# Liquid Surface Scattering at ILL

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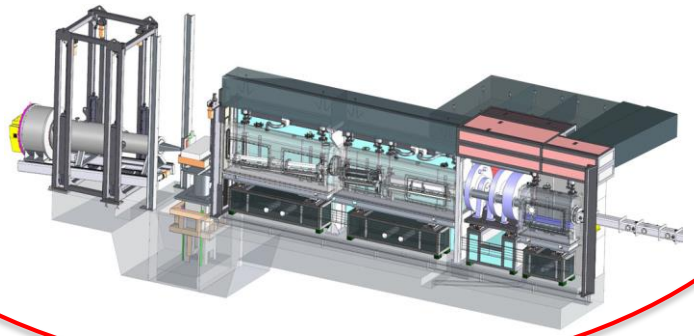
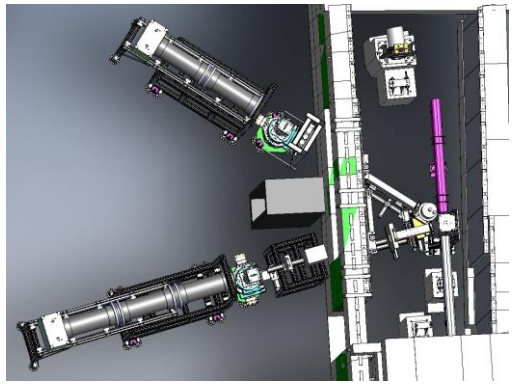
# Liquid Surface Scattering machines at ILL

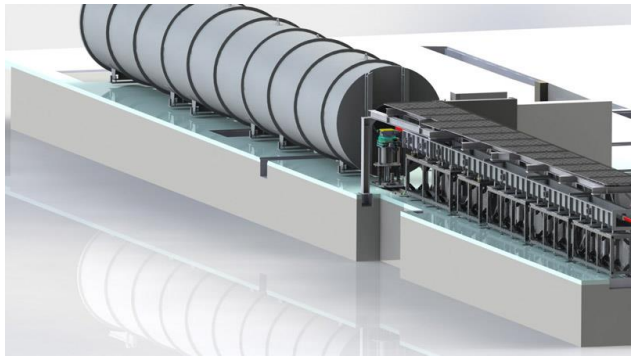
FIGARO
(horizontal reflectometer):



Super-ADAM
(vertical monochromatic Reflectometer
with horizontal Pseudo-GISANS option):

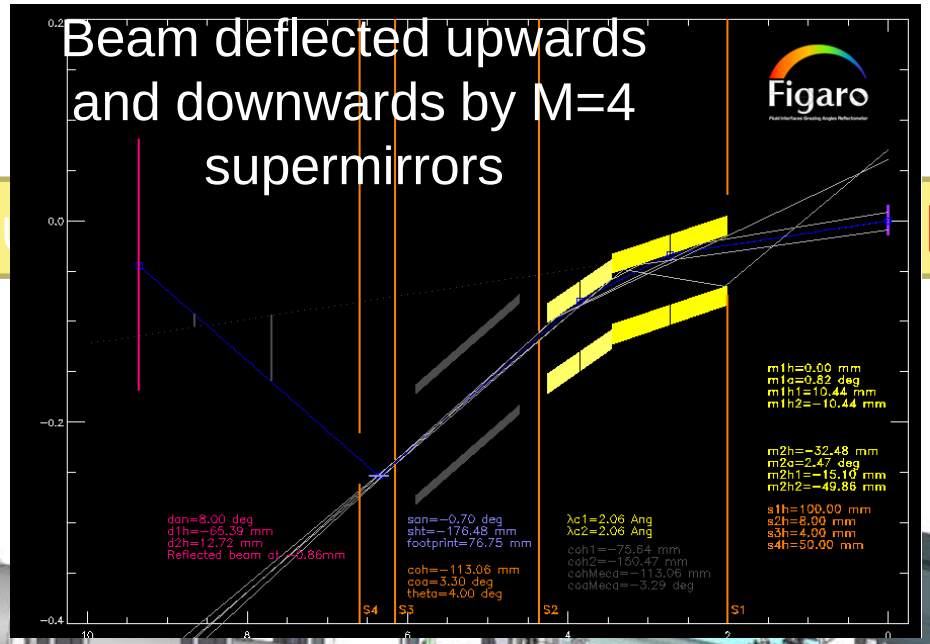


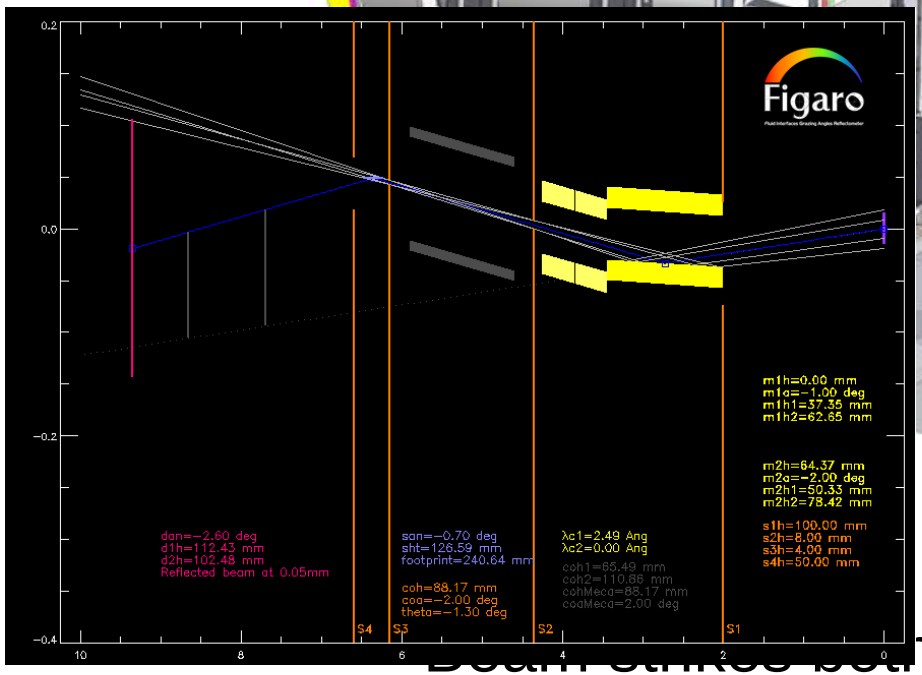
D22
(SANS machine
with GISANS option):

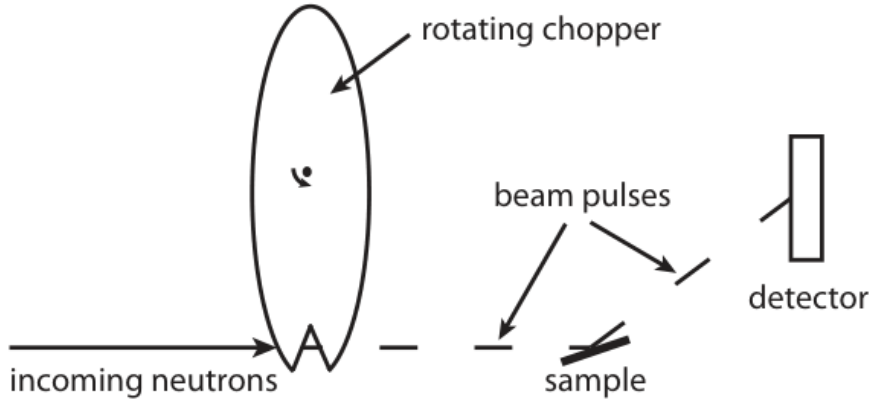


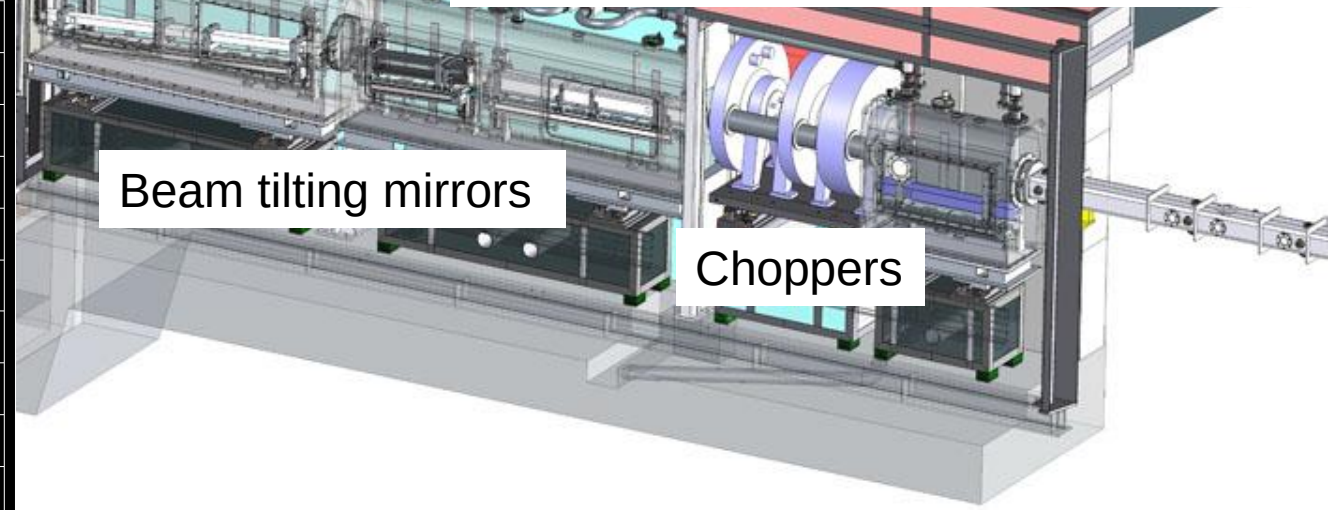
Figaro
Fluid Interfaces Grazing Angles Reflectometer

Beam deflected upwards and downwards by M=4 supermirrors



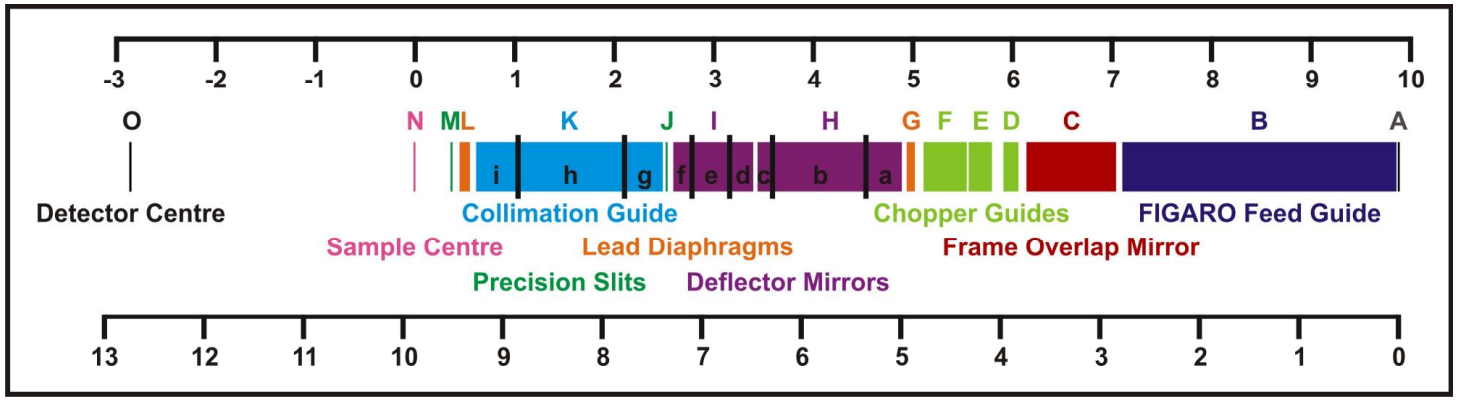



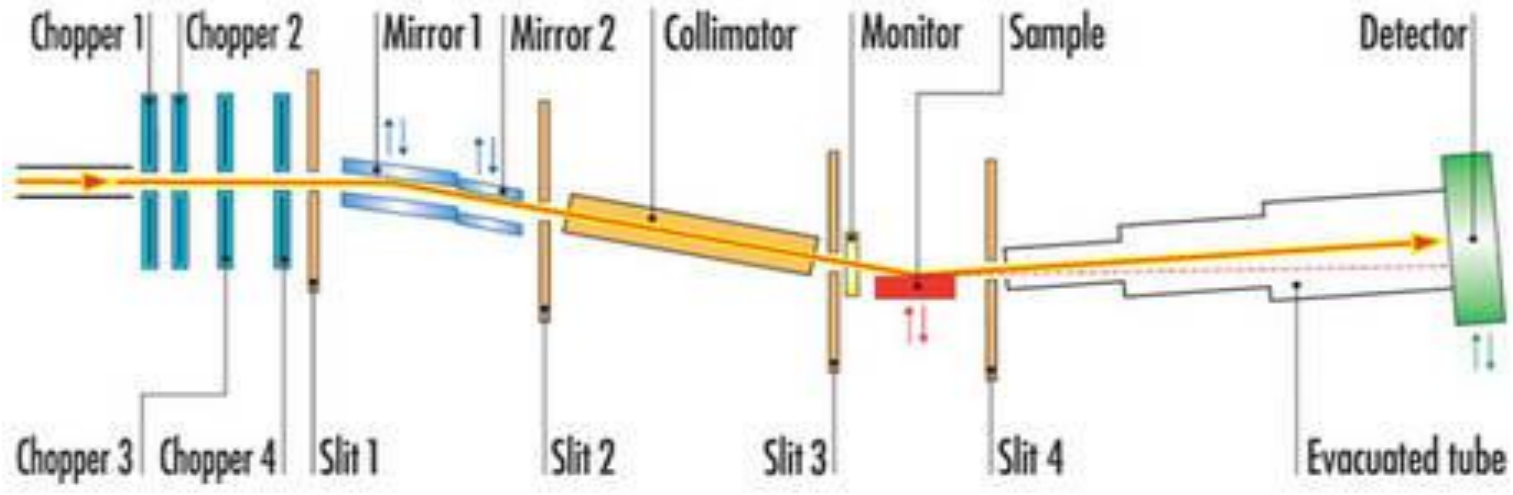

Campbell, R. *et al.* Eur. Phys. J. Plus, (2011) **126**, 107.

Beam strikes both sides of interfaces

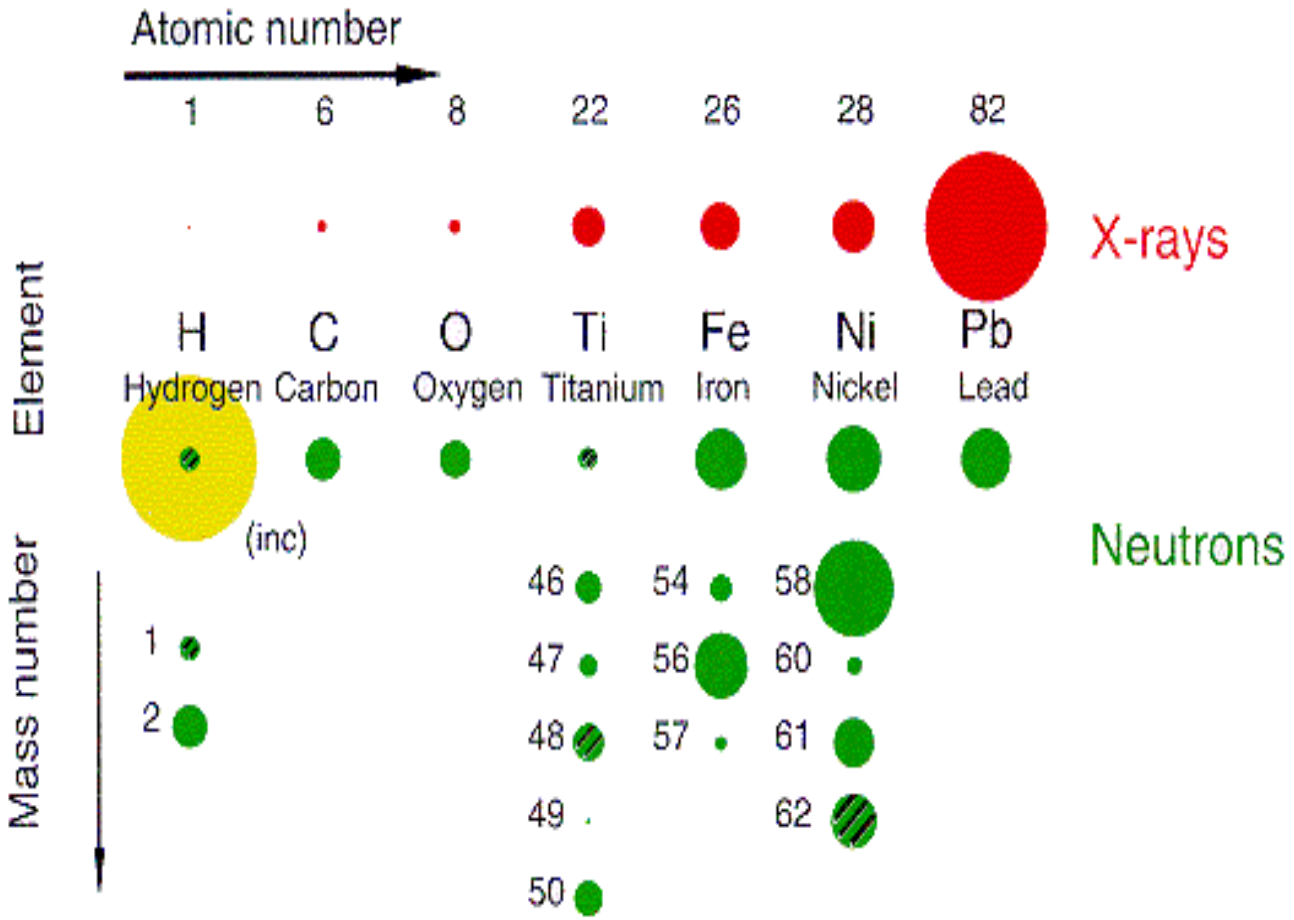
# FIGARO

Typical incoming beam divergence (5 m collimation) (v x h) FWHM: 0.005°- 0.1° x 0.05 - 0.1°
Detector resolution at 2.8 m (v x h) FWHM: 0.045° x 0.09°



# Scattering cross sections for neutrons and X-rays




The diameters of the circles shown scale with the scattering amplitude $f_x$ ($\sin\Theta = 0$) for x-rays, and $b_{coh}$ * 10 for neutrons. Hatching indicates negative scattering amplitudes.

- Origins of scattering differ for the different methods.
- X-rays dominated by number of electrons.
- Neutrons rely on contrast of nucleus: similar for many different elements, but show strong variations from different isotopes of same element, especially hydrogen.
- Absorption cross-section orders of magnitude lower than scattering cross-section for neutrons in most materials.

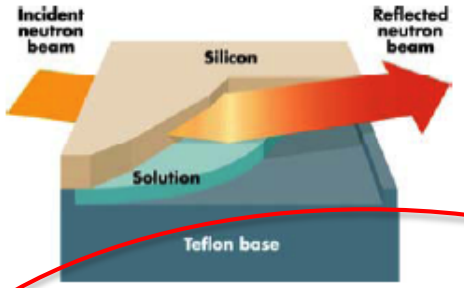
# Applications of Neutron Reflectometry

## Kinetics

- Polymer Diffusion
- Critical exponents in SCF
- Protein unfolding
- Non equilibrium surfactant films
- Temporal resolution of
  - Ion transfers
  - Solvent transfers
  - Polymer structure

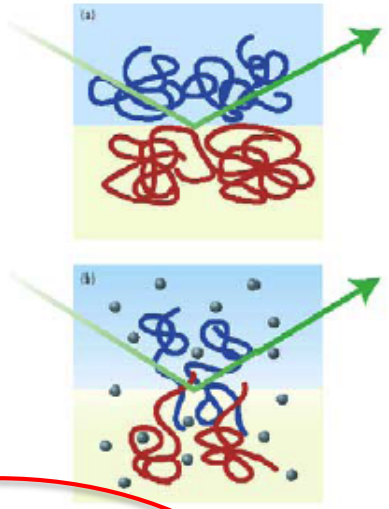
## Electrochemistry

- Electrodeposition and Surface nucleation
- Self Assembly of systems
  - Metal Hydroxide electroprecipitation (batteries)
  - Novel templating mechanisms



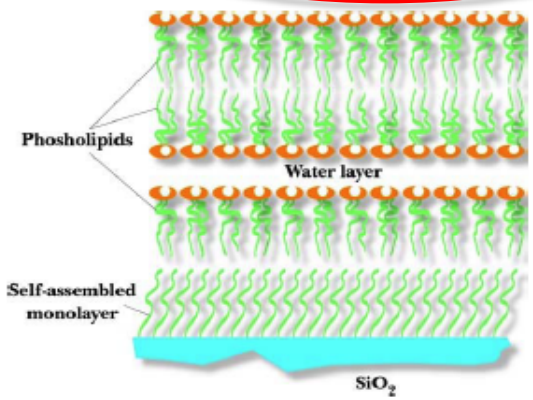

## Model Devices

- Thin polymer films (finite size effects)
- Spin coating



## Surfactants

- Parametric Studies
- Liquid/Liquid Interface
- Reduce Label size in Structural Studies
- Self Assembly
- Foams



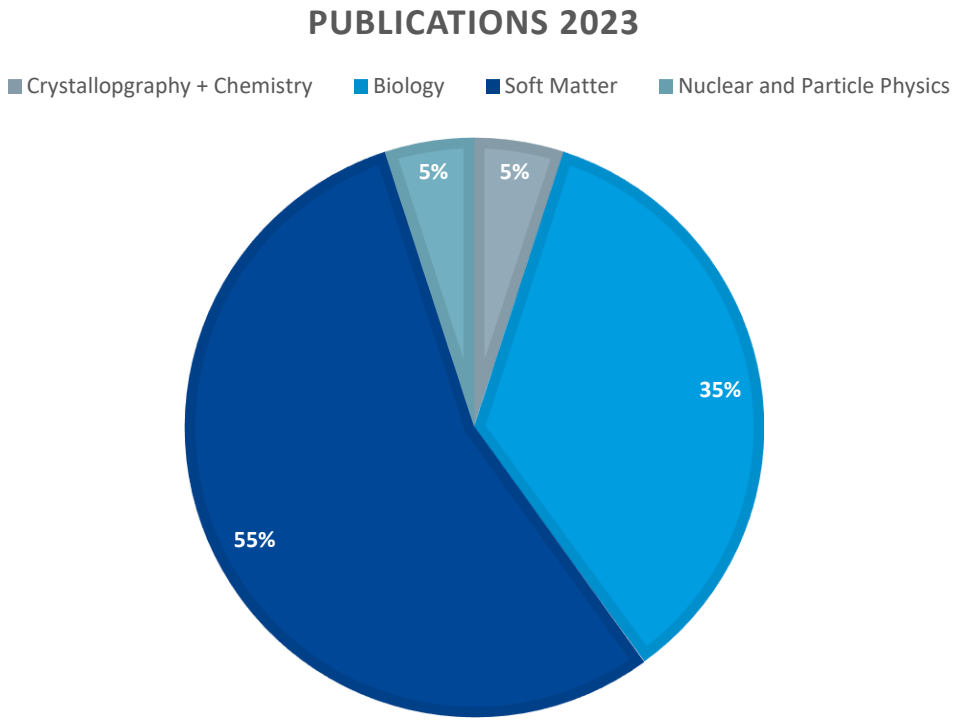

## Biology

- Protein adsorption
- Biocompatible polymers
- Drug transport
- Anaesthesia mechanisms

## Magnetism:

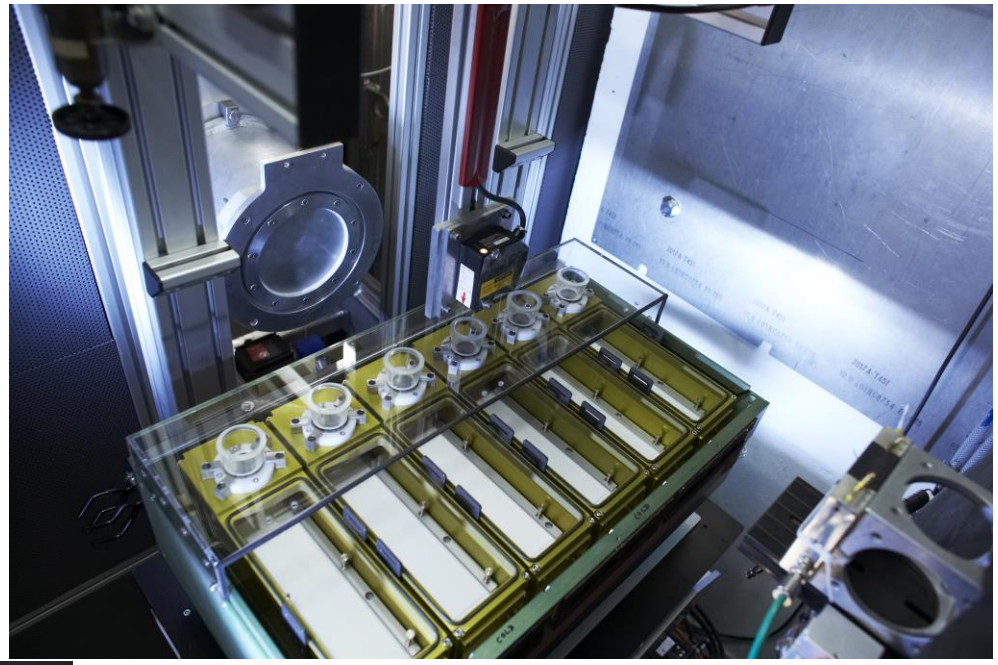
- Magnetic multilayers
- Thin magnetic films
- Thin film magnetometry

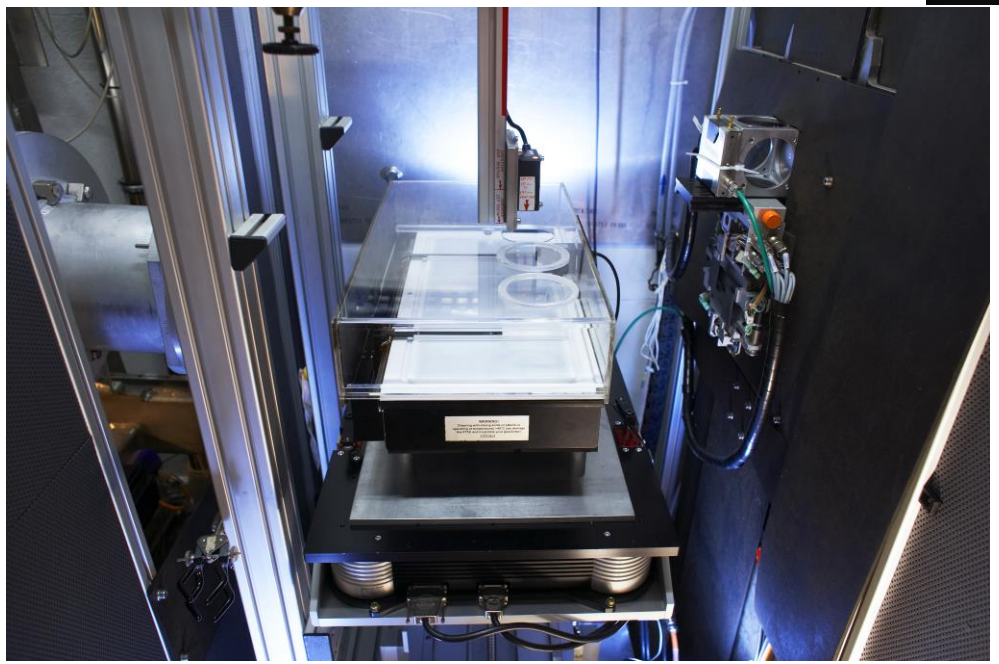
# SUMMARY OF SCIENTIFIC ACTIVITY



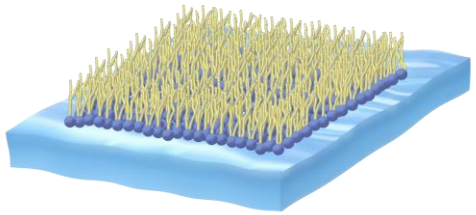

- Main scientific areas on FIGARO are Soft Matter and Biology.

# SAMPLE ENVIRONMENT

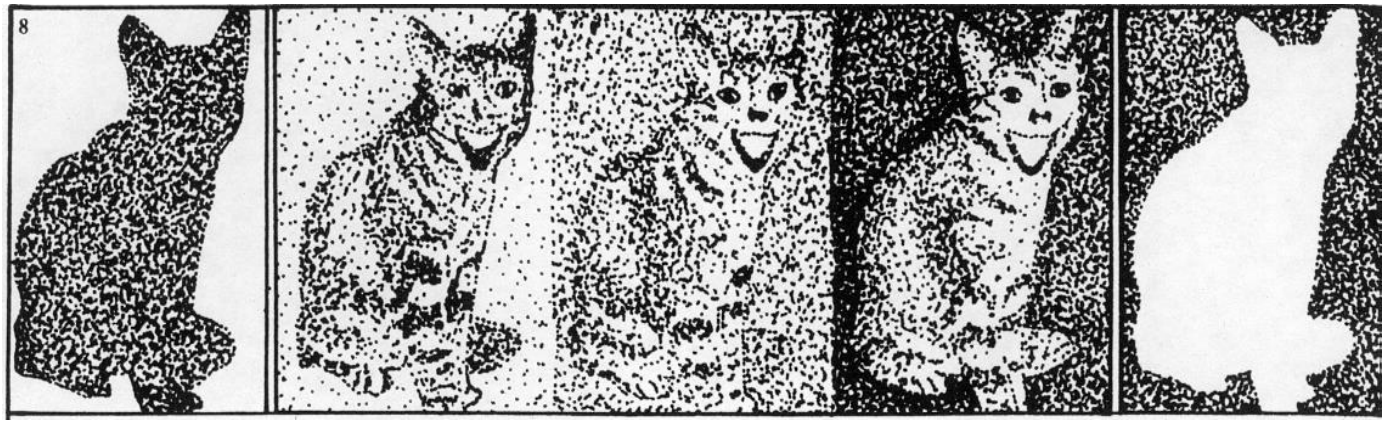




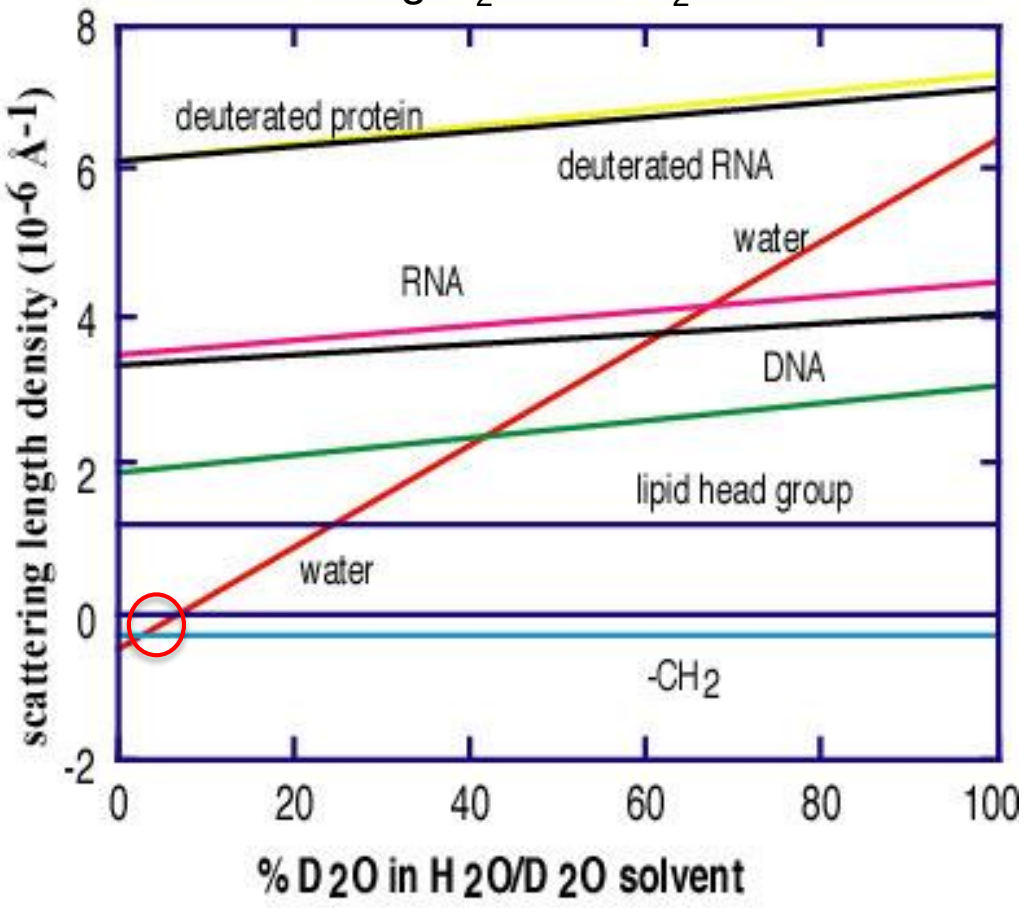
Langmuir trough for insoluble monolayers



# Example I: Direct surface excess, composition and structural measurements by scattering contrast matching



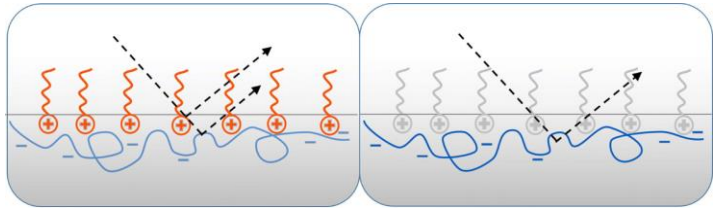
Mixing $D_2O$ and $H_2O$:




*For: $q^*\sigma \ll 1$ and $q^*d \ll 1$*

$$R \approx (4\pi/q)2(b * \Gamma)^2$$

Zero-SLD-matched water

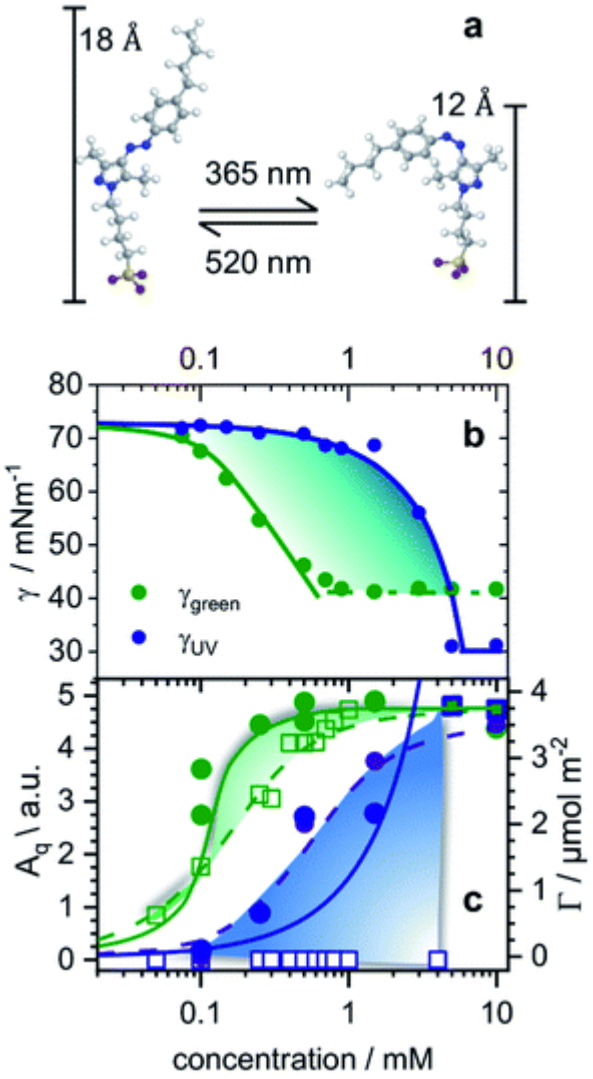


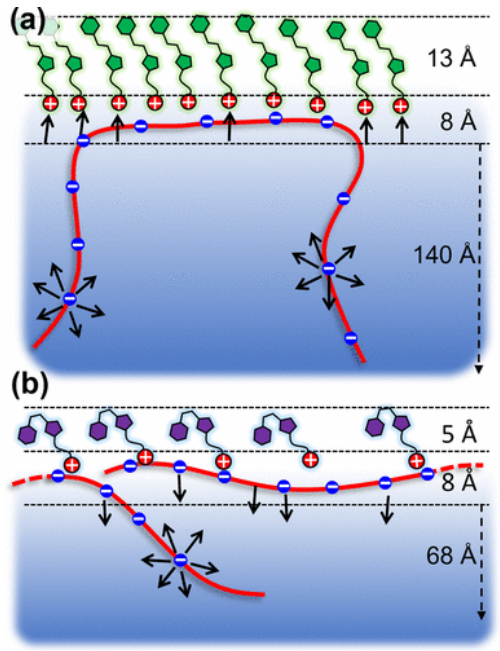
Braun *et al.*, *Adv. Coll. Interf. Sci.* **247** ( 130-148) 2017

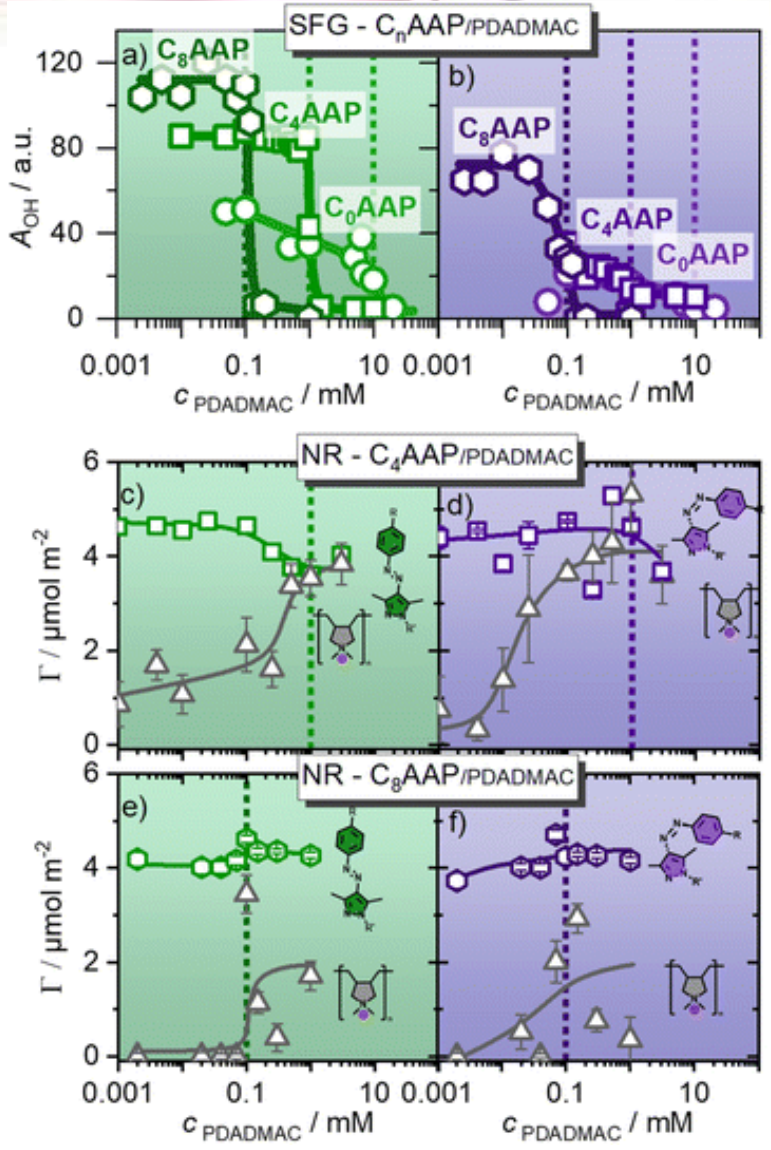
# Example Ia: Polymer/Surfactant mixtures at the air-water interface

# Photo-switchable surfactants and P/S mixtures

## Individual kinetic surface excess and structure revealed by NR



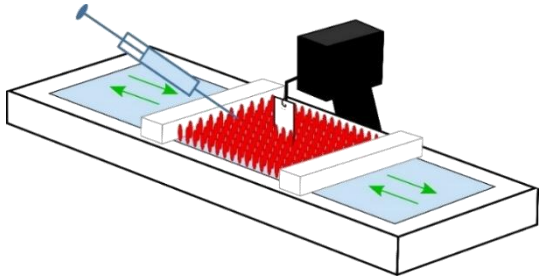



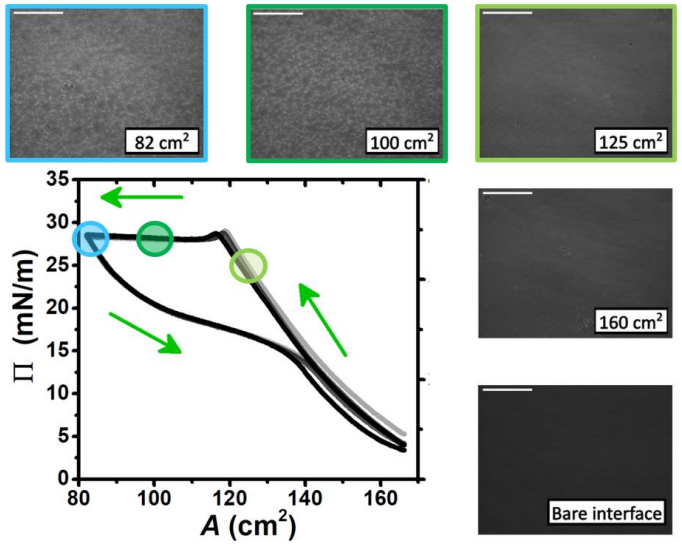


Honnigfort *et al.*, *Chem. Sci*. **11** 2085-2092 (2020)
Schnurbus *et al.*, *J. Phys. Chem. B.* **124** 31 (2020)
Schnurbus *et al.*, *ACS Appl. Mat. Interf.* **14** 3 (2022)
Hardt *et al.*, *Langmuir* **39** 16 (2023)
Hardt *et al.*, *Nanoscale* **16** 9975-9984 (2024)

# 3D CONTROL OF EXTENDED STRUCTURES IN POLYELECTROLYTE/SURFACTANT FILMS

Spread P/S films at the air/water interface

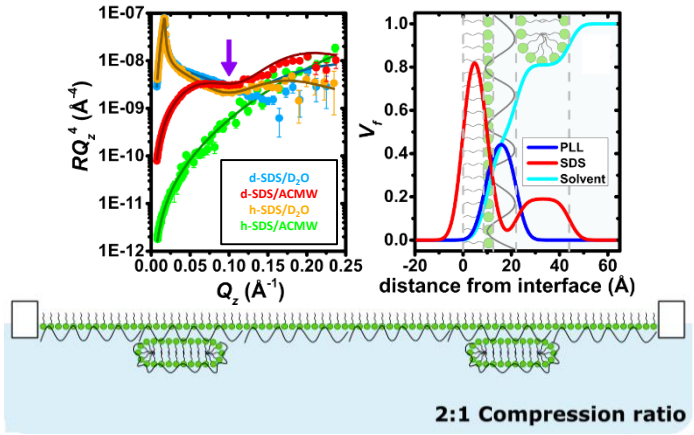




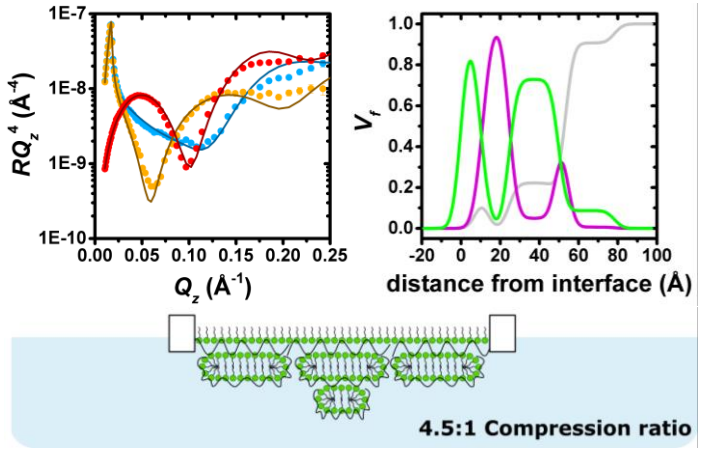

- **Monolayer's coverage control**
- **Switch on/off 3D extended structures**
- **3D extended structures' coverage control**

## LINEAR POLYPEPTIDES

Structural control via **compression ratio**



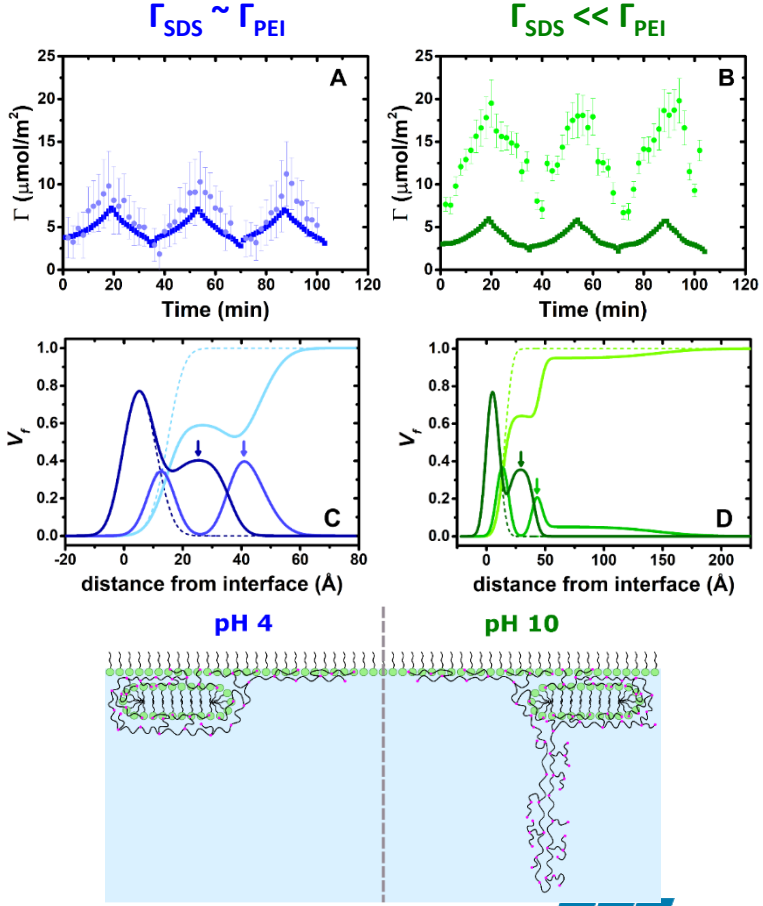

*Carrascosa-Tejedor, J., et al. Chem. Commun. 58 (**2022**)*




*Carrascosa-Tejedor, J., et al. Nanoscale 15 (**2023**)*

## HYPERBRANCHED POLYELECTROLYTES

Structural control via **pH**

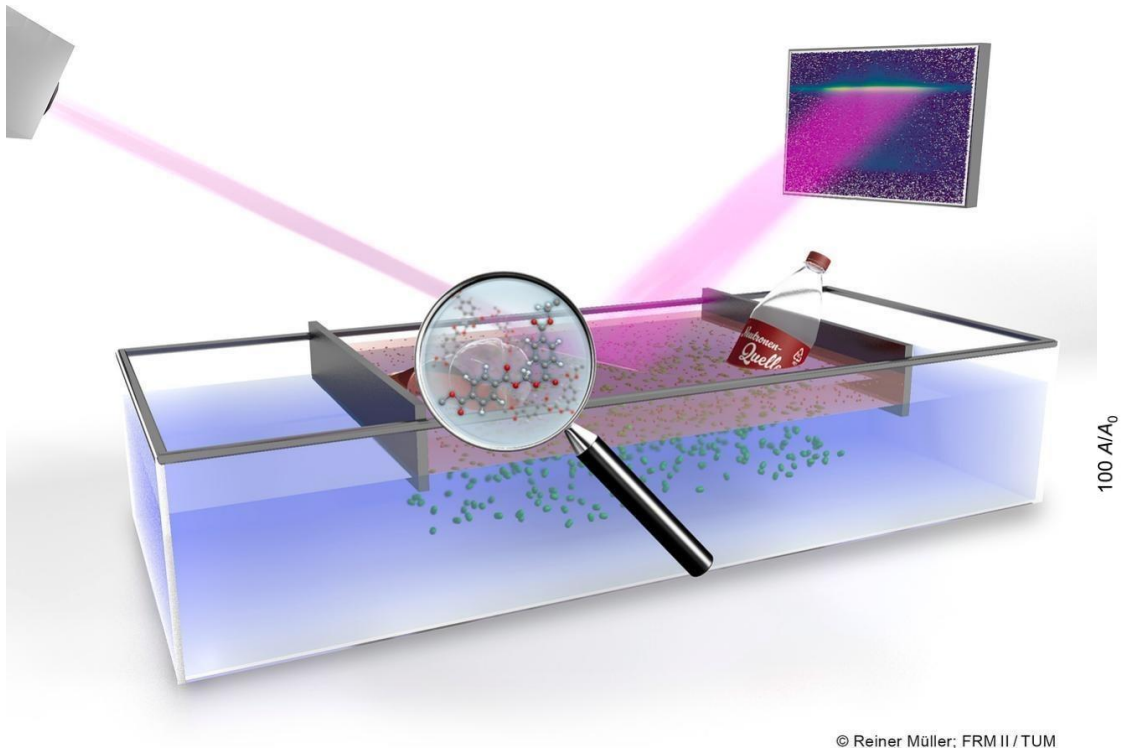


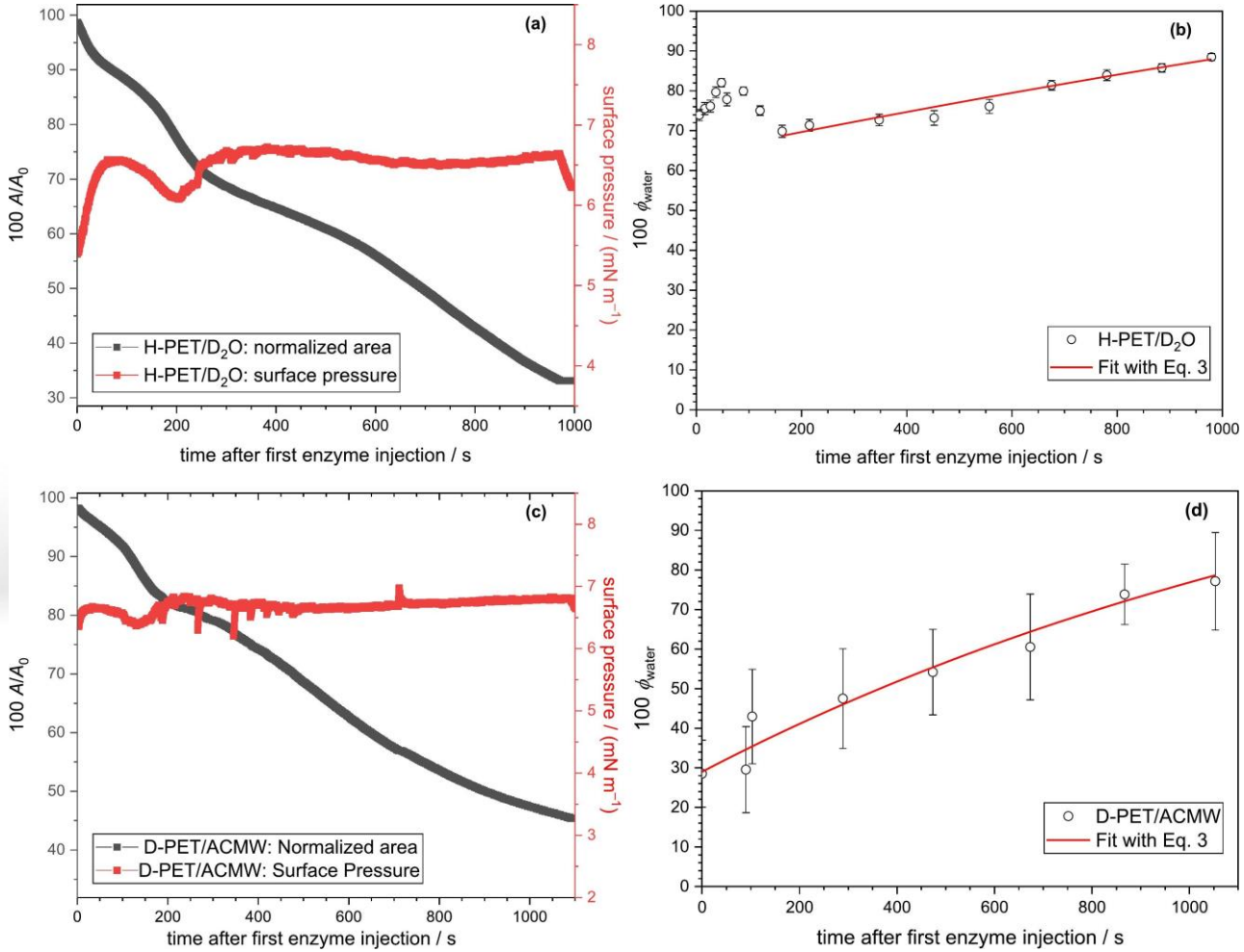

*Carrascosa-Tejedor, J., et al. Langmuir 39 (**2023**)*

# Example Ib: Enzyme activity at the air-water and oil-water interface

# enzymatic poly(ethylene terephthalate) hydrolysis

## Kinetics of PET hydragion from NR



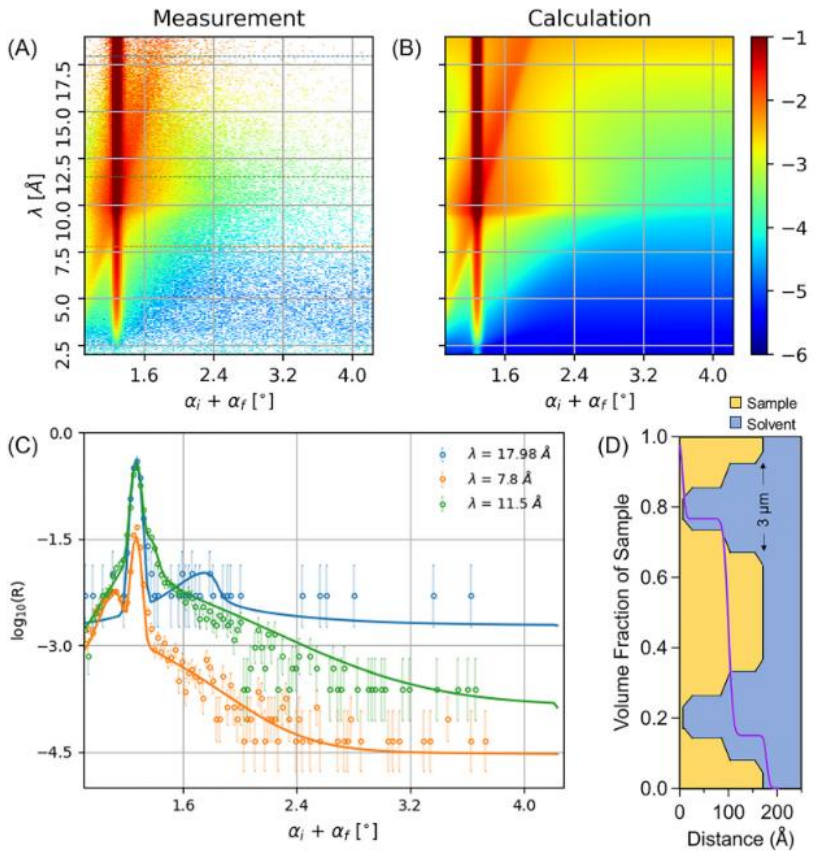




Machatschek *et al.*, *J. Coll. Interf. Sci.* **698** 138021 (2025).

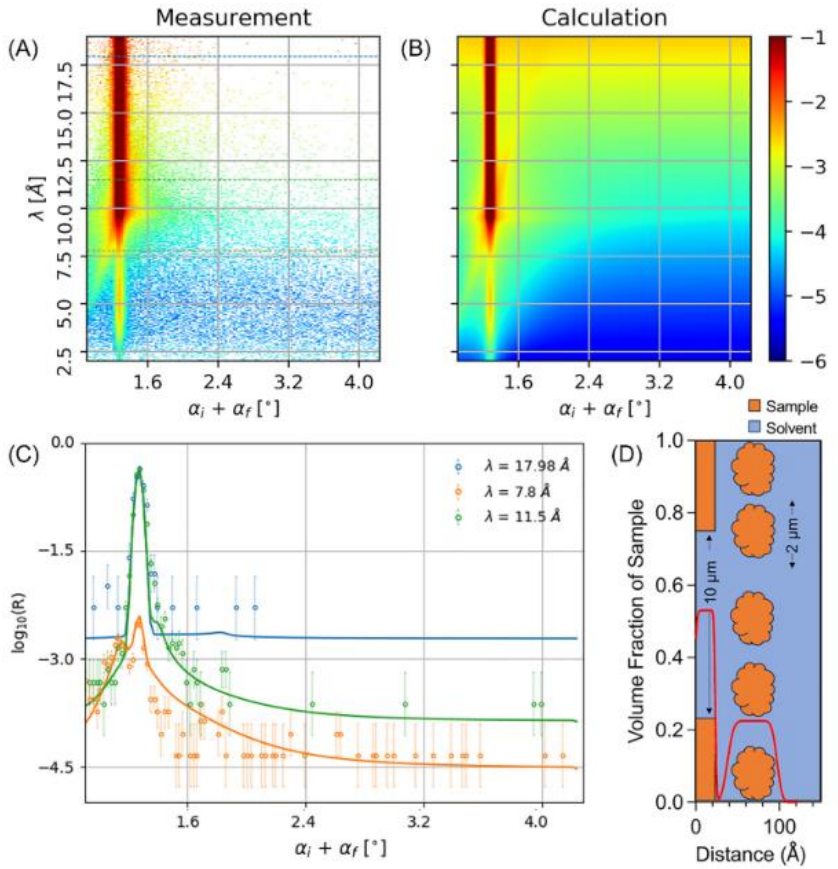
# Structural changes of triolein films during lipolysis

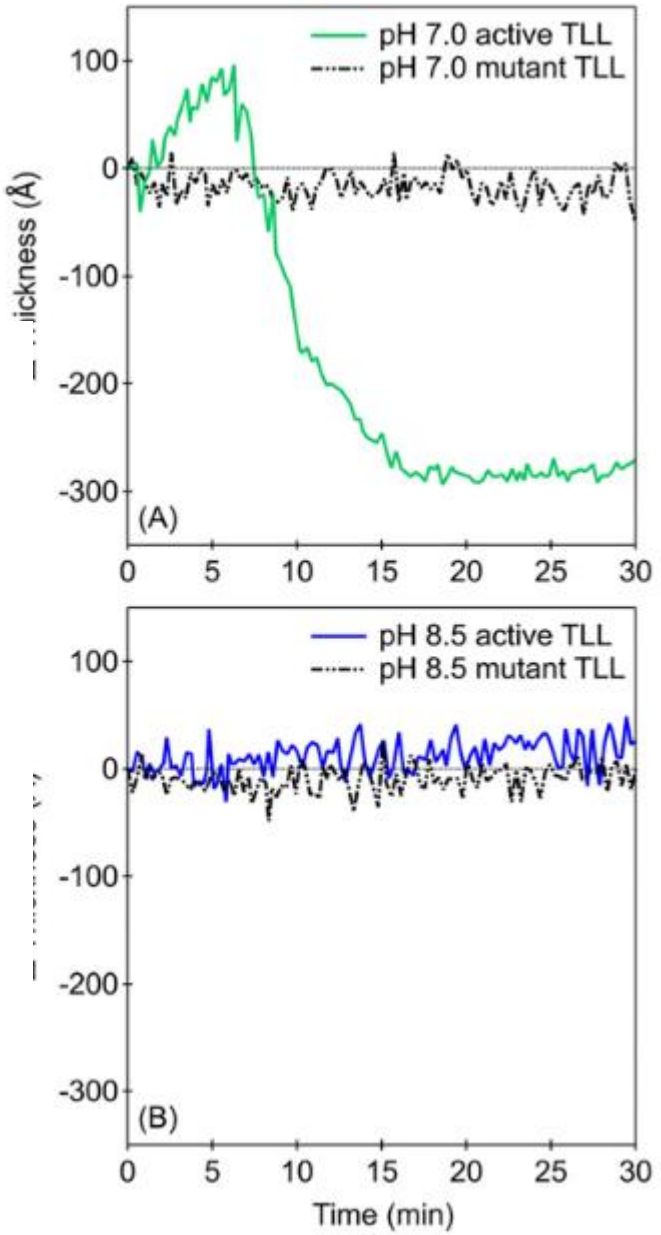
Triolin oil digestion kinetics from NR
In-plane struicture from OSS

Before digestion:




After digestion:



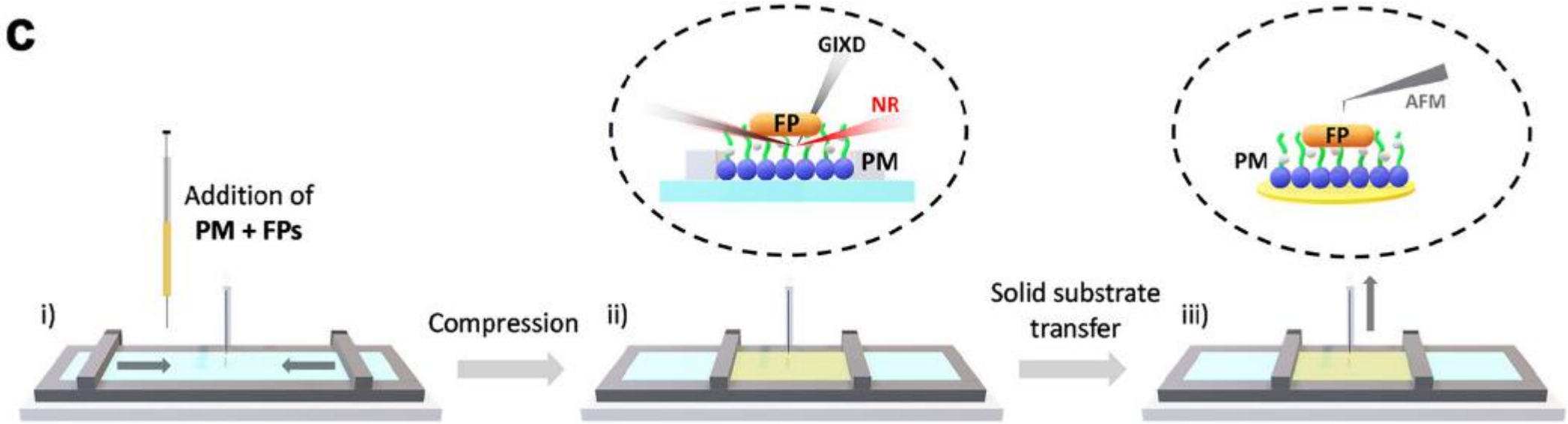




Humphreys *et al.*, *Soft. Matt.* **22** 343-354 (2026).

# Example Ic: Protein/membrane interactions at the air-water interface

# Interaction of sars-cov-2 fusion peptides with biomimetic plasma membranes

## Monolayer composition extracted from contrast matching




Pawar *et al.*, *Nat. Commun*. **17** 915 (2026).

# Peptide assembly at the air/liquid interface

## Structure/orientation of peptides

ADVANCED SCIENCE NEWS
www.advancedsciencenews.com

ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

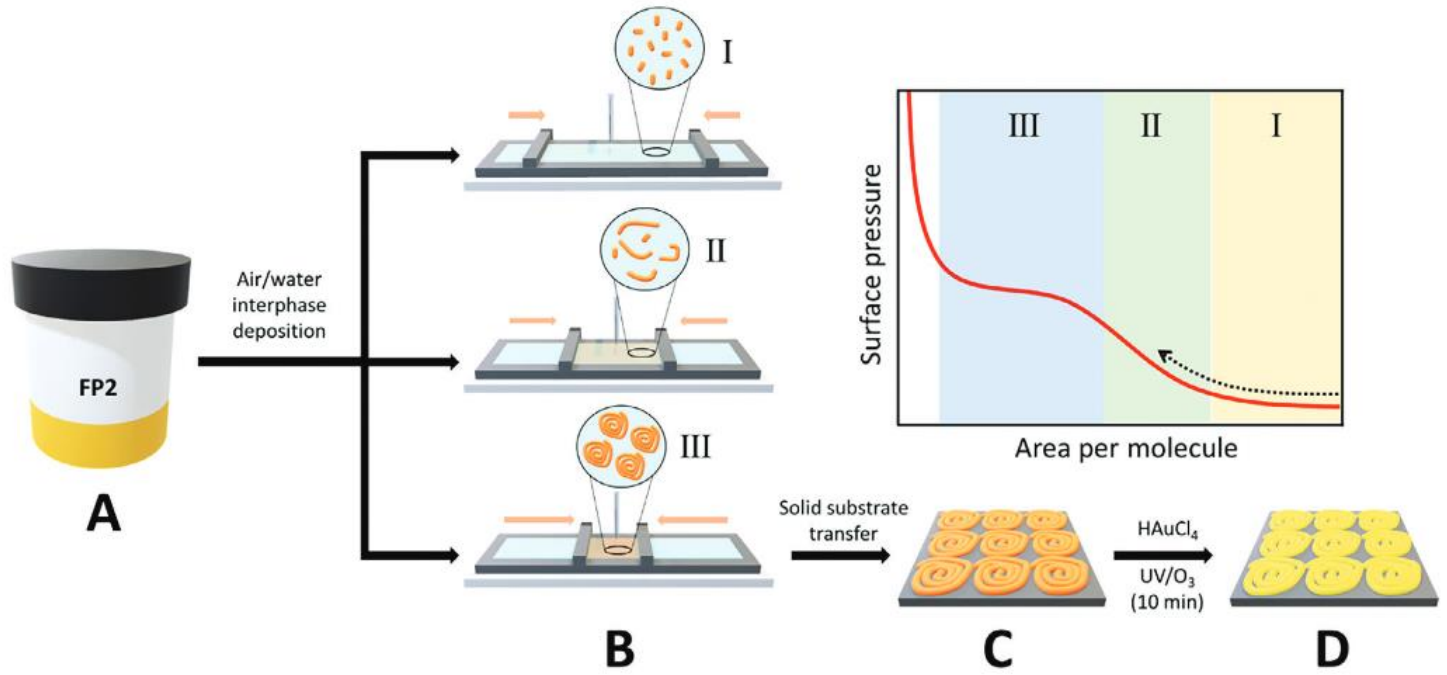



**Figure 1.** Schematic summary of the experimental approach. A) Preparation of the peptide solution into DMF. B) Deposition at the air–water interface and compression using a LB set-up. C) Transfer to mica substrate. D) Selective impregnation with metallic salt and peptide removal with $UV/O_3$.

Combination with interfacial rheology:

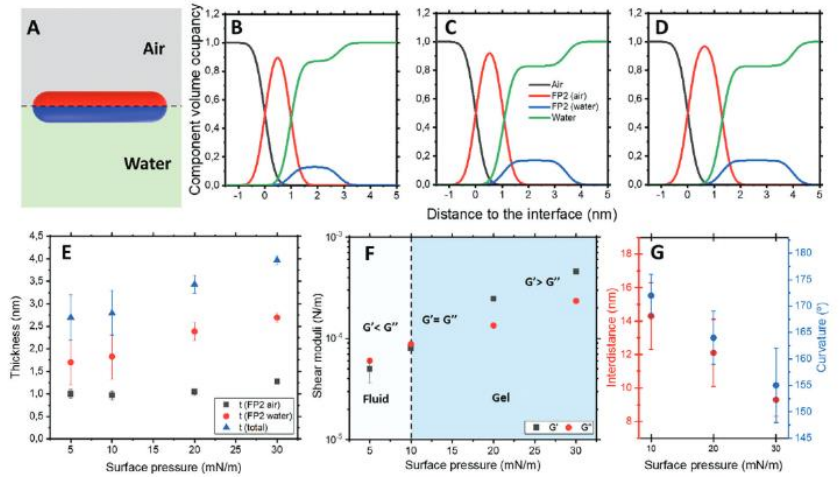
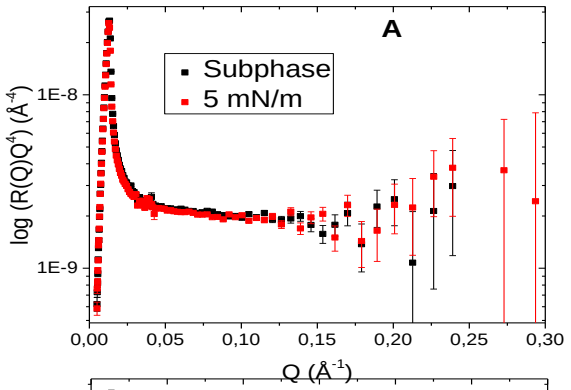



**Figure 4.** A) Schematic of the model used to fit NR data. Density profiles of the interfaces at B) 10, C) 20, and D) 30 mN $m^{-1}$. E) The total thickness of the fibers obtained by NR. F) Interfacial shear rheological measurements. G) Interdistance and curvature of the fibers were obtained by analysis of the AFM images.

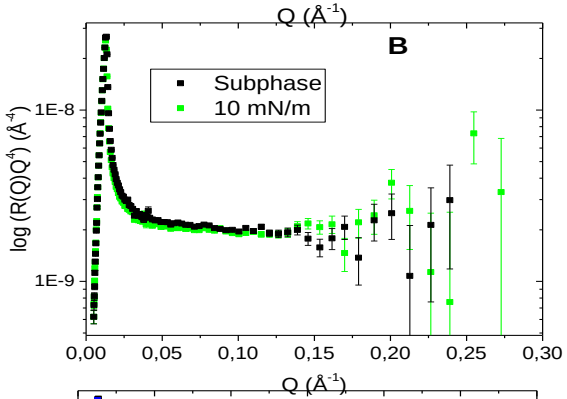
Alvarez-Fernandez *et al.*, *Advanced Functional Materials* **35** 2411061 (2025).

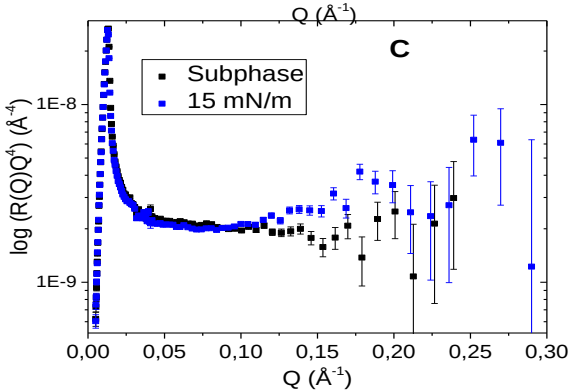
# Example Id: Polymer blend phase separation at the air-water interface

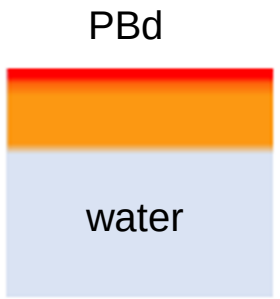
# Co-polymer Langmuir monolayers





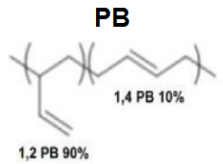


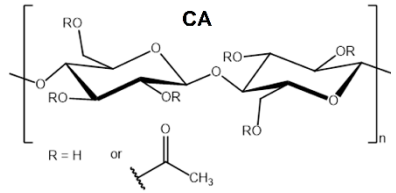



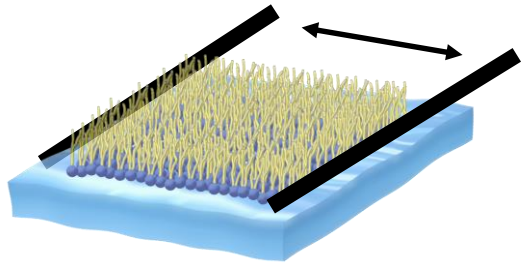

Structure of hydrophobic (polybutadiene)/ hydrophilic (cellulose acetate) polymer blend at the air/water interface.

$Nb_{PBd} = 5.72.10^{-6}$ Å$^{-2}$ $Nb_{CA} = 1.23.10^{-6}$ Å$^{-2}$




Barriers

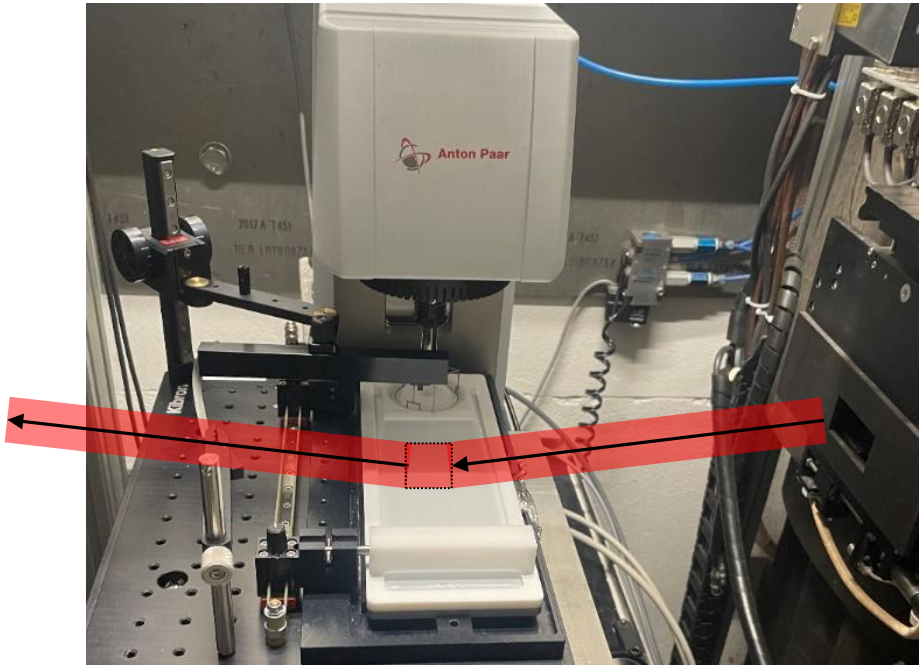


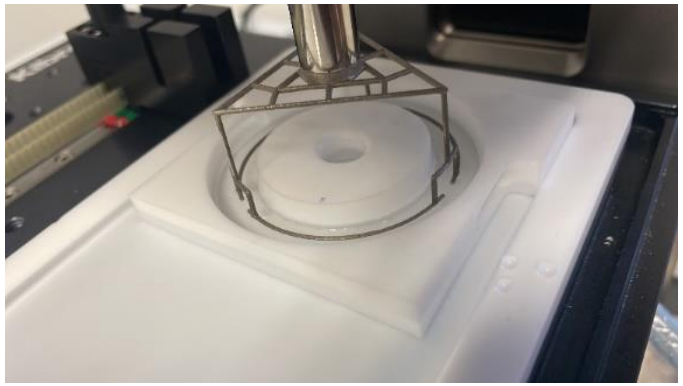
Water contrast-matched to CA/BP mixture

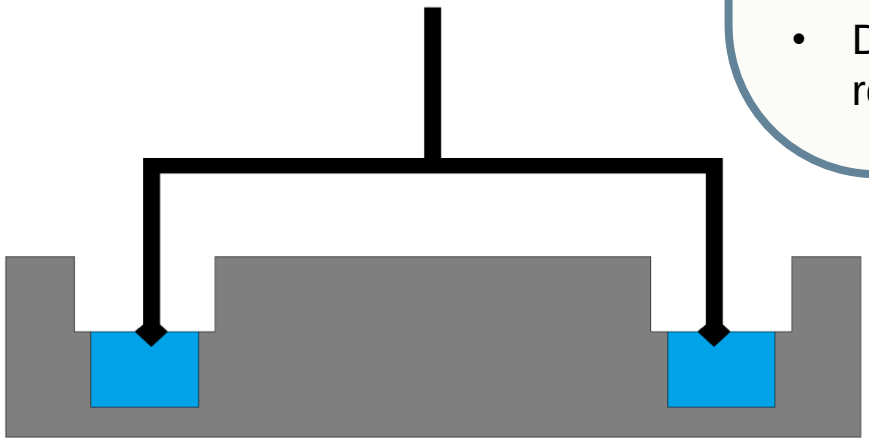

Vaillard *et al.*, *Langmuir* **37** ( 5717–5730) 2021
Vaillard *et al.*, *Langmuir* **38** ( 2538–2549) 2022
Backus *et al.*, *Langmuir* ( in print) 2026

# Example II: Combination of NR and interfacial rheology

# In situ interfacial rheology and Langmuir trough





**Double-wall ring**

**Pros:**

- High shear stresses.
- Large frequency range.
- Area in contact with bulk phases much smaller than in bicone.
- Large interfacial contact line.
- Small probe inertia.
- Measurement lower limit:
  $10^{-6}$ N/m $\leq G''_s$.

**Drawback:**

- Drive inertia limits frequency response.


S. Vandebril et al, *Rheol. Acta* 49, 131-144, (2010)

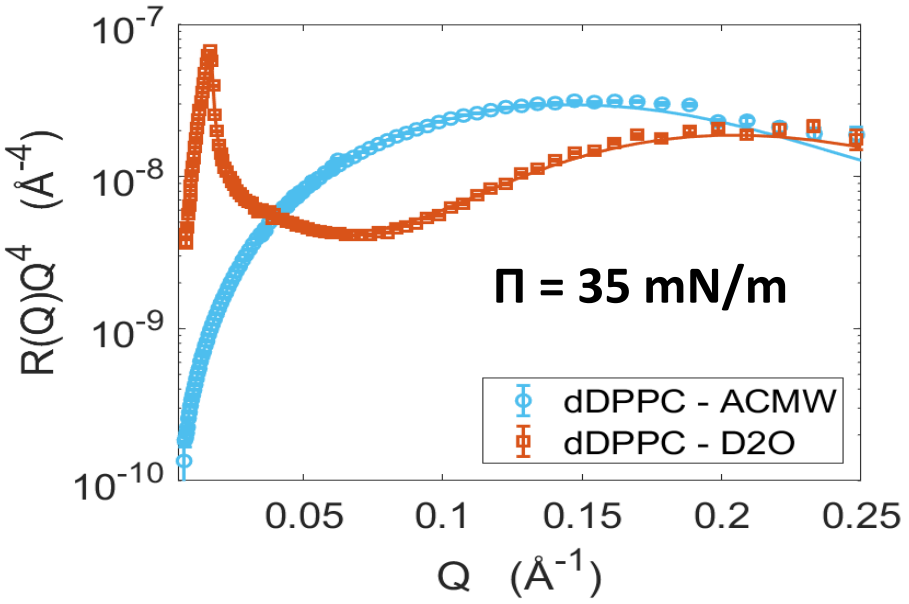
B. Schroyen et al. *Rheol. Acta* 56, 1-10, (2017)

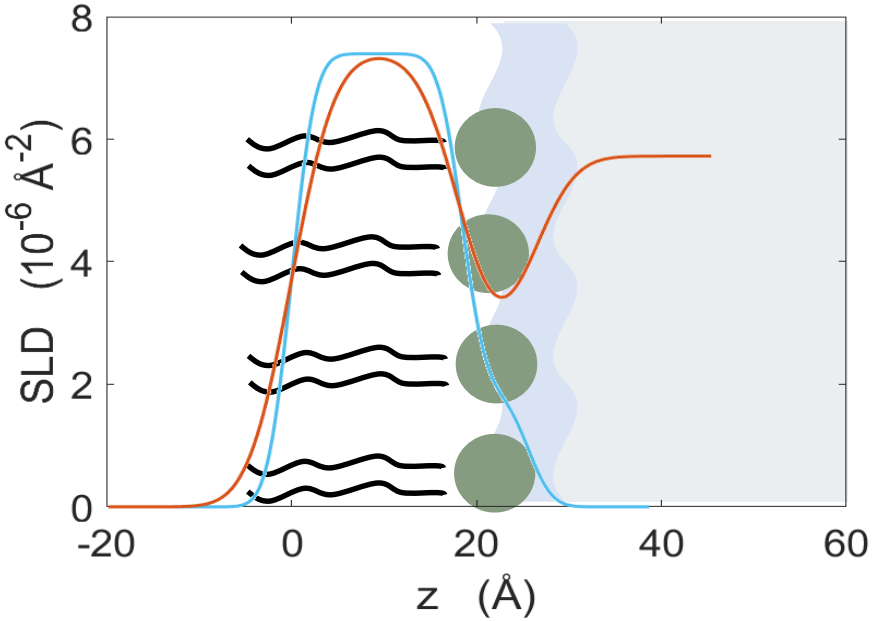
D. Renggli et al., *J. Rheol*. 64(141), (2020)


P. Sanchez-Puga *et al. J. Appl. Cryst.* (In print) 2026.

# Double-wall ring set-up

## DPPC – Structural analysis using NR



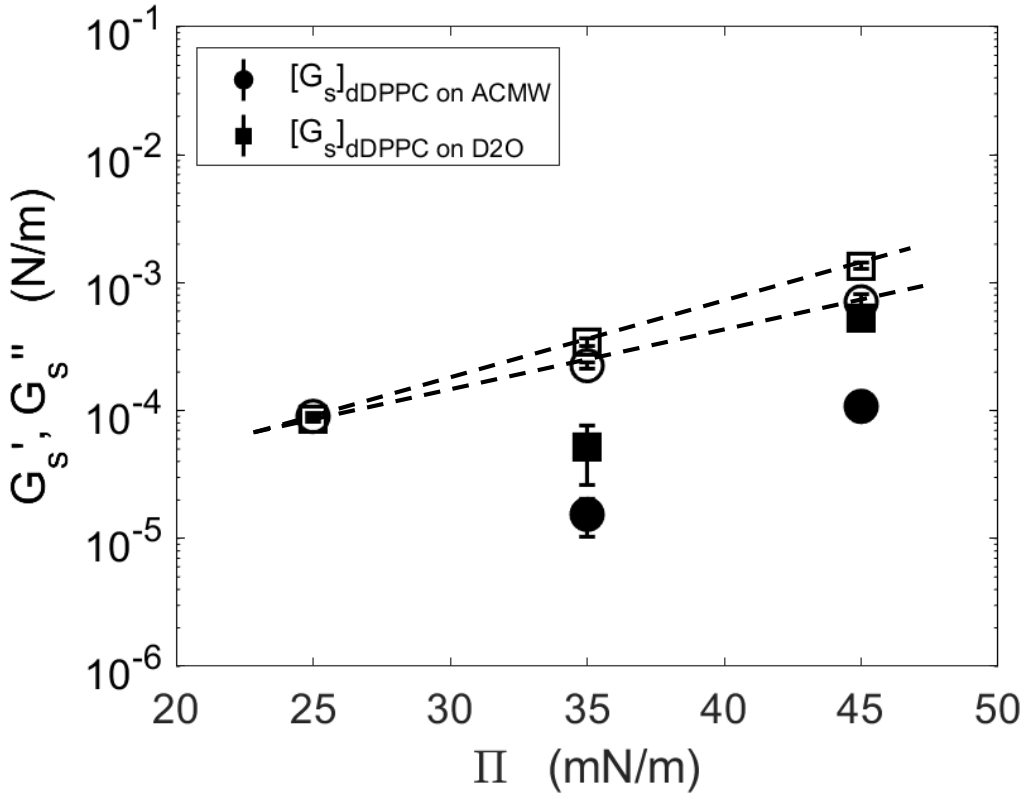

R. A. Campbell *JCIS* (2018)

| Π (mN/m) | Chains thickness (Å) | Headgroup thickness (Å) | Area per molecule (Å²) |
|---|---|---|---|
| 25 | 18.10 | 8 | 48.95 |
| 35 | 18.47 | 7.16 | 44.91 |
| 45 | 18.77 | 7.28 | 44.21 |

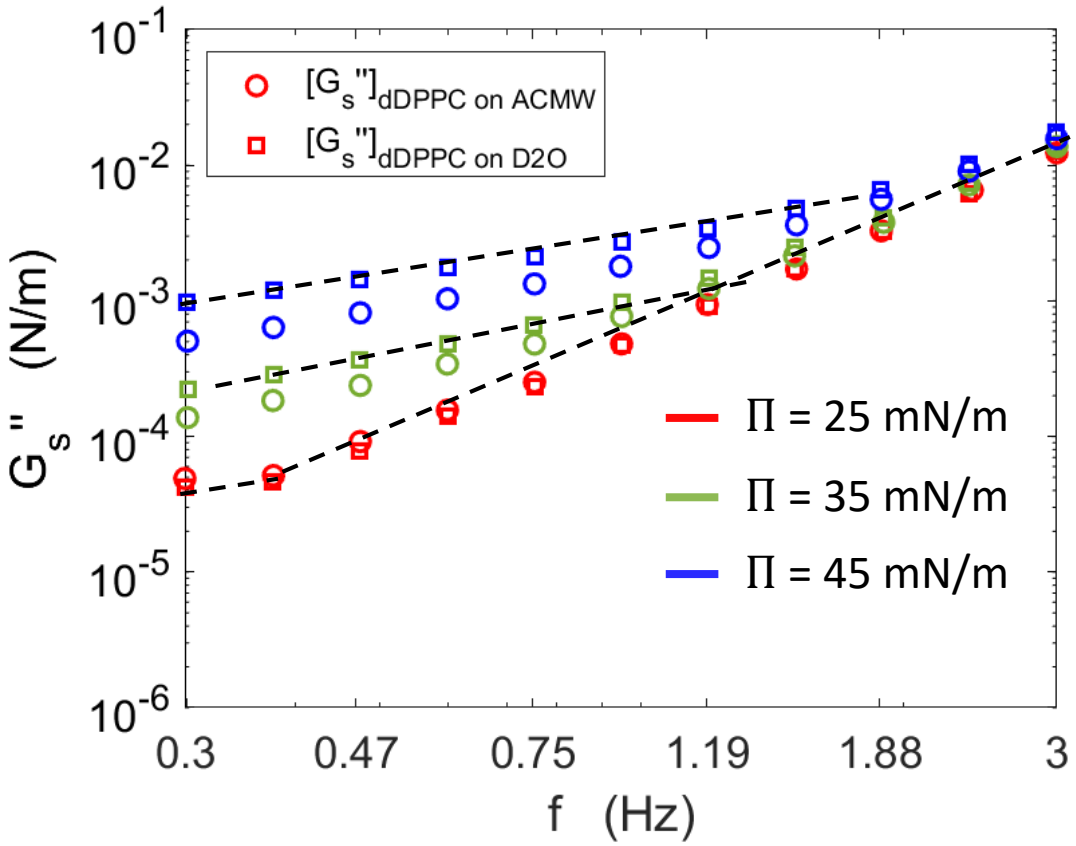
# Double-wall ring set-up

## DPPC - Rheology

**3% Strain, f = 0.5 Hz**




**3% Strain, f = 0.3 – 3 Hz**

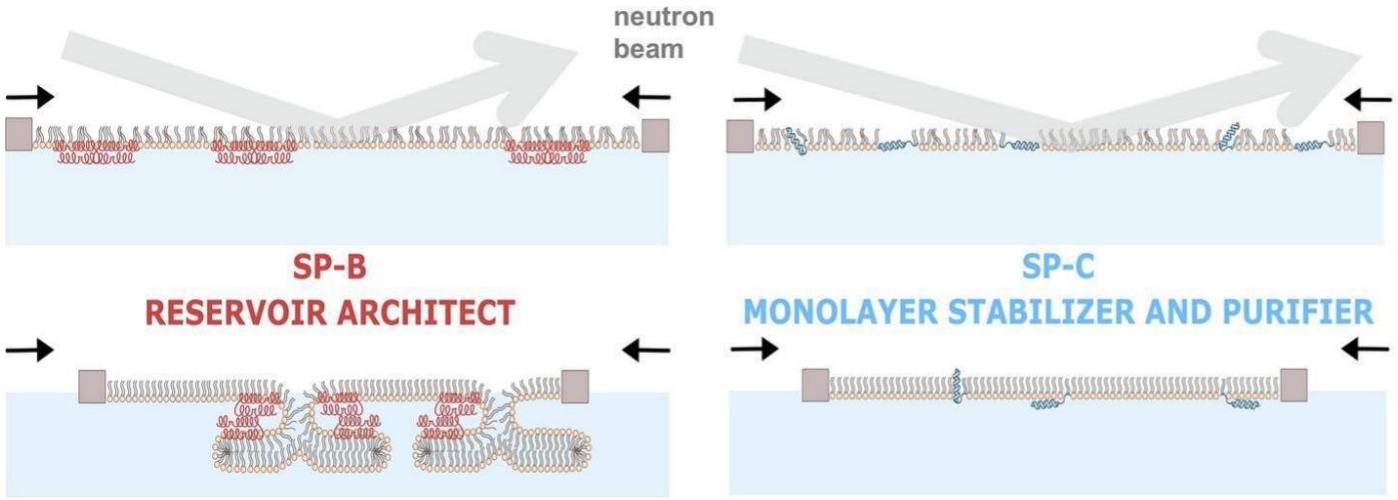


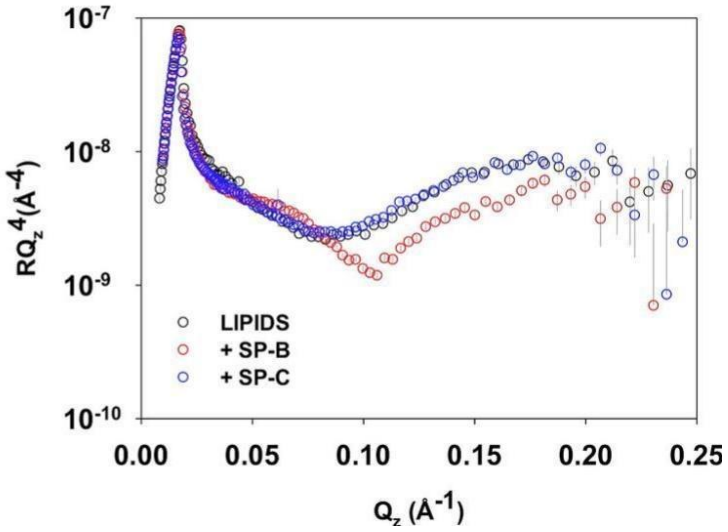

$G_s'$ → Filled symbols

$G_s''$ → Open symbols

E. Hermans *et al. Soft Matter* 2014

# Example IIb: Lung surfactant structure at the air-liquid interface

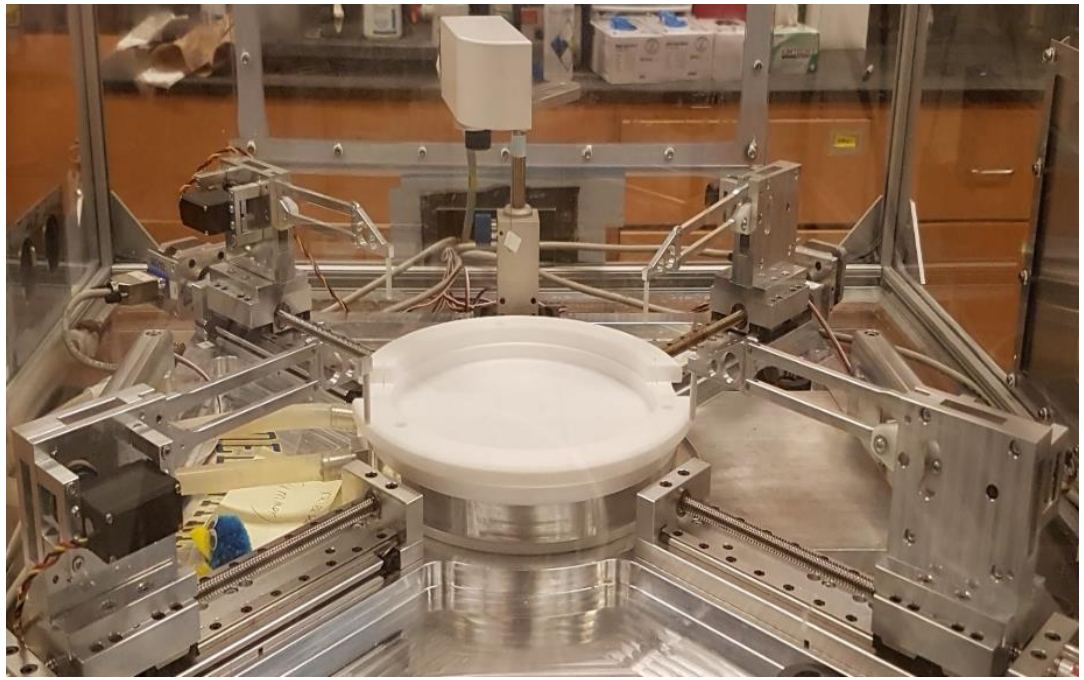


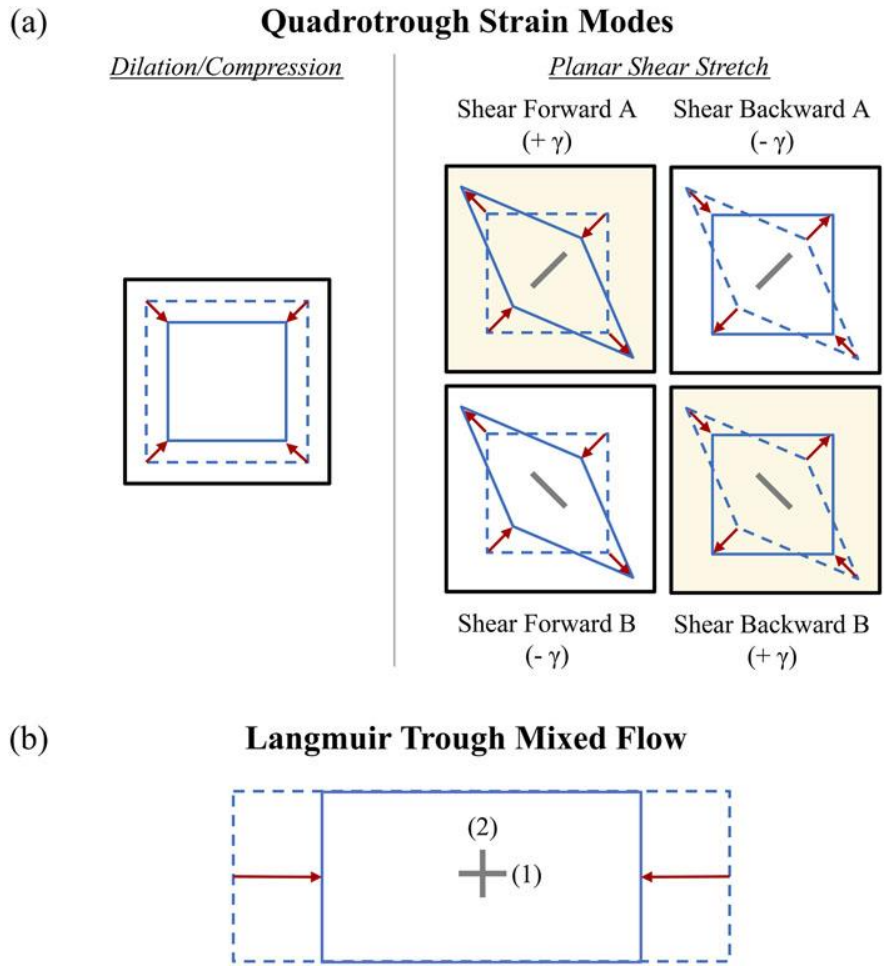




Collada *et al., J. Coll. Interf. Sci.* **701** 138769 (2026).

# QT trough

**Quadrotrough: *In situ* Dilation or shear of Langmuir monolayers**






Tein *et al.* Rev. Sci. Instrum.. 2022;93(9).

ETH zürich

Jan Vermant

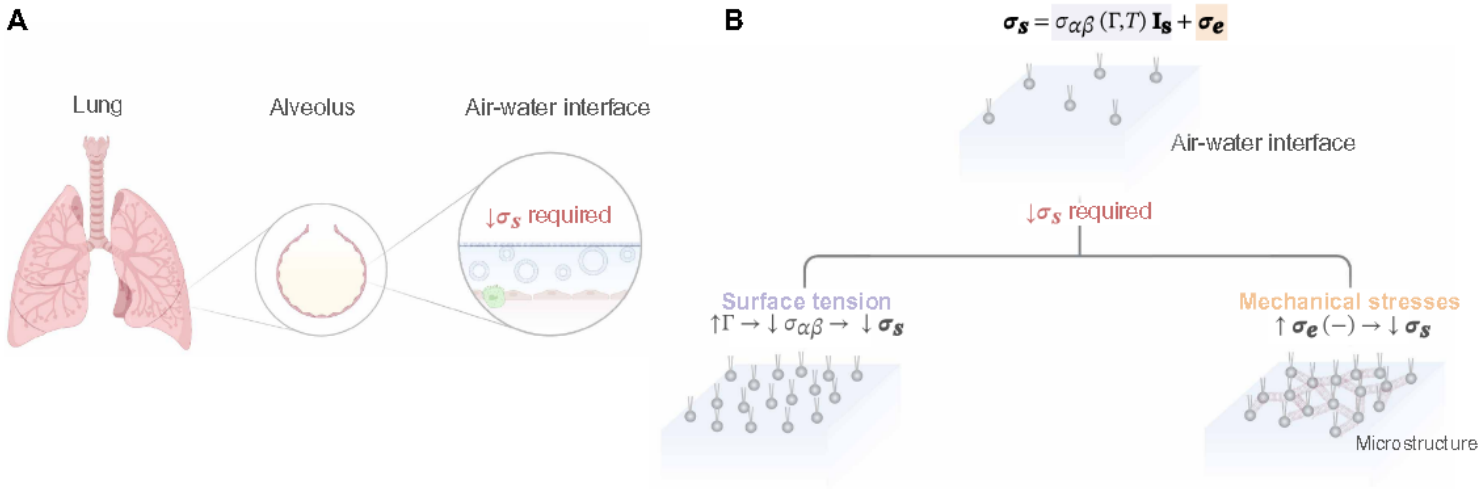
UNIVERSITY OF DELAWARE

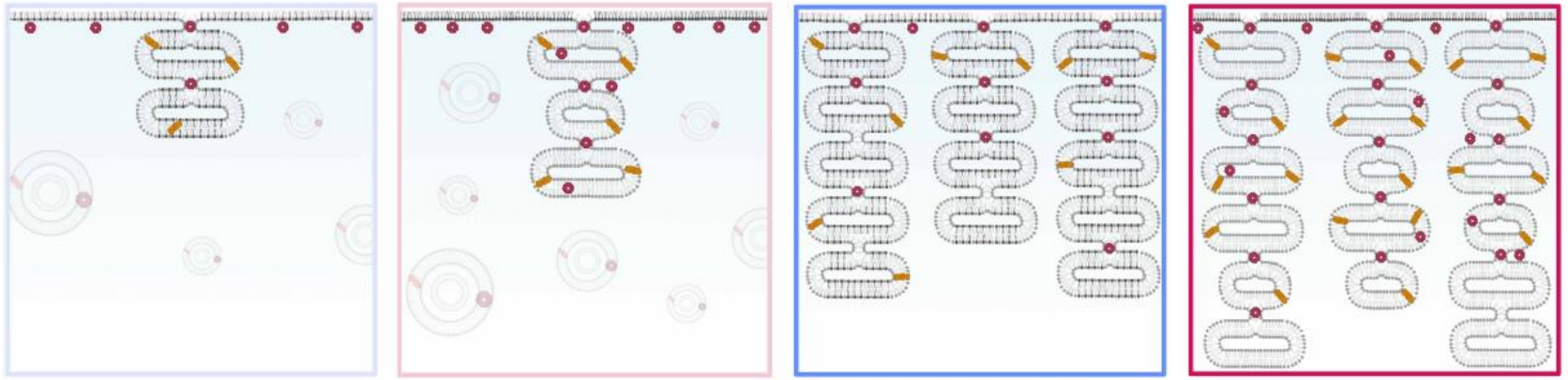
Norman Wagner

# QT trough

## Quadrotrough: *In situ* Lungsurfactant microstructure

SCIENCE ADVANCES | RESEARCH ARTICLE



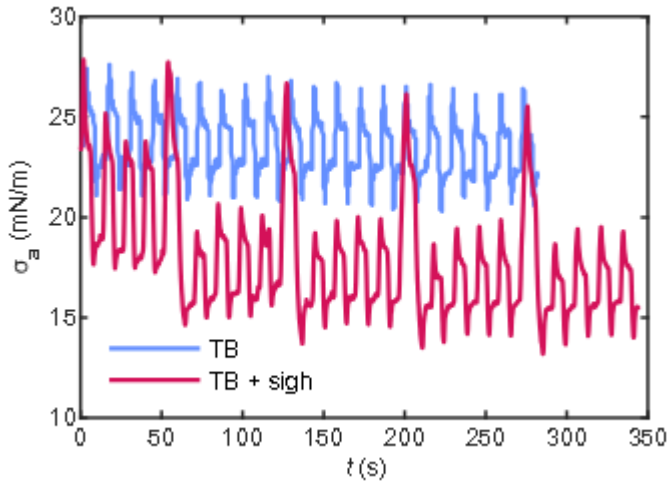
TB
$t$ < 80 min

TB + sigh
$t$ < 80 min

TB
$t$ > 80 min

TB + sigh
$t$ > 80 min

## Mimicking breathing cycles




Novaes-Silva *et al.*, *Soft Matter* **21** 7963 (2025).
Novaes-Silva *et al.*, *Sci. Adv.* **11** eadx6034 (2025).

# Example III: Bulk oil/water interface

# Why liquid/liquid? Why FIGARO?

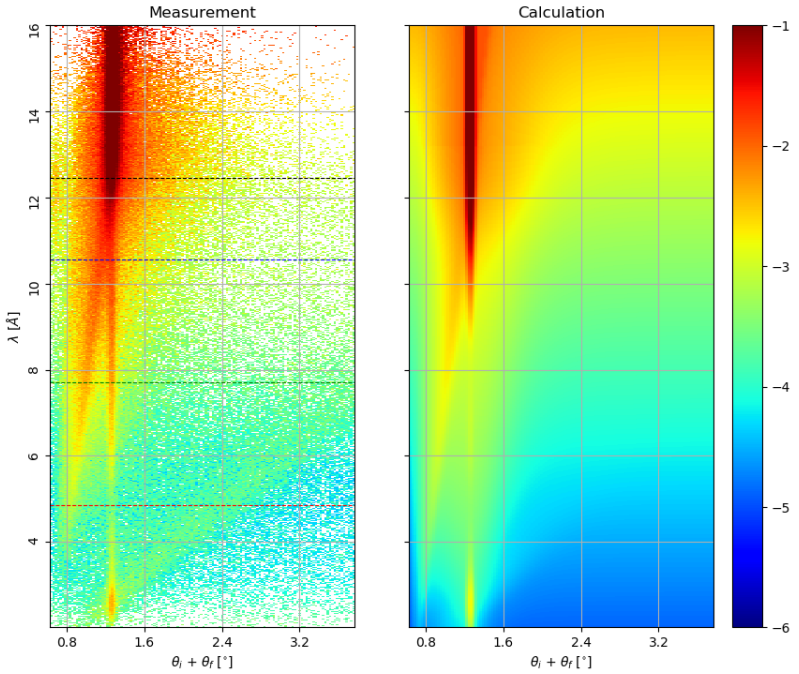
Liquid/liquid interface important for:

- Stabilisation of emulsion
- Mixed surfactants and cold water cleaning
- Transport properties of cell membrane
- Proteins (and surfactants) at Oil / Water
- Diverse range of colloids

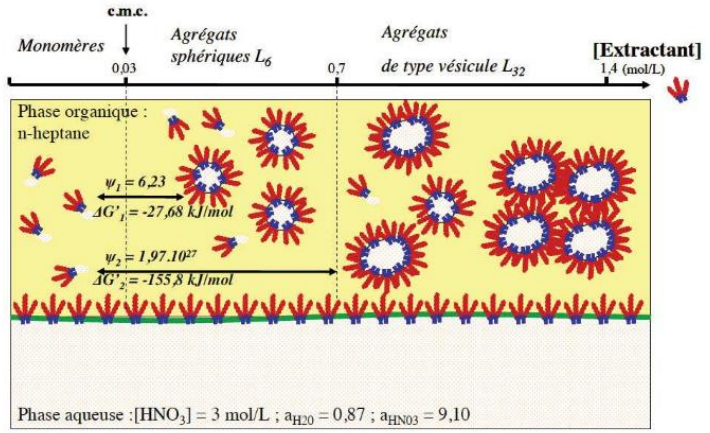
FIGARO is very flexible, can reflect up or down,

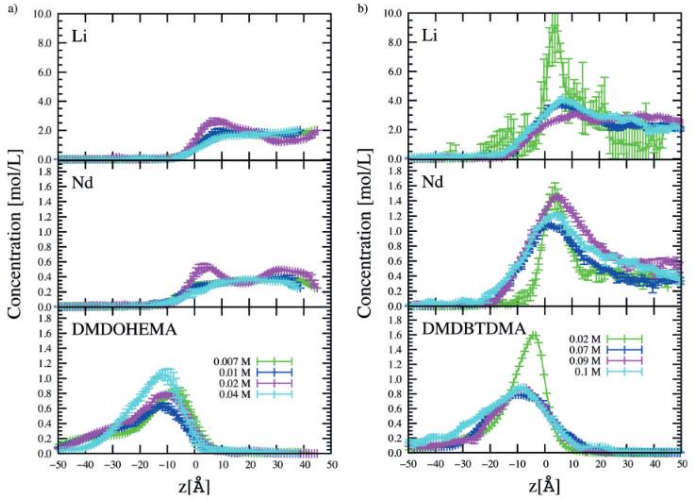
High flux, 2D detector

Off-specular scattering of lipid multilayer
At the oil/water interface:

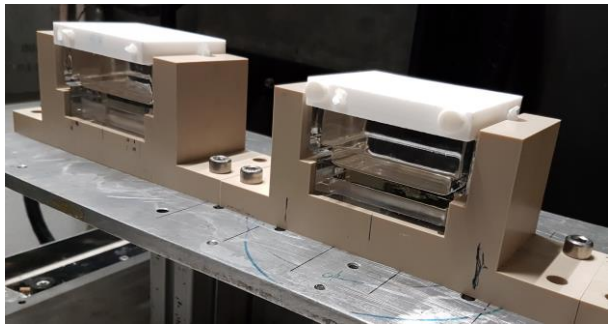



Liquid/liquid interface in solvent extraction:




Current design:



Drawbacks of current design:

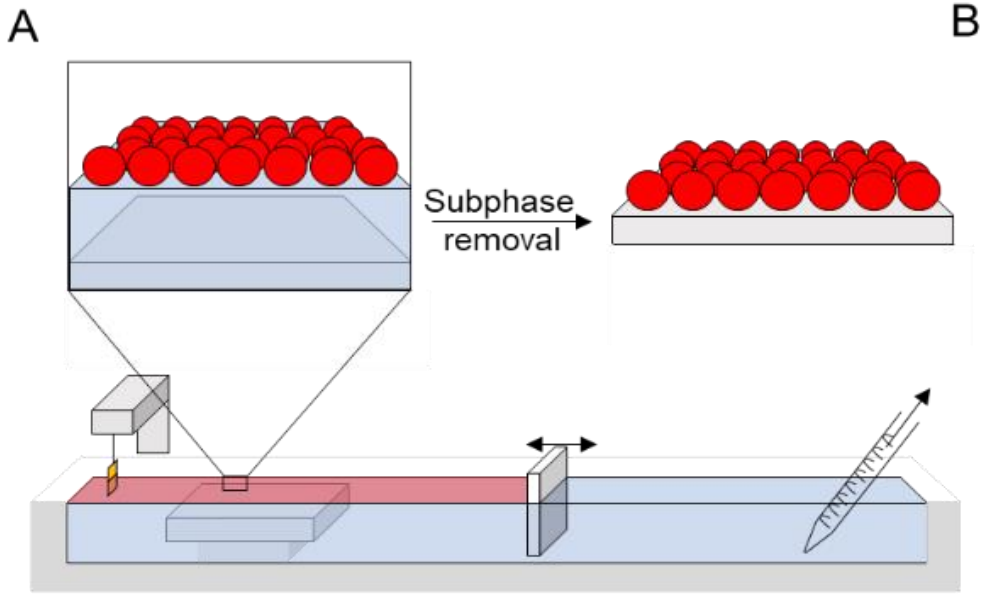
- Designed only for liquid/liquid interface, hence solid/liquid interface not (easily) accessible.
- Not machined, so edges are not sharp -> Difficult alignment.

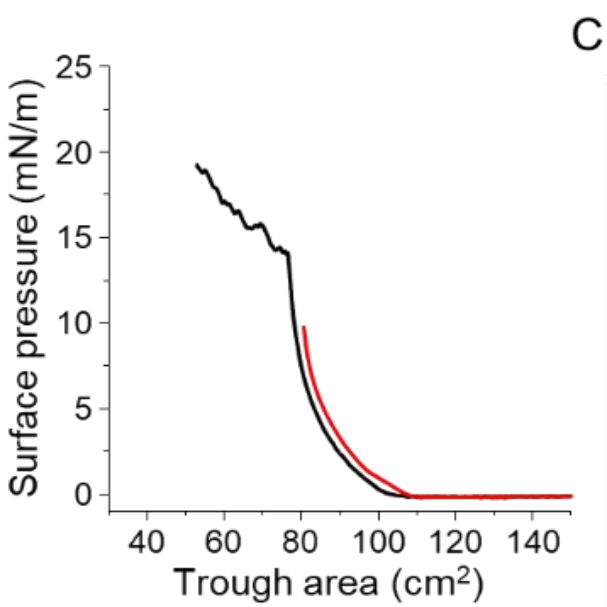
Scoppola *et al., Angew. Chem.* **128** 94572 (2016).

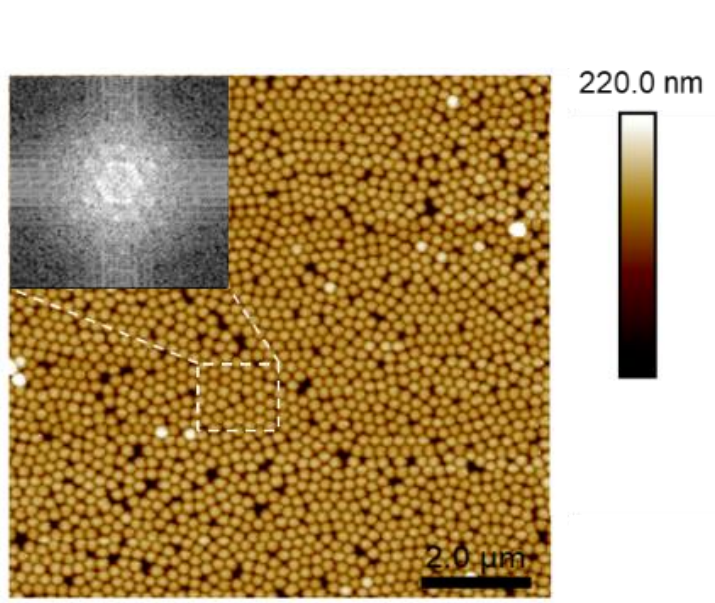
# Example IV: NPs at the silicon-water and air-water interface (FIGARO (NR+OSS) and D22 (GISANS))

Nico Paracini, Max Wolff, Marite Cardenas

neutrons

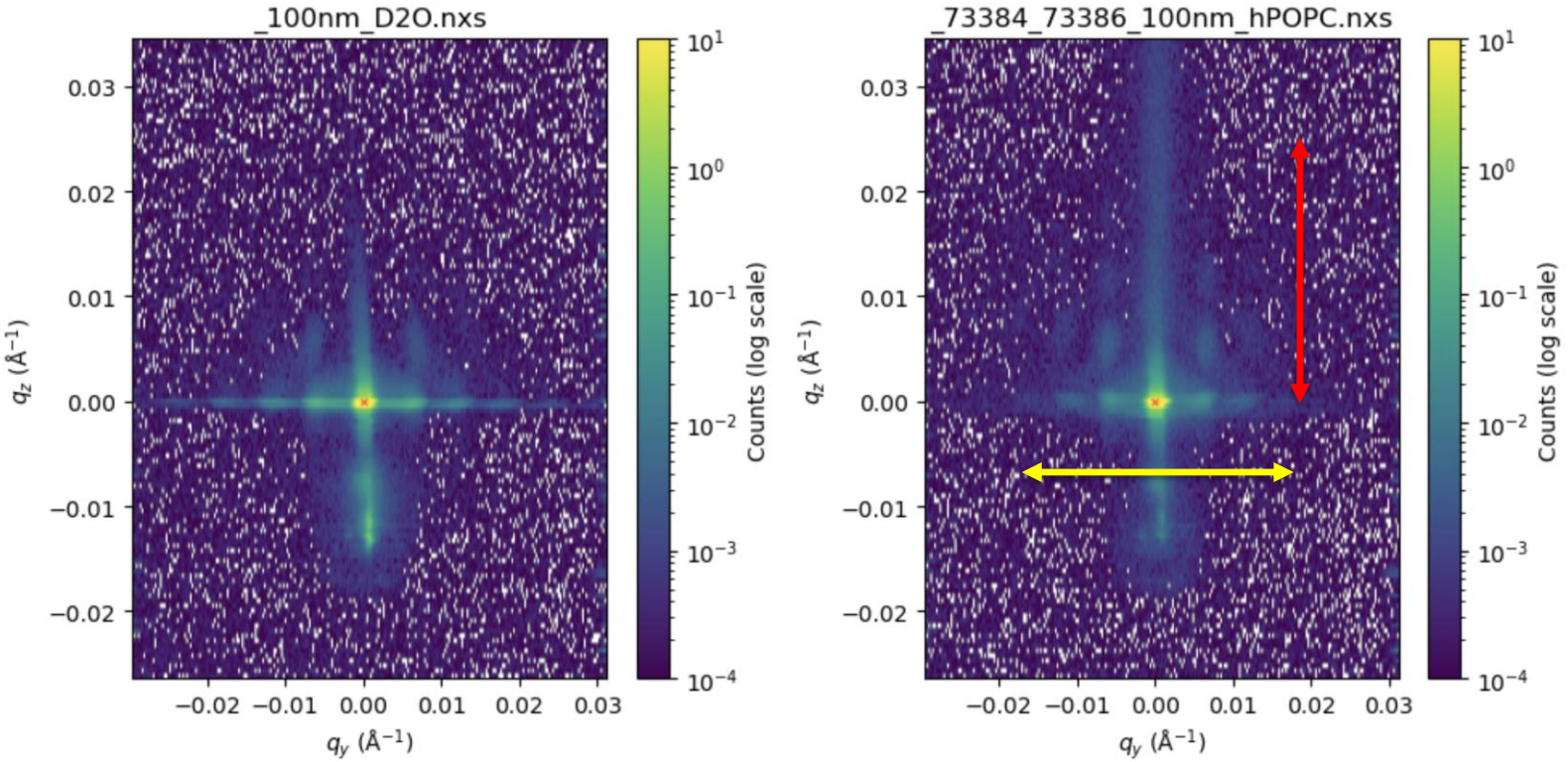


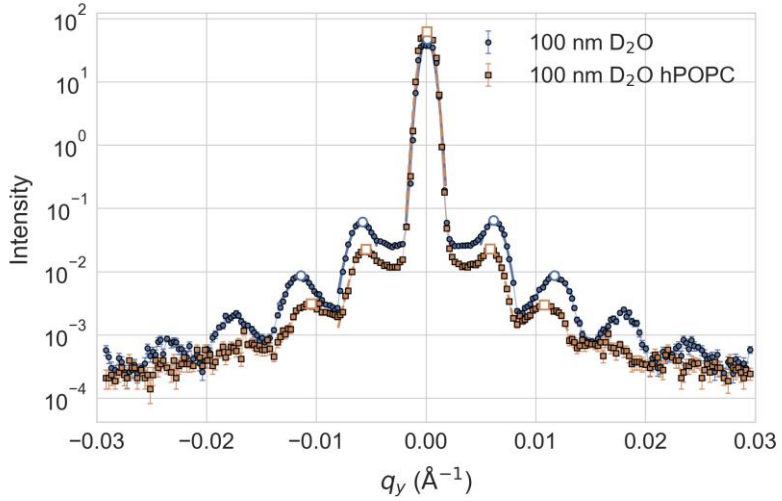



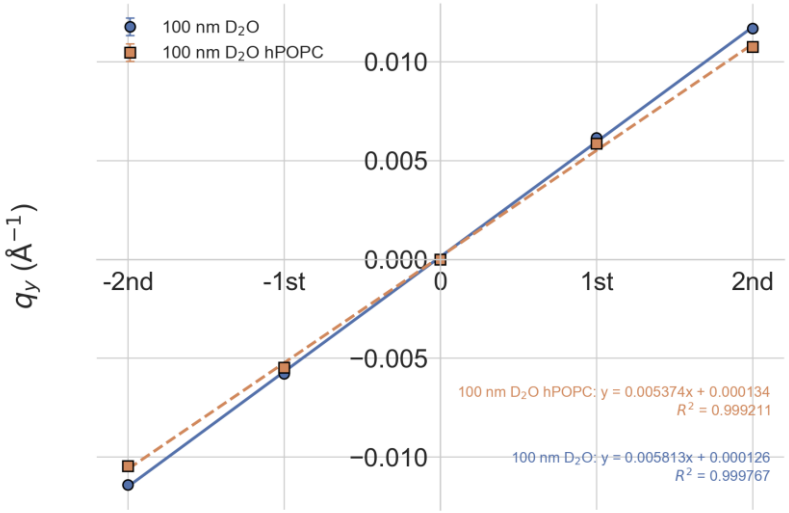



# **100 nm** – from **$D_2O$** to **$D_2O$+hPOPC**

N. Paracini, P. Gutfreund *et al.* - Structural Characterization of Nanoparticle-Supported Lipid Bilayer Arrays by Grazing Incidence X-ray and Neutron Scattering, *ACS Applied Materials & Interfaces* **15** 3772-3780 (2023).




Addition of lipids on 100 nm causes shift in peak position compatible with bilayer formation

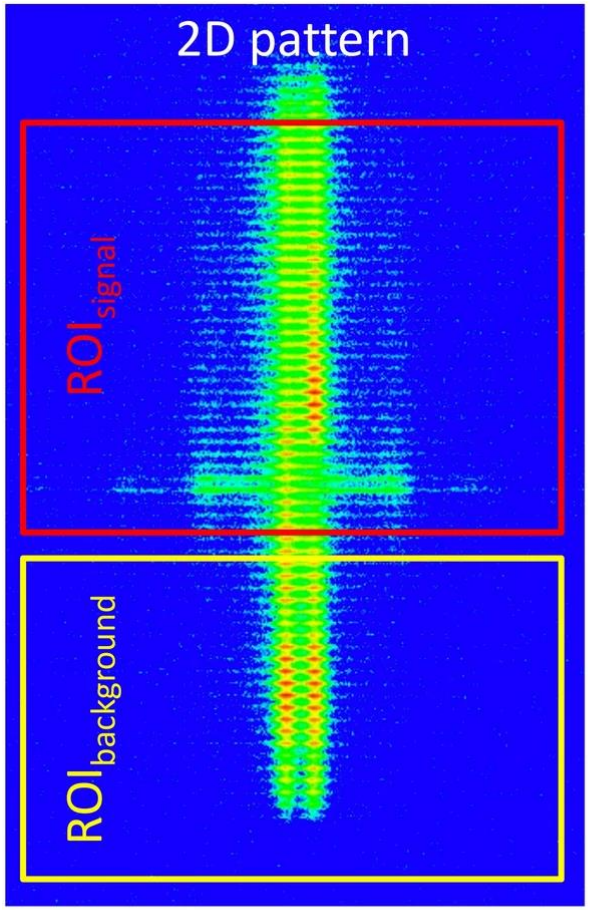
Significant loss of intensity in $q_y$ after adding the lipids
Increased intensity along $q_z$

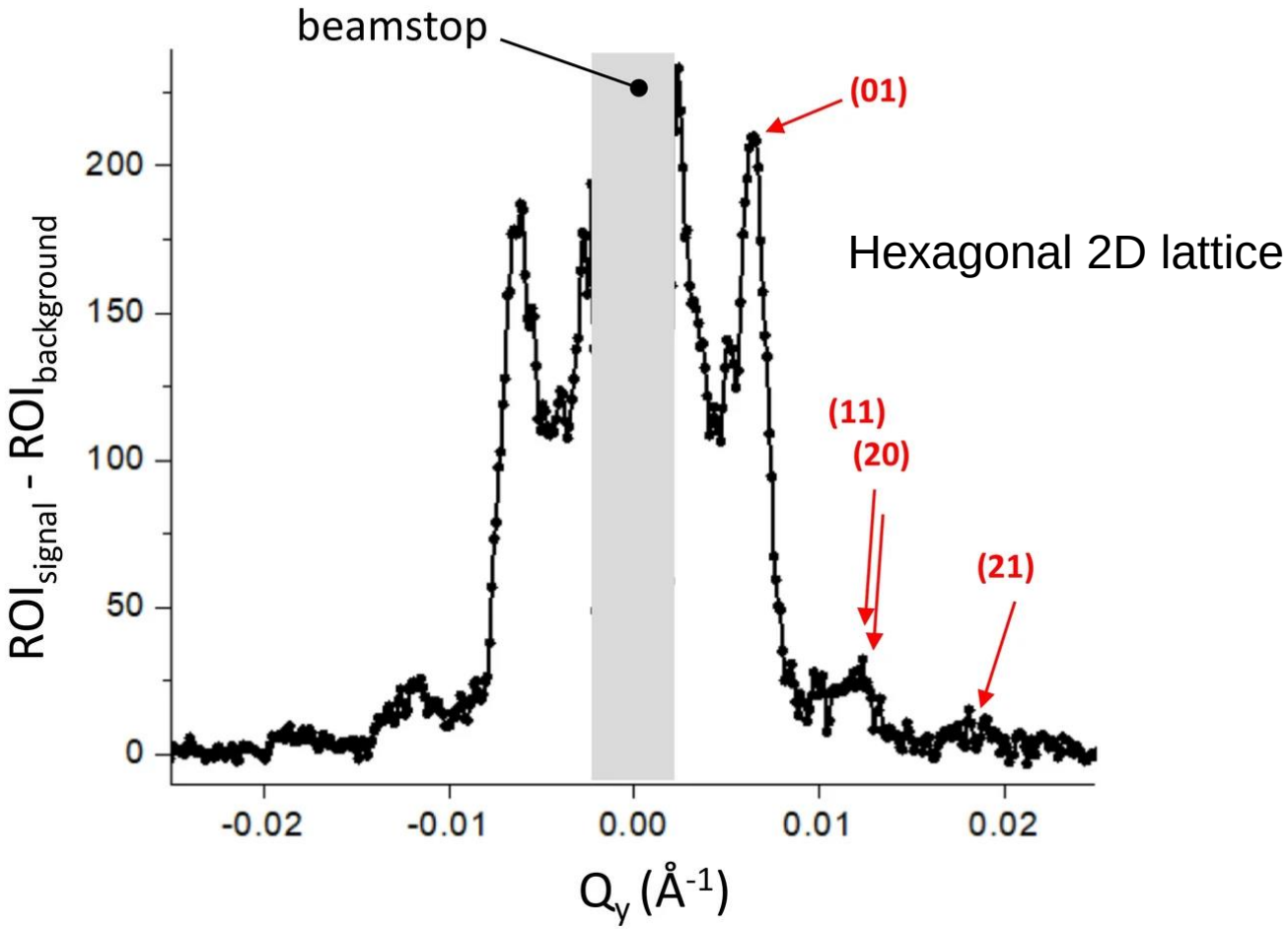
NR shows no bilayer formation on flat silica

Δd D2O = 1080.8 Å
Δd D2O hPOPC: d = 1169.2 Å
difference = 88.3 Bilayer formation

# NPs at air-water interface

Pseudo-GISANS on S-ADAM 100 nm NPs:



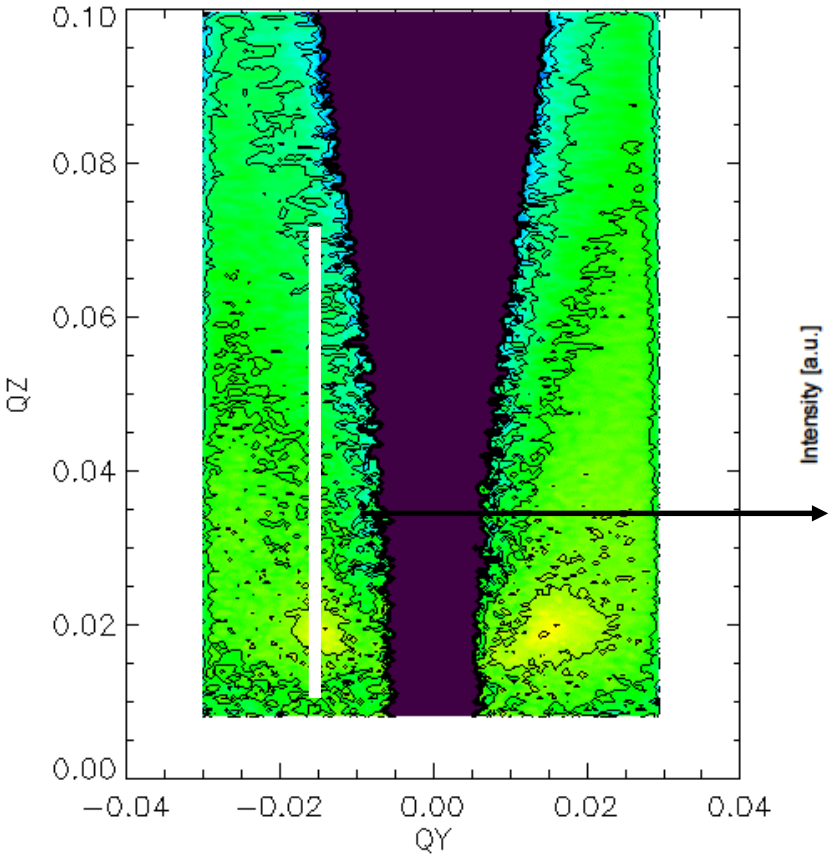

Vorobiev, A. *et al.*, *Scientific Reports* (2021) **11**, 17786.

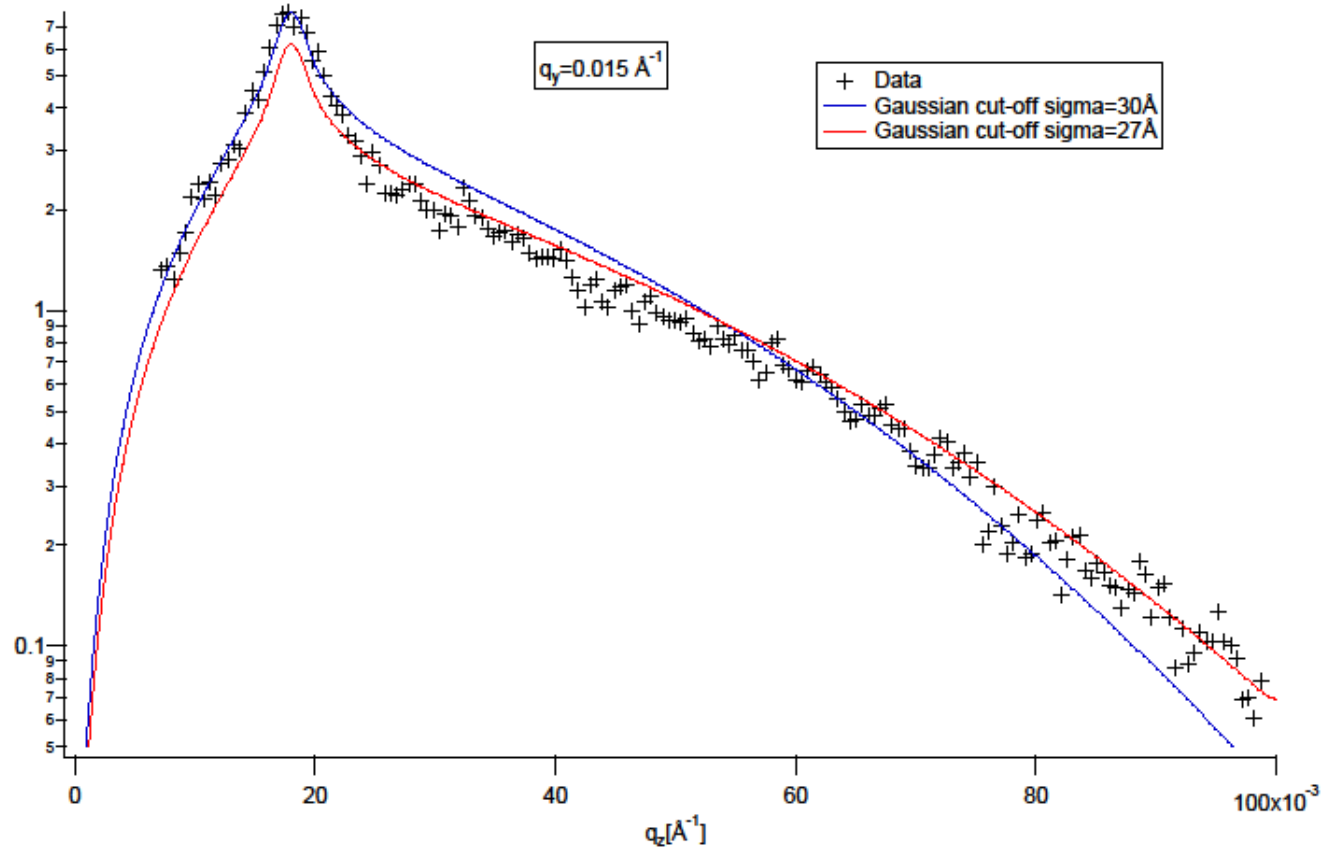
Pseudo- GISANS allows to extract the mean in-plane distance/lattice and/or size between NPs.

# NPs at air-water interface

GISANS on FIGARO 30 nm NPs
With C-TAB:

Mean in-plane distance between NPs: 41 nm
Part of NP particle in air: 10 nm




→ GISANS allows to extract the mean in-plane and out-of-plane size.

GISA

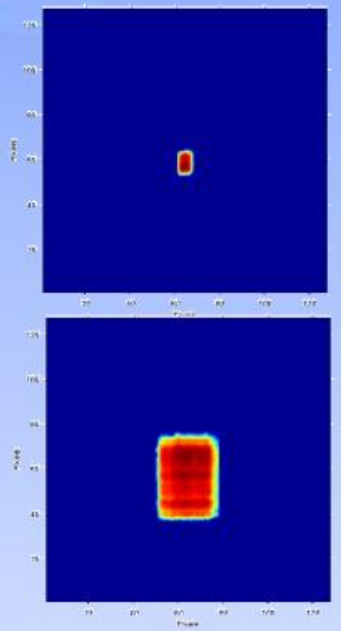
New free

Velocity selector

300

## Small-Angle Neutron Scattering: Resolution effects

- **Beam Divergence, δθ, determined by collimation distance and source aperture size**
  - Try to keep within the 'pin-hole' approximation for the sample size
  - Beam 'size' on the detector
  - Most important for detector pixels close to the beam centre

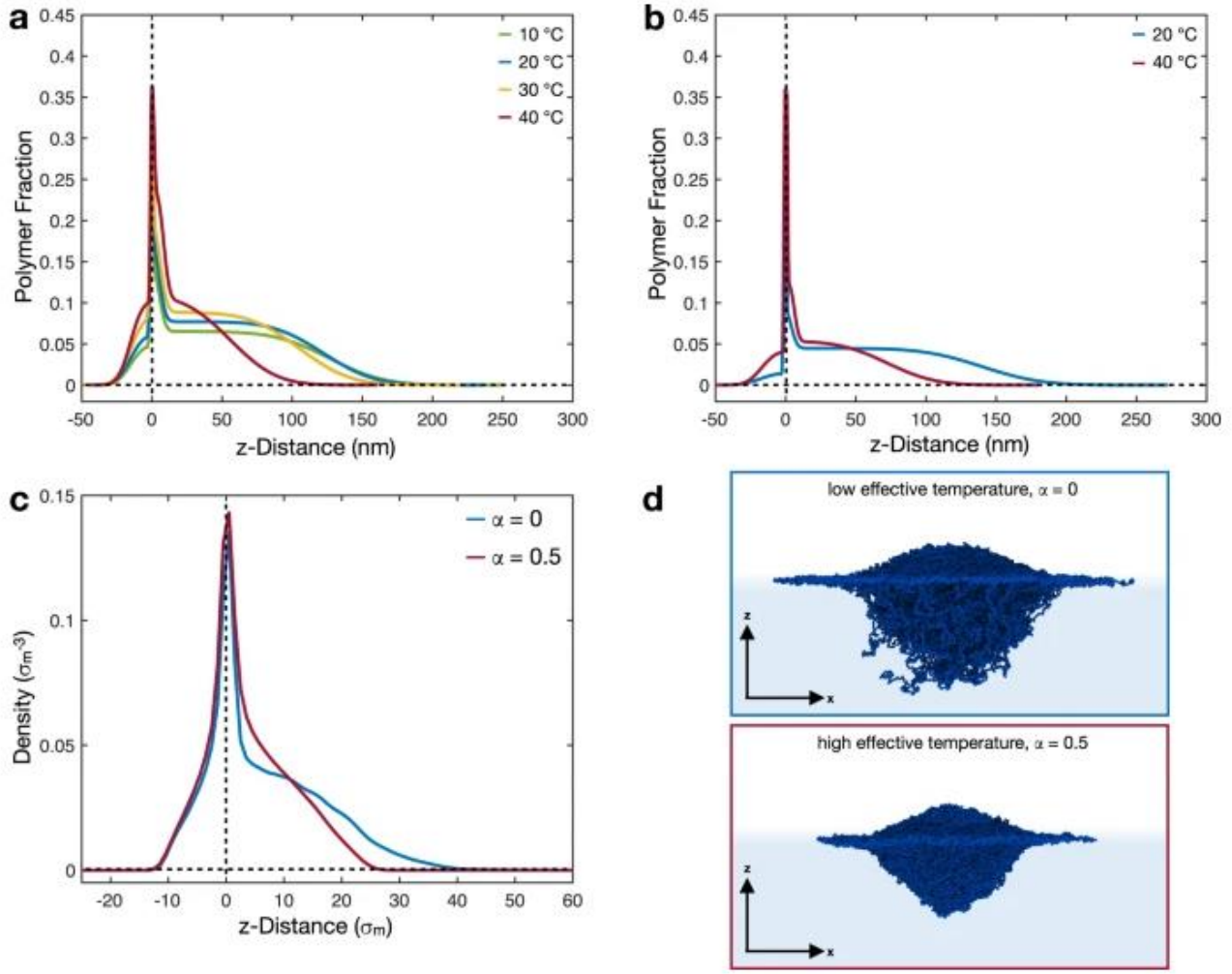



- **Wavelength spread, δλ/λ:**
  - Typically 10% from a velocity selector
  - **δλ** leads to a radial (|q|) smearing of data
  - Most important for scattering at higher angles .....
    ..... and could be relaxed further under some conditions to gain flux .....
    ..... but need also an option for higher resolution for some highly ordered systems

Paracini *et a*

# Microgels at the air/liquid interface

**Fig. 2: Structure of 5 mol% cross-linked microgels at liquid interfaces.**




Boschenek *et al.*, Nature Communications **13** 3744 (2022).