Seventh Annual Conference On The Physics, Chemistry And Biology Of Water

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Seventh Annual Conference On The Physics, Chemistry And Biology Of Water

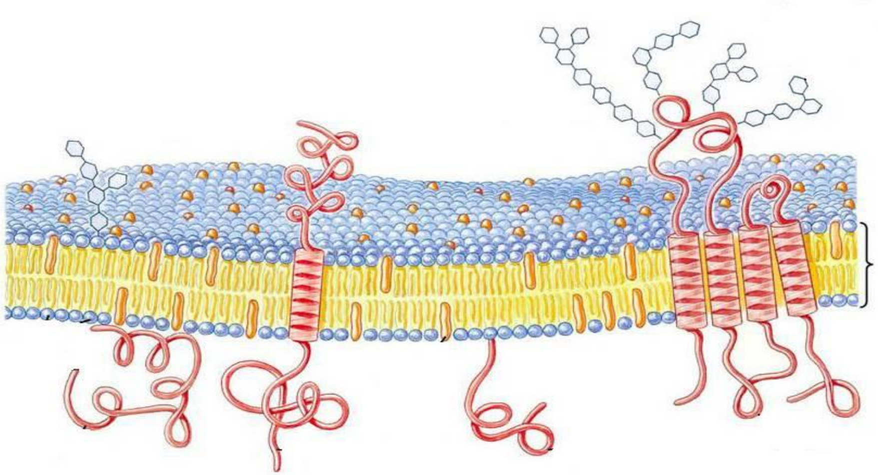
WATER POCKETS IN LIPID MEMBRANES EVALUATED BY FTIR SPECTROSCOPY

Signicance of Water interphase for peptide/enzymes activities in Lipid Membranes

MEMBRANES OR WATER

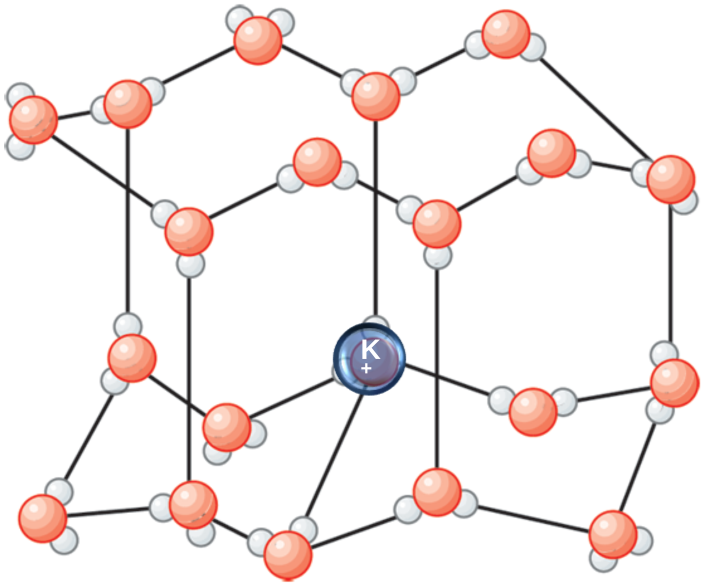
MEMBRANE THEORY

Bilayer as a dielectric slab



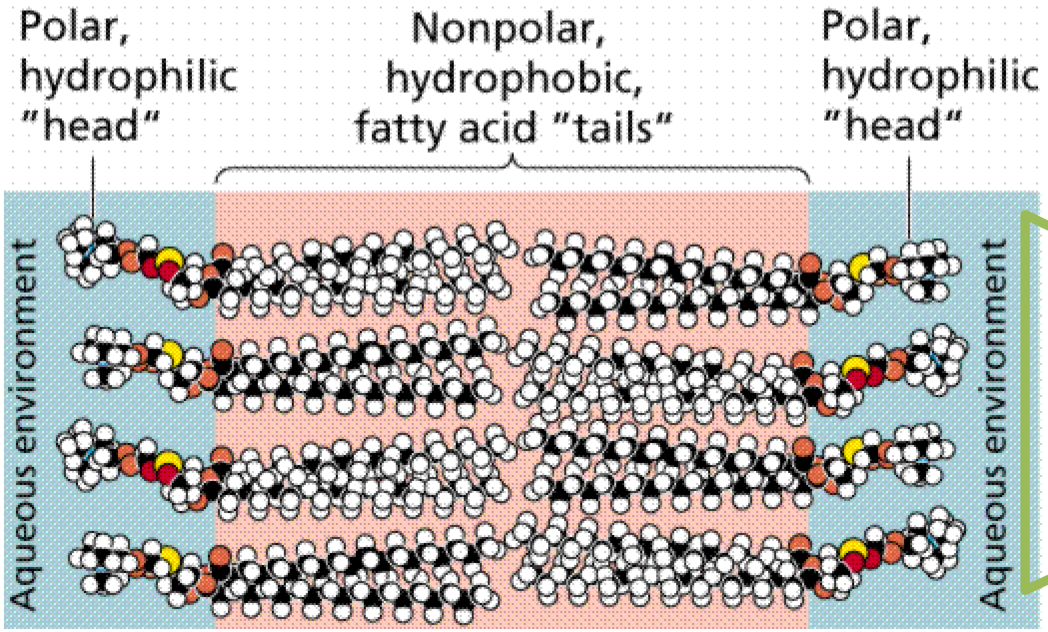
Permeability barrier for water and ions

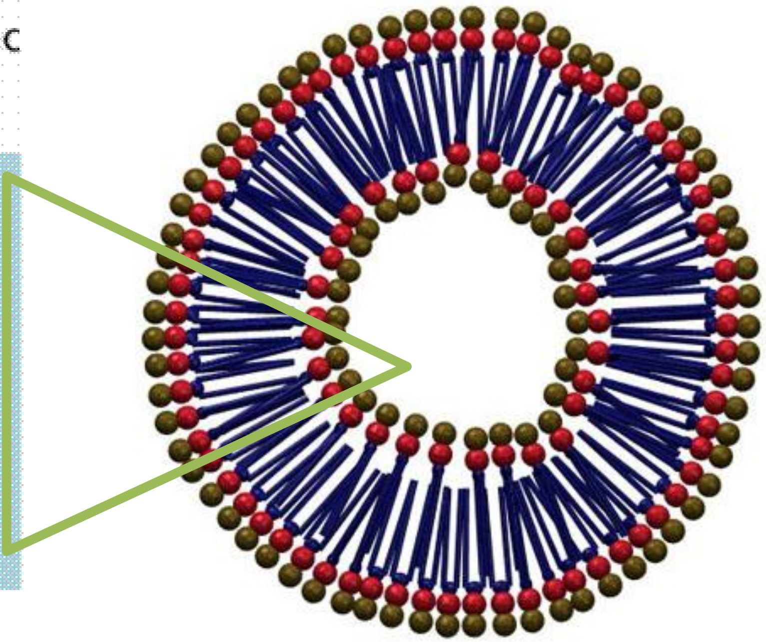
ASSOCIATION INDUCTION HYPOTHESIS



WATER IN MEMBRANES

(Disalvo De Gier, 1983)



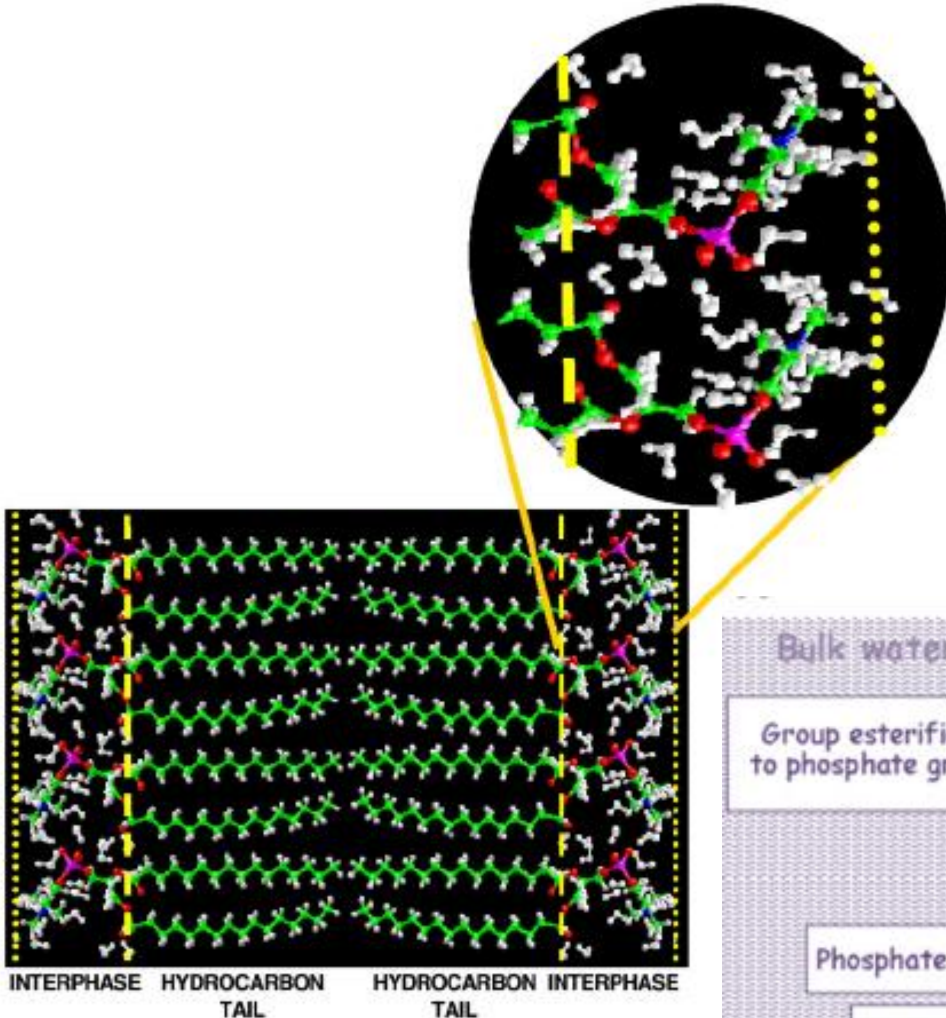


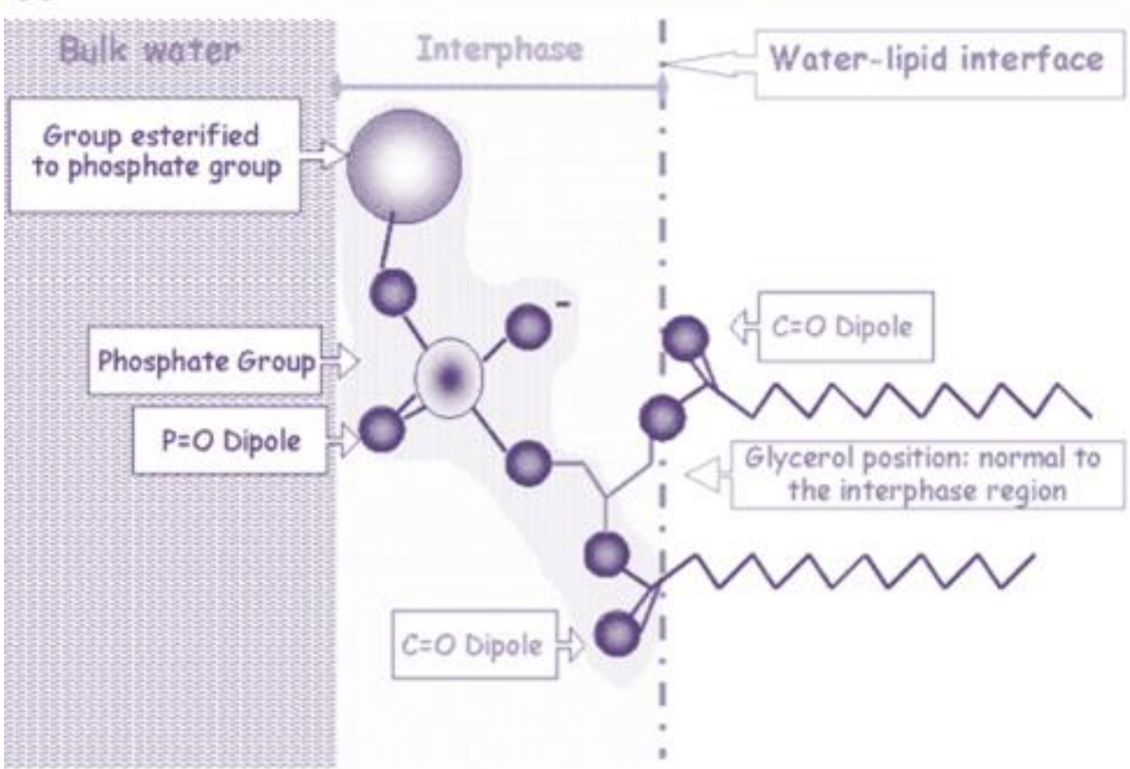
Water layers adjacent to lipid bilayer are 1 nm thickness with 20 water molecules per lipid .

Excluded volume for polar solutes. Exclusion zone

WATER INTERPHASE

NOT INTERFACIAL WATER





PURPOSES

To show

ELECTRICAL

THERMO DYNAMICAL

STRUCTURAL PROPERTIES

of water interphases in relation to:

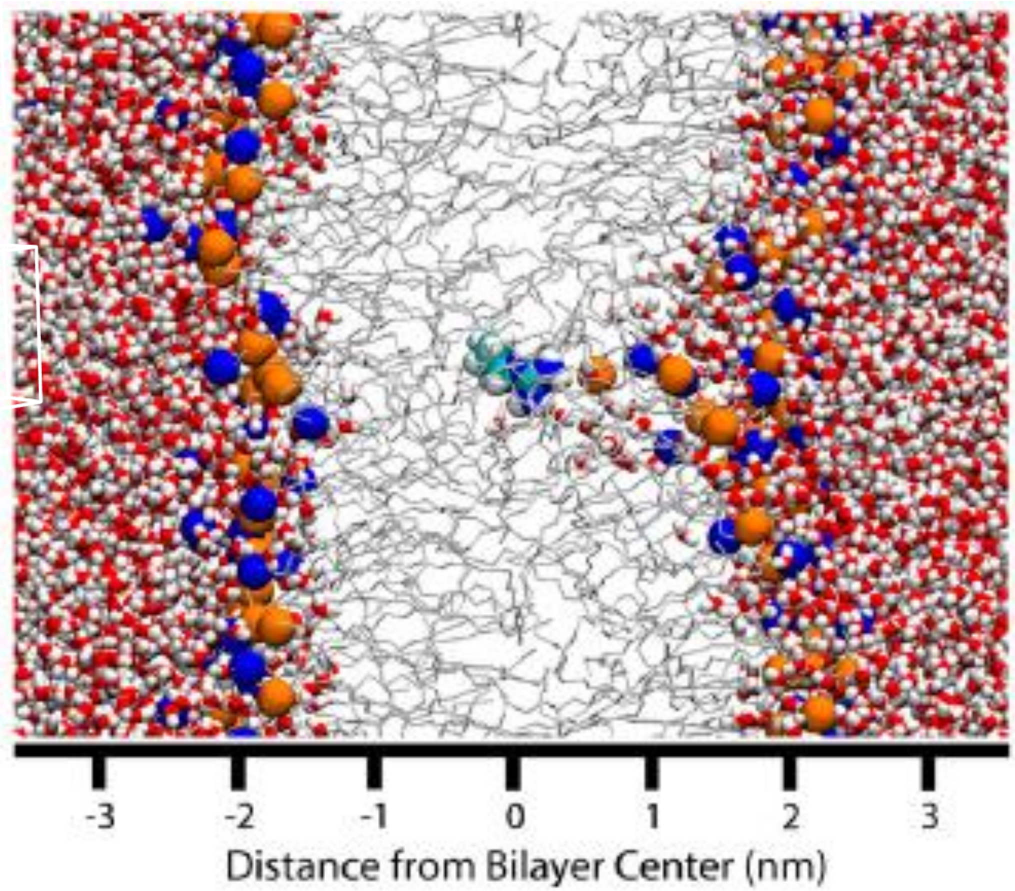
Stability and reactivity of enzymes → ***Insertion of signal peptides*** → ***Regulation*** → ***Information***

PRESENT CHALLENGES

Toxin and signal peptides with polar and positive aminoacids enter the bilayer

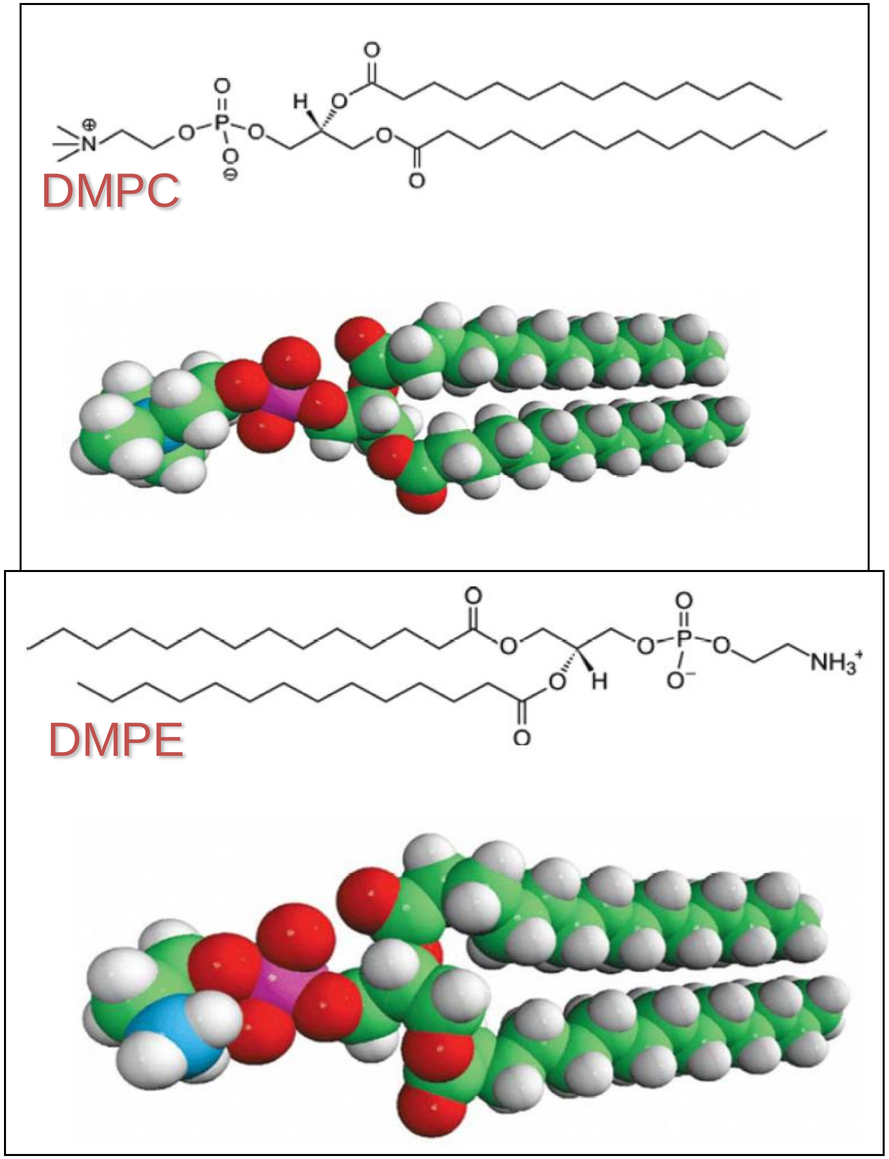
The dielectric slab is hypothesis not consistent

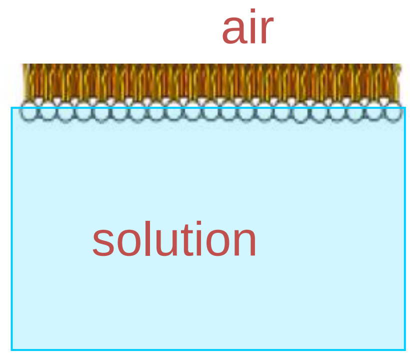
Water inside the membrane

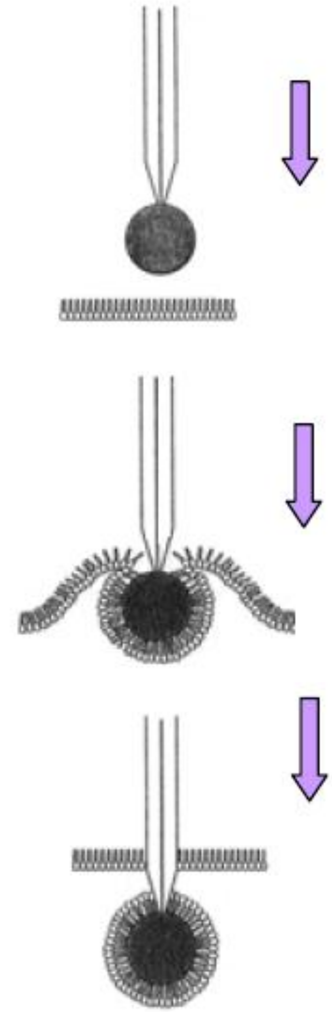


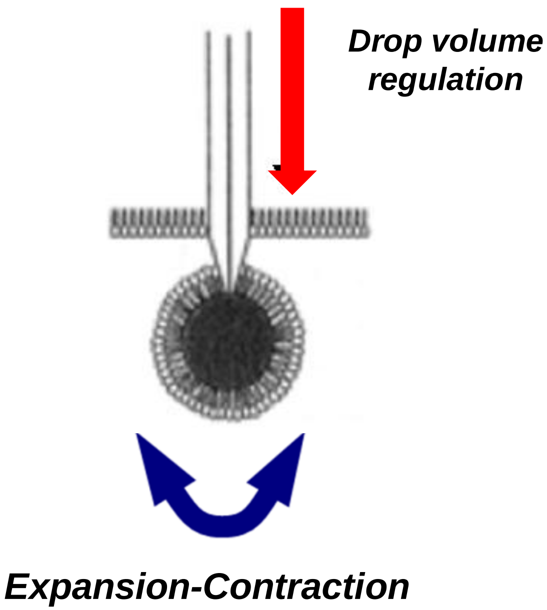
ELECTRICAL PROPERTIES

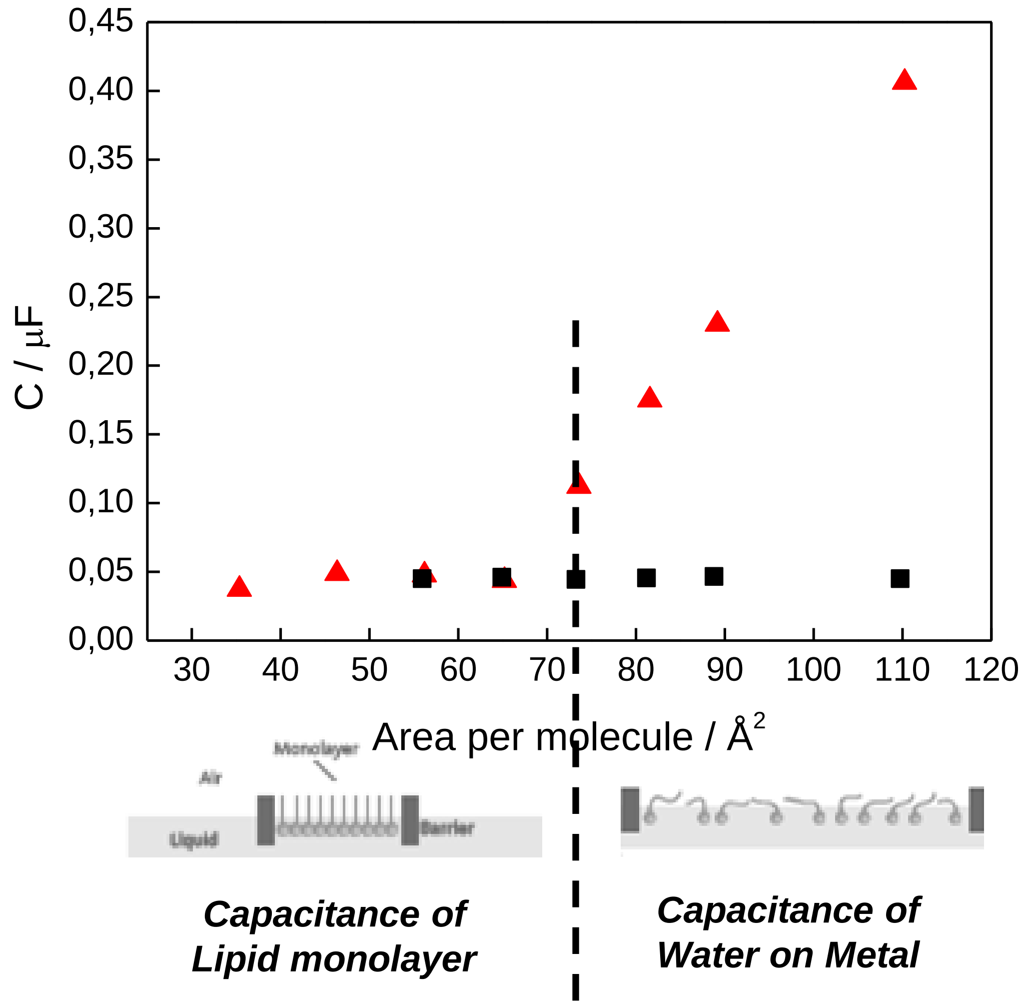
LIPID ORGANIZED AS MONOLAYER AT AIR WATER INTERFACE









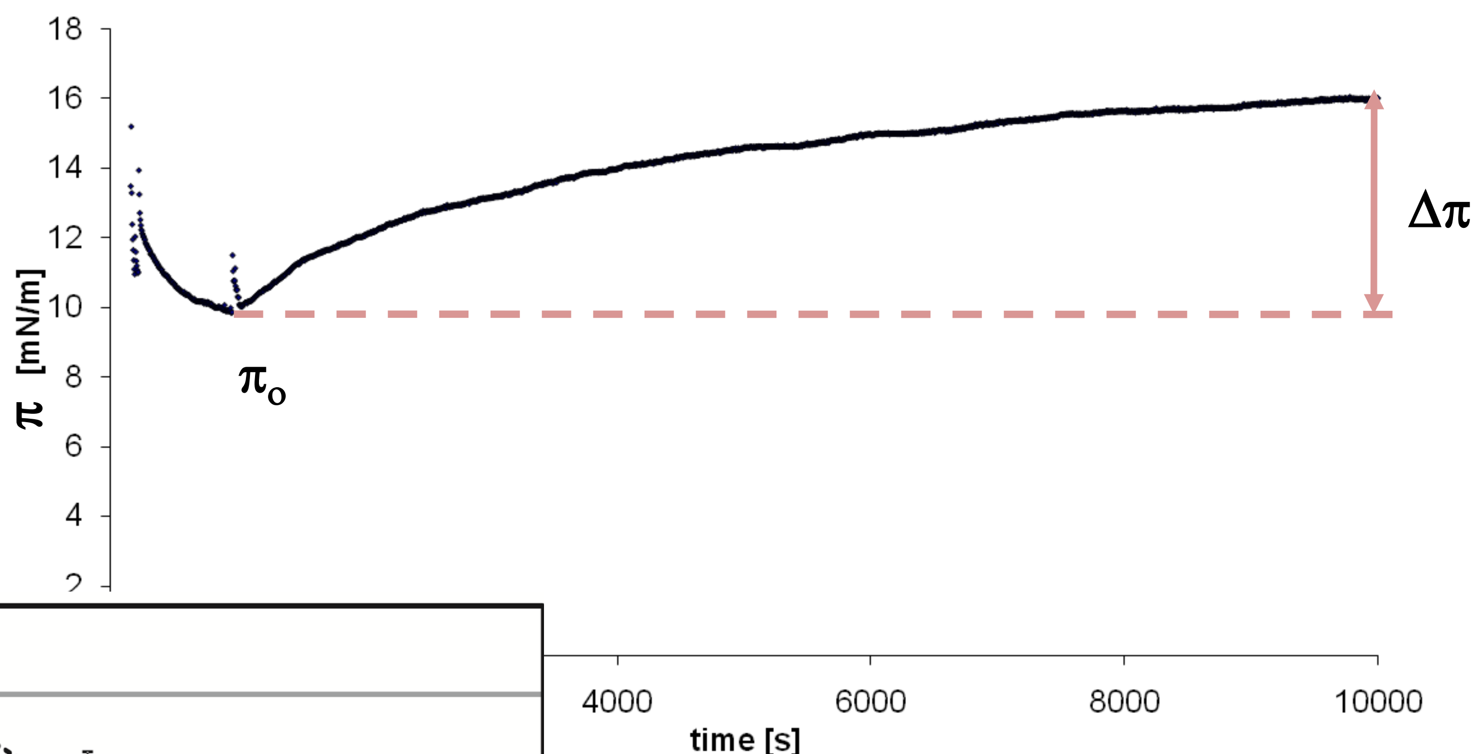


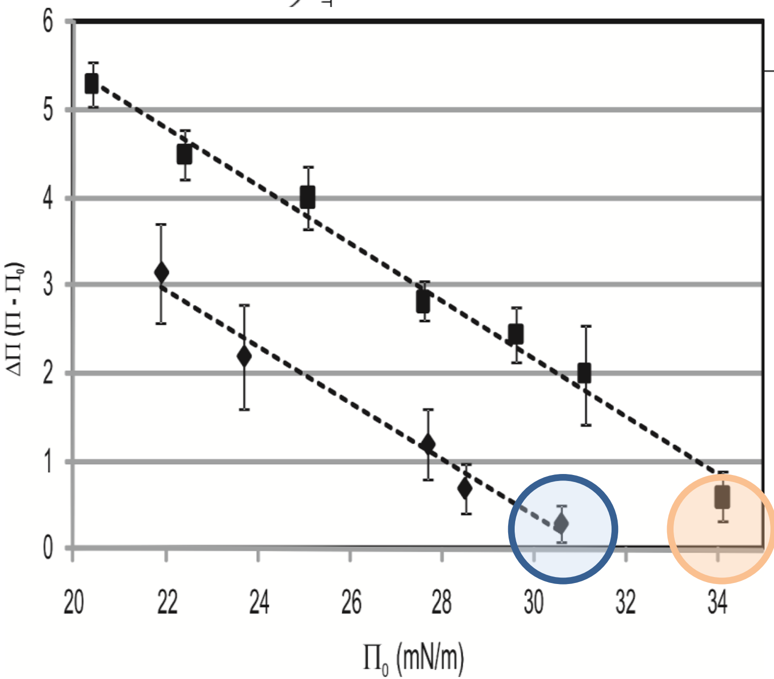
4% increase of the area

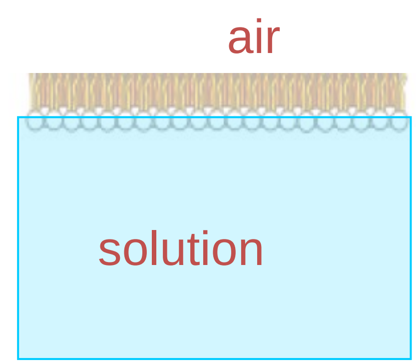
THERMODYNAMIC PROPERTIES

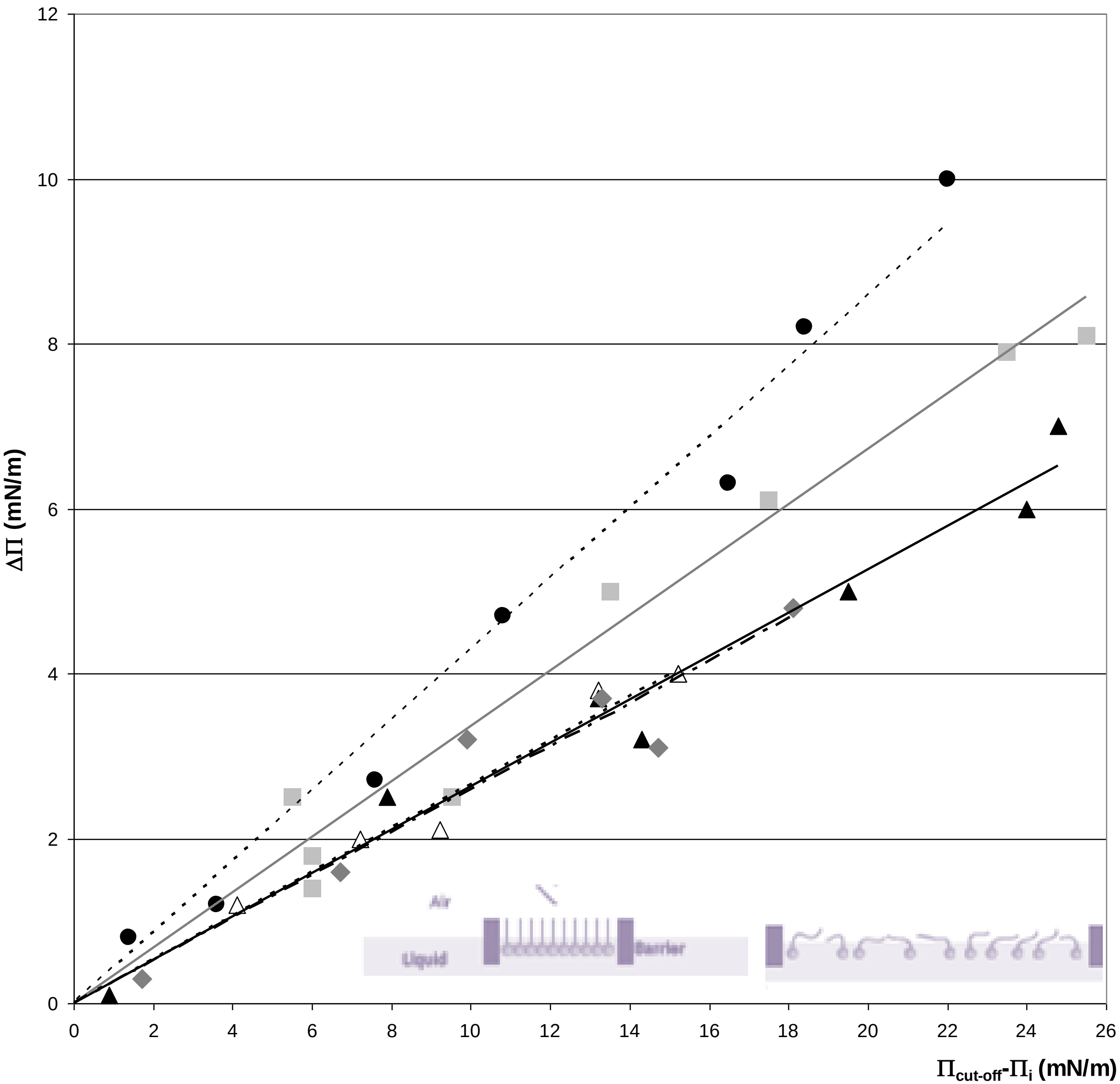
Surface free energy = surface tension changes

INSERTION OF AQUEOUS PROTEINS INTO LIPID MONOLAYERS



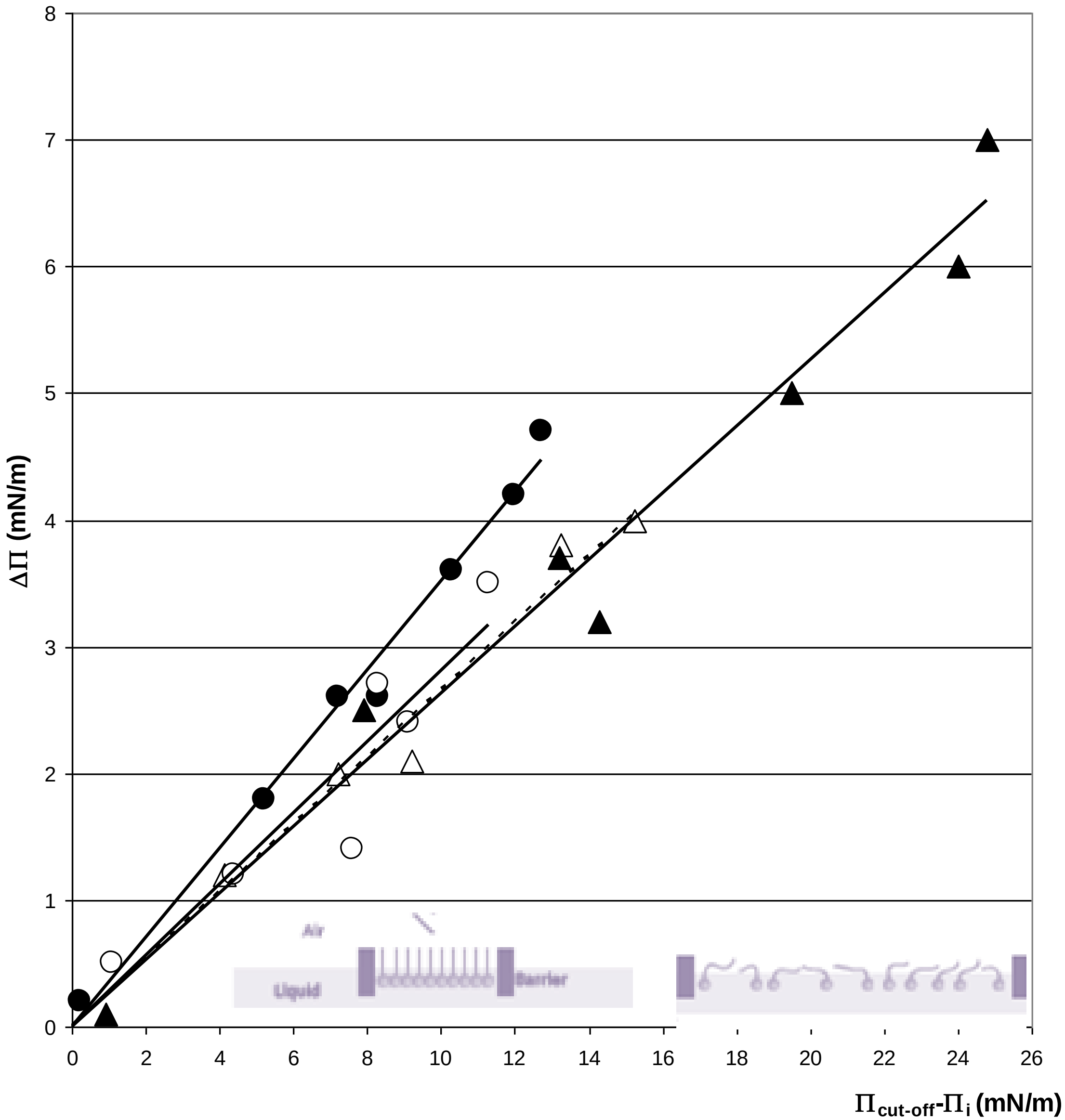






Lipid	*m*	*Cut-off*
DMPC	0.263	41.5
DPPC	0.259	39.5
DOPC	0.336	41.5
DPhPC	0.429	39.6
DMPE	0.266	30.8

DECREASE IN SURFACE PRESSURE Π_c - Π

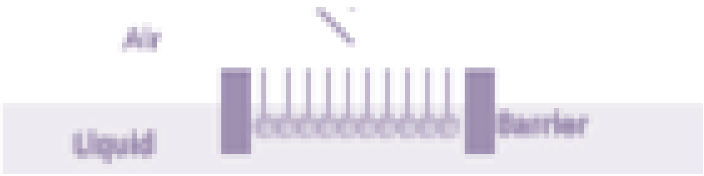


Lipid	*m*	*Cut-off*
DMPC	0.263	41.5
DMPE	0.266	30.8
D(Ether)PC	0.352	31.8
D(Ether)PE	0.280	29.4

DECREASE IN SURFACE PRESSURE Π_c - Π

DECREASE IN SURFACE PRESSURE $P_c - P$

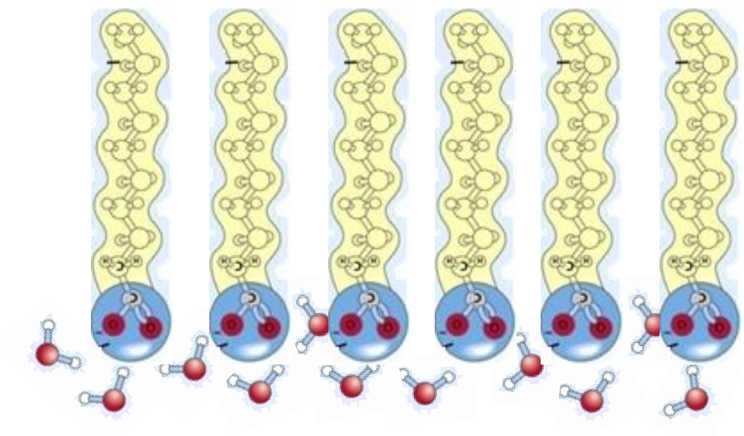
is related to the increase of water beyond **the hydration water (confined water)**

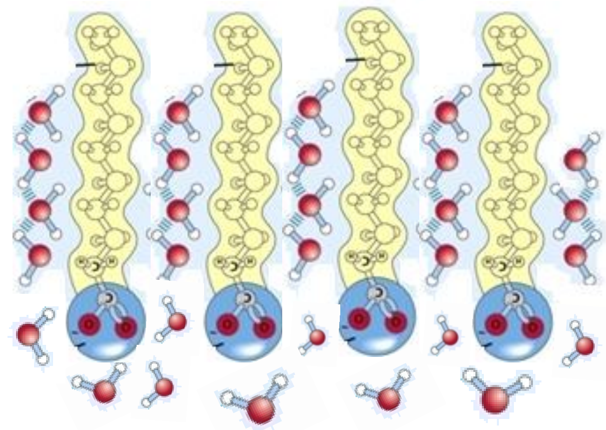


hydration water
(critical packing)

confined water

SURFACE PRESSURE PERTURBATION IS RELATED WITH WATER INTERPHASE ACTIVITY





$$\Pi = n_w \, RT \, \ln a_w$$

$$K = \ln\left(a_w | a_{wp}\right) / ln \, \left(a_c | a_{wc}\right)$$

Bidimensional Solution Of Hydrated Head Groups (Defay & Prigogine 1966; Evans & Skalak, 1978)

Pairs of membrane-protein or peptides

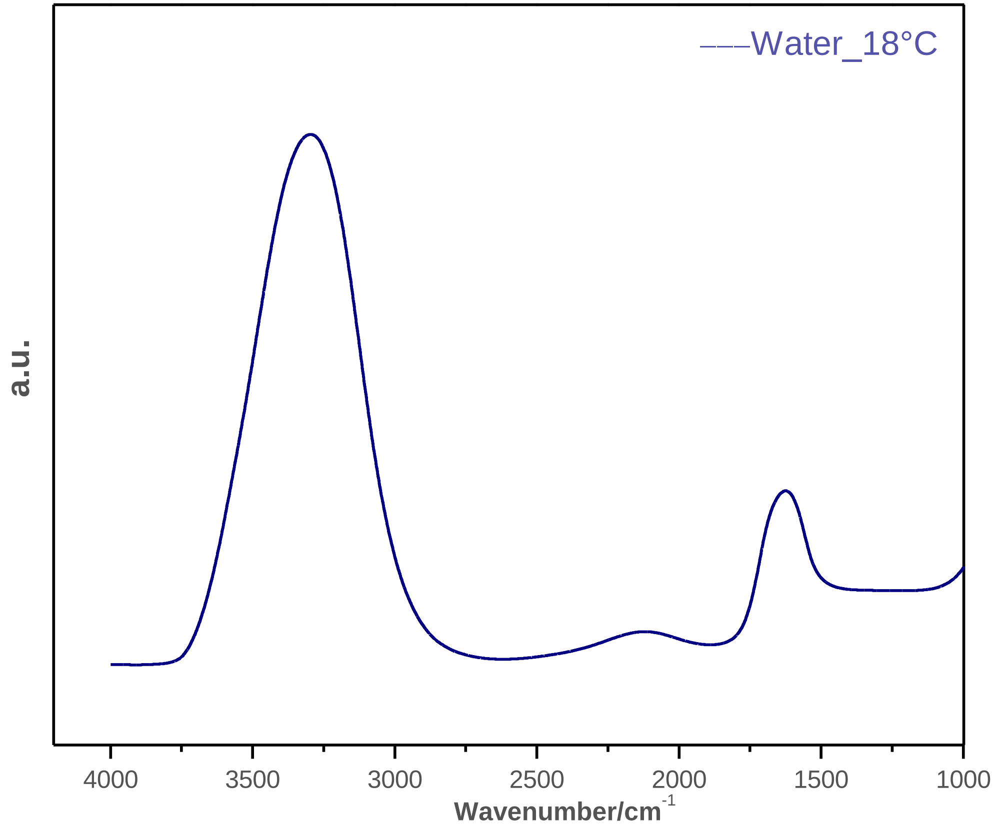
Membrane composition	K	Cut off	Protein
DMPC	0.264	41.5	Aqueous protease
DMPE	0.266	30.8	Aqueous protease
Di(ether)PC	0.351	31.8	Aqueous protease
Di(ether)PE	0.282	29.4	Aqueous protease
DPPC	0.259	39.5	Aqueous protease
DOPC	0.336	41.5	Aqueous protease
DPhPC	0.428	39.6	Aqueous protease
PC:SA (10:1)	0.685	35.18	Bacterial S-layer
PC:Chol:SA (10:2.5:1)	0.519	34.6	Bacterial S-layer
PC:Chol:SA (10:5:1)	0.328	36.64	Bacterial S-layer

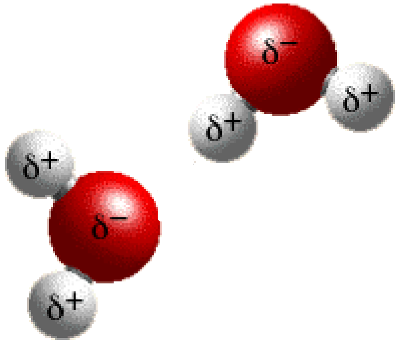
Water is the common intermediary in the interaction of different proteins, peptides or aminocids with lipid membranes

$$K = \ln\left(a_w | a_{wp}\right) / \ln\left(a_c | a_{wc}\right)$$

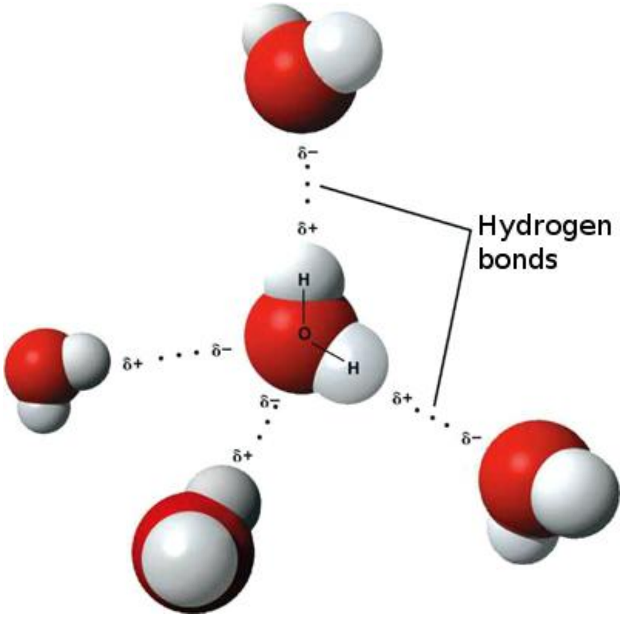
STRUCTURAL PROPERTIES OF WATER INTERPHASE

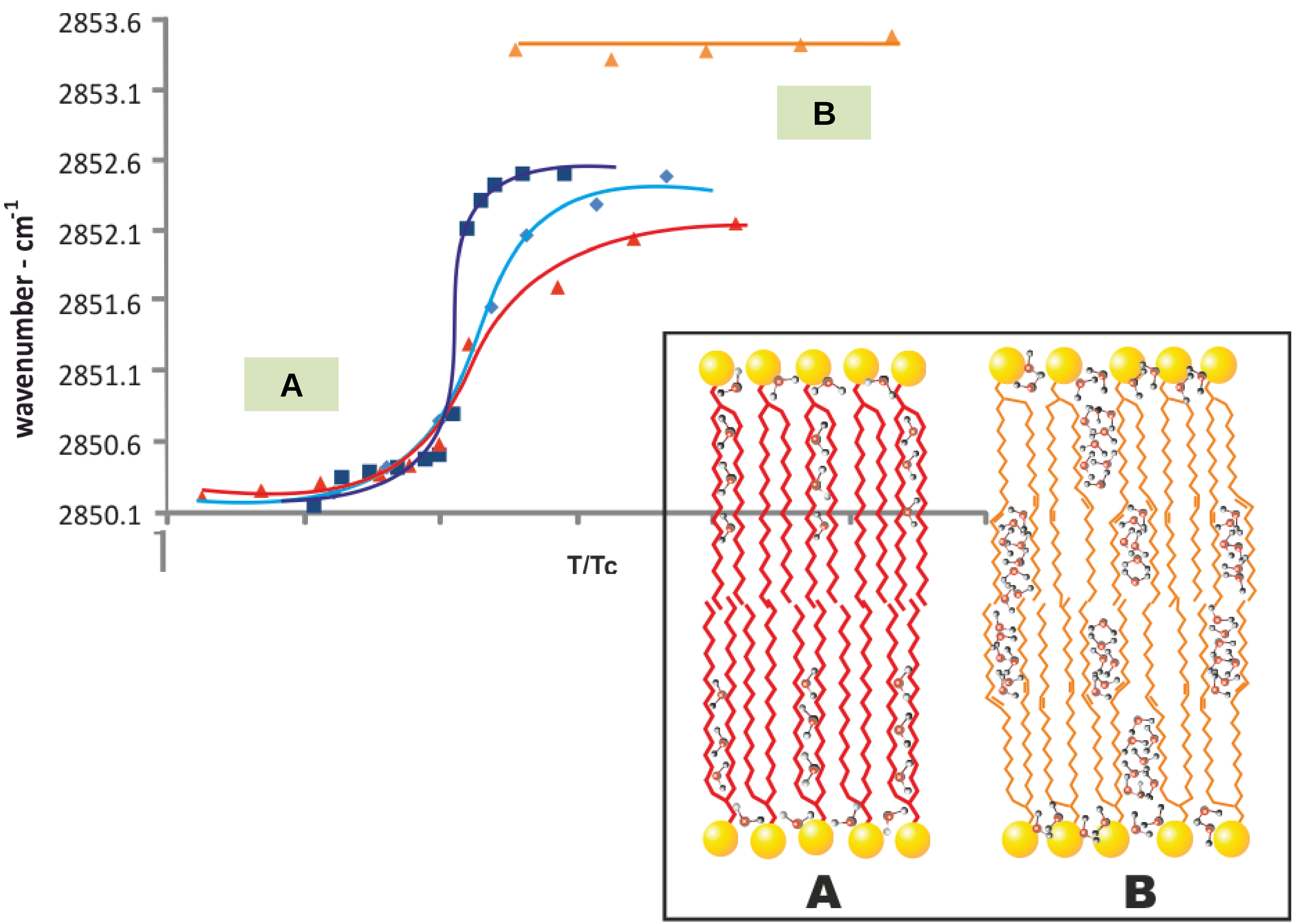
OH Stretching mode





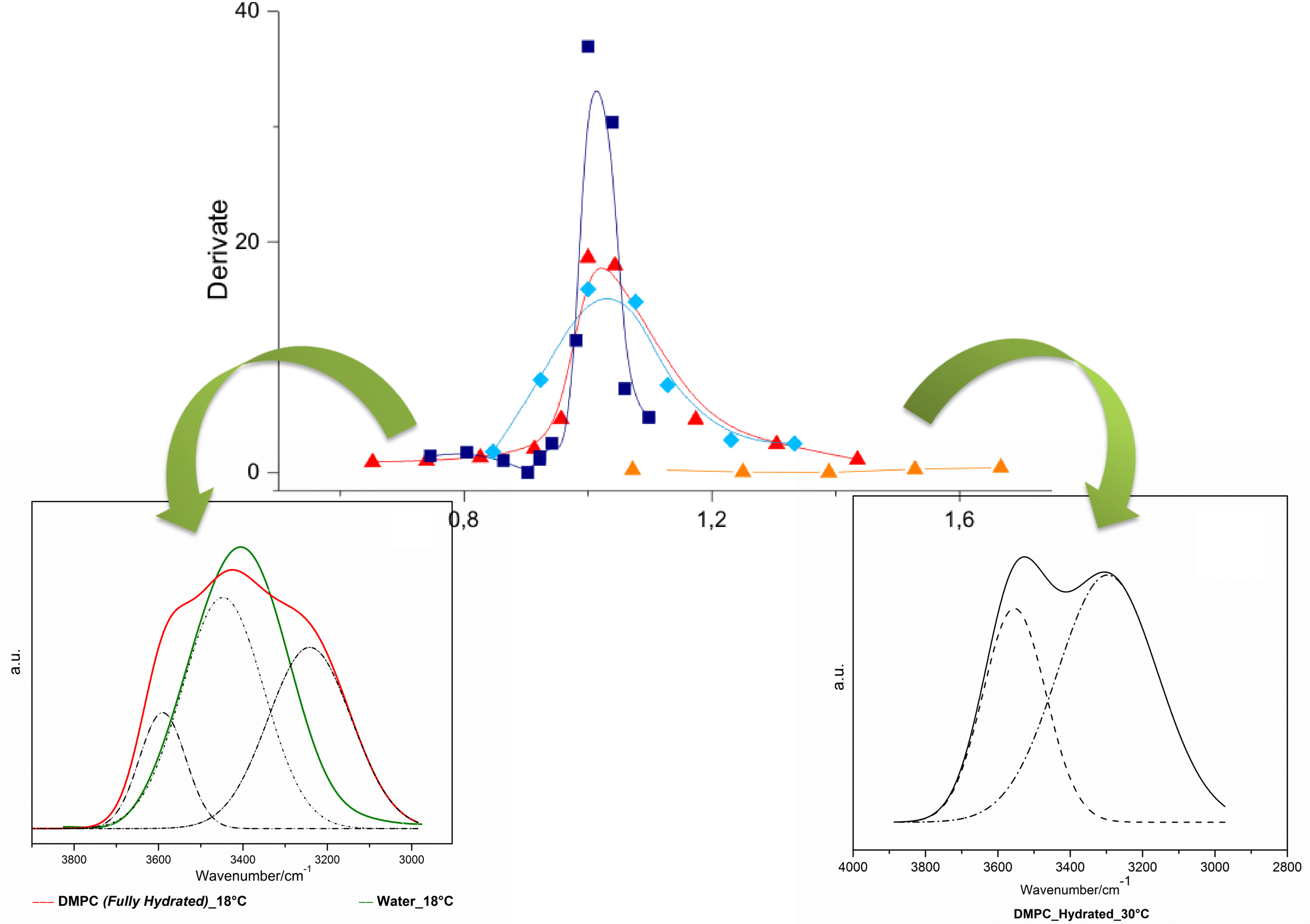
$$\nu = 1/2\Pi \sqrt{k / \mu}$$





2853.6
2853.1
2852.6
2852.1
2851.6
2851.1
2850.6
2850.1
wavenumber - cm-1
T/Tc
A
B
A
B

WATER STATE AROUND THE LIPID PHASE TRANSITION



CONCLUSION

- **Different water populations are found according to the lipid are in a condensed or expanded state.**

- **Confined water seems to appear in expanded lipid states**

Thermodynamic and structural link

$$\Pi = n_w RT \ln a_w$$

Defay & Prigogine 1966; Evans & Skalak (1978)

$$\Pi = n_w RT \ln g_w C_w$$

$$g_w = A + BT + CT^2 + \ldots\ldots\ldots$$

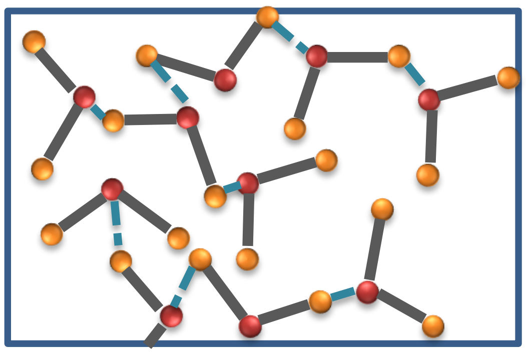
A = molecules without H-bond

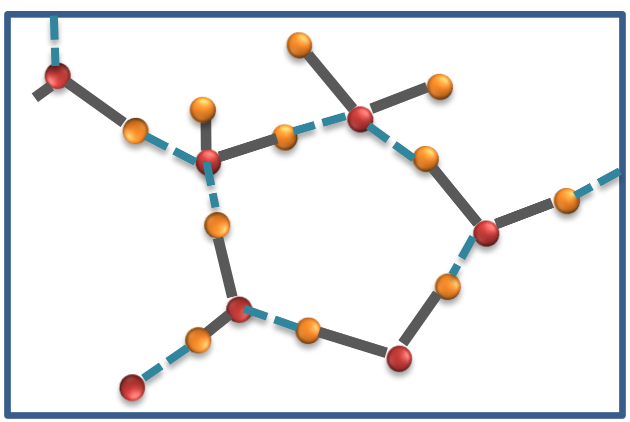
B = molecules with 1 H-bond

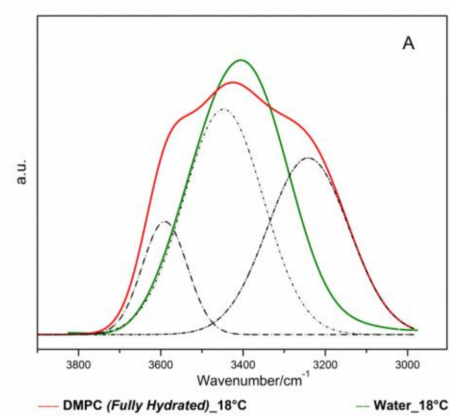
C = molecules with 2 H-bond

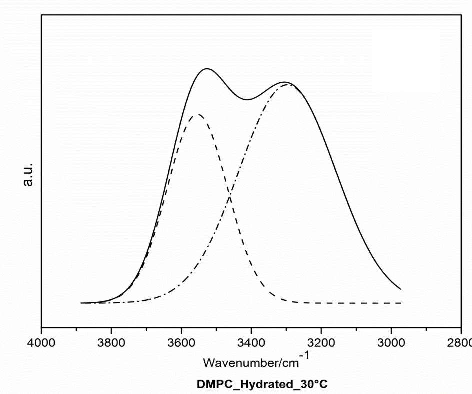
D = molecules with 3 H-bond

E = molecules with 4 H-bond

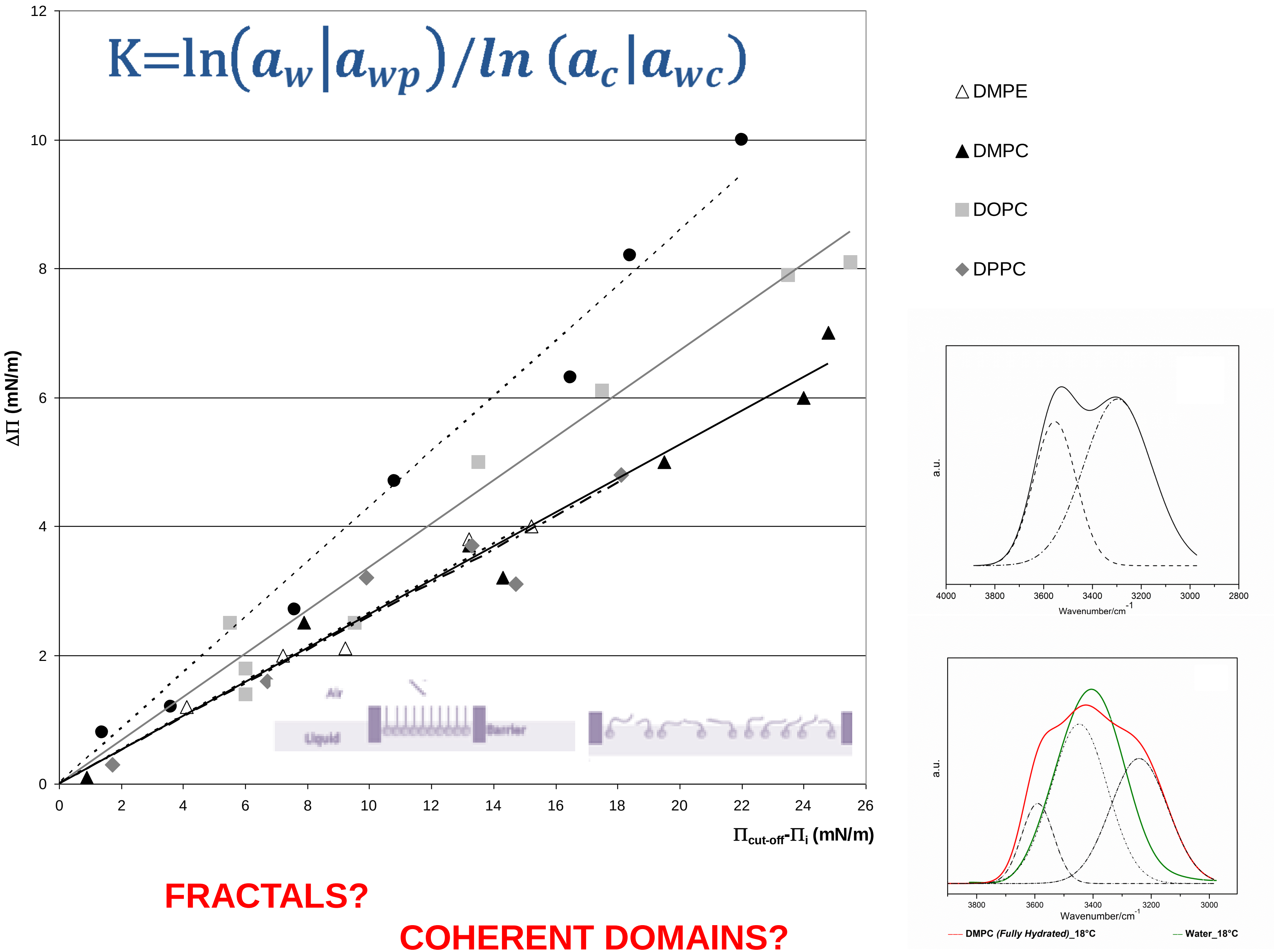








A variety of water populations



FRACTALS?

COHERENT DOMAINS?

Summary

- **Water domains of confined water appears beyond the hard core hydration shell of lipids.**

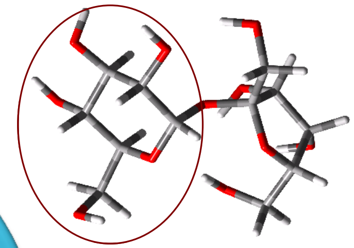
- **Confined water determines the surface free energy of lipid interphases.**

- **The thermodynamic activity of water confined in the interphase region is correlated with different water structural arrangements according to the lipid state.**

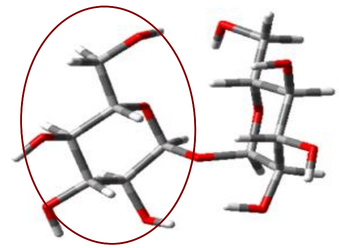
- **Confined water domains appear to be modified by lateral pressure.**

DYNAMICS

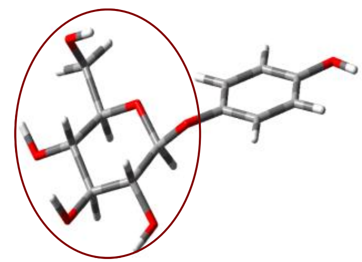
Water can be replaced by trehalose, glicerol,arbutin or sucrose to maintain biological structures in anhidrous state



Sucrose



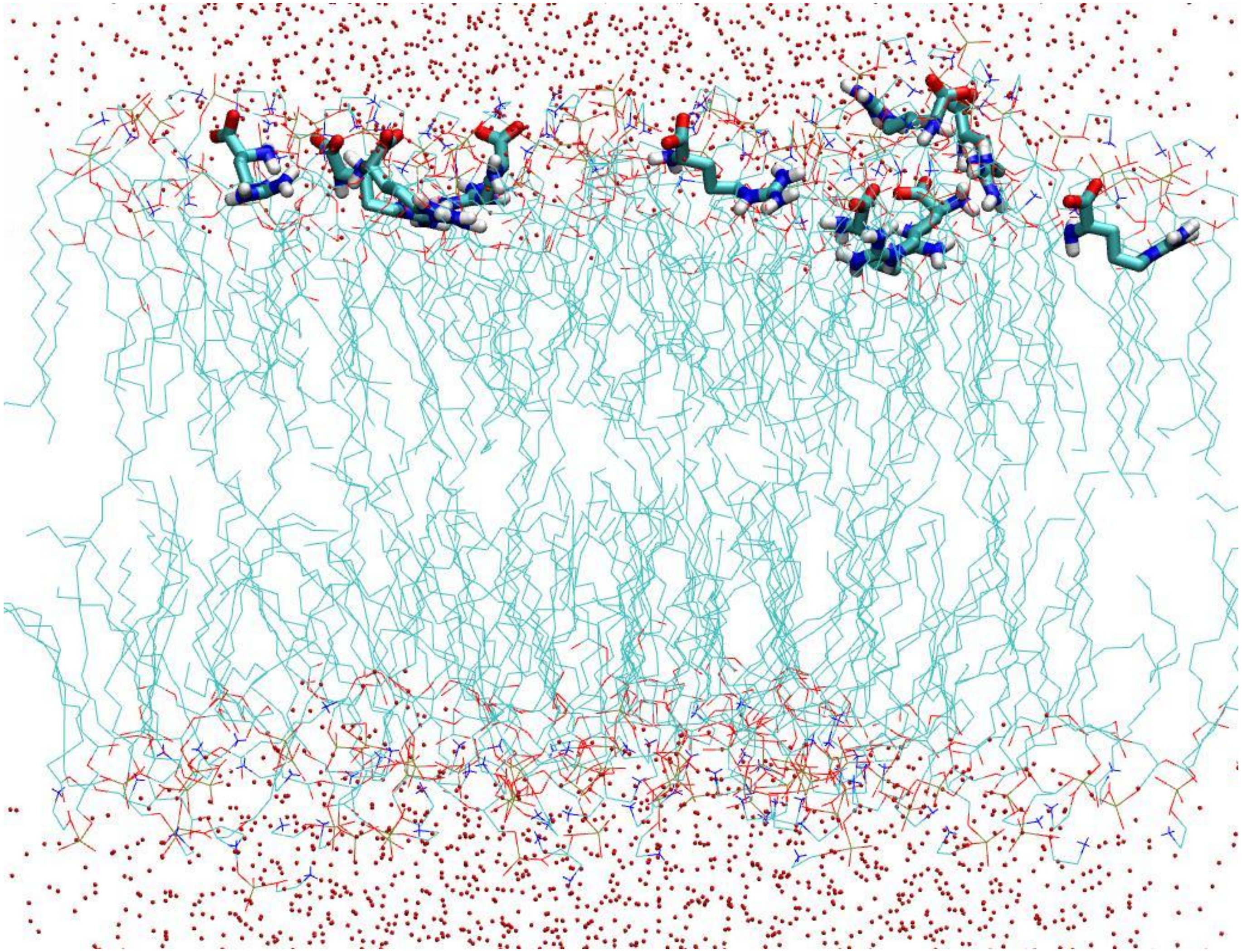
Trehalose



Arbutin

Water must be restored for function in order to provide confined water levels

ENZYME ACTIVITY INCREASES 40% IN RESTRICTED WATER DOMAINS (REVERSE MICELLES OR LIPID INTERPHASES)



Enzymes activities is sensitive to the different water qualities in the different lipid membranes.

LIPID- WATER RATIO IN DIFFERENT LIPID ENSAMBLES OF DMPC AND DMPE

	Water per lipid at the break of Bragg spacing (64)	Water per lipid in monolayers(50, 52)	Water per lipid in micelles(65)	Water at phosphate (FTIR) (66, 67)
DMPC	12	11	12-14	6
DMPE	ND	9	4	ND

[50] F. Lairion, E.A. Disalvo, Langmuir 20 (2004) 9151–9155.
[52] F. Lairion, E.A. Disalvo, Chem. Phys. Lipids 150 (2) (2007) 117–124.

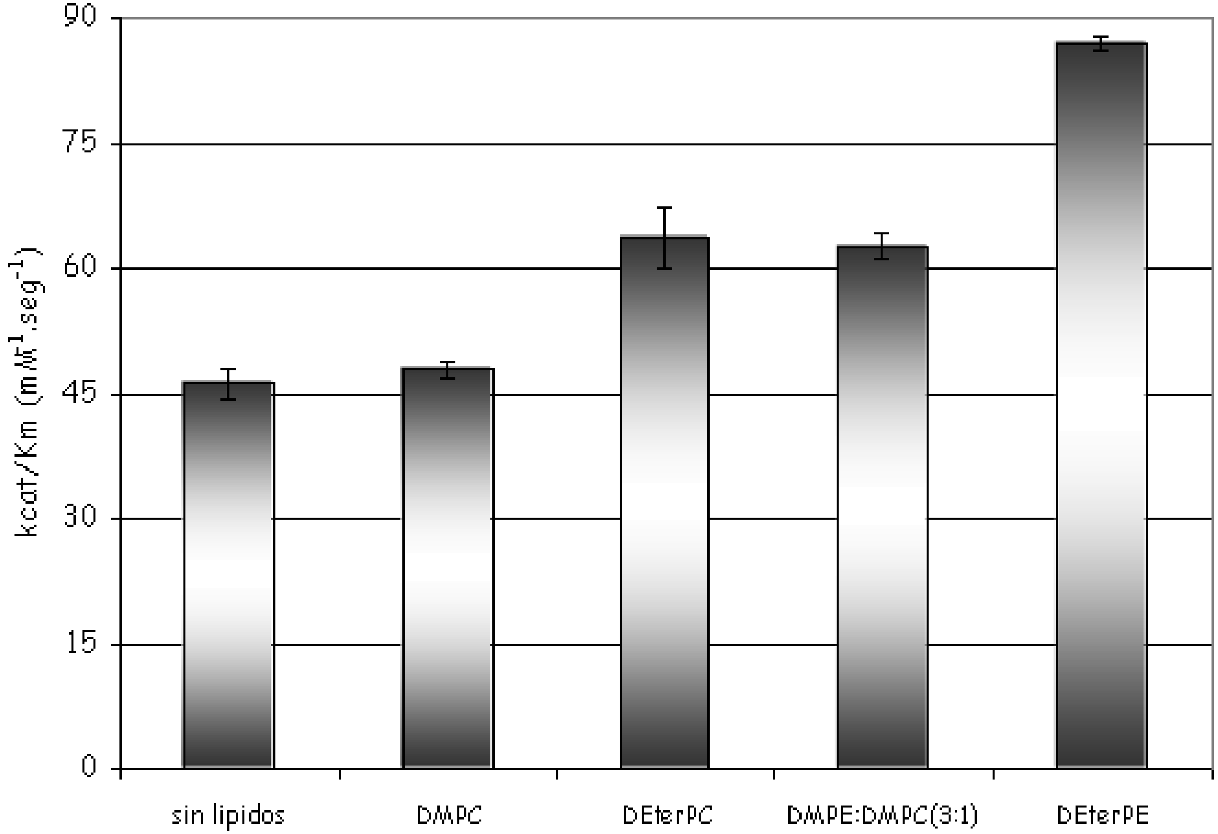
[64] R.J. Mashl, H.L. Scott, S. Subramaniam, E.r.i.c. Jakobsson, Biophys. J. 81 (2001) 3005–3015.
[65] F. Lairion, R. Filler, E.A. Disalvo, Colloids Surf. B Biointerfaces 25 (4) (2002) 369–371.

[66] J.L. Arrondo, F.M. Goñi, J.M. Macarulla, Biochim. Biophys. Acta 794 (1) (1984) 165–168.
[67] F.M. Goñi, J.L. Arrondo, Faraday Discuss. Chem. Soc. 81 (1986) 117–126.

CATALYTIC EFFICIENCY PARAMETER [K_{CAT}/K_M ($mM^{-1}.seg^{-1}$)]

OF PROTEOLITIC ACTIVITY OF RENNET FROM *MUCOR MIEHEI*

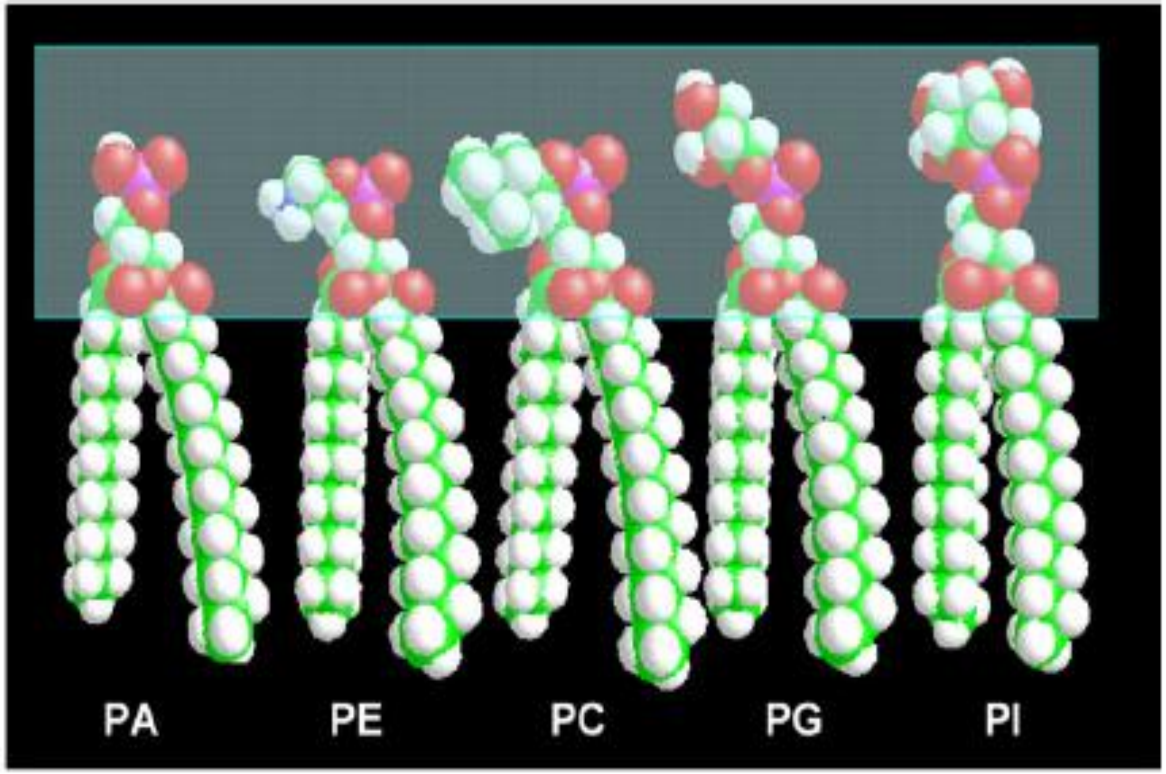
ADSORBED TO DIFFERENT LIPID INTERPHASE.



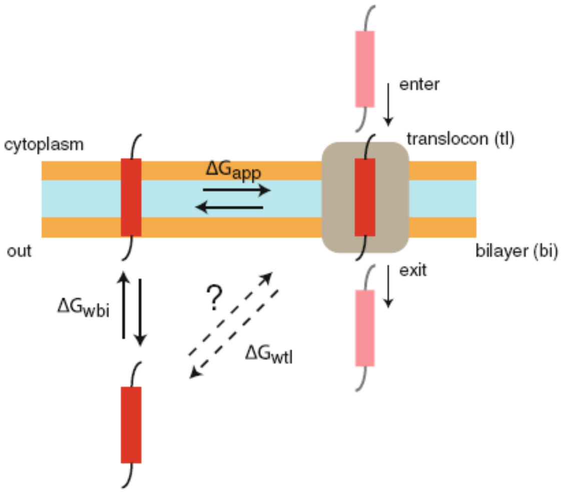
INFORMATION

Genomics ===➔Lipidomics =➔ aquaomics

Adapted from R. Tsenkova

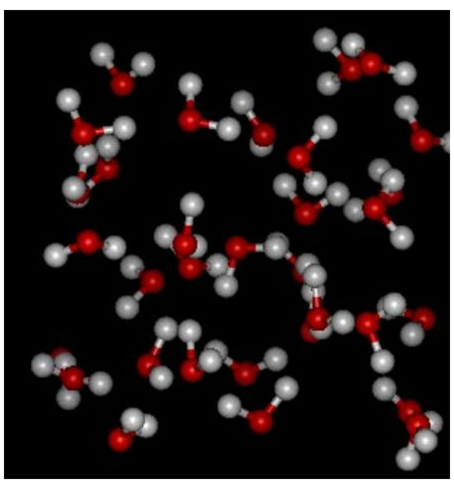


SPECULATIONS



Translocons

(based on geometrical criteria)



Waterons

(based on changes in the multiple water populations in the lipid interphase with different free energy content)

EXPERIMENTS IN PROCESS

See you in 2013

MUCHAS GRACIAS-THANK YOU!