Thank you: Roberto/Francesco

- 600-page book **Liquid Polymorphism**, edited by HES
  ~~~~~~~~Adv Chem Phys, vol.152 [S.A. Rice, Series Editor]

INVITATION: please come to Boston
..i will welcome you at any time!

1. for a visit...of any length
2. for your Ph.D. program
3. for your postdoc
4. for your sabbatical
5. for a fun meal

or...at least....sit back and address a fascinating question NOW!
  ~~~~~~~~

"Experimental Tests of the Liquid-Liquid Phase Transition Hypothesis"

> 50 teachers, 15 EXPERIMENTALISTS (in upper case), 11 are HERE (denoted **:
C.A.ANGELL, M.C. Barbosa, M.C. BELLISSENT, L.BOSIO, F.BRUNI, X Q CHU,S. V. Buldyrev, M.Canpolat, S.-H. CHEN**, D. Corradini, C. CORSARO**, P. G. Debenedetti**, U.Essmann, G.Franzese**, G.GALLI, P.Gallo**, A. Geiger, N. Giovambattista, S.Han, M.Hemmati, H.J.Herrmann, T. Kesselring, P. Kumar, E. Lascaris, J.Luo, E.La Nave, G.Malescio, F.MALLAMACE**,D. MALLAMACE**, P BAGLIONI, M.Marques, M. G. Mazza, O.MISHIMA, P.Netz, A.NILSSON**, L.G.Pettersson**, P.H.Poole, P.J.Rossky, R. Sadr, S. Sastry, A. Scala, D. Schlesinger, F. Sciortino, A. Skibinsky, E. Strekalova, F.W.Starr, K.C. Stokely,Z Su, J.TEIXEIRA, K. T. Wikfeldt, L.Xu**, M.Yamada, Z. Yan, YANG ZHANG**

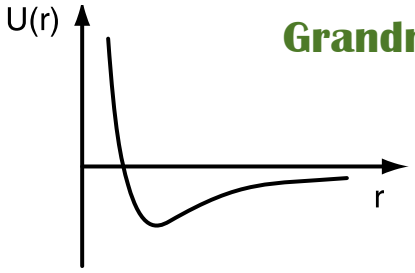
Question: Water is a prototype complex liquid: simple at first sight but 72 anomalies...**can liquid-liquid phase transition hypothesis offer a conceptual framework?**

TAKE-HOME MESSAGE

1. What matters: TWO characteristic length/energy scales
2. Widom line: a "smoking gun" for L-L critical point: ~228K,~1kbar
3. "protein" "glass" "transition" NOT protein, NOT glass, & NOT even a transition! Rather is crossover in water structure at Widom line.

QUESTION: Under what conditions a L-L phase transition?

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

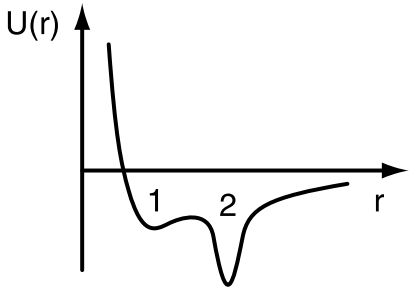


Grandma: "How does a liquid know to condense?"

(a)

Q: How can a liquid exist in 1 phase???

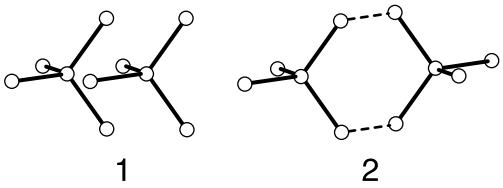
ex: Lennard-Jones: 1 length scale, 1 liquid



(b)

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

ex: 2 wells => 2 length scales => 2 liquids

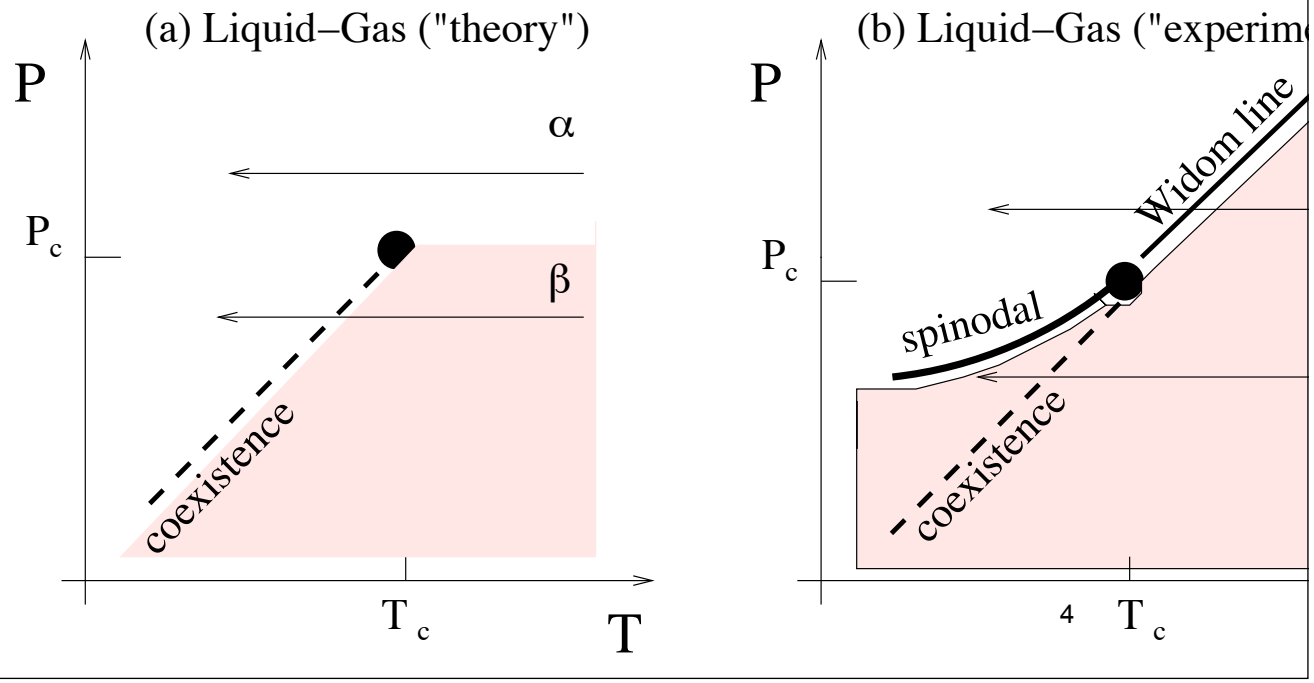


(c) LOCAL geometry for each well

Q: TESTING IF THERE IS A LIQUID LIQUID TRANSITION??

concept of a "critical region"....up to 2T_c

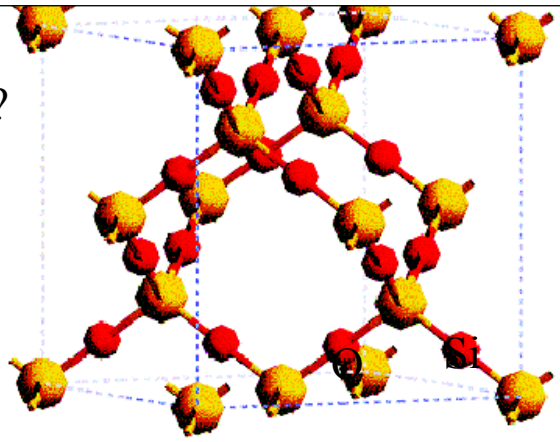
Near T_c : response functions (compressibility., specific heat, thermal.expansion) are proportional to correlation length to some power. Hence all 3 functions have maxima at the Widom line.



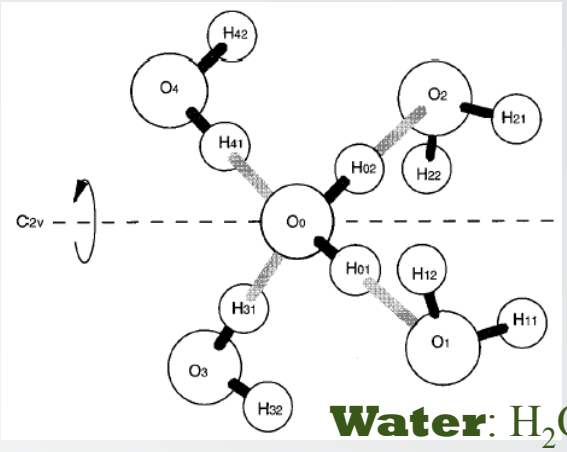
***TEST #1: Other Liquids with Local Tetrahedral Symmetry???

Three ubiquitous substances have in common local tetrahedral structure and hence **TWO** length scales in their interaction potentials.

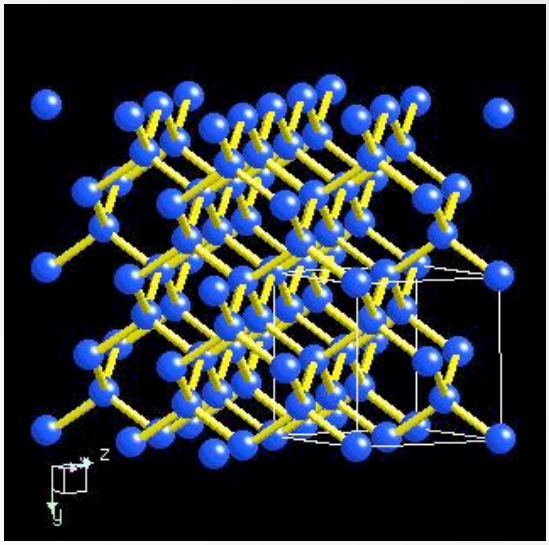
Q: Do all 3 show a liquid-liquid transition?



Silica (Lascaris ...): SiO_2

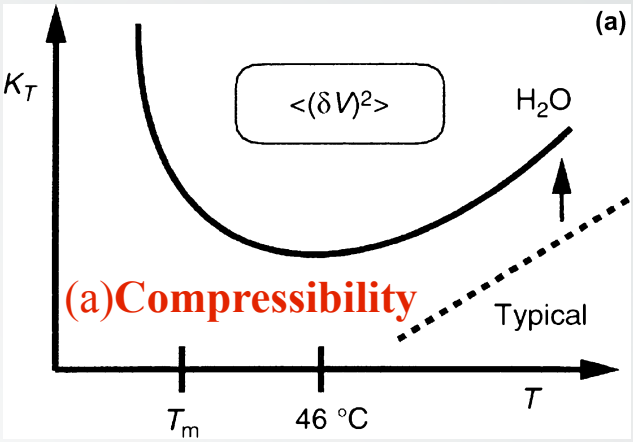


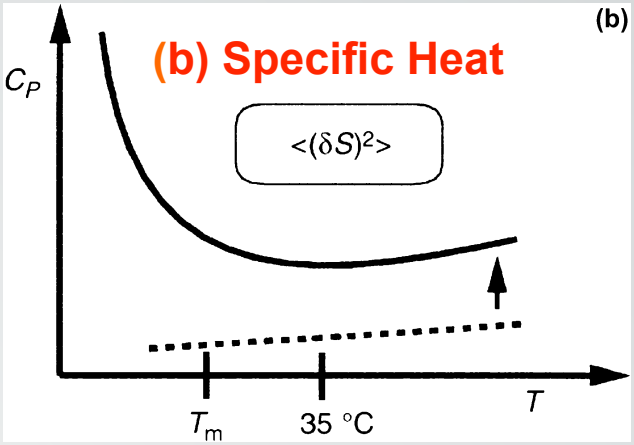
Water: H_2O

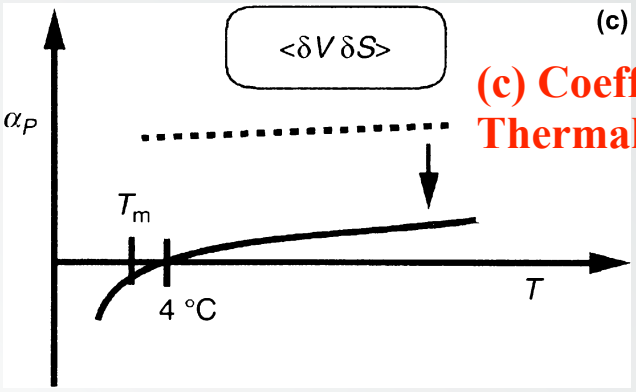


Silicon: Si (Sastry,Widom.Beye)

***TEST # 2: Thermodynamic response functions quantify fluctuations







Q: Is apparent singularity about -45 C the Widom line **???**

Test #3 (Sim):

SIMULATIONS: ST2,TIP4P, TIP5P,SPC,TIP4P2005)

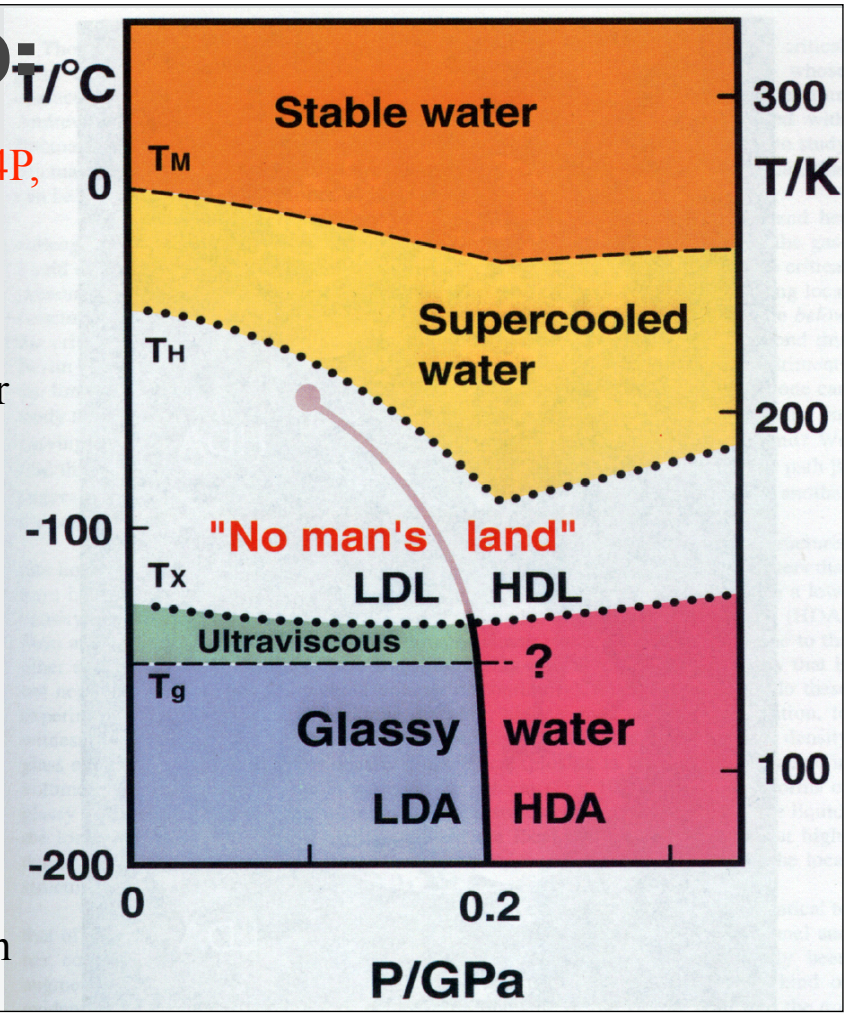
ex:2718 state points in PT plane (Poole et al 2005) each studied for 1728 water "molecules" (ST2), others: TIP5p,SPC,TIP4p/2005...)

RESULTS:

(a) Line of L-L phase transitions (LLPT line)

(b) Terminates @ L-L Critical Point (LLCP)

(c) Extends to glassy region



QUESTION: Expeimental Tests of Water Polymorphism???

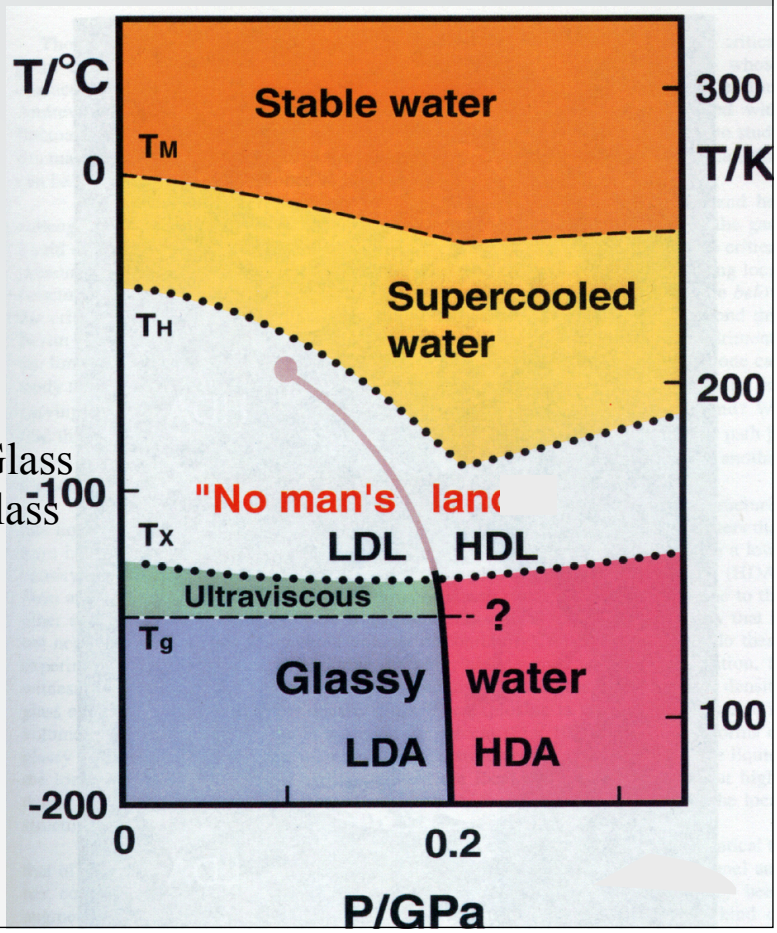
Exptl.Test #4:

Poole et al 1992 predict:
2 kinds of glassy water,
separated by 1. order ph tr.
Experiments 2 years later:
Mishima 1994 (2 + 1992)

LDA: Low-Density Amorph .Glass
HDA: High-Density Amoph Glass
****

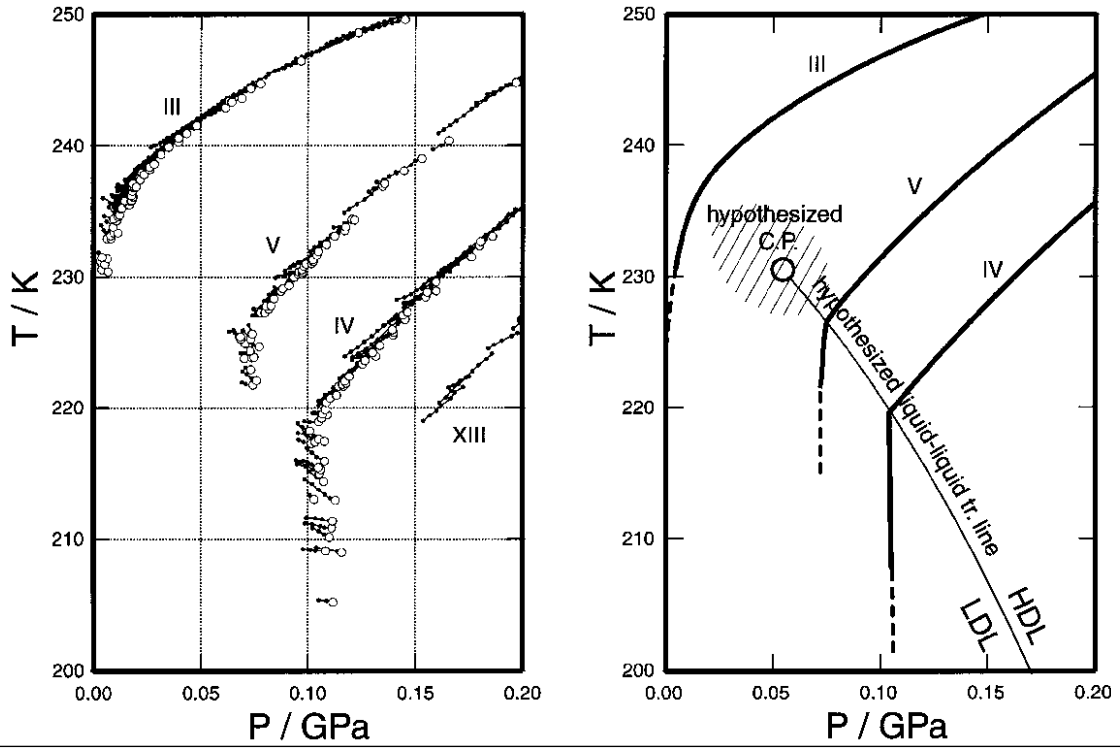
LDL: Low-Density Liquid
HDL: High-Density Liquid
****

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



Exptl test #5: Water Polymorphism

Melting ice polymorphs: Mishima/HES Nature98



Exptl. Test #6:

V = dG/dP

EXPERIMENTAL V(P,T) Equation of State

How?

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).

O.MISHIMA/ HES

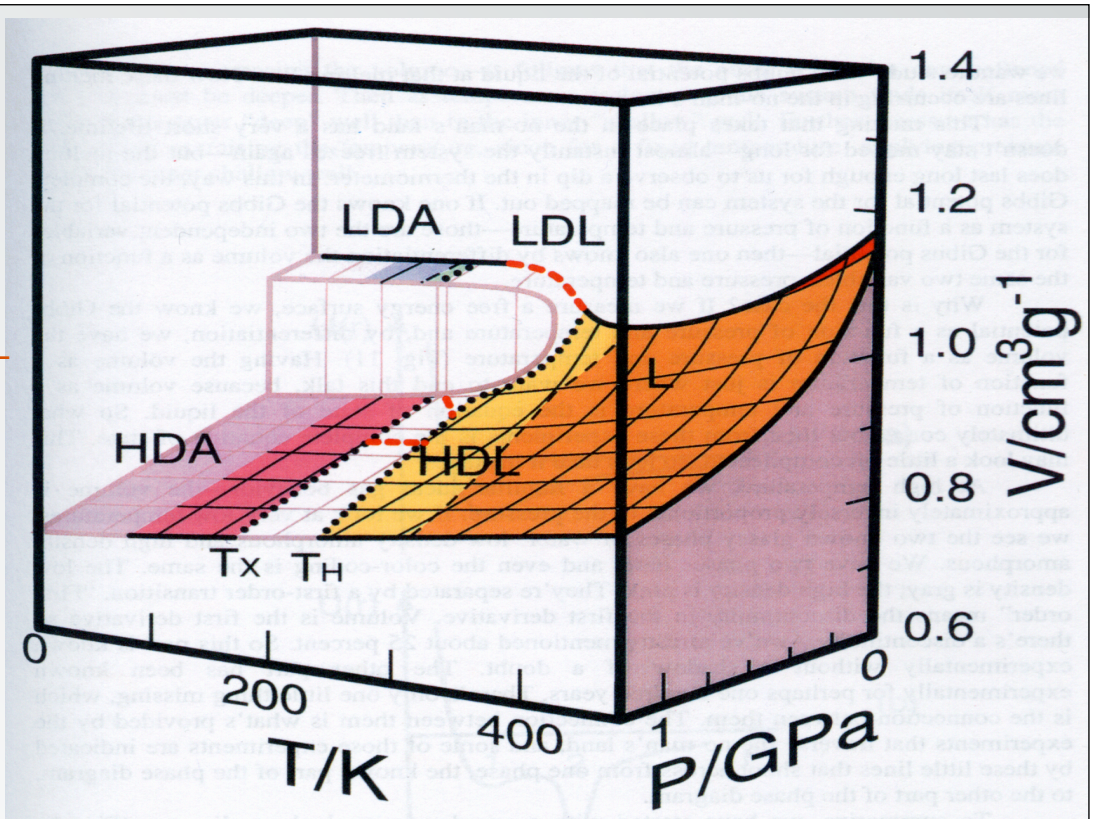
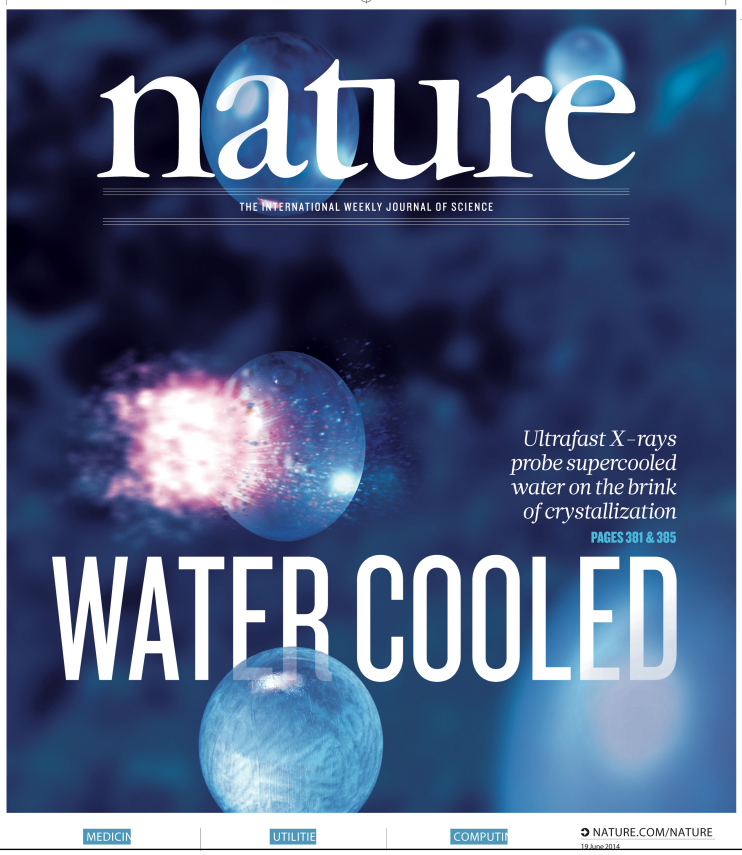


Figure 11: Experimentally-derived [56] thermodynamics equation of state V=V(P,T), using the same color coding as in Figs. 1 and 9. The specific volumes of the amorphous phases are known for the region below T_X [6]. Solid lines are the specific volume along the melting lines of ice IV and XIV. The high-temperature 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.

Exptl test #7:

BIG REMAINING CHALLENGE: How to enter "no-man's land" (below -38 C)???

ANSWER #1: NILSSON, PETTERSSON,... shooting at falling drops



Artist's perspective

A 12 μm droplet falls in vacuum and is hit by the 3 μm x-ray pulse generated by the 1 km long FEL…

Exptl test #8:

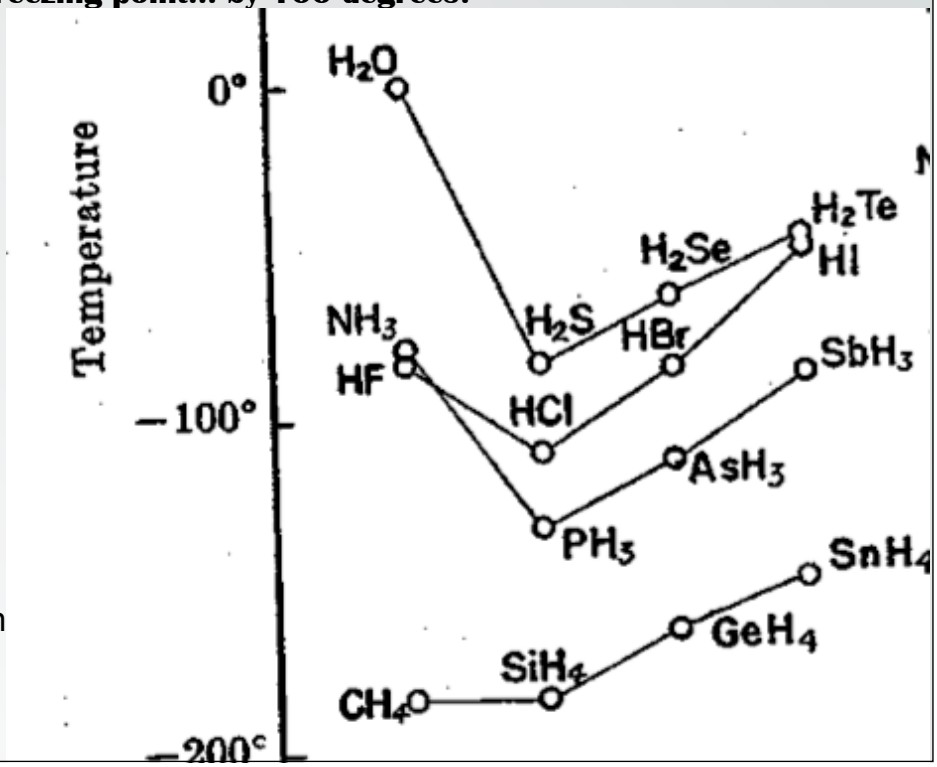
BIG REMAINING CHALLENGE: How to enter "no-man's land" (below -38 C)???

ANSWER #2: Study 64-year old Bible: Linus Pauling,"General Chemistry"1947."NANOCONFINEMENT" distorts water's "perfect" hydrogen bond network. **lowers freezing point... by 100 degrees!**

Linus Pauling 1947:
"Water would freeze about -100 Celcius IF water posessed no H bonds"

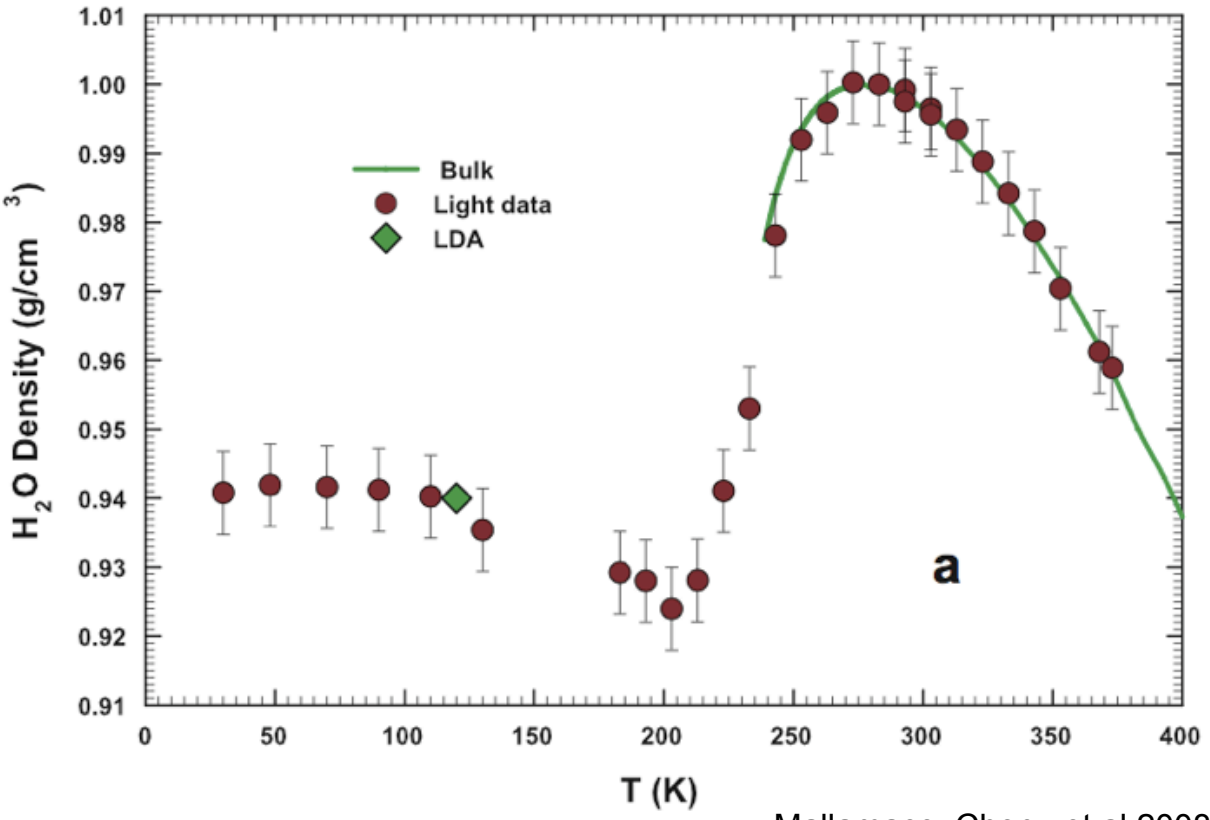
WORRY:
Does nanoconfinment destroy cooperative interactions also?

ANSWER:
NO! Nanoconfinement Destroys phase transition ONLY after correlation length = pore size.



Exptl. Test #9 (confined water = bulk?)

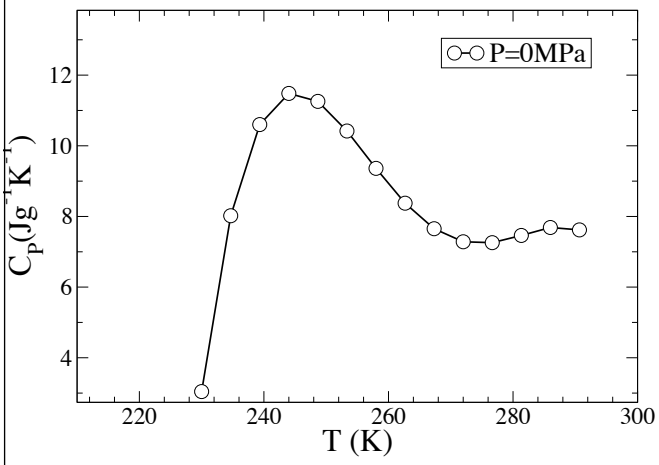
Thermodynamic anomalies & the Widom temp.: bulk water vs. confined "water":



Mallamace, Chen, et al 2008 PNAS

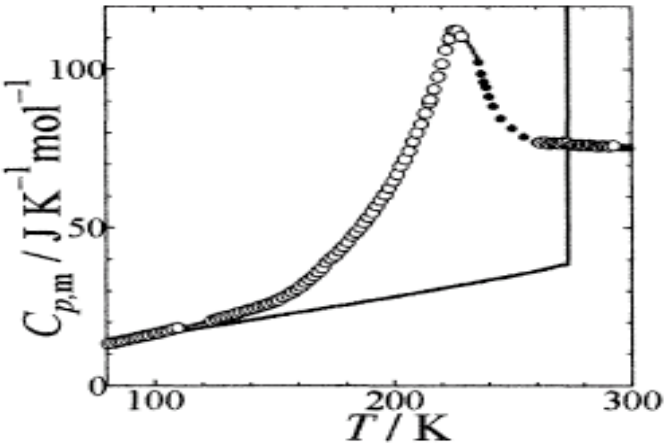
Expt'l Test #10: Also Specific heat peak (entropy fluctuations) locates Widom line: Simulations consistent with Oguni specific heat experiments

TIP5P **Simulation** [[Boston]]



L. Xu, P. Kumar, S.V. Buldyrev, S.H. Chen, P.H. Poole, F. Sciortino, HES, *PNAS* ***102****,16558* (2005).

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

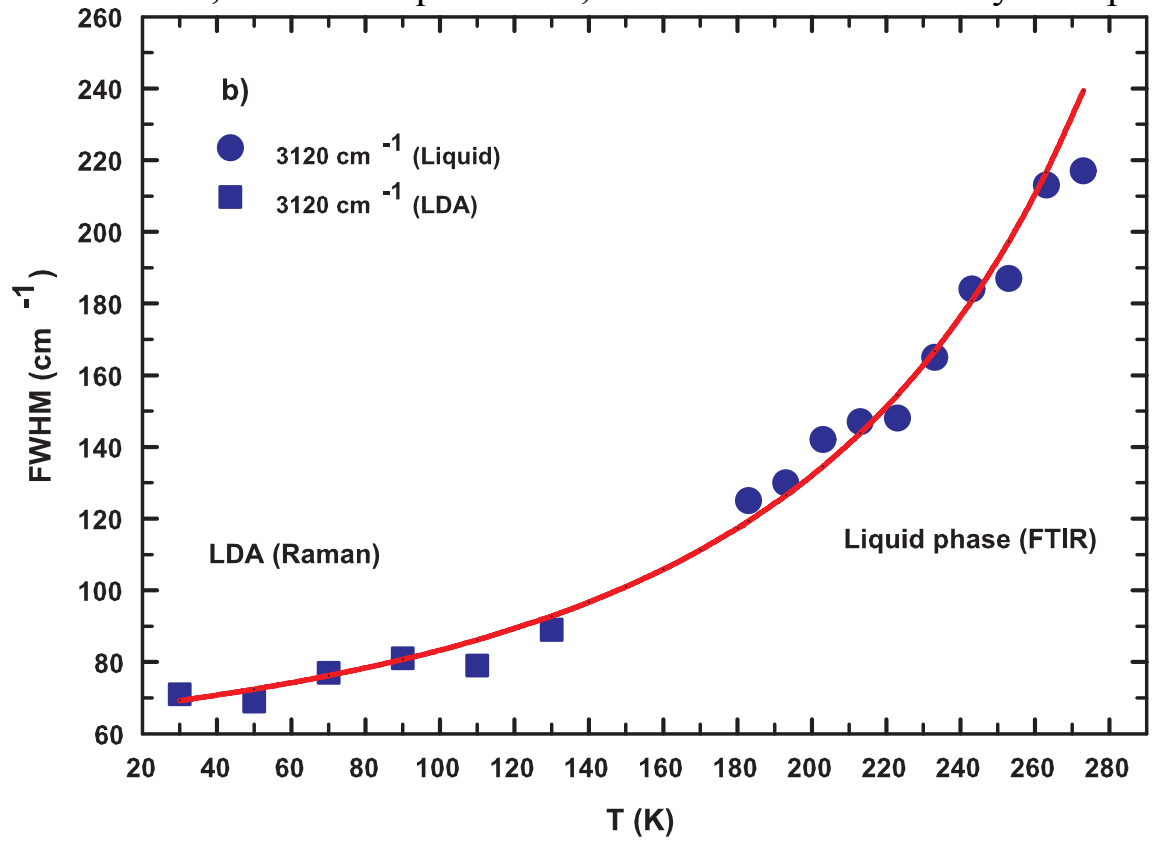


S. Maruyama, K. Wakabayashi, **M. OGUNI** "Thermal Properties of Supercooled Water Confined within Silica Gel Pores," AIP conference proceedings 708, 67 (2004)).

Experimental Test #11:

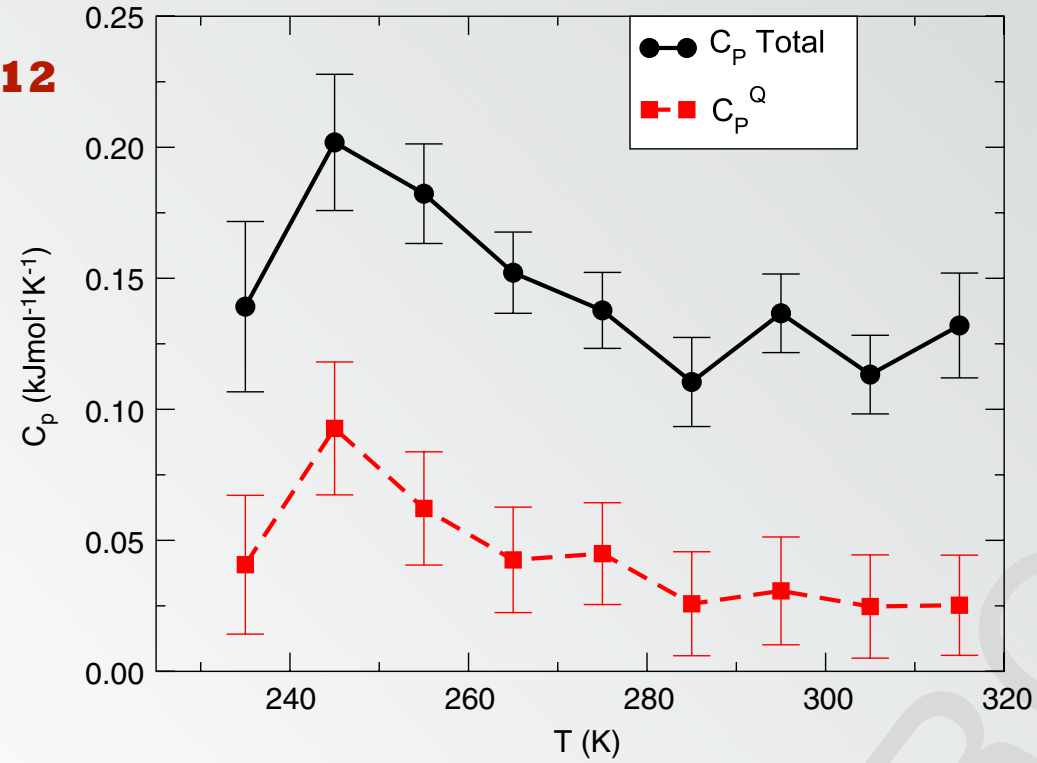
Q: Is room-T water continuous with low-density amorphous solid water?

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



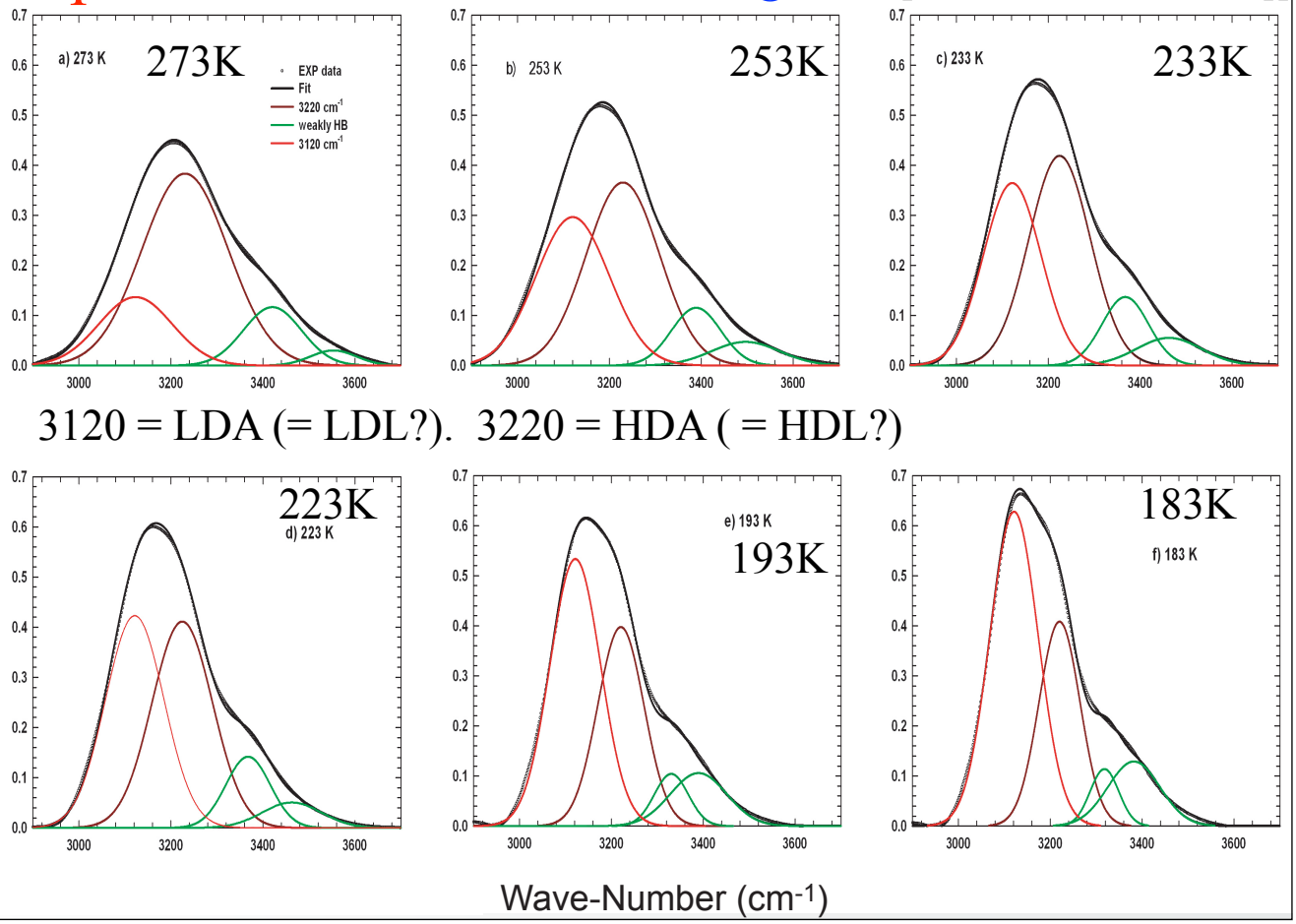
Temp.derivative of orientational order is contribution to specific heat from the orientational part of entropy. Also peaks at Widom line.

TEST #12



Kumar-Stanley, PNAS 2009

Exptl Test #13: Cross Widom line @225 K[Mallamace-Chen07]]

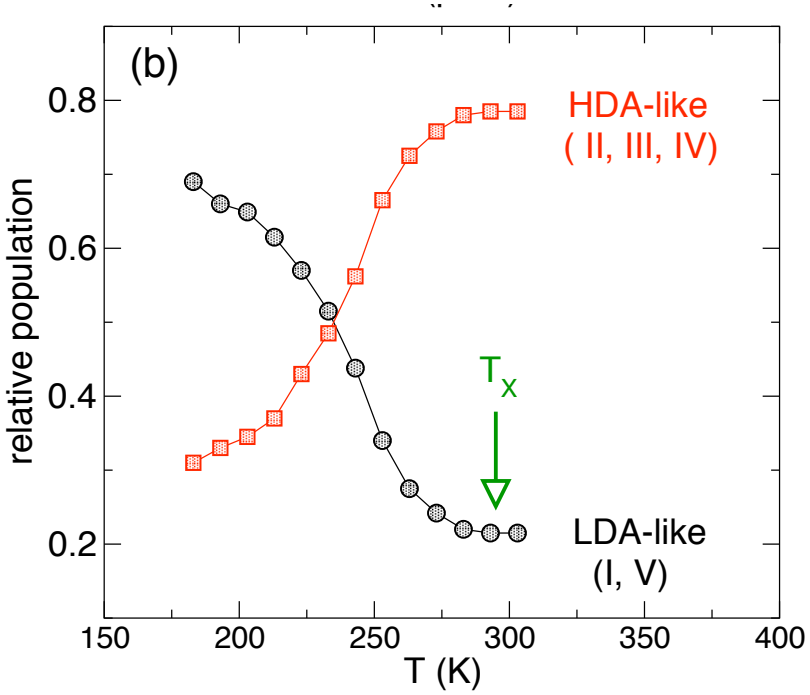


3120 = LDA (= LDL?). 3220 = HDA (= HDL?)

Wave-Number (cm^{-1})

Onset Temp of Breakdown: possible structural interpretation
namely when the LDL starts to condense out of the HDL

Exptl. Test #14:
Analysis of Mallamace FTIR experiments for relative populations of LDL vs HDL local structures

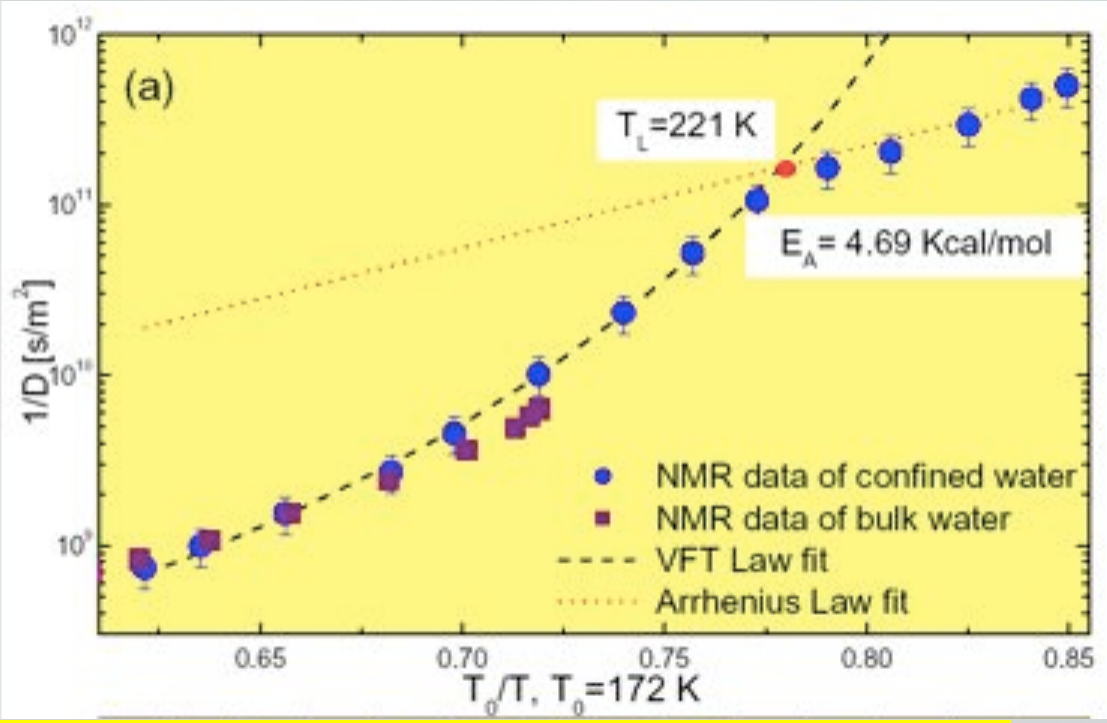


Xu,Mallamace,Starr,Yan,Buldyrev,HES: Nature Physics 2009

Experimental TEST 15: Dynamic Anomaly: confined "water"

Q: WHAT MAKES CONFINED WATER DIFFERENT FROM WATER?

A. There is a dynamic crossover ("Fragile to Strong") near the Widom line



Mallamace/Chen/several gifted students & others: 2005-present

Fragile-to-Strong Crossover for Hydrated MCM-41-S-14

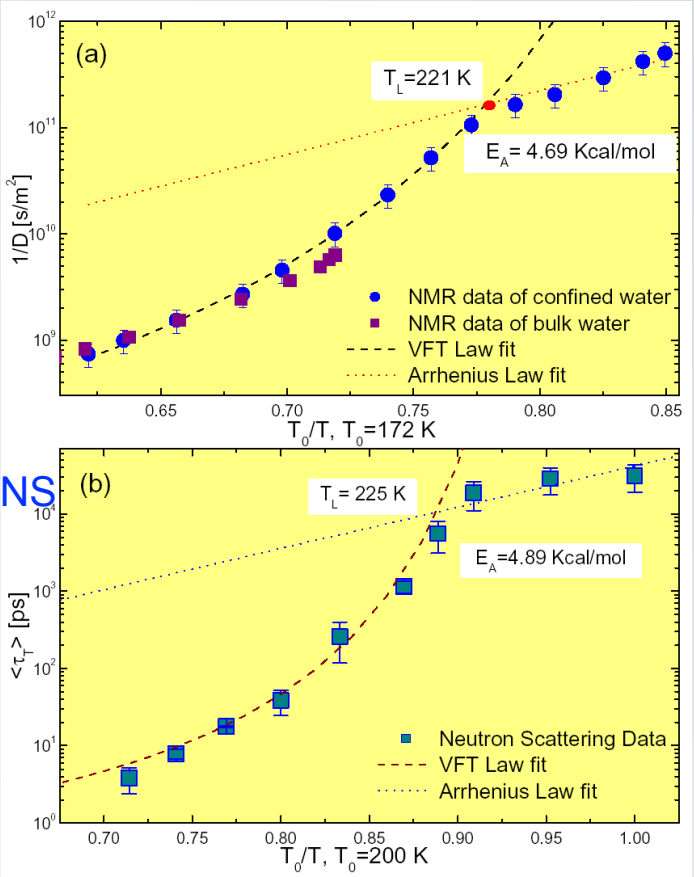
EXPT'L TEST 16: DIFFERENT MEASUREMENTS AGREE

Meas. #1: Self Diffusion by NMR

F. Mallamace *et al*., JCP (2006)

Meas. #2: α-relaxation time by QENS

A. Faraone et al, *JCP* **121**, 10843 (2004)

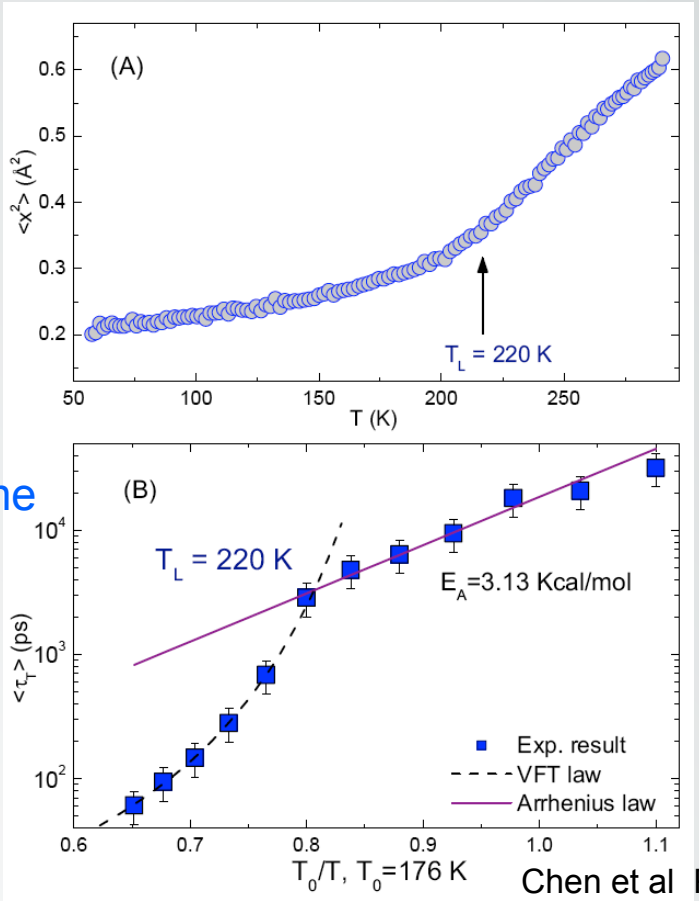


Experiments display dynamic crossover at 222 K in Protein Hydration Water

EXPTL TEST #17

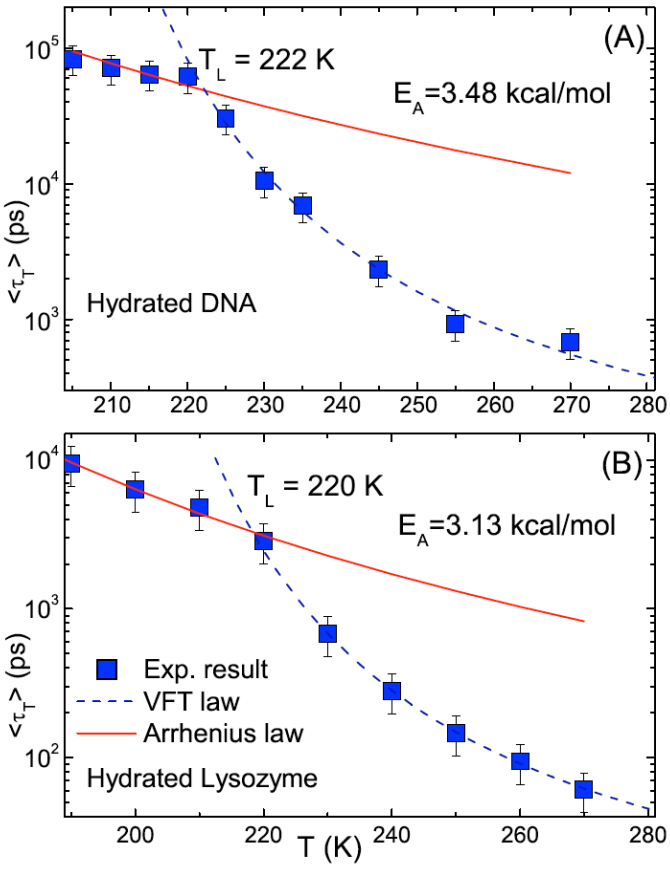
mean square displacement vs. temperature

log of characteristic time vs. inverse temperature



Chen et al PNAS

TEST #18: Compare FSC in DNA & in lysozyme hydration water



Comparison of the temperature dependence of the average translational relaxation times of hydration water:

(A) in hydrated DNA

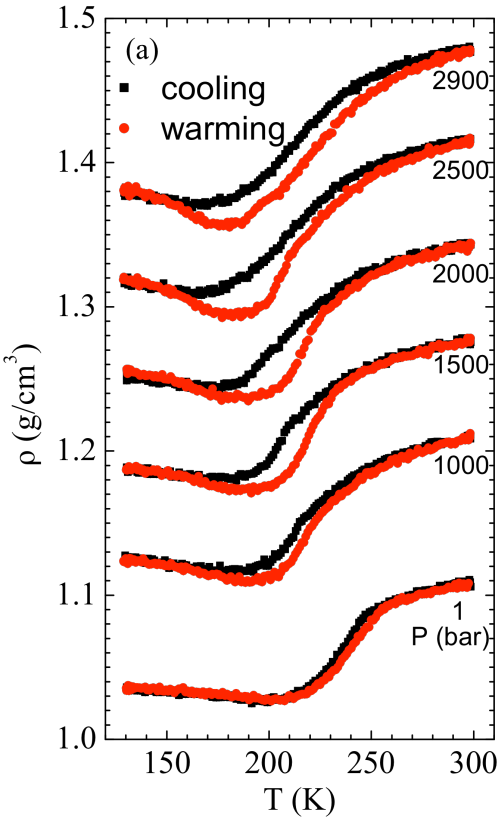
(B) in hydrated protein.

They both show a cusp-like dynamic crossover phenomenon at temperatures around 220 K. Dash line and solid line are VFT law and Arrehnius law fits respectively.

S.-H. Chen et al., "Experimental Evidence of Fragile-to-Strong Dynamic Crossover in DNA Hydration Water," preprint in http://arxiv.org/abs/cond-mat/0605314.

S.-H. Chen et al.,"Observation of fragile-to-strong dynamic crossover in protein hydration water", PNAS **103**, 9012-9016 (2006).

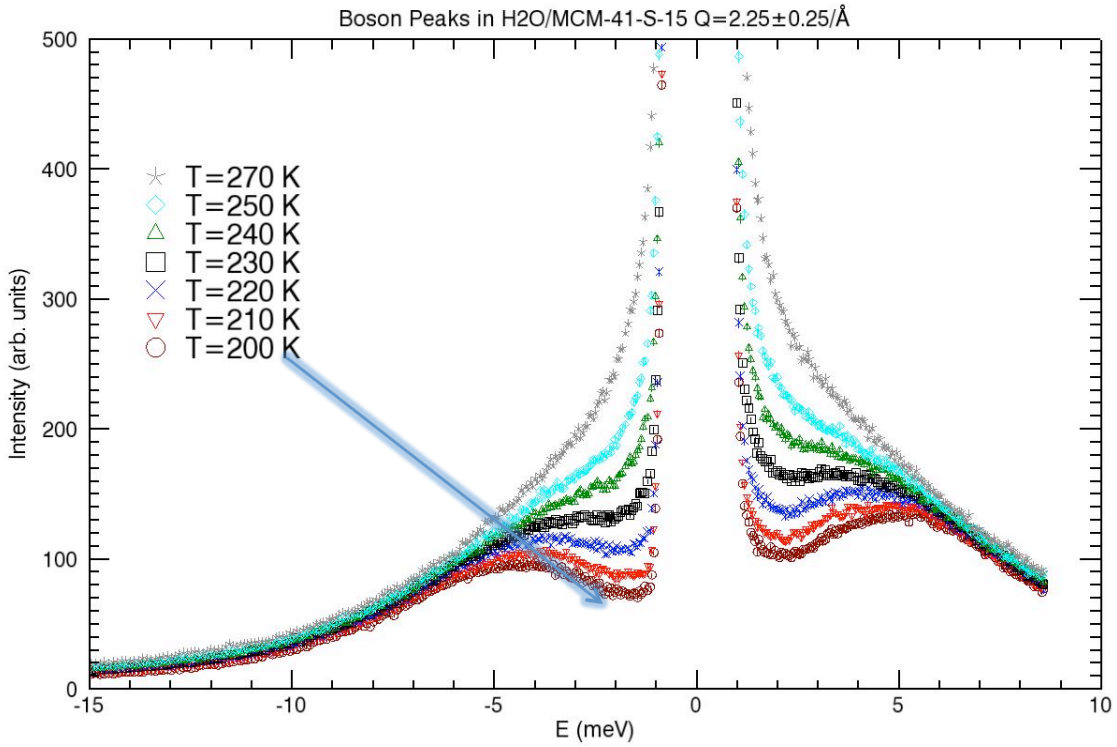
TEST 19: Evidence of 1st-order Liquid-Liquid Phase Trans.



Y Zhang, A Faraone, WA Kamitakahara, KH Liu, CY Mou, JB Leao, S Chang, SH Chen, PNAS 2011

+ Test #20: Boson Peak

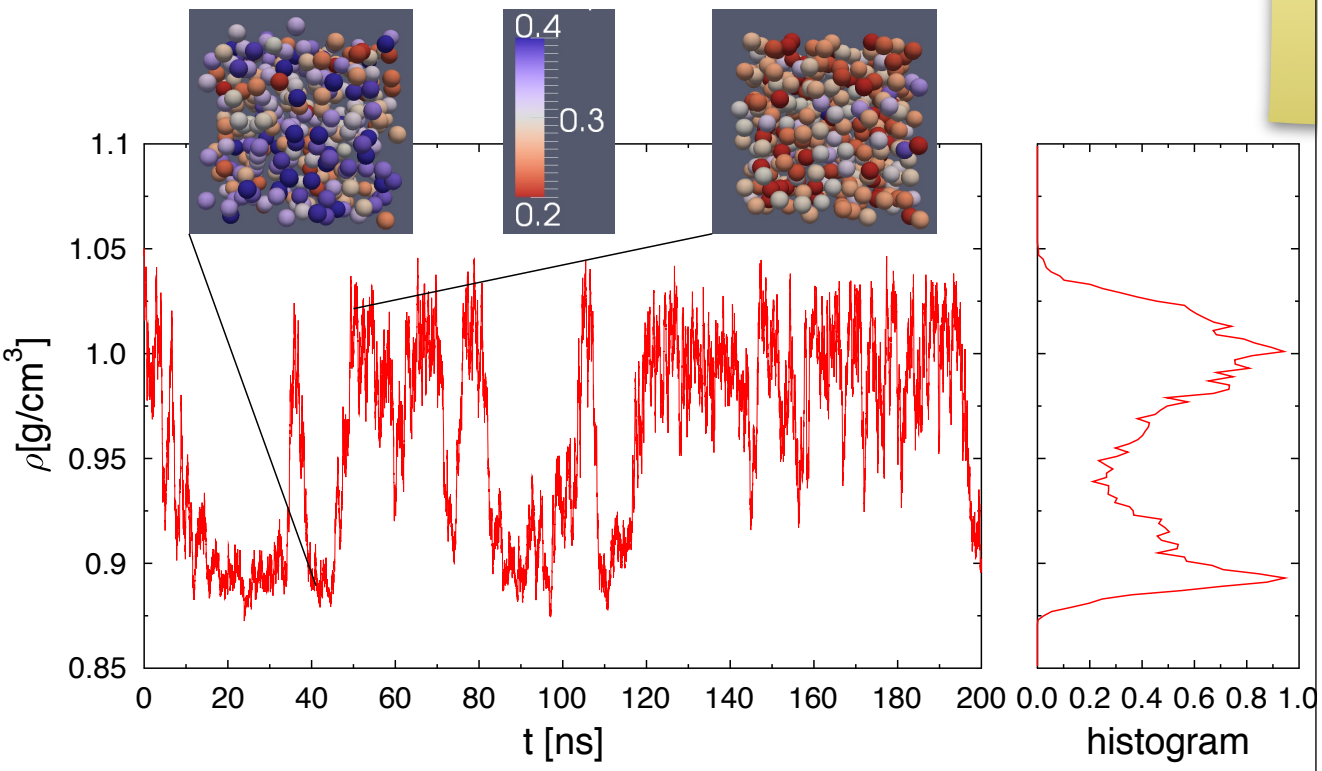
Y Zhang,etal, A Cupane et al.

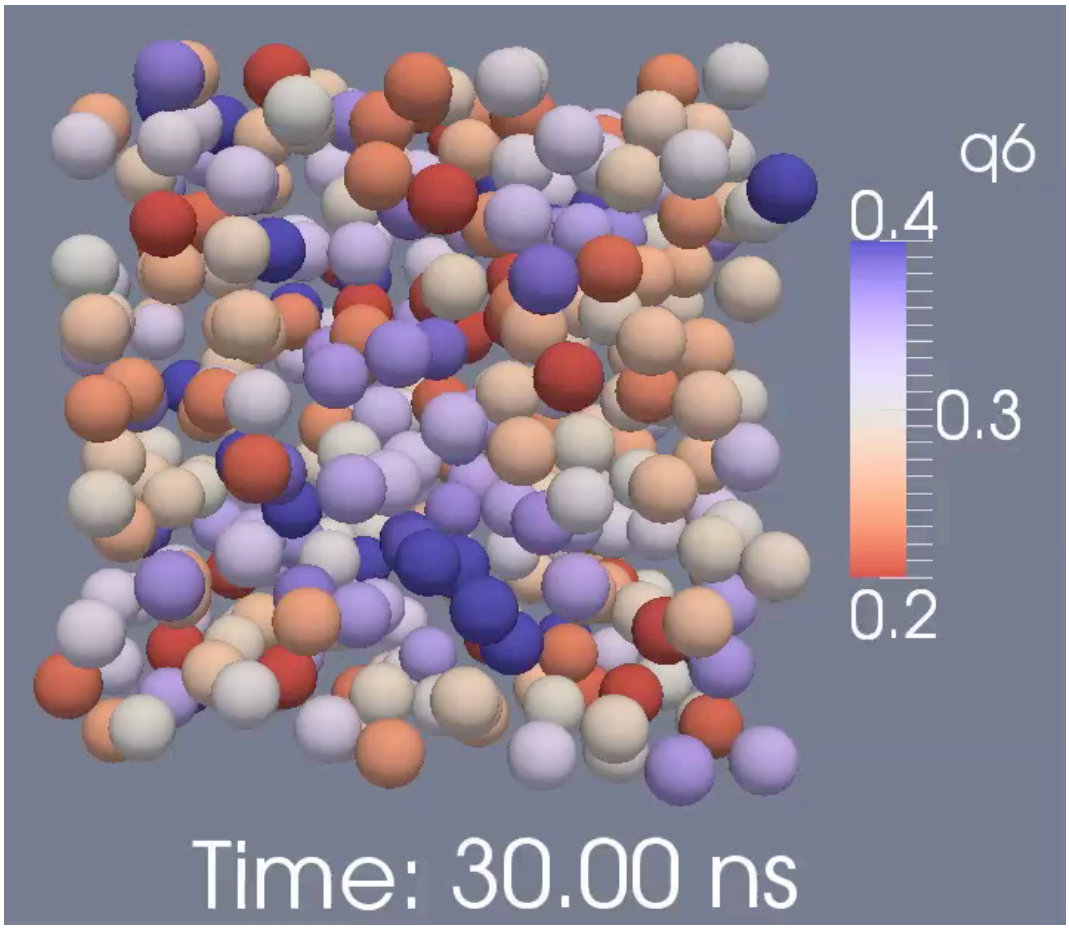


P. Kumar, K. T. Wikfeldt, D. Schlesinger, L. G. M. Pettersson, and H. E. Stanley, "The Boson Peak in Supercooled Water," Nature Sci. Rep. 3, 1980 (2013)

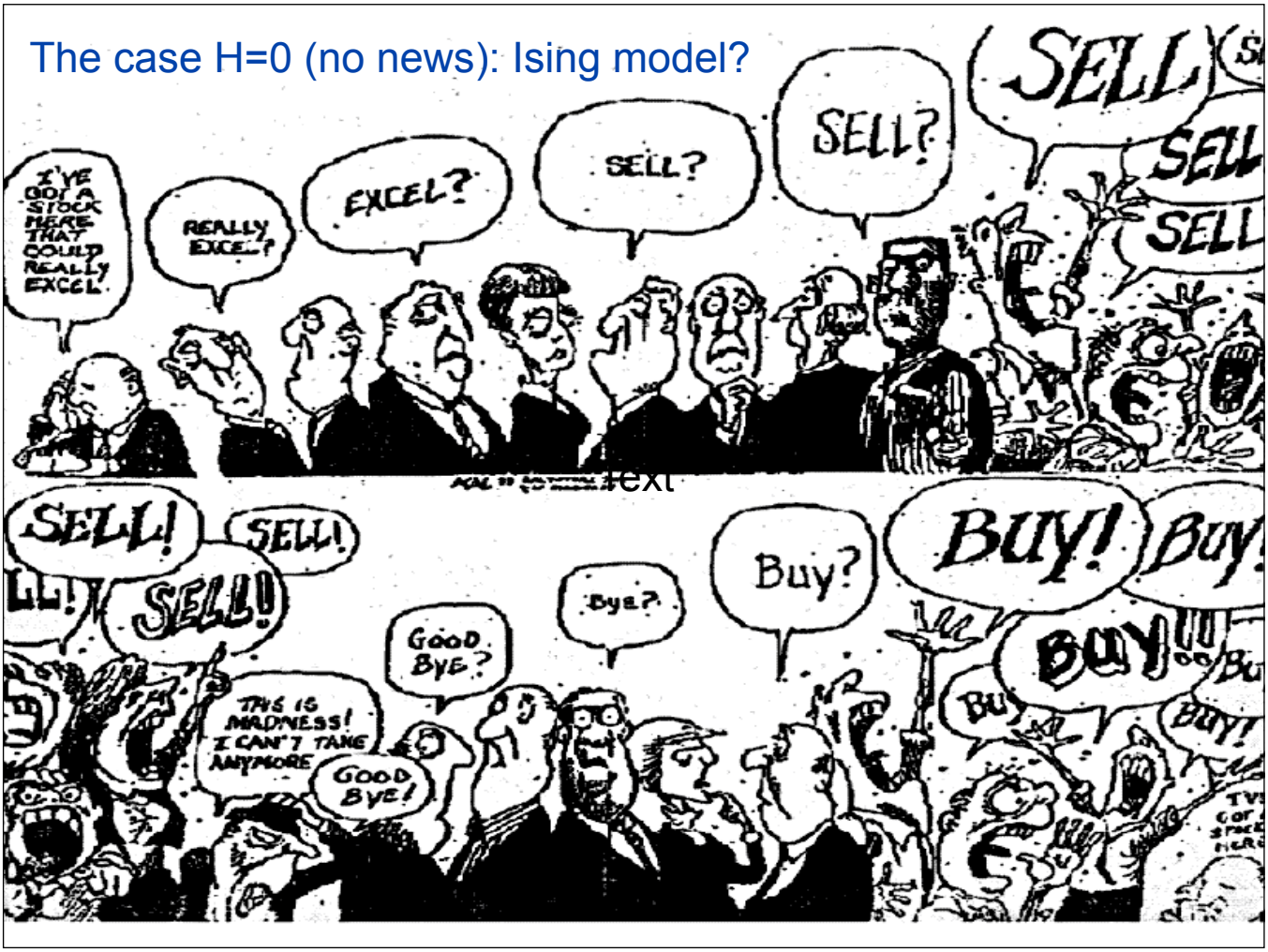
Test # 21: *time dep. for 1 state point near ph. trans. line:*

Kesselring,Lascaris, Franzese, Buldyrev, Herrmann,HES: Nature Sci.Rep.2012; JCP 2013




q6
0.4
0.3
0.2
Time: 30.00 ns

The case H=0 (no news): Ising model?



"How?" "Models?": Herd vs. News?

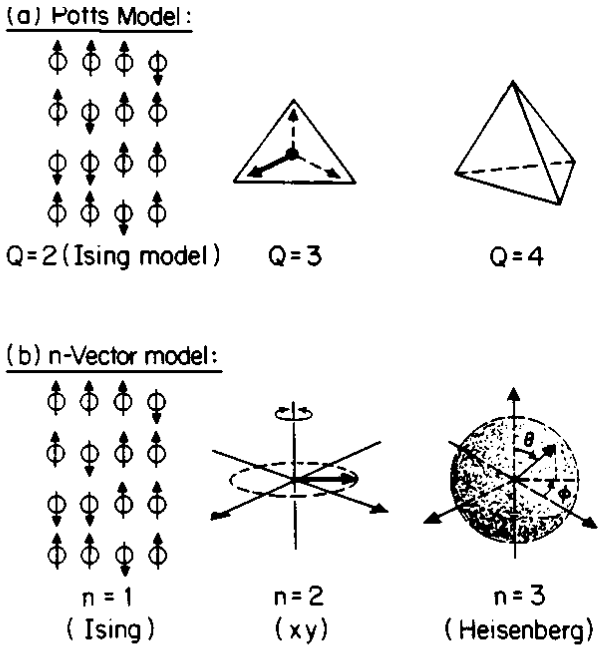
(1) "**herd** effect" (exchange int. J). (2) "**news** effect" (external field H)

Each stock is a unit, interacting with other stocks (units) and bathed in a magnetic field H (news). J depends on the two stocks, and H depends on the stock. Both can change with time.

Possible models:
(a) Units can be in Q different DISCRETE states: "Potts Model" (Potts 1952).

(b) n-dimensional units. Each can be in a CONTINUUM of states: "n-Vector Model" (HES 1969)

(c) ***modified Edwards-Anderson "spin glass"*** with TIME-dependent LONG-range interactions both signs



Can a law describe bubbles and crashes in financial markets?

Goal: every trade---msec level...

Tobias Preis [1,2] and H. Eugene Stanley [1]

Physics World, May 2011

DETAILS IN:

T. Preis, J. Schneider, HES``Switching Processes in Financial Markets," PNAS 108, 7674

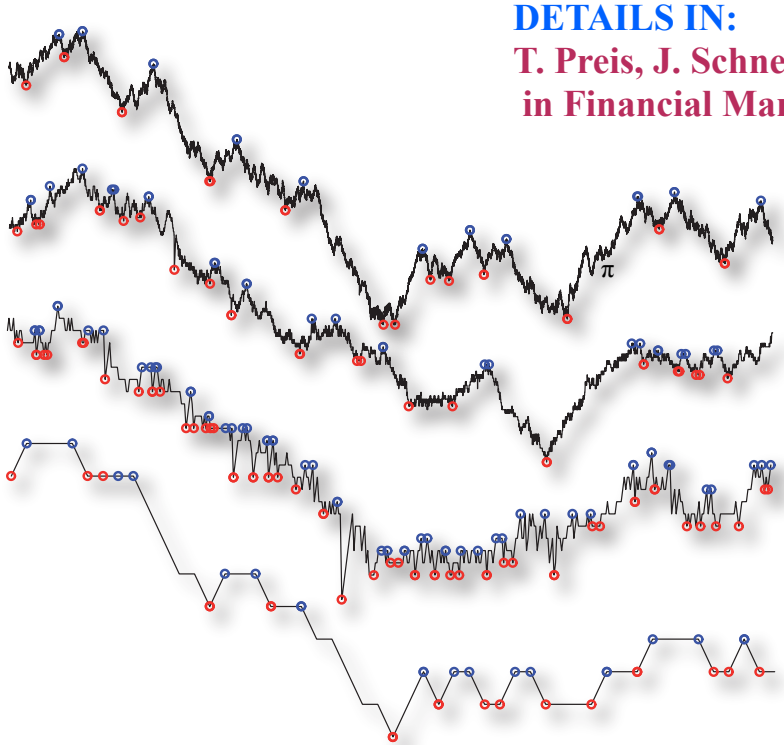
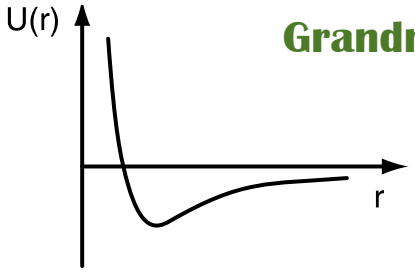


Figure 1 | Scale-free behavior of financial market fluctuations. Financial market time series feature identical properties on very different time scales. All four curves are subsets of a 14 million transactions dataset taken from a German DAX future time series. The price curves cover time periods of roughly 1 day (top curve), 1 hour, 10 minutes, and 1 minute (bottom curve). Local maximum and minimum values are marked as blue and red circles.

QUESTION: Under what conditions a L-L phase transition?

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

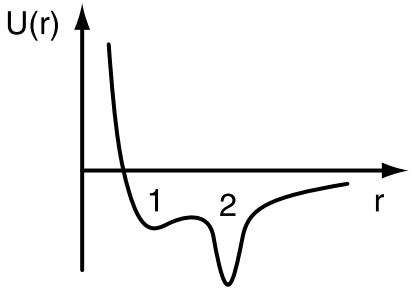


Grandma: "How does a liquid know to condense?"

(a)

Q: How can a liquid exist in 1 phase???

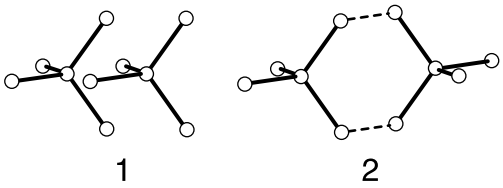
ex: Lennard-Jones: 1 length scale, 1 liquid



(b)

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

ex: 2 wells => 2 length scales => 2 liquids



(c) LOCAL geometry for each well

"SCIENTIFIC CHALLENGE":

Limmer/Chandler: JCP 2011,2013

- On the "imagined" L-L Phase Transition

"This paper reports the results of a numerical study aimed at elucidating the purported [1, 2] liquid-liquid phase transition in supercooled liquid water. The results indicate that this **imagined polyamorphism does not exist** in atomistic models of water."

Responses:

Palmer, Liu,Car, Debenedetti,.... Nature
Poole/Sciortino: PCCP, JCP
Gallo/Sciortino: PRL
Kesselring/Lascaris/Franzese/Buldyrev/Herrmann/Stanley:
Nature Scientific Reports 2012, JCP 2013