Water in heterogeneous/biological systems
Interfacial water—from the ordered structures to the single hydrated shell

Yuri Feldman

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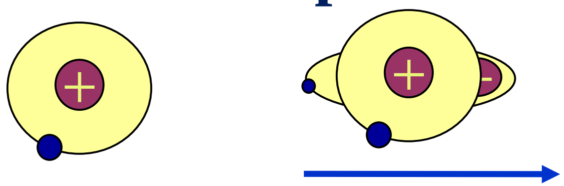
Introduction-Dielectric Spectroscopy

Dielectric spectroscopy is sensitive to relaxation processes

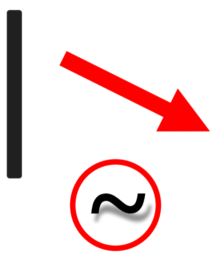
Types of polarization

Deformation polarization

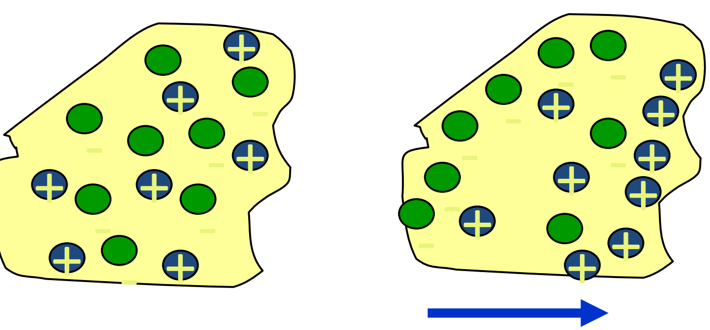


Electric Field

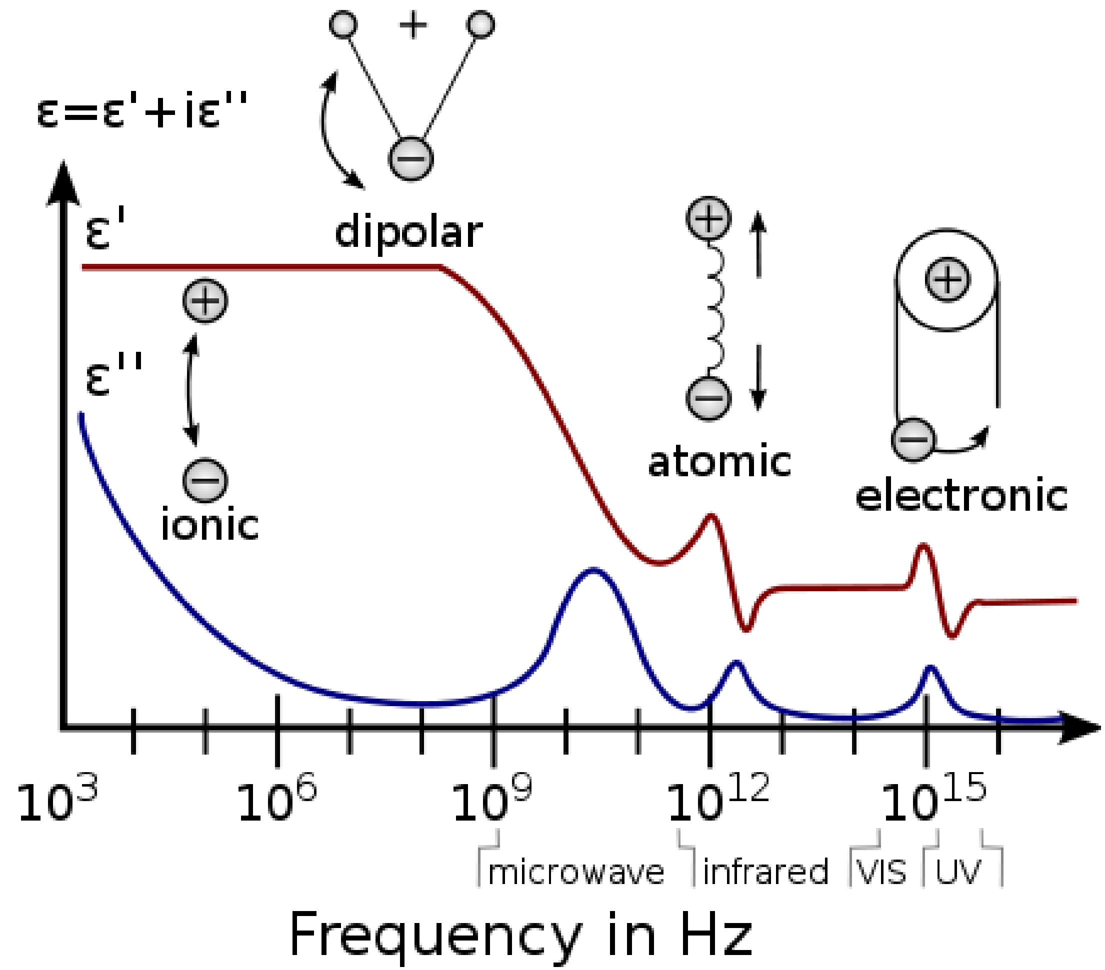
Orientation polarization:



Ionic Polarization:



Electric Field



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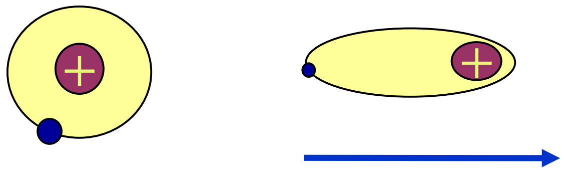
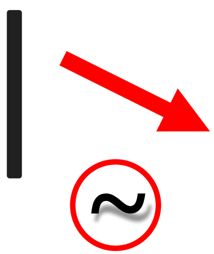


Electric Field

Orientation polarization:



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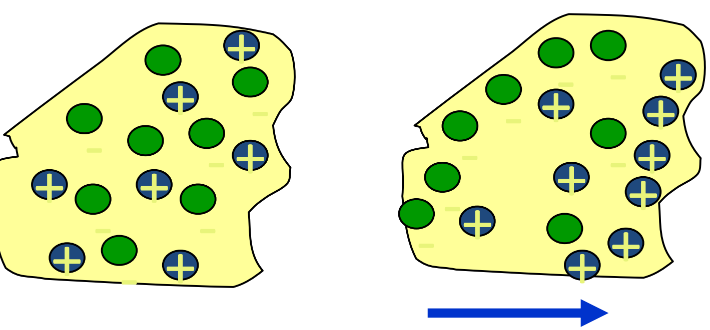
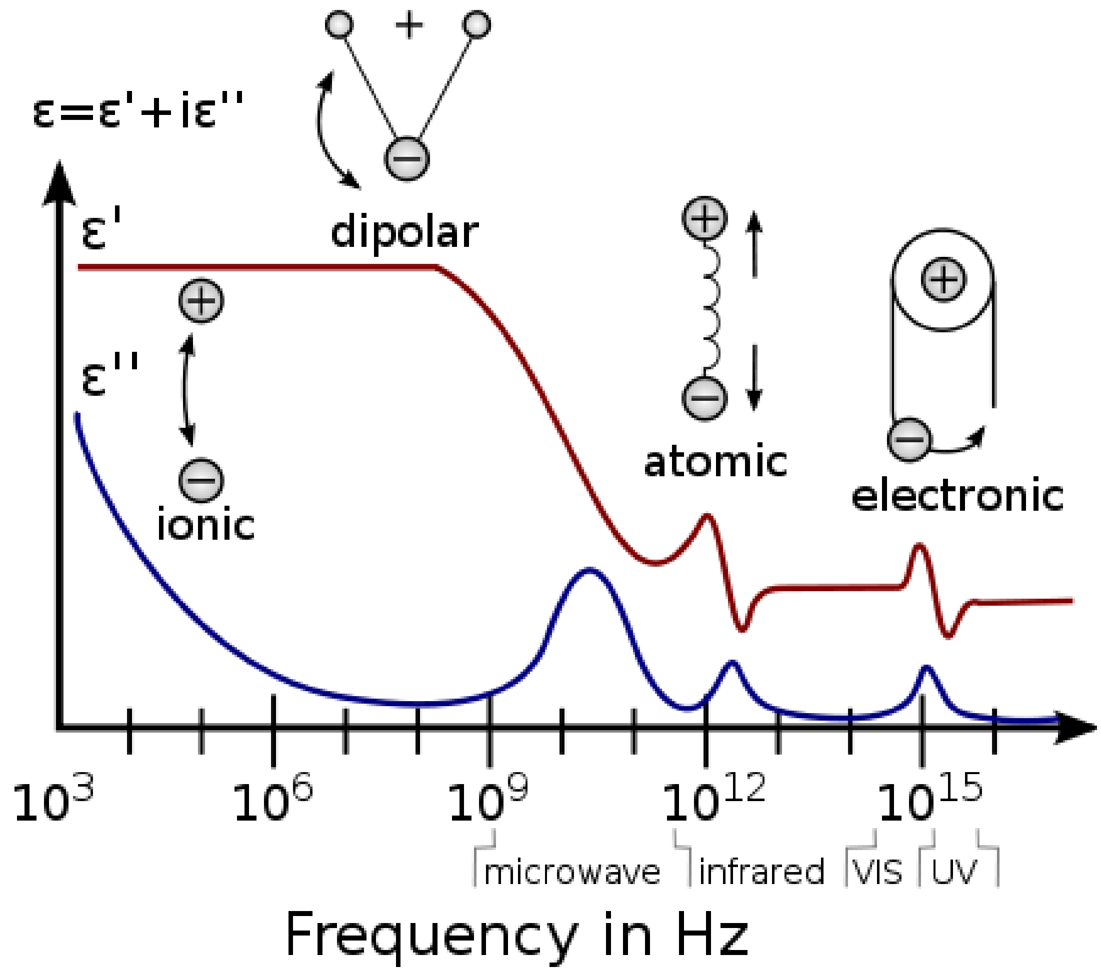
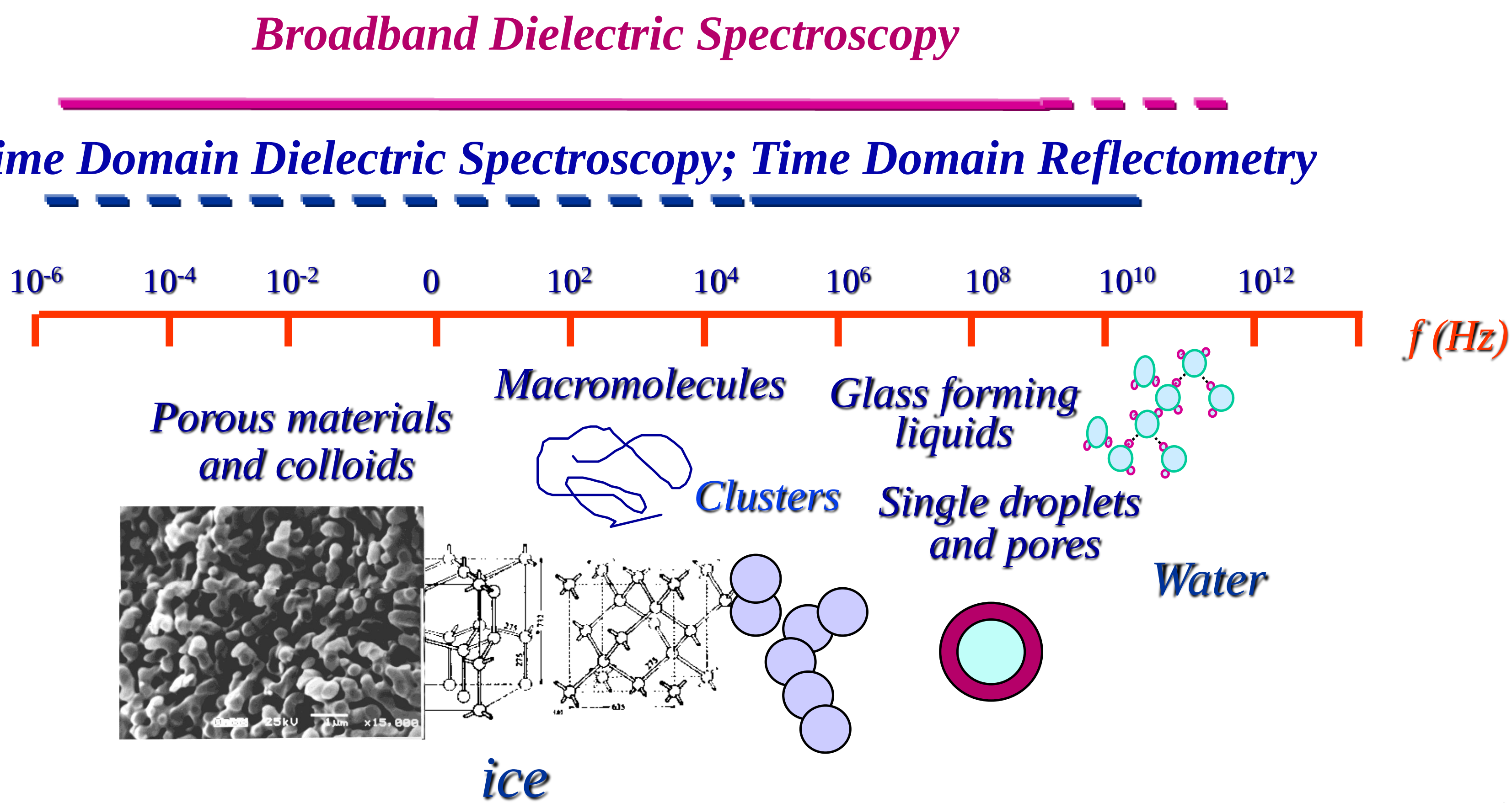


Electric Field

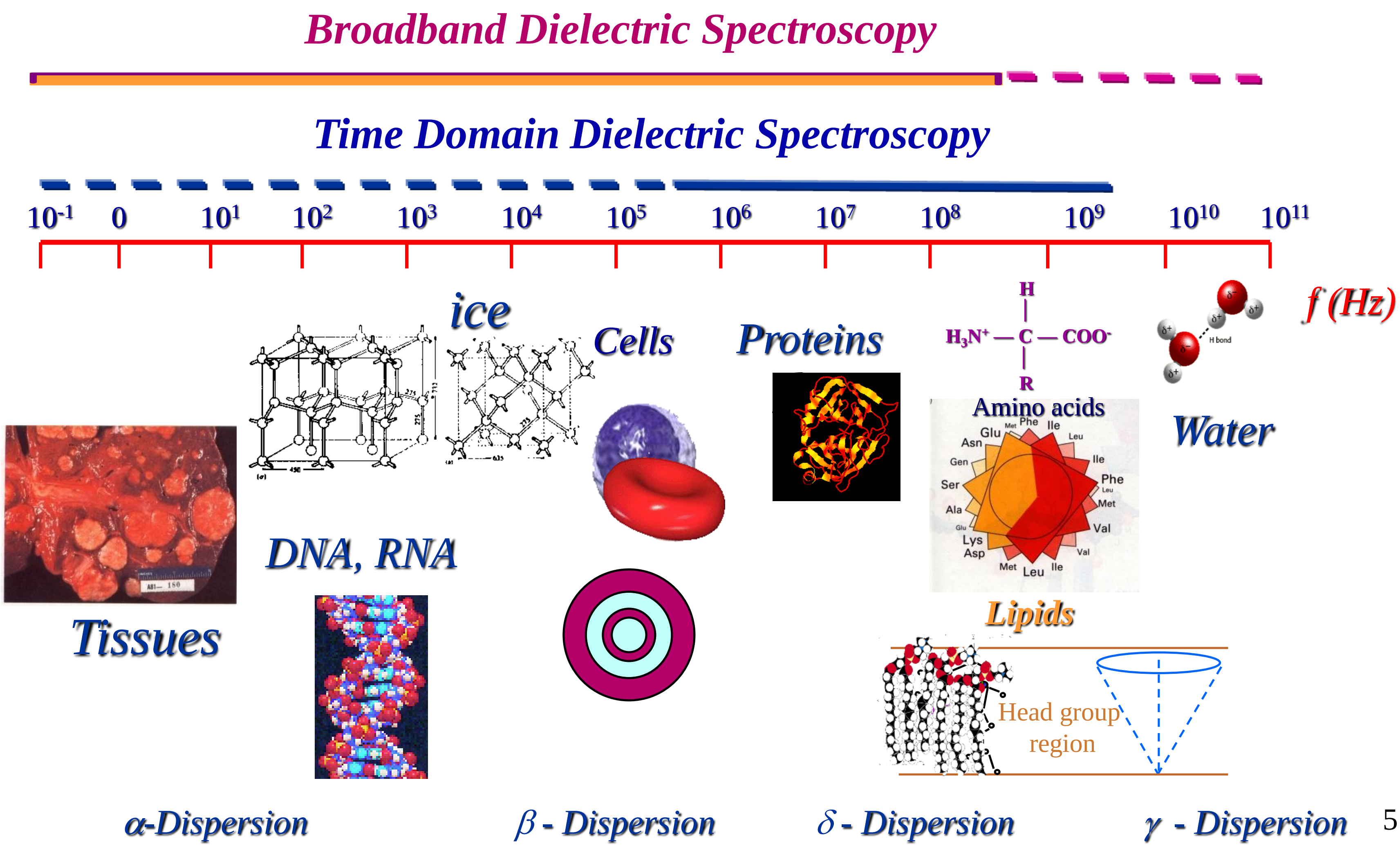


Dielectric response on mesoscale

Dielectric spectroscopy is sensitive to relaxation processes in an extremely wide range of characteristic times (10^{5} - 10^{-12} s)



Dielectric Response in Biological Systems



Water as a marker in the dielectric spectroscopy measurements

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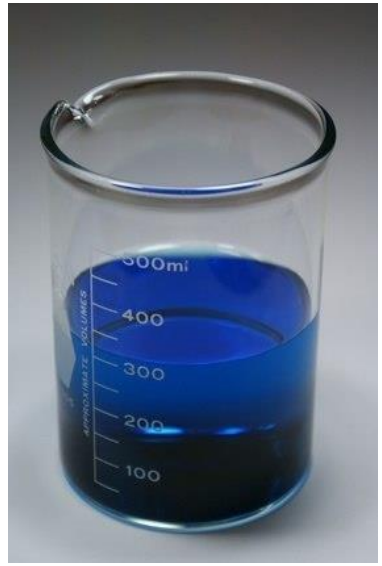
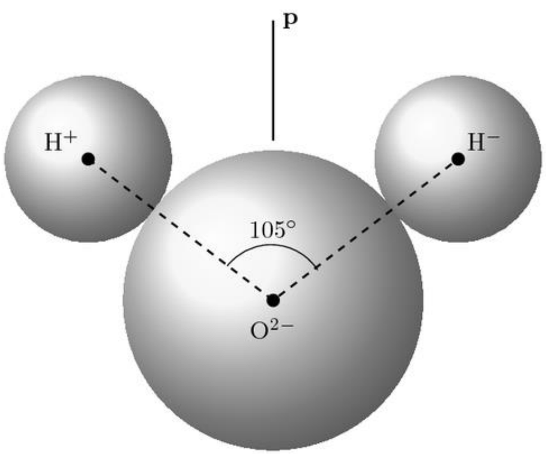


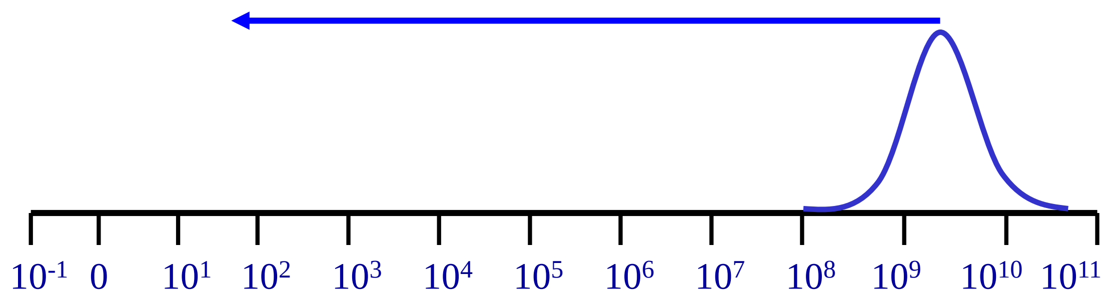
=

1.8-3 D

(large dipole moment)

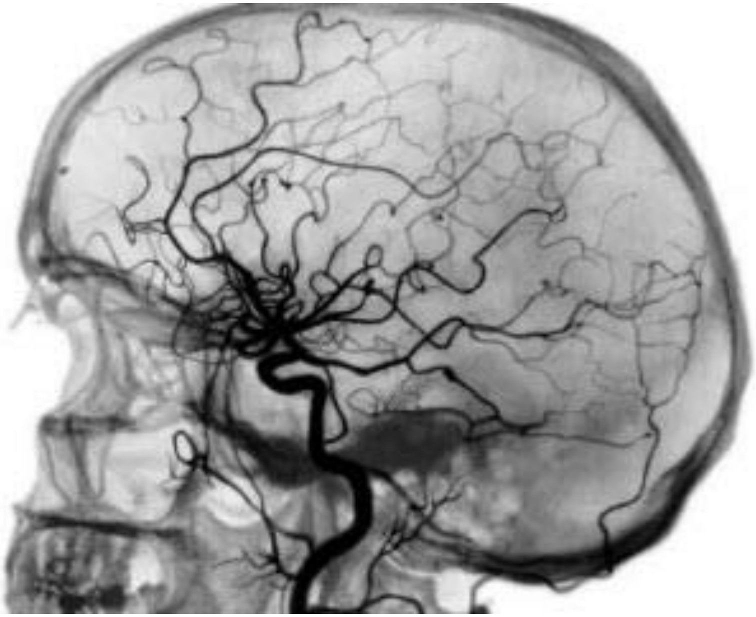


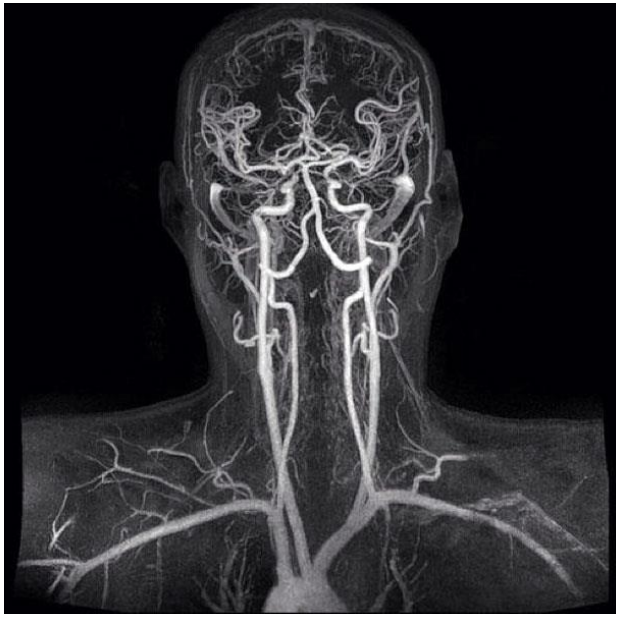
Decreasing temperature/
Confined conditions



Water is the "contrast" in dielectric measurements!!!

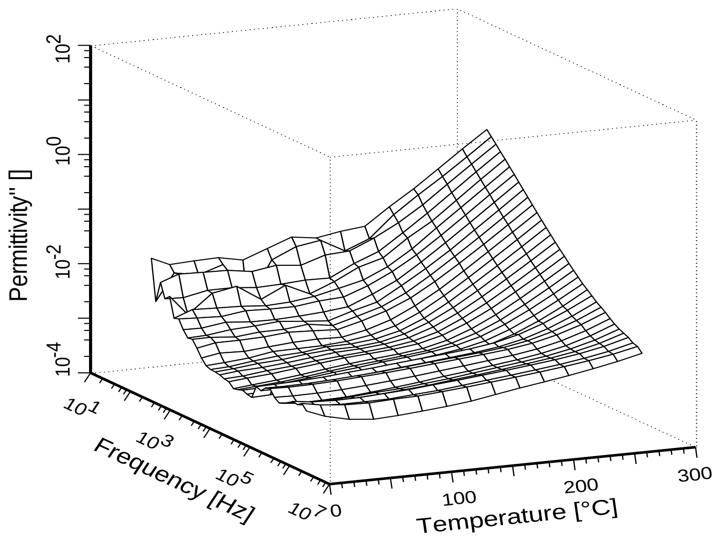
Water as a marker in the dielectric spectroscopy measurements



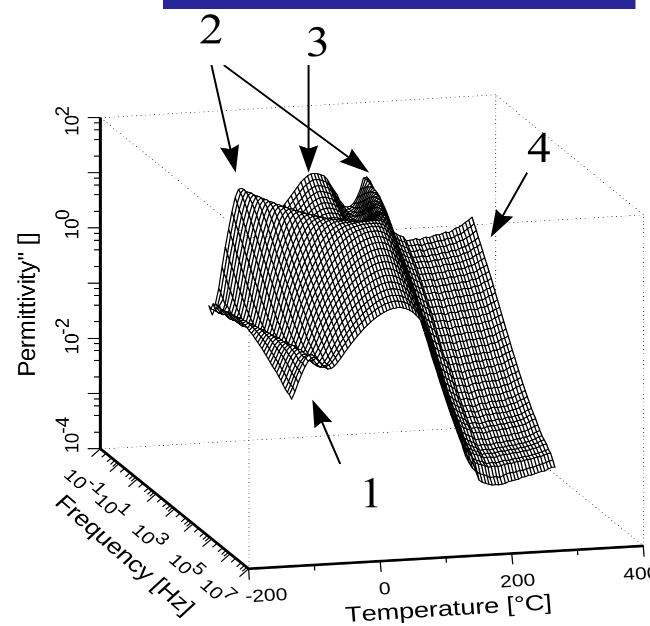


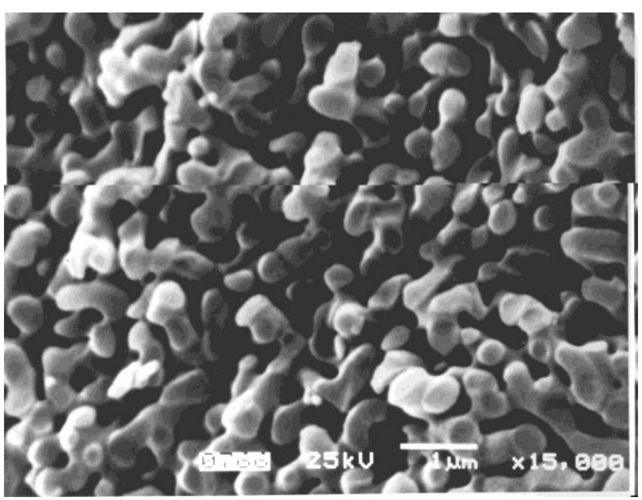
Water as a marker in the dielectric spectroscopy measurements

Dehydrated sample



Hydrated sample





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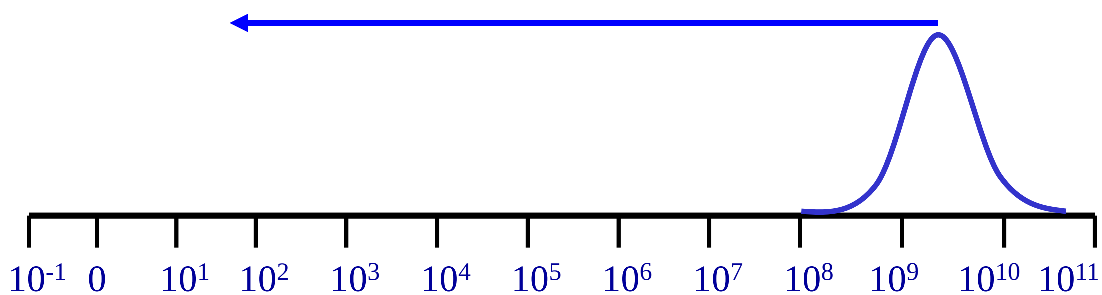


Water is the "contrast" in dielectric measurements!!!

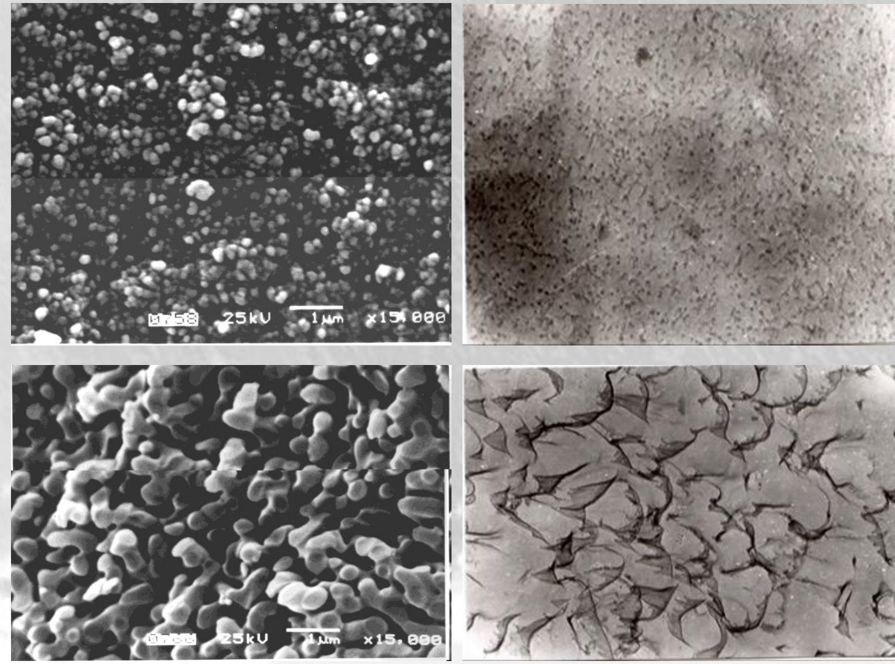
Water in **non organic** systems:

1) Silica glasses

a. 62.6% SiO_2, 30.4% B_2O_3,7%Na_2O

b. 70% SiO_2, 23% B_2O_3, 7% Na_2O,

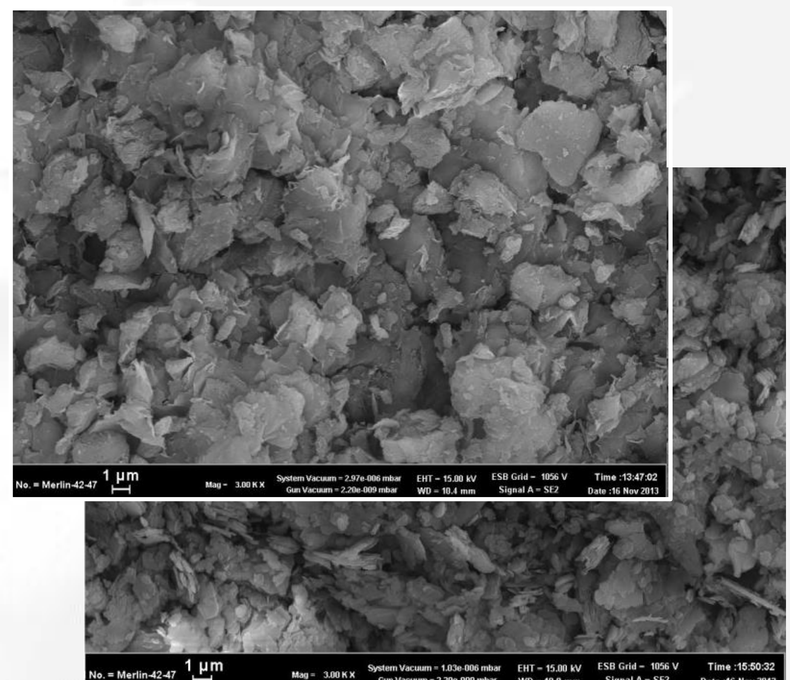
Microporous and Mesoporous Materials
58 (2003) 237–254
PRL (2010) Vol. 105, pp. 037601-4



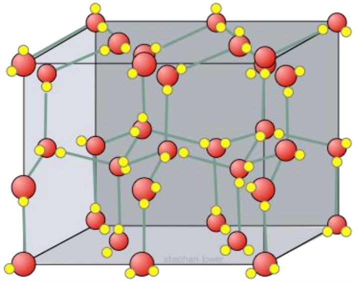
2) The study of confined water dynamics in clay minerals with different doped ions (K, Co, Ni)

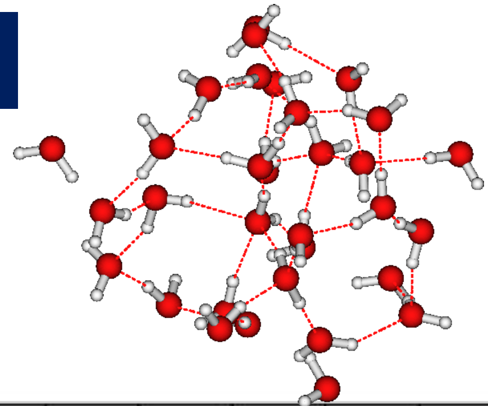
a. Montmorillonite
b. Kaolinite

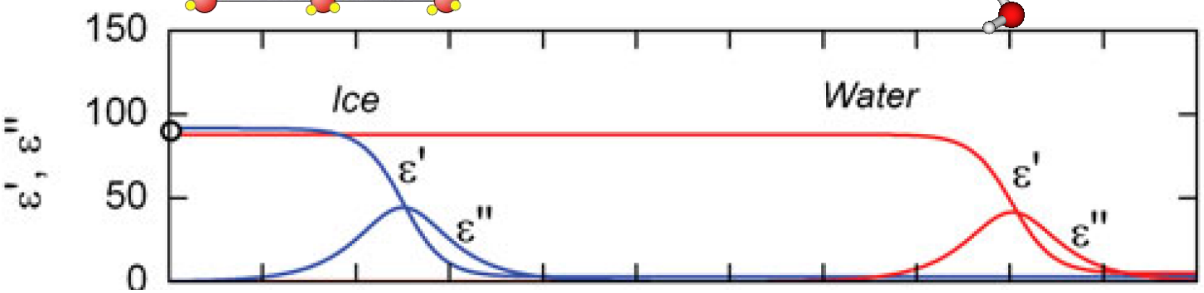
Clays and Clay Minerals (2014), Vol. 62, pp. 62–73

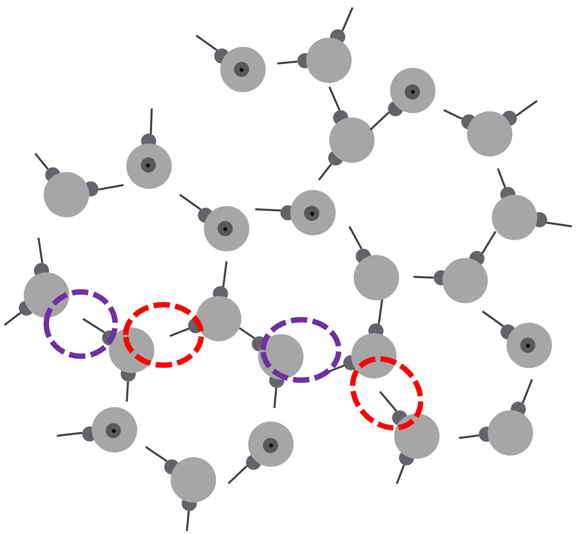


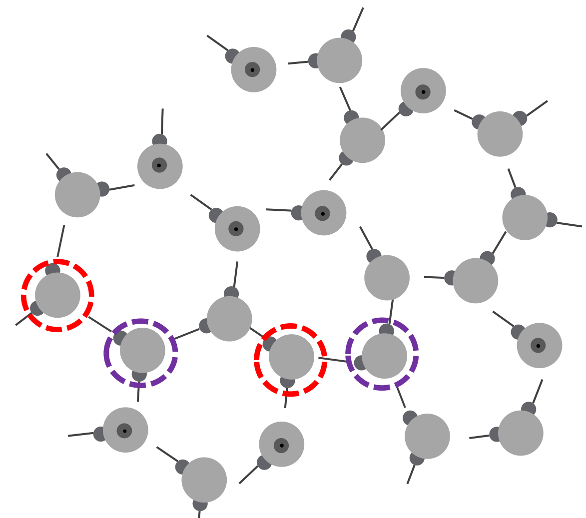
Dielectric relaxation in ice and water











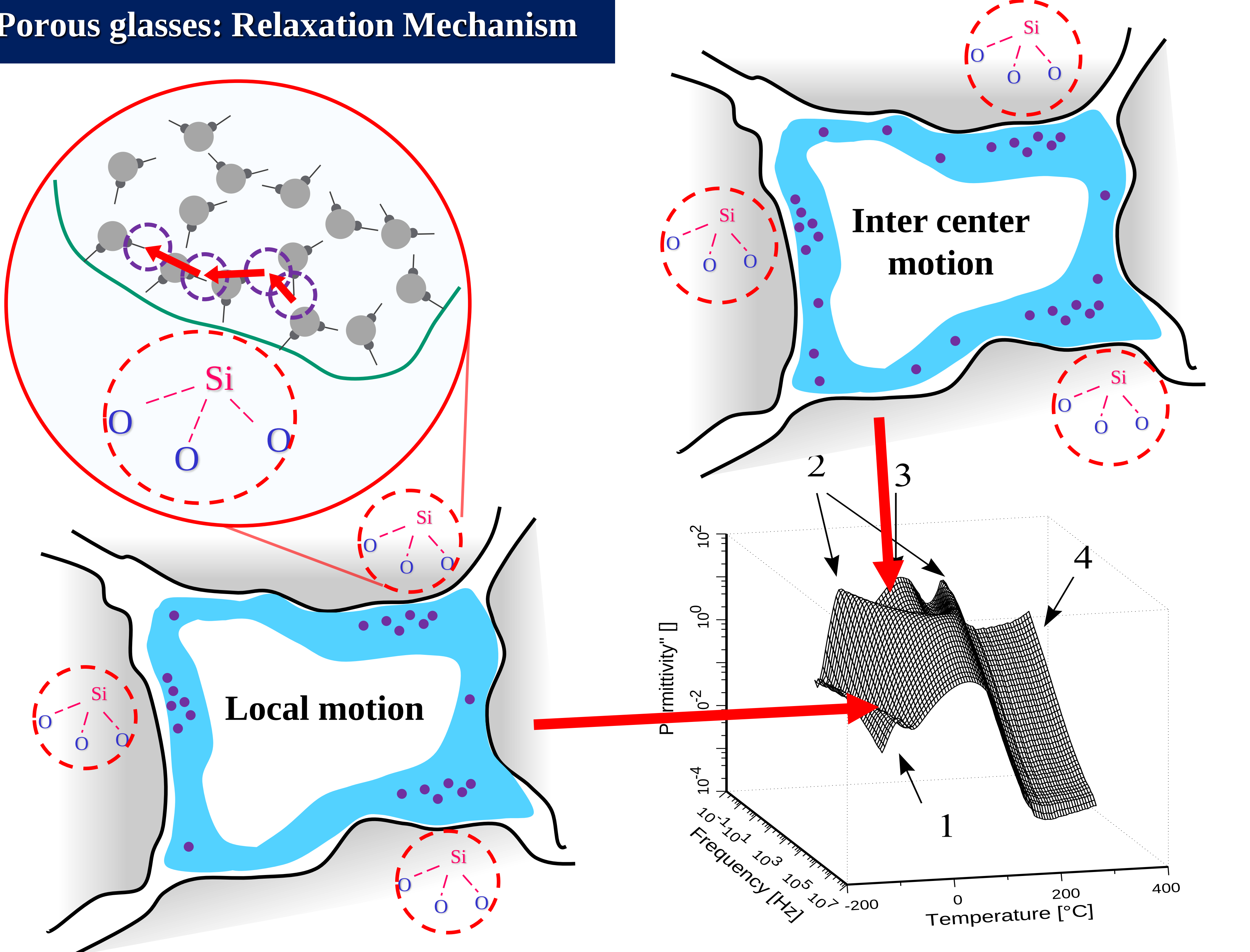
Ionic defects

Orientation defects

L-defects **D-defects**

OH^- **OH^{3+}**

Porous glasses: Relaxation Mechanism



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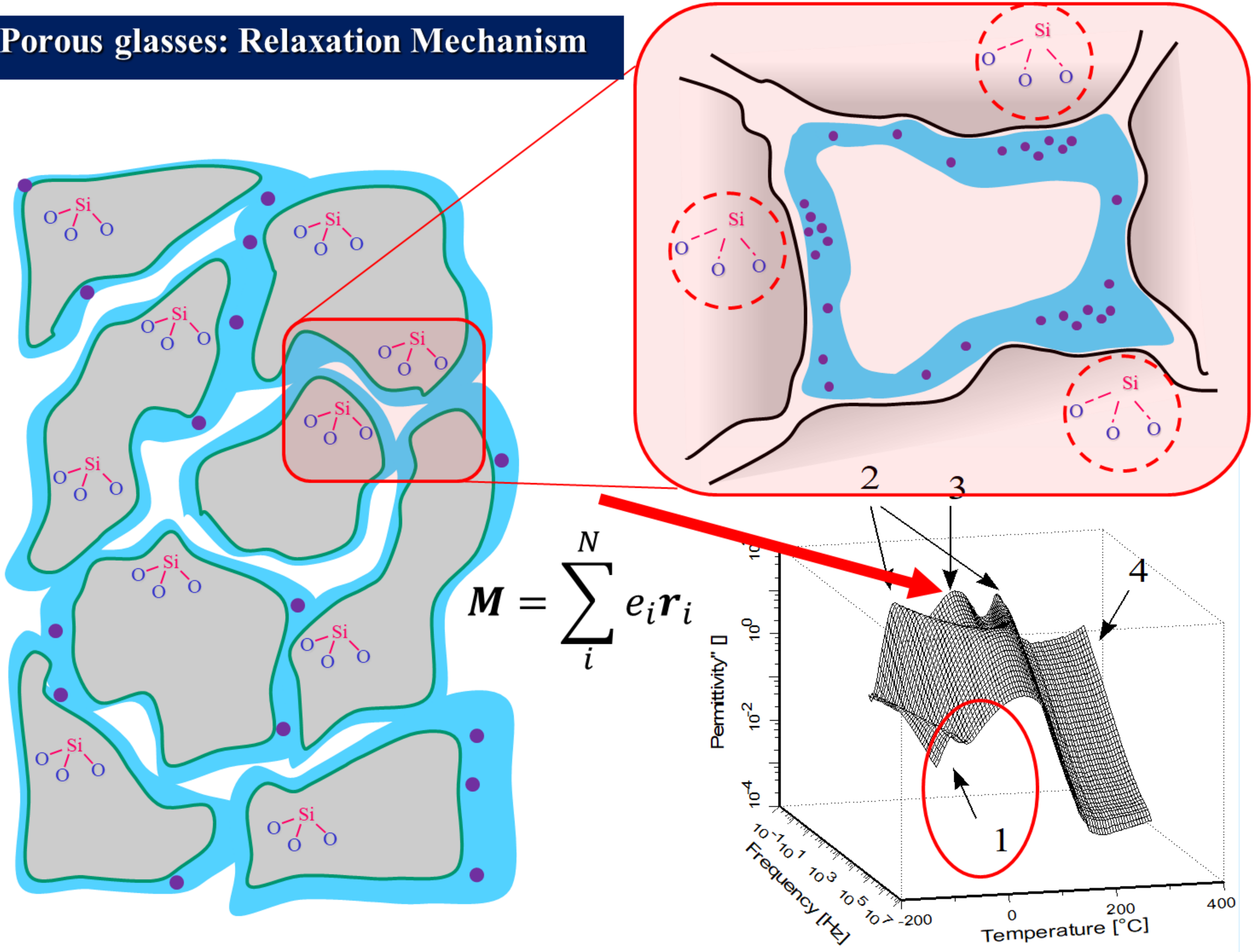
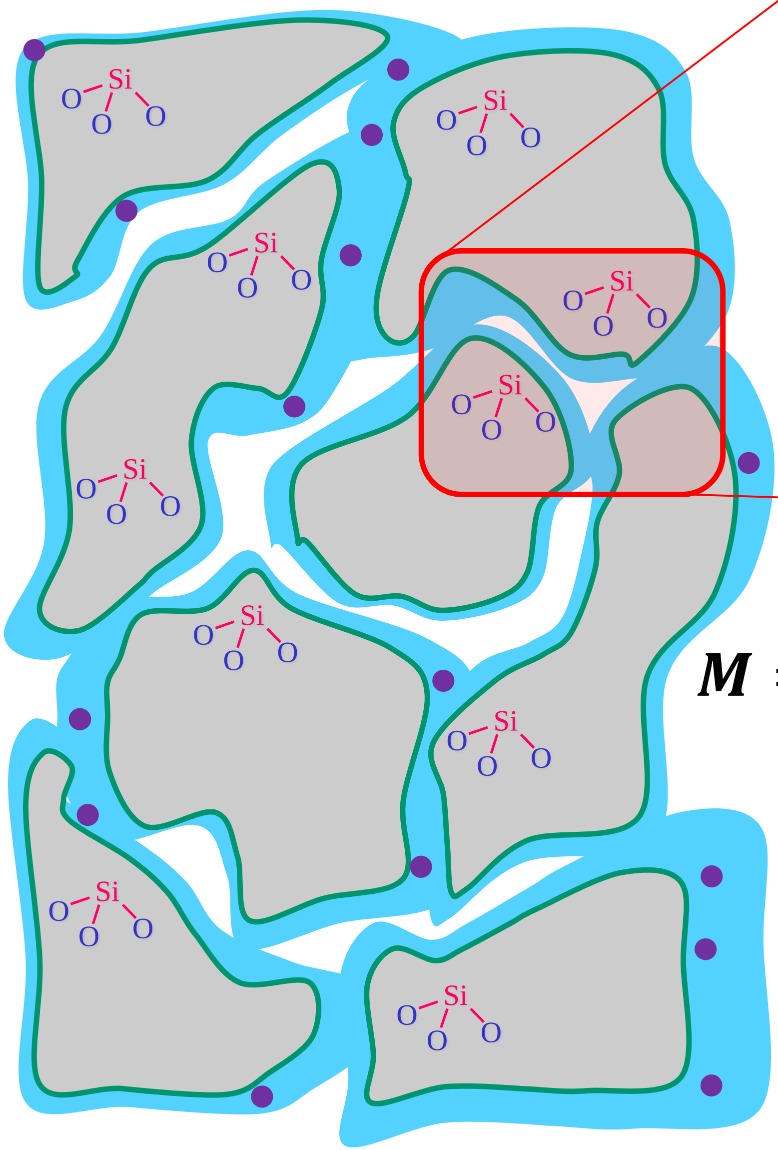
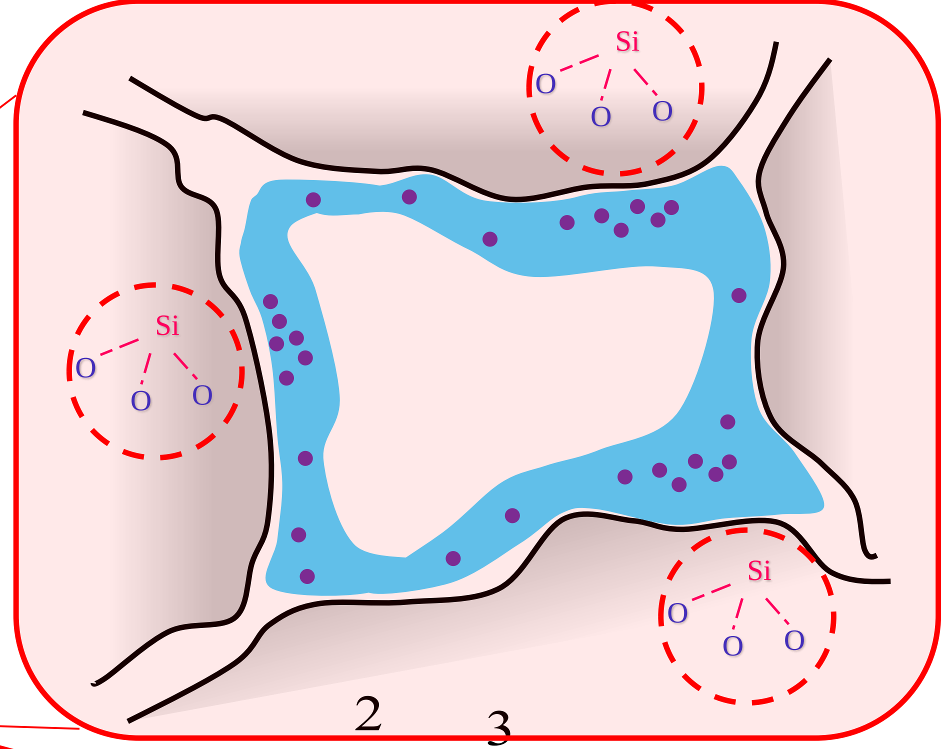


$$\boldsymbol{M} = \sum_{i}^{N} e_i \boldsymbol{r}_i$$

Porous glasses: Relaxation Mechanism





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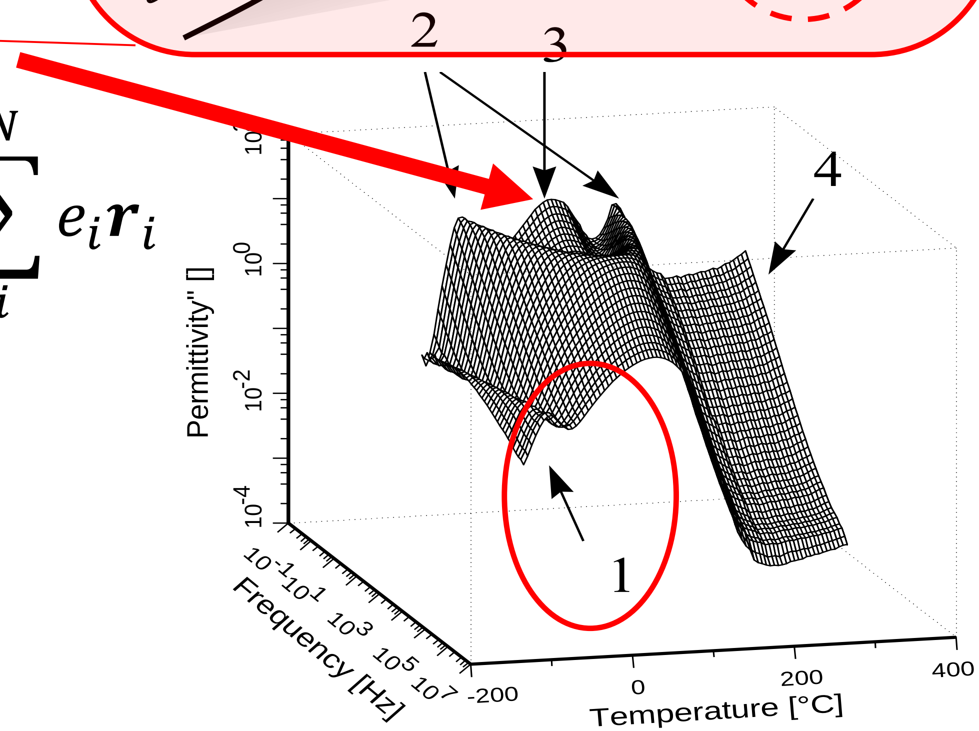
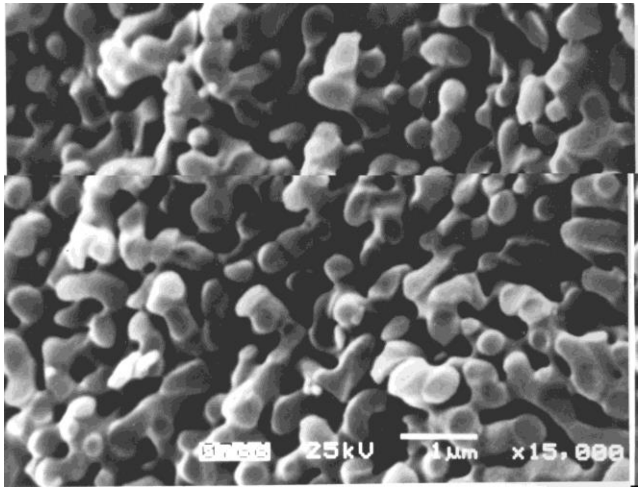
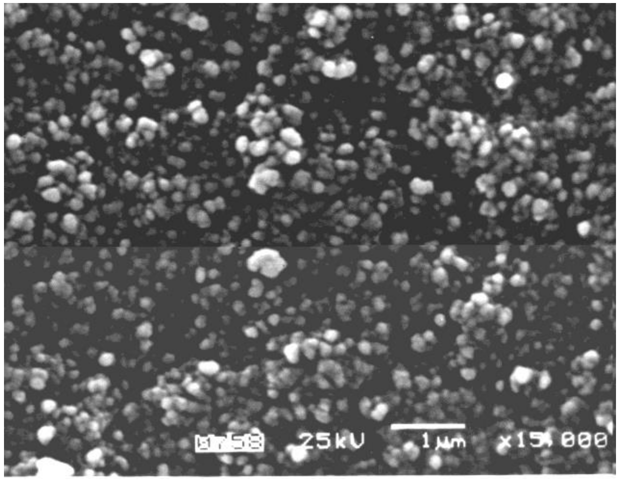
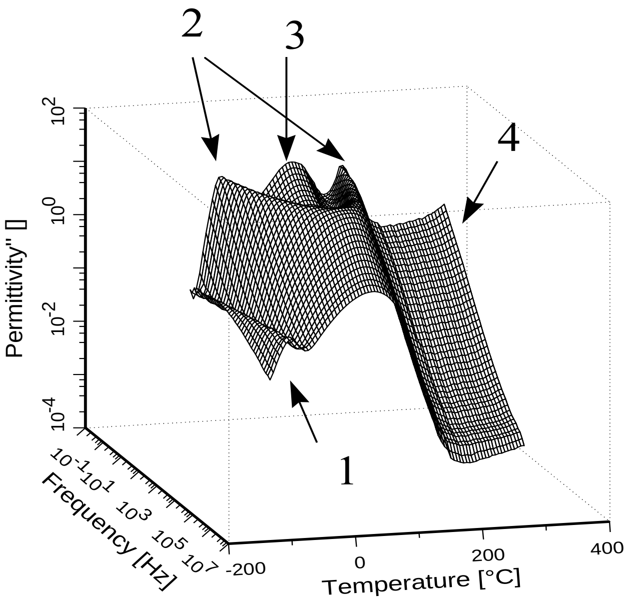


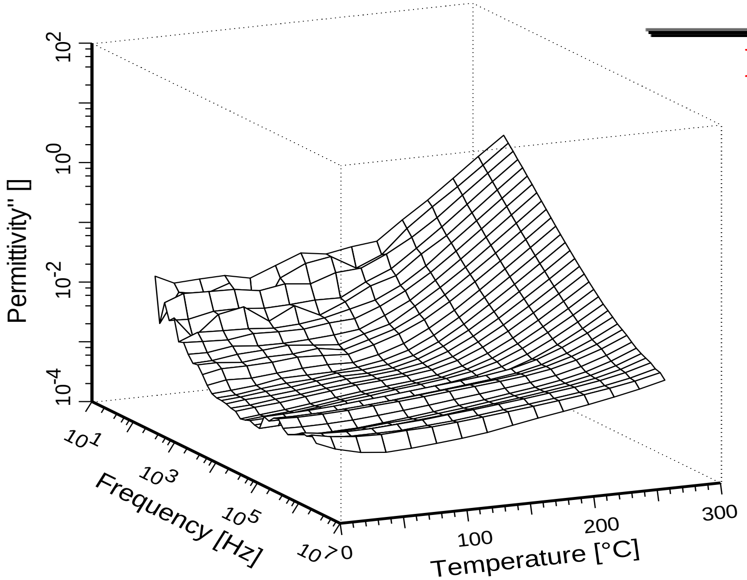
Porous glasses





Samples	Humidity , *h* %
II	0.63
A	1.2
B	1.4
D	1.6
C	3.2
III	3.39
I	3.6





A - 50 kJ/mol

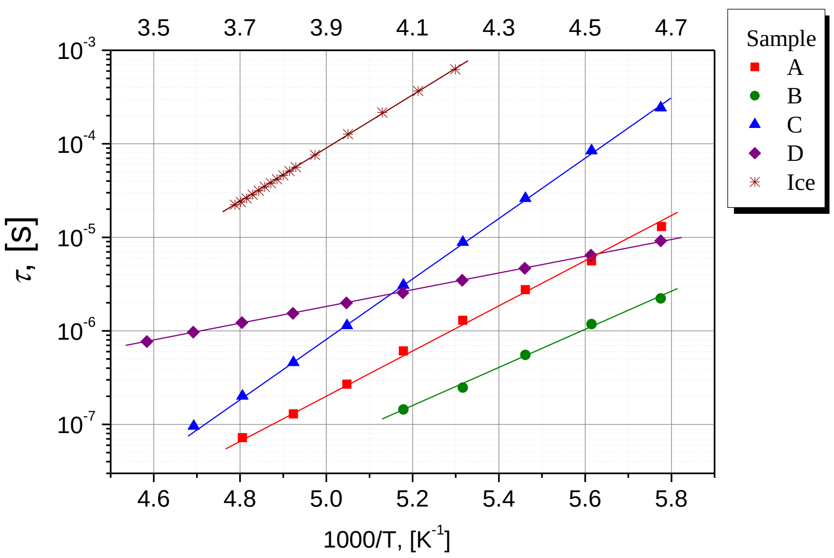
B - 42 kJ/mol

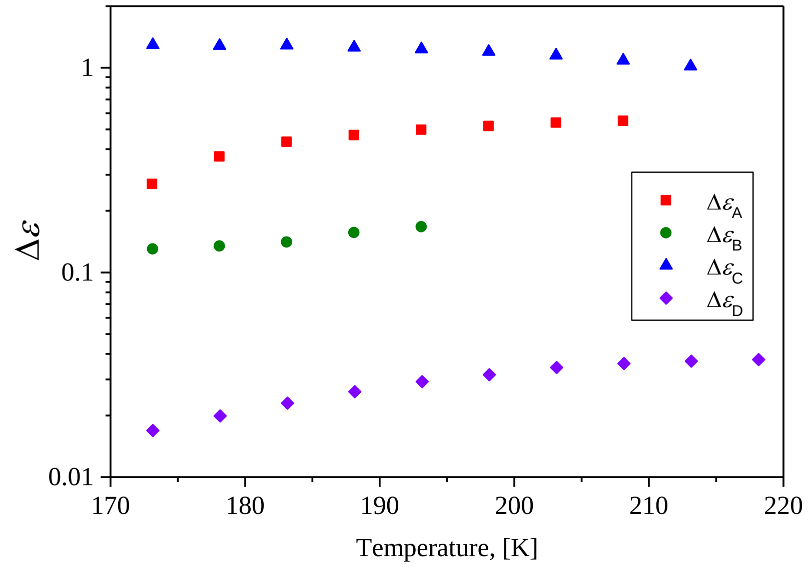
C - 67 kJ/mol

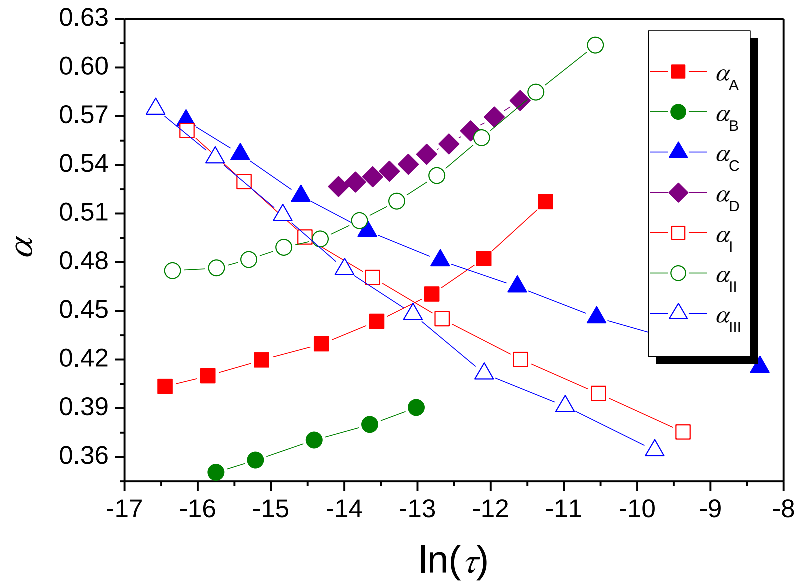
D - 19 kJ/mol

Ice - 60 kJ/mol

Porous glasses







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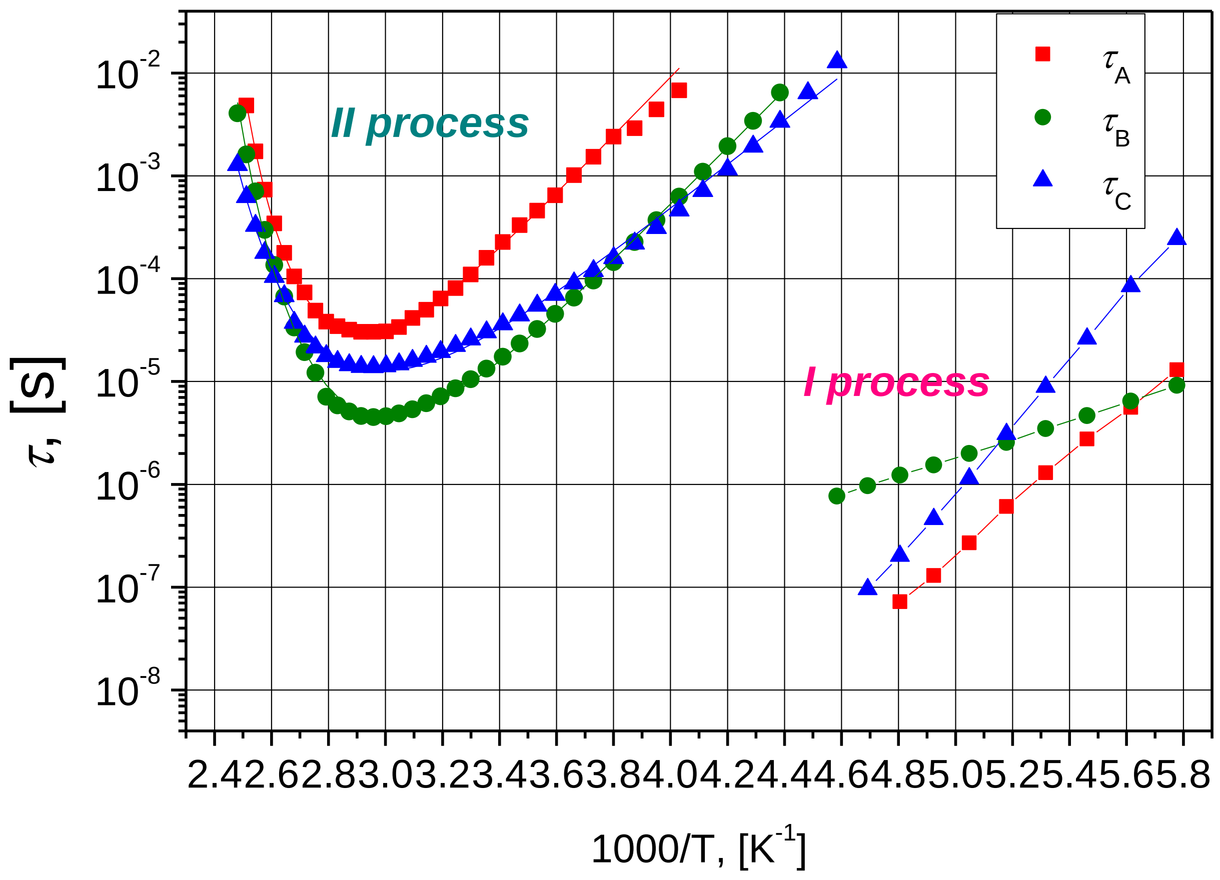
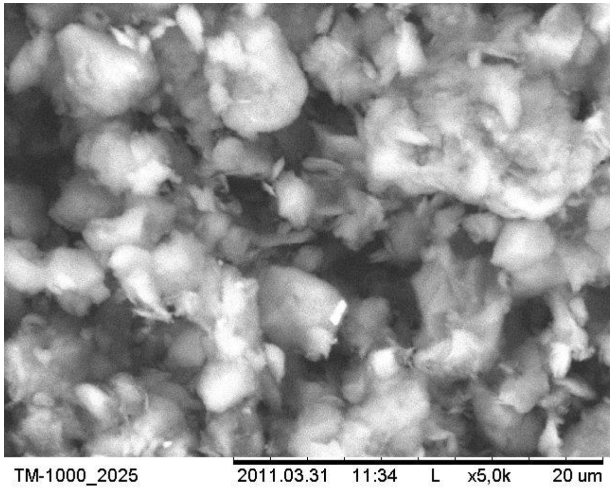
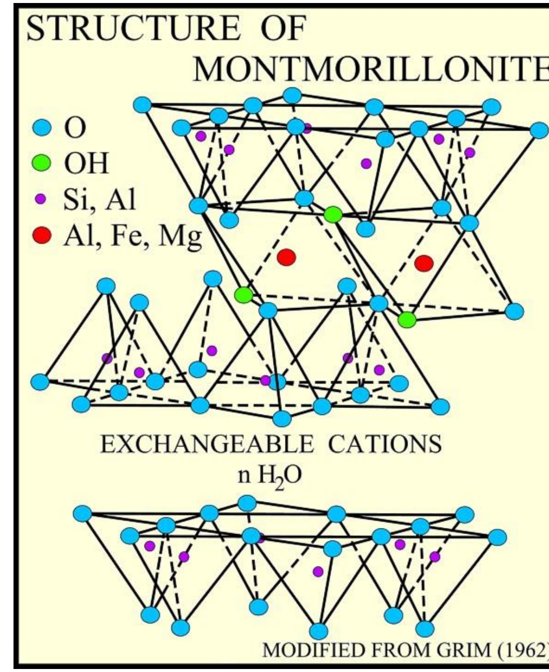
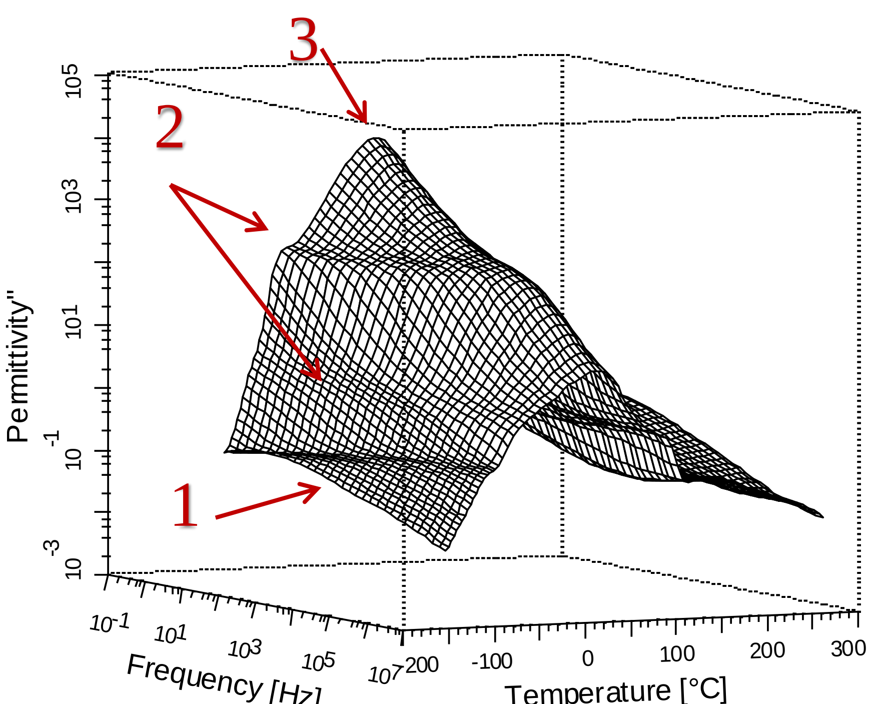
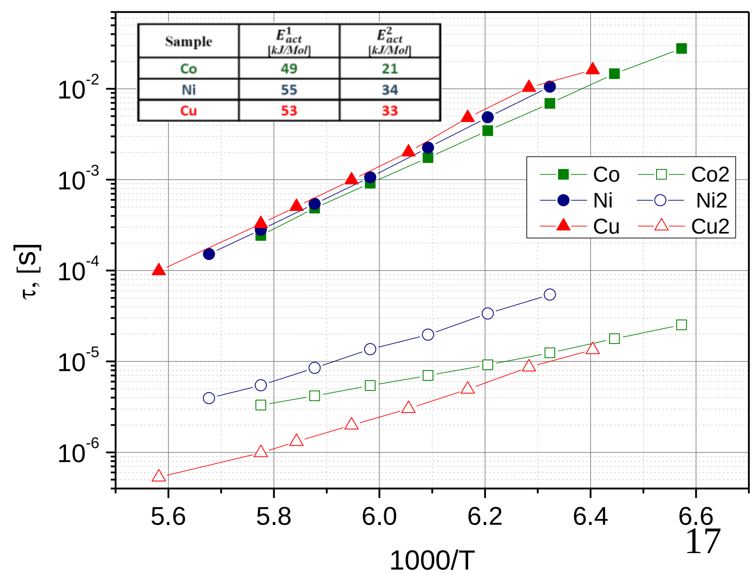


Aluminosilicates: Montmorillonite Ni









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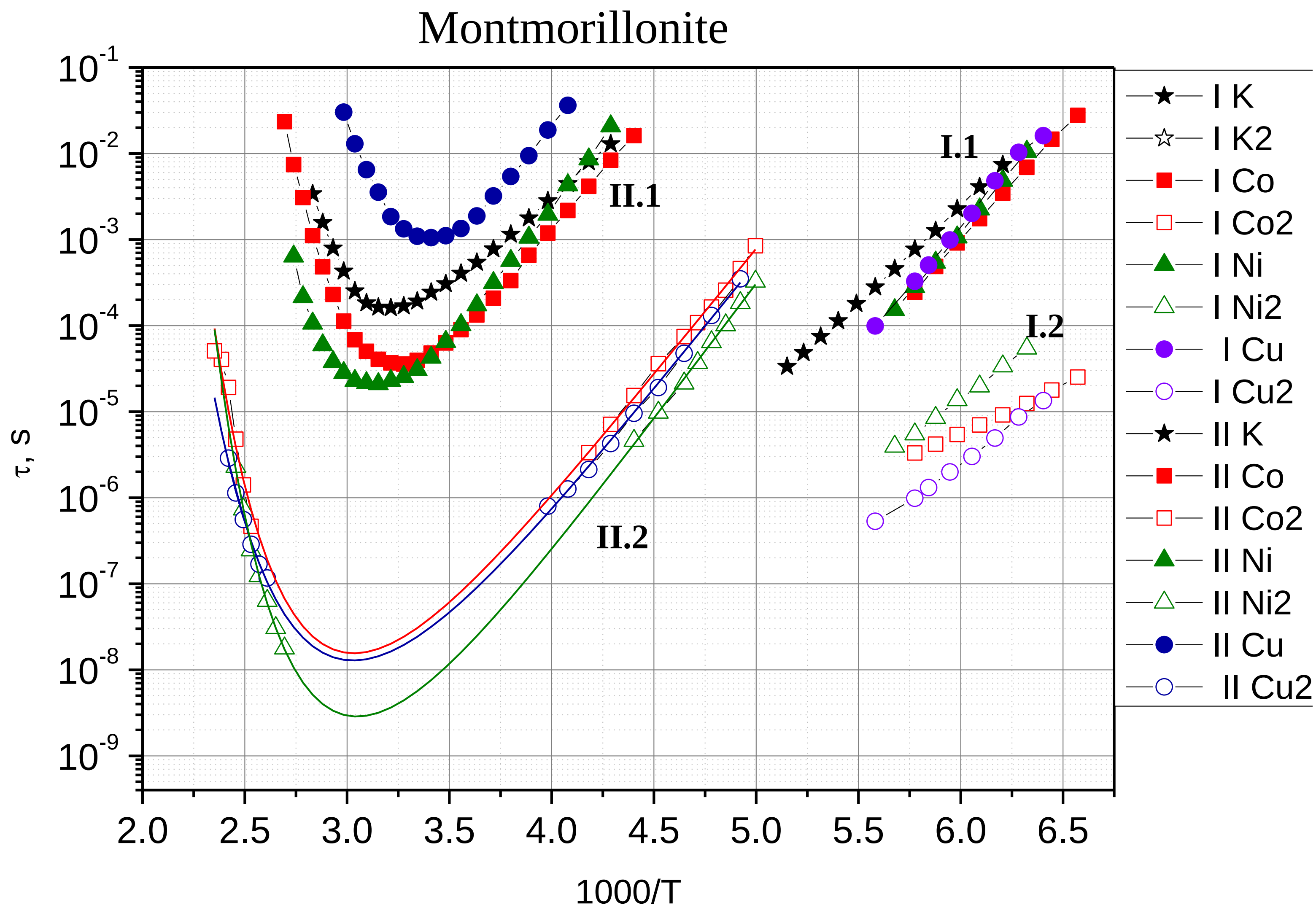


From **non organic** to **organic** systems

Using the water as a marker in porous system we can find:

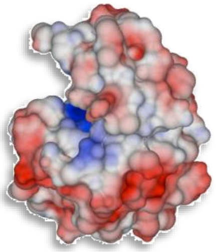
1) The dynamics of water in the regime of the tight confinement
2) The influence of the various ions on the water dynamic
3) Structural properties of the sample: percolation cluster, fractal dimension and porosity

In organic systems additional effects appear:

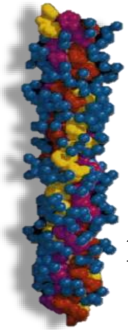
Inert interfacial water as apposed to the actively solvating molecule

Specific structure of the protein surface

Concentration of the hydrophilic centers in one place



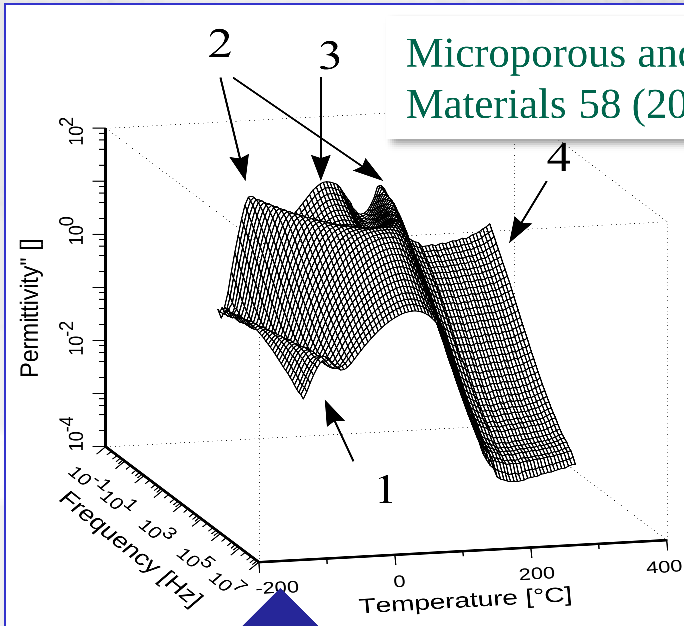
Anisotropic properties. Ordered structures



Dielectric Responses of the confined water are similar in non organic and organic systems

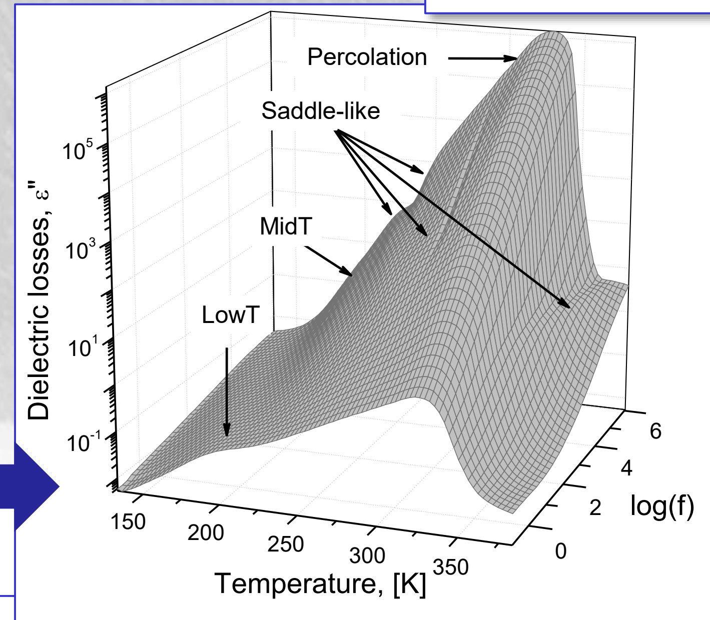
PCCP (2016), V.18, pp. 10992-10999

Microporous and Mesoporous Materials 58 (2003) 237–254

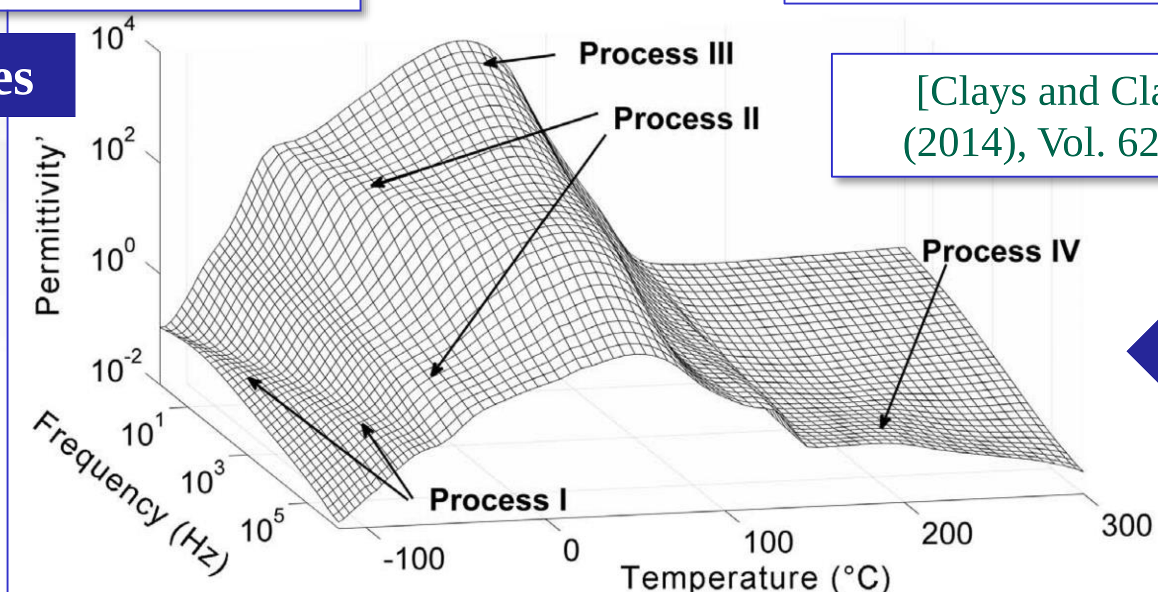


Porous glasses

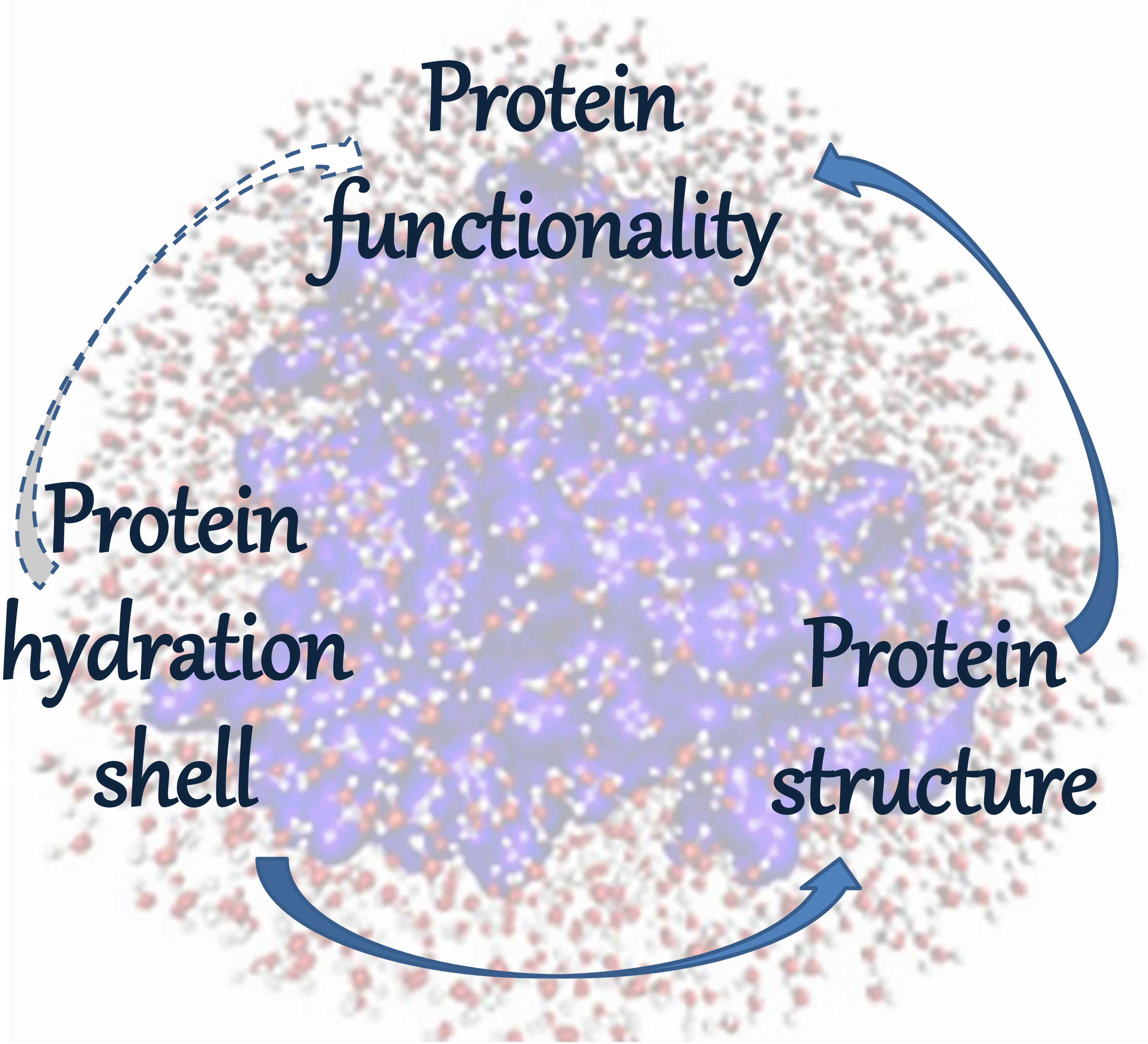
Hydrated proteins (Lysozyme)



[Clays and Clay Minerals (2014), Vol. 62, pp. 62–73]

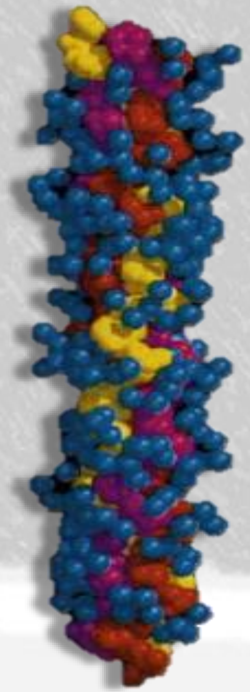


Clays

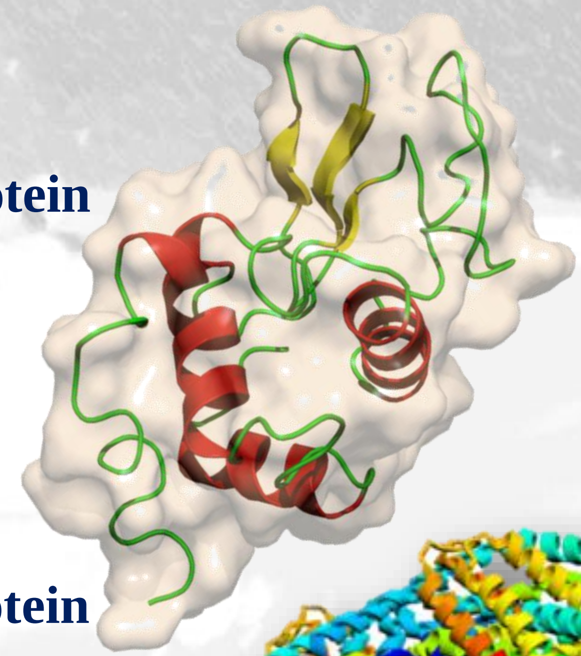

Protein functionality
Protein hydration shell
Protein structure

Water in **organic** systems. Hydration shell dynamics in proteins:

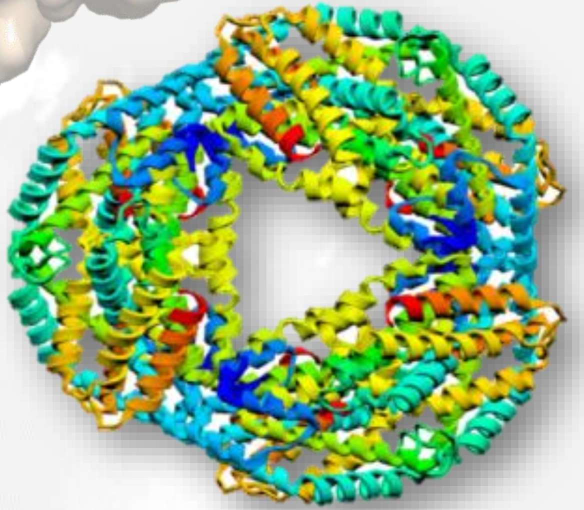
1) Hydration shell dynamics of a fibril protein (Collagen type 1).



2) Hydration shell dynamics of a globular protein (Lysozyme).

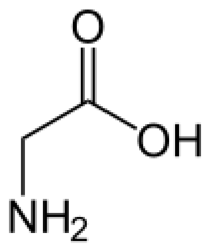


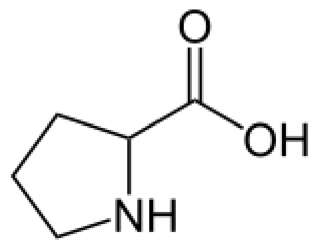
3) Hydration shell dynamics of a ring like protein (Phycocyanin).

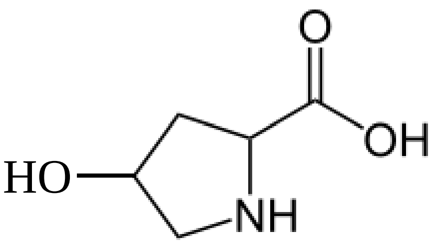


Collagen is a protein consisted of $(X\text{-}Y\text{-}Gly)_n$ repeating sequences

Gly is the Glycine   X or Y is the Proline or 4-HydroxyProline



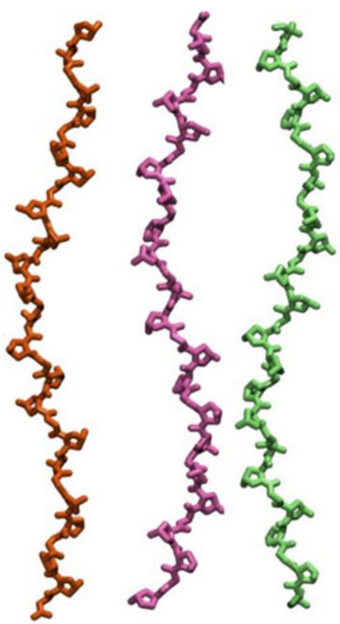


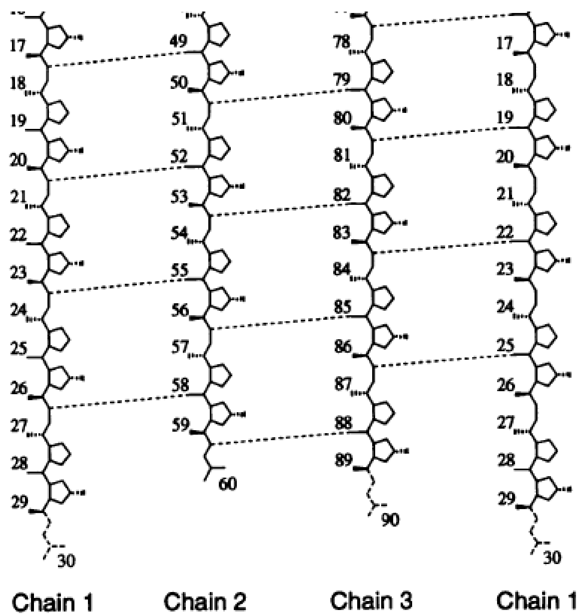


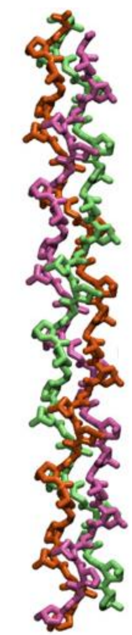
Steric effect stabilizes the extended nature of the individual chains

Hydrogen bonds (Gly: NH···O=C: X) leads to triple helixes organization

Stable triple helixes structure

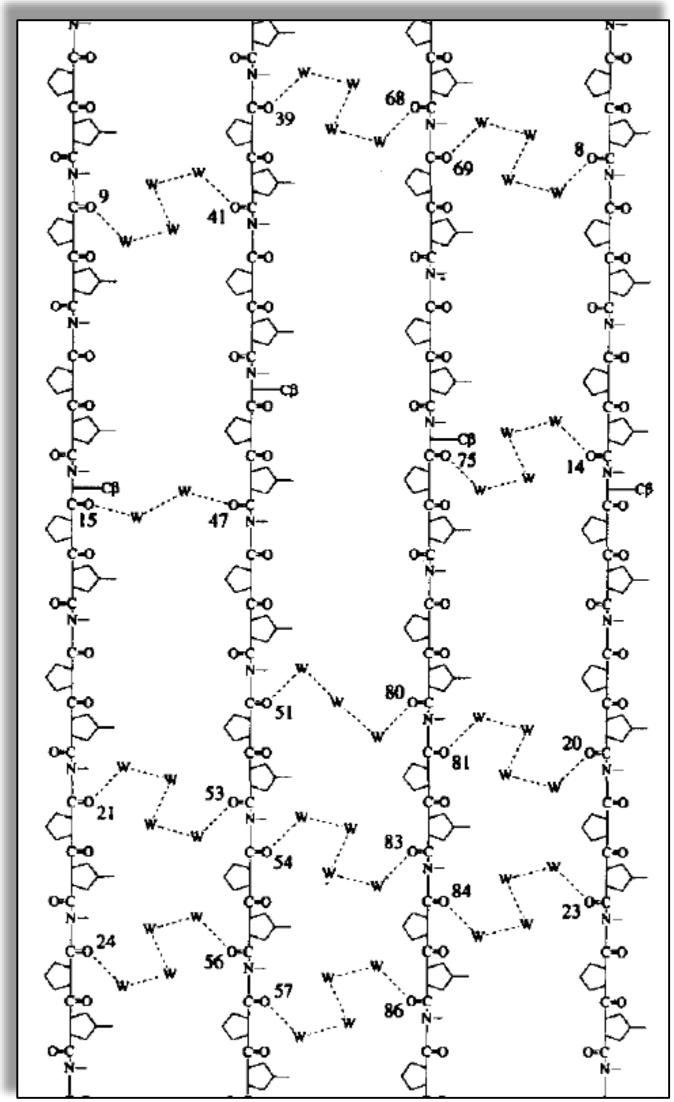




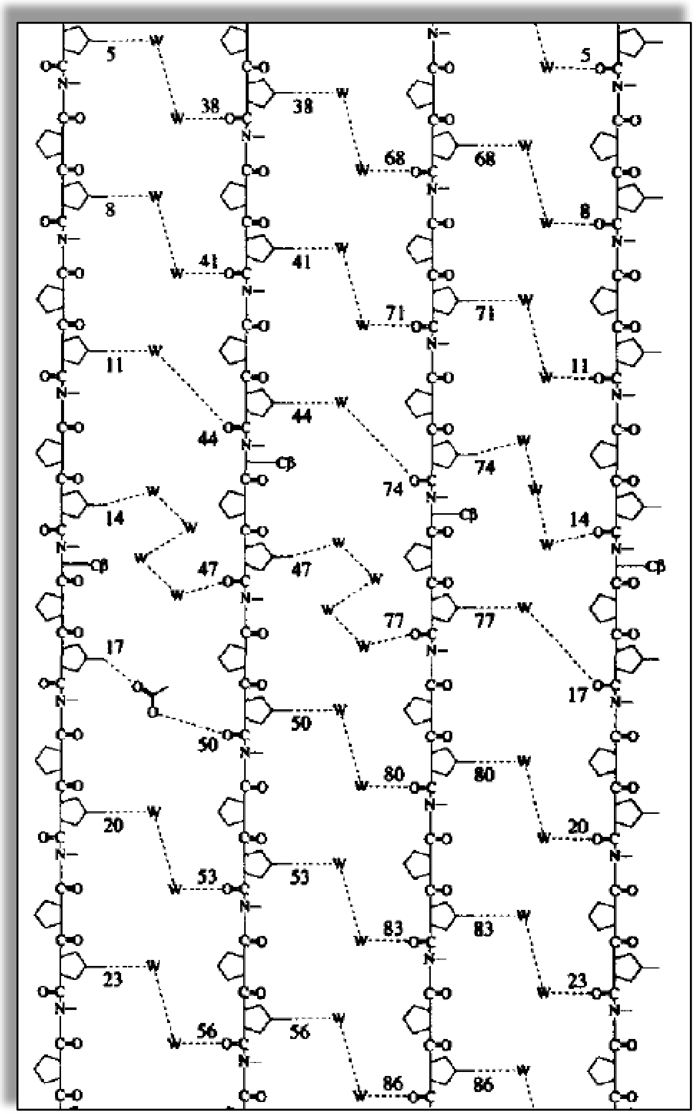


Introduction to collagen: Water bridges

Water molecules embed into triple helixes creating water bridges, that stabilizes collagen structure [*J. Bella et al Science, 1994*]

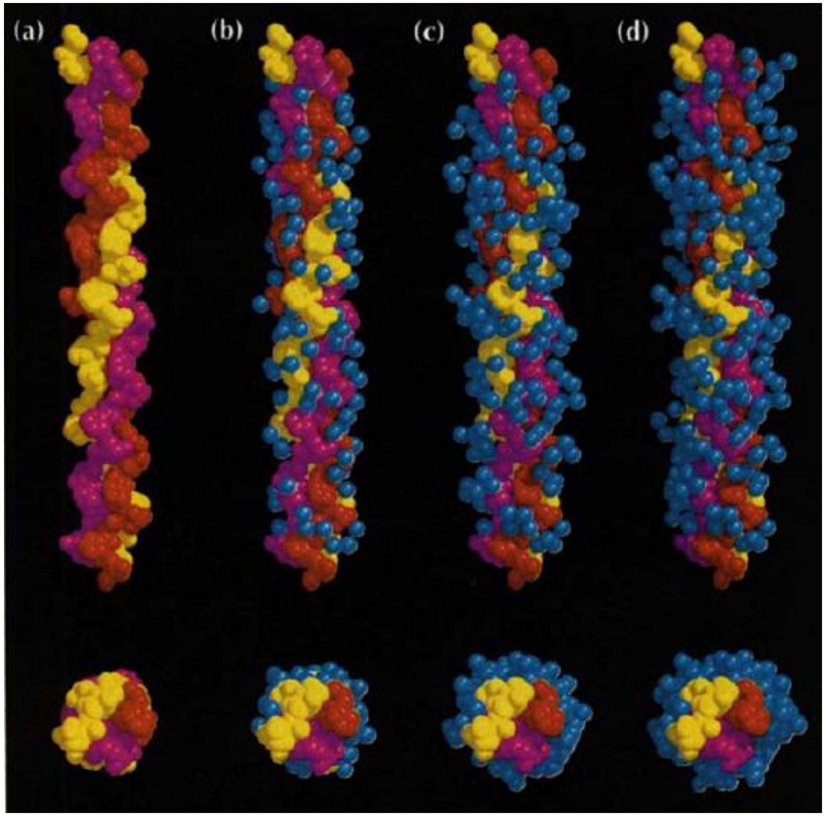


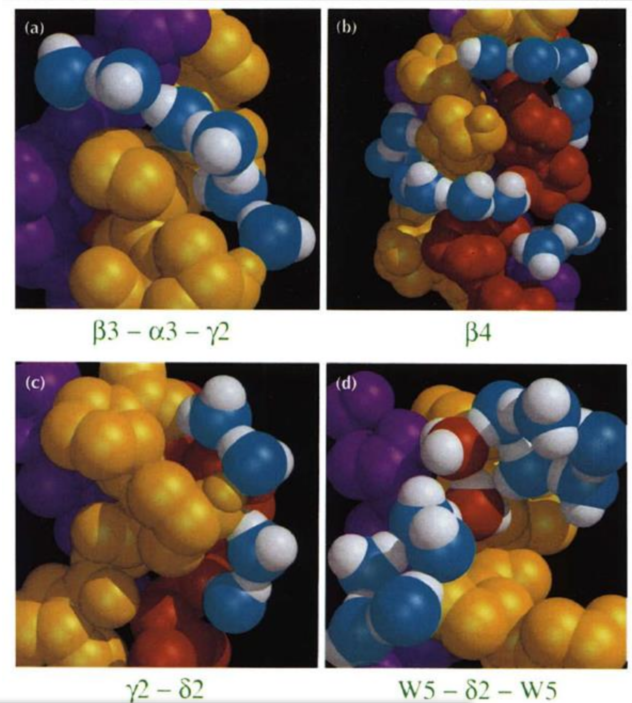
Water bridges appear as a
surface bridges surround the triple helixes.

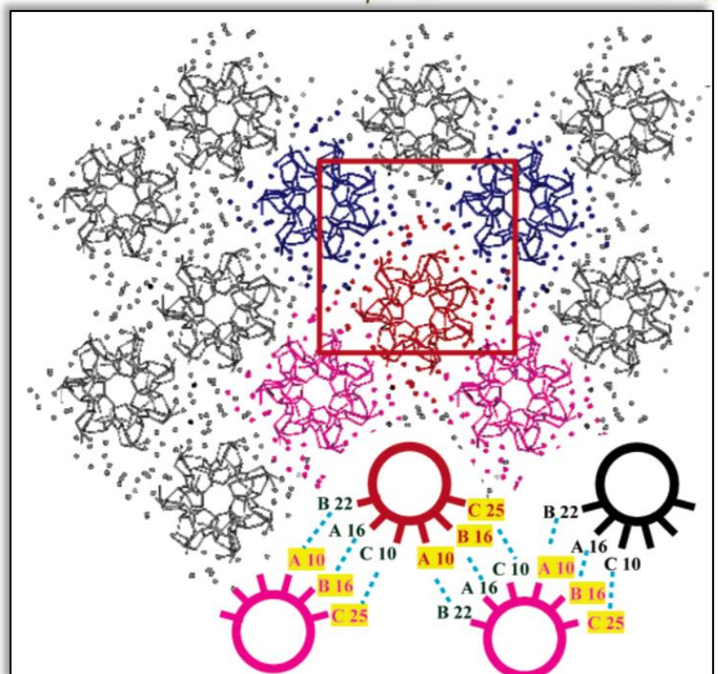


Introduction to collagen: Water bridges

The hydration shells connect between each other creating stabilized collagen filaments [*K. Kawahara et al, Biochemistry, 2005*]

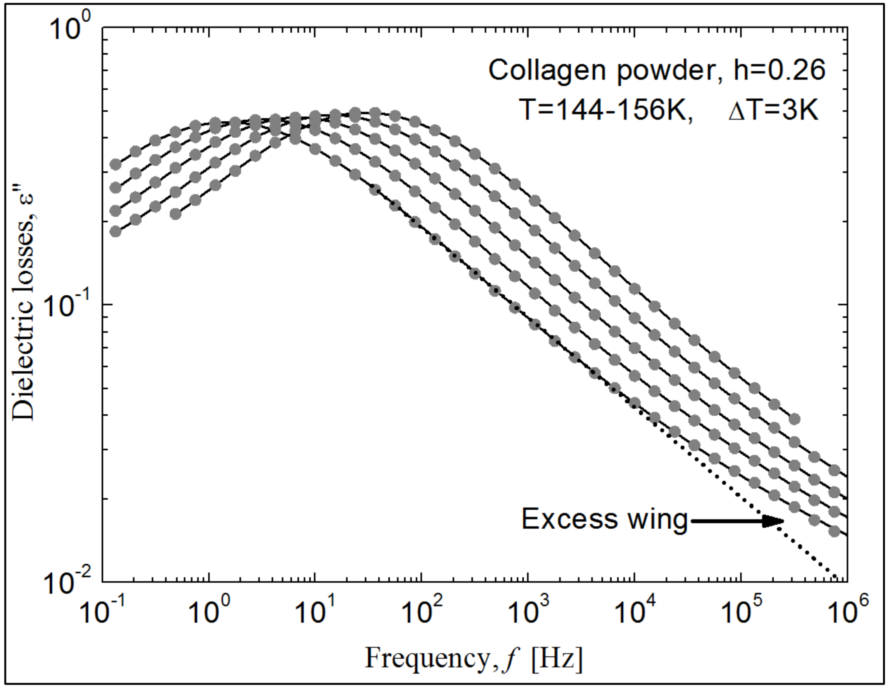


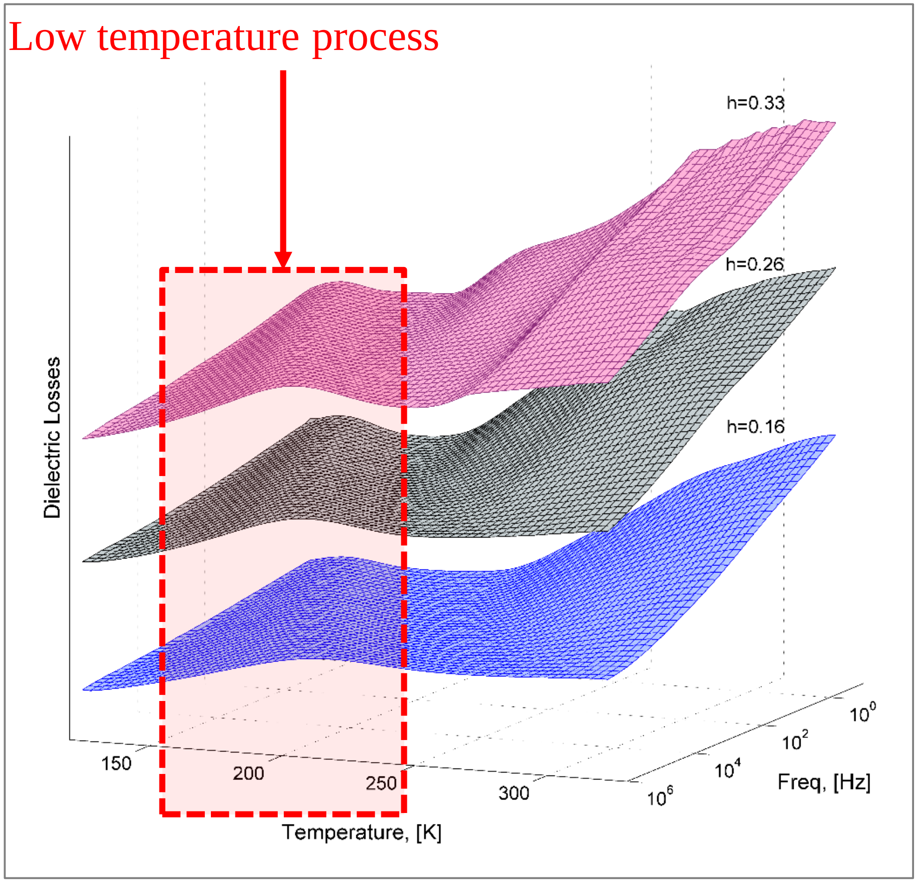




The problem: **What is the differences between hydration shell of globular and fibrillar proteins**

Dielectric measurements of the hydrated collagen powders





S. A. Lusceac, et al Proteins and Proteomics, 2010

3D plot of dielectric losses of the hydrated collagen powders

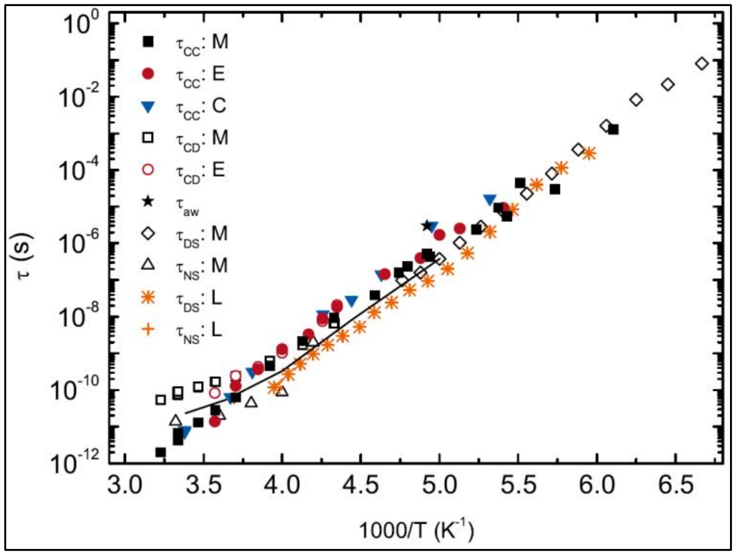
h=0.16 =0.26 =0.33

Dielectric measurements of the hydrated collagen powders

S. A. Lusceac, et al J. Non-Cryst. Solids (2011)

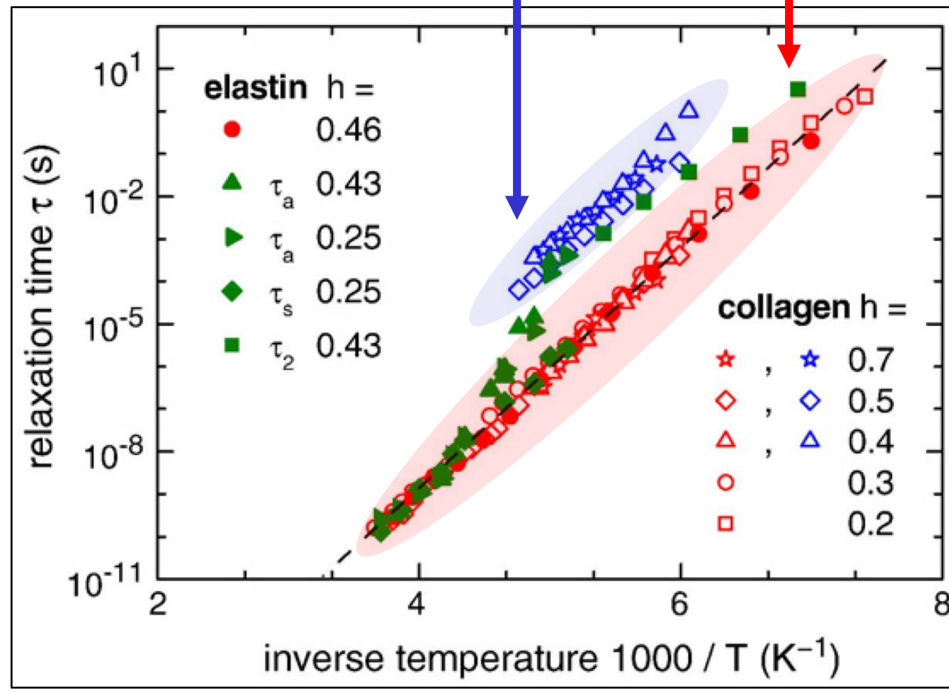
Ice process appears at high hydration level h>0.4

S. A. Lusceac, et al Proteins and Proteomics, 2010



Ice process

Main process



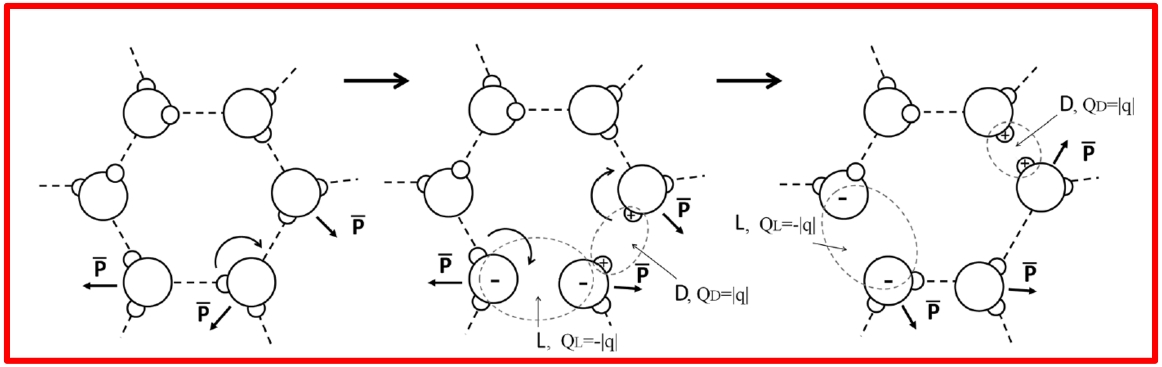
1. **Main process doesn’t depend on the shape of the protein and is observed in the various proteins.**
2. **It is attributed to the large-angle jumps of the water molecule**
3. **The present models are ignored the excess wing at the high frequency**

New approach in the data description: Excess wing explanation

The proposed large-angle jumps can be corresponded with the migration of the H-bond network defect [I. Popov, A. Puzenko, A. Khamzin and Y. Feldman PCCP, 2015]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \left[\dfrac{i\omega n q^2 \left\langle r_{or}^{*2}(\omega)\right\rangle}{6 k_B T \varepsilon_0}\right]^{-1}}$$

Orientation defect



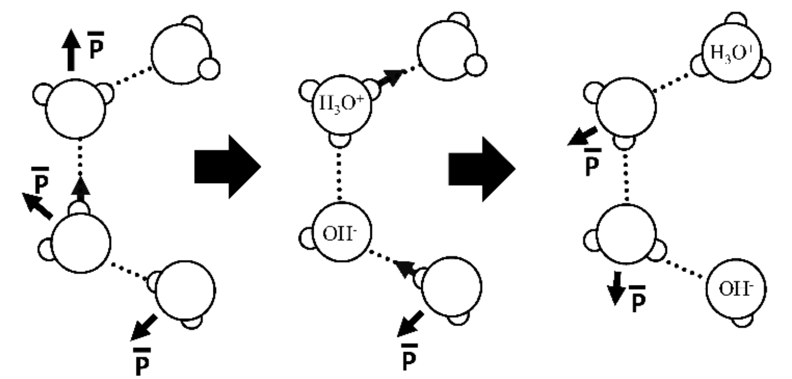
$$\underbrace{\left\langle r_{or}^2(t)\right\rangle = \lambda^2 \left(t/\tau_h\right)^{\alpha_{or}} \Rightarrow \left\langle r_{or}^{*2}(\omega)\right\rangle \sim (i\omega)^{-\alpha_{or}-1}}$$

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \left(i\omega\tau_{or}\right)^{\alpha_{or}}}$$

If we take into account an ionic defect

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \left[\dfrac{i\omega}{6 k_B T \varepsilon_0} \sum_{i=1}^{2} n_i q_i^2 \left\langle r_i^{*2}(\omega)\right\rangle\right]^{-1}}$$

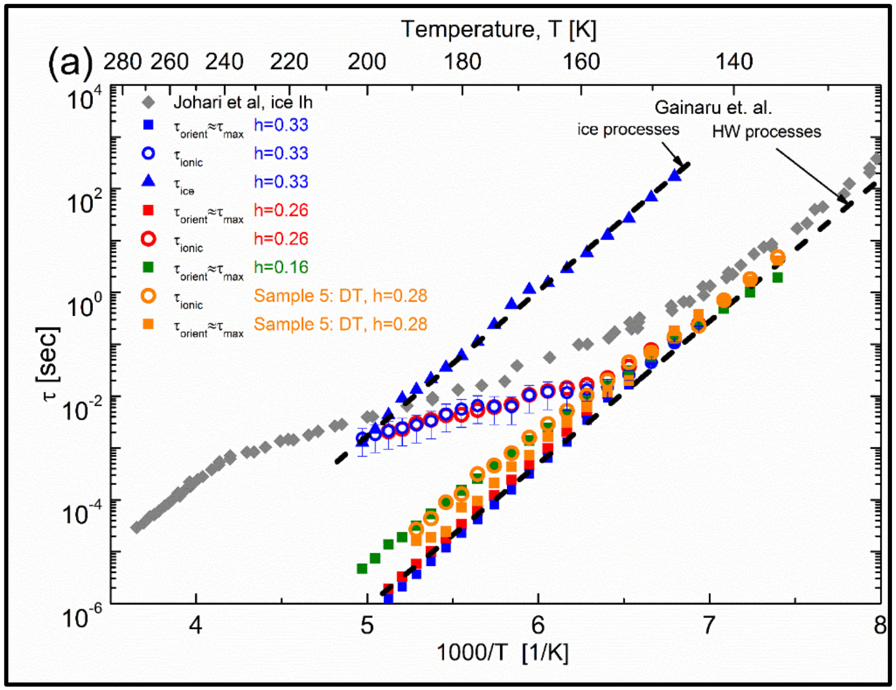
Ionic defect

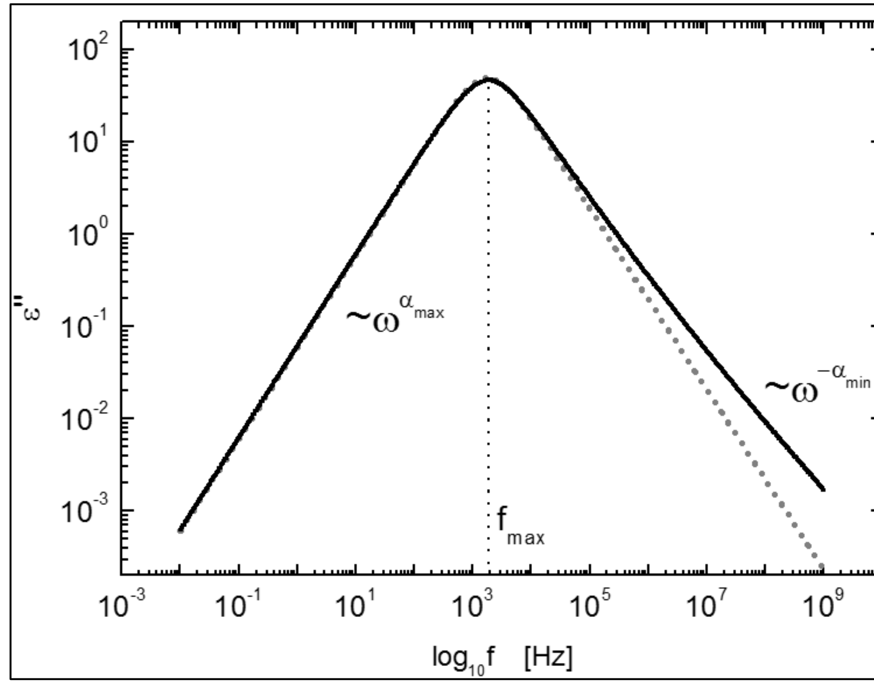


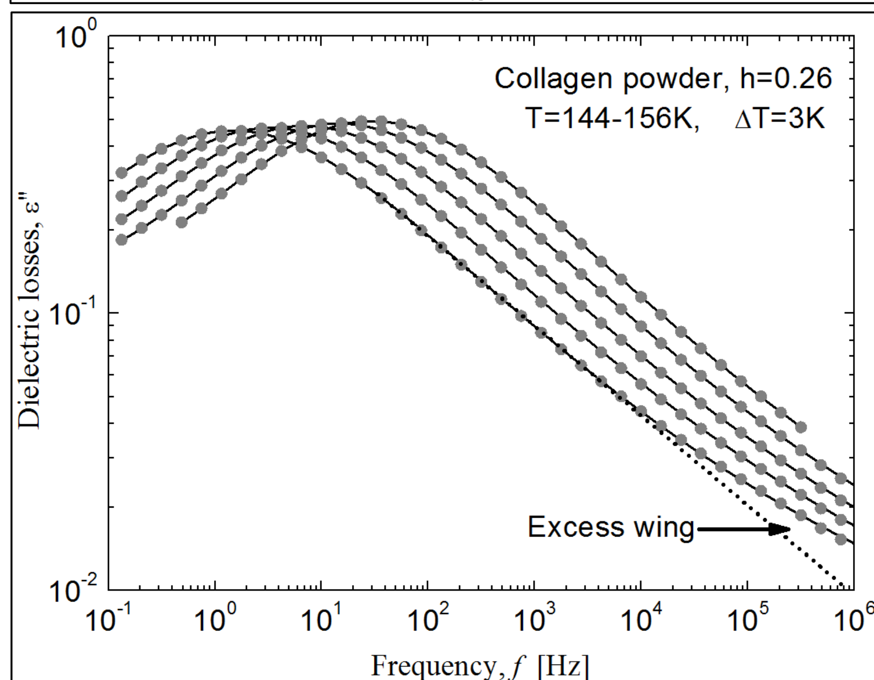
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \left[\left(i\omega\tau_{or}\right)^{-\alpha_{or}} + \left(i\omega\tau_{ion}\right)^{-\alpha_{ion}}\right]^{-1}}$$

Collagen data treatment

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\Delta\varepsilon}{1+\left[\left(i\omega\tau_{or}\right)^{-\alpha_{or}}+\left(i\omega\tau_{ion}\right)^{-\alpha_{ion}}\right]^{-1}}$$

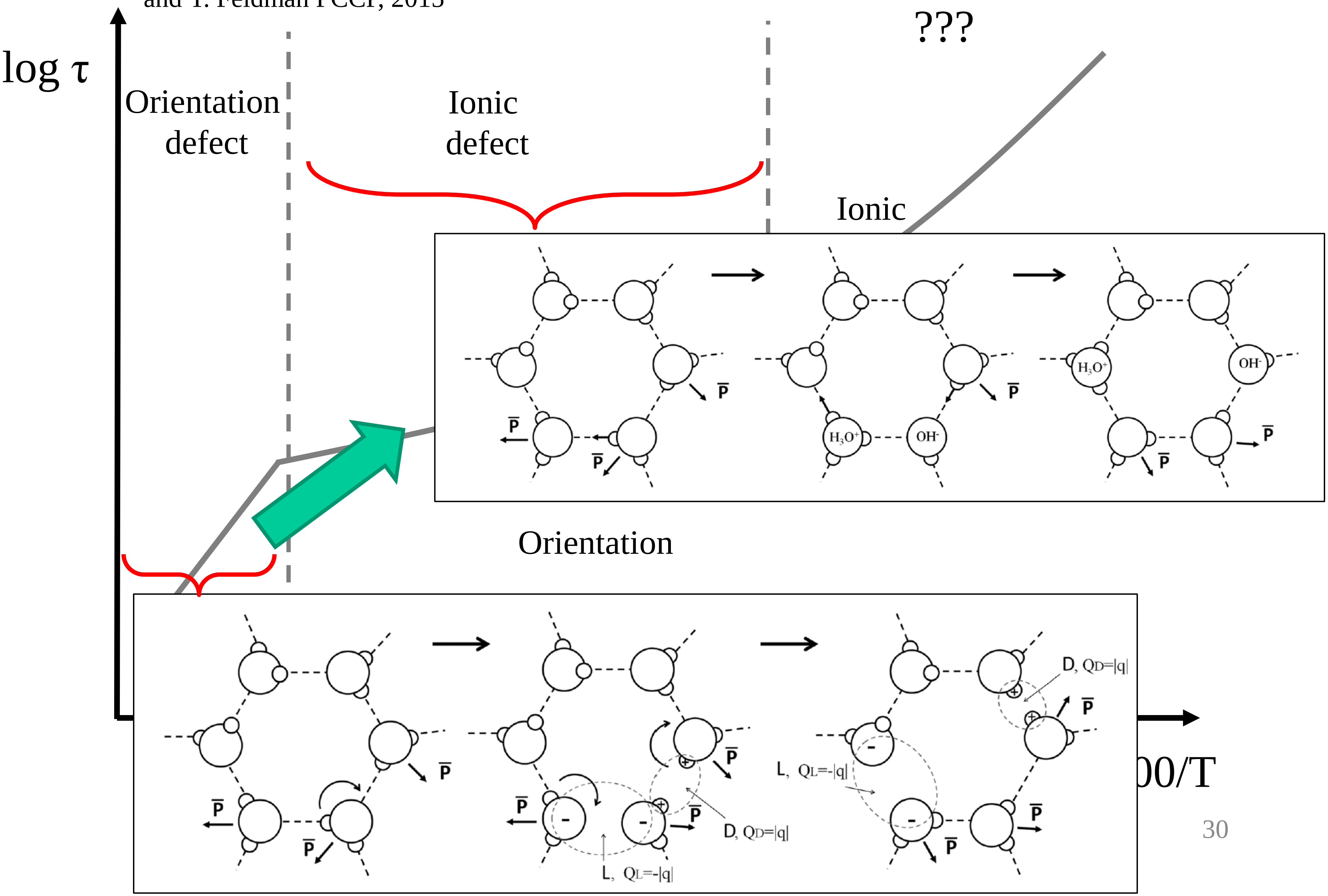






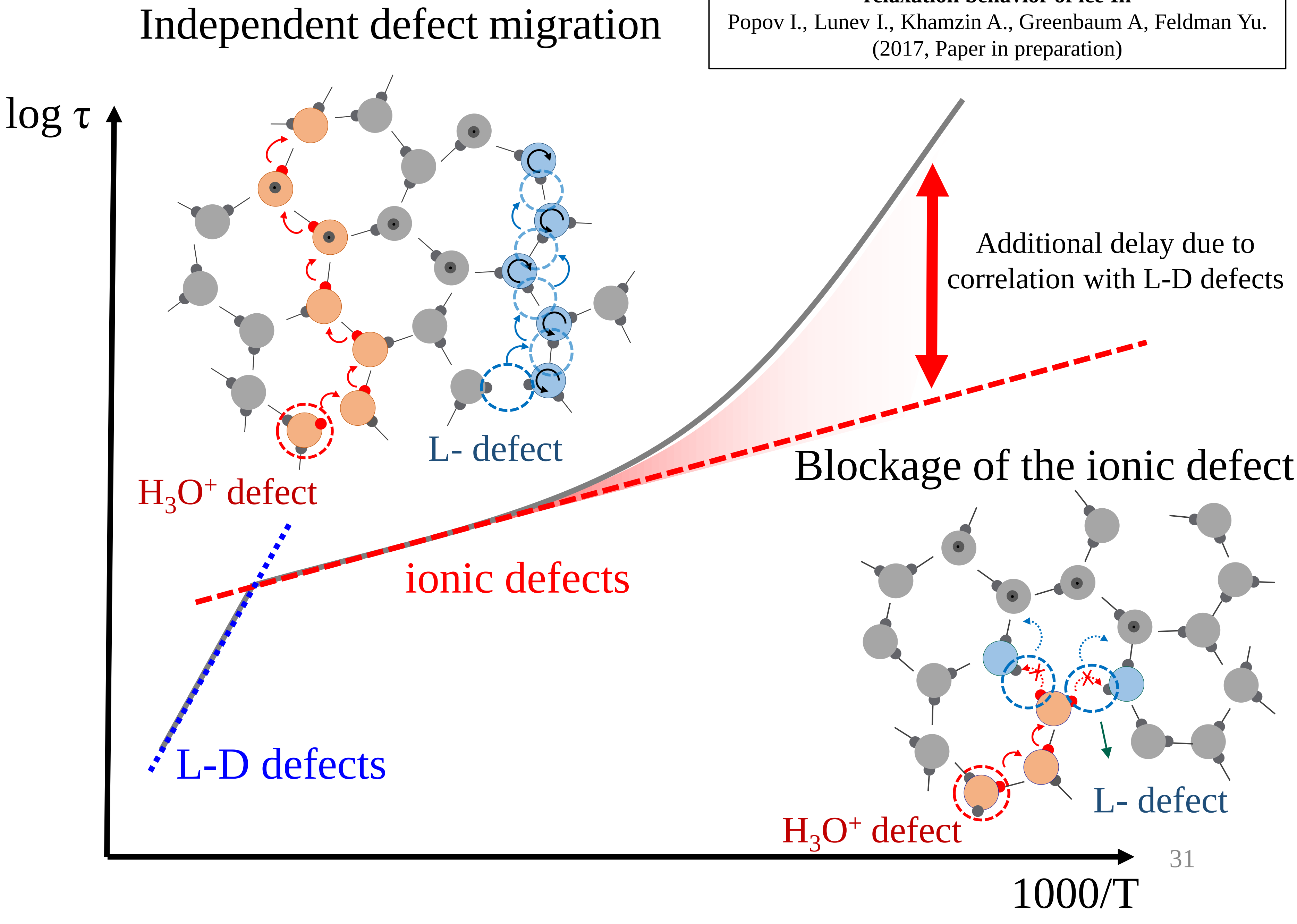
Relaxation in ice

I. Popov, A. Puzenko, A. Khamzin and Y. Feldman PCCP, 2015



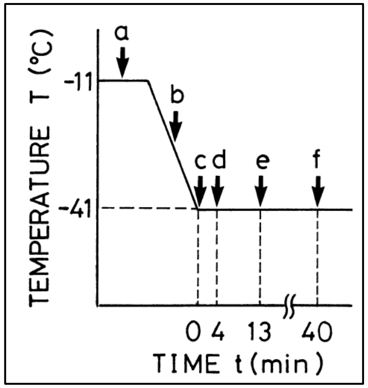
Relaxation in ice

The low-temperature dynamic crossover in dielectric relaxation behavior of ice Ih
Popov I., Lunev I., Khamzin A., Greenbaum A, Feldman Yu. (2017, Paper in preparation)

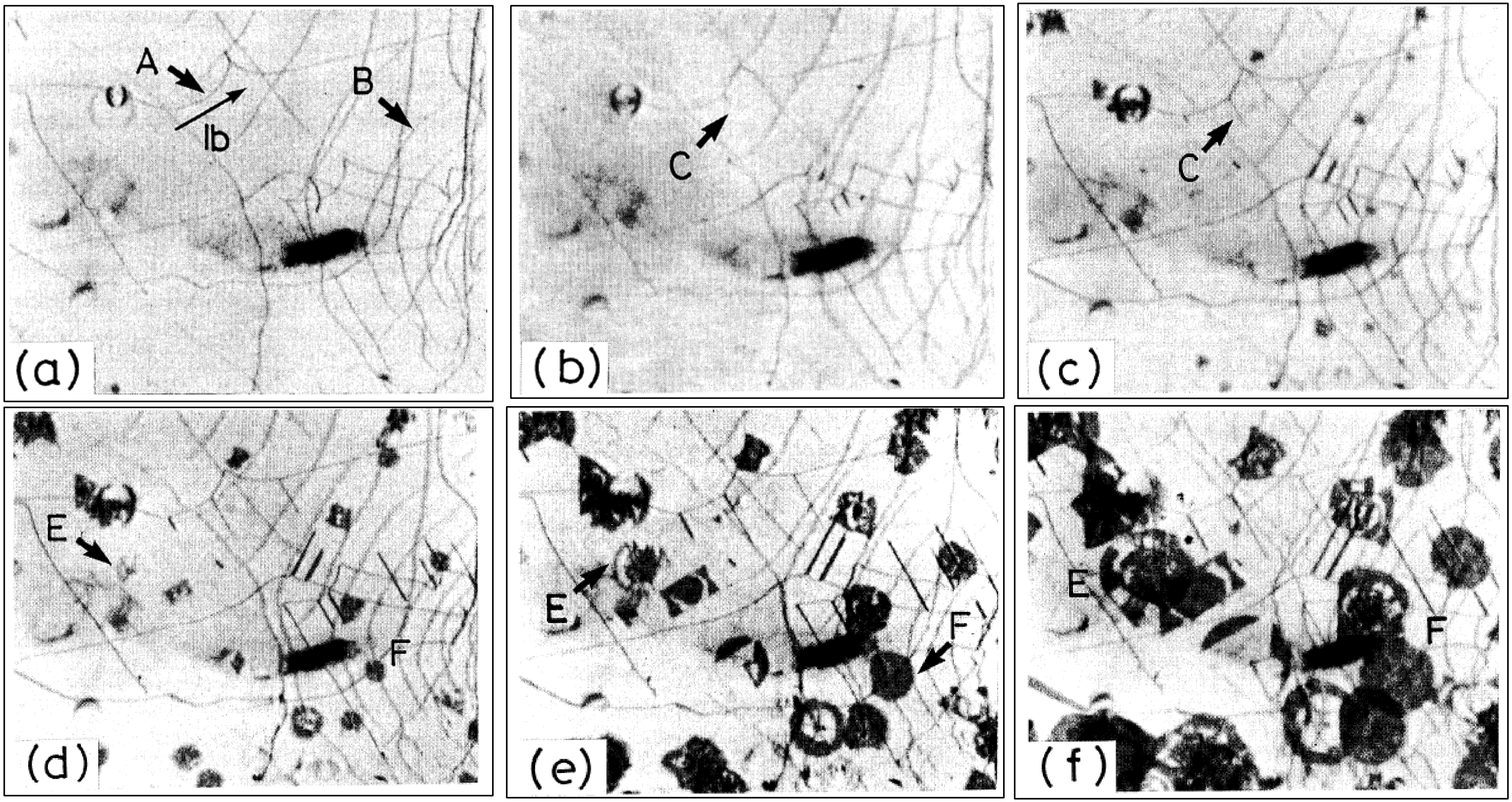


Relaxation in ice

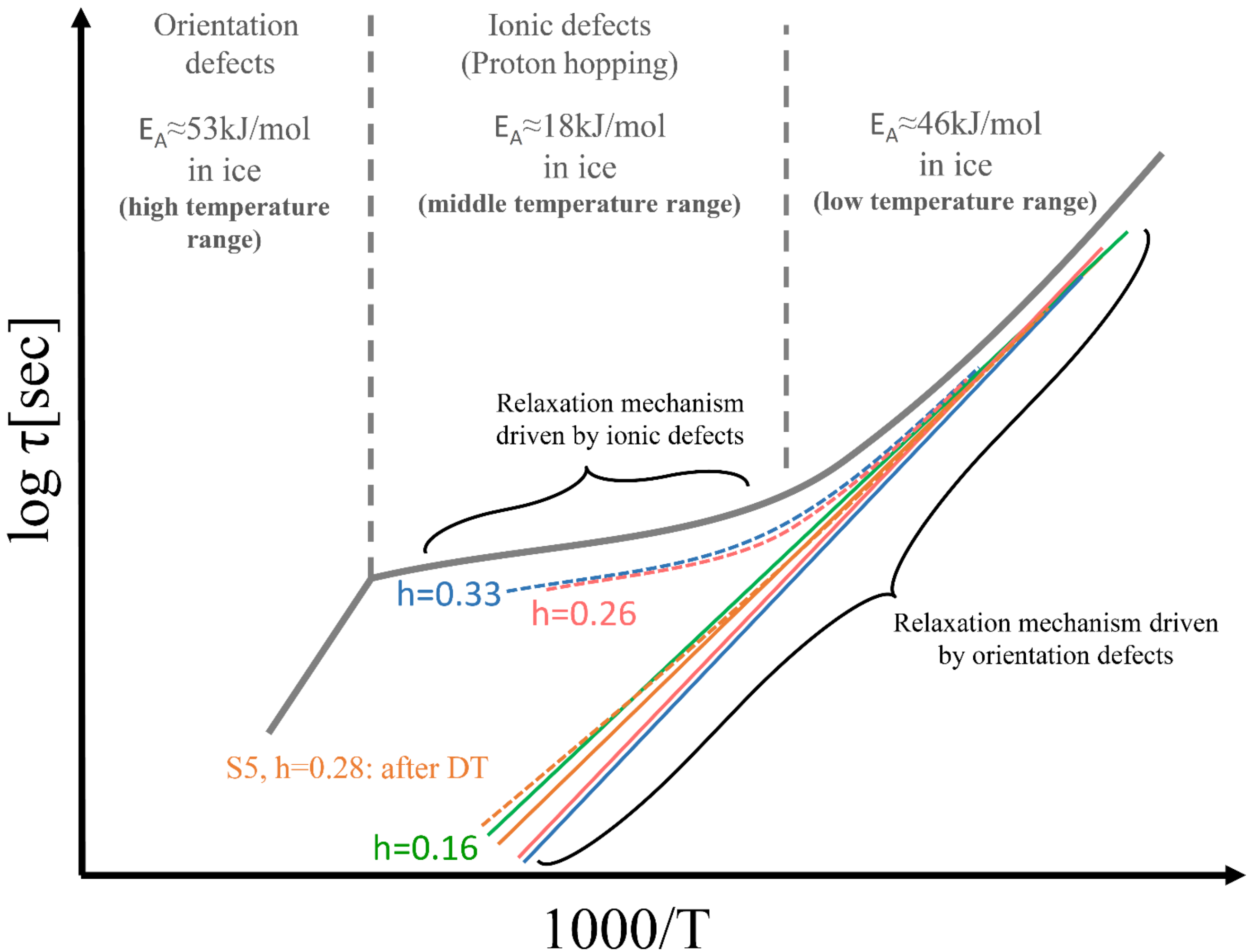
K.Goto et al Japanese J. of Applied Phys. (1986) pp.351-357

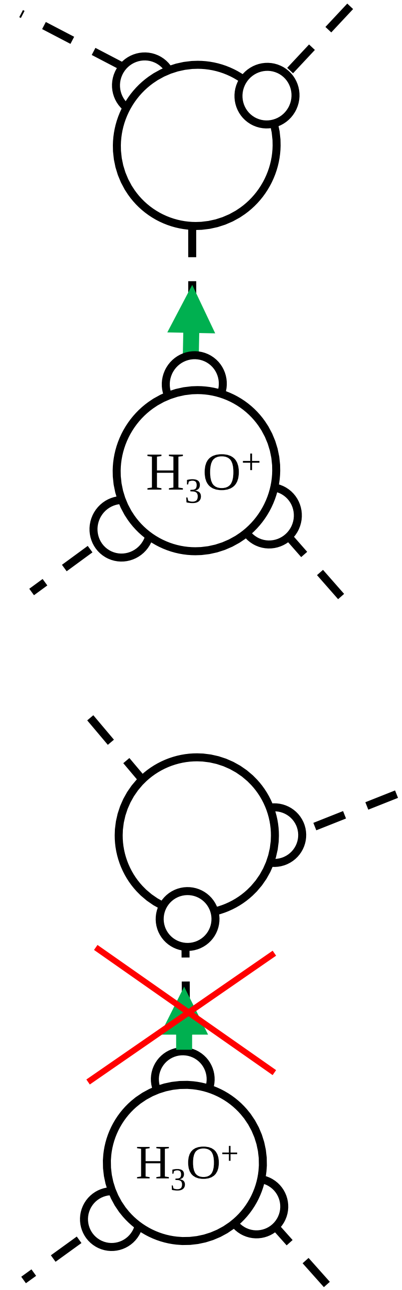


At low temperature the crack appearance leads to the suppression of the ionic defect and transition back to the mechanism of the orientation defect.



Hydration water ~ Distorted ice

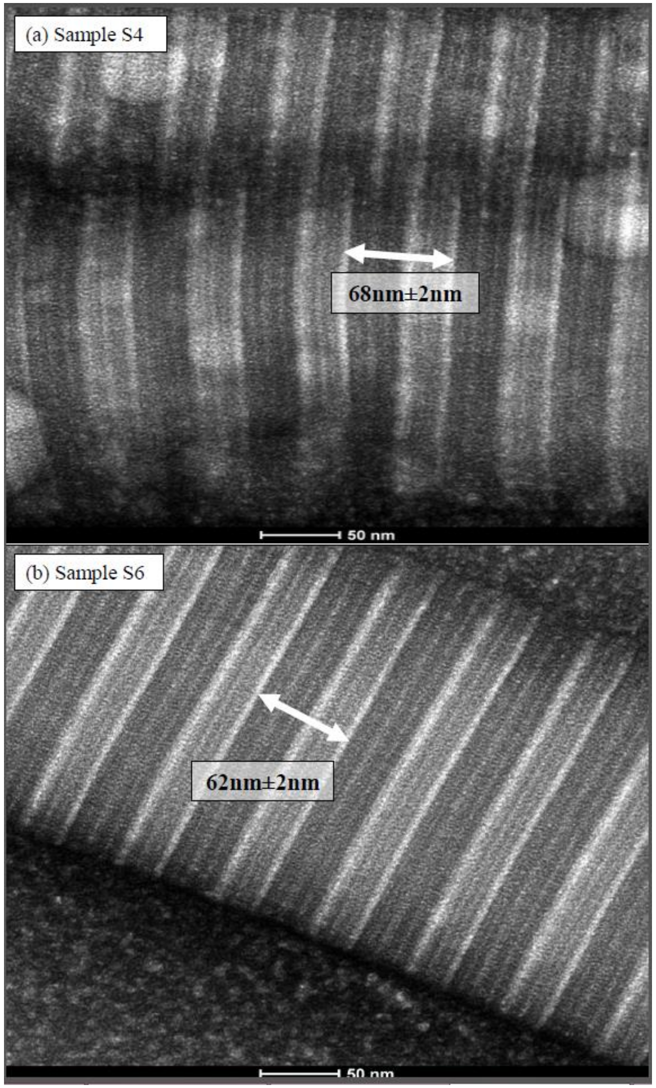


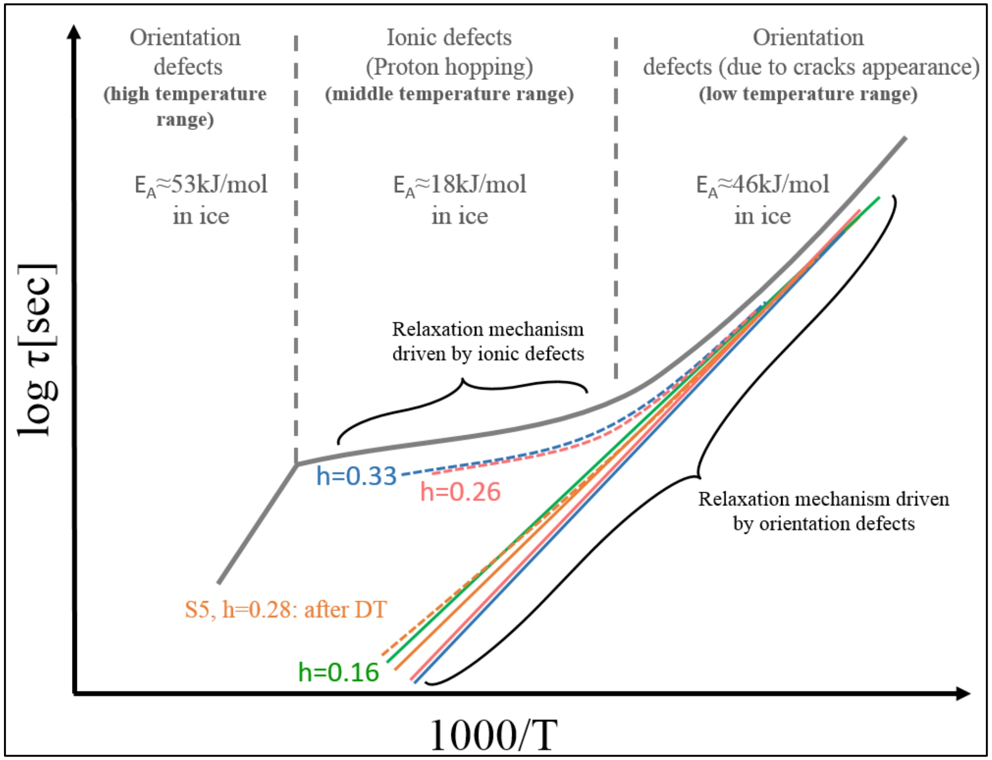


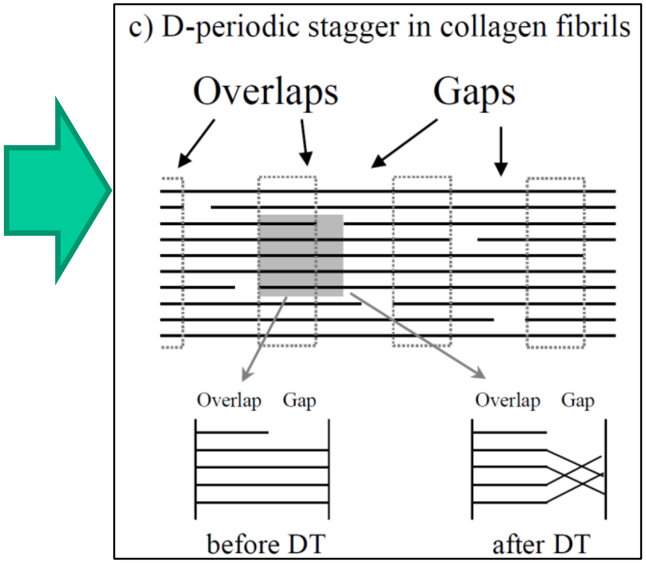
Relaxation by ionic defect cannot be faster than relaxation by orientation defect

Dehydrothermal Treatment:

After Heating and Keeping the collagen at 120 ^{0}C for 30 min, proton hopping mechanism slows down



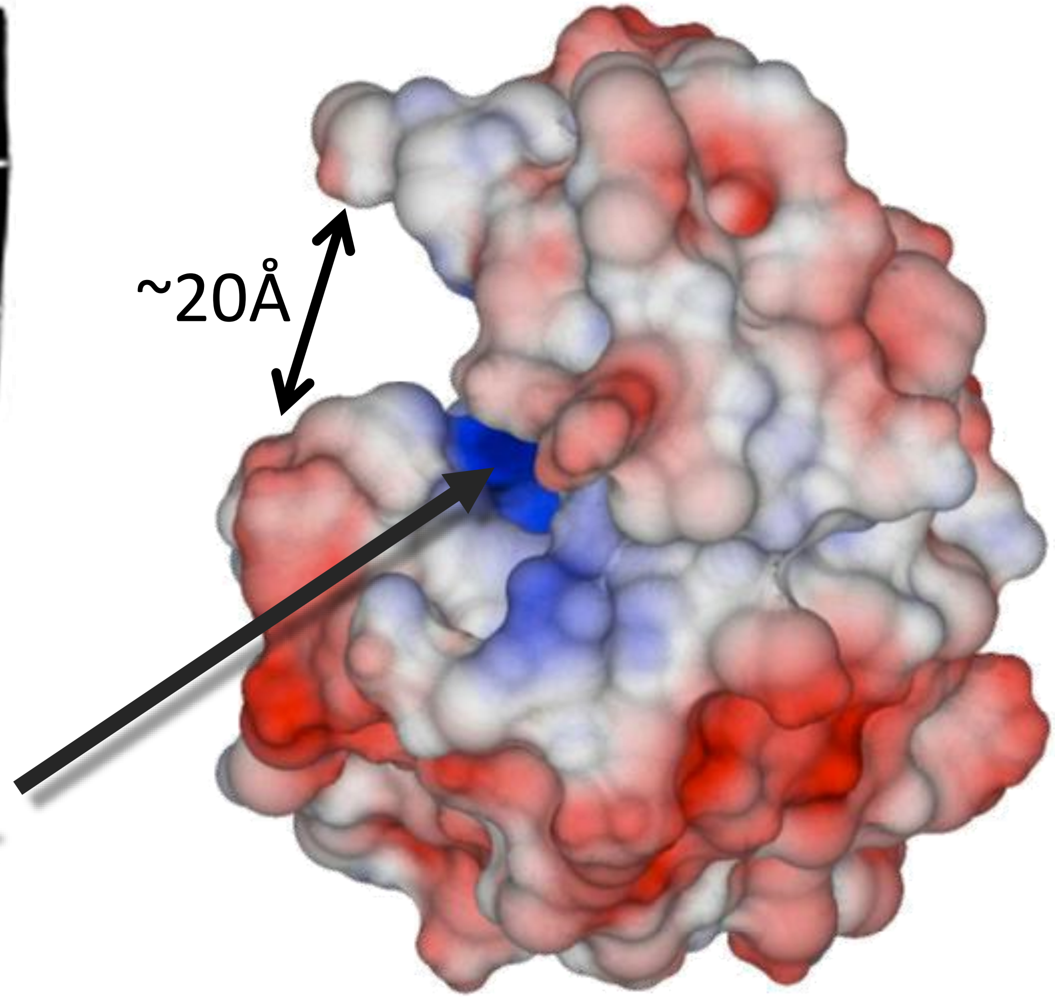




Chains tilting prevents the formation of the long range water structure.

Relaxation occurs in local compartments, where contribution of the L-D and ionic defect are comparable

Lysozyme

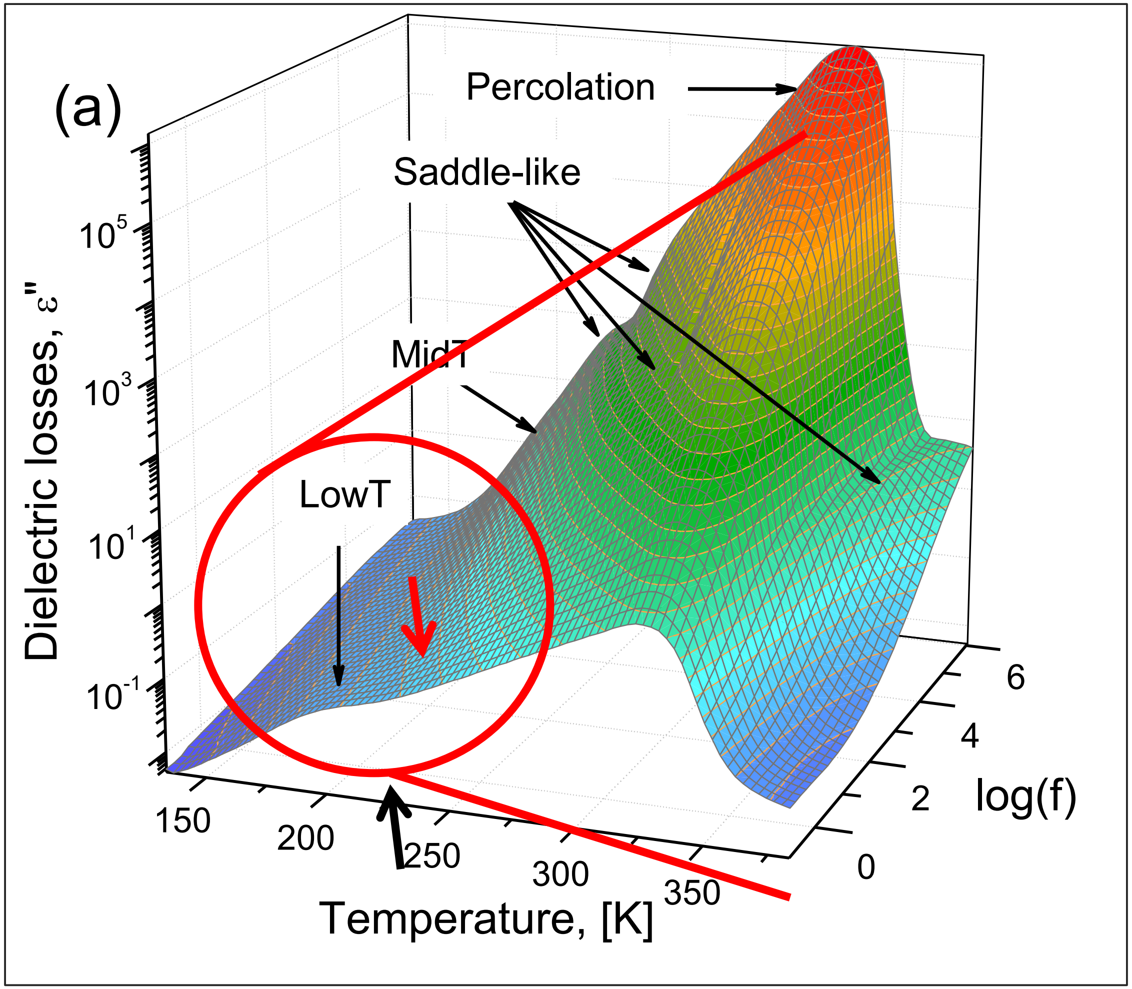


Charged active center

Lysozyme: Surface charge plot
[Christopher D. Cooper at el. 2013]

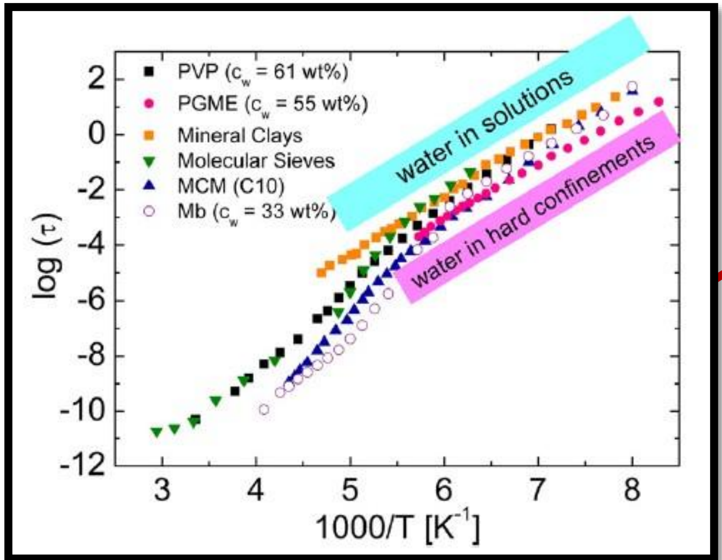
BDS Measurements: Lysozyme h=0.28 and h=0.16

The typical dielectric spectra

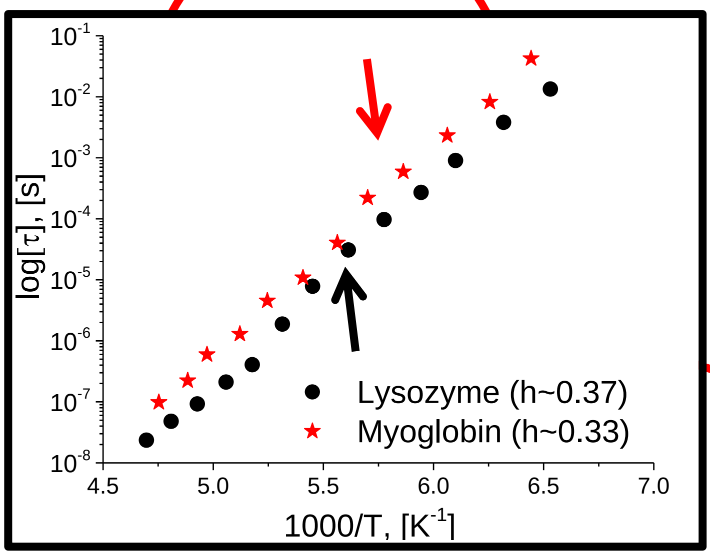


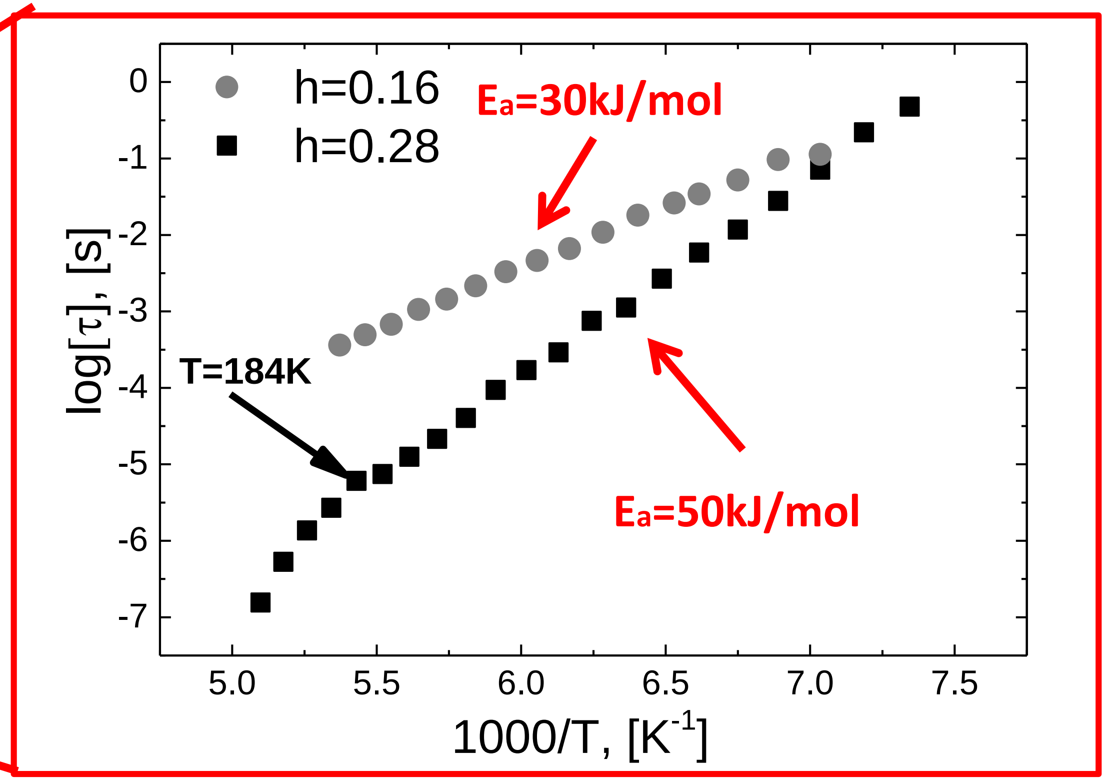
[Khodadadi and A.P.Sokolov 2015]

BDS Measurements: Lysozyme h=0.28 and h=0.16



Swenson and CerVeny 2015



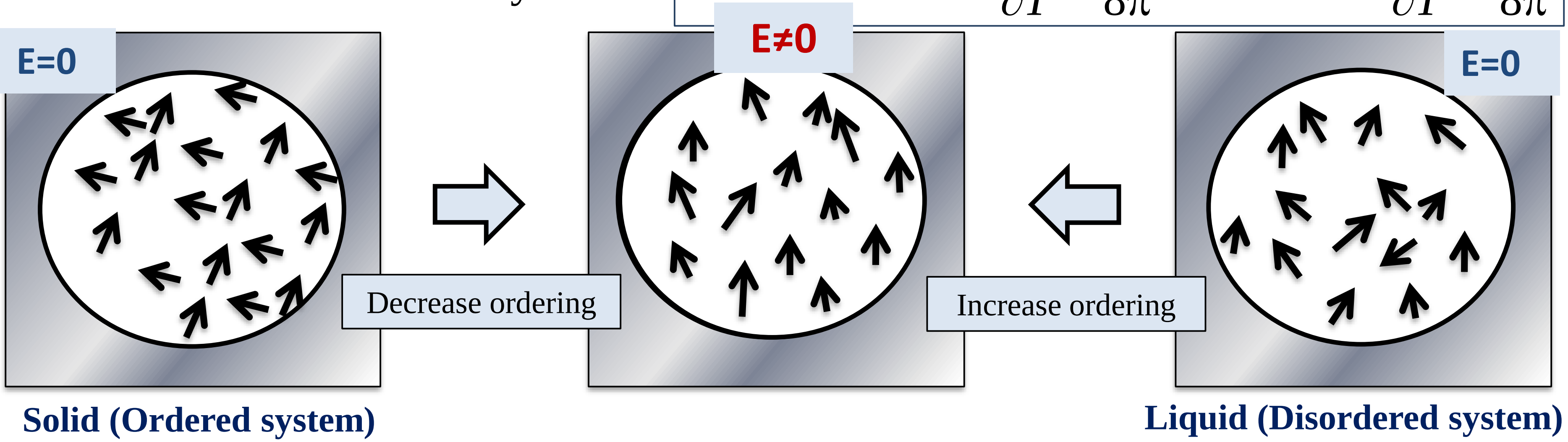


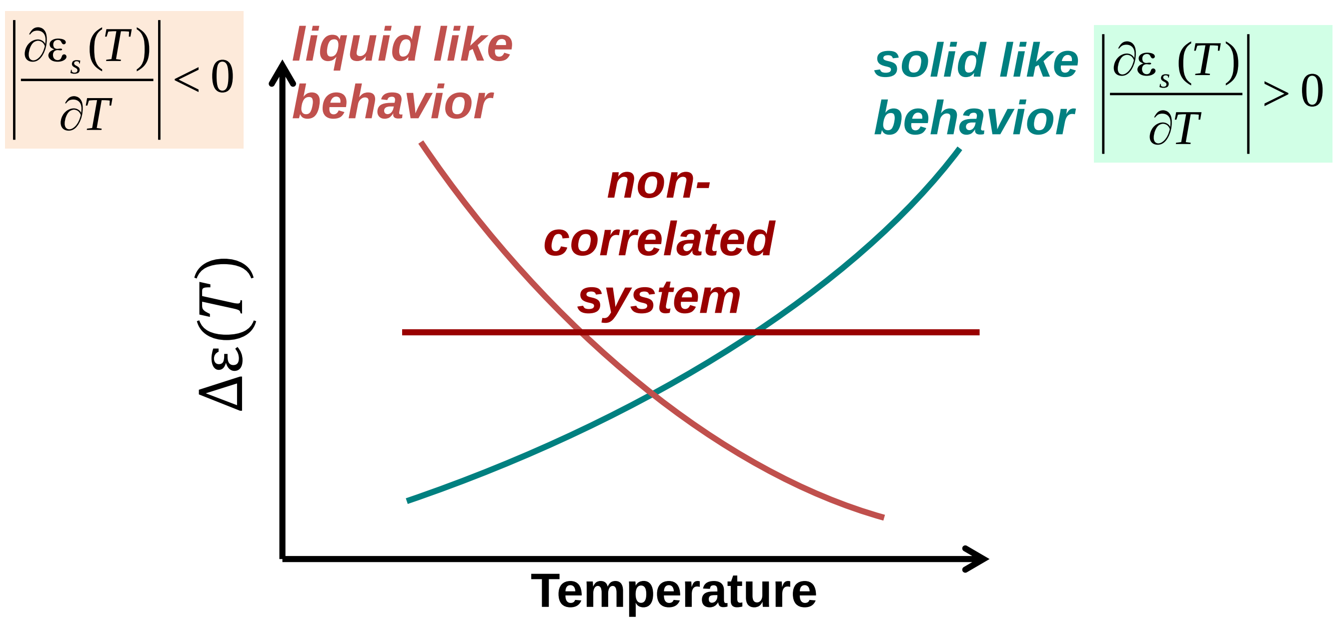
[Khodadadi and A.P.Sokolov 2015]

Dielectric Polarization and Entropy of the System

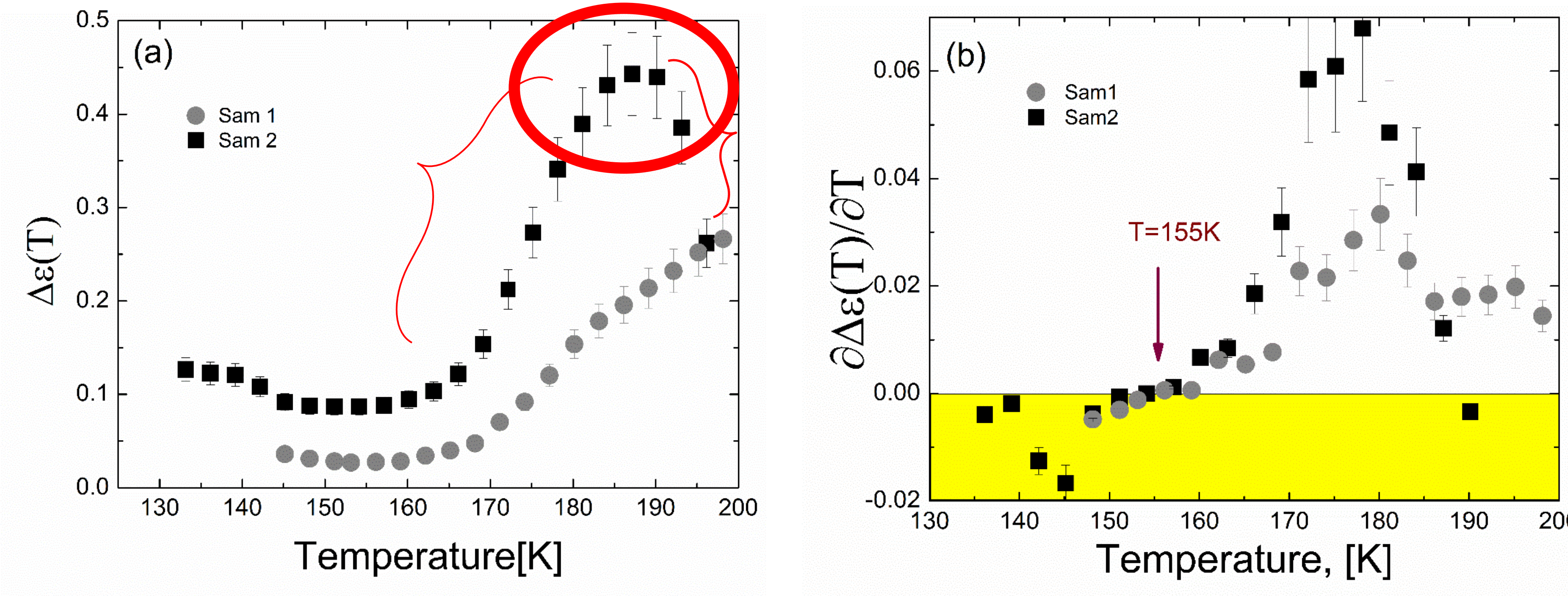
Entropy and
Static Dielectric Permittivity

$$S(T) = S_0(\mathrm{T}) + \frac{\partial \varepsilon_s(T)}{\partial T}\frac{E^2}{8\pi} \approx S_0(\mathrm{T}) + \frac{\partial \Delta\varepsilon(T)}{\partial T}\frac{E^2}{8\pi}$$





BDS Measurements: Lysozyme h=0.28 and h=0.16

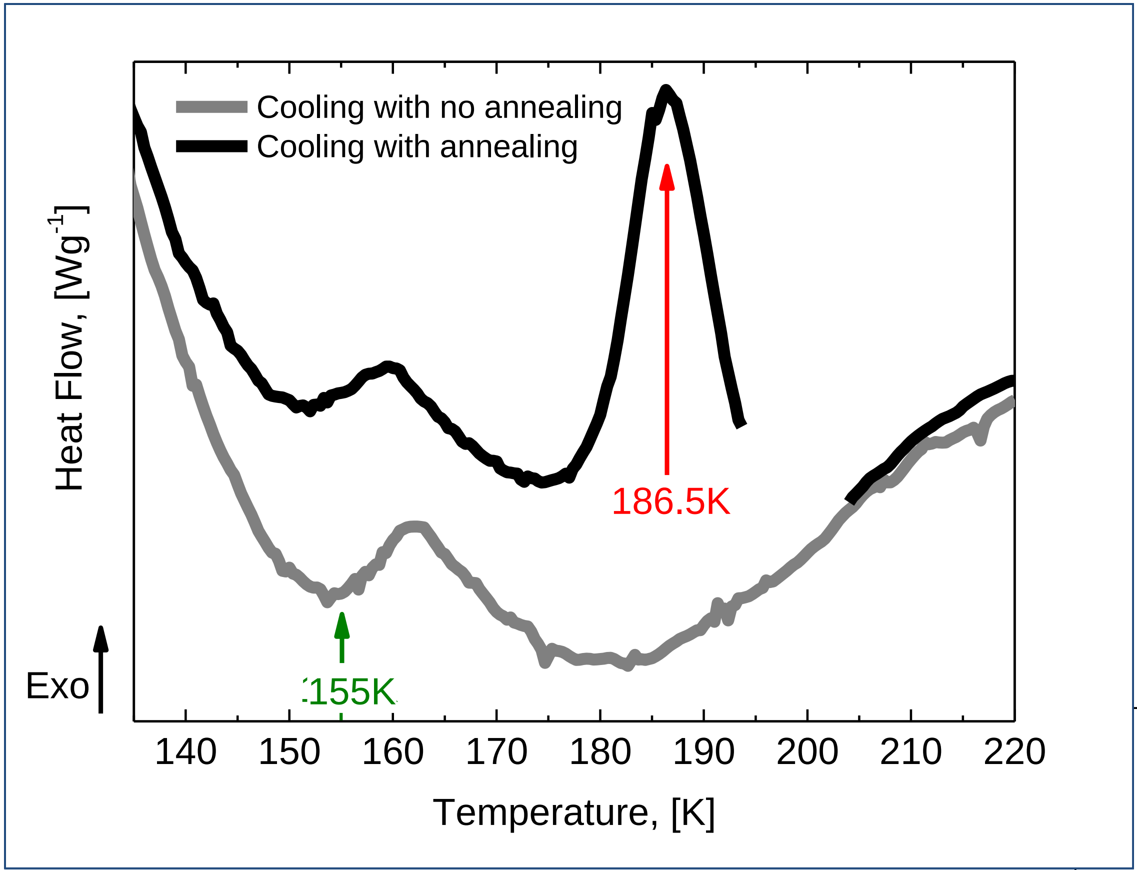


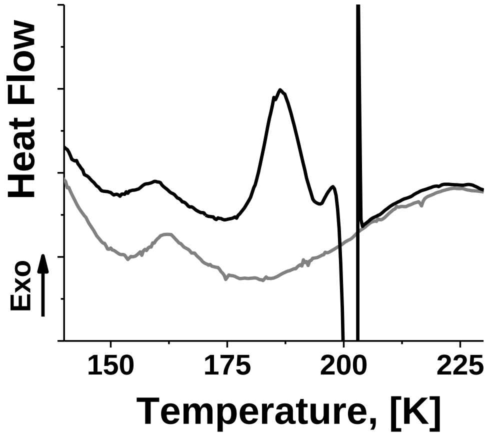
$d\Delta\varepsilon/dT$>0 tendency to solid-like dipole orientation

$d\Delta\varepsilon/dT$<0 tendency points to a liquid-like behavior.

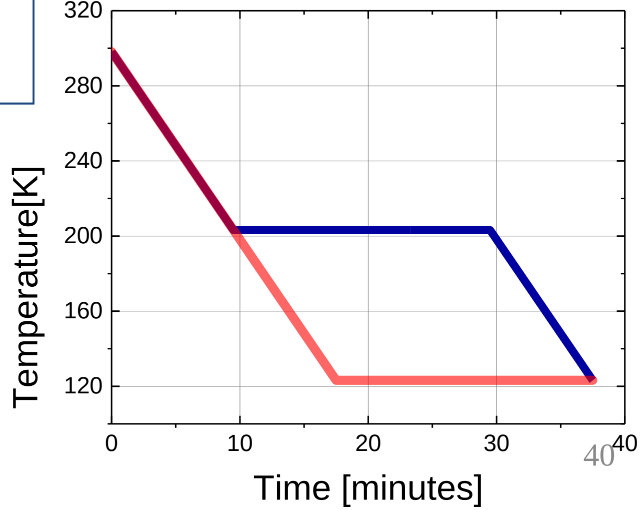
T<155K	155K<T<187K	T>187K
Short-range antiparallel orientation of the water dipoles, typical for the amorphous system	Tendency to solid like behavior	Tendency to liquid like behavior

DSC Measurements: Lysozyme h=0.2



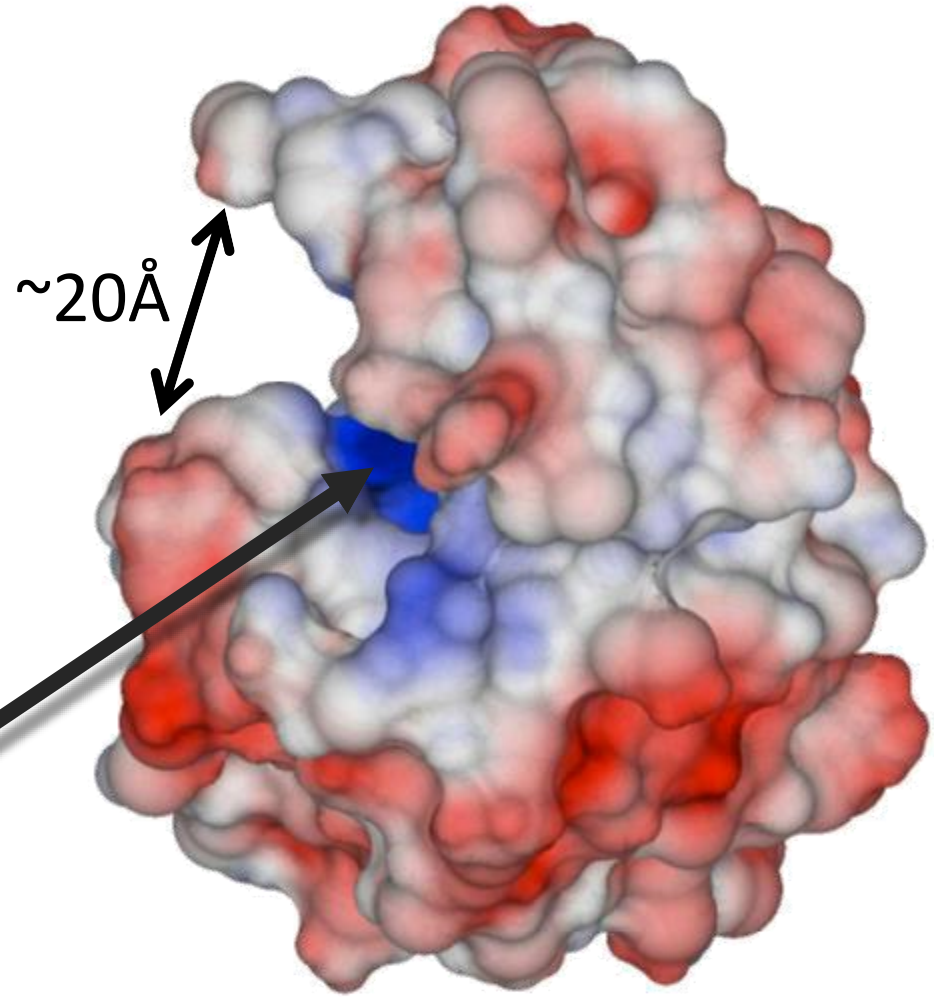


Protocol



Explanation of the Results

Charged active center

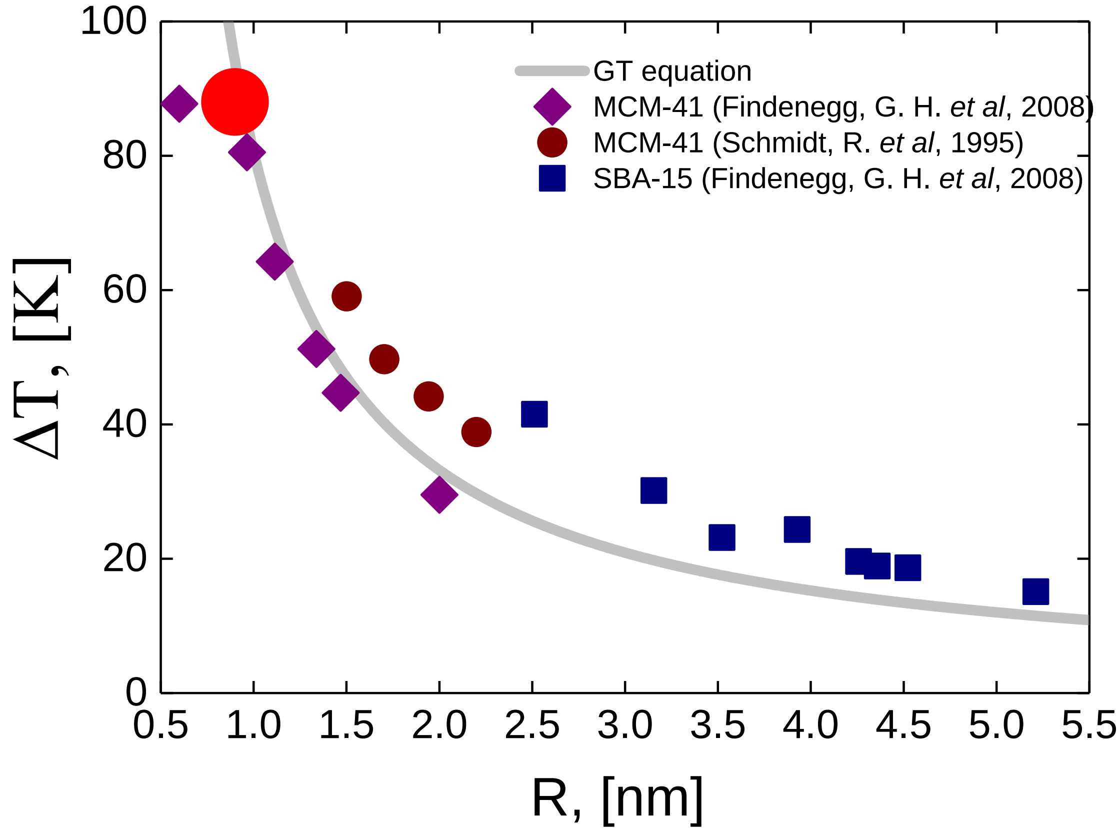


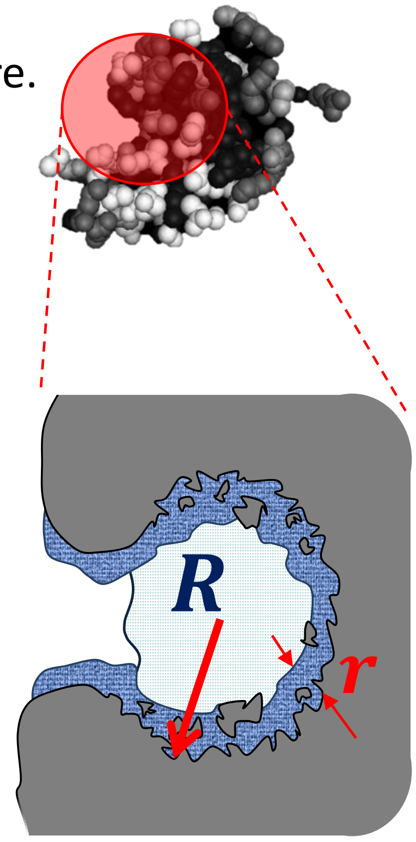
Lysozyme: Surface charge plot
[Christopher D. Cooper at el. 2013]

Gibbs-Thompson Fit for Silica Nano pores

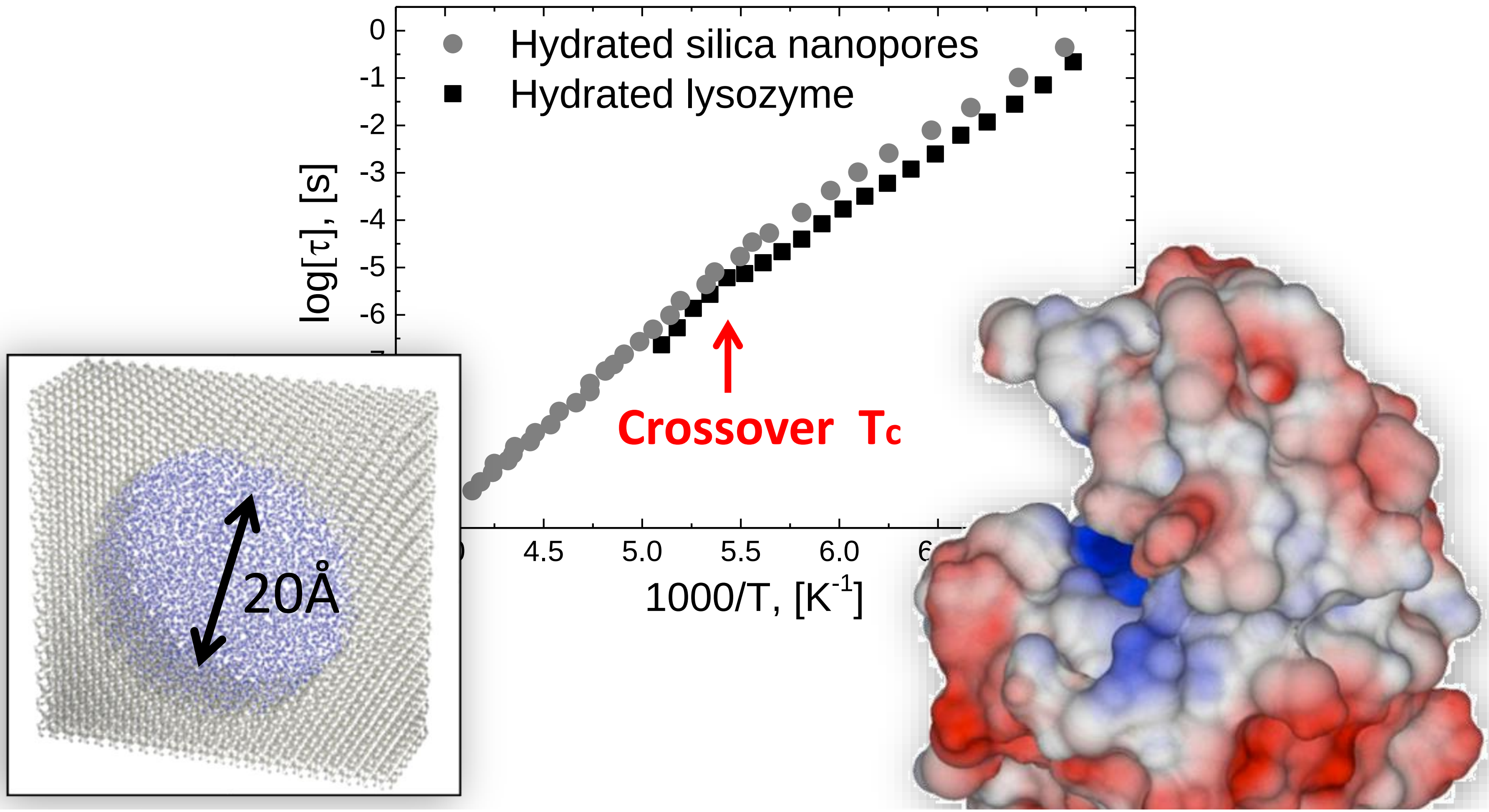
$$\boxed{\Delta T_f(R) = C_{GT}/(R - r)}$$

$\Delta T_f = T_f(bulk) - T_f(pore)$- The depression of the confined water melting temperature.
C_{GT}-The Gibbs-Thompson Coefficient.
R - The radius of the pore.
r - The thickness of a liquid-like layer at the relevant melting temperature.





Relaxation Times of Hydrated Lysozyme and Confined Water in Silica Nanopores



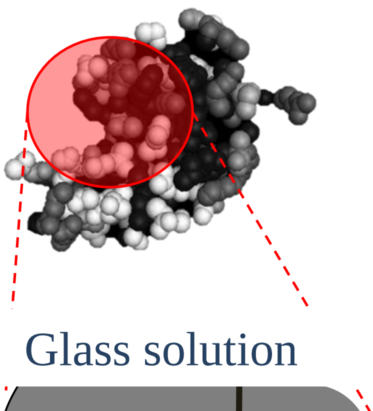
Silica nanopore with pore diameter equaled to **20A**

[Eliodoro Chiavazzoet al 2014]

Lysozyme with diameter cavity inside equaled to **20A**

[Christopher D. Cooper at el. 2013]

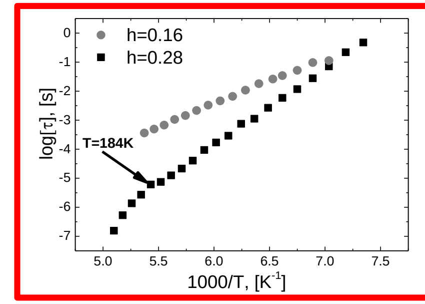
The Model

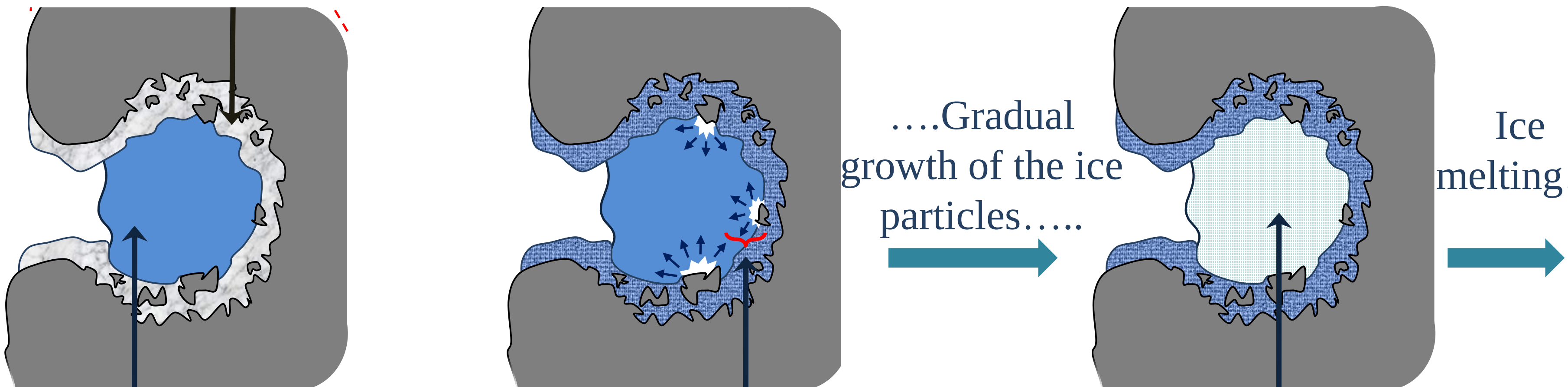


Glass solution

T=155K:
1) Glass transition of the solution
2) Onset of the crystallization

T=184K:
Phase Transition of the ice inside the pore.





….Gradual growth of the ice particles…..

Ice melting…

Glass-state water

Nucleation growth of the ice particles

Ice particle inside the pore

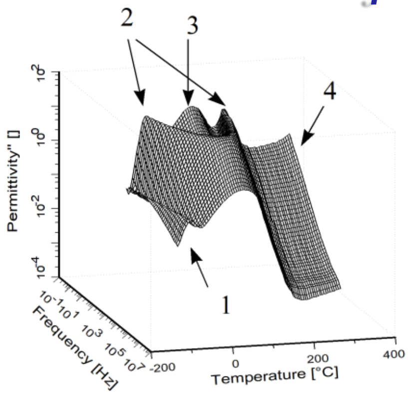
T=155K

T=184K

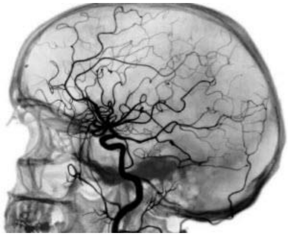
Temperature, [K]

Conclusions

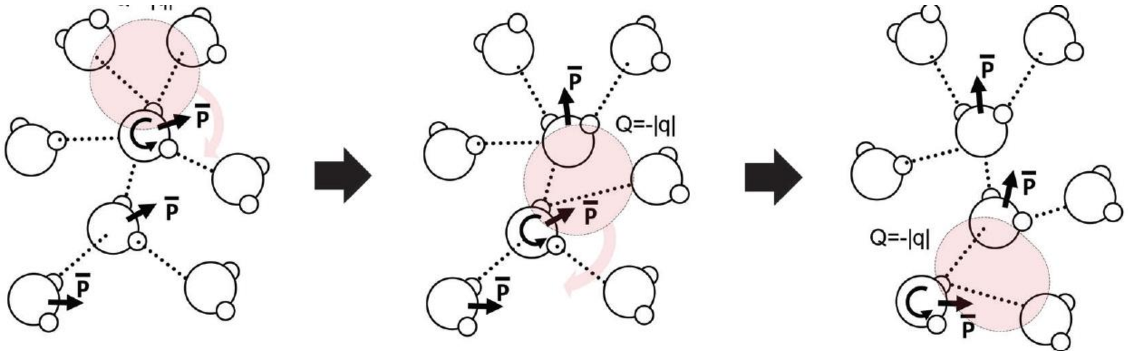
1) The morphology, dynamics and the dielectric properties of the matrixes will have an influence on the nature of the relaxation of hydrated water.



2) Water can be considered as a marker or a contrast in Dielectric Spectroscopy. The structural and dynamical properties of the matriex can be studied via its hydrating.



3) Defect migration model can be used as an universal approach in description of the dynamic of the hydration process.



Acknowledgements

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