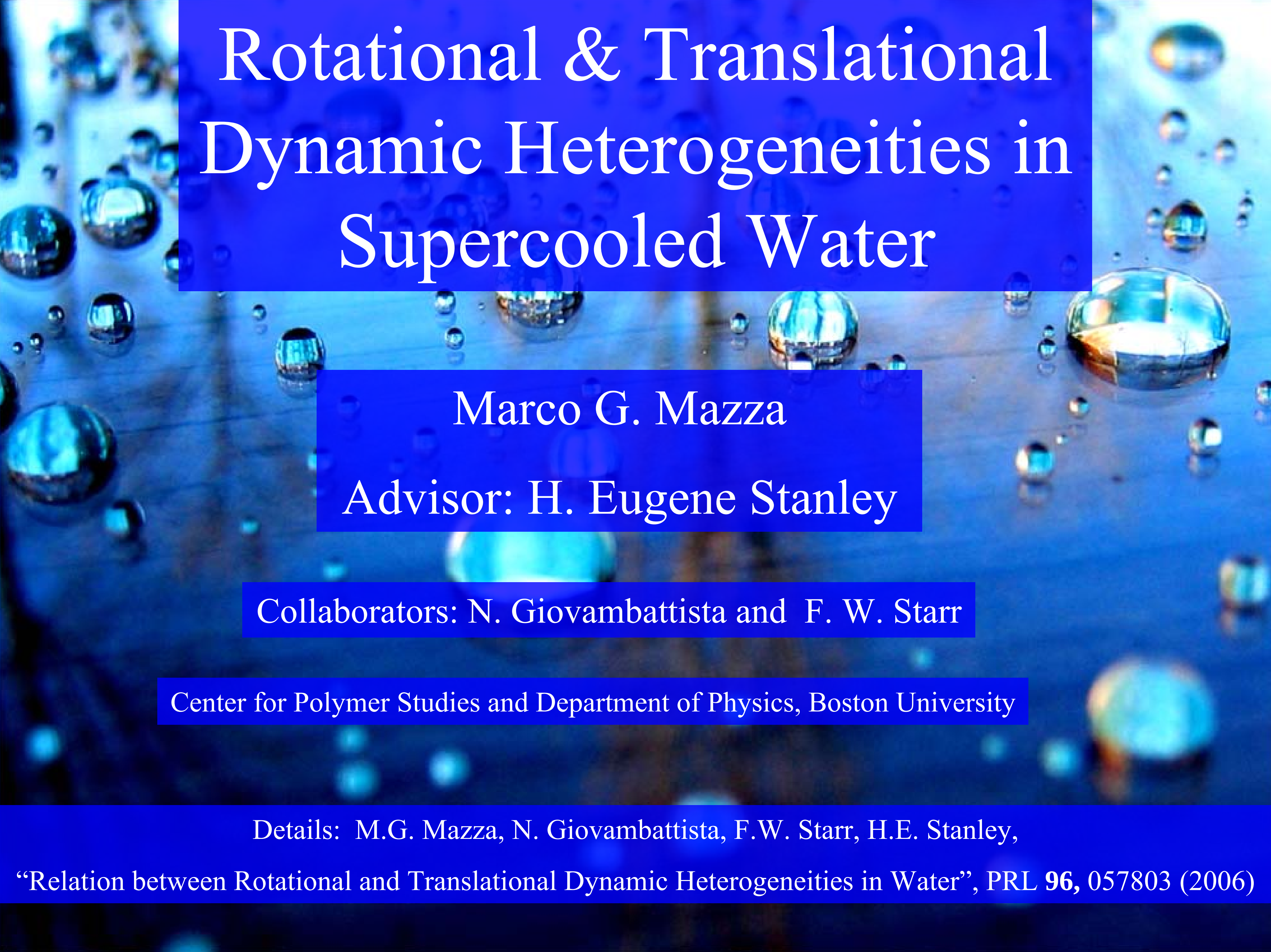

# Rotational & Translational Dynamic Heterogeneities in Supercooled Water

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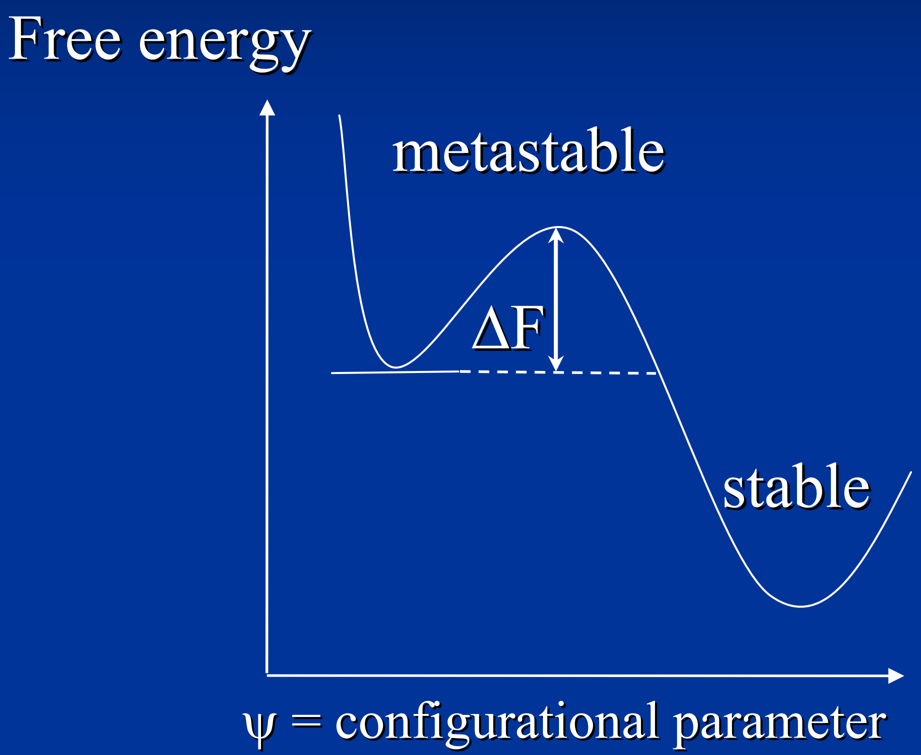
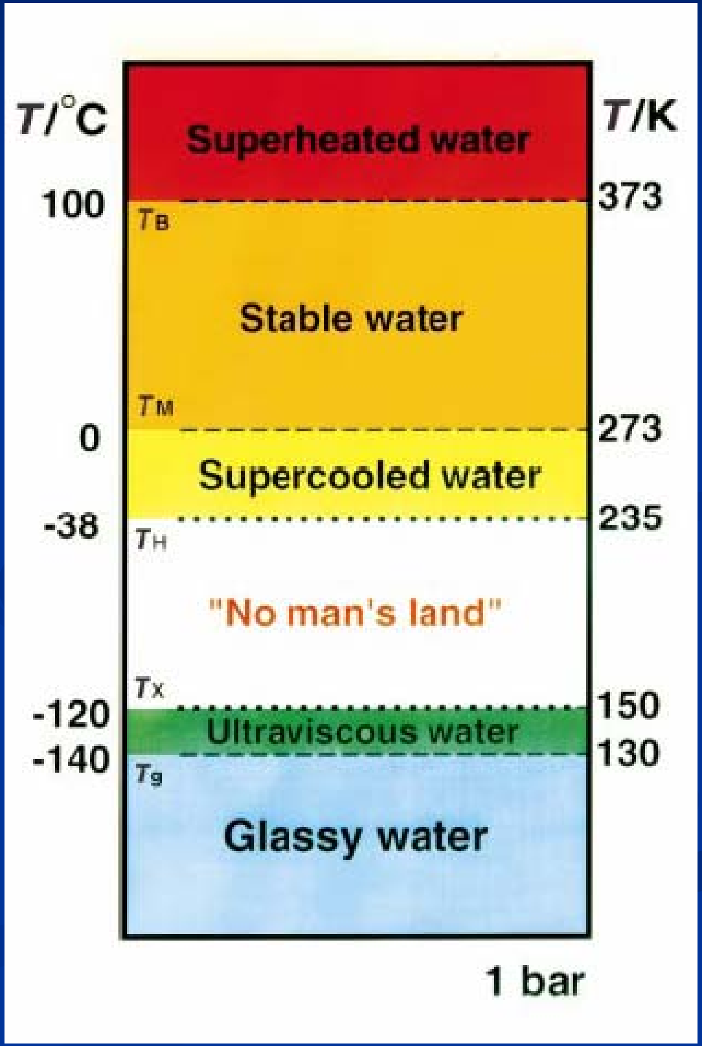
Details: M.G. Mazza, N. Giovambattista, F.W. Starr, H.E. Stanley,
“Relation between Rotational and Translational Dynamic Heterogeneities in Water”, PRL **96,** 057803 (2006)

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

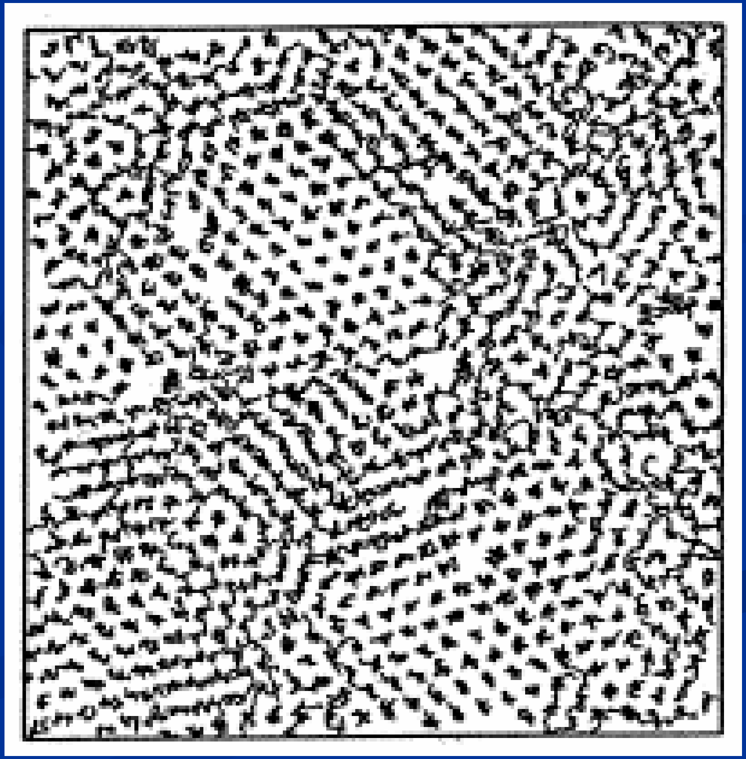




- Water is metastable because it cannot overcome the free energy barrier ΔF
- Upon cooling the energy barrier decreases, until ΔF ≈ kT, leading to homogeneous nucleation

- Ordinary single-component liquids in standard conditions are correctly described as homogeneous
- Overwhelming experimental evidence that supercooled liquids are instead heterogeneous

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



Overlapped snapshots of 2d atoms

# Why bother?

- Heterogeneous dynamics gives a mechanism for diffusion at very low T: necessity of cooperative regions to overcome the energy barriers
- Heterogeneous dynamics explains relaxation in experimental correlation functions, which are not simple exponentials

$$C(t) \approx \exp[-(t/\tau)^{\beta}] = \int_{0}^{\infty} P(\alpha) e^{-t/\alpha} d\alpha$$

$P(\alpha)$: spatial distribution of relaxation times $\alpha$

# Questions:

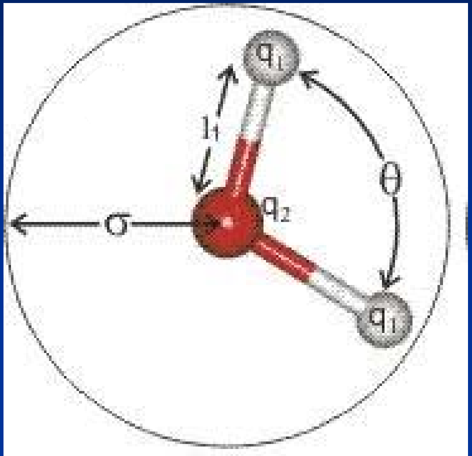
1. In addition to the well-studied translational heterogeneities, are there also rotational heterogeneities?
2. If so, are rotational heterogeneities related to the translational heterogeneities.?

# 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



$\sigma = 3.166$ Å

$\varepsilon = 0.650$ kJ/mol

$l_1 = 1.0$ Å

$\theta = 109.47°$

$q_1 = +0.4238$ (e)

$q_2 = -0.8476$ (e)

Molecular dynamics simulation: Integrate numerically Newton’s equations in the canonical ensemble (NVT)

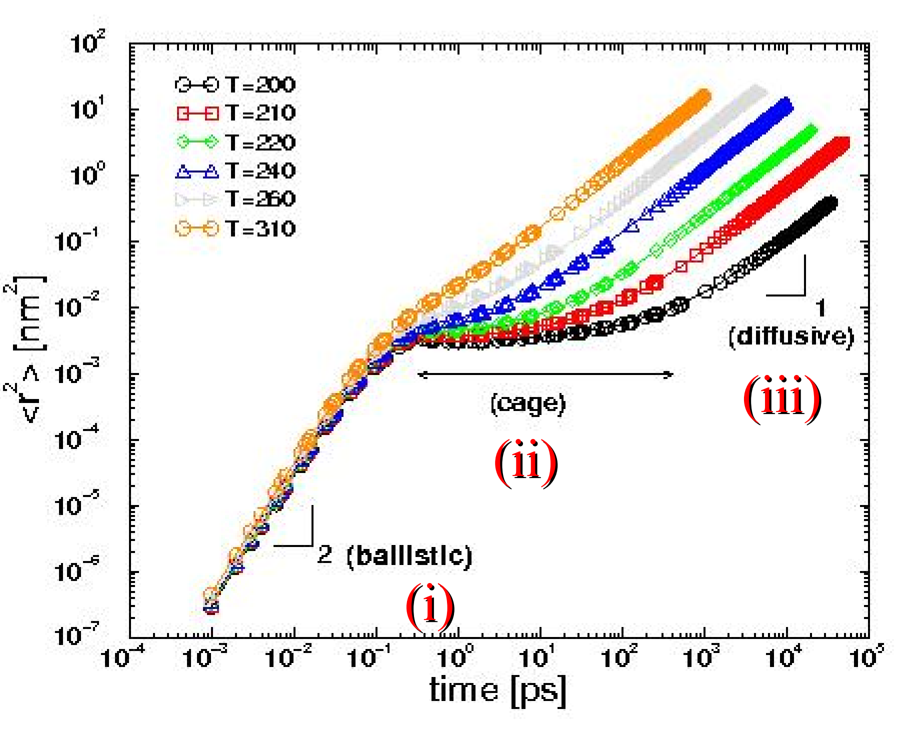
N=1728 water molecules

$V = 51.7\ \mathrm{nm}^3$

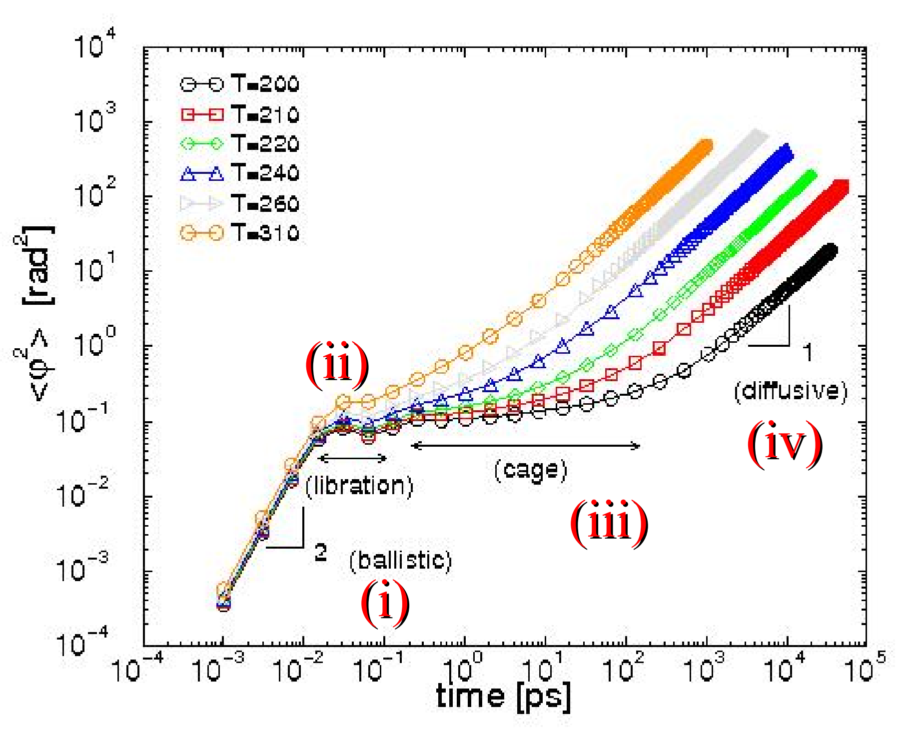
T=200 – 350 K

# First Results:

## Translational mean square displacement



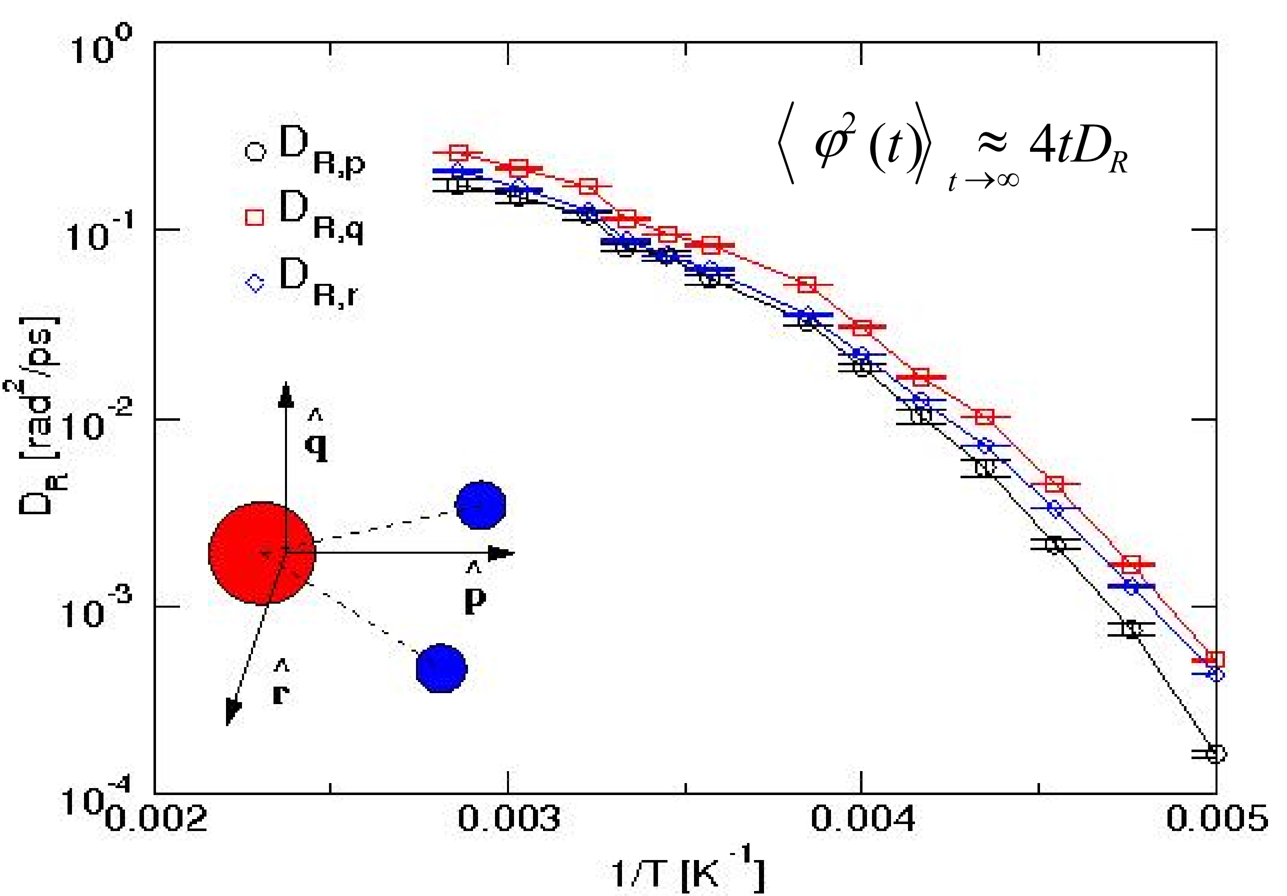
## Rotational mean square displacement



Mazza et al., PRL **96**, 057803 (2006)

- Three dynamical regimes for translational mean square displacement described by $\langle r^2 \rangle$
- Four dynamical regimes for rotational mean square displacement described by $\langle \varphi^2 \rangle$

# Rotational Diffusivities for the three principal directions

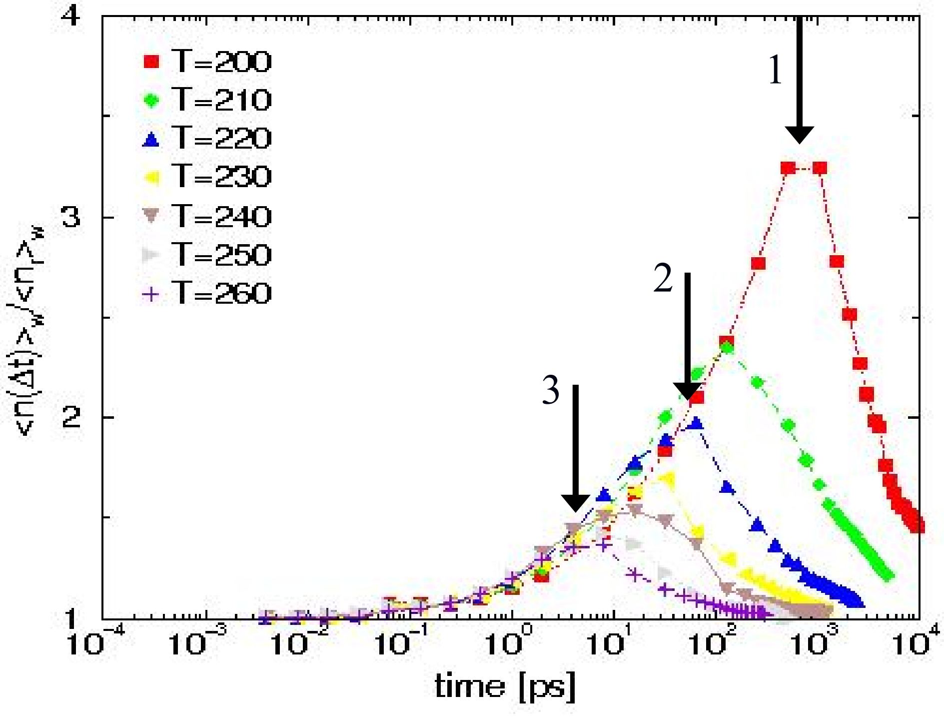


- The rotational diffusivity decreases by ≈ 3 orders of magnitude
- We need clusters of more mobile molecules: significant molecular motion in a cold, dense fluid can only occur if the molecules rearrange their positions in a concerted, cooperative manner.

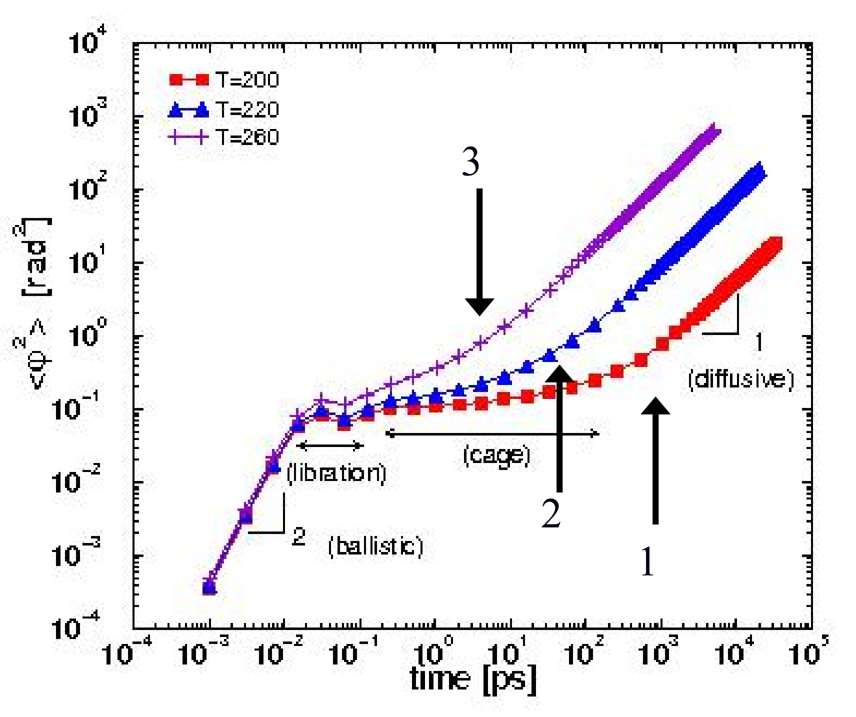
# Cluster definition

1. Rotational Mobility: maximum angular displacement in $\Delta t$
2. Select the 7% of the most rotationally mobile molecules
3. Define cluster at time $t_0$ for observation time $\Delta t$ as those molecules whose O-O distance is less than 0.315 nm

Average size of rotational clusters

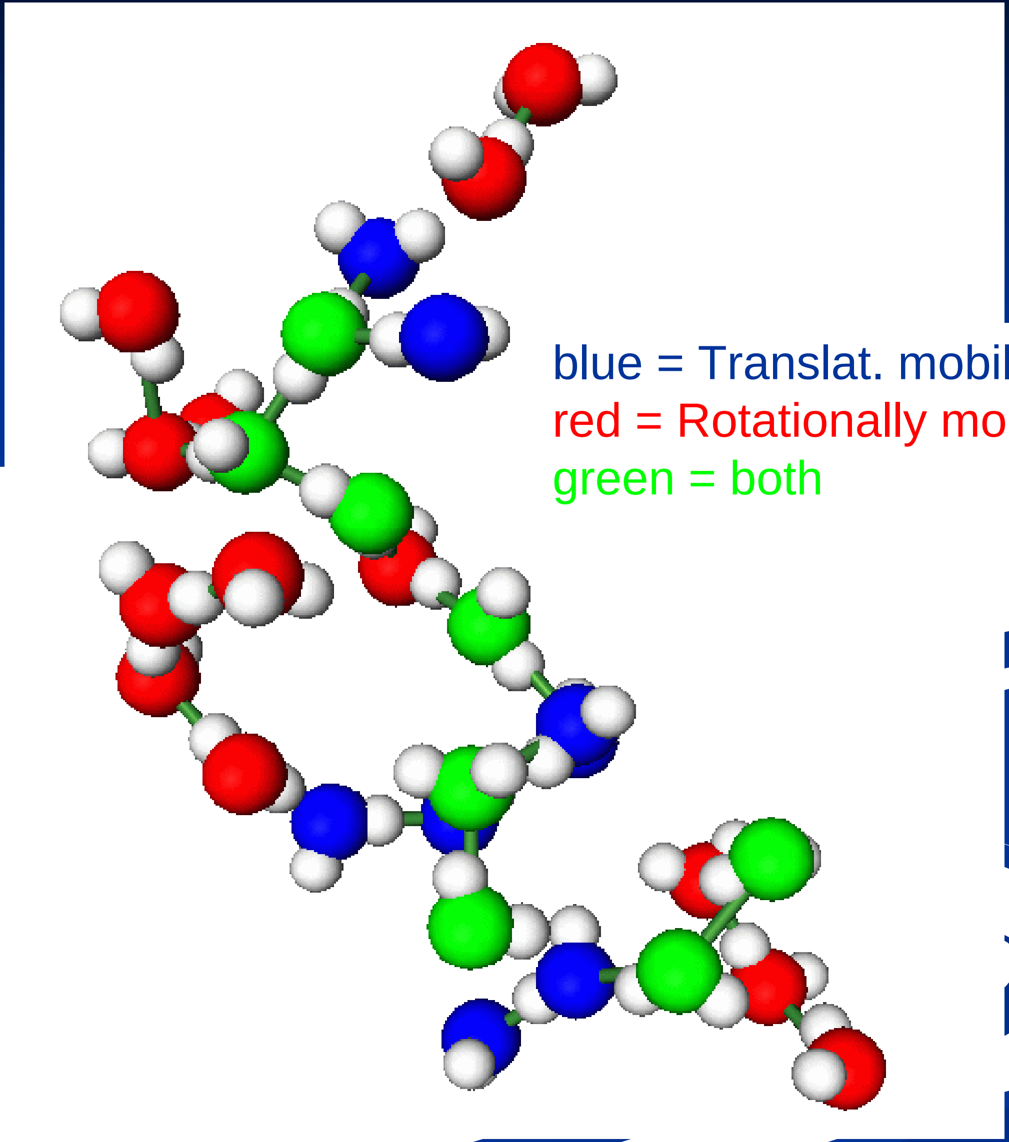


Rotational mean square displacement



- Answer to question 1: yes, 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).

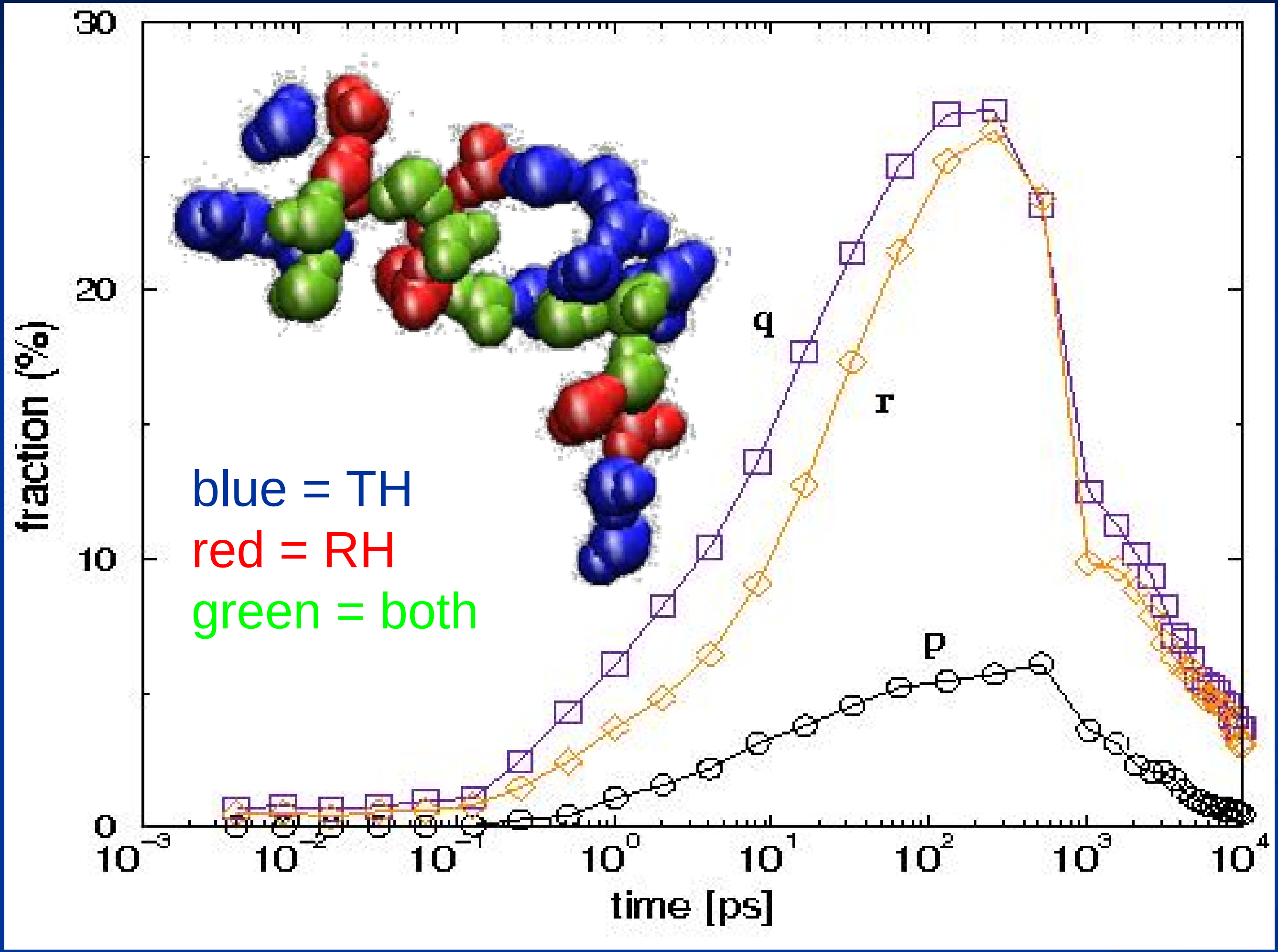
# Clusters of rotationally mobile molecules

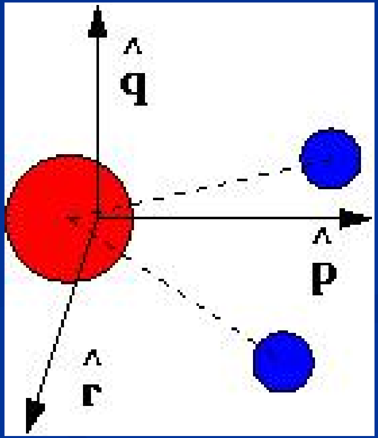


blue = Translat. mobile clusters
red = Rotationally mobile clusters
green = both

- Disconnected clusters are part of a larger region of cooperative motion

# Fraction of molecules in both rotational & translational heterogeneities

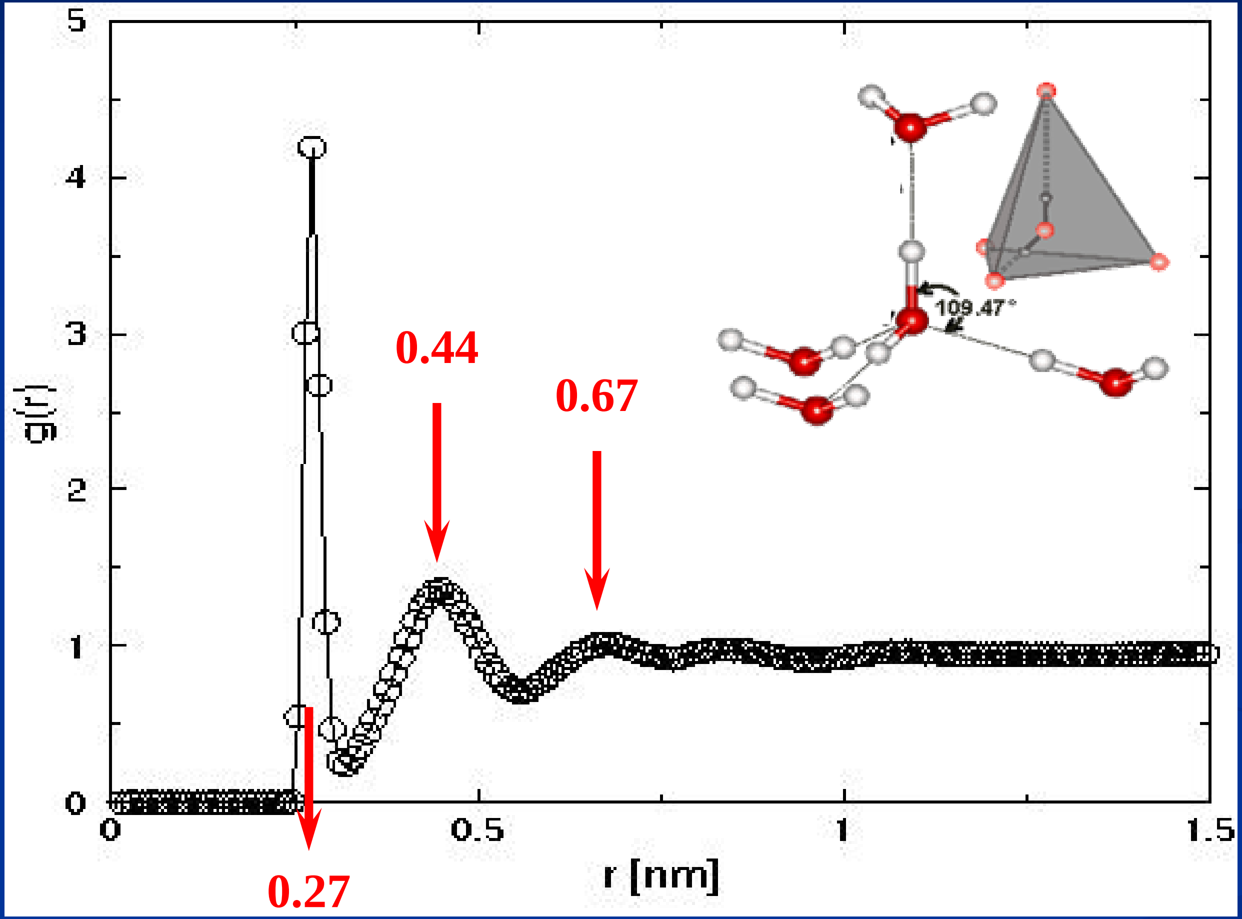




- This fraction (of the clusters) can be as high as almost 30%

Review:

# Oxygen-Oxygen radial distribution function

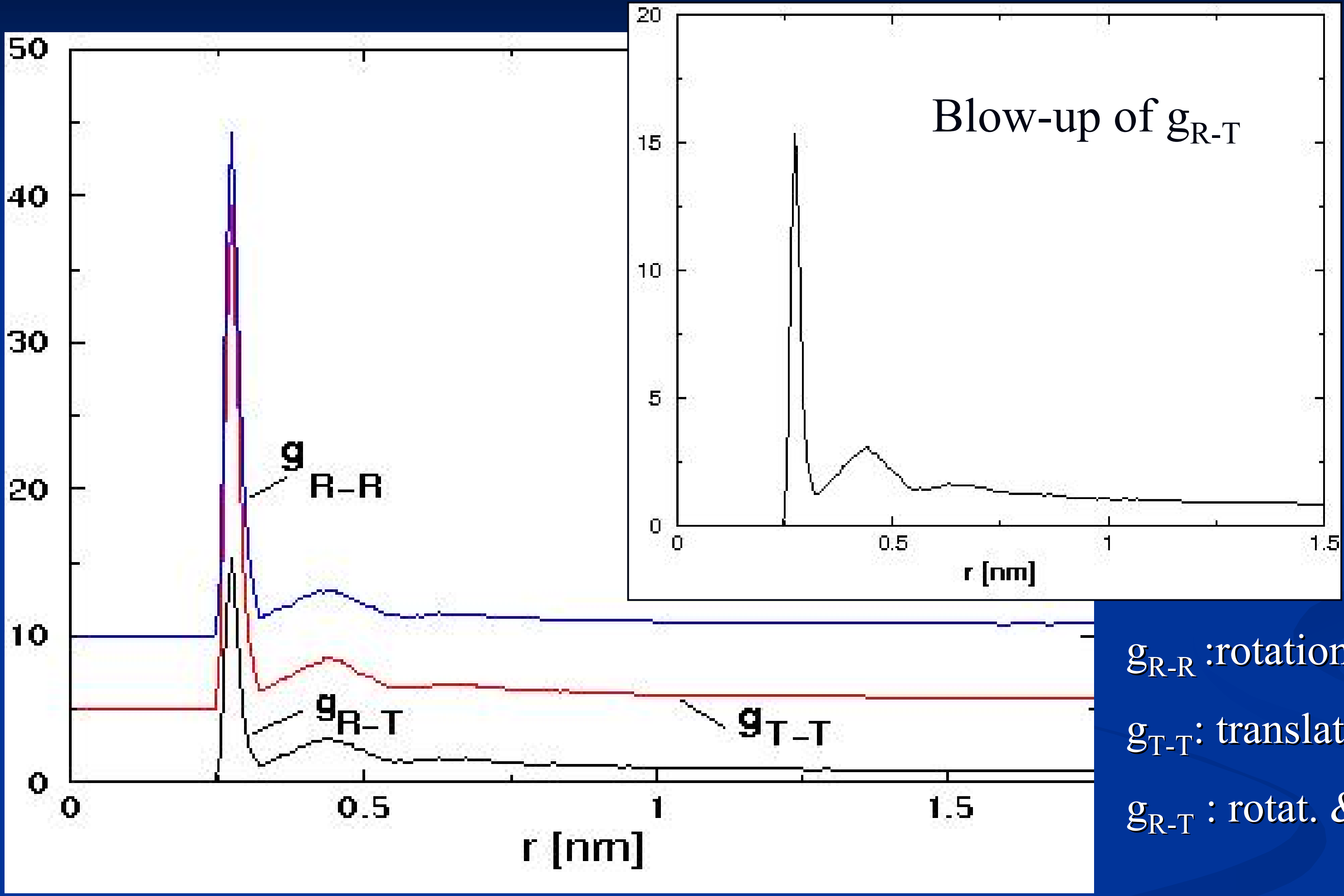


- water forms a tetrahedral structure with its neighbors

probability of finding two molecules separated by distance *r*

Short range order, long range disorder

# Three oxygen-oxygen radial distribution functions for heterogeneities



$g_{R-R}$ :rotational clusters

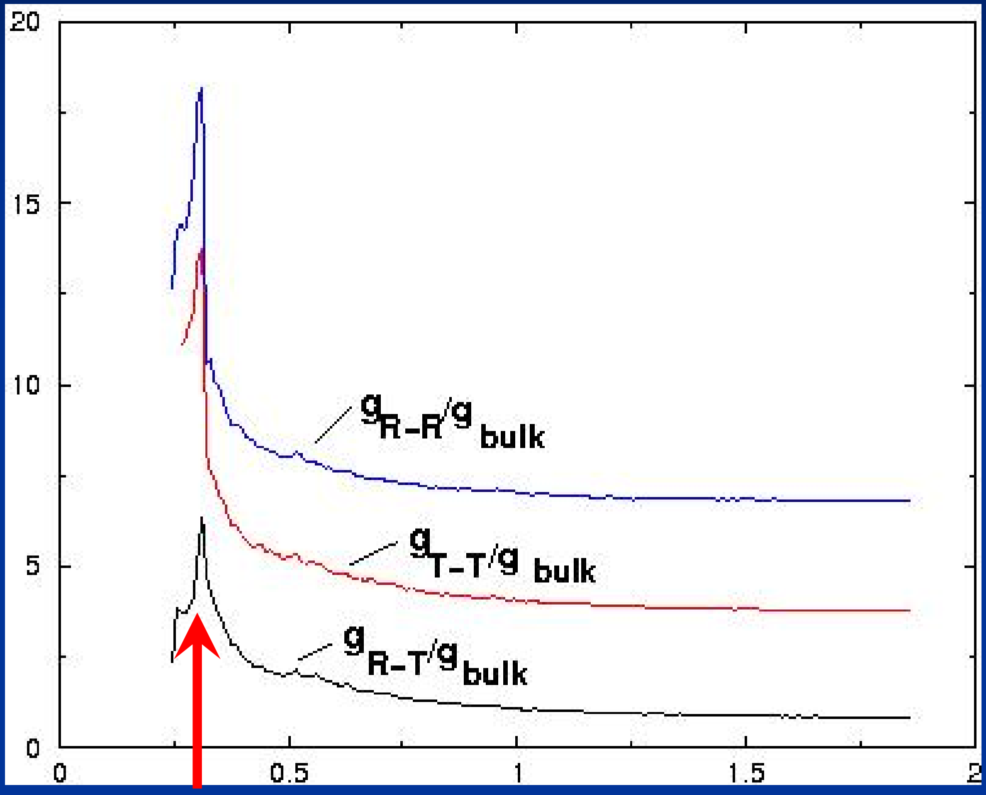
$g_{T-T}$: translational clusters

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

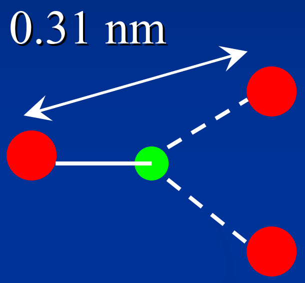
- $g_{R-R}$, $g_{T-T}$, $g_{R-T}$ are similar to standard oxygen-oxygen radial distr. function
- rotational and translational heterog. are correlated in space (answer to question 2)

# Normalization by the "standard" radial distribution function

Motivation: measure of some "extra" order beyond the bulk structure



0.31



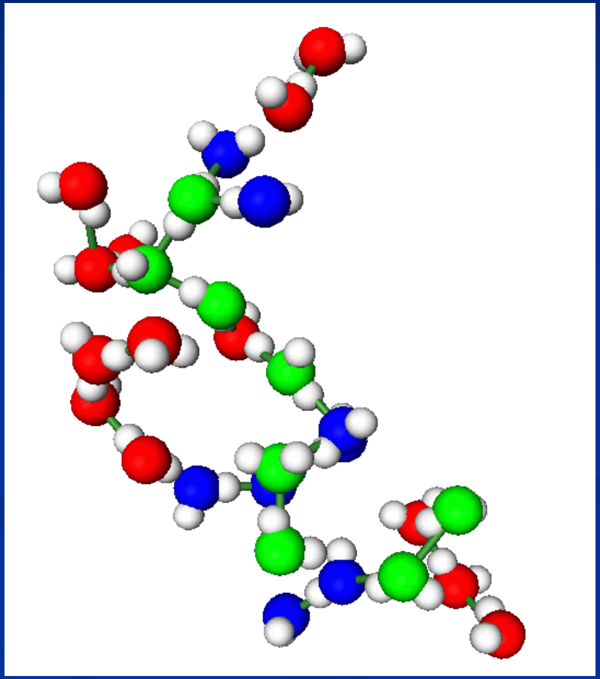
bifurcated bond: a hydrogen shared between 2 other oxygens

- 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.

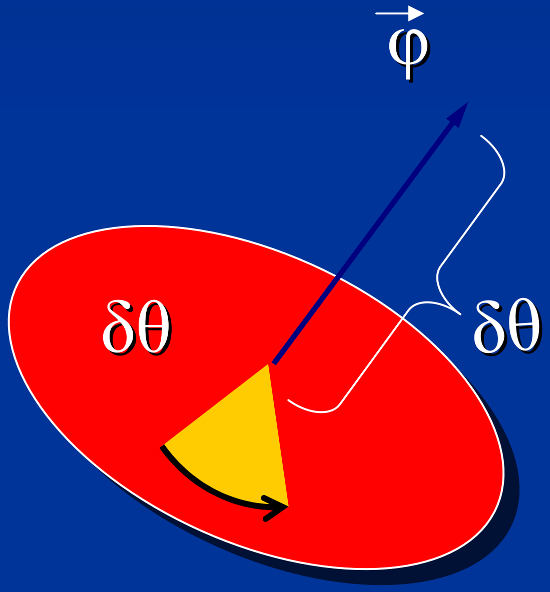
# Conclusions

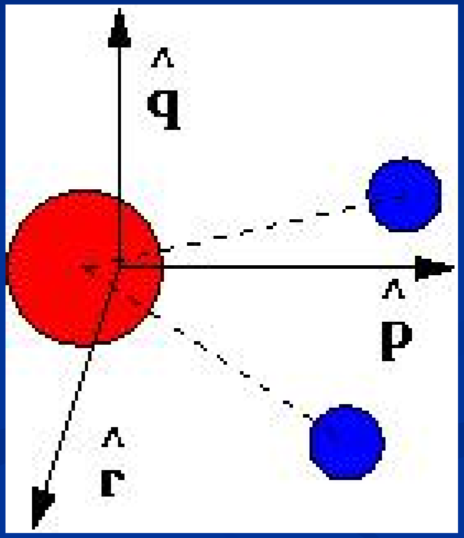
1. Rotational and translational heterogeneities form together a larger more complex region of cooperative motion.

2. The presence of a fifth oxygen (inside the nearest neighbor shell) acts as “catalyst” for the restructuring of the hydrogen-bonded network, therefore allowing a mechanism for diffusion in cold water.



# Description of rotations



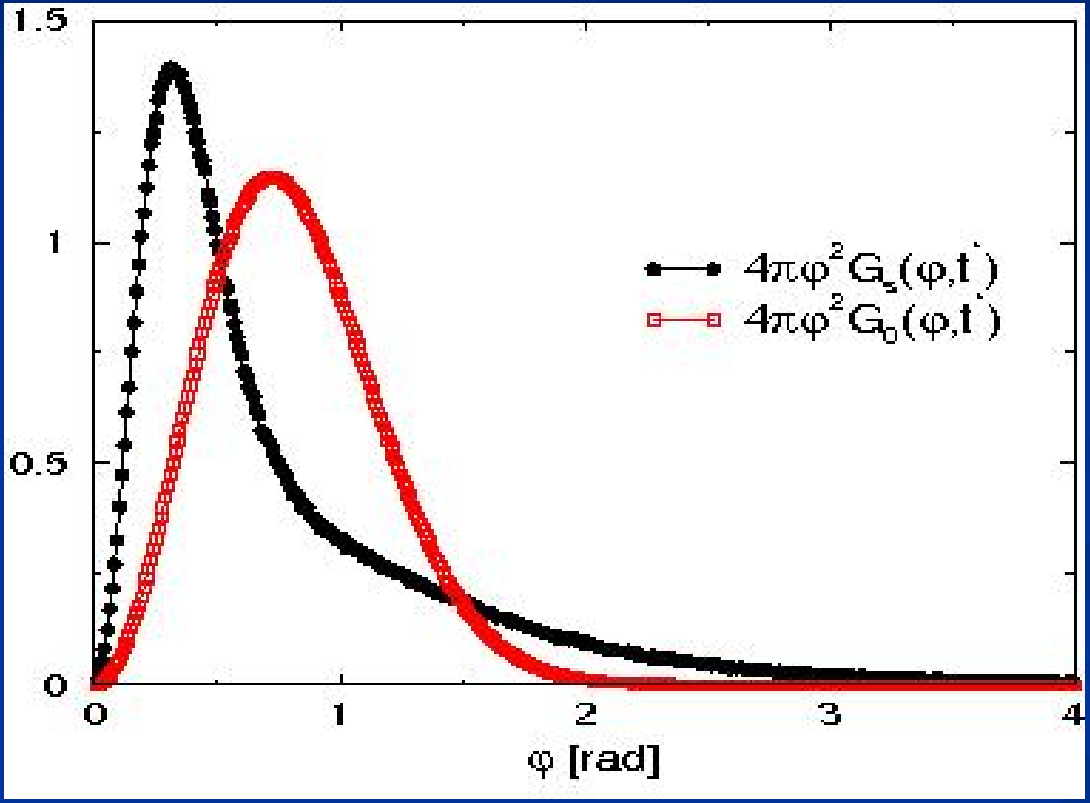


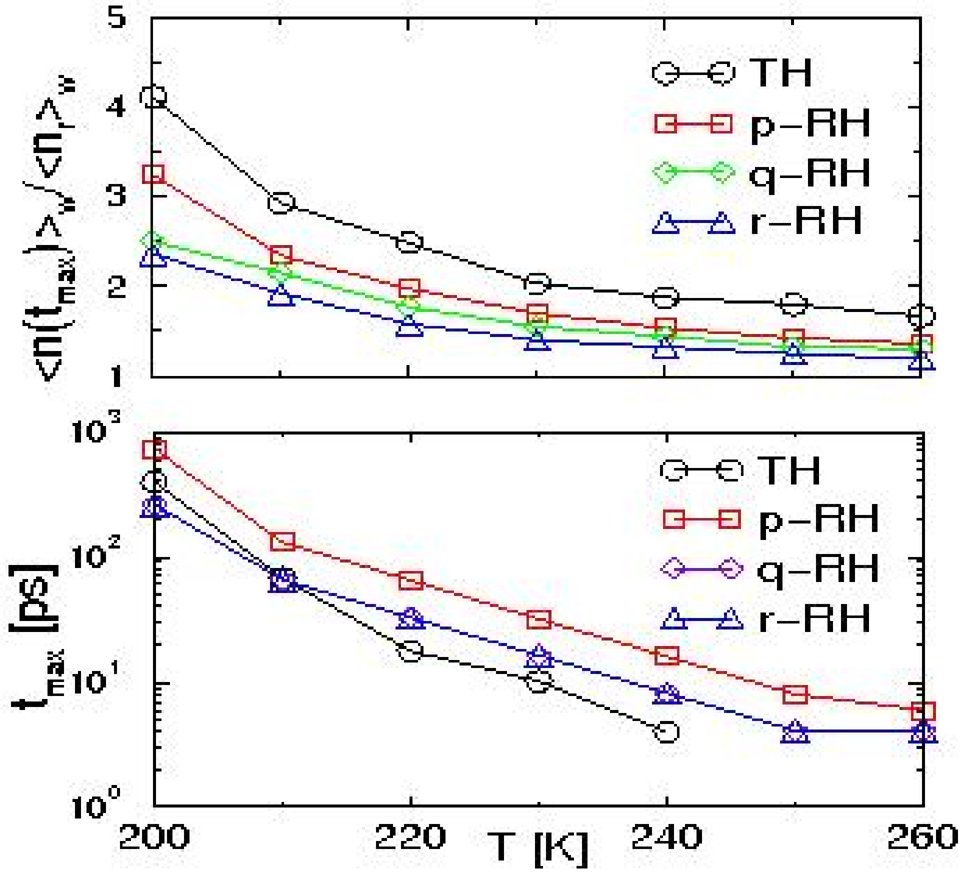
Moments of Inertia

r: 2.9376 x $10^{-40}$ g $cm^2$

p: 1.9187 x $10^{-40}$ g $cm^2$

q: 1.0220 x $10^{-40}$ g $cm^2$


1.5
1
0.5
0
0
1
2
3
4
φ [rad]
$4\pi\varphi^2 G_s(\varphi,t^*)$
$4\pi\varphi^2 G_0(\varphi,t^*)$


$\langle n(t_{max})\rangle_s / \langle n_r \rangle_s$
5
4
3
2
1
TH
p–RH
q–RH
r–RH
$t_{max}$ [ps]
$10^3$
$10^2$
$10^1$
$10^0$
TH
p–RH
q–RH
r–RH
200
220
T [K]
240
260