Properties of an Organic-Inorganic Langmuir Monolayer and *in-situ* Investigation of its Induced Decomposition

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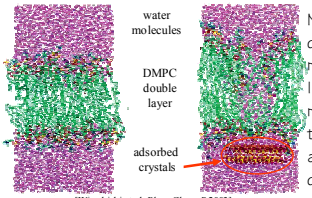
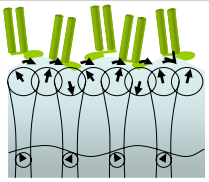
Introduction

Langmuir monolayers at the air water interface are exposed to lateral and normal fluctuations of the liquid subphase disturbing the ordering of the surfactant molecules. Complex fluids like hydrosols exhibit tunable physical properties which offer possibilities to damp surface fluctuations and manipulate the self-assembly process of amphiphilic molecules at the surface. The coupling of inorganic clay nano-particles with bio-molecules result in new hybrid monolayers with strongly altered thermodynamic and structural properties.



[Wierzbicki et al. *Phys. Chem. B* 2003]

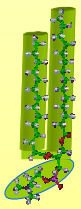
Molecular Dynamic simulations suggest, that charged crystal surfaces also play an important role in membranolysis (the rupture of cellular membranes): the lipid layer in contact with the crystal reveal reduced mobility of individual molecules leading to a separation of the bilayer. This process is believed to be important for arthritic cellular diseases like gout where the charged crystals are uric acid crystals.



scientific interest

- investigation of thermodynamic and structural properties of organic-inorganic hybridlayer
- crystal surface charge induced nucleation processes
- induced decomposition of the compound layer

The System



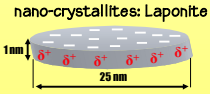
DMPC
the prevailing phospholipid in human celluar-membranes

hydrophobic chains (C_{14}) ≈17.5Å long

hydrophilic headgroup (~8Å) zwitteronic with positive charge in the tip

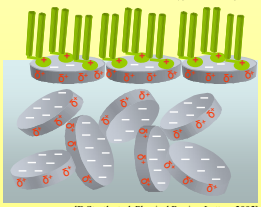
DPPC: same structure with C_{16} alkane chains

nano-crystallites: Laponite



synthetic clay with surface charge deficit

self-assembled hybrid layer

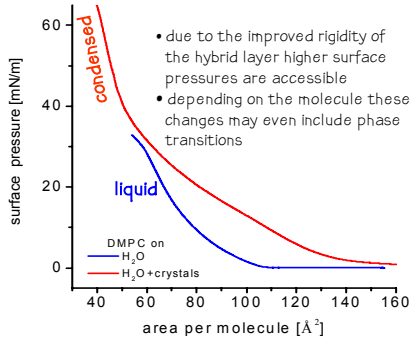


[B.Struth et al, Physical Review Letters *2002*]

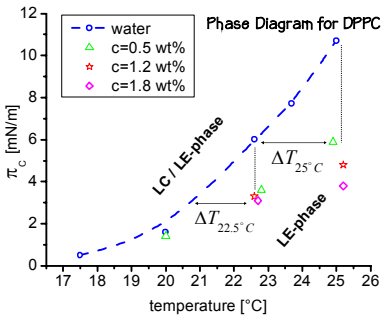
electrostatic interaction →
- adsorbed mineral monolayer
- formation of a bulk network

Thermodynamic properties

results from Langmuir pressure /area isotherms

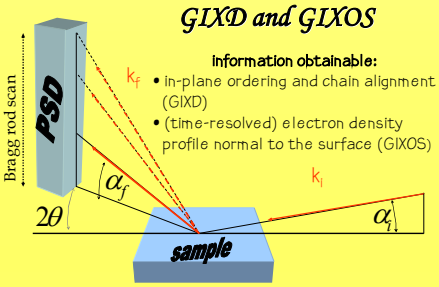


- due to the improved rigidity of the hybrid layer higher surface pressures are accessible
- depending on the molecule these changes may even include phase transitions

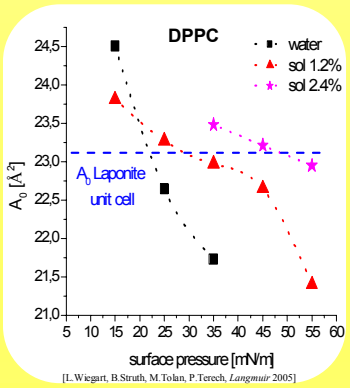


shifts in the phase diagram are similar to a temperature reduction → 'virtual cooling'

Surface Sensitive X-ray Scattering: GIXD and GIXOS

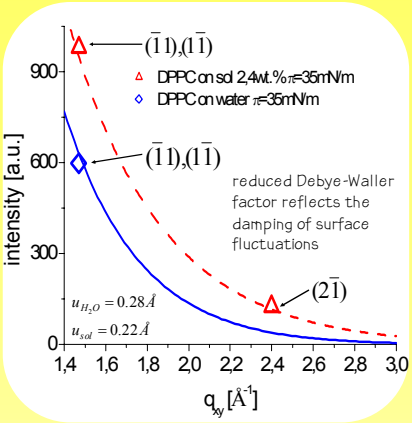


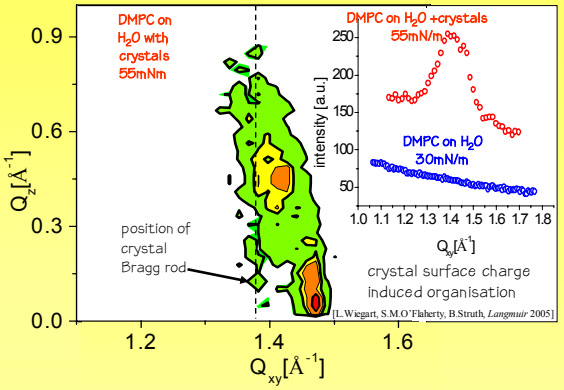
information obtainable:
- in-plane ordering and chain alignment (GIXD)
- (time-resolved) electron density profile normal to the surface (GIXOS)



[L.Wiegart, B.Struth, M.Tolan, P.Terech, *Langmuir* 2005]

The area requirement adapt to the crystal templates.
The external force (surface pressure) needed to overcome this mapping depends on the strength of the bulk network which increases with the clay concentration.

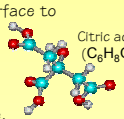




[L.Wiegart, S.M.O'Flaherty, B.Struth, *Langmuir* 2005]

Induced decomposition

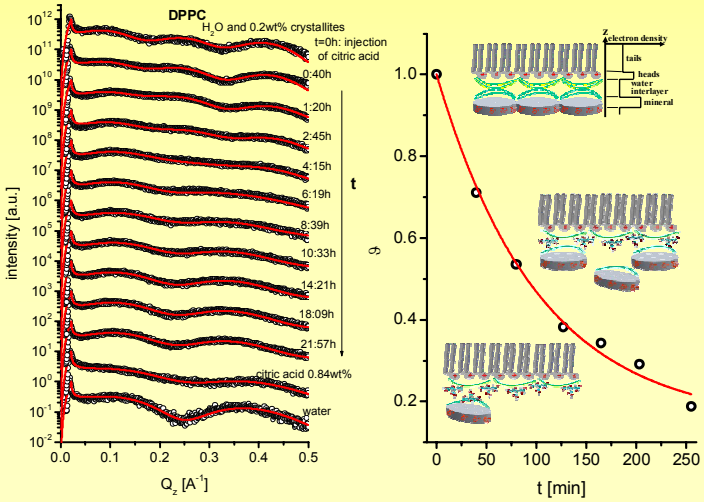
Idea: screen the charges between the lipid headgroups and the crystal surface to remove the crystal layer.
A small and negatively charged molecule like citric acid can substitute the nano-crystals at the membrane.



The desorption process is monitored in-situ via the electron density profile. The newly developed GIXOS technique (~30s instead of ~1.5h for conventional XSR) allows for the investigation of the related kinetics.
The interface coverage ϑ with crystallites has been fitted to a Langmuir model:

$$\vartheta(t) = \left[\frac{k_a c}{k_a c + k_d} + \left(1 - \frac{k_a c}{k_a c + k_d}\right) e^{-(k_a c + k_d)t}\right]$$

leading to k_a=0.72 cm³ min⁻¹ g⁻¹ and k_d=0.00144 min⁻¹



Conclusions

- the surface charge of the crystallites act as anchors for the zwitterionic headgroups of the surfactant
- the crystals function as templates for the self-assembling process of the membranes
- the improved rigidity of the hybridlayer and the accompanied damping of fluctations is refleted both in the thermodybamic and structural properties
- first direct observation of the crystal induced demobilisation of the lipids in a membrane
- the compound layer can be decomposed by screening the electrostatic interaction e.g. by the injection of citric acid
- the new developed GIXOS technique allows for the investigation of the kinetics of the induced desorption

Outlook

Direct investigation of the dynamic of the hybrid layer by means of X-ray Photon Correlation Spectroscopy (XPCS)