BOSTON UNIVERSITY

Role of orientational dynamics in supercooled water

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Thesis Defense

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1. MGM, N. Giovambattista, F.W. Starr, H. E. Stanley, ***Relation between rotational and translational dynamic heterogeneities in water,*** Phys. Rev. Lett. **96,** 057803 (2006).
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3. MGM, K. Stokely, H.E. Stanley, G. Franzese, ***Anomalous specific heat of supercooled water,*** arXiv:0807.4267.
4. 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. **180**, 497 (2009).
5. K. Stokely, MGM, H.E. Stanley, G. Franzese, ***Effect of hydrogen bond cooperativity on the behavior of water***, arXiv:0805.3468***.***

Physical Question:

Role of orientational dynamics in understanding water dynamics and thermodynamics

Two examples:

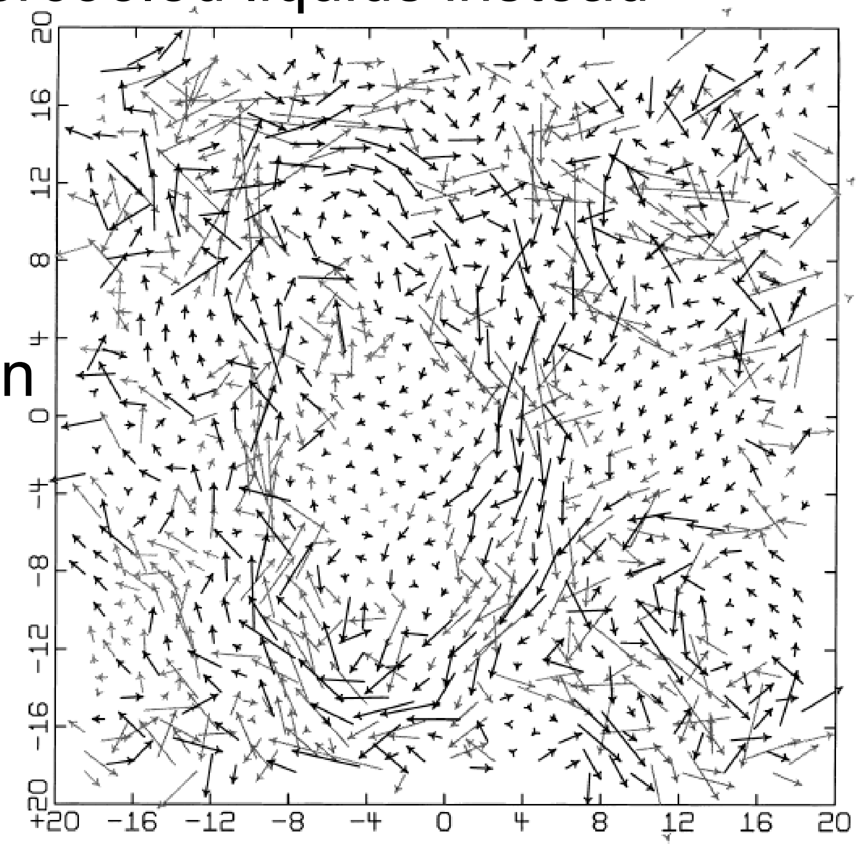
- Heterogeneous Dynamics
- Behavior of liquid-liquid transition line

Puzzle:

- Ordinary single-component liquids in standard conditions correctly described as homogeneous

- Experimental evidence that supercooled liquids instead heterogeneous

HETEROGENEITY = in one region molecular translational motion is orders of magnitude faster than in another region a few nm distant



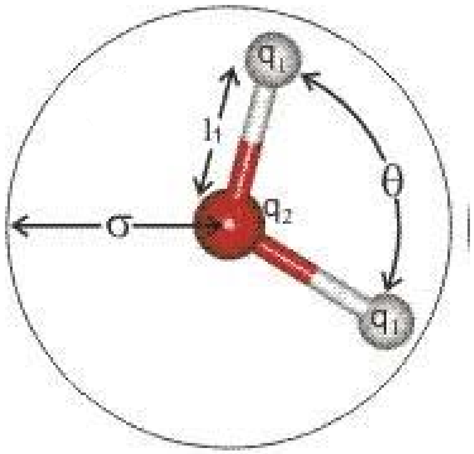
Perera, Harrowell, J. Non-Cryst. Sol.235-237, 314 (1998)

Model: SPC/E (extended simple point charge potential)

- Lennard-Jones interaction between oxygen atoms

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- Electrostatic interaction between all charged sites



σ = 3.166 Å

ε = 0.650 kJ/mol

l_1= 1.0 Å

θ= 109.47°

q_1= +0.4238 (e)

q_2= -0.8476 (e)

Molecular dynamics simulation: numerical integration Newton equations in the canonical ensemble (NVT)

N=1728 water molecules

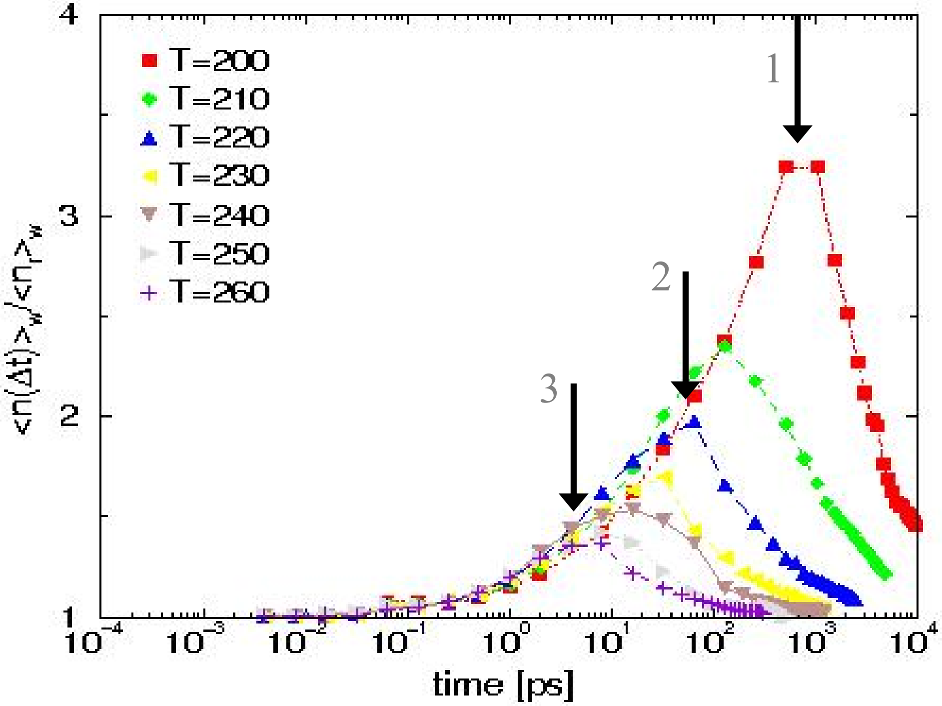
V=51.7 nm^3

T=200 – 350 K

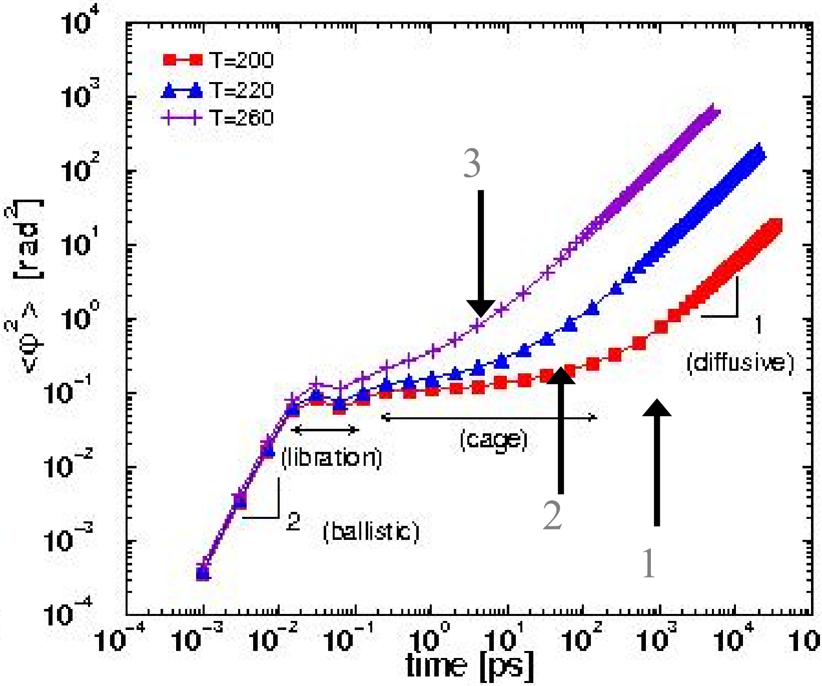
Rotationally mobile cluster

1. Rotational Mobility: maximum angular displacement in observation time Δt (10^{-3} ps$<\Delta t<10^{4}$ ps)
2. Select 7% of most rotationally mobile molecules
3. Define cluster at time t_0 for observation time Δt as those selected molecules whose O-O distance is less than 0.315 nm

Average size of rotational clusters

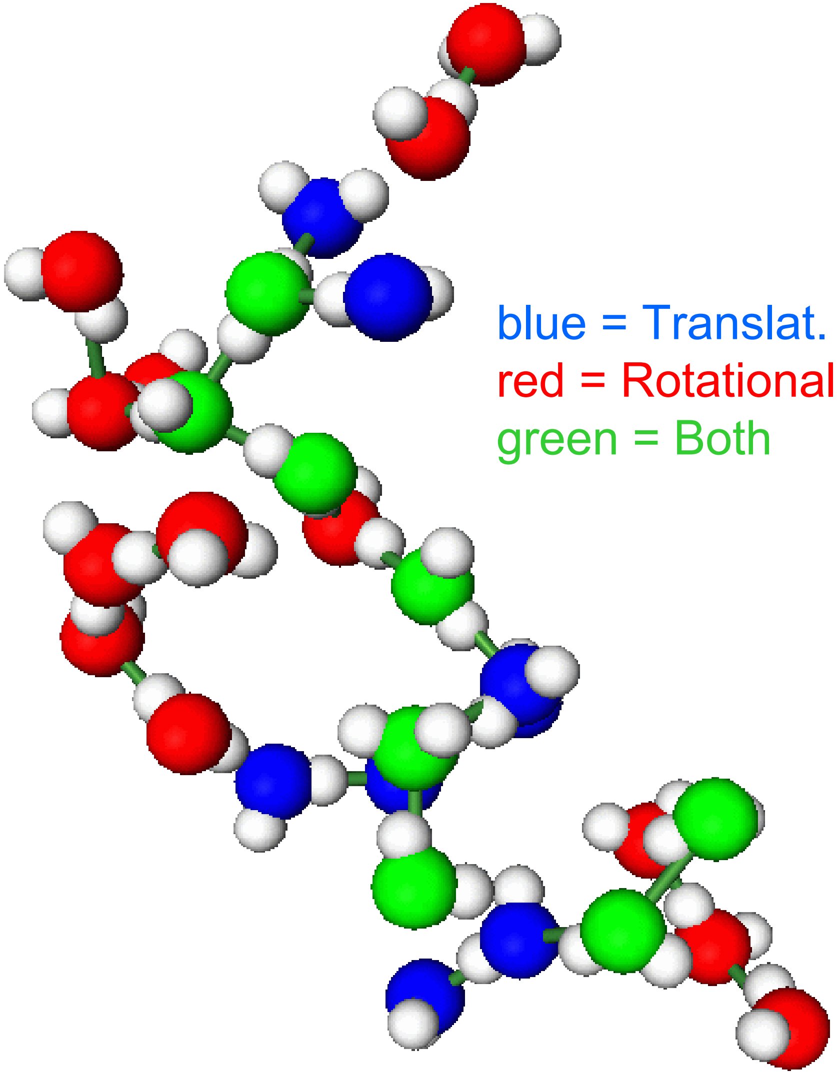


Rotational MSD



- the most rotationally mobile molecules tend to form clusters.
- The maximum size of these clusters occurs at the end of the cage time regime (arrows).

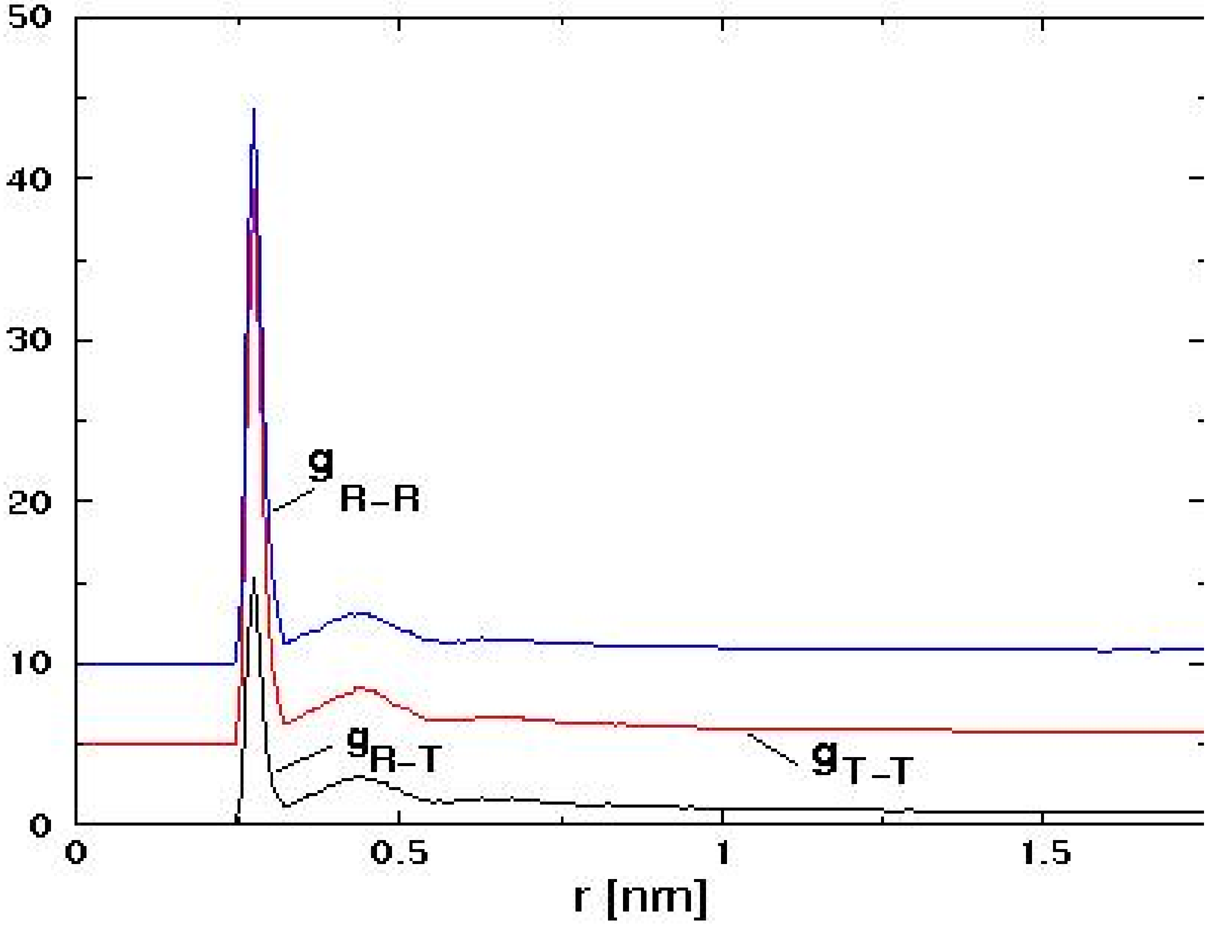
Two kinds of clusters



blue = Translat. mobile clusters
red = Rotationally mobile clusters
green = Both

Disconnected clusters are part of a larger region of cooperative motion

Three oxygen-oxygen radial distribution functions for heterogeneities



g_{R-R} :rotational clusters

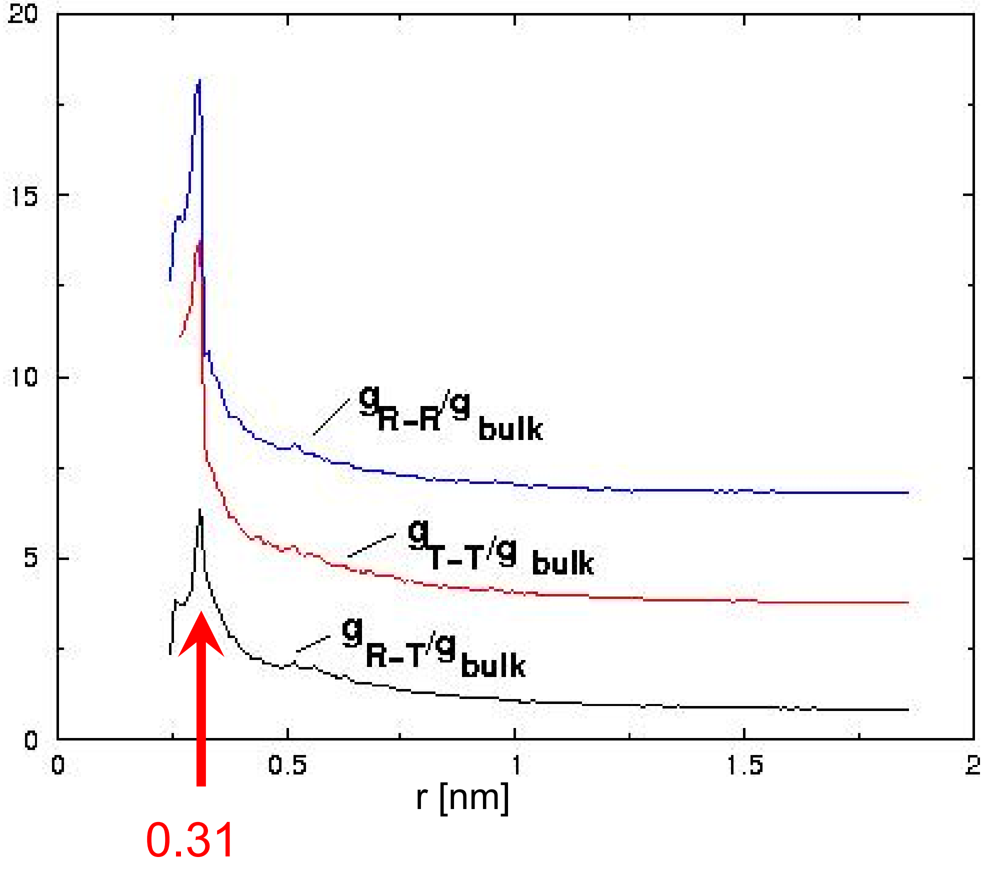
g_{T-T}: translational clusters

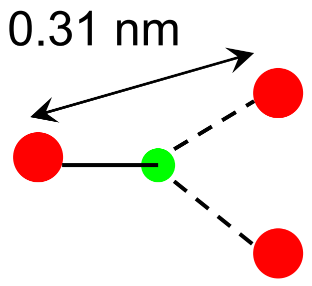
g_{R-T} : rotat. & transl. clusters

- g_{R-R}, g_{T-T}, g_{R-T} are similar to standard oxygen-oxygen radial distr. function
- rotational and translational heterog. are correlated in space

Normalization by the “standard” radial distribution function

Motivation: measure of some “extra” order beyond the bulk structure



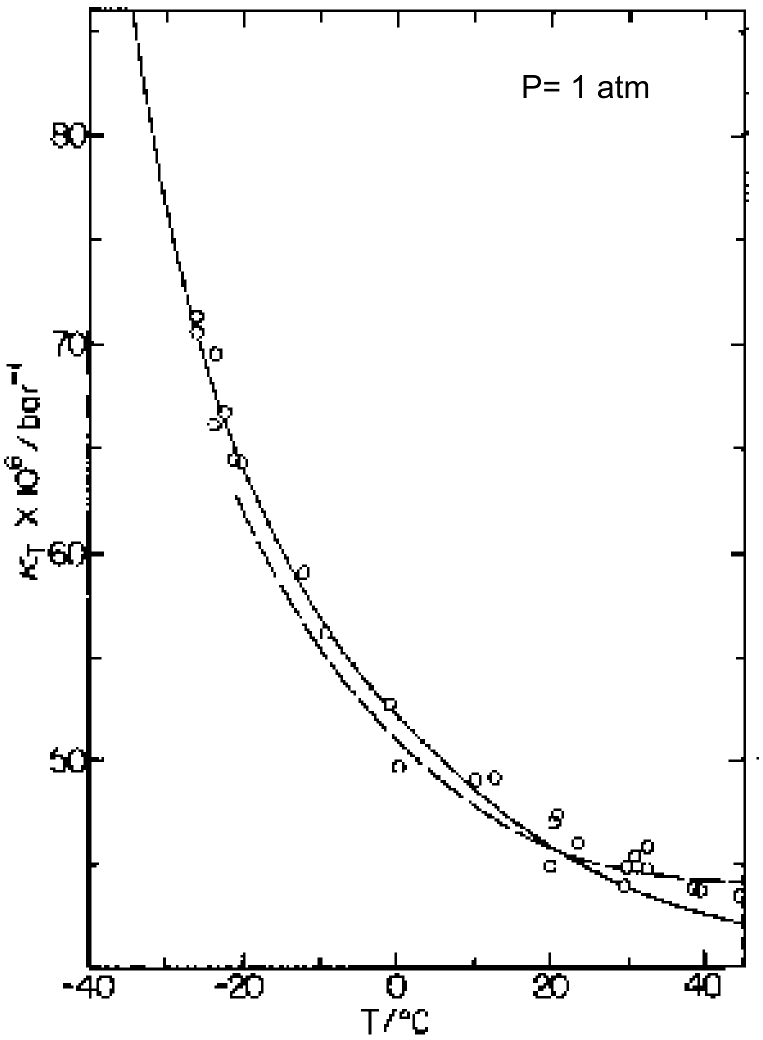


bifurcated bond: a hydrogen shared between 2 other oxygens

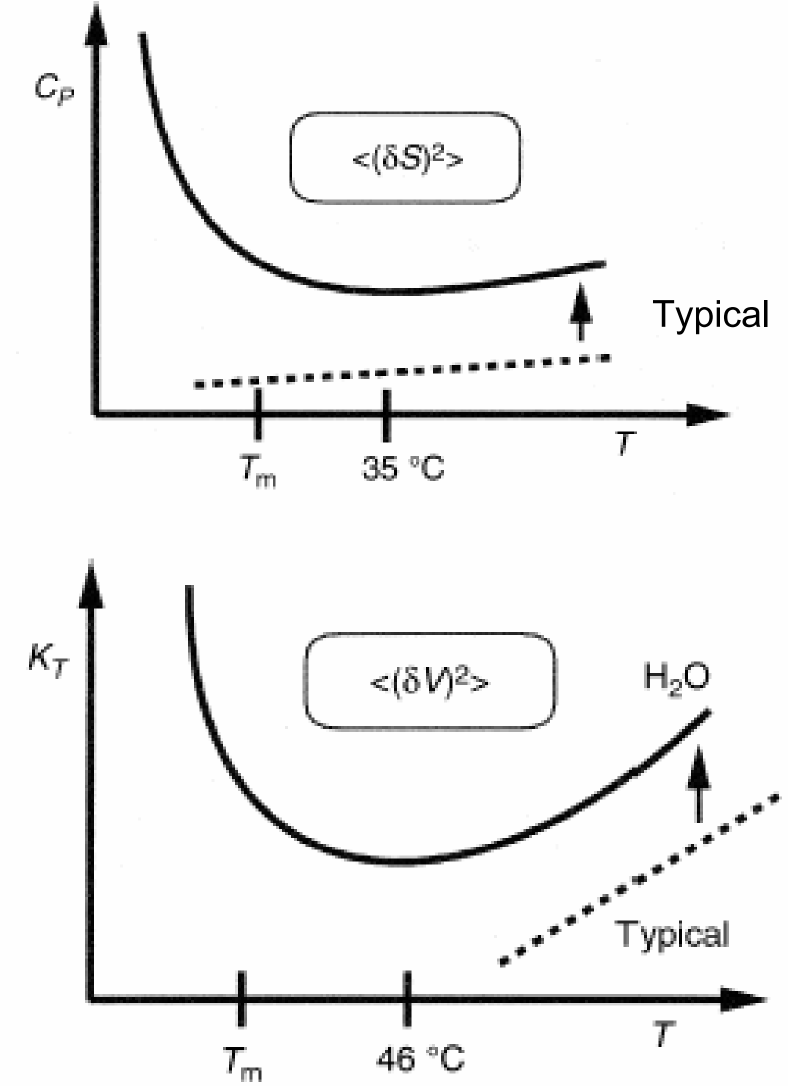
- Peak at ≈ 0.31 nm → bifurcated bond present in both rotational and translational heterogeneities.
- Bifurcated bonds provide extra mobility to molecules belonging to a heterogeneity.

Role of orientational dynamics in thermodynamics

Puzzle:

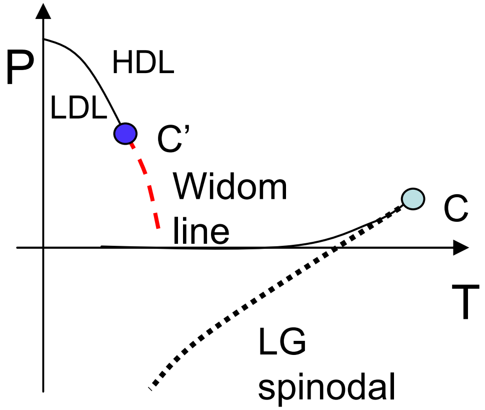


Exp. data from R.J. Speedy and C.A. Angell, (1976)



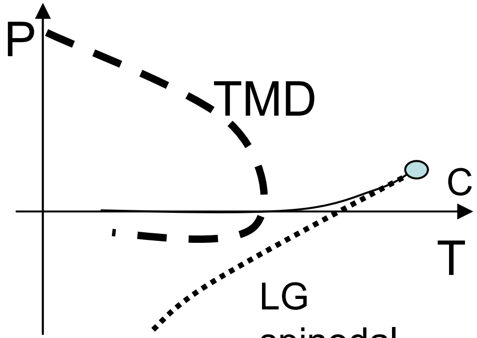
Large increase of the thermodynamic response functions

1. LLCP



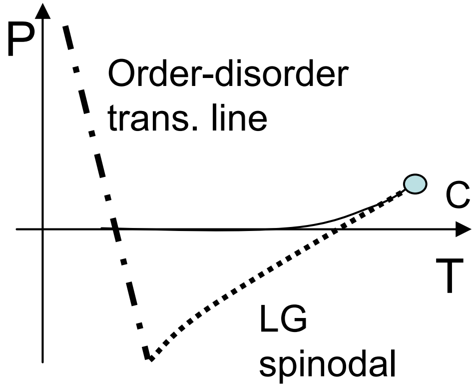
The anomalous increase of response functions is due to the Widom line (locus of corr. length maxima)

2. SF



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

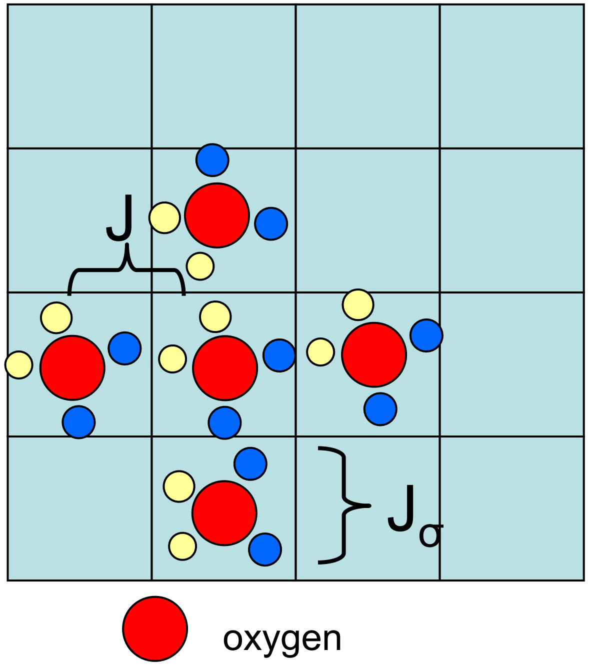
3. CPF



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

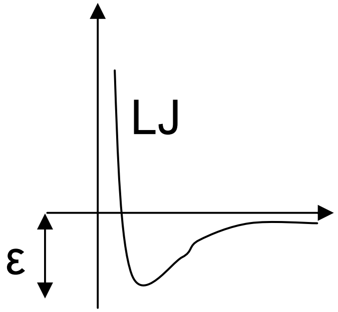
What we did: Monte Carlo simulations of a cell model

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



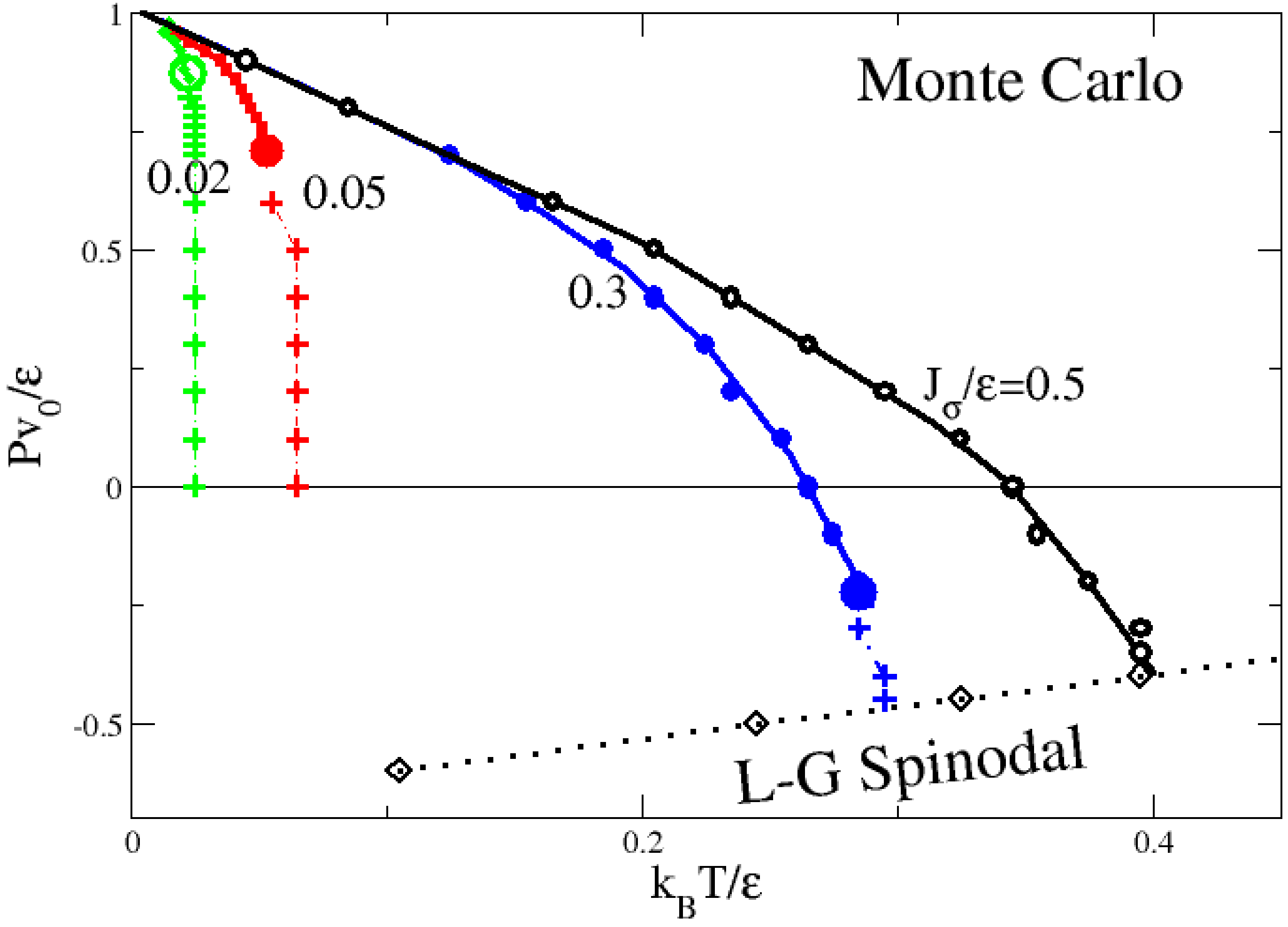
Interactions:

1. Lennard-Jones → $\varepsilon>0$
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)

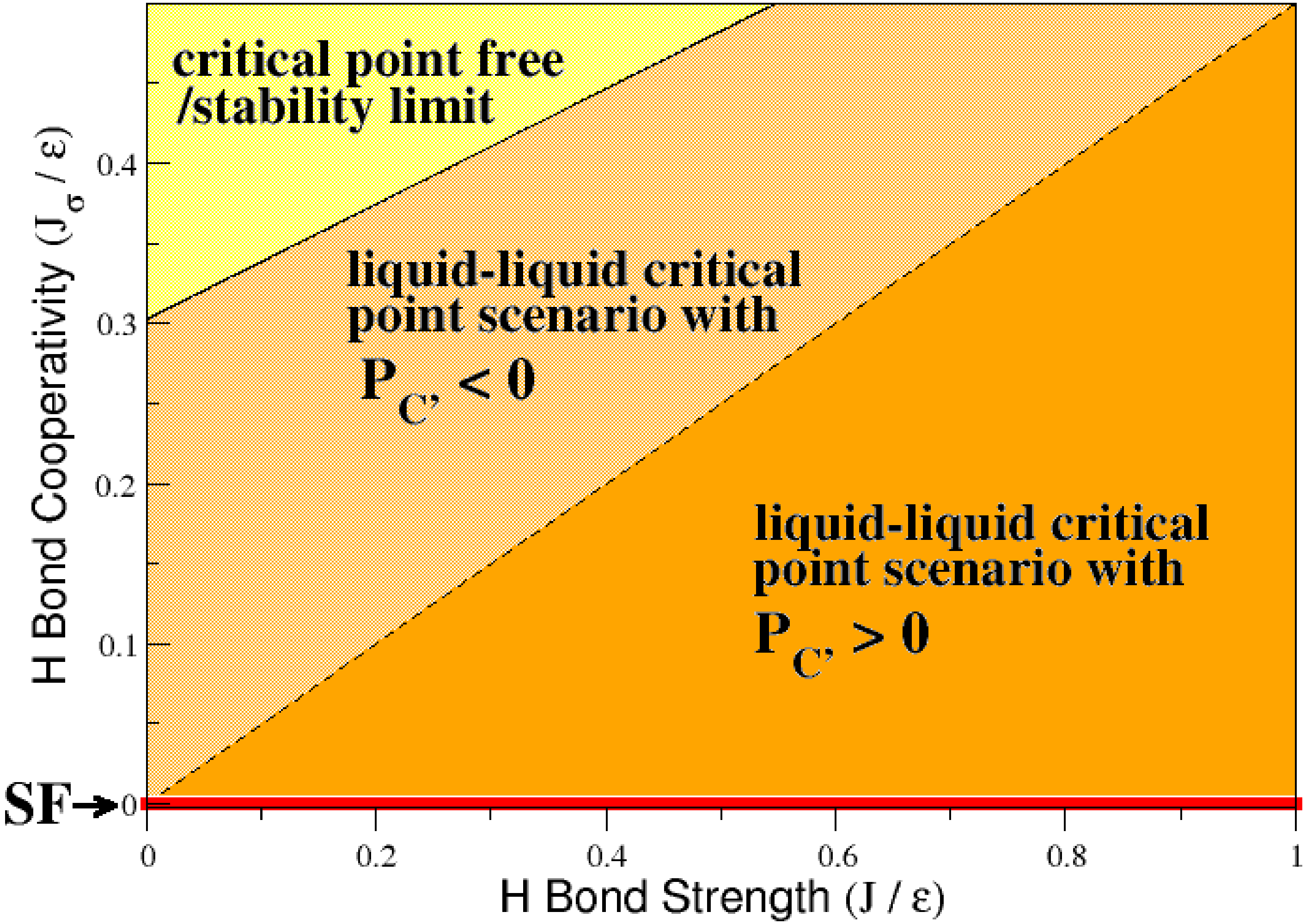
volume allowed to fluctuate: H bond format. leads to increase in volume

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



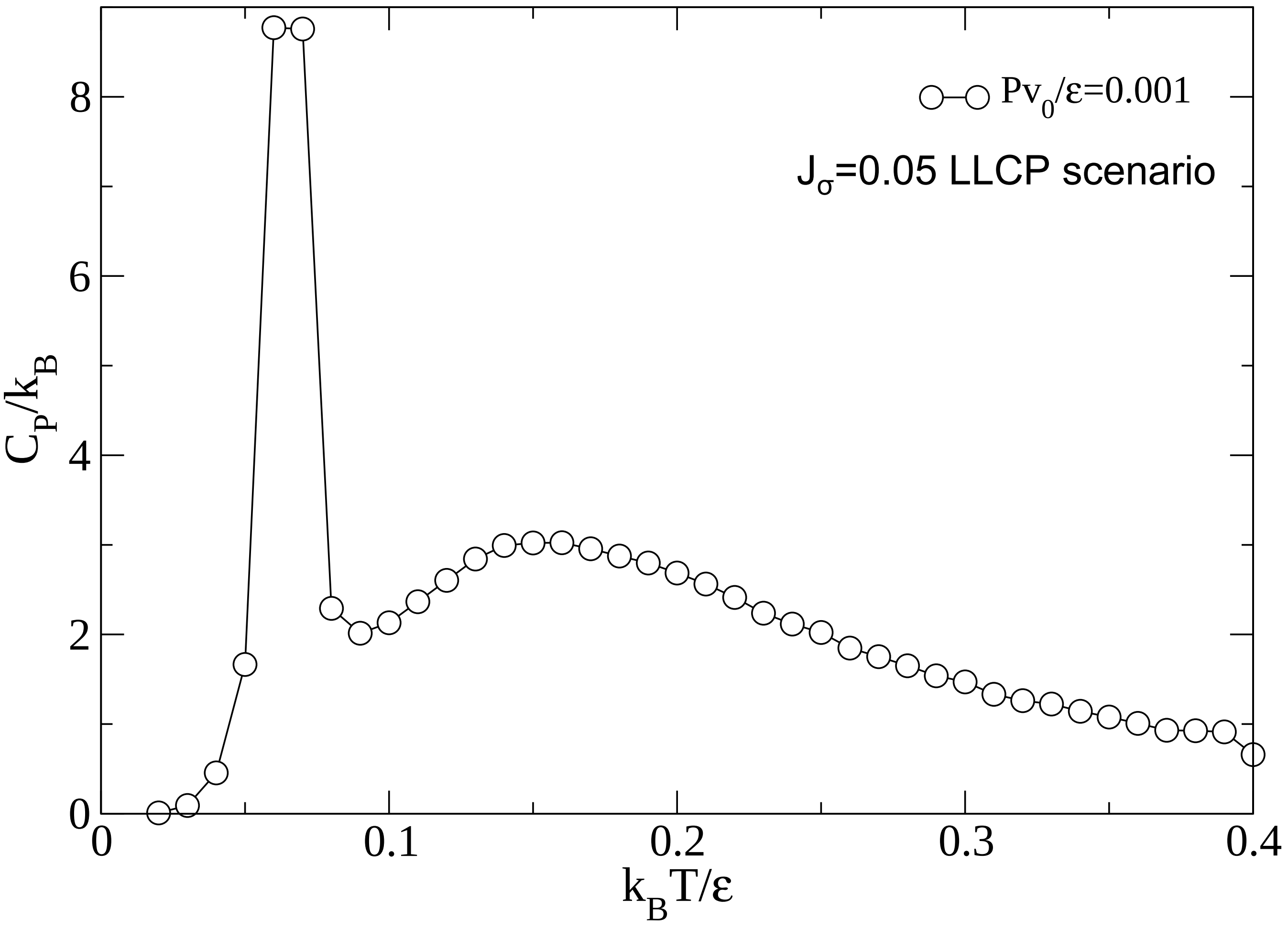
We recover all 3 scenarios upon changing the H bond cooperativity (J_σ)

Parameter space:



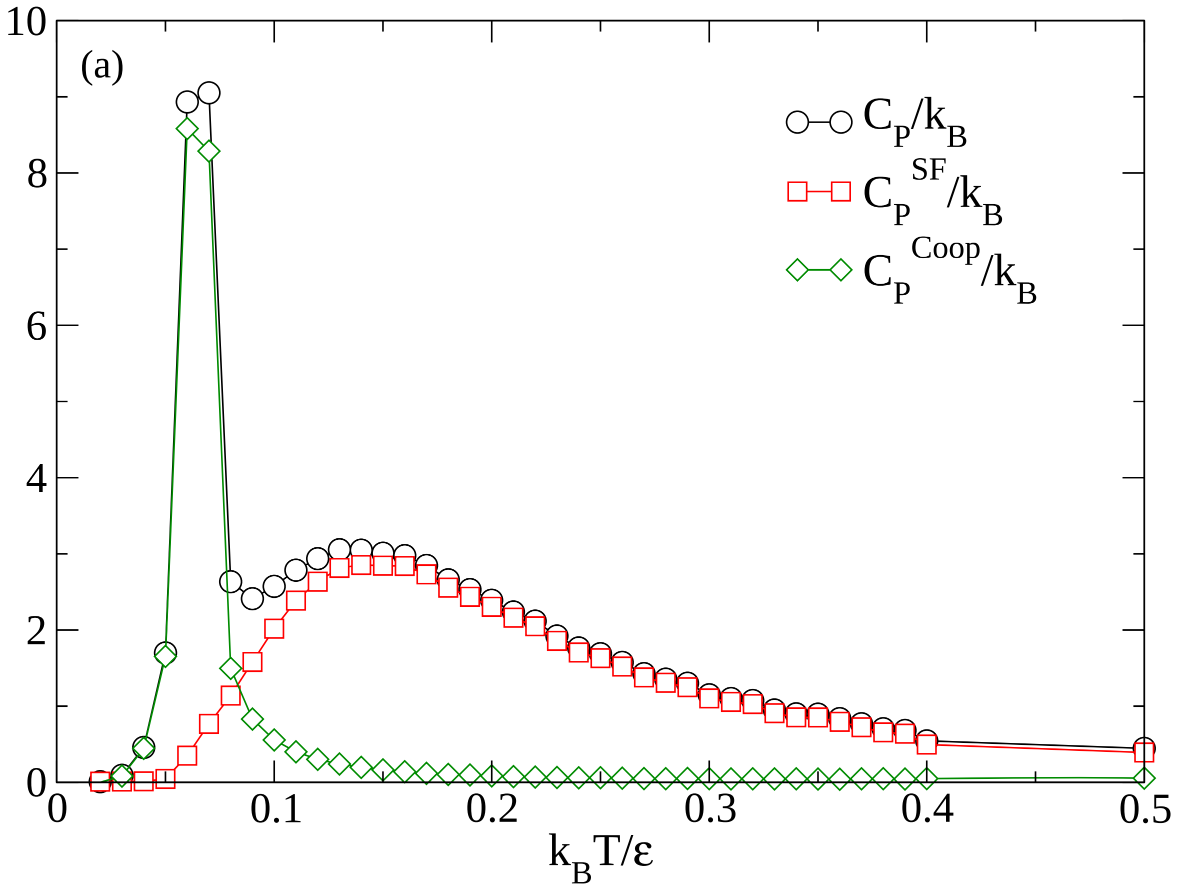
Using mean-field and MC we map out the 3 scenarios proposed

An interesting prediction:



Two maxima in the specific heat

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

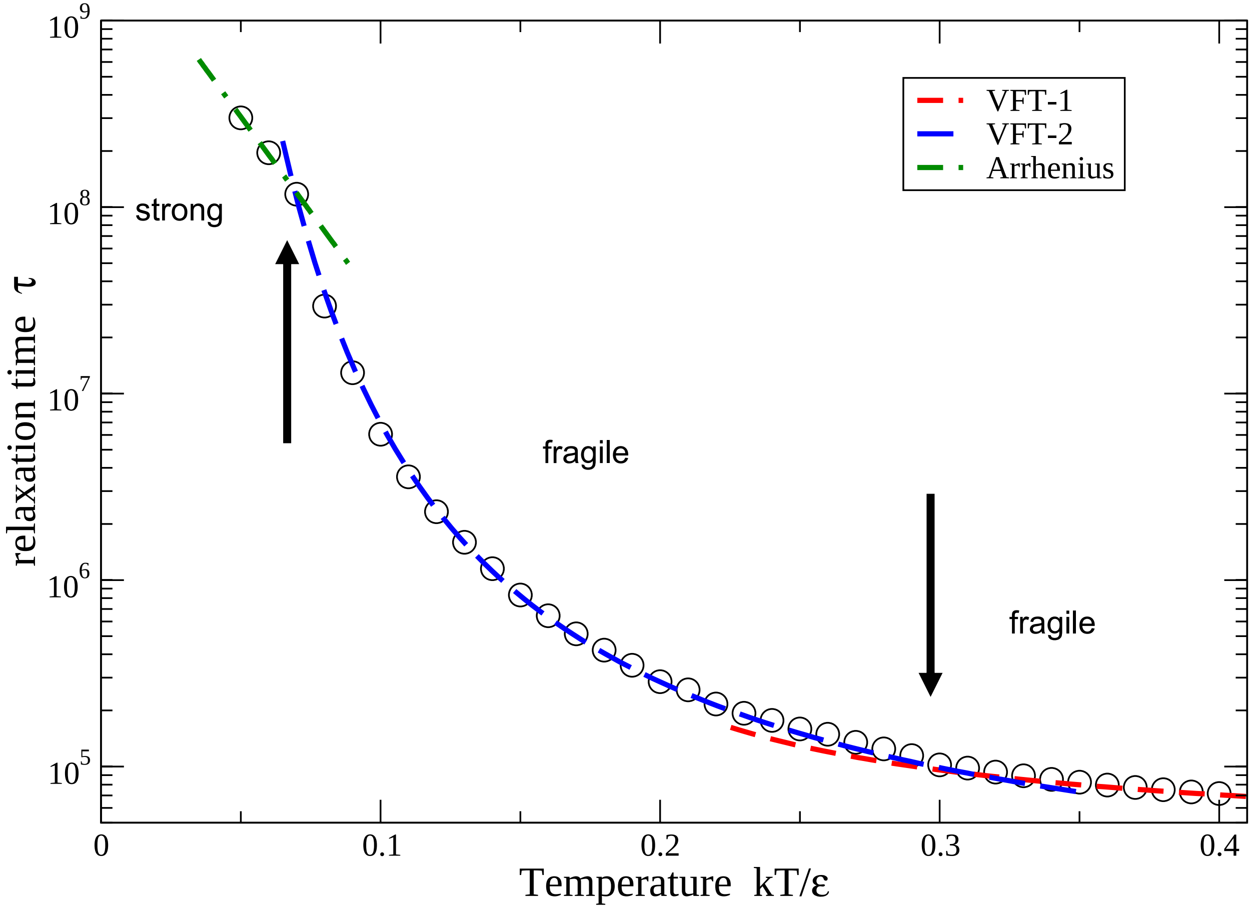
But the configurational entropy is related to C_P

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

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.:

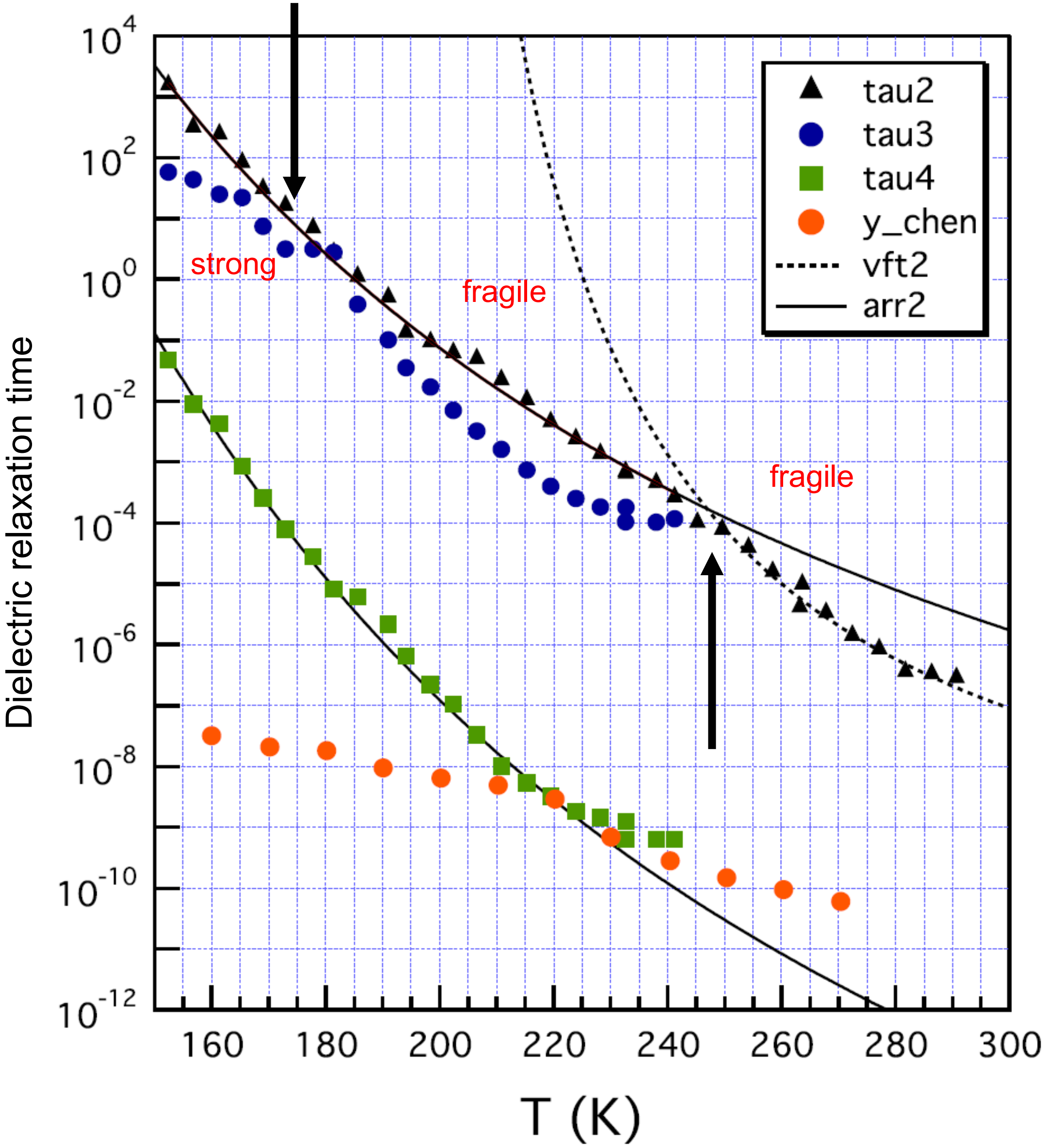
$$\tau \propto \exp[A/(T - T_0)]$$

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

- Rotational dynamics shows heterogeneities: key factor for diffusion
- 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)

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