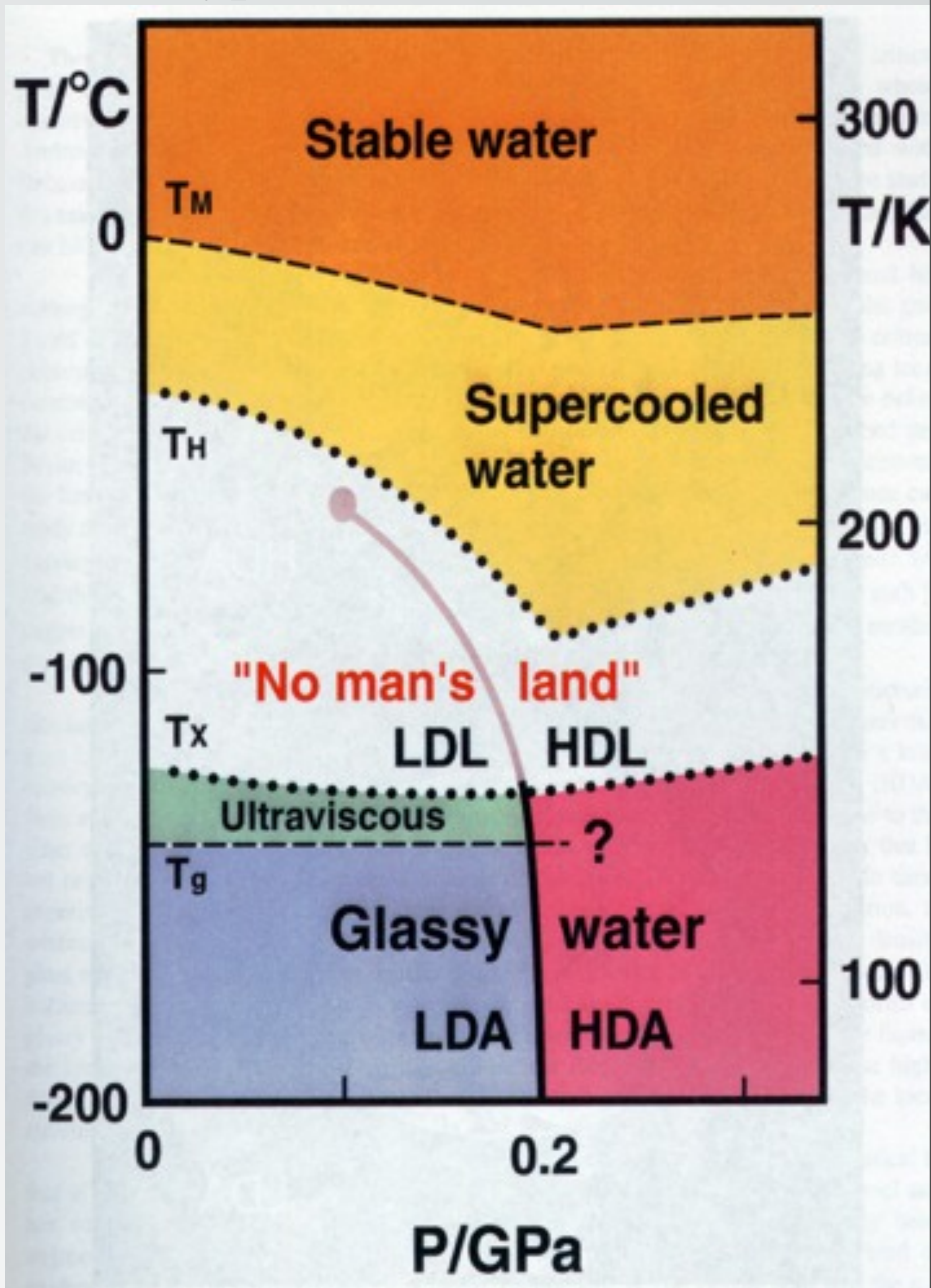
**QUESTION 3: What do we actually do?



TRUE!



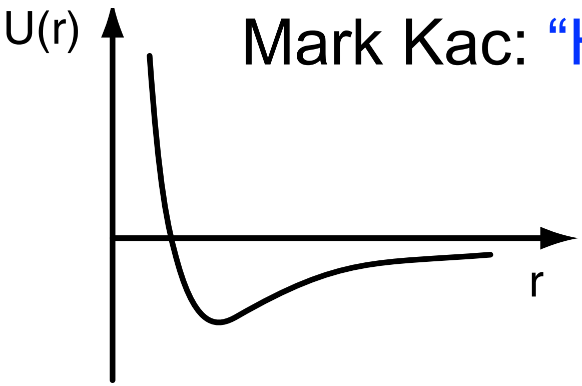
1992 Hypothesis (PHP/FS/UE/HES)



QUESTION: How can 2 liquid phases co-exist?

Answer: 2 length scales ---> Liquid-Liquid Phase Transition

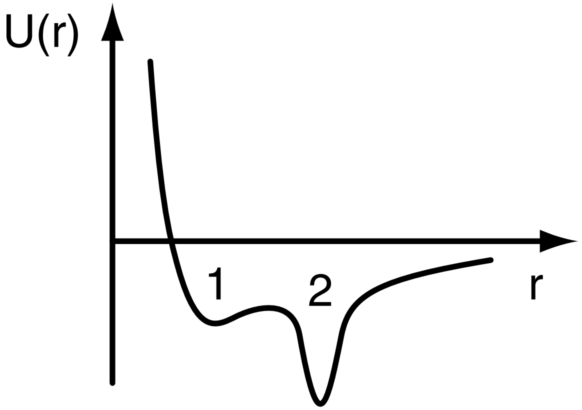
Mark Kac: "How does a liquid know when to condense?"



(a)

How can a liquid exist in 1 phase???

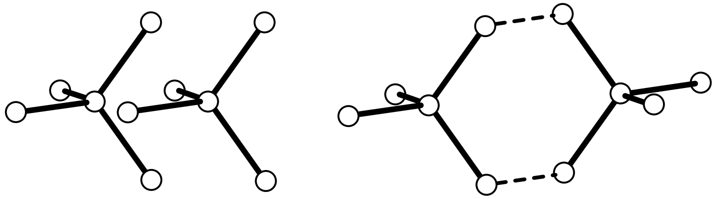
ex: Lennard-Jones: 1 length scale, 1 liquid



(b)

How can a liquid exist in 2 diff phases???

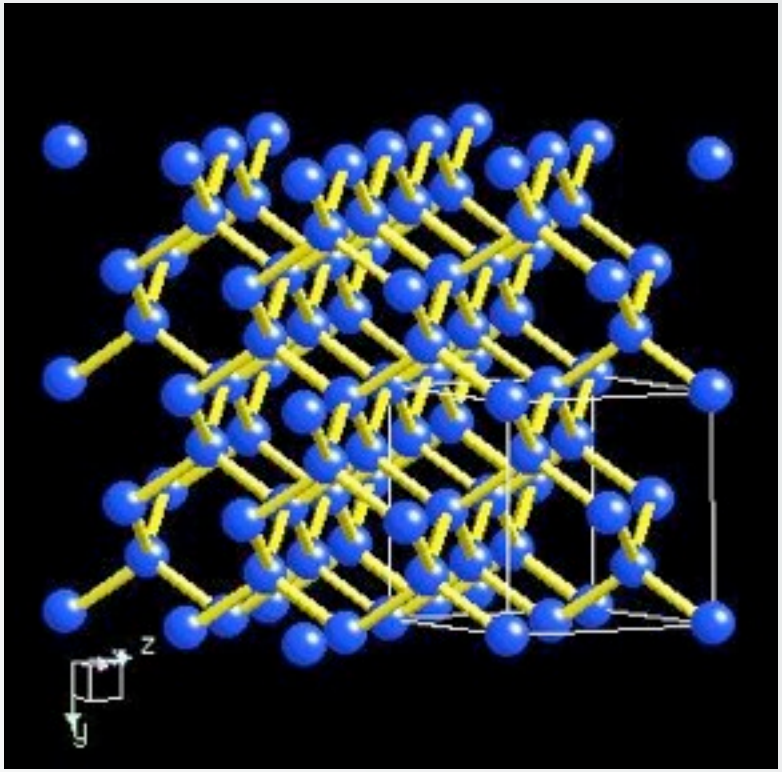
ex: 2-well L-Jones: 2 length scales,2 liquids



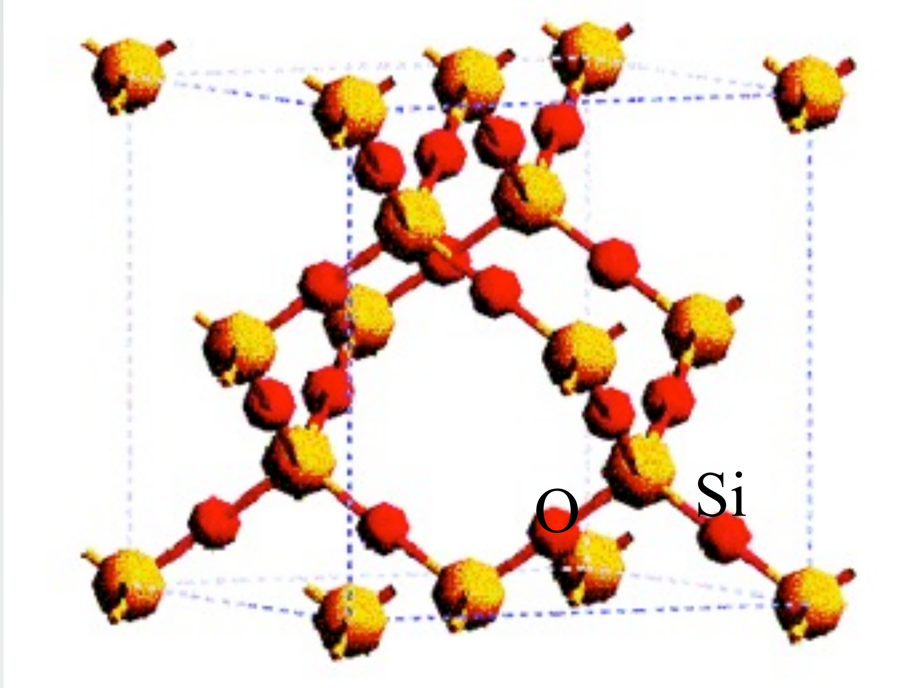
(c) LOCAL geometry for each well

1 2

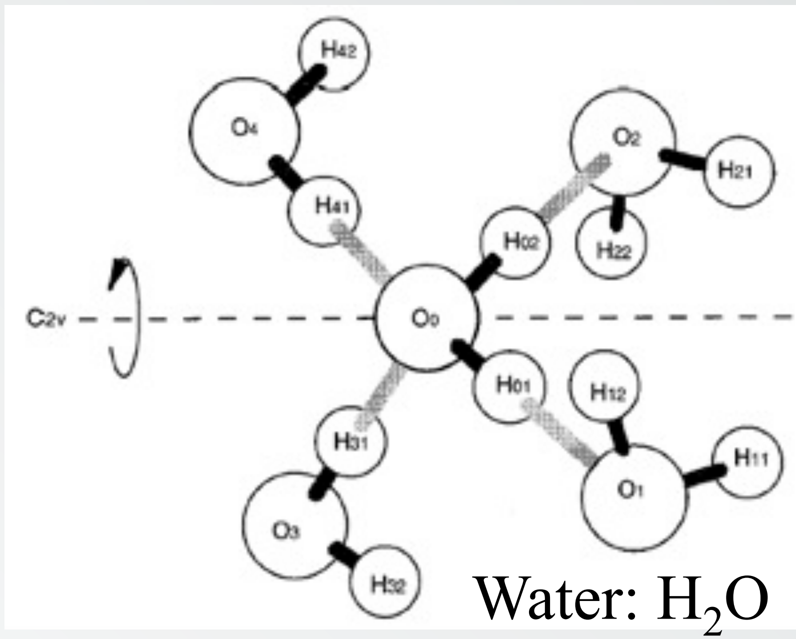
QUESTION: Why 2 length scales implies L L Phase Transition???



Silicon: Si (Sastry 2010 PNAS)



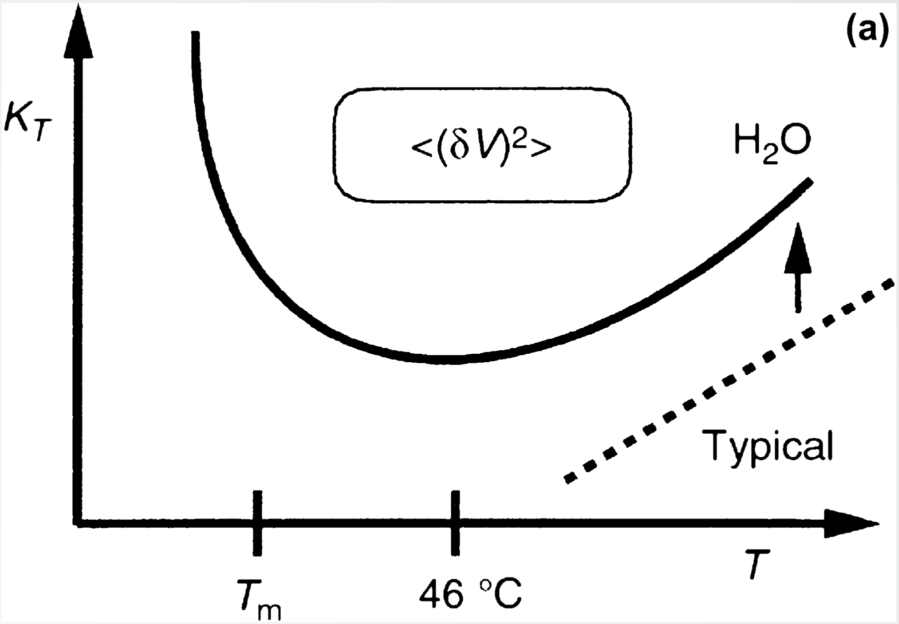
Poole/Angell: Silica: SiO_2

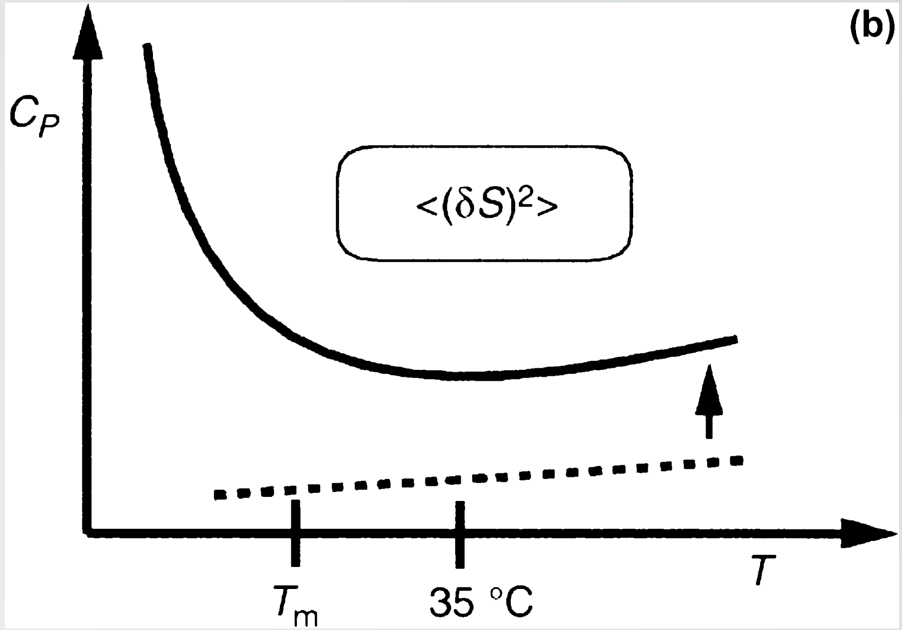


Three ubiquitous substances have in common local tetrahedral structure and hence more than one length scale in their interaction potentials.

Do all 3 show a liquid-liquid transition?

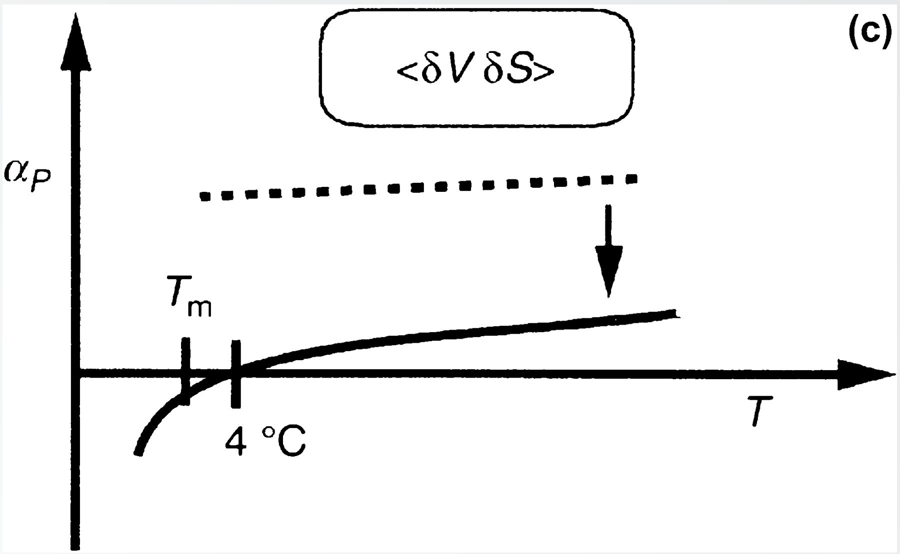
Example: 3 of the 64 anomalies: 3 thermodynamic response functions





(b) Specific Heat

(a)Compressibility



(c) Coeff. Thermal Expansion

QUESTION: Why apparent singularity about -50 C ??

QUESTION: How to TEST the liquid-liquid Phase Trans. Hypothesis???

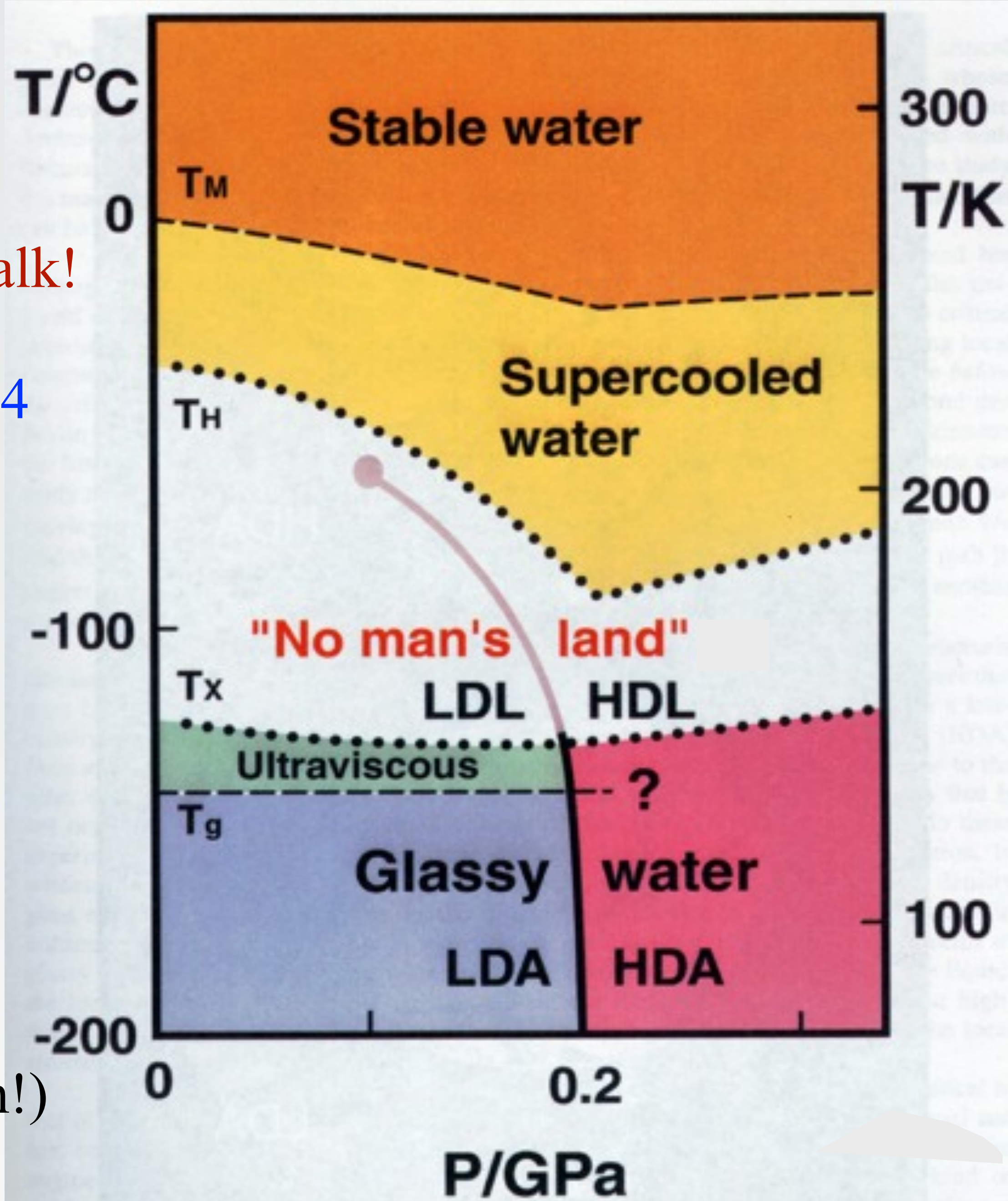
3 ANSWERS:
1. Models--(2 scale models)
2. Simulations--about 100
3. Experiments--rest of this talk!

EXPT TEST 1: Mishima 1994
2 kinds of glassy water

LDA: Low-Density Amorphous Glass
HDA: High-Density Amorphous Glass

LDL: Low-Density Liquid
HDL: High-Density Liquid

P_c approx 1 kbar (M.Trench!)
T_c approx. - 50 C



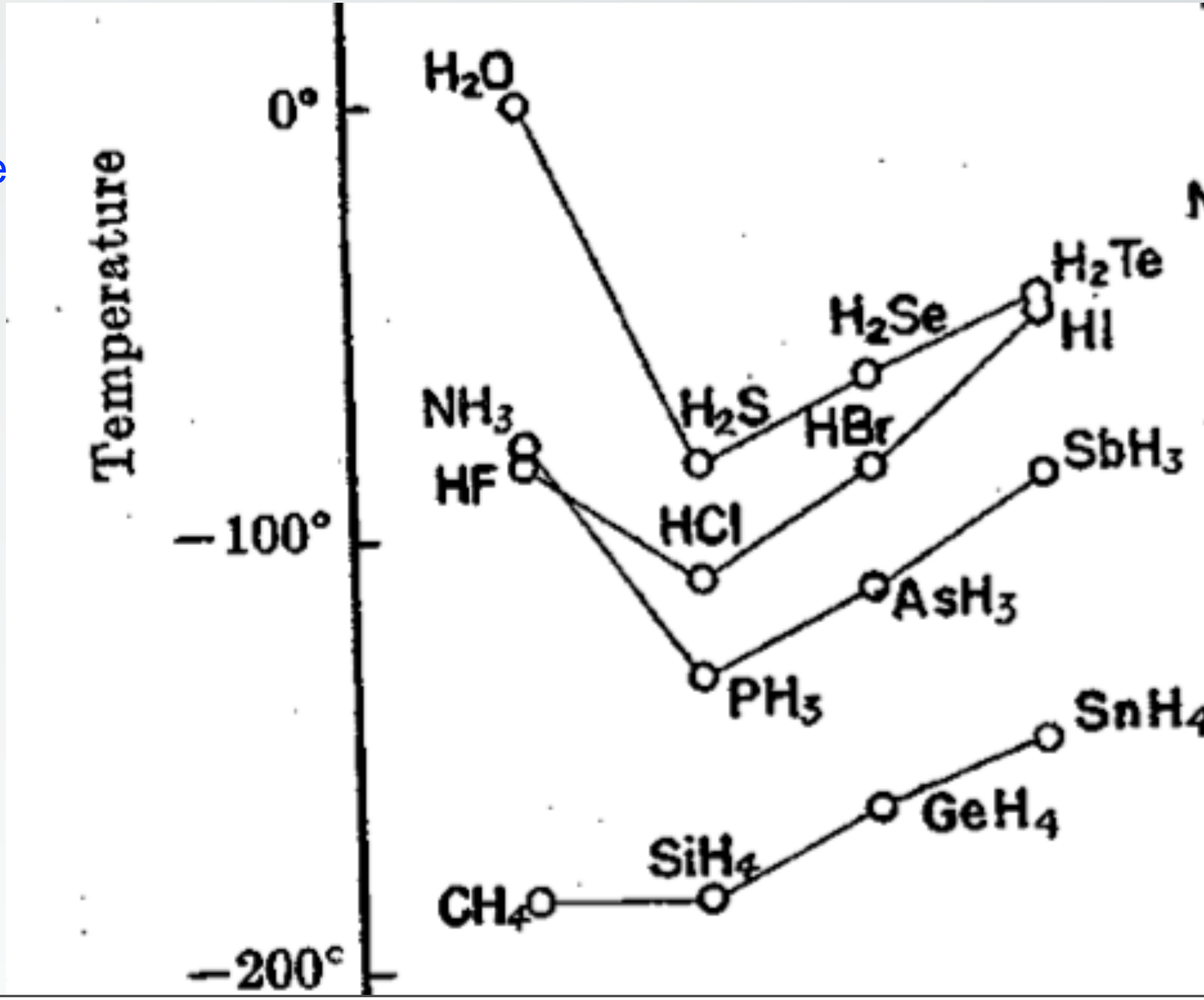
BIG REMAINING CHALLENGE: How to enter “no-man’s land” (below -38 C)???

ANSWER: Study the 62-year old Bible: Linus Pauling 1947.
“NANOCONFINEMENT” distorts water’s “perfect” hydrogen bond network.

Pauling “miracle”: nanoconfinement lowers freezing point... by 100 degrees!!

Linus Pauling 1947:

“Water would freeze about 150-170 K IF water had no H bonds”

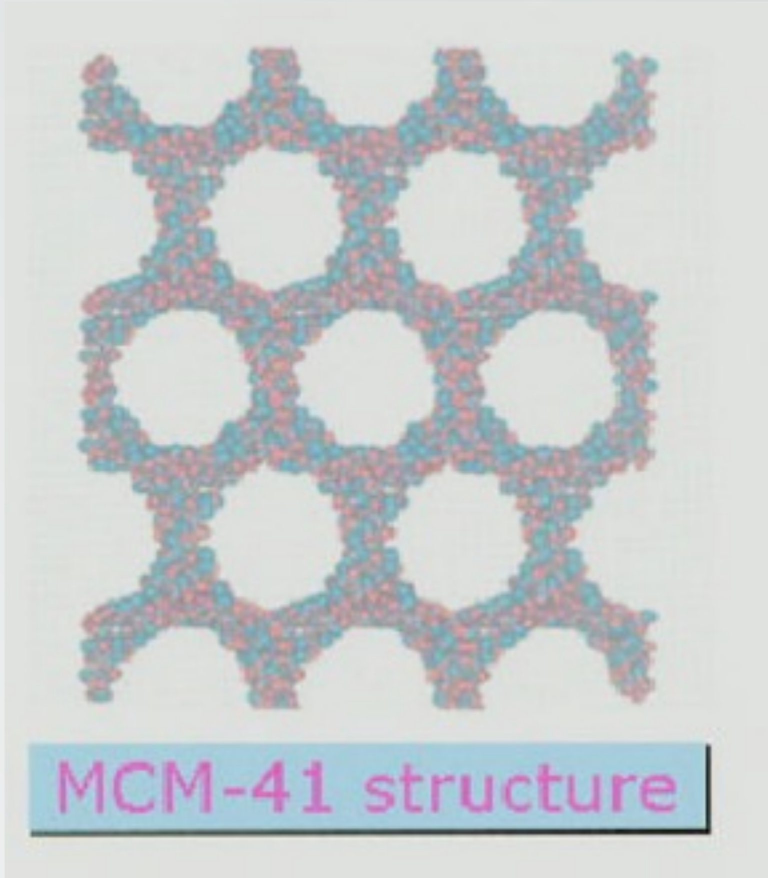


WORRY: Does nanoconfinment destroy cooperative interactions also?

ANSWER: NO (Ising)
Destroys phase transition ONLY after correlation length = pore size.

MCM-41-S: Unfreezable “water”

MCM-41-S is well ordered with hexagonal symmetry.

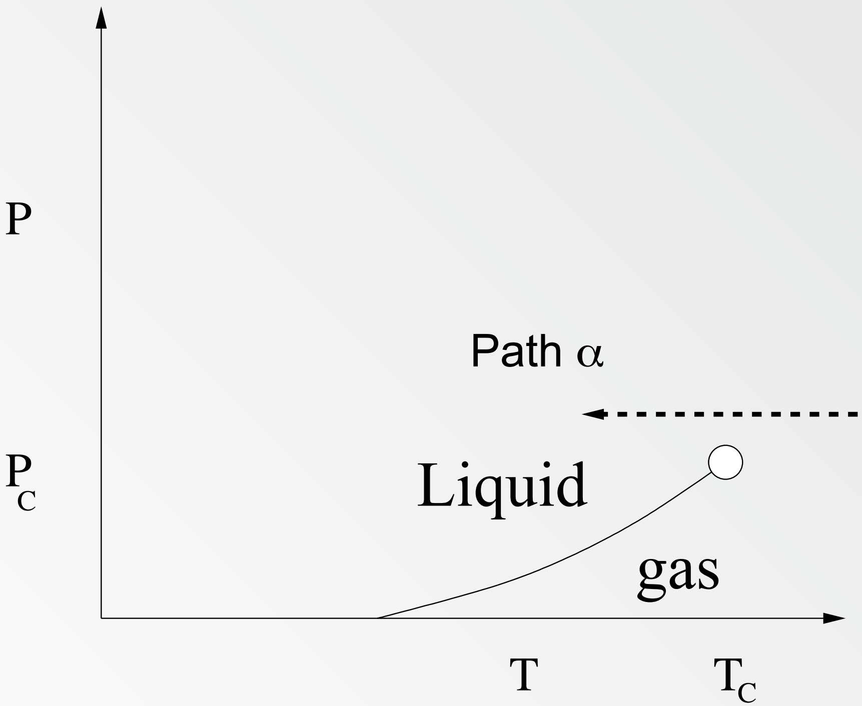


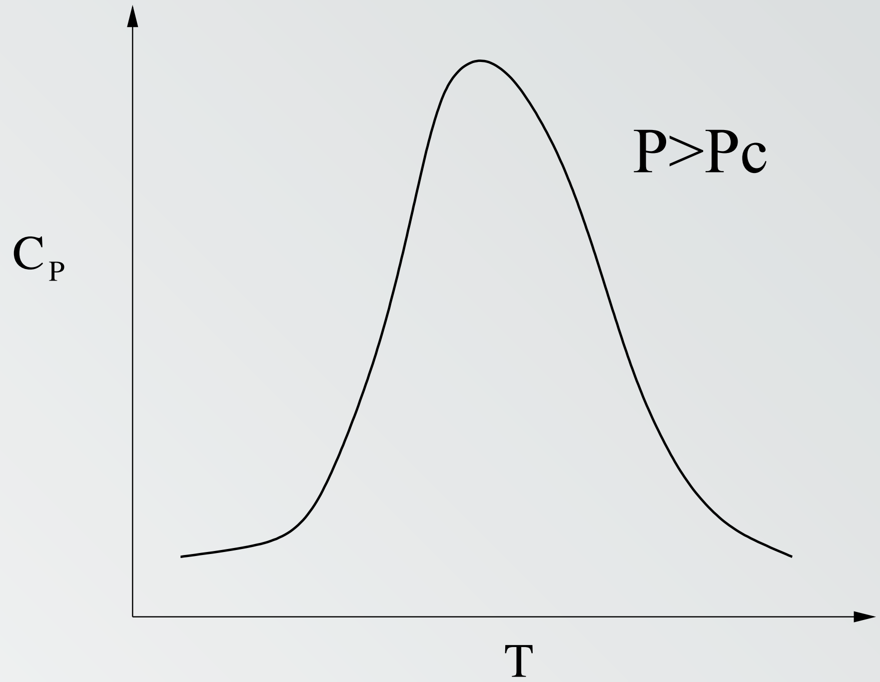
Four MCM-41-S samples, fully hydrated:

1. MCM-41-S-10, with pore size <10 Å,
2. MCM-41-S-12, with pore size 12 Å,
3. MCM-41-S-14, with pore size 14 Å,
4. MCM-41-S-18, with pore size 18 Å,

C.-Y. Mou, Taiwan

DIRECT test for a Critical point???
The case of the ordinary liquid-gas system





Widom line: Locus of correlation length maxima. Response functions proportional to powers of correlation length, so they also have maxima.

Hence, response function maxima even far above the critical point => Signature of Widom line. WHY response function maxima???

DIRECT test for a Critical point???
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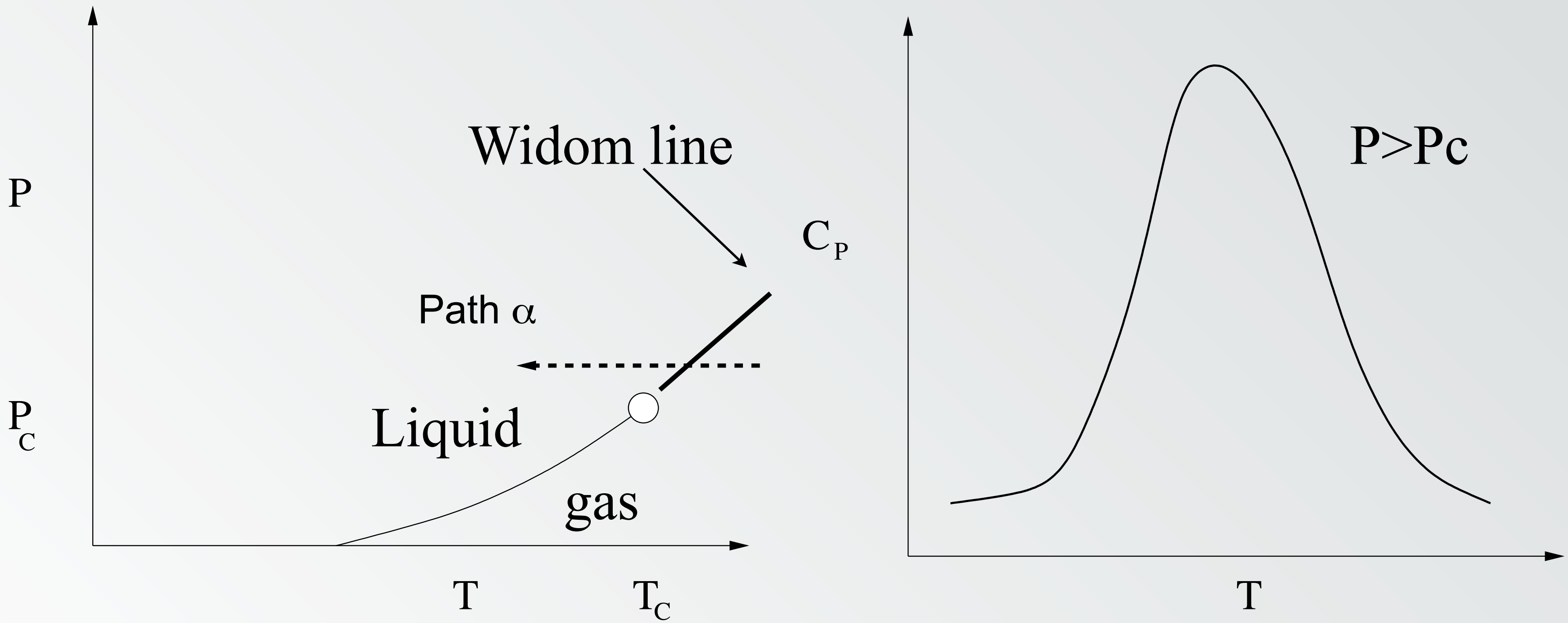

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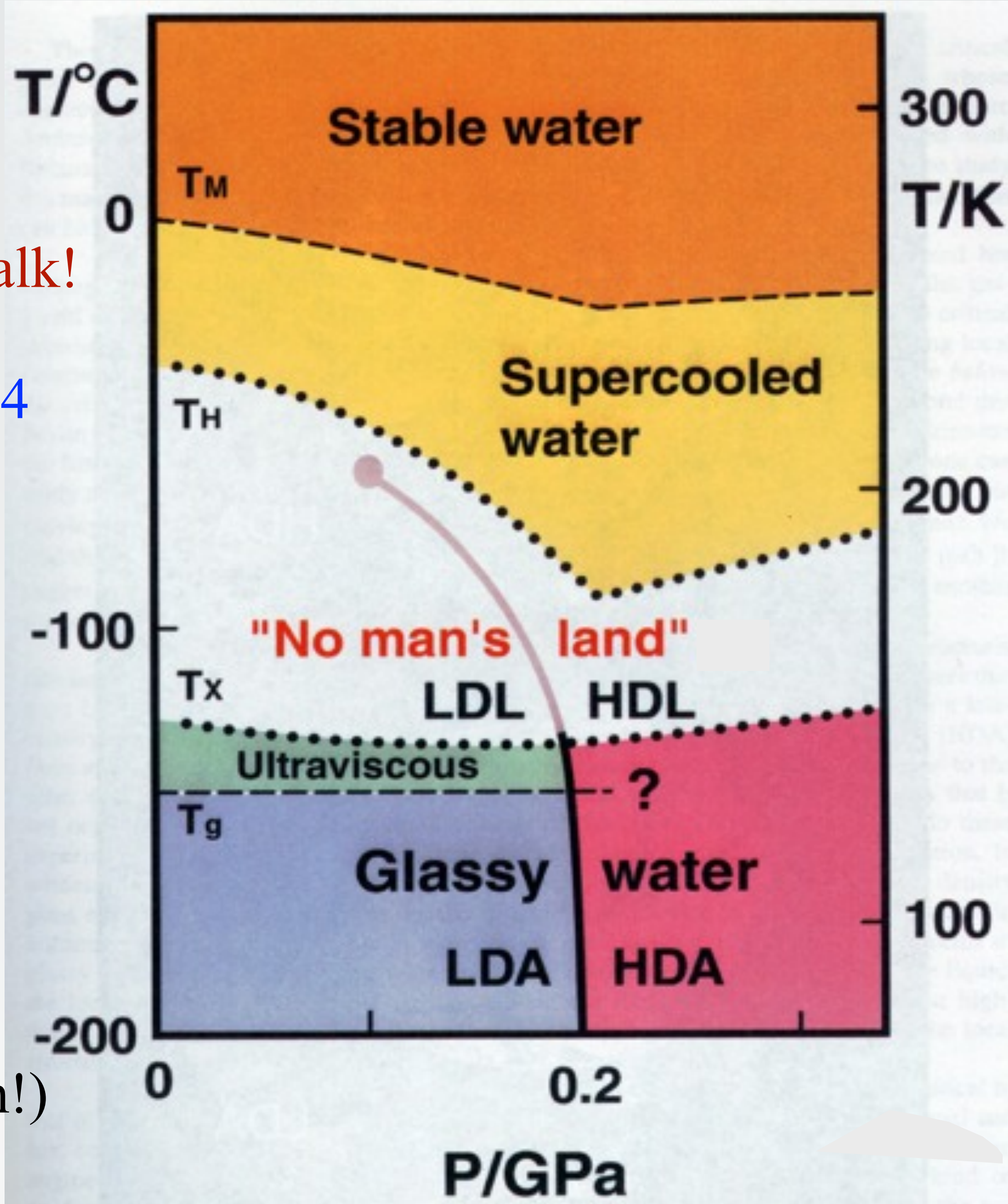
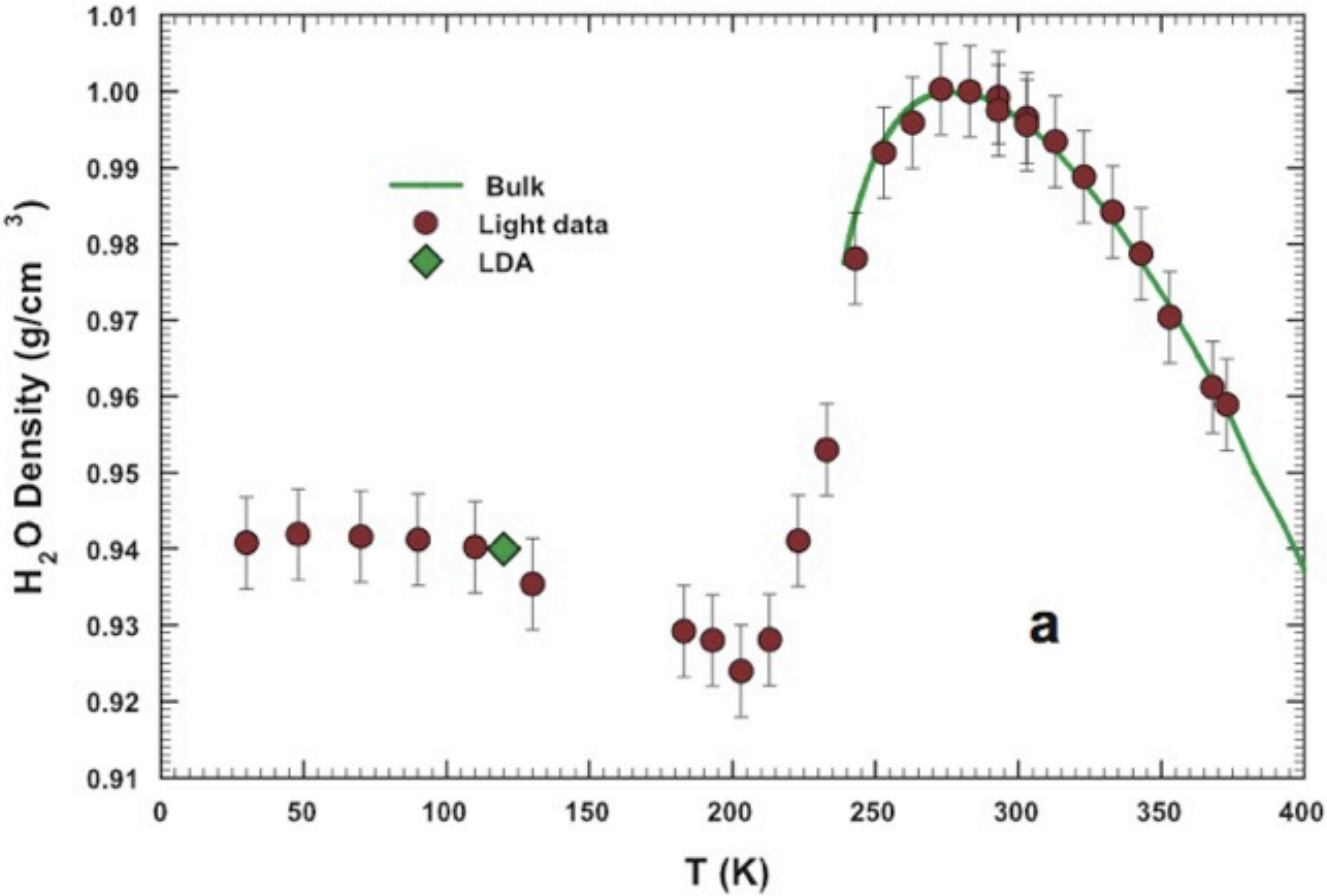
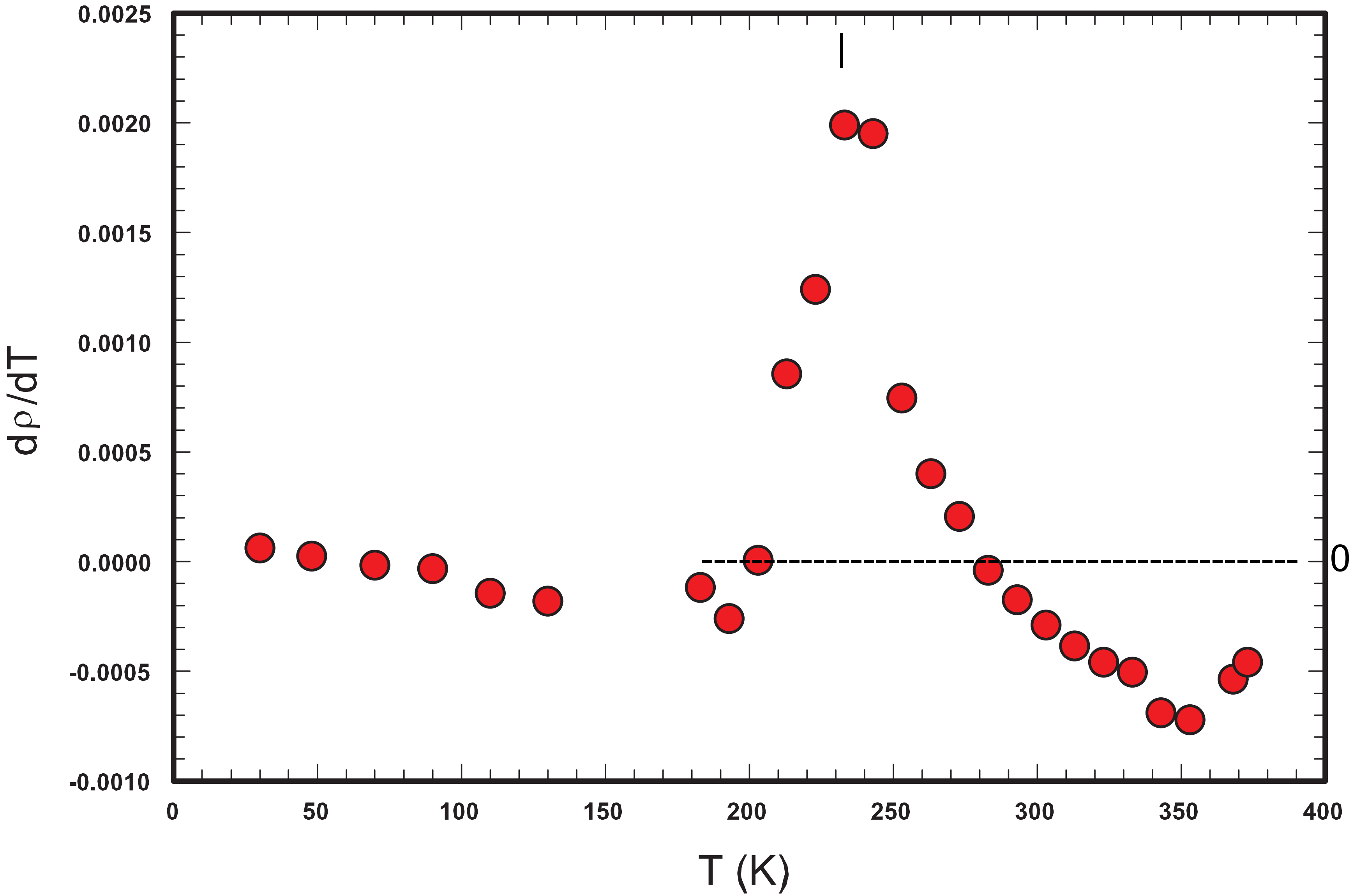


Thermodynamic anomalies & the Widom temperature: water vs. confined "water":



Mallamace, Chen, et al 2008 PNAS

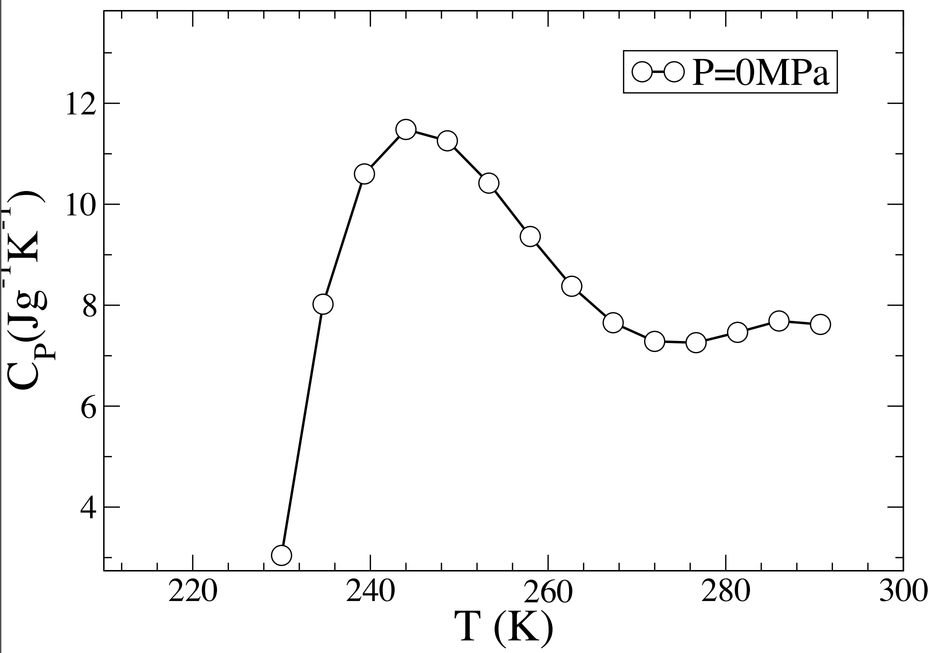
IDEA: Use thermal expansion peak (entropy/volume cross fluctuations) to locate Widom temperature...occurs exactly where simulations predict--about 230K



Expt: F. Mallamace et al, PNAS 2008. MD: Paschek, Poole et al,, Xu et al, Molinero.

IDEA: Use specific heat peak (entropy flucts.) to locate Widom temp: Simulations consistent with Oguni specific heat experiments

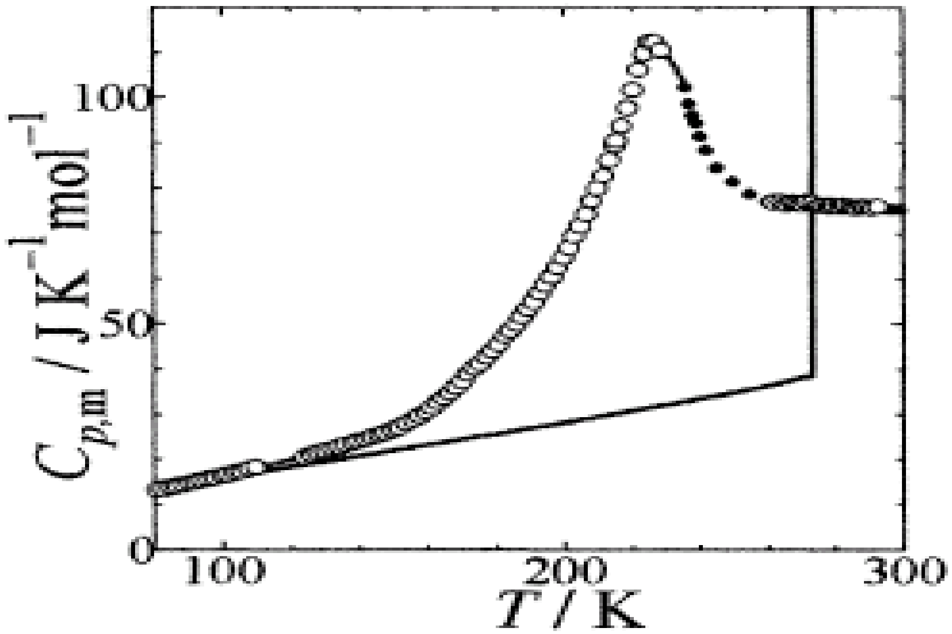
TIP5P Simulation
[[Boston 2005]]



L. Xu, P. Kumar, S.V. Buldyrev, S.H. Chen, P.H. Poole, F. Sciortino, H.E. Stanley,

PNAS ***102***,*16558* (2005).

Experiments (peak: 225K)
[[Sendai 2003]]

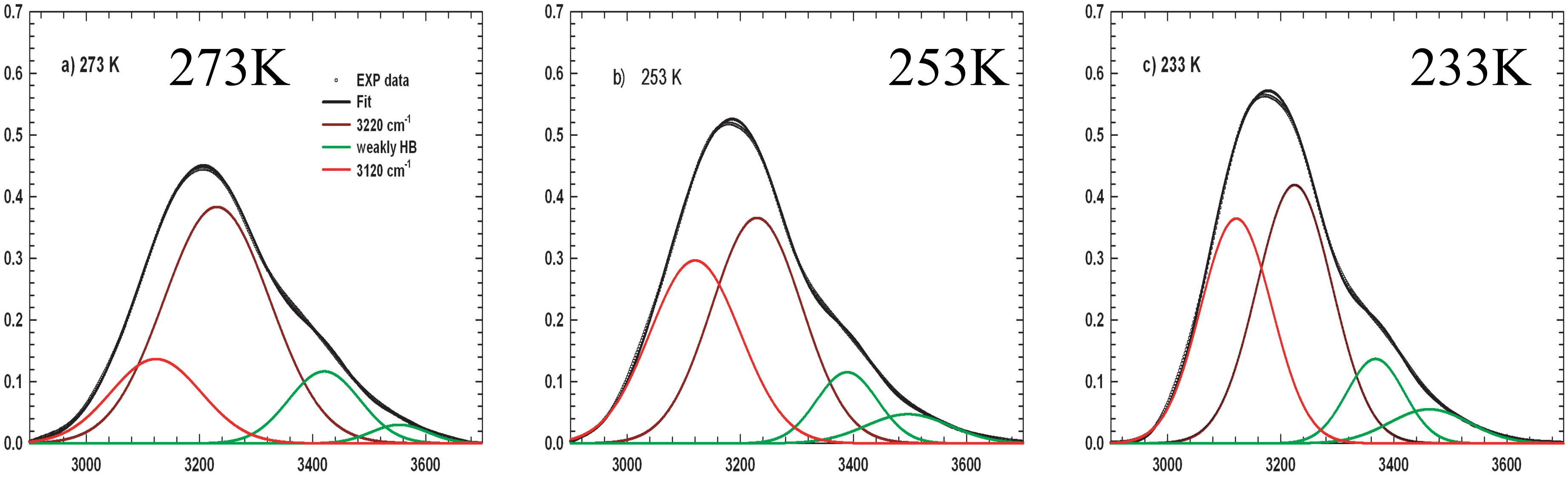


S. Maruyama, K. Wakabayashi, M. Oguni,

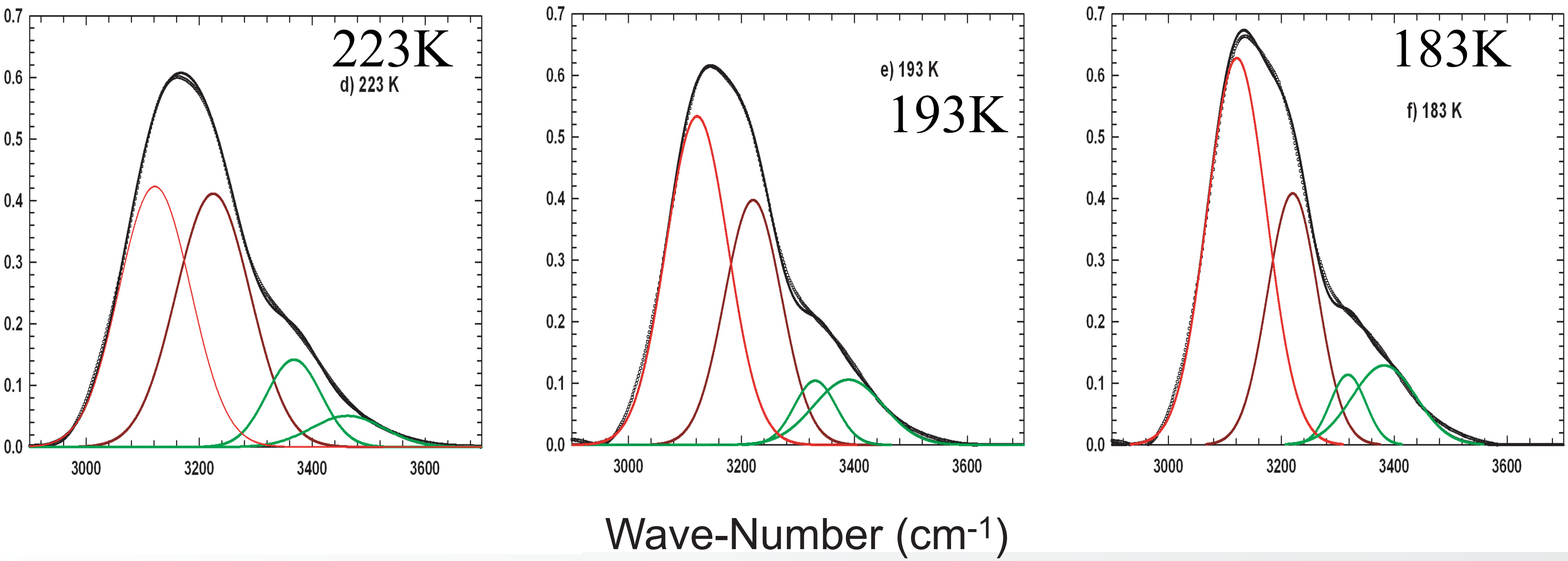
"Thermal Properties of Supercooled Water Confined within Silica Gel Pores,"

AIP conference proceedings 708, 67 (2004)).

Crossing the Widom line at 223 K [[Mallamace et al 2007]]

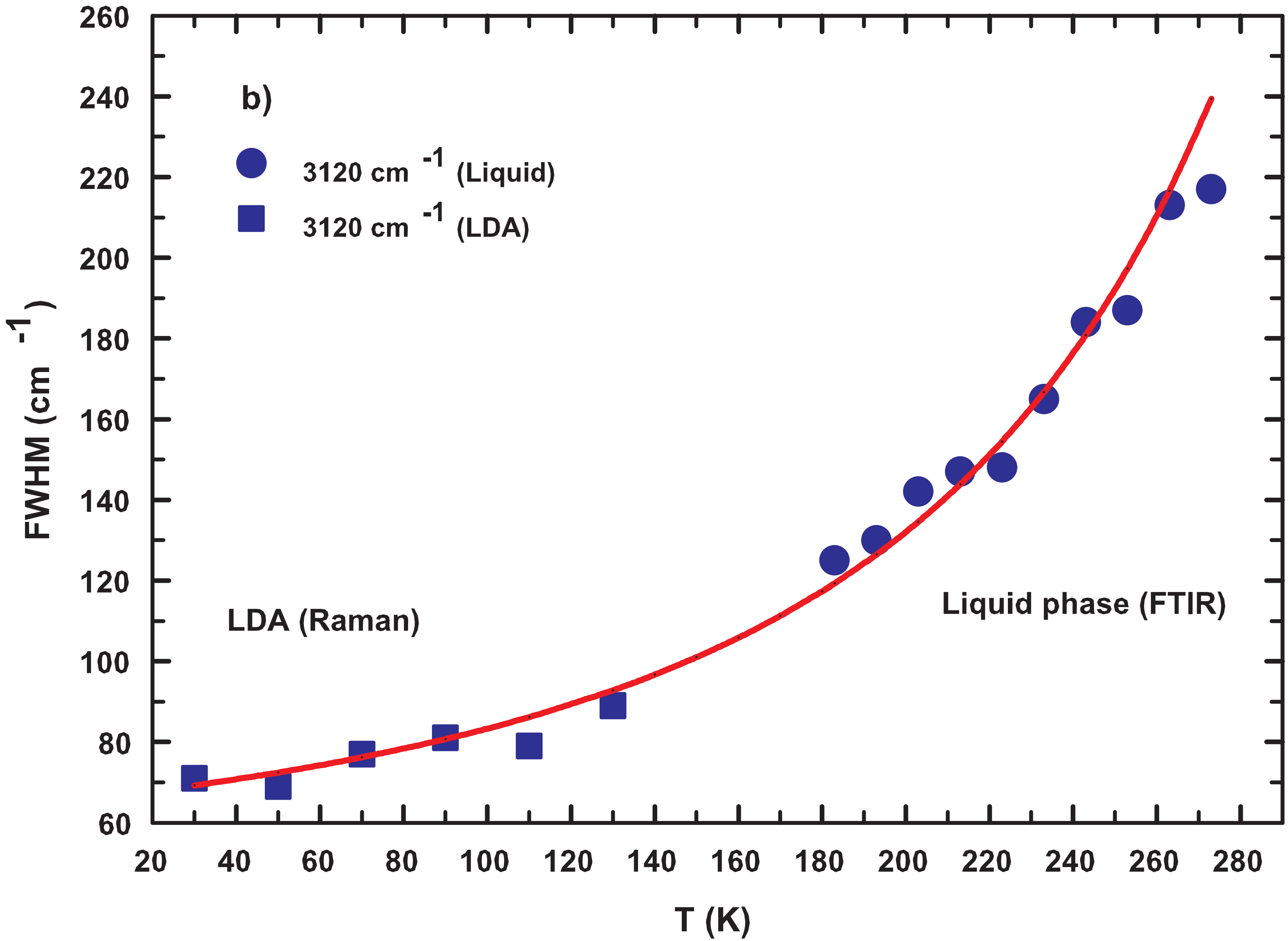


3120 = LDA (= LDL?). 3220 = HDA (= HDL?)



Q: Is room-T water continuous with low-density amorphous solid water?

A: Mallamace, 2007 for liquid water; S.A.Rice for low-density amorphous solid



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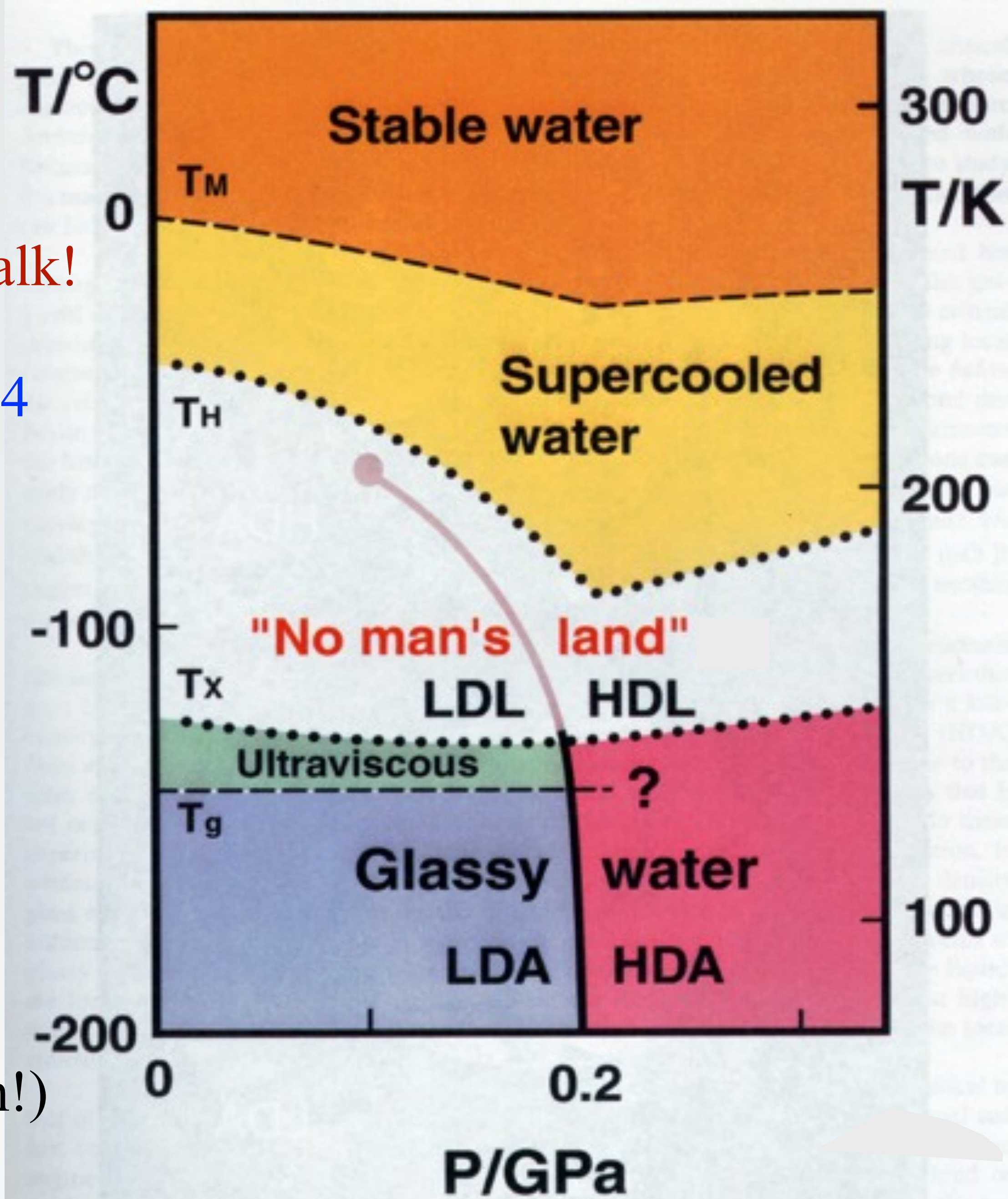
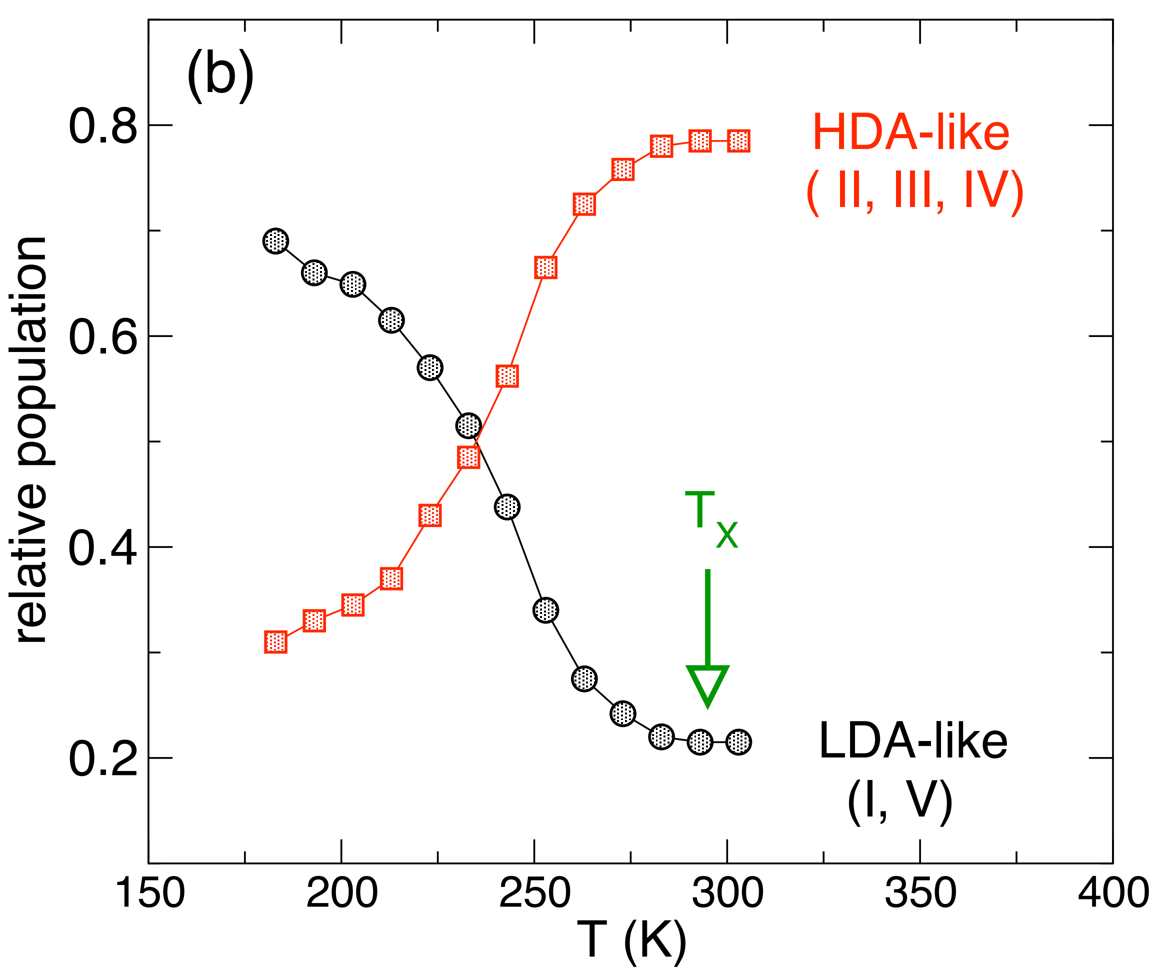


Onset Temp of Breakdown: possible structural interpretation

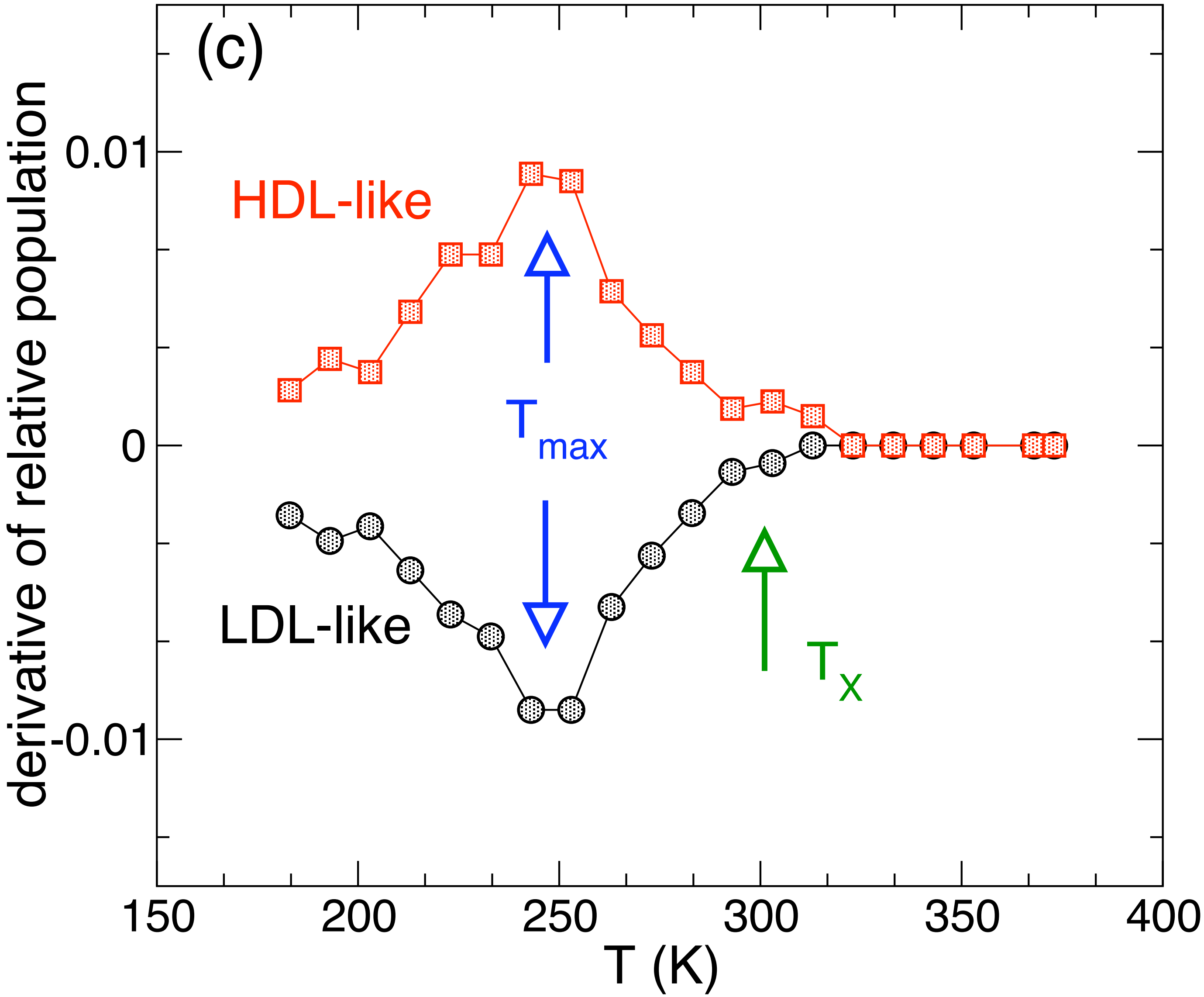
namely when the LDL starts to condense out of the HDL

Analysis of Mallamace FTIR experiments for relative populations of LDL vs HDL local structures



Xu,Mallamace,Starr,Yan,Buldyrev,HES,Nature Phys(2009 August)

T derivative has maximum on crossing the Widom line



Xu,Mallamace,Starr,Yan,Buldyrev,HES,Nature Phys.2009 August)

NEW: EXPERIMENTAL V(P,T) EOS

Get G(P,T) by knowing G for liquid and solid same along melting lines....by interpolation get G(P,T) for all (P,T).

V = dG/dP

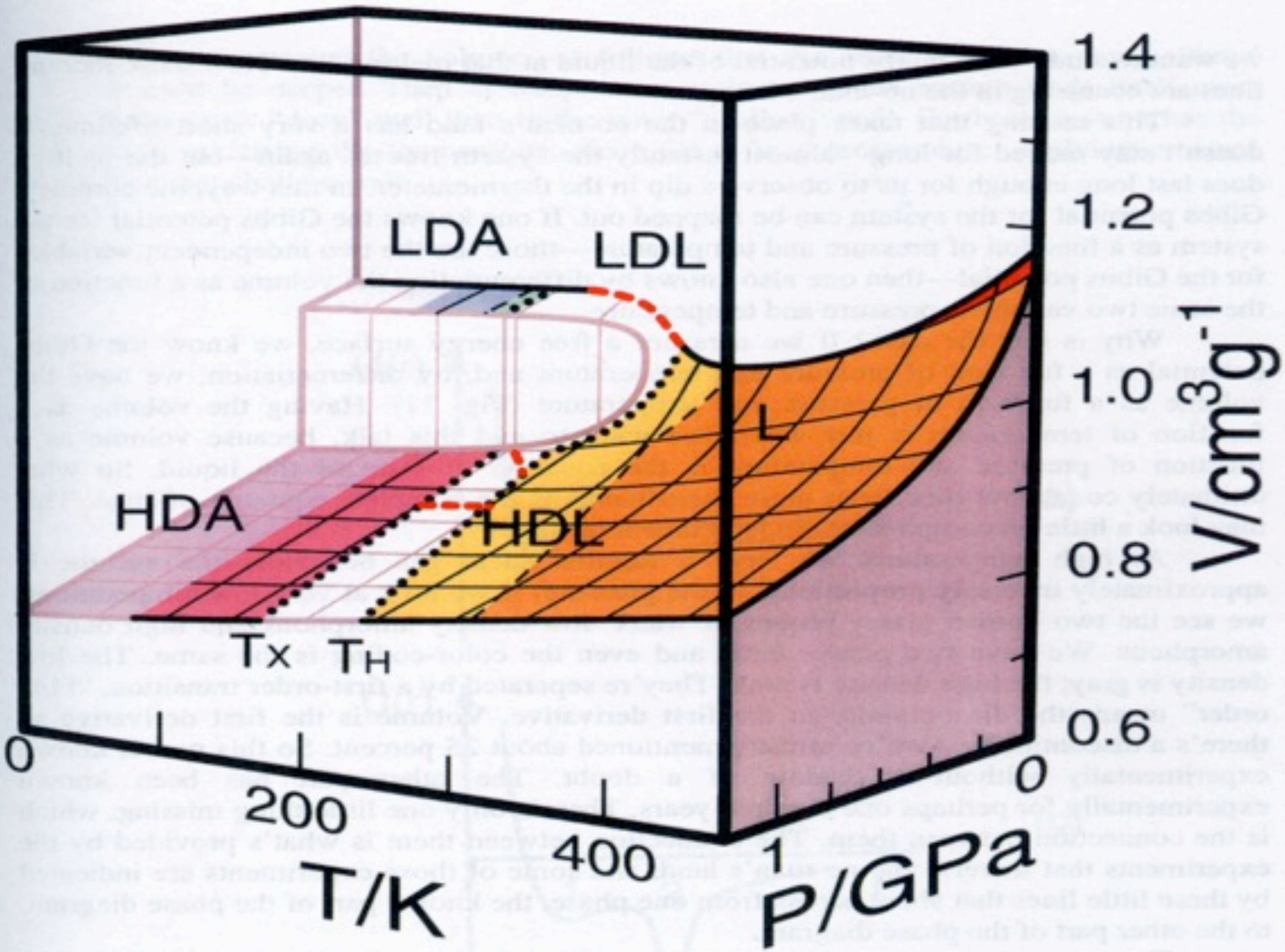
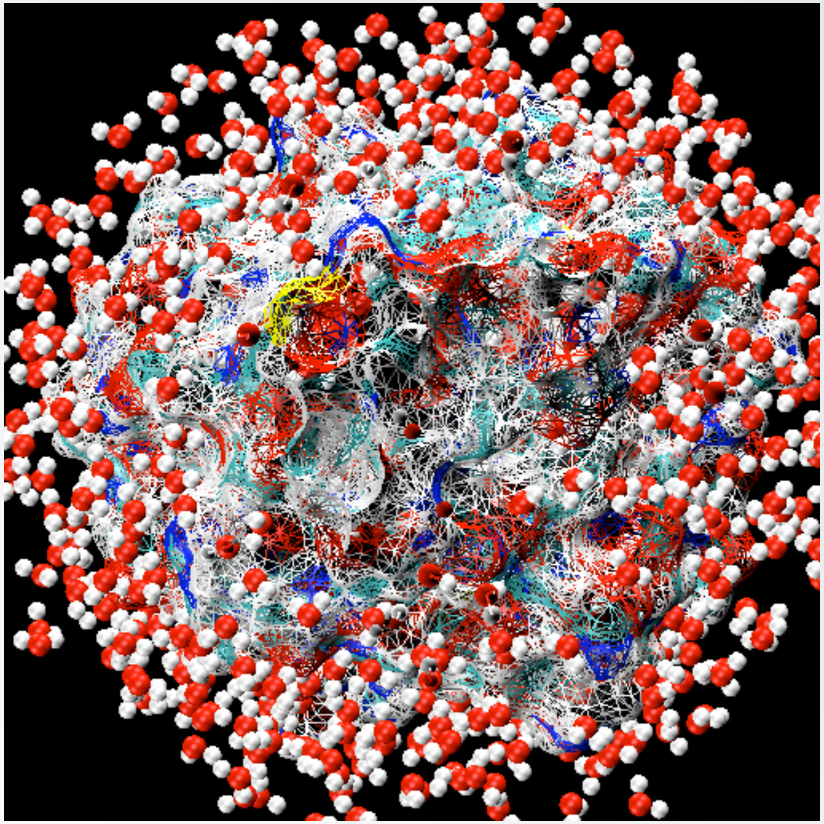


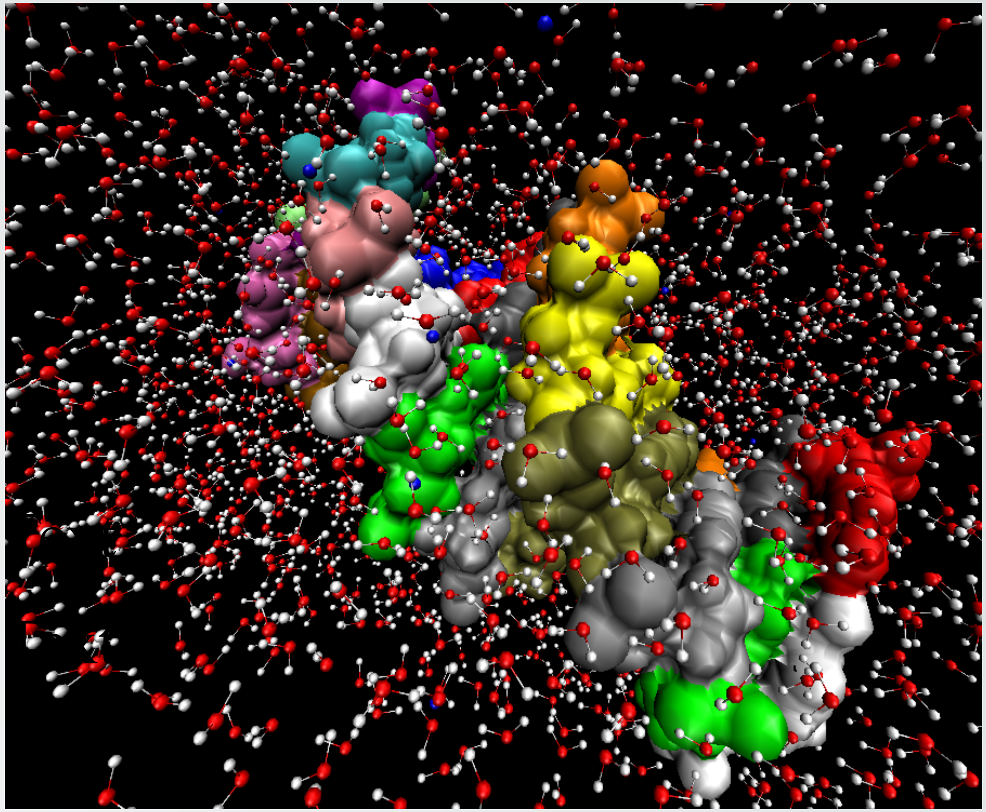
Figure 11: Experimentally-derived [56] thermodynamics equation of state V=V(P,T), using the same color coding as in Figs. 1 and 9. The specific volumes of the amorphous phases are known for the region below T_X [6]. Solid lines are the specific volume along the melting lines of ice IV and XIV. The high-temperature liquid appears to separate into two low-temperature liquid phases just below the critical point located at around 0.1 GPa and 220 K. These two liquid phases are continuous with the two amorphous phases that are known to exist below about 150 K.

O.MISHIMA/ HES

Q: Are anomalies of confined "water" due to silica MCM41walls?

A. Consider "wall-free" protein hydration water: same Widom temp.





Proteins (Lysozyme, ...) surrounded by water molecules

DNA (also RNA,...) surrounded by water molecules

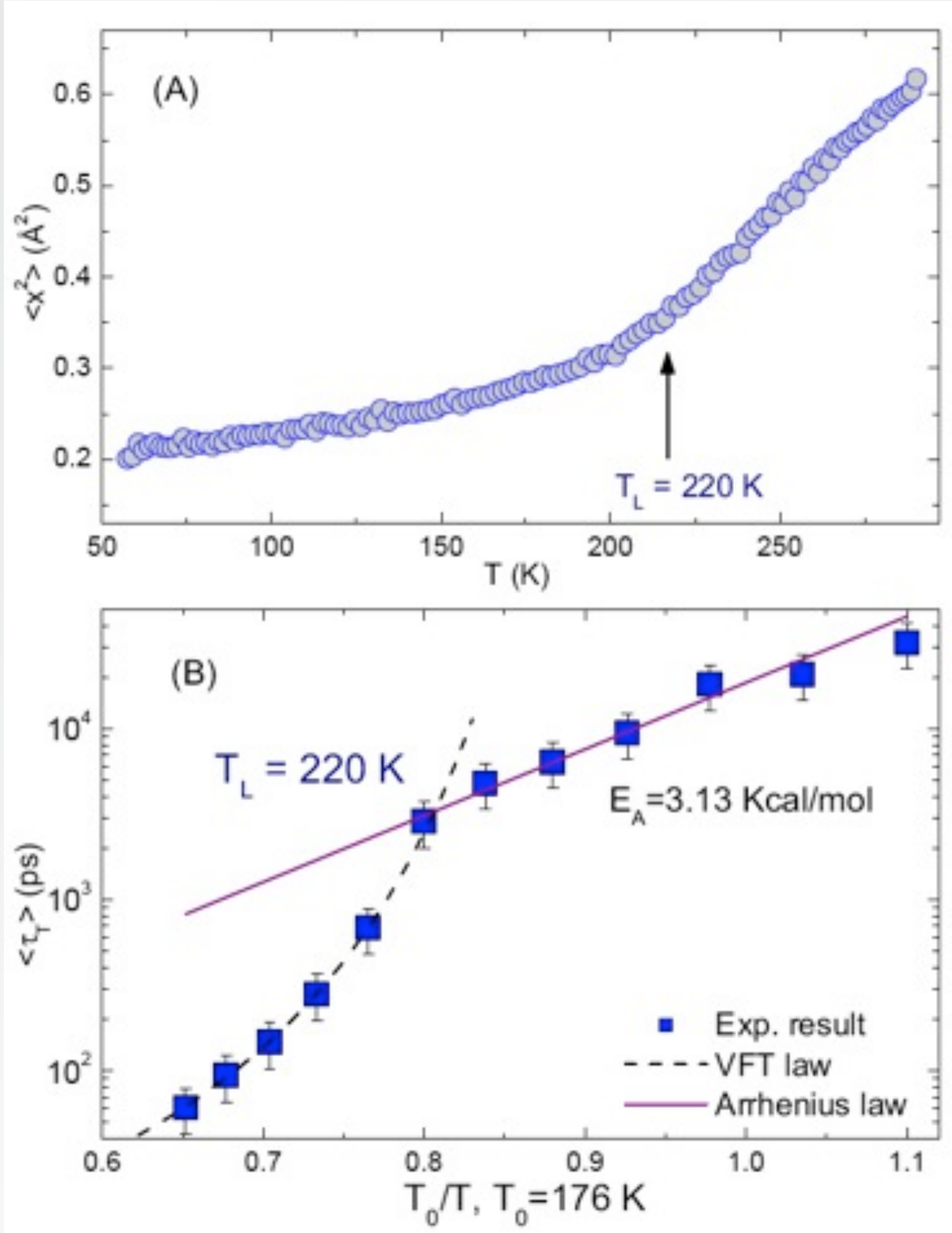
EXPTS: Chen/Mallamace and their many gifted students: same Angell Temp

MD SIMS: Kumar,Yan,Xu,Mazza,Buldyrev,Chen,Sastry,Stanley(PRL 06)

Experiments display dynamic crossover at 220 K in Protein Hydration Water

mean square displacement
vs.
temperature

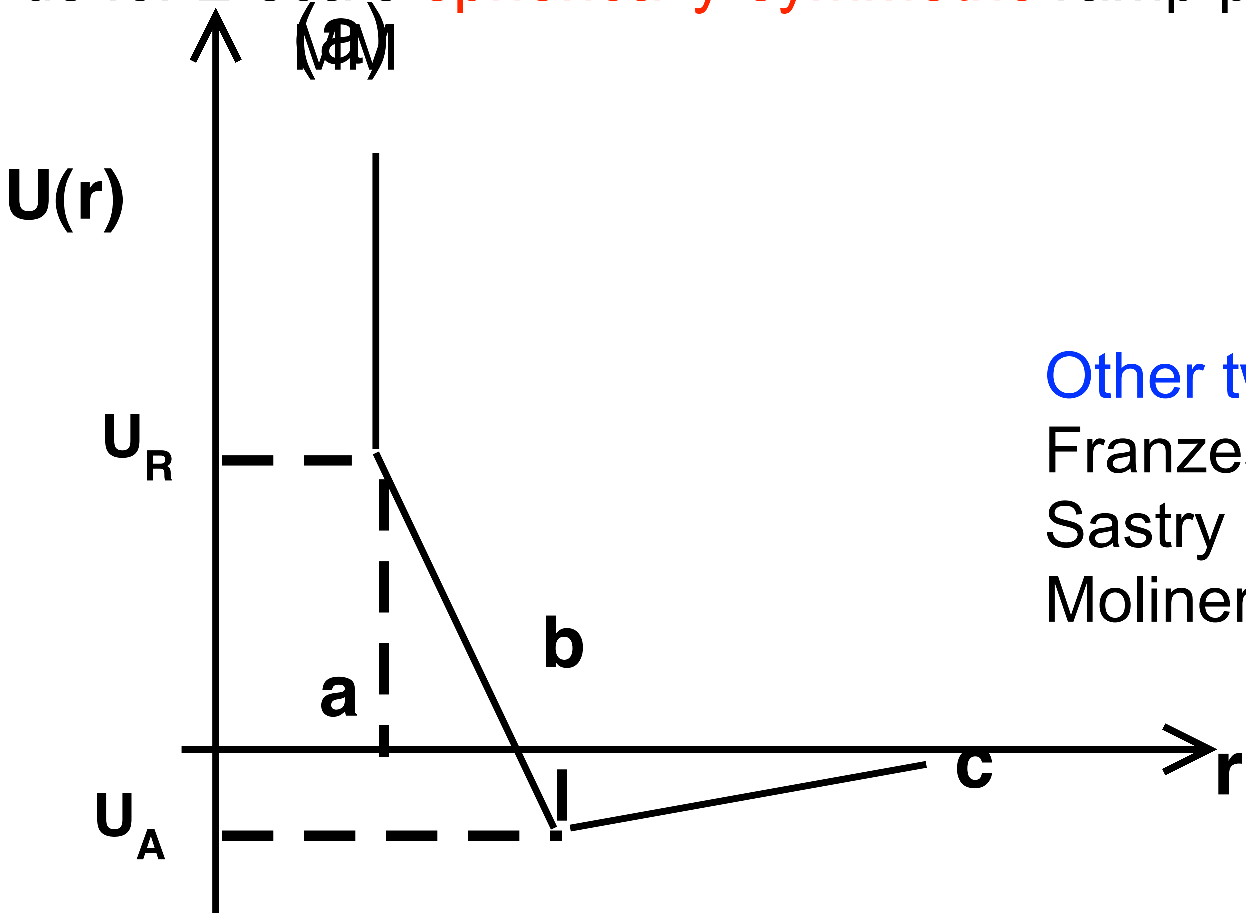
Charachteristic time
vs.
temperature



from Chen et al 2006 PNAS

How general is this picture?? That breakdown starts when LDL starts to condense out?
And Widom line is where two structural populations balance?

Holds for ANY 2-scale potential? For metallic glasses?
Holds for 2-scale spherically-symmetric ramp potential (Jagla)!



Other two-scale potentials:
Franzese
Sastry
Molinero

TAKE-HOME MESSAGE:

1. What makes water special: TWO characteristic length/energy scales

2. Widom line is a "smoking gun" for L-L critical point: (228K,1kbar)

3. "protein" "glass" "transition" possibly NOT protein, NOT glass, and NOT a transition; rather is crossover in water structure at Widom line.

("Liquid Polymorphism" S.A.Rice, Adv Chem.Phys, 2010

C.A.ANGELL**, M. C. Barbosa, M.C. BELLISSENT, L.BOSIO**, F.BRUNI**, S. V. Buldyrev, M.Canpolat, S.-H. CHEN**, P. G. Debenedetti, U.Essmann,G.Franzese, A. Geiger N. Giovambattista, S.Han, P. Kumar, E.La Nave,G.Malescio, F.MALLAMACE**, M. G. Mazza, O.MISHIMA**, P.Netz, P.H.Poole, P.J.Rossky, R. Sadr,S. Sastry, A. Scala, F. Sciortino, A. Skibinsky, F.W.Starr, K.C. Stokely J.TEIXEIRA **, L.Xu, Z. Yan (32 teachers!

thank you