

*Dynamics of hydration water and its
implication for biomolecular dynamics*

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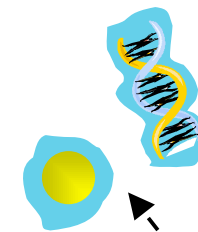
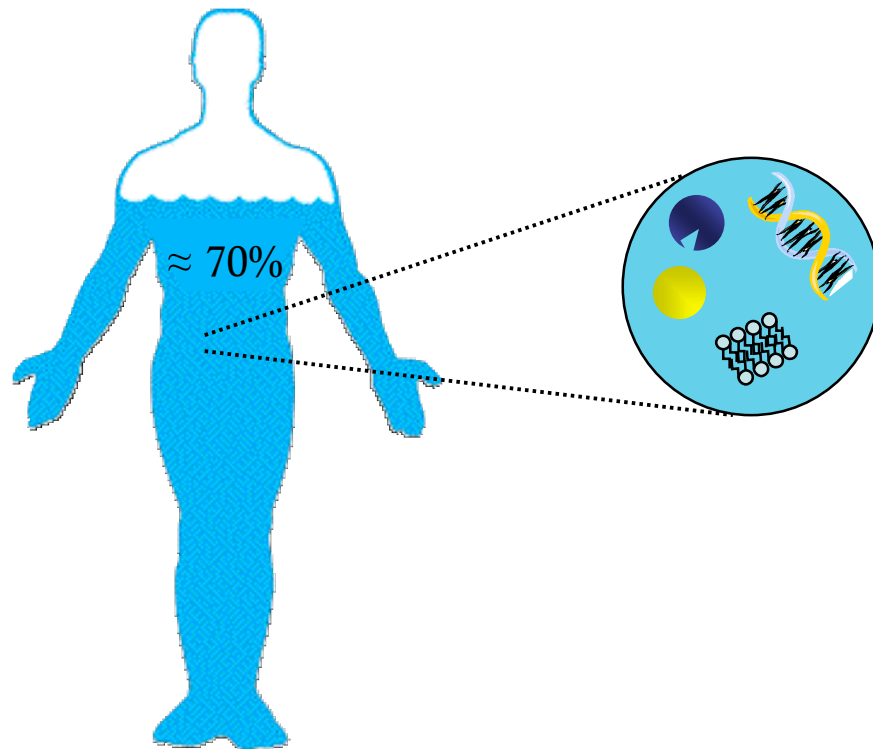
Los Alamos:

Hans Frauenfelder

Outline

- **Introduction to interfacial and biological water**
- **Confined supercooled water**
 - "Normal" liquid behaviour
 - Relaxation processes in confined water
 - Diffusion of confined water
 - "Problems" and relation to bulk water
- **Proteins in different solvents**
 - Introduction to the idea of solvent-slaved protein dynamics
 - Dielectric data on myoglobin in water-glycerol solvents
 - QENS data on hemoglobin in water, glycerol and methanol
- **Conclusions**

Water in a body



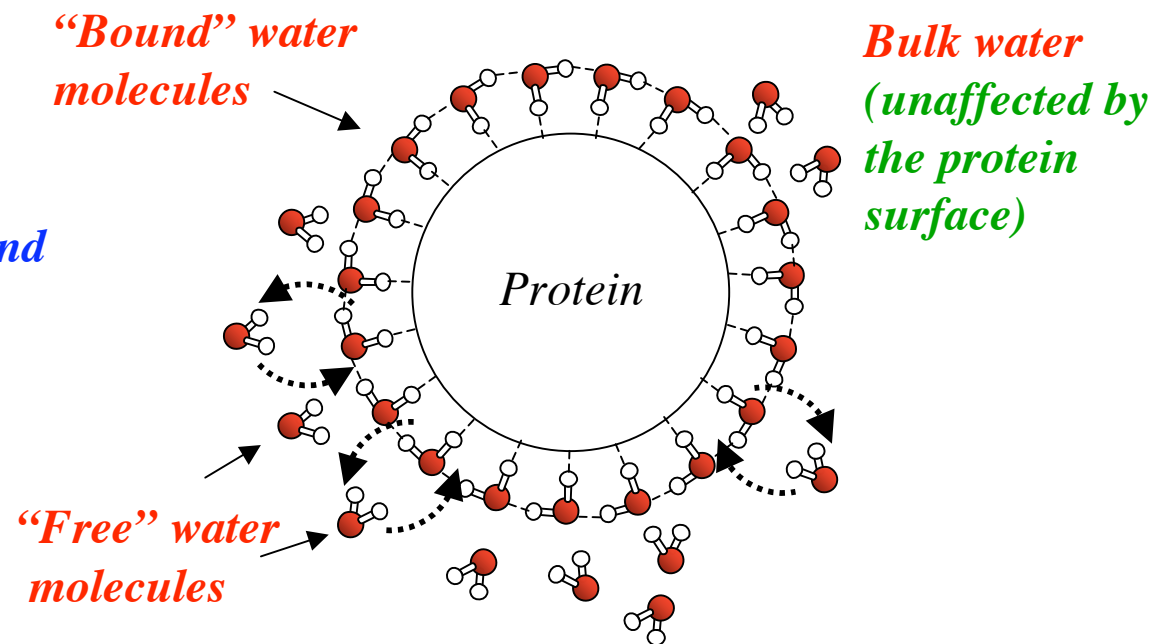
water molecules attached to
or located in the vicinity of
surfaces of different kinds

interfacial/confined water

Biological water

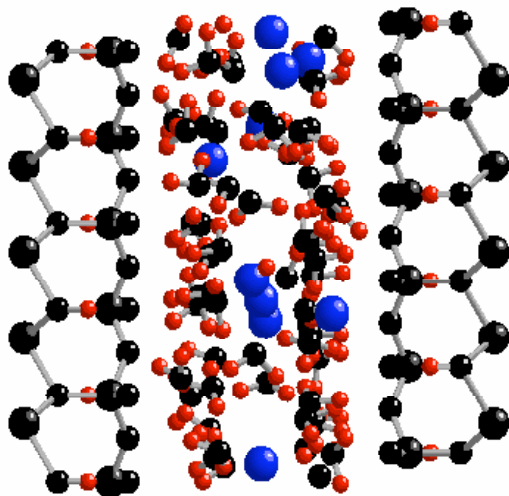
Hydration water

- ◆ *Tightly (H-) bonded water*
- ◆ *More loosely bonded water*
- ◆ *Dynamical exchange between the two molecular layers*
- ◆ *Hydration shell = first and second hydration layers*
- ◆ *Enables protein motion necessary for protein function*



Confined water

- What is special with confined water?
- Why study confined water?
- What do we know about confined water?
- Structure and dynamics is altered.
- Important for processes in biology, geology and technology.
- A way to enter "no man's land".
- Molecular layering
- Affected H-bonded network
- Slower dynamics at surfaces



Two molecular layers of water confined in a Na-vermiculite clay. From N. T. Skipper *et al.* in ISIS Facility Annual Report (1998), page 47

*Dynamics of confined
supercooled water*

How does supercooled water behave in "no man's land" (150-235 K)?

- **Fragile or strong?**

R. S. Smith and B. D. Kay, *Nature* (1999)

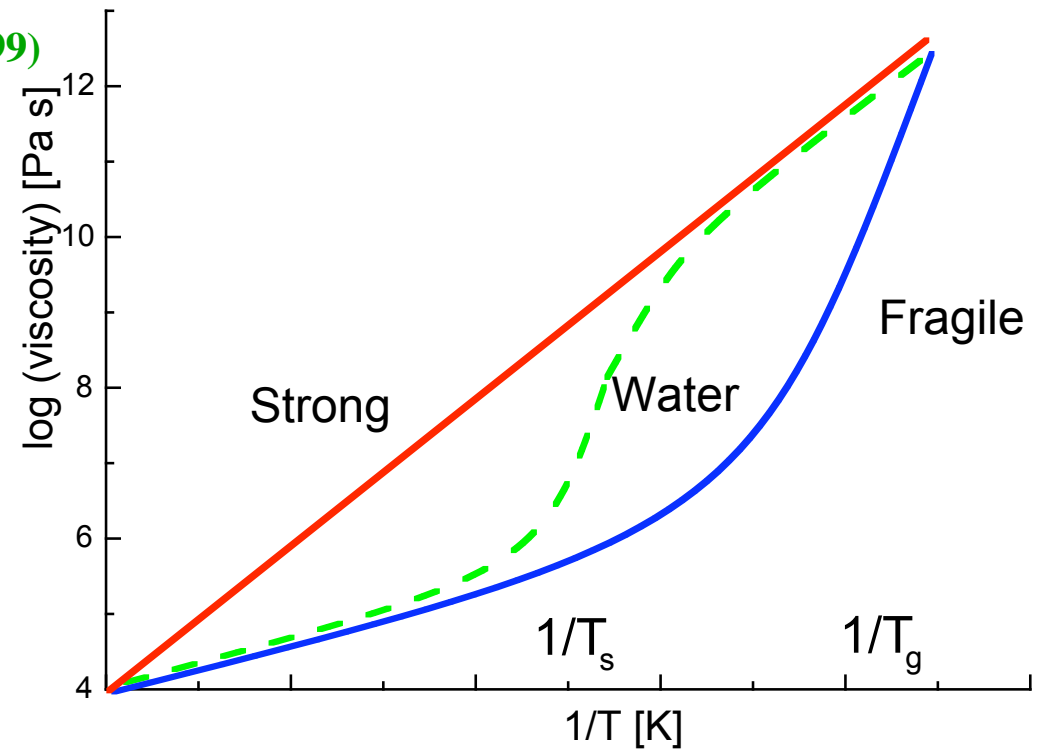
K. Ito et al., *Nature* (1999)

- **Where is T_g located,**

~ 130 K or ~ 165 K?

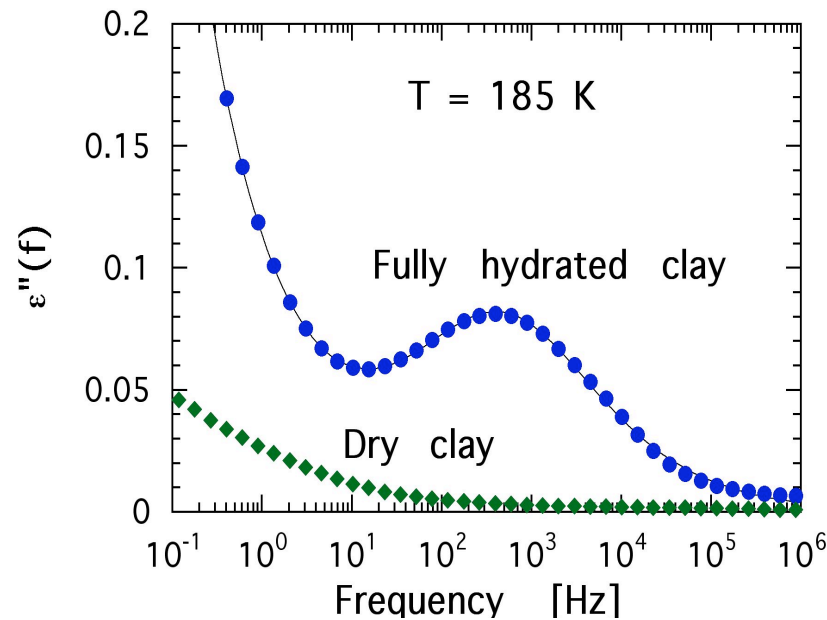
G. P. Johari et al., *Nature* (1987)

C. A. Angell et al., *Science* (2001),
Nature (2004)

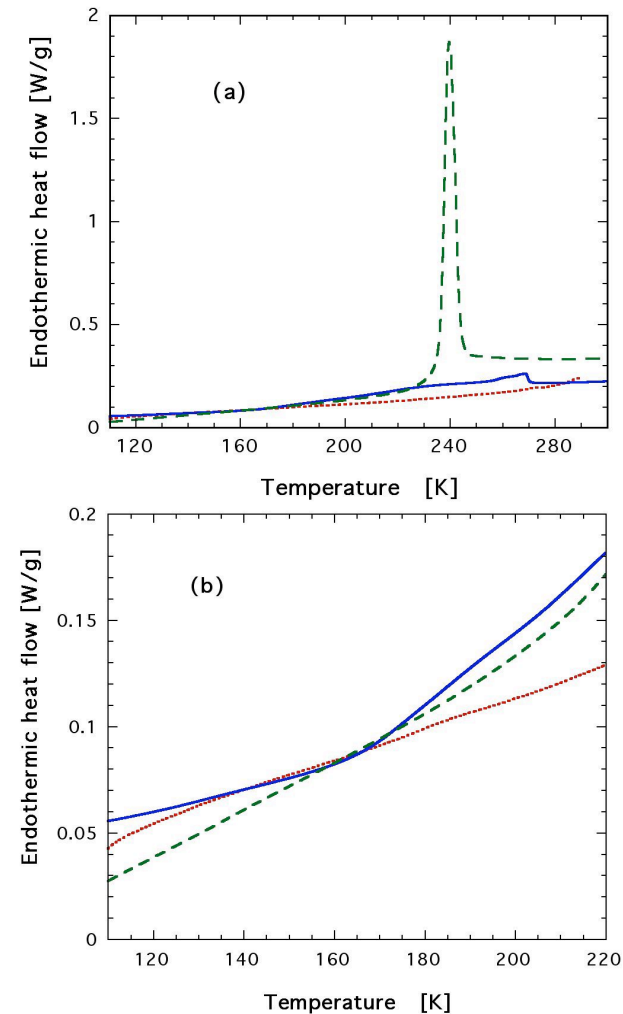


Studies of confined water

Dielectric and DSC data on confined water

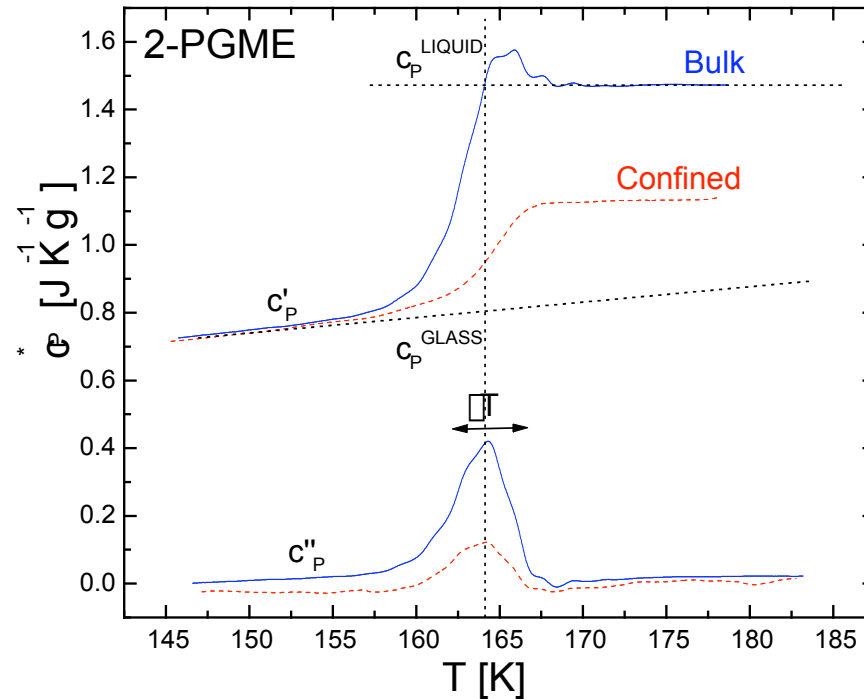


Imaginary part of the dielectric permittivity of vermiculite clay at 185 K. A clear dielectric loss peak is observed for the fully hydrated clay. R. Bergman and J. Swenson, Nature 403, 283 (2000).



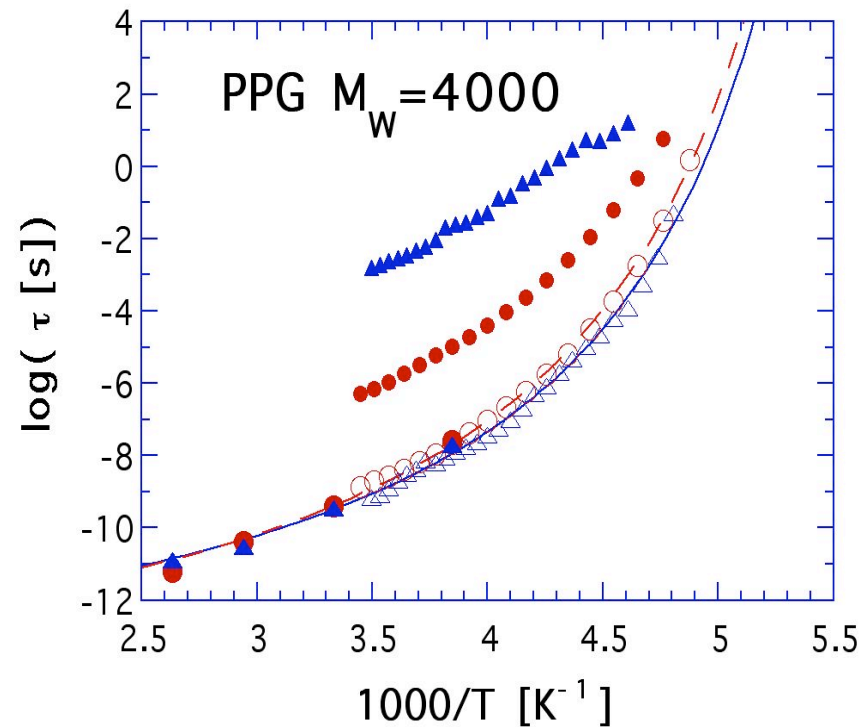
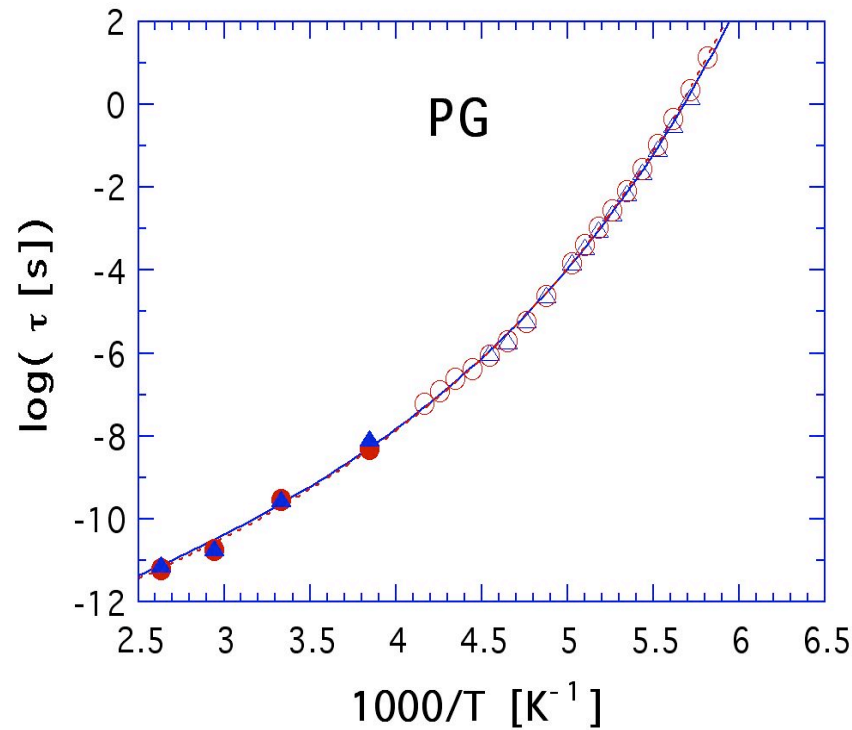
DSC measurement of endothermic heat flow during reheating (10 K/min) of fully hydrated clay and MCM-41 with pore diameters 21 Å and 36 Å. No clear glass transition can be observed.

Typical glass transition for liquids confined in clay



Calorimetric T_g for di-(proylene glycol monomethyl ether) (2-PGME) confined in a Na-vermiculite clay.
S. Cervený et al., J. Phys. Chem. B 108, 11596 (2004).

Relaxation times of PG and PPG confined in clay



□=confined

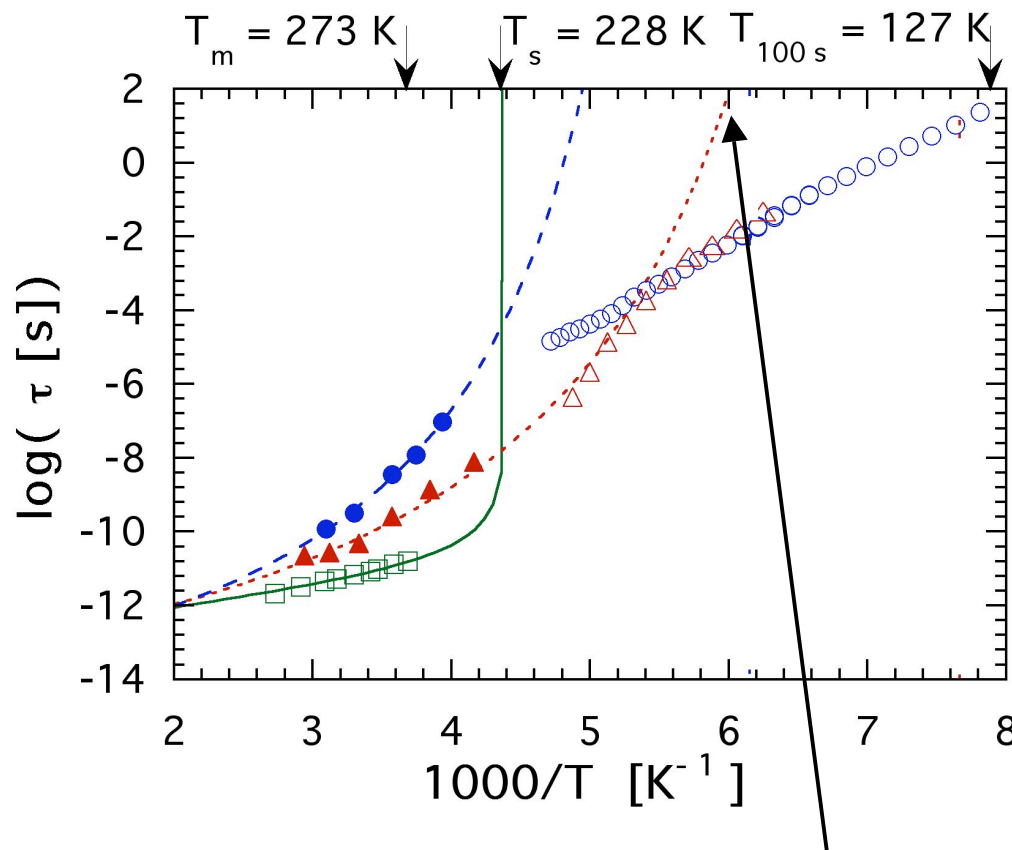
●=bulk

J. Swenson et al. Eur.
Phys. J. E12, 179 (2003)

- Average relaxation time from QENS ($Q=1 \text{ \AA}^{-1}$) \approx dielectric □-relaxation time.
- These relaxation times are almost unaffected by the confinement.

Relaxation times of water confined in clay and 10 Å molecular sieves

Fragile-to-strong transition?



O = vermiculite clay

□ = molecular sieve (diameter=10 Å)

Squares = dielectric data of bulk water
(C. Rønne *et al.*, *Phys. Rev. Lett.*
82 (1999) 2888)

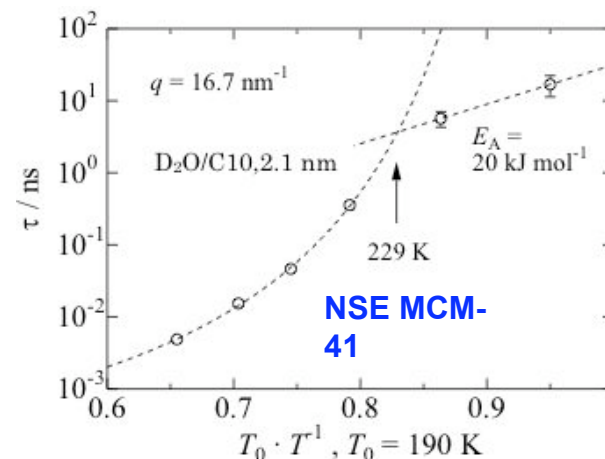
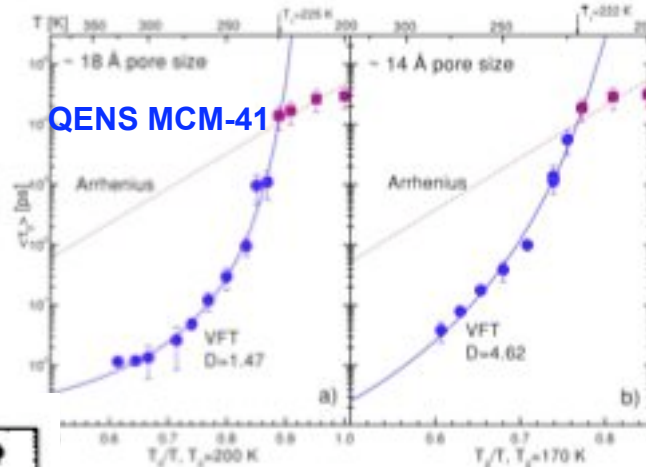
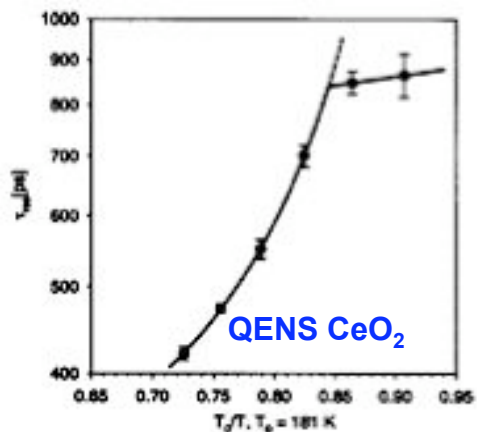
Solid symbols = average relaxation
times from neutron spin-echo

Empty symbols = dielectric relaxation
times.

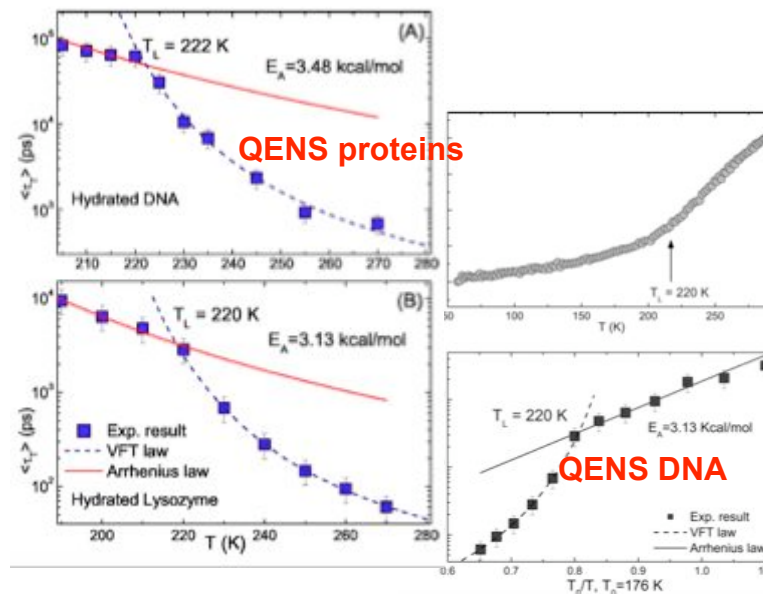
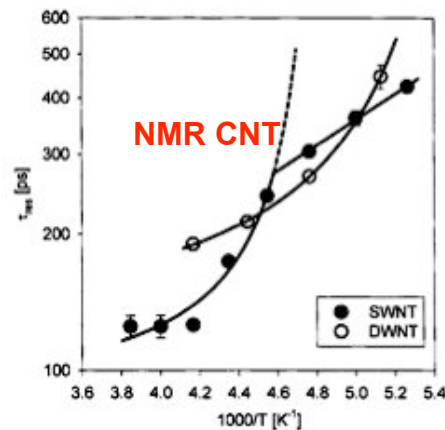
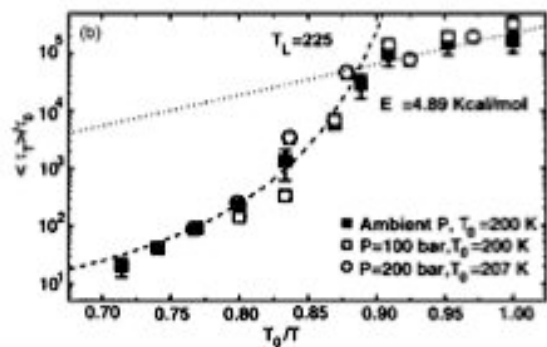
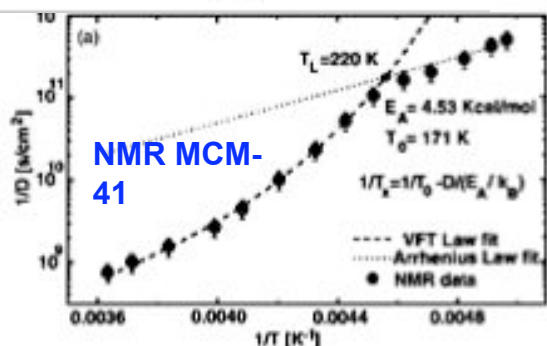
The solid line represents the power law
behaviour of bulk water proposed by
C. A. Angell *et al.*

T_g at 160 K? (From adiabatic calorimetry of 1.1 nm pores, M. Oguni *et al.* *Chem. Asien J.* 2, 514 (2007))

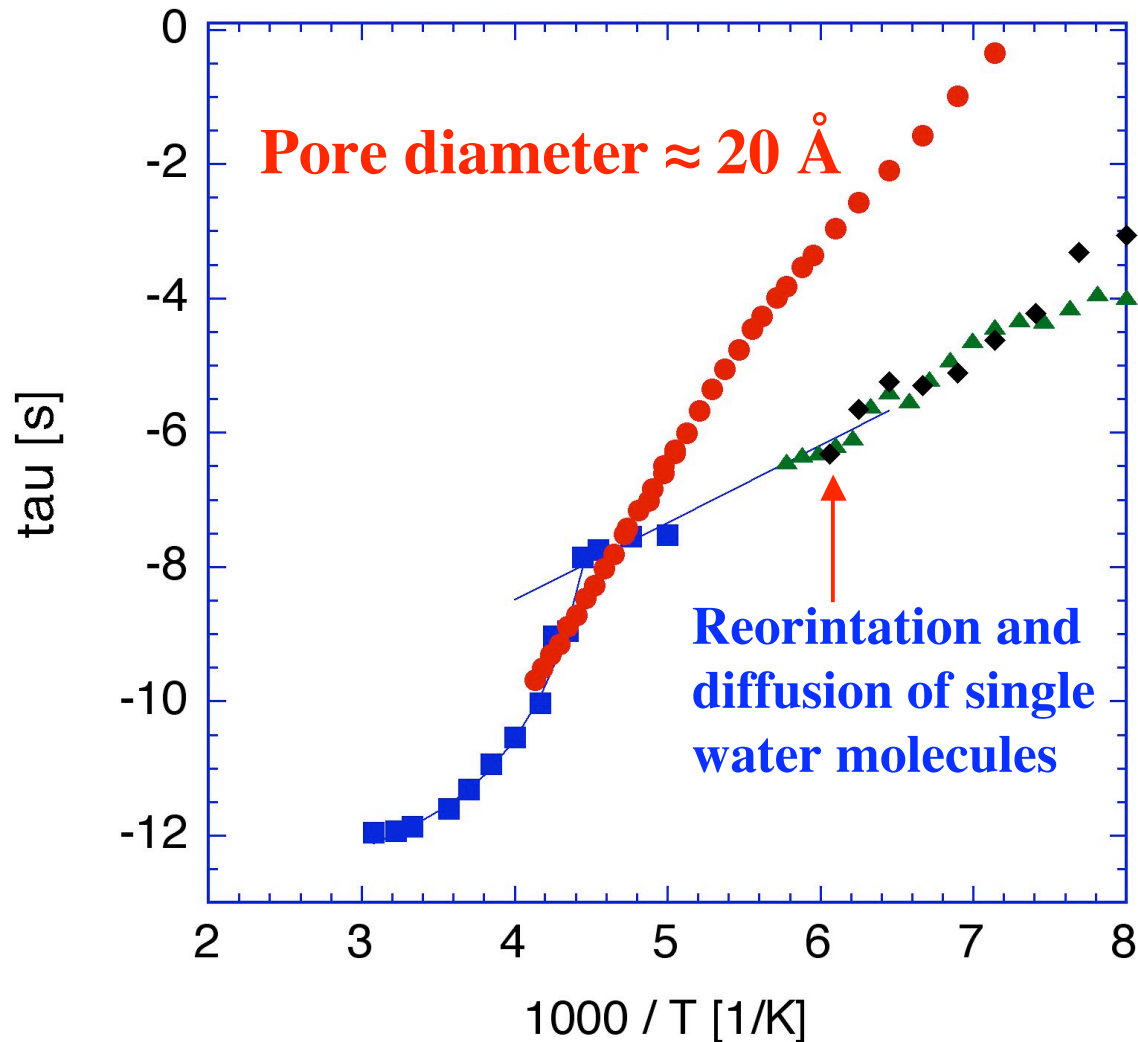
Another apparent "fragile-to-strong transition" of interfacial water



Kittaka et al.



Relaxation times of water confined in MCM-41 from QENS and dielectric spectroscopy



Blue symbols: QENS data from
A. Faraone *et al.*, *J. Chem.
Phys.* 121, 10843 (2004)

Red symbols: Our dielectric
data

Green symbols: Fastest process
in hydrated clay

Black symbols: Fastest water
process in hydrated myoglobin

**Fragile-to-strong
transition?**

Related crossover in the diffusivity of interfacial water

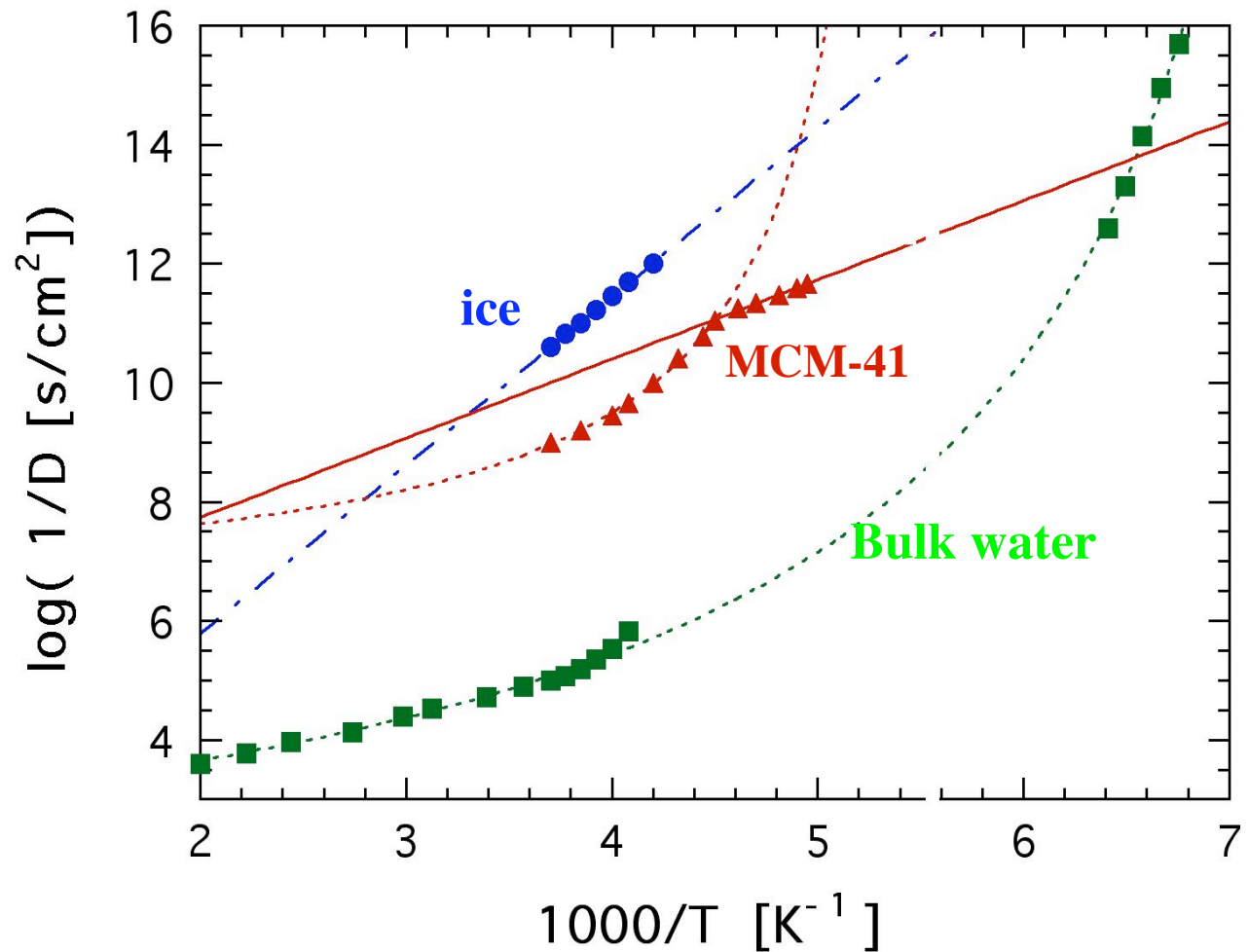
Bulk water (□)

Ice (○)

From R. S. Smith and B. D. Kay, *Nature* 398, 788 (1999) and references therein.

Water confined in MCM-41-S with 14 Å pores (△)

From F. Mallamace et al, *J. Chem. Phys.* 124, 161102 (2006).

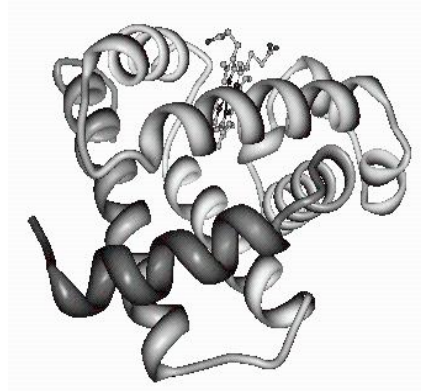


- * No clear consistency between confined and bulk water.
- * Moderately supercooled bulk water does not follow VFT.

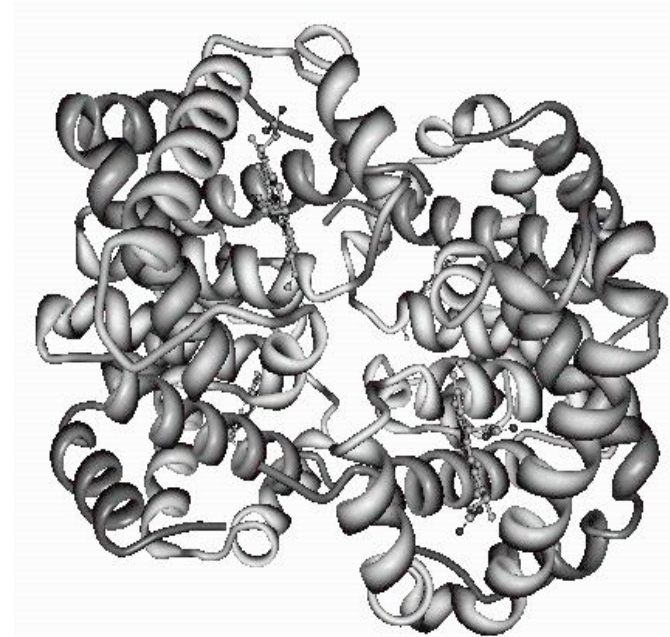
Conclusions confined supercooled water

- * In (most?) systems of confined water the cooperative α -relaxation cannot be observed at low temperatures. An apparent fragile to strong transition occurs when the merged $\alpha\beta$ process transforms to a pure α process.**
- * Another dynamic cross-over occurs for the water diffusivity when it decouples from the structural relaxation process (the merged $\alpha\beta$ process).**
- * How are the findings for confined water related to bulk water? Every interpretation seems to be contradicted by at least one experimental study.**

Dynamics of proteins in different solvents



Myoglobin



Hemoglobin

Biological water

Important for structure, stability, dynamics and function

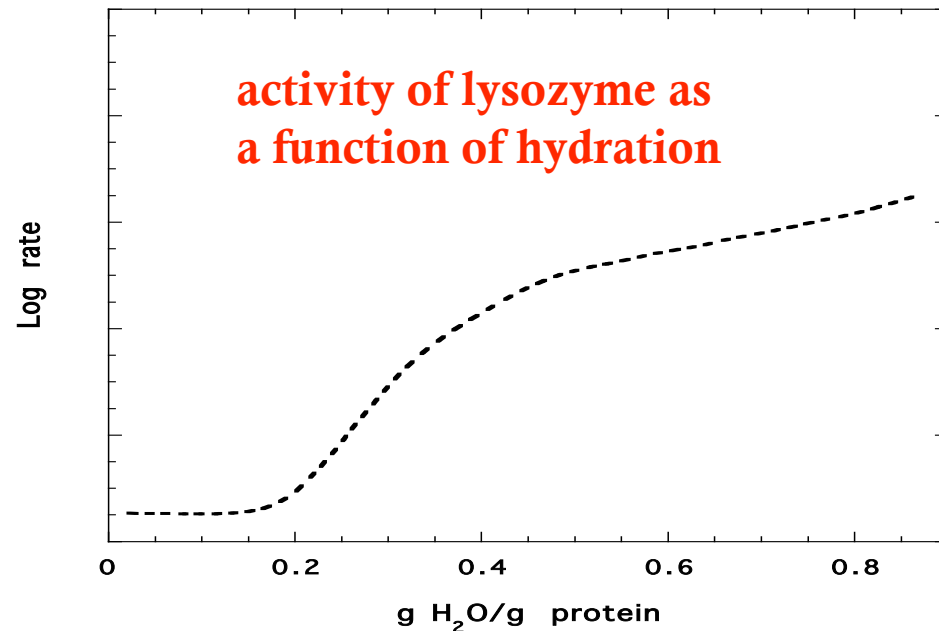
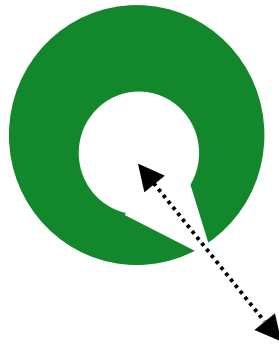
motions necessary for function

hydration necessary for function

“closed”



“open”

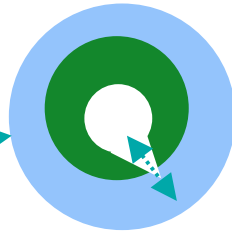


Rupley et al. Trends. Biol. Sci. 1983

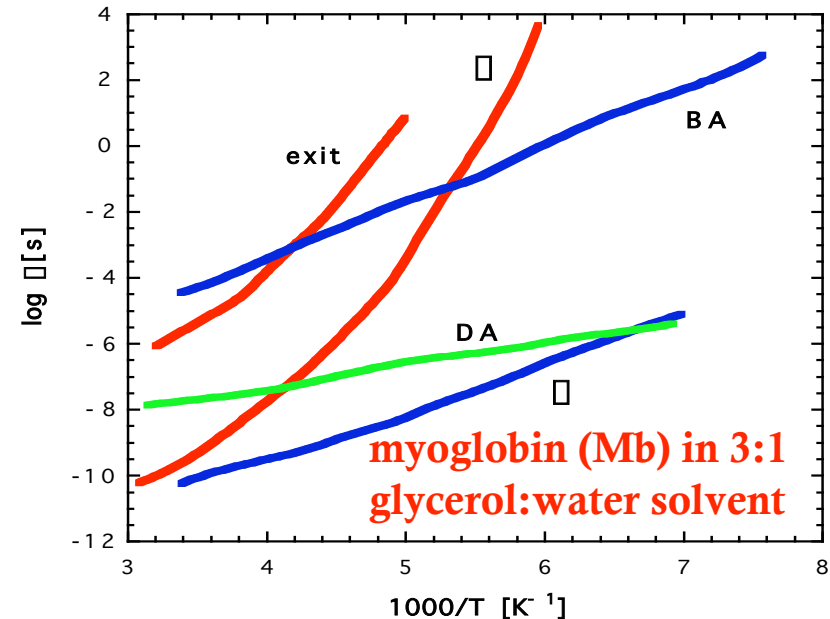
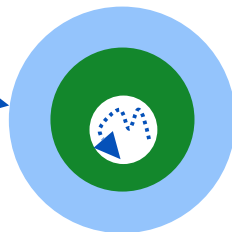
The “slaving concept”

Protein dynamics and function are coupled to motions in the surrounding environment.

- **solvent-slaved**
absent in dehydrated proteins
and proteins in solid environments

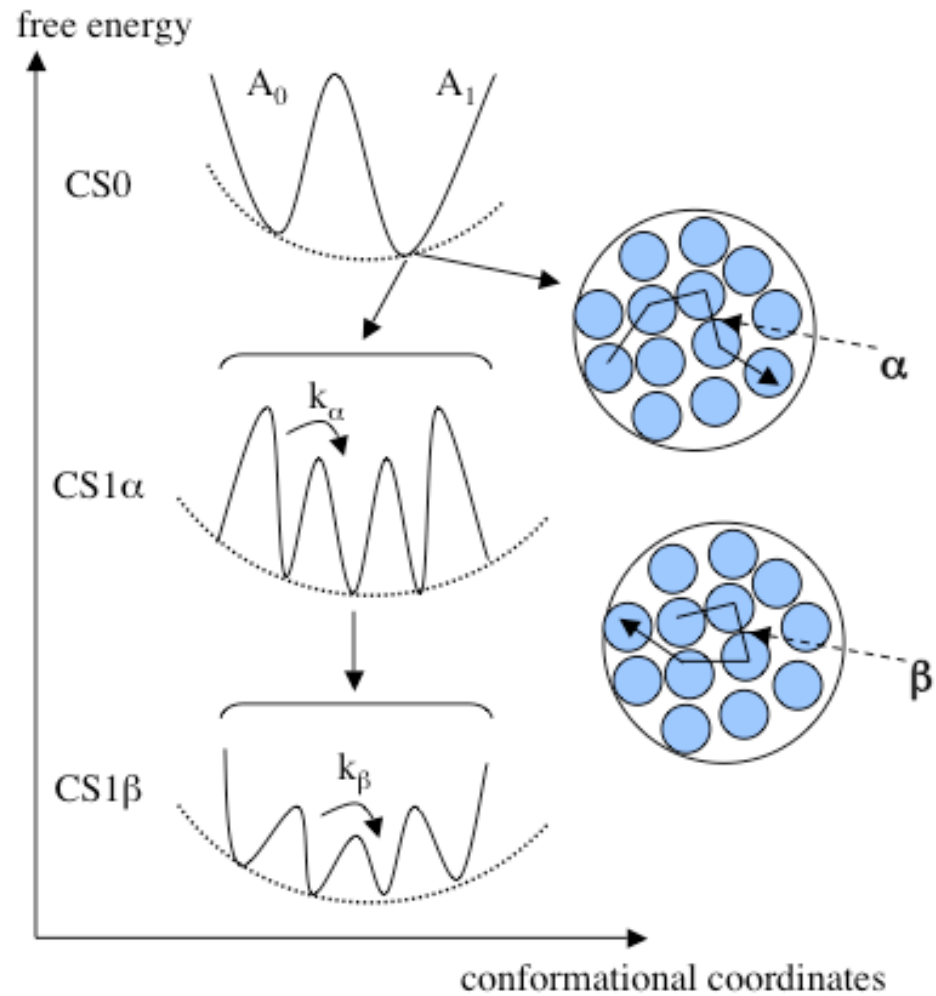


- **hydration-shell-coupled**
absent in dehydrated state
- **vibrational (non-slaved)**
independent of the surrounding



exit (escape of CO from Mb) is determined by the τ -relaxation in the solvent, whereas local CO migration (**BA**) within Mb is determined by the τ -relaxation.

The energy landscape



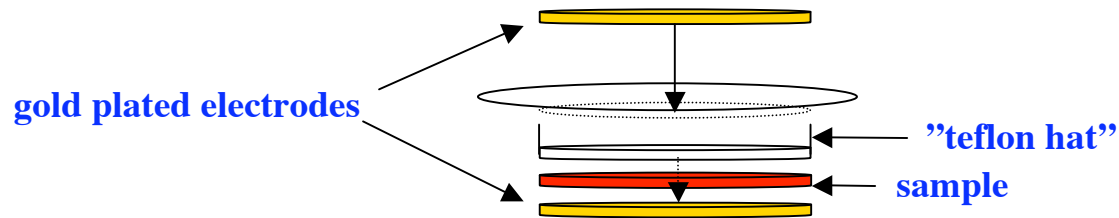
P. W. Fenimore, H. Frauenfelder et al., PNAS 110, 14408 (2004)

*Relation between solvent and protein dynamics;
A way to understand the importance of water for
biological processes*

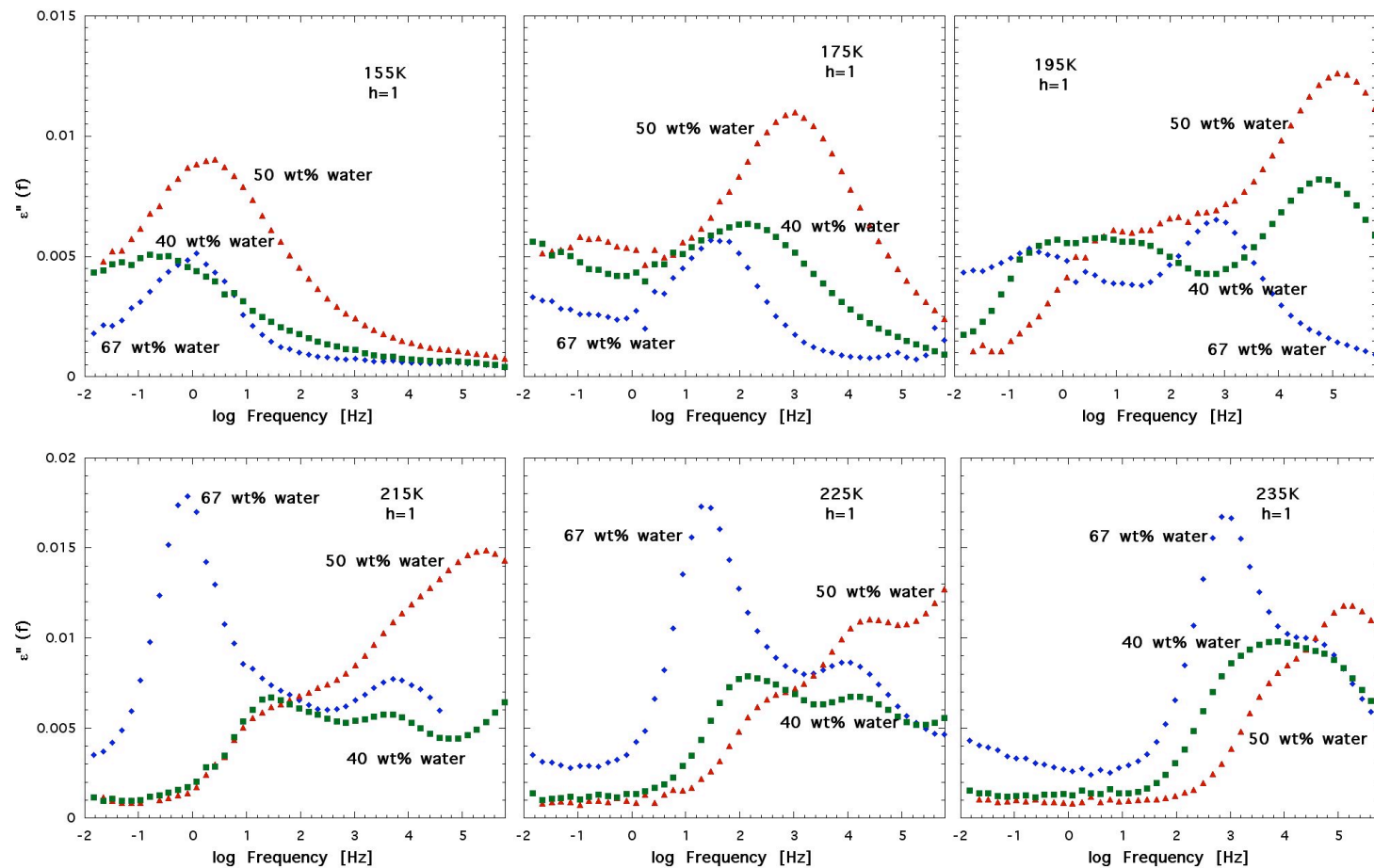
- Are protein dynamics and functions determined by solvent dynamics?
- Does water exhibit unique properties as solvent?
- What is the role of hydrogen bonds?

These questions can only be answered by comparing protein and solvent dynamics for different types of solvents.

Dynamics of myoglobin in water-glycerol solvents by dielectric spectroscopy



Conductivity and electrode polarisation were prevented by using a "teflon hat".



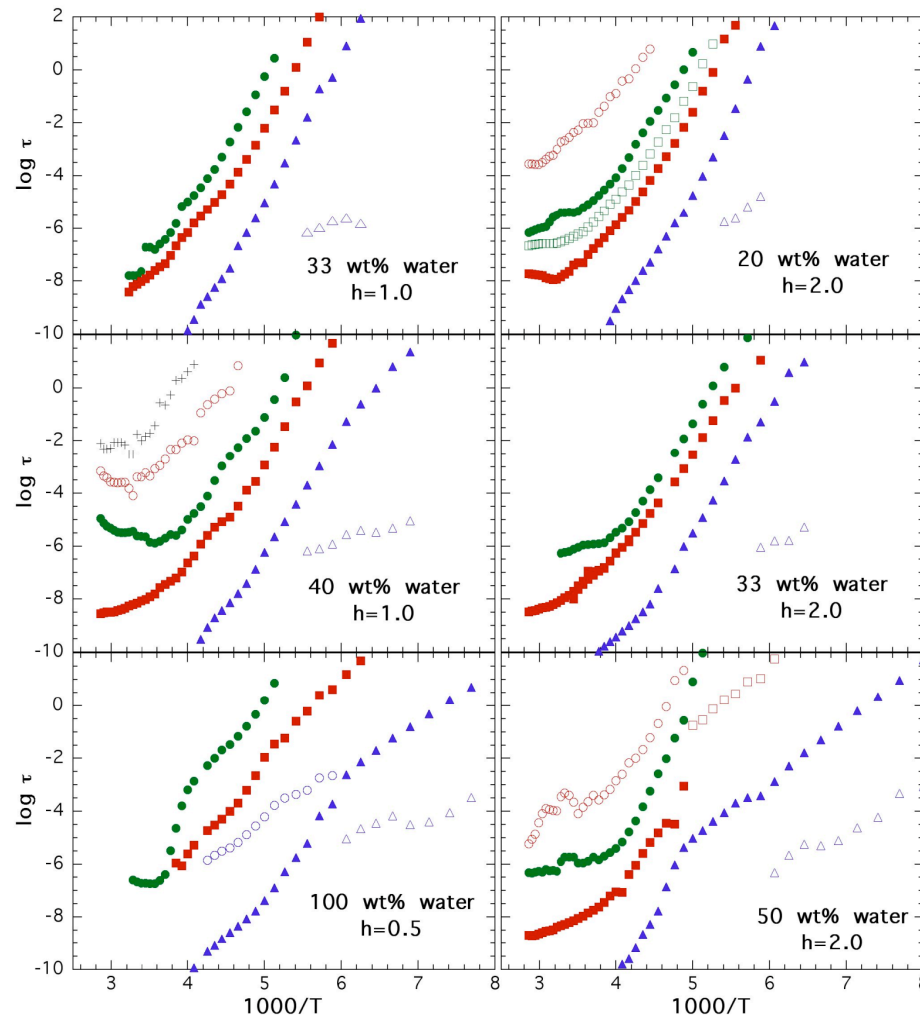
Dynamics of myoglobin in water-glycerol solvents

Interpretations:

Blue symbols = solvent relaxations

Solid red symbols = motions of polar side groups

Solid green symbols = conformational protein fluctuations (with possible contribution from Maxwell-Wagner polarisation)



* Similar T dependence for both protein and solvent

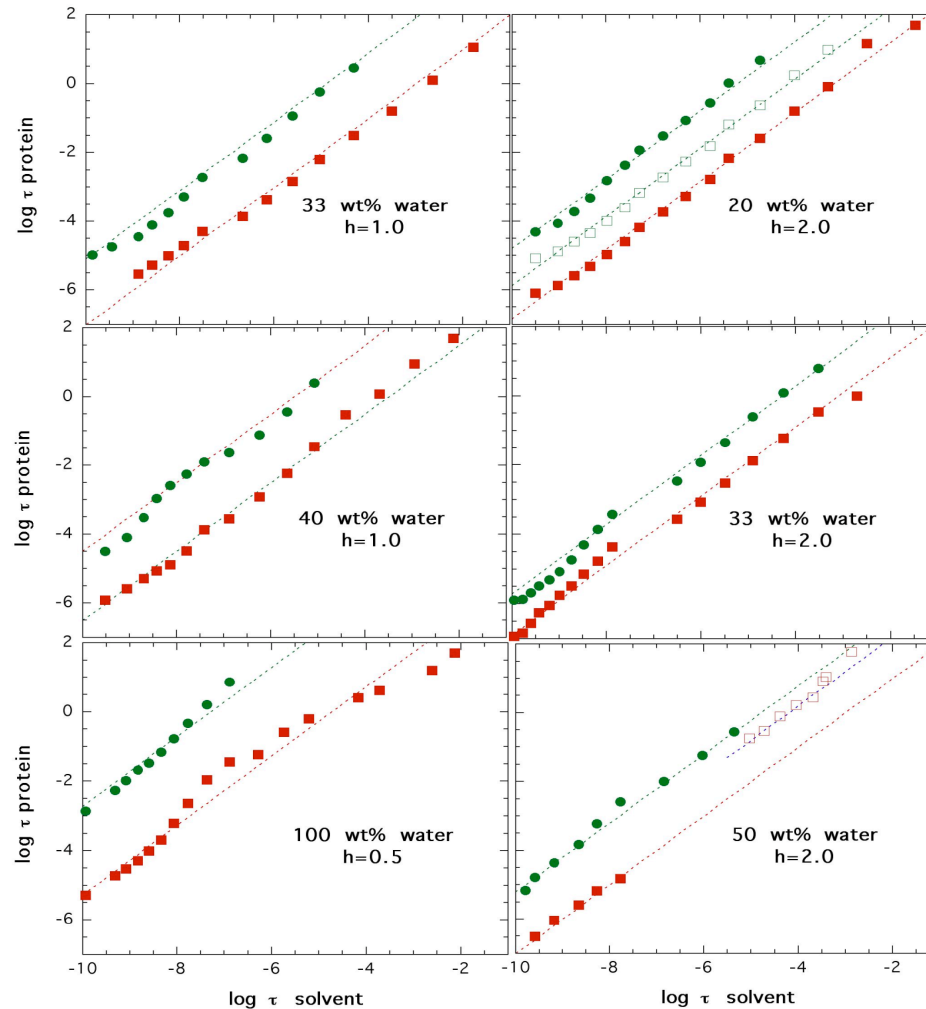
* Crossover in T dependence for water rich samples for both protein and solvent

* High water content and low T; only local \square -relaxation in the solvent

* High water content and high T; local \square -relaxation seems to remain in parts of hydration shell

Relaxation times for different solvent and protein processes in samples of different hydration levels ($h = \text{g solvent/ g protein}$) and weight fractions of water in the solvent.

Relation between the main solvent process and the fastest protein processes



* Linear dependence between solvent τ -relaxation and the fastest protein processes

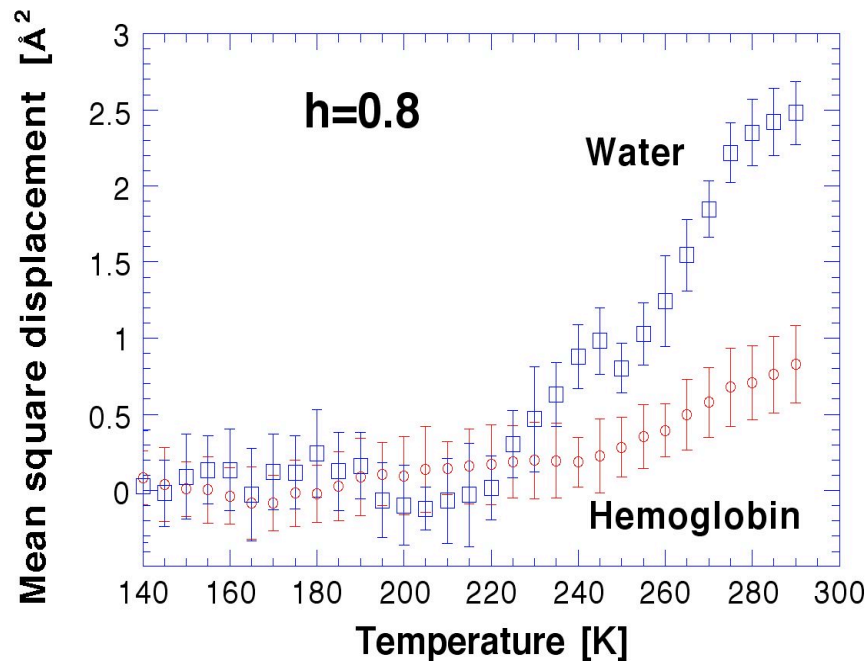
* For the highest water contents an additional local protein process is related to solvent τ -process

Solid red symbols = motions of polar side groups

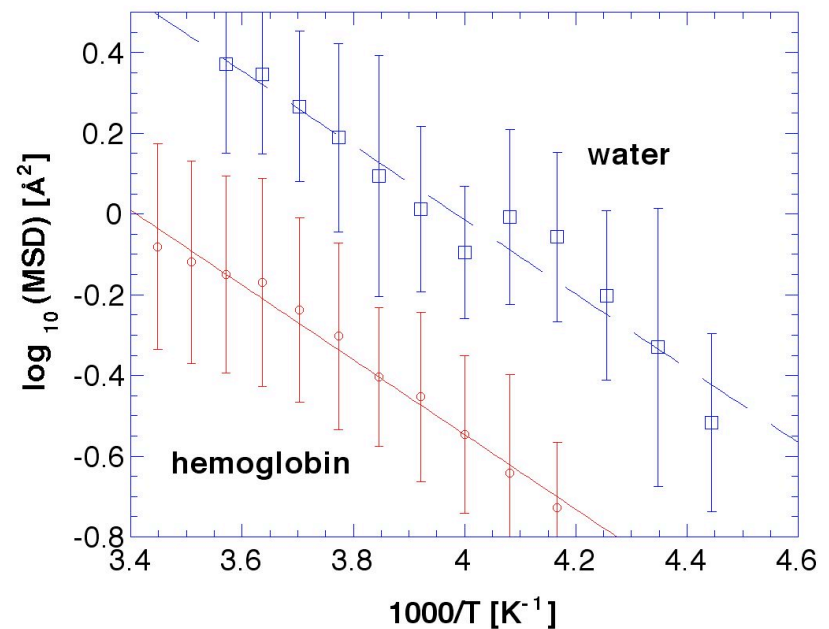
Solid green symbols = conformational protein fluctuations (or M-W polarisation)

Mean square displacement from neutron scattering

Hemoglobin in water



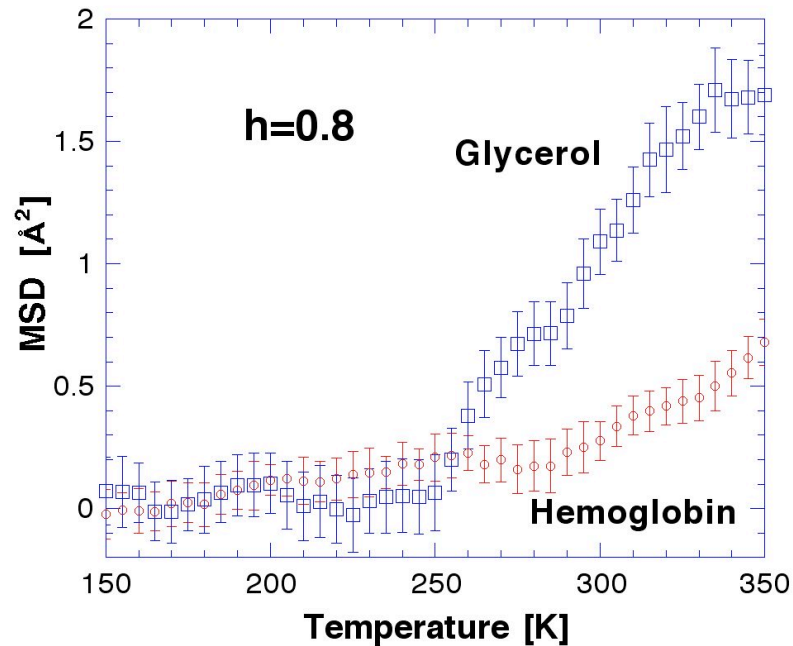
Onset of anharmonic protein motions at 240 K and water dynamics at 220 K.



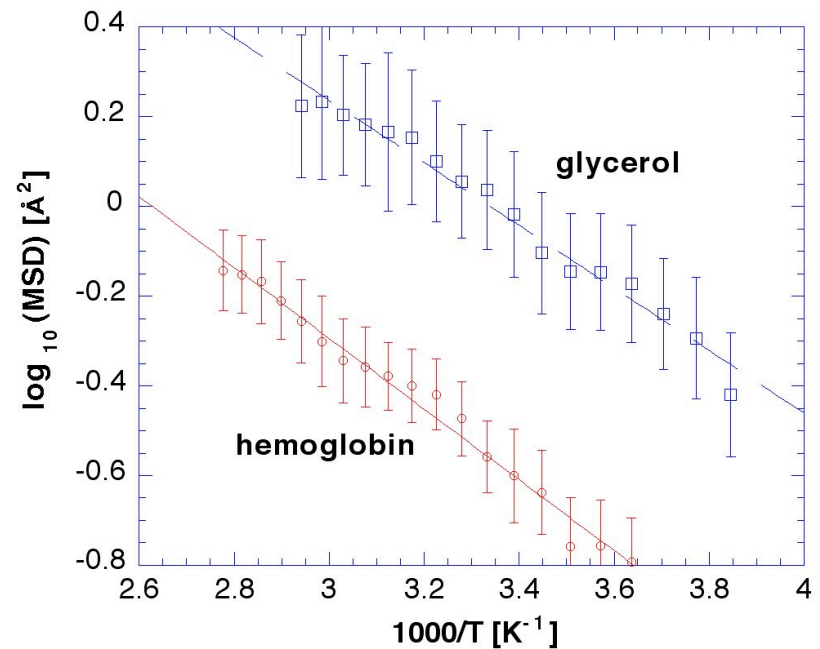
These fast local motions have an activation energy of 0.18 eV for both the protein and the water, suggesting that these protein motions are slaved by the water dynamics.

How is it for other solvents?

Glycerol



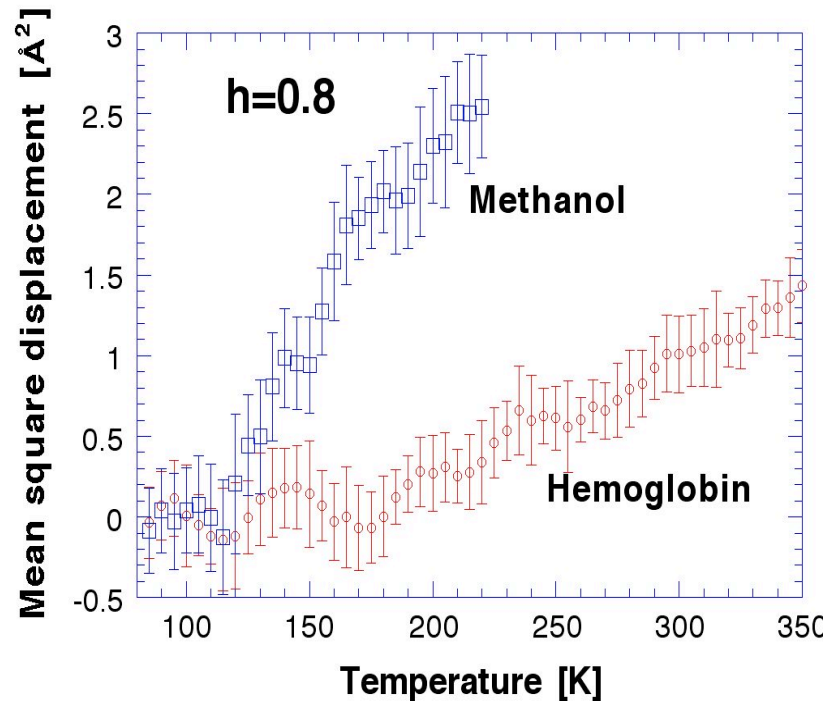
Onset of anharmonic protein motions at 280 K and glycerol dynamics at 250 K.



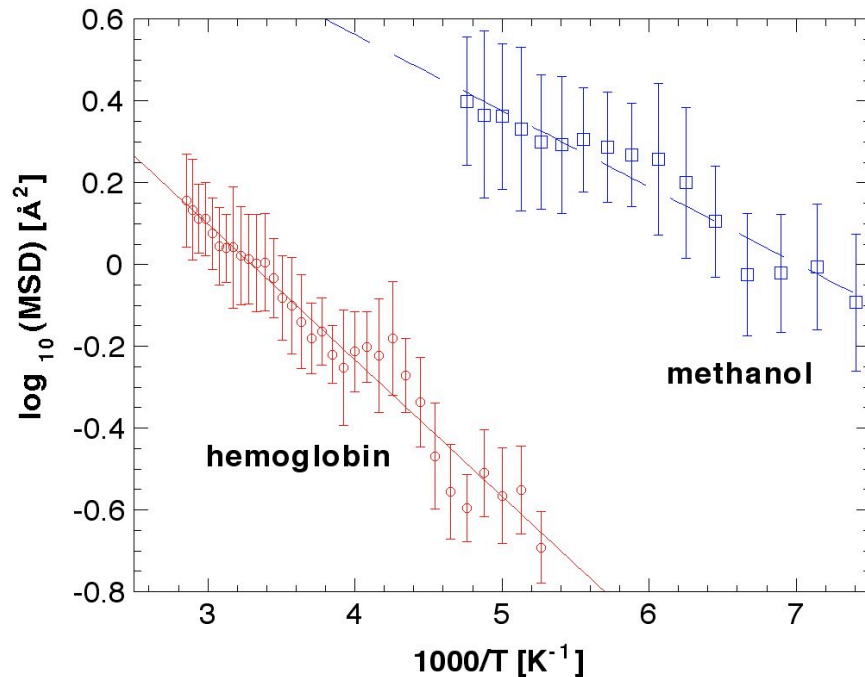
In this case, the fast local motions have an activation energy of 0.16 eV for both the protein and the glycerol, suggesting a similar slaving relation as for water.

Methanol

(Myoglobin denaturated)



Onset of anharmonic protein motions at 170 K and methanol dynamics at 120 K. This low temperature solvent dynamics is due to the methyl group rotation.



The fast local protein motions have an activation energy of 0.07 eV and the solvent dynamics only 0.04 eV, i.e. the methyl group rotation does not promote any protein dynamics. Thus, no slaving in this case.

Conclusions protein-solvent dynamics

* As for other systems of confined water the cooperative β -relaxation cannot be observed at low temperatures and water rich solvents. A cross-over in the relaxation dynamics occurs when the merged $\beta\beta\beta$ process transforms to a pure β process.

* A similar dynamic cross-over occurs for the protein at the same temperature.

* In parts of the hydration shell the β -relaxation seems to remain at high temperatures.

* The findings support that large scale conformational protein fluctuations are determined by the β -relaxation in the solvent, whereas local protein motions are determined by local (β) motions in the hydration shell.

(as suggested by P. W. Fenimore, H. Frauenfelder *et al.*, PNAS 110, 14408 (2004))

* Has solvent (or water) a similar role for other biological systems?