Cooperativity and scenarios for supercooled water

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- Giancarlo Franzese, Universitat de Barcelona
- Advisor: H. Eugene Stanley, BU

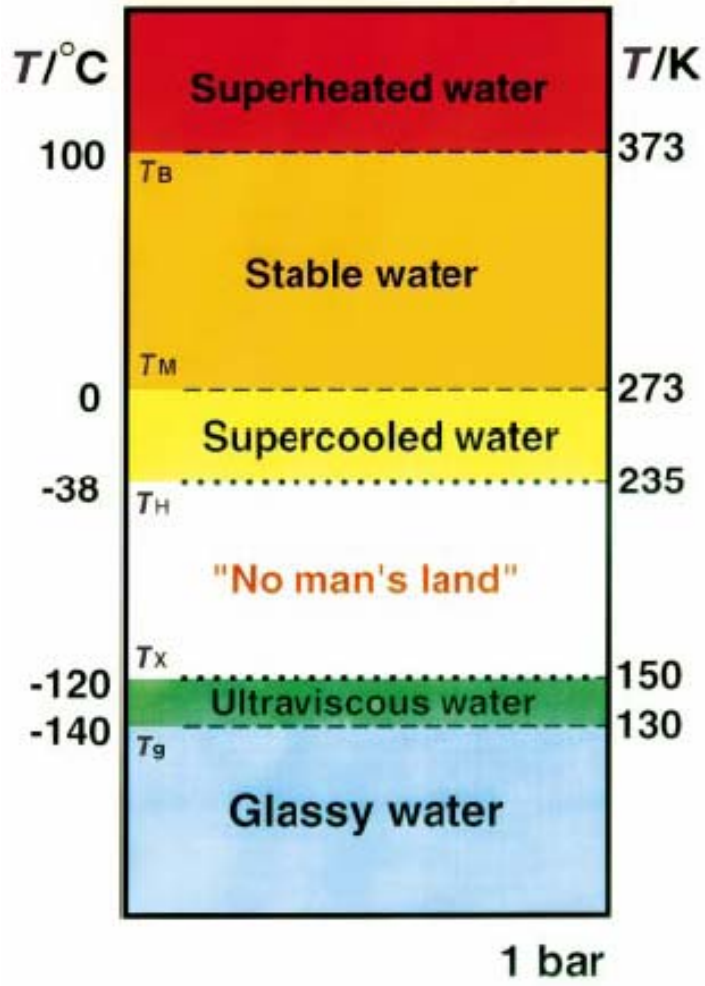
Physical Question:

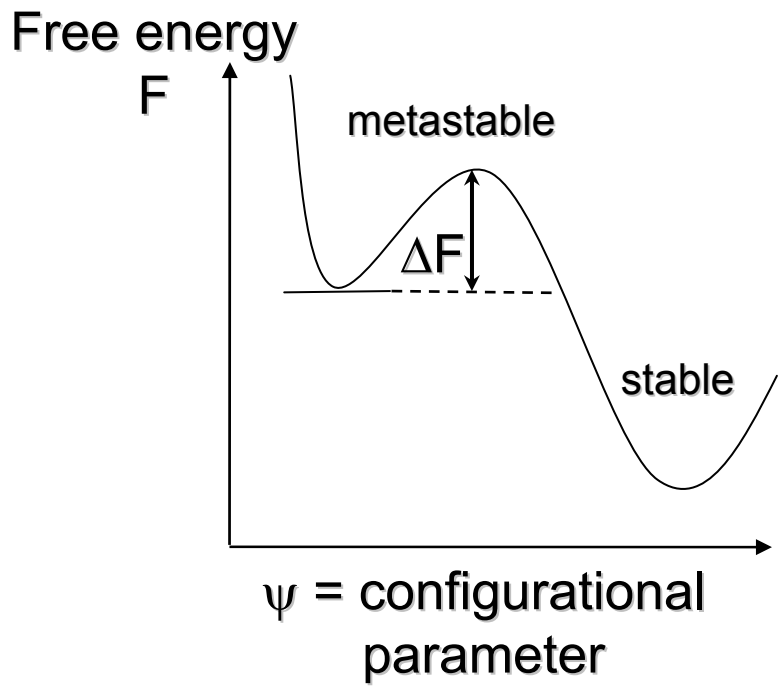
connection among 3 possible scenarios for water

two practical problems:

1. Need of fast simulations to explore extensively the phase diagram predicted by the different scenarios → simple model
2. Need of equilibrating to very low T → accelerated dynamics

1. MGM, K. Stokely, H.E. Stanley, G. Franzese, arXiv:0807.4267, ***Anomalous specific heat of supercooled water***.
2. MGM, K. Stokely, E.G. Strekalova, H.E. Stanley, G. Franzese, ***Cluster Monte Carlo and numerical mean field analysis for the water liquid--liquid phase transition,*** Comp. Phys. Comm. (in press), (arXiv:0810.4688).
3. K. Stokely, MGM, H.E. Stanley, G. Franzese, arXiv:0805.3468, ***Effect of hydrogen bond cooperativity on the behavior of water.***



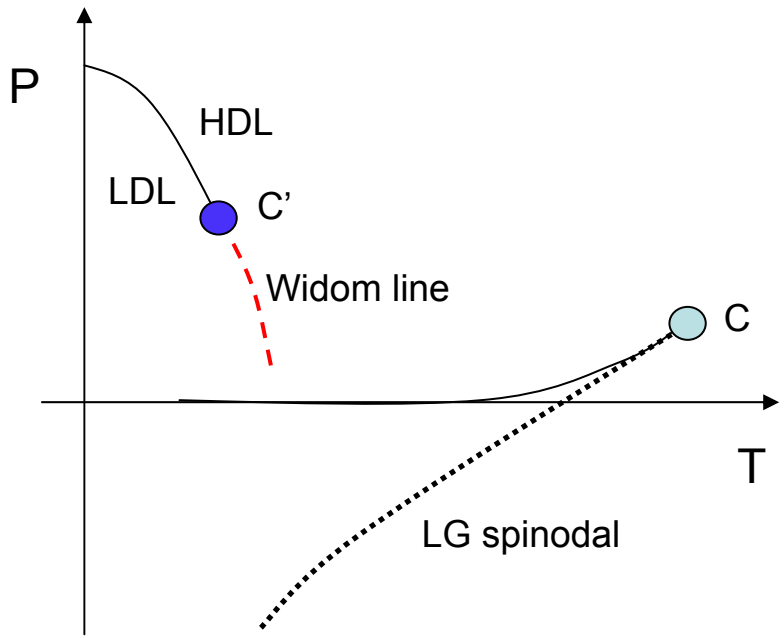


Supercooling is the process of cooling a liquid below its freezing point, without it becoming solid.

- Water is metastable because it cannot overcome the nucleation free energy barrier ΔF
- Upon cooling the energy barrier decreases, until $\Delta F \approx kT$, leading to homogeneous nucleation

First scenario: liquid-liquid critical point (LLCP)

From MD simulations Poole et al. (1992) found indication of a line of first-order phase transition between a low density liq. (LDL) and a high density liq. (HDL) terminating on a critical point (Poole *et al*. Nature 1992)



HDL: high density liq.

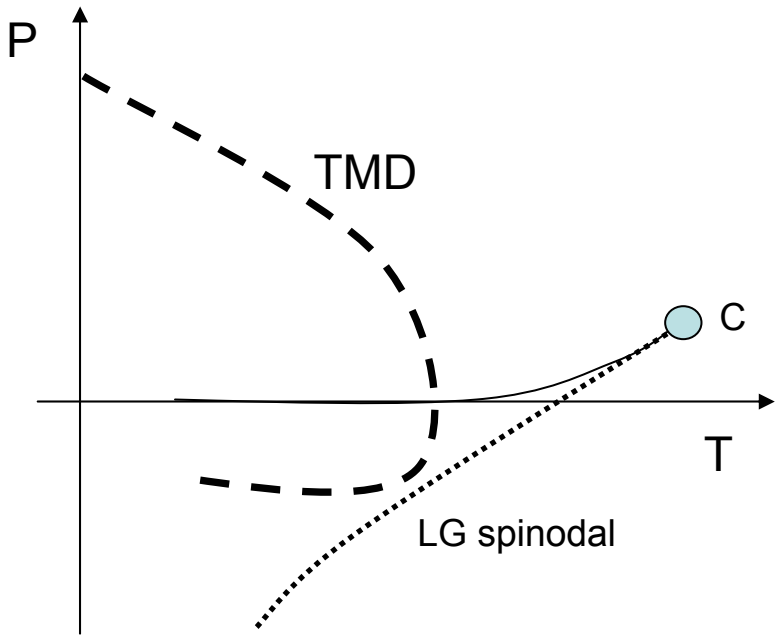
LDL: low density liq.

Widom line: locus of maximum correlation length ξ

Second scenario: Singularity free scenario (SF)

- TMD: locus of temperature where density is max

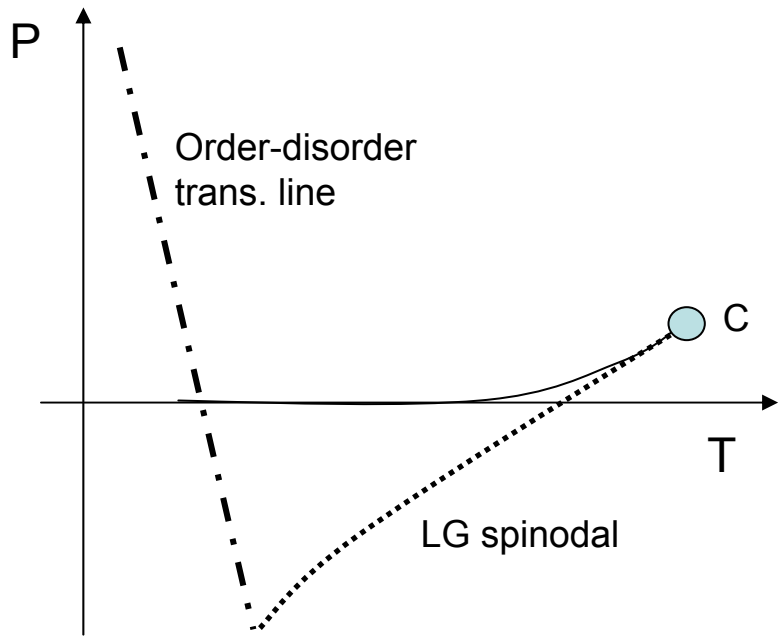
- When the TMD has negative slope in the (P-T) plane, K_T increases upon cooling without diverging



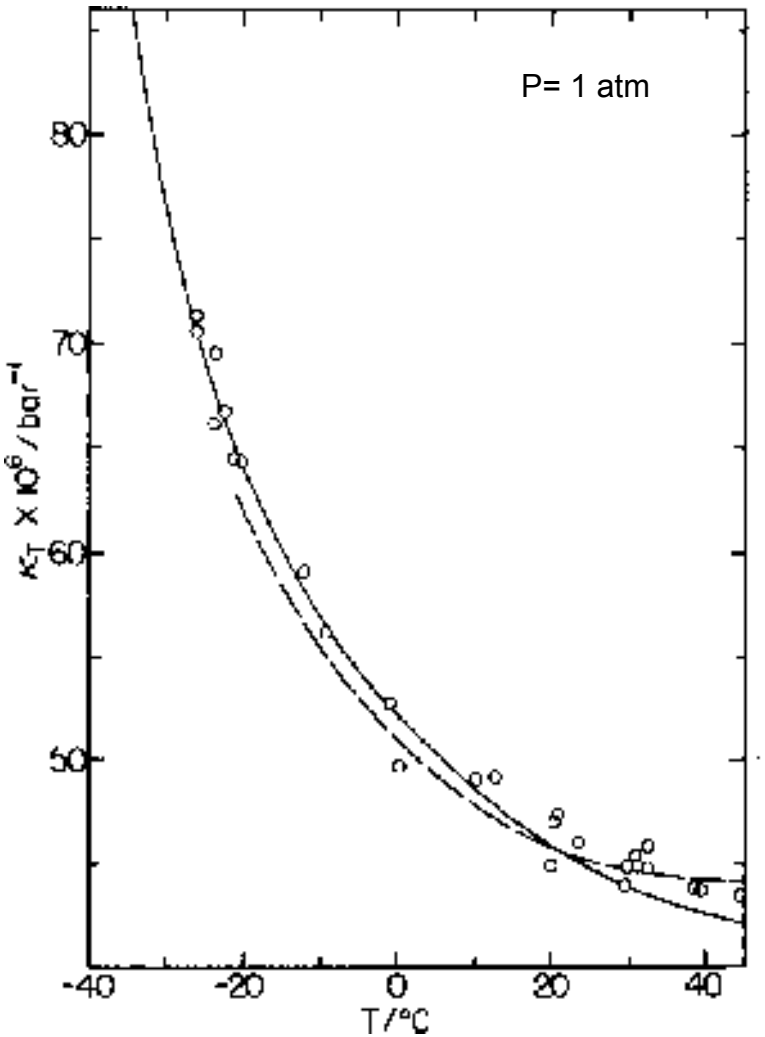
S. Sastry *et al*., Phys. Rev. E **53**, 6144 (1996)

Third scenario: Critical point-free (CPF)

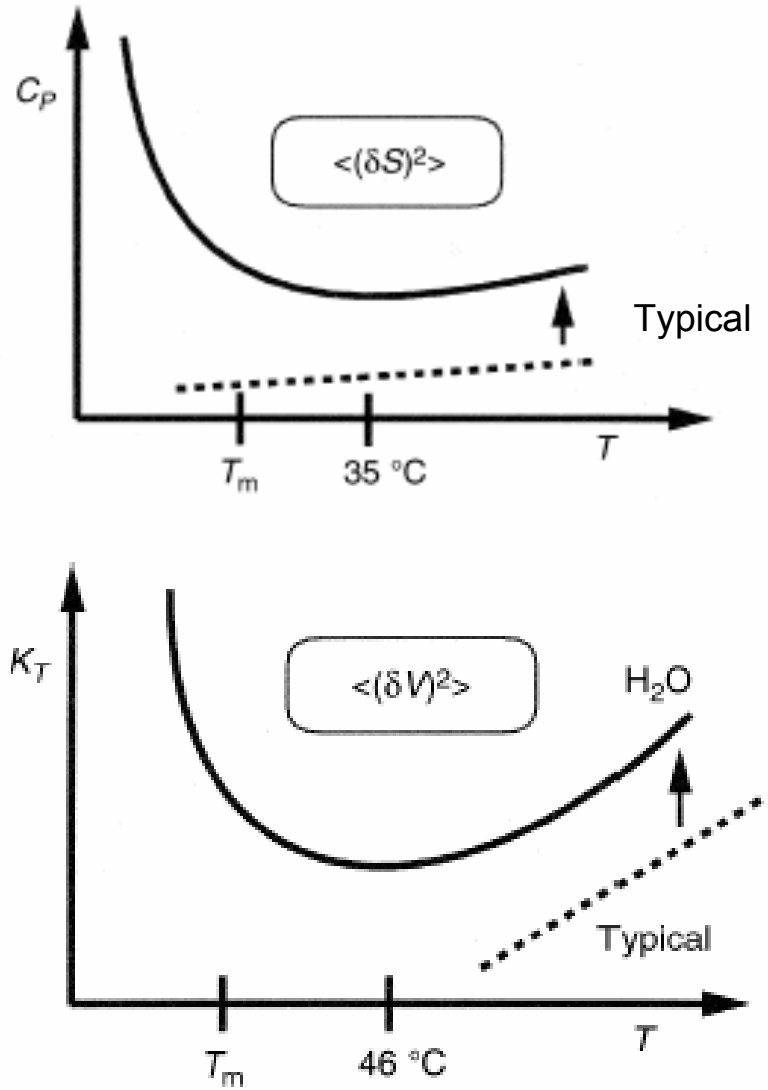
"order-disorder transition that occurs in the "anomalous regime," 150 to 250 K. This order-disorder transition, which may include some weak first-order character" C. Austen Angell, Science **319**, 582 (2008)



Motivation:

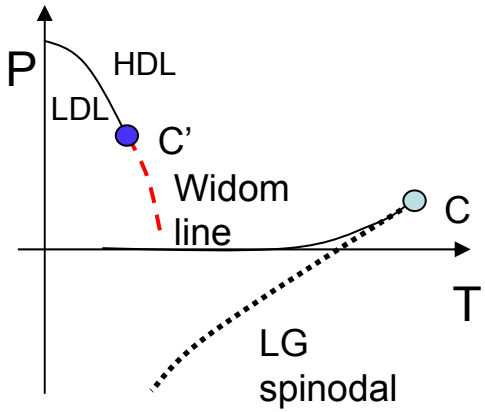


Exp. data from R.J. Speedy and C.A. Angell, (1976)



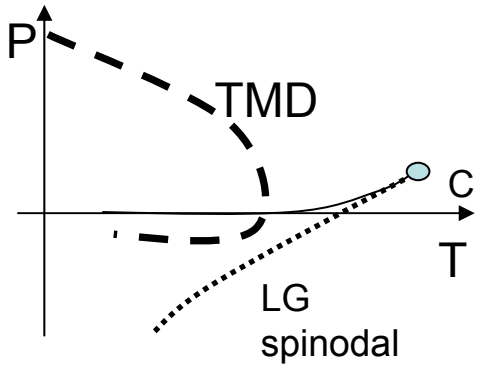
Large increase of the thermodynamic response functions

1. LLCP



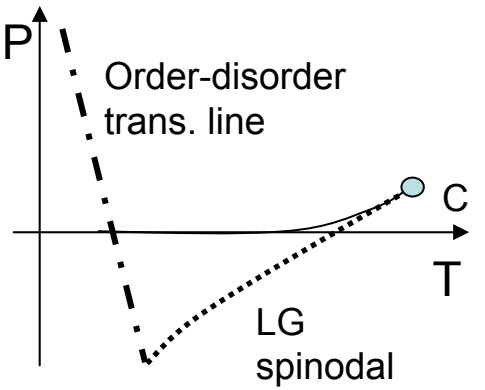
The anomalous increase of response functions is due to the Widom line (locus of corr. length maxima)

2. SF



The anomalous increase of response functions is due to the negative slope of TMD

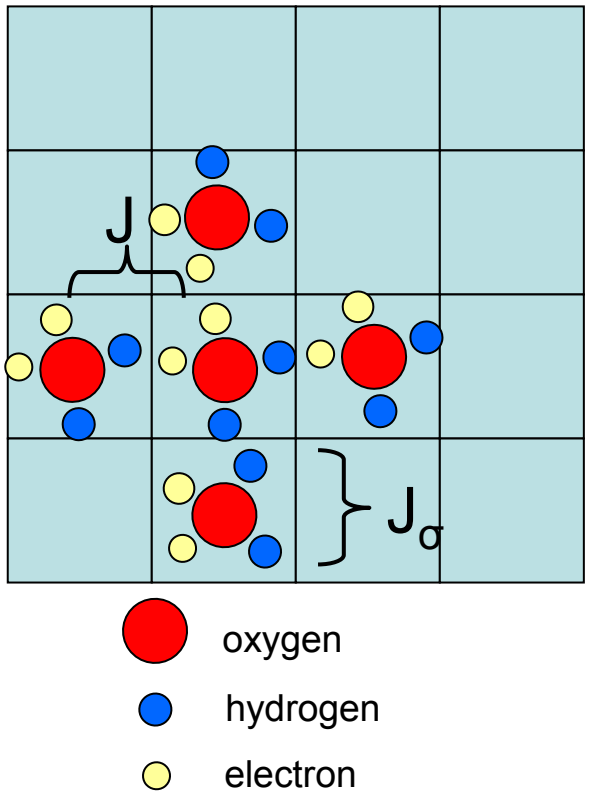
3. CPF



The anomalous increase of response functions is due to the presence of an order-disorder transit. line

What we did: Monte Carlo simulations of a cell model

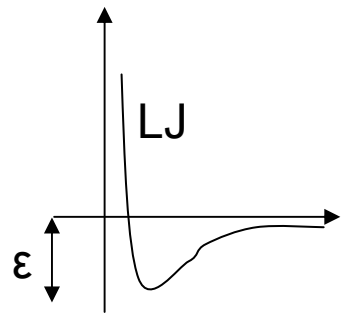
Necessity of a simple model to explore extensively the phase diagram



G. Franzese *et al.*, PRE 67, 011103 (2003)

- The fluid is divided into N cells
- One molecule per cell
- 4 first neighbors to bond
- the 4 arms of each molecule are treated as Potts variable

Interactions:



1. Lennard-Jones → ε>0
2. Molec. form H bonds → J>0
3. Molec. assume tetrahedral config. → $J_\sigma \geq 0$

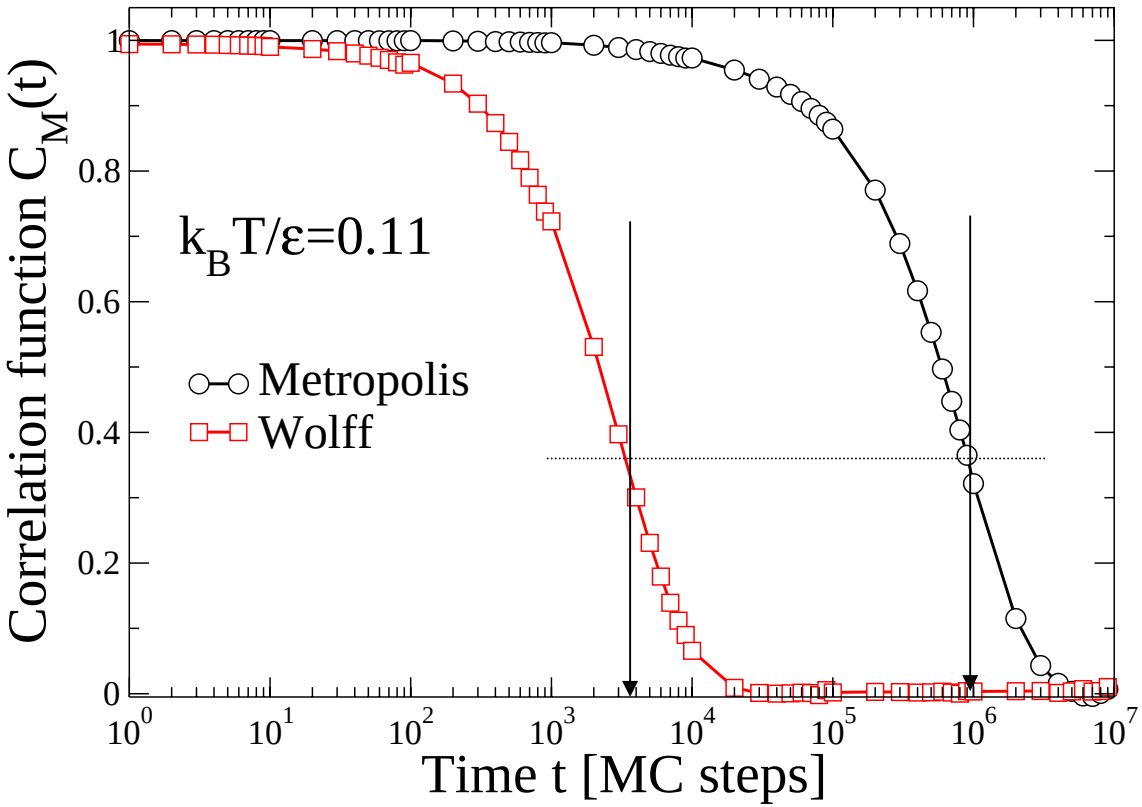
energy scales: $J_\sigma < J < \varepsilon$ ($\varepsilon \approx 0.6$ kJ/mol)

volume allowed to fluctuate: H bond format. leads to increase in volume

Cooperativity between H bonds corresponds to O-O-O correlation

How we did it:

using Wolff dynamics, to speed-up equilibration

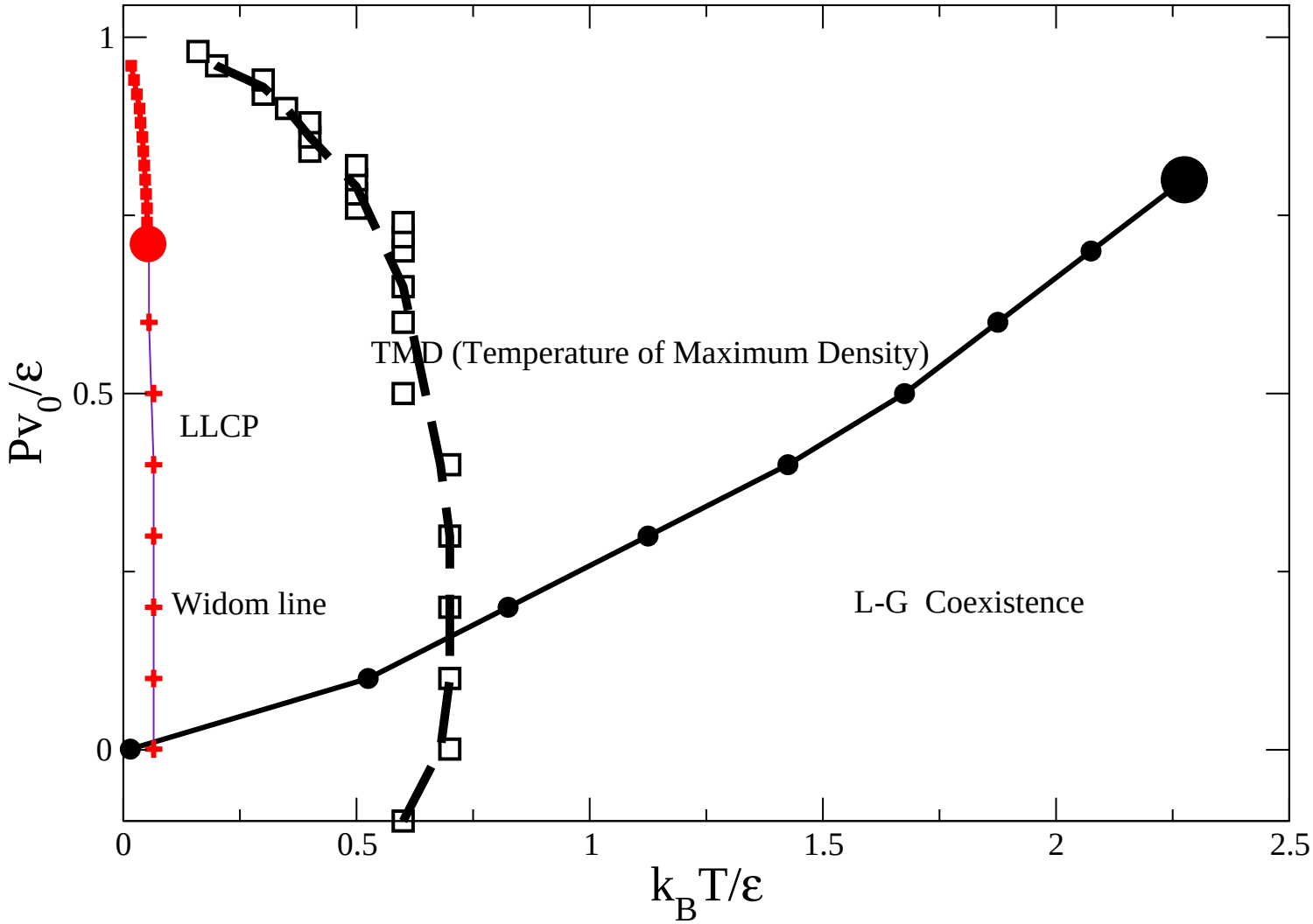


- Metropolis: single-spin flip
- Wolff: clusters of correlated spins are flipped

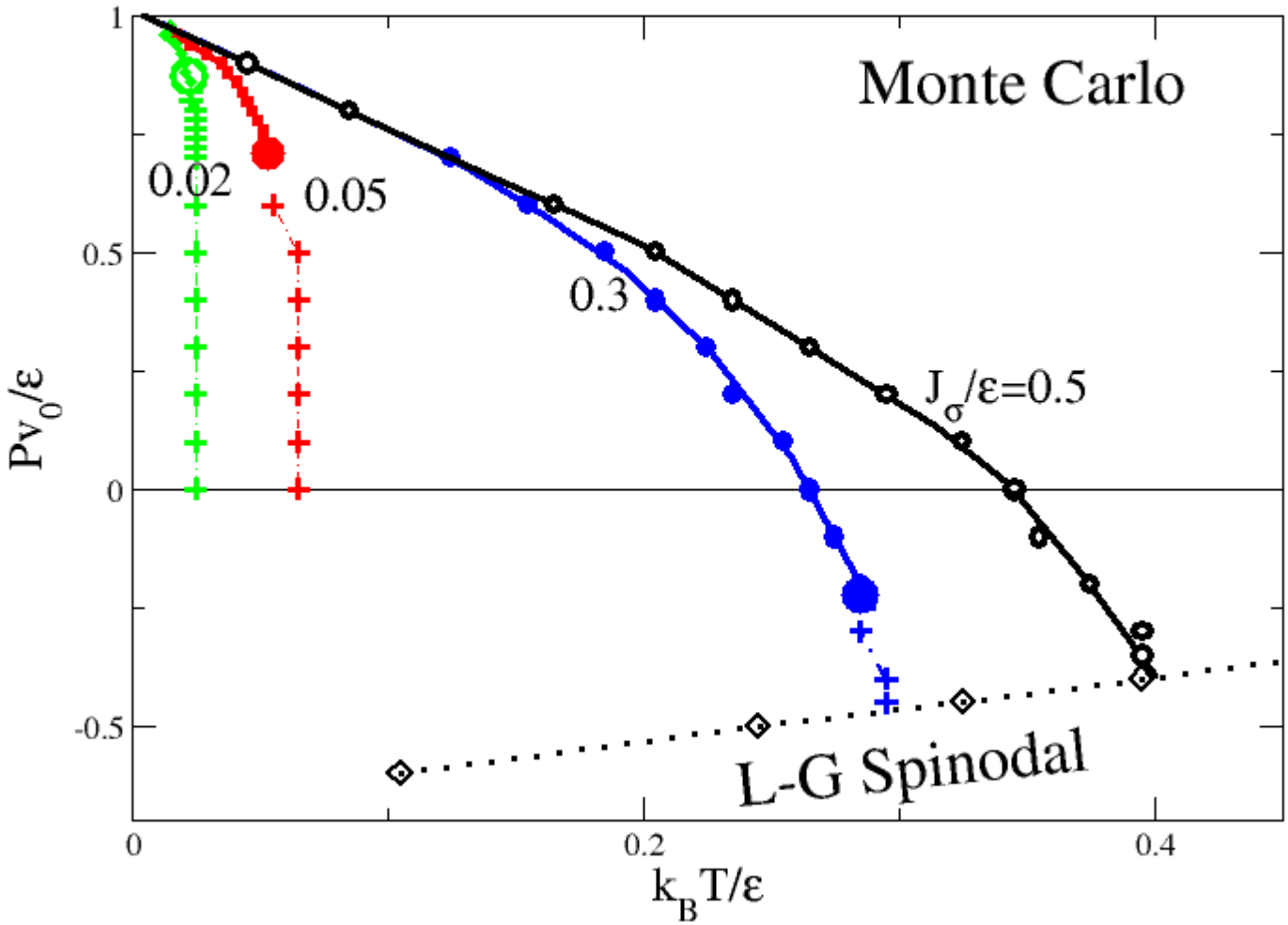
M: average molecular orientation

factor ≈ 10^3 of speed-up

Phase diagram – Monte Carlo simulations (NPT ensemble)

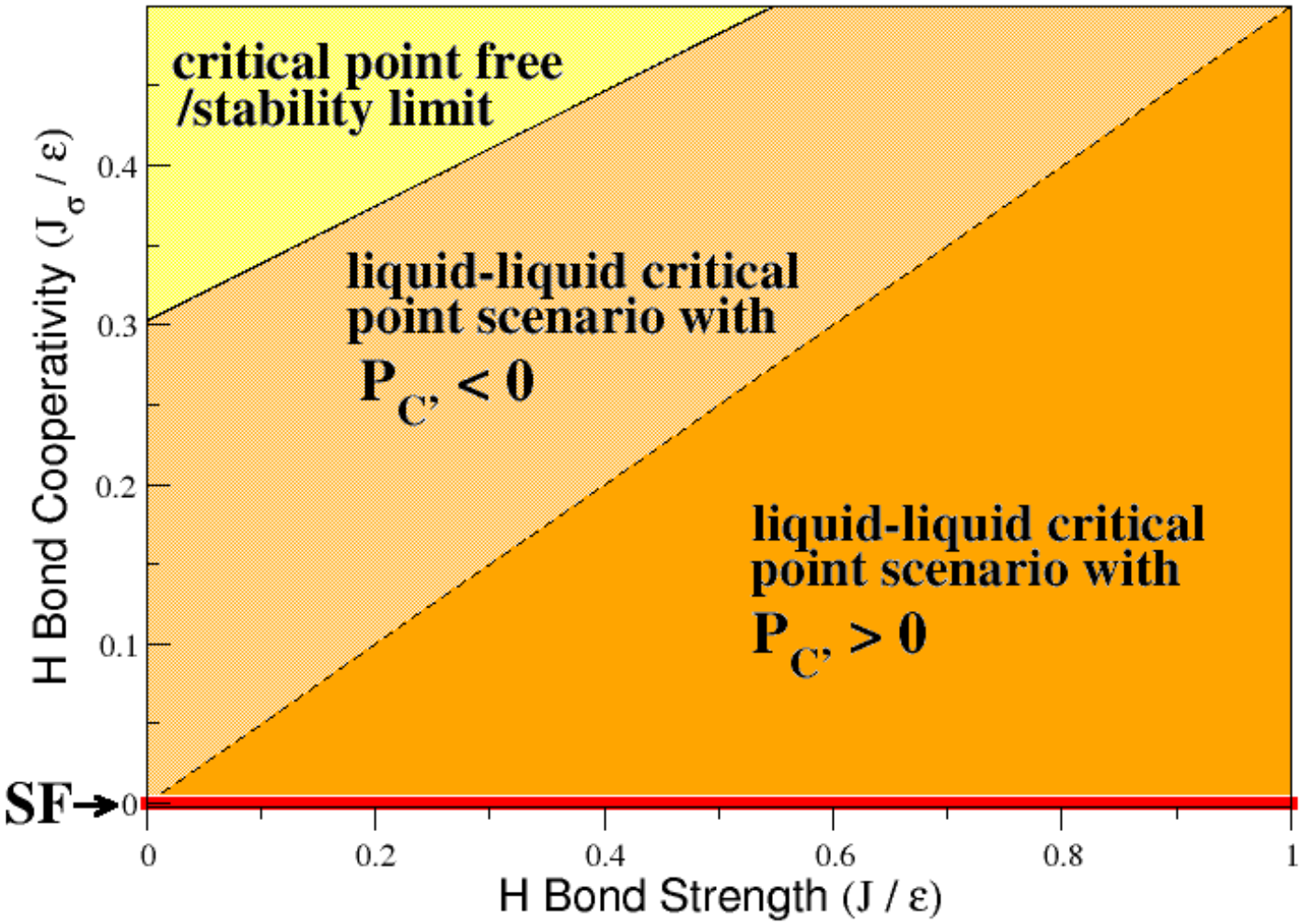


This simple cell model can reproduce the main thermodynamic features of water



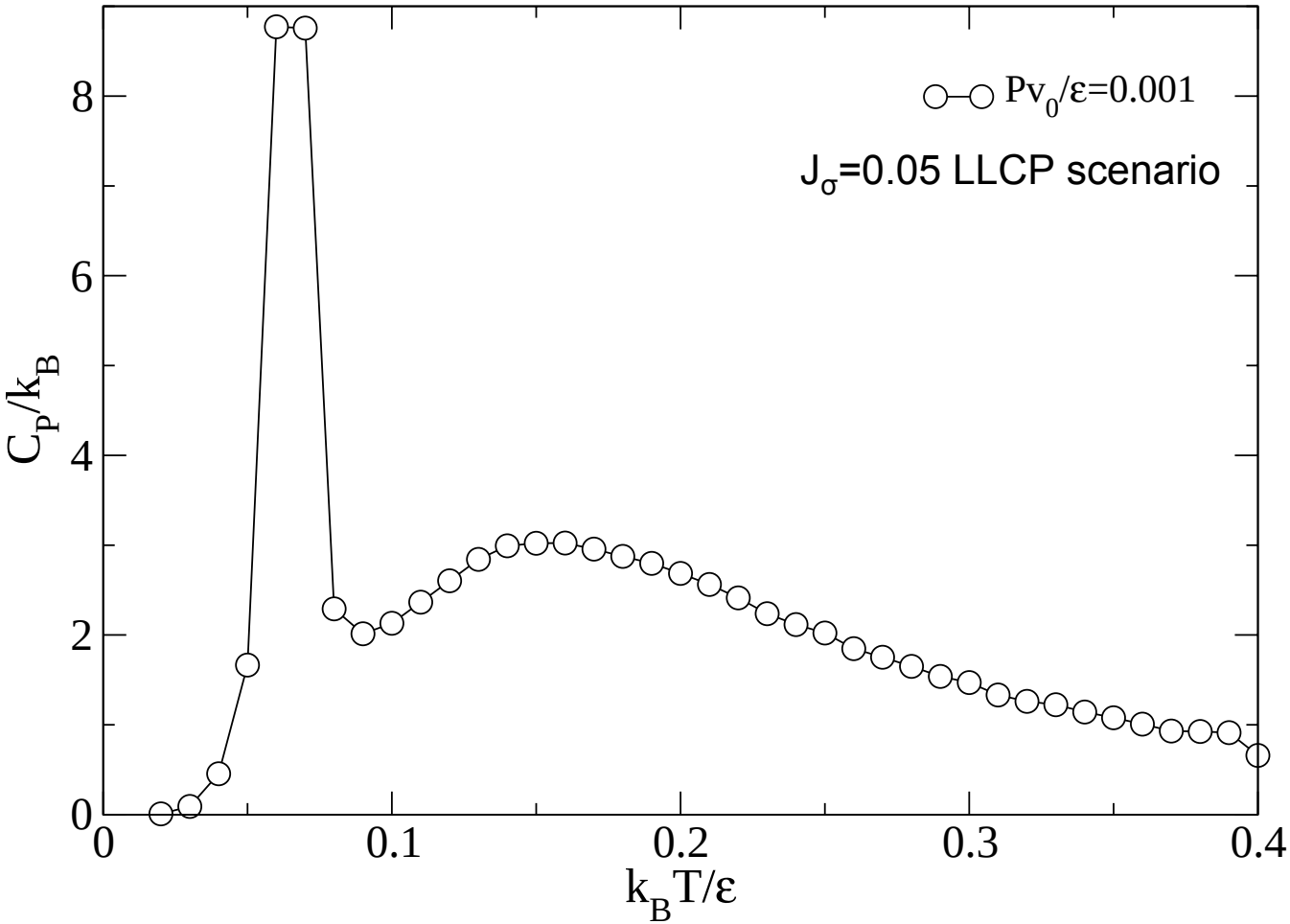
We recover all 3 scenarios upon changing the H bond cooperativity (J_σ)

Parameter space:

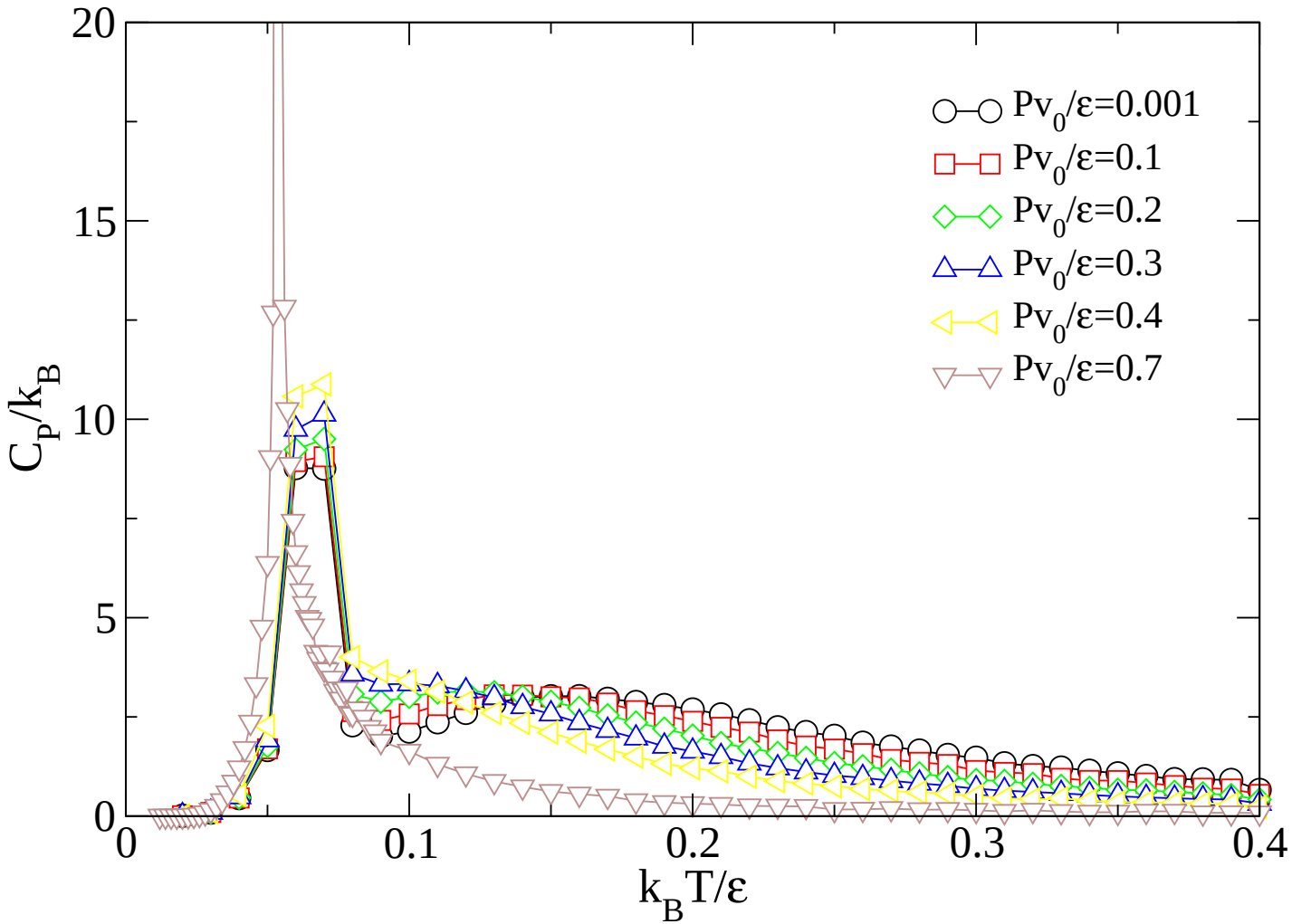


Using mean-field and MC we map out the 3 scenarios proposed

An interesting prediction:

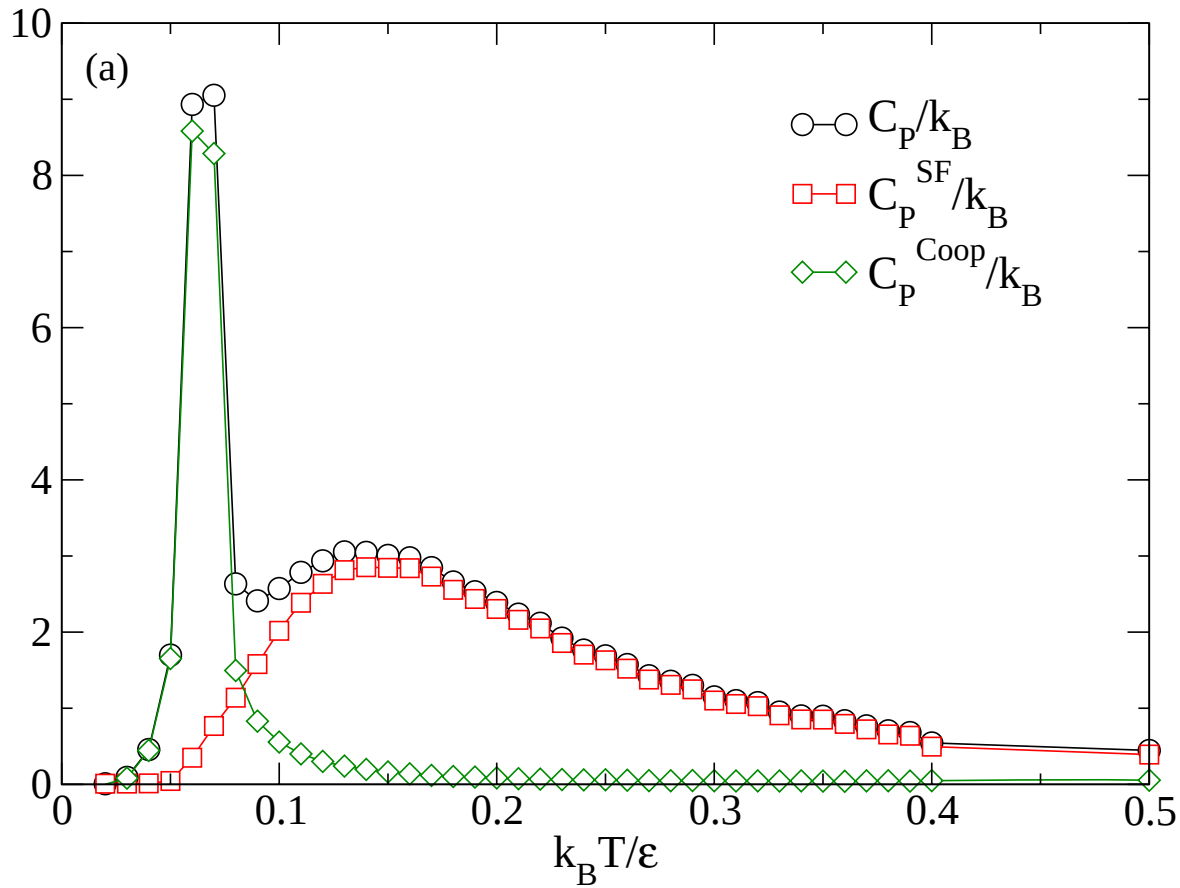


Cooperativity gives rise to a second maximum in the specific heat



- The broad max shifts to lower T upon increasing P
- The narrow max (at lower T) increases in height

Decomposition of C_P as the sum of two terms: SF + cooperative component



C_P^{SF}: fluctuations of HB formation

C_P^{Coop}: fluctuations of HB correlation

Consequence of 2 max in C_P

From Adam-Gibbs theory:

$$\tau = \tau_0 \exp[B/TS_c]$$ S_c: configurational entropy

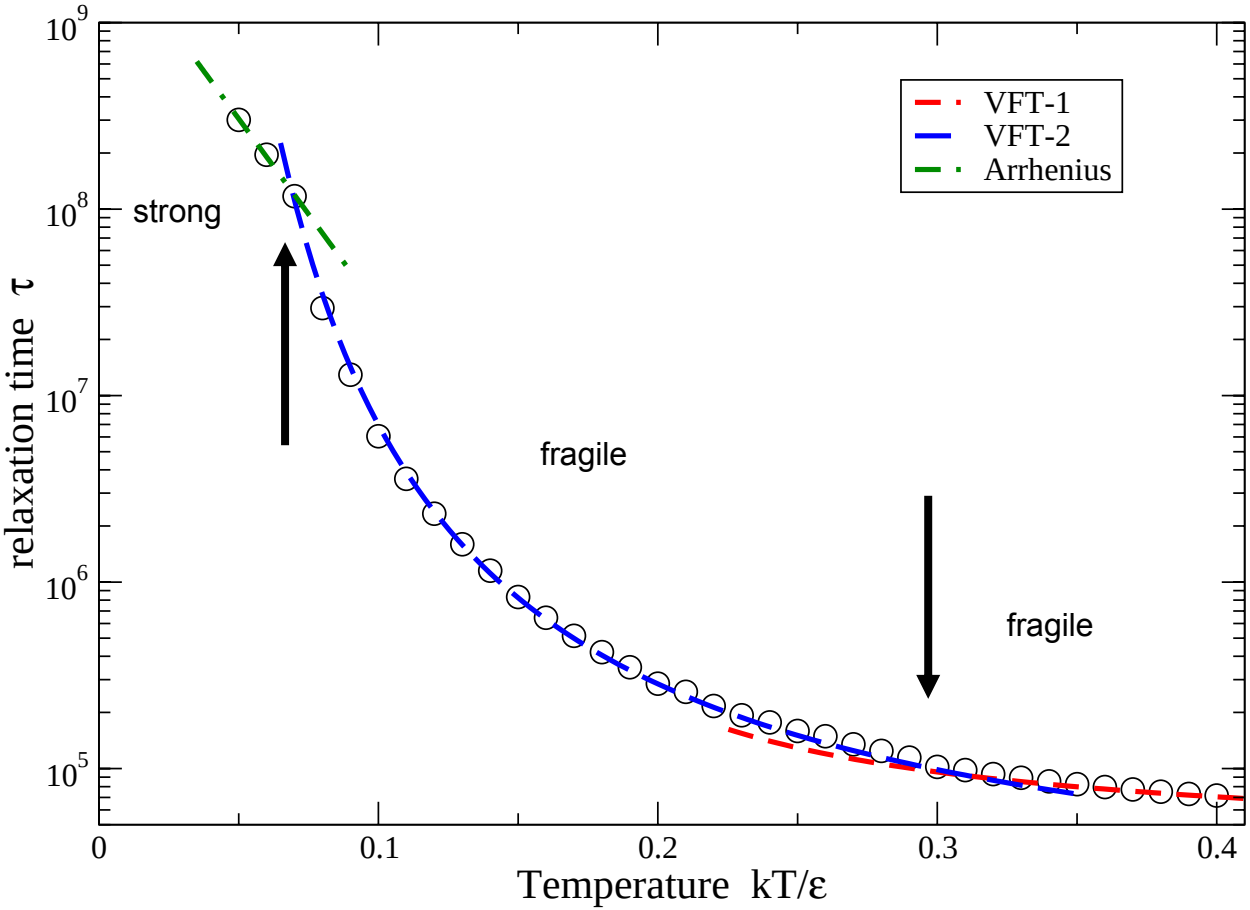
But the configurational entropy is related to C_P

$$S_c \approx S = \int \frac{C_P}{T} dT$$

Thus, from a max in C_P we expect a crossover in relaxation time

from 2 max in C_P we expect 2 crossovers in relaxation time

We compute the relaxation time from the MC correlation functions



Vogel-Fulcher-Tamman (VFT) for "fragile" liq.:

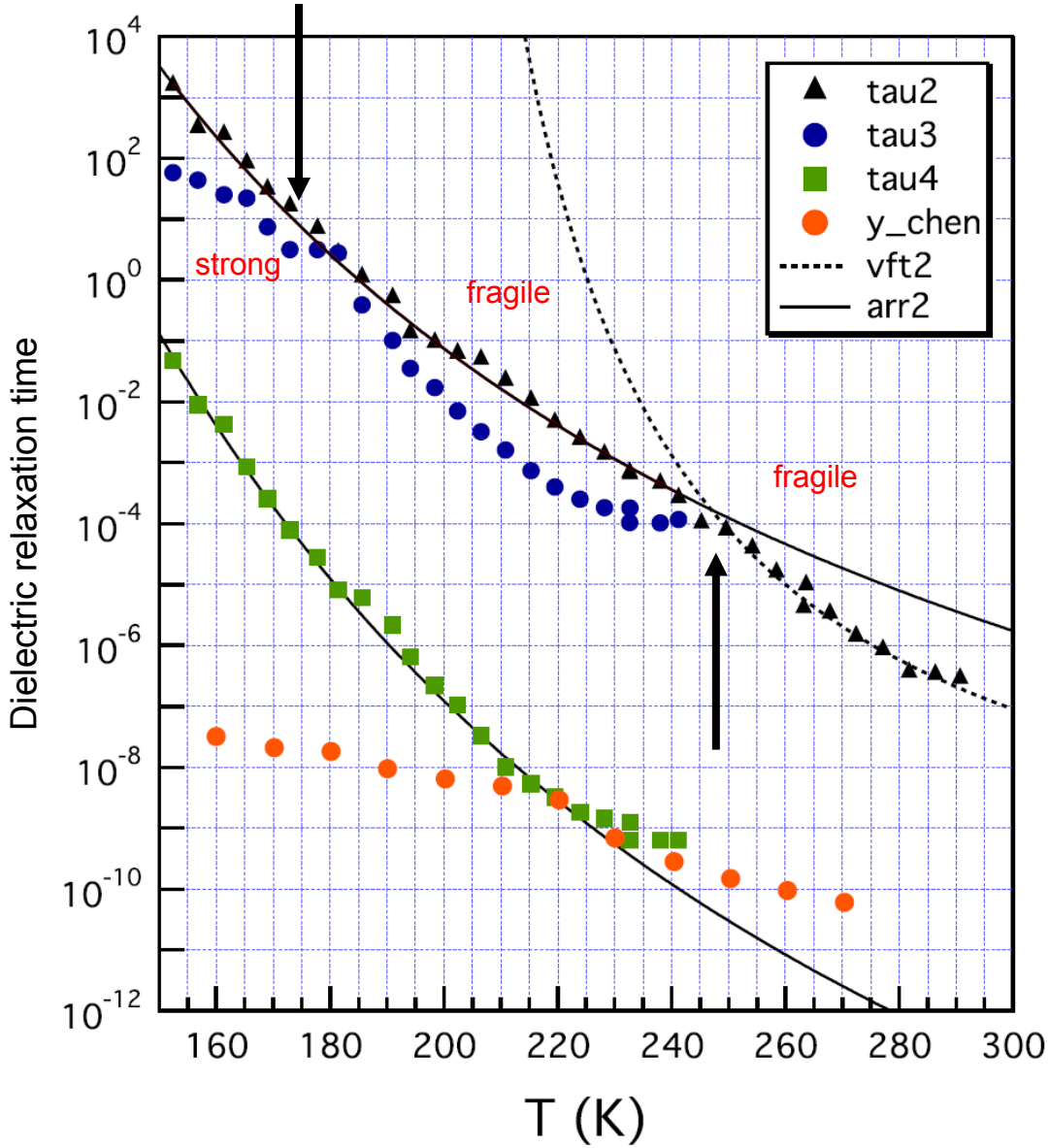
$$\tau \propto \exp[A/(T-T_0)]$$

Arrhenius for "strong" liq :

$$\tau \propto \exp[-B/kT]$$

(very) preliminary results show 2 crossovers in relaxation time

Experimental evidence:



preliminary experimental evidence of 2 crossovers

F. Bruni (private communication)

Conclusions

- H bond cooperativity can provide a unifying description of the different scenarios proposed for the phase diagram of water.
- The interesting possibility of two maxima in the specific heat is predicted
- Two crossovers are found in the relaxation time: fragile-to-fragile and fragile-to-strong (supported by some preliminary exp. results)

1. MGM, K. Stokely, H.E. Stanley, G. Franzese, arXiv:0807.4267, ***Anomalous specific heat of supercooled water***.
2. MGM, K. Stokely, E.G. Strekalova, H.E. Stanley, G. Franzese, Comp. Phys. Comm. (in press), ***Cluster Monte Carlo and numerical mean field analysis for the water liquid--liquid phase transition*** (arXiv:0810.4688).
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Possible improvements

- The model should take into account the possibility of more than 4 first-neighbors
- More realistic 3d topology
- More detailed interactions

References

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