

Collapse Process of Langmuir Monolayers Monitored by Imaging Ellipsometry

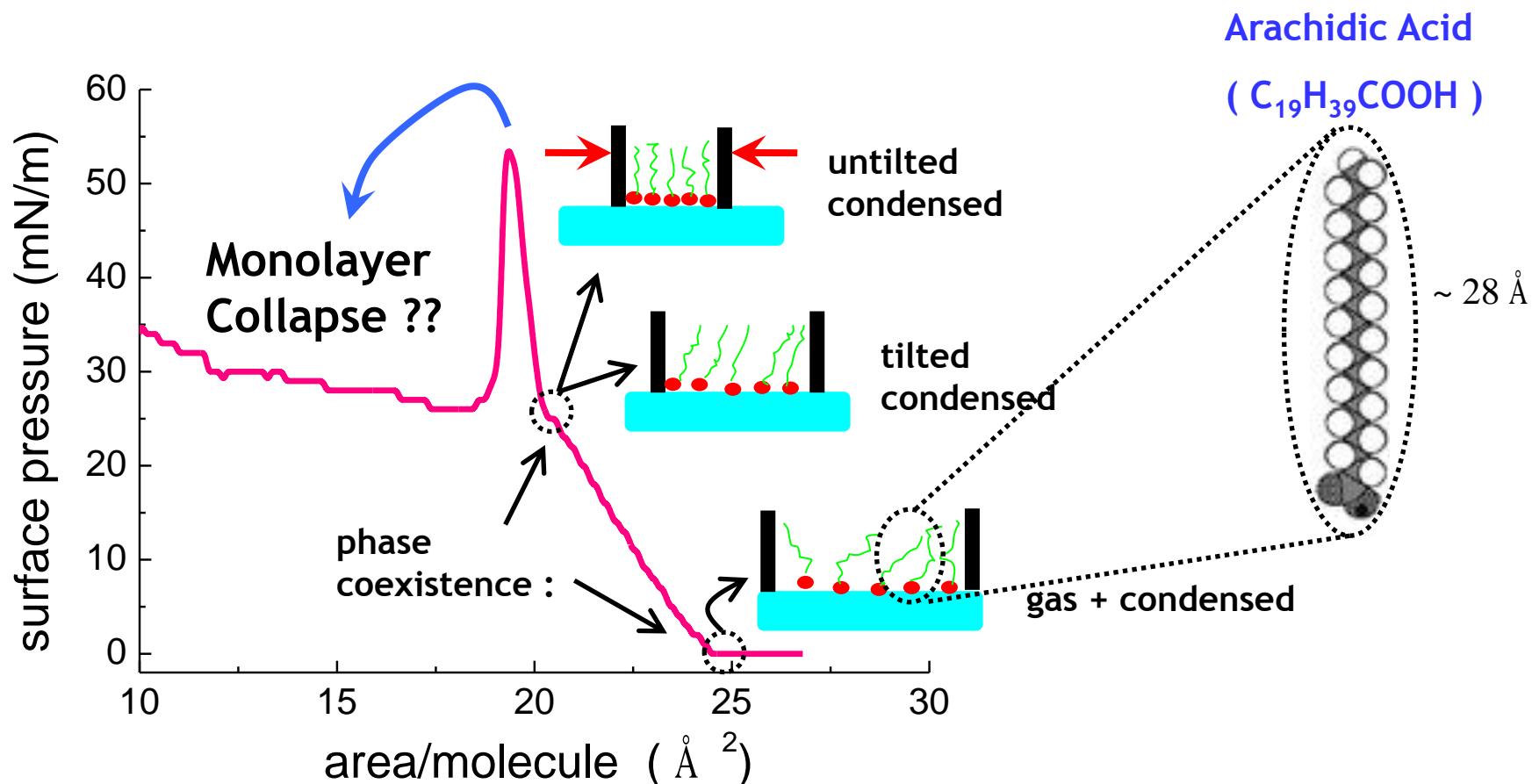
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³*Ames Laboratory, Iowa state University*

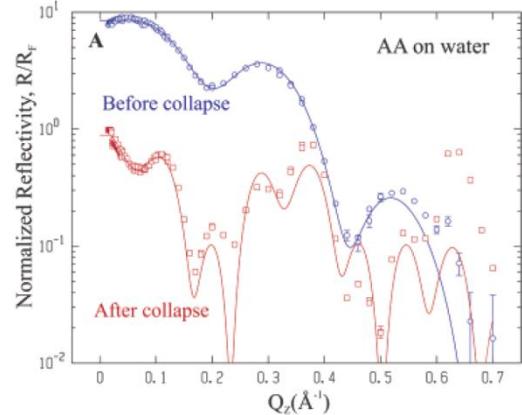
Introduction - Phase diagram of Langmuir monolayer



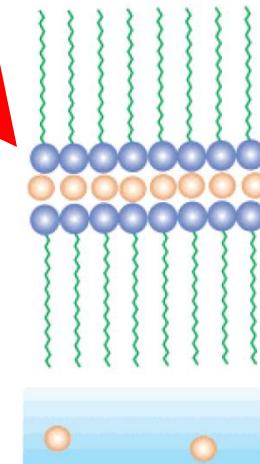
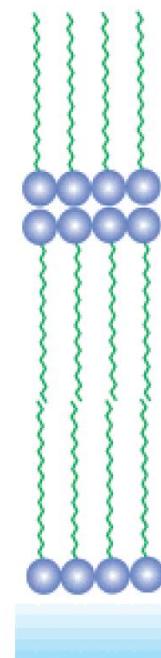
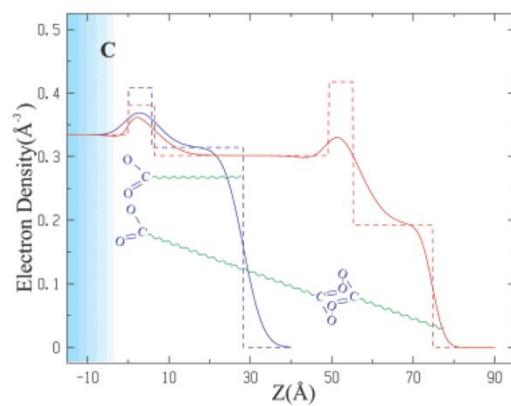
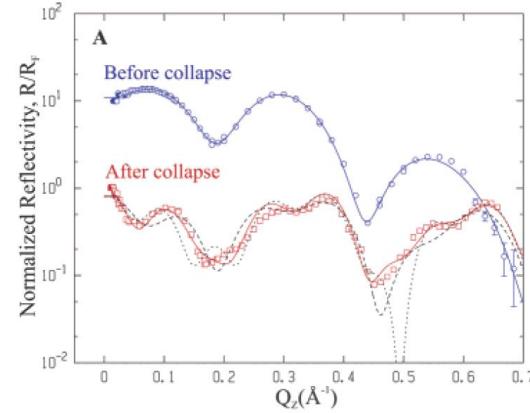
Collapse of the Langmuir monolayer

X-ray reflectivity

Fatty acid on pure water

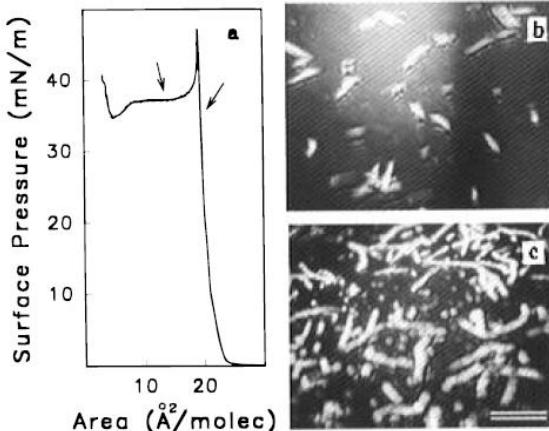


Fatty acid on 1 mM CaCl_2 solution

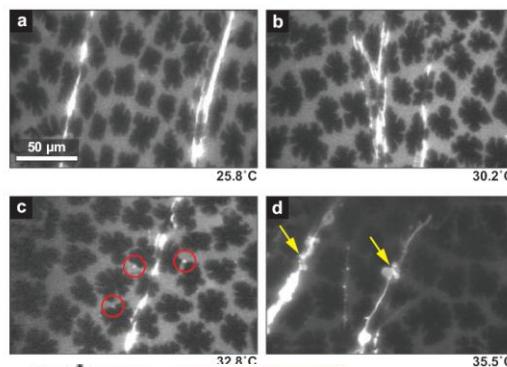


(Vaknin et al., Langmuir (2007))

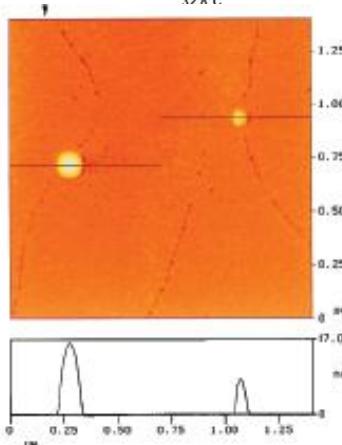
Collapse of the Langmuir monolayer: previous experiments



Brewster Angle Microscopy (BAM)
(Angelova et al., J. Phys. Chem. (1996))

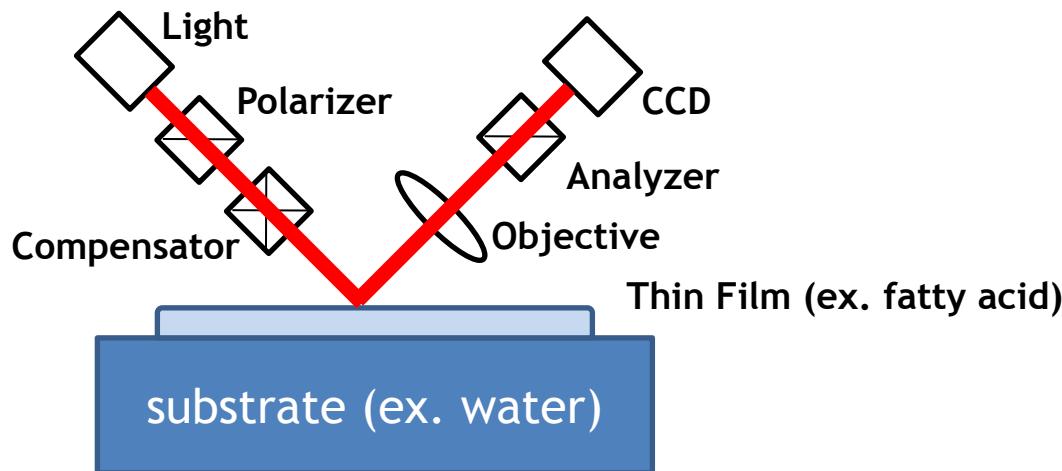


Fluorescence Microscopy
(Lee, Annu. Rev. Phys. Chem. (2008))



AFM on DPPC films transferred to mica
(Schief. J. Phys. Chem. B (2000))

Experimental setup - imaging ellipsometer

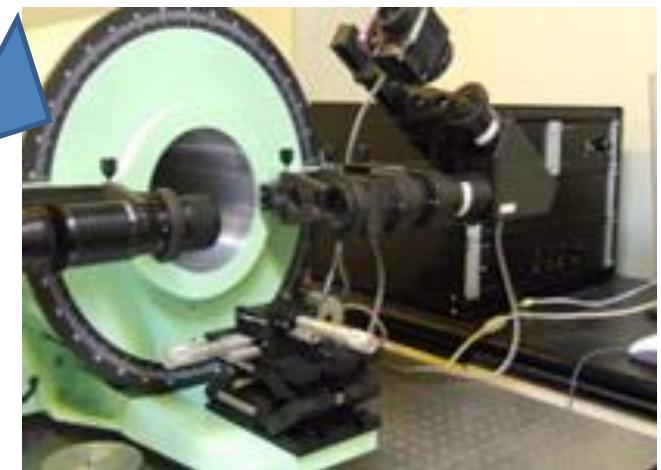
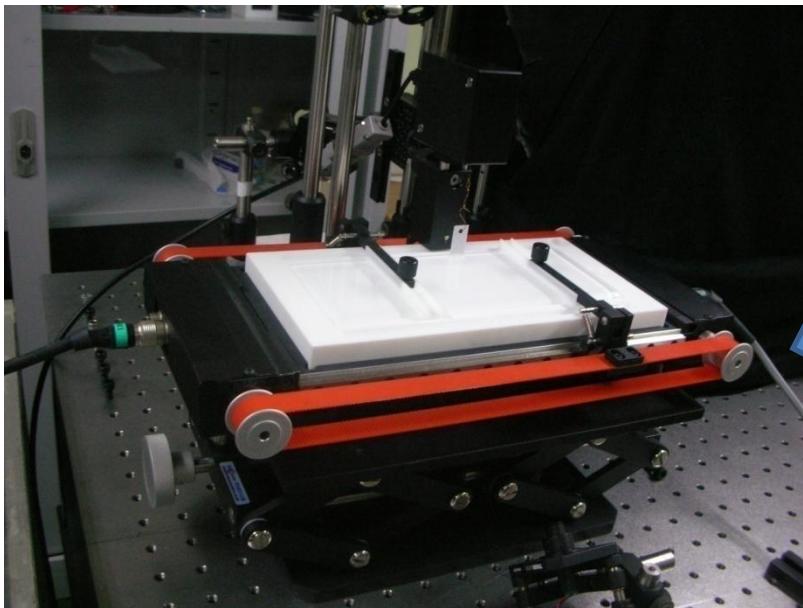


$$r_p / r_s = (\tan \psi) e^{i\Delta} : \text{complex reflectance ratio}$$

→ Δ, ψ : ellipsometric angle obtained

→ n, d : thickness and refractive index of the film

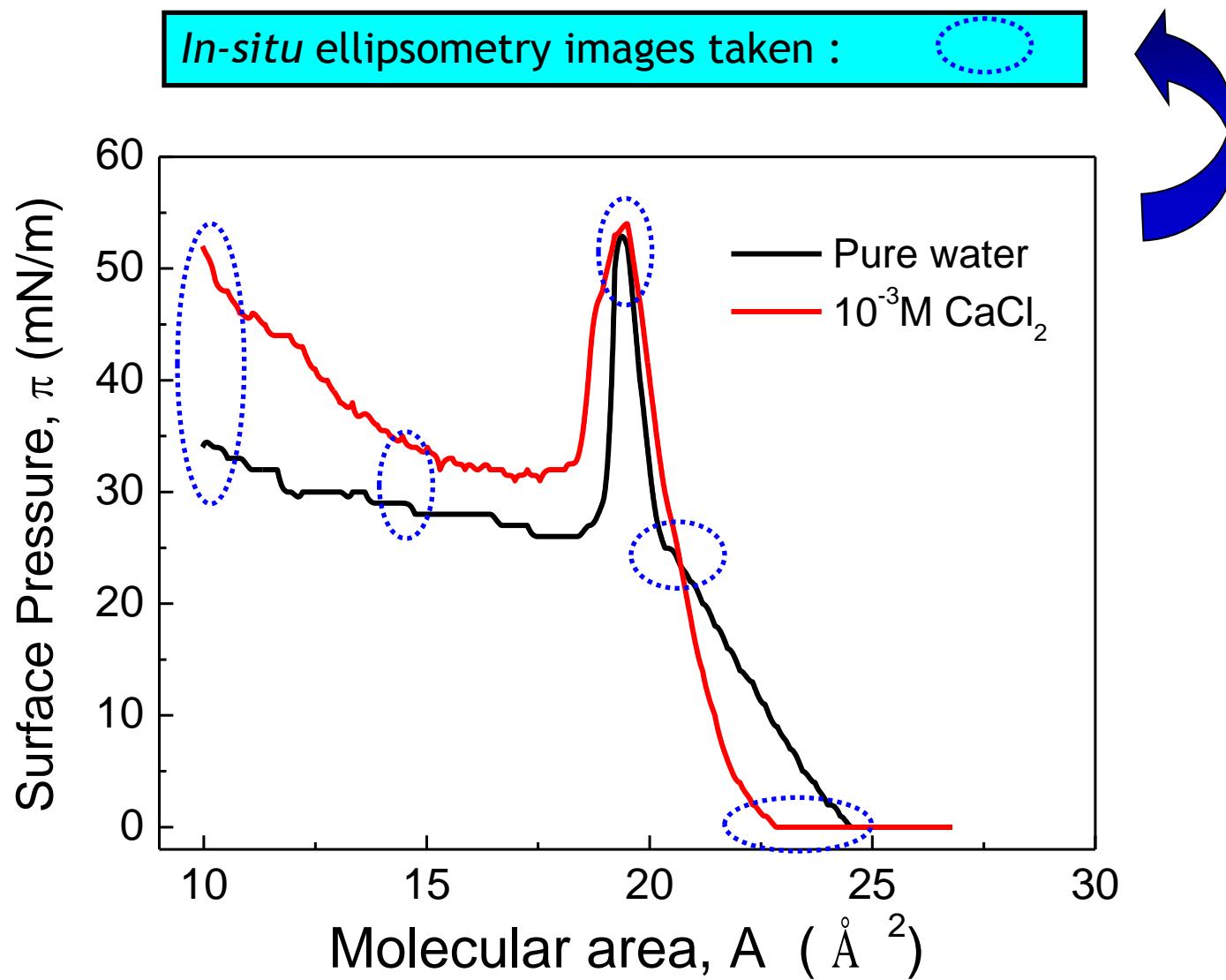
Experimental setup - sample preparation



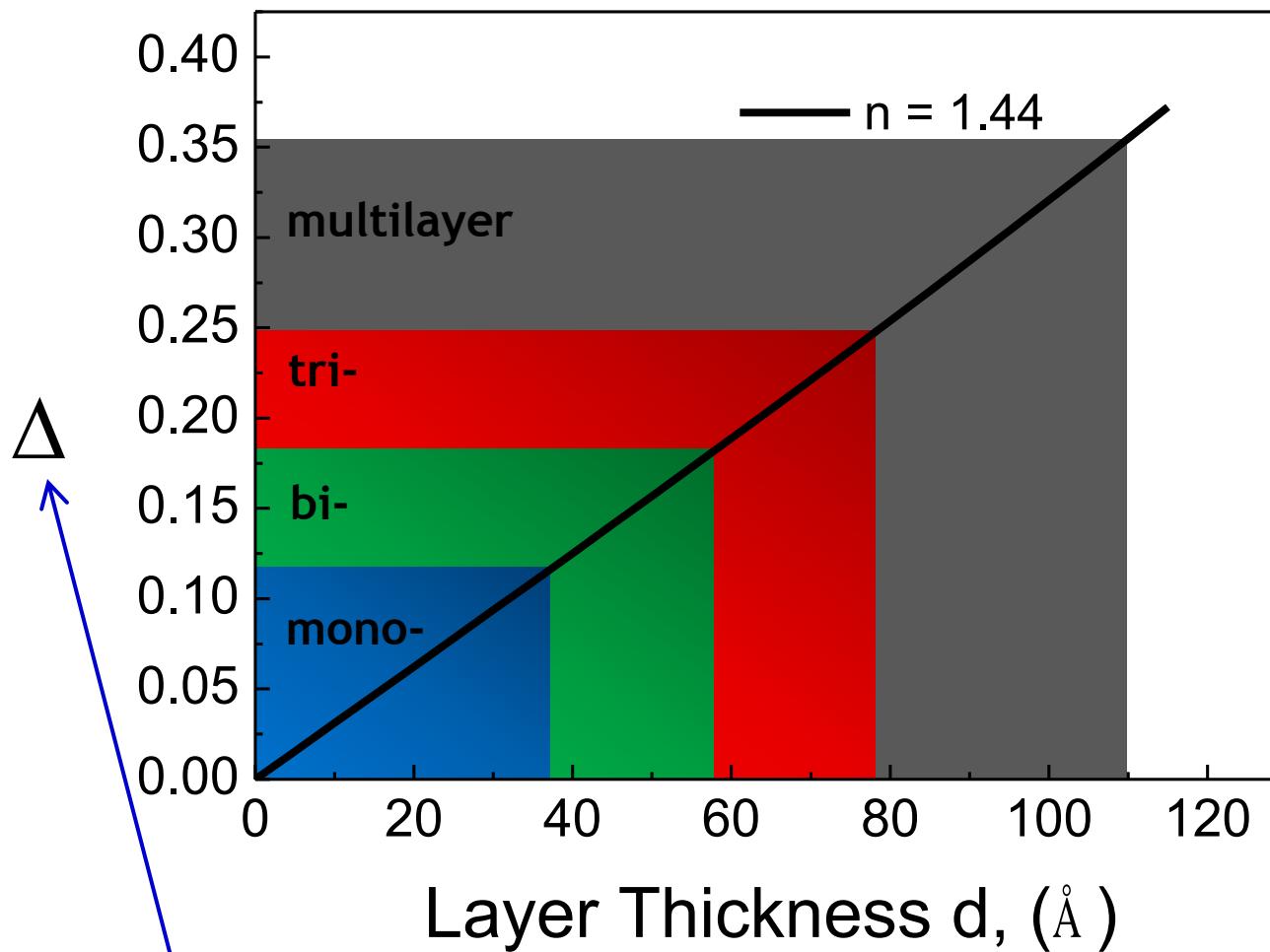
- wavelength : 632 nm
- incidence angle : 55°

- Molecule: arachidic acid (AA, $C_{19}H_{39}COOH$) : $n_1 = 1.44$
(Ducharme et al., Langmuir (2001))
- π -A isotherm barrier speed : ~ 0.58 Å²/min
- subphase: pure water or 10⁻³ M CaCl₂ solution: $n_2 = 1.33$

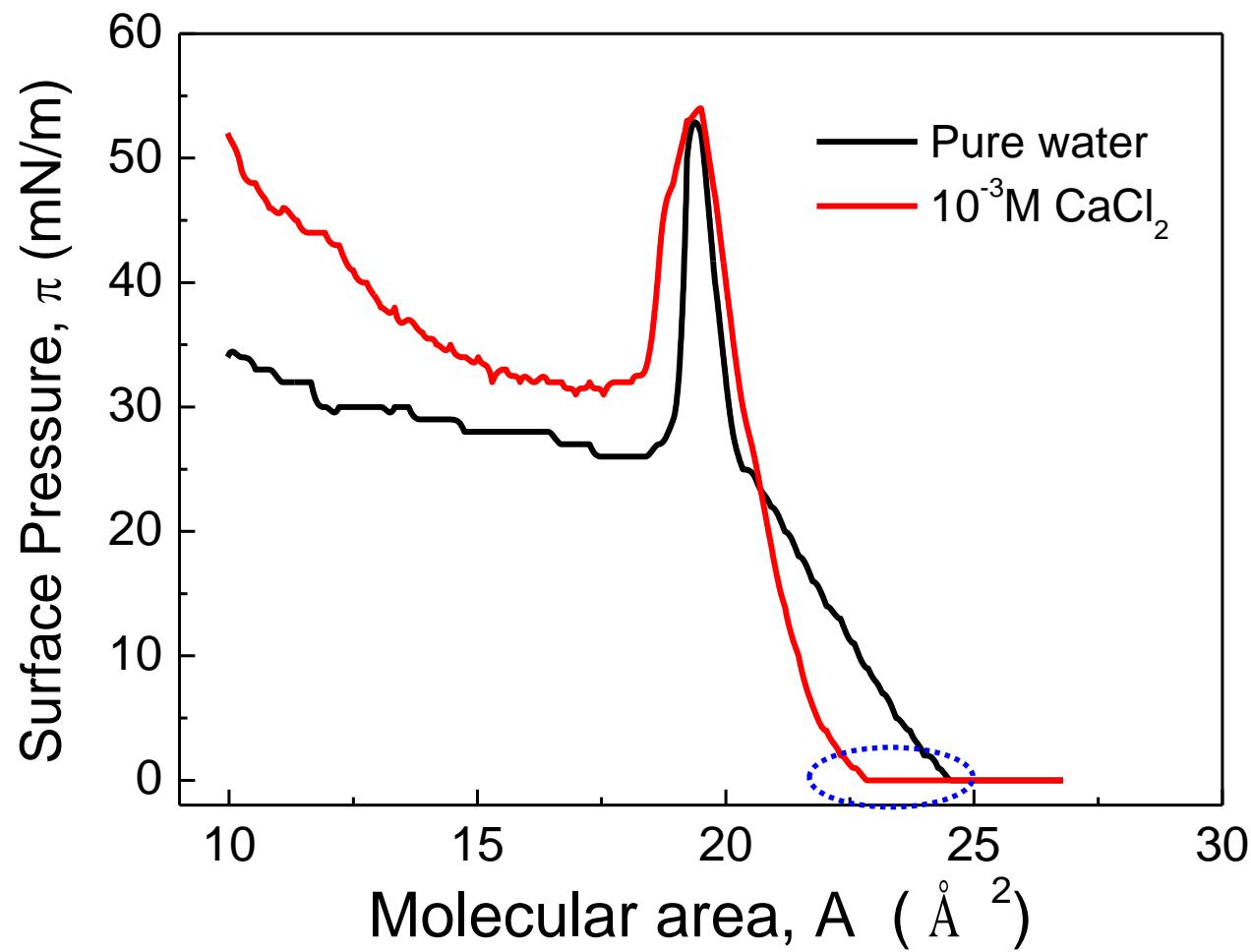
Experimental result - π -A isotherm of AA monolayer



Film thickness from calculation

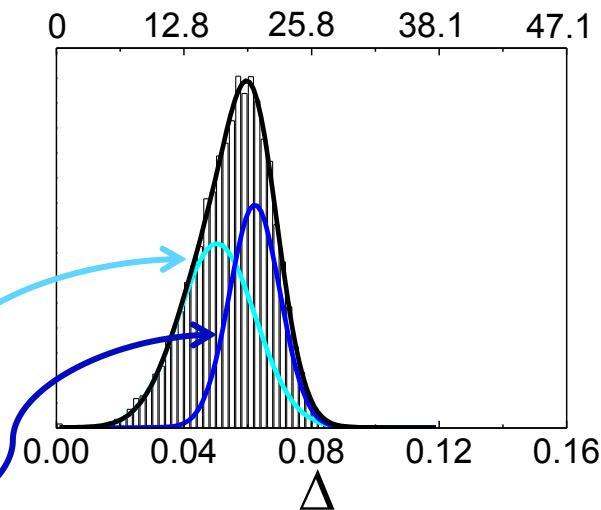
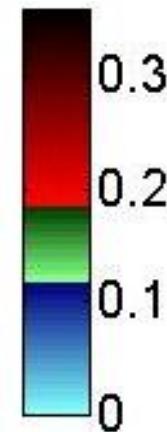
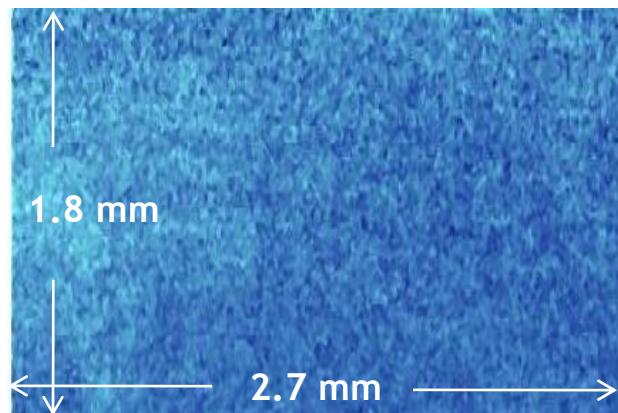


$r_p / r_s = (\tan \psi) e^{i\Delta}$: complex reflectance ratio



Experimental result - gas + condensed phase/ Δ mapping

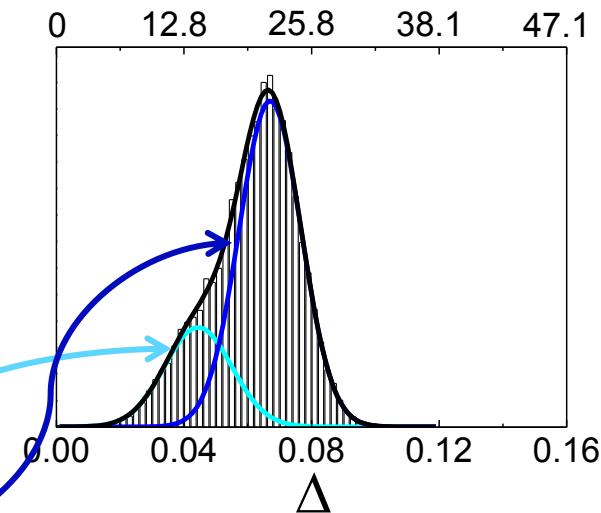
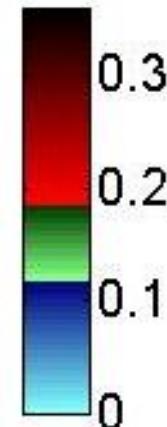
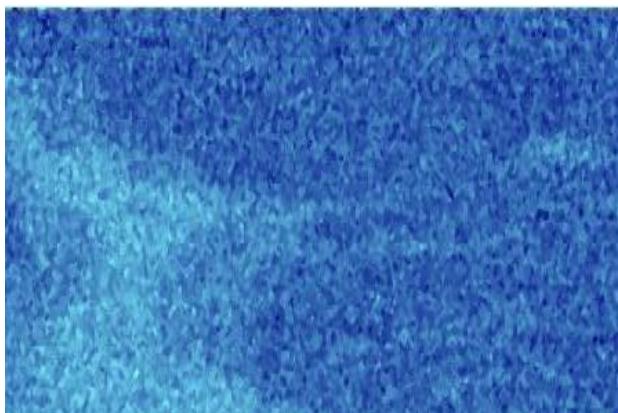
- Pure water / at 24 \AA^2



» gas : $\Delta = 0.0503$ ($d_s \sim 16.1 \text{ \AA}$), $65.3 \% \pm 3.3$

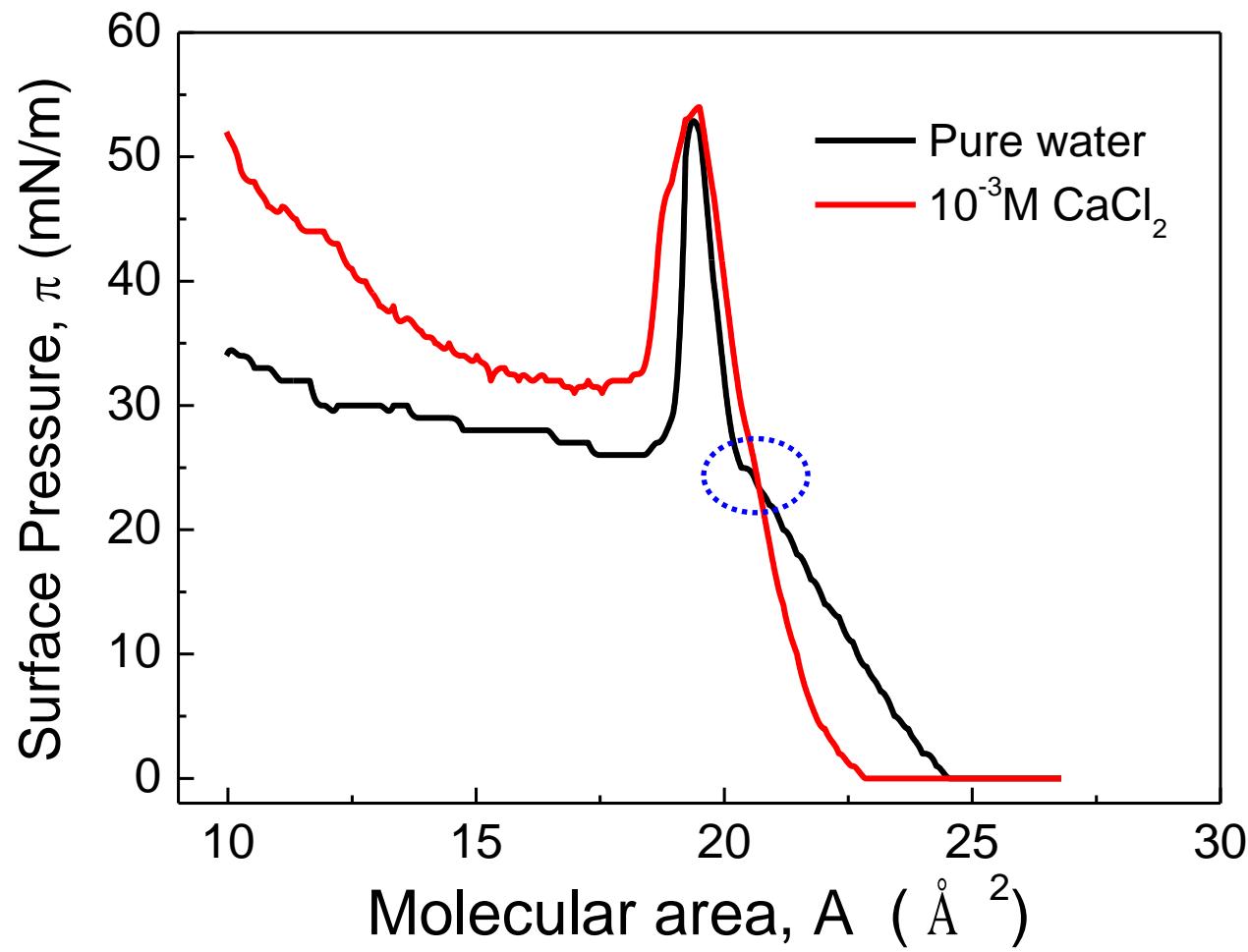
» condensed : $\Delta = 0.062$ ($d_s \sim 20.0 \text{ \AA}$), $34.7 \% \pm 3.1$

- 10^{-3} M CaCl_2 / at 22.5 \AA^2



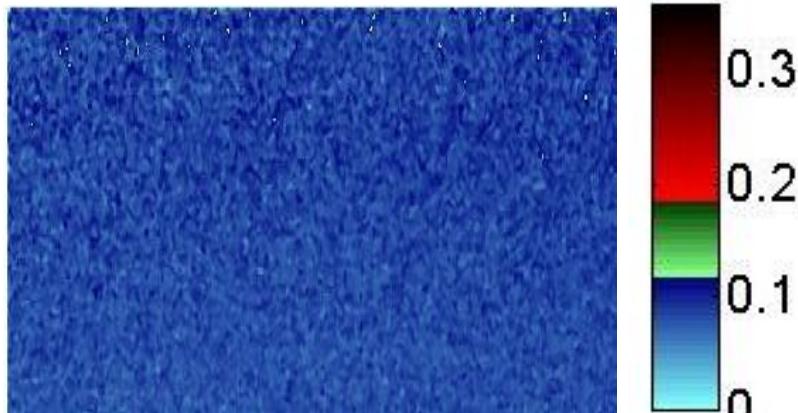
» gas : $\Delta = 0.044$ ($d_s \sim 14.2 \text{ \AA}$), $26.6 \% \pm 0.87$

» condensed : $\Delta = 0.067$ ($d_s \sim 21.5 \text{ \AA}$), $73.4 \% \pm 0.08$

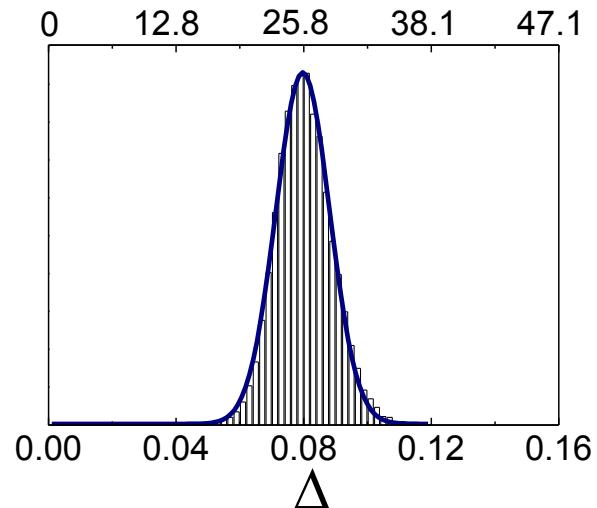


Experimental result - the onset of the untilted phase/ Δ mapping

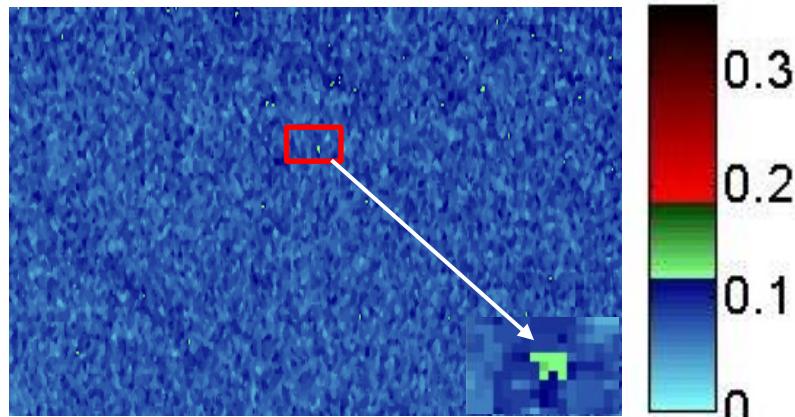
- Pure water / at 20.5 Å²



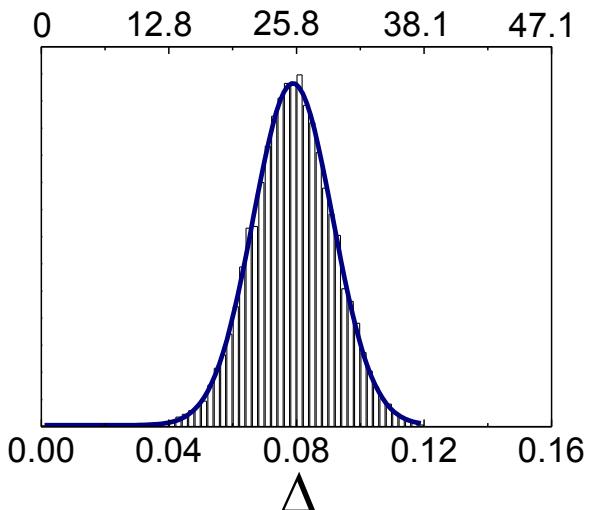
» untilted : $\Delta = 0.079$ ($d_s \sim 25.4$ Å)

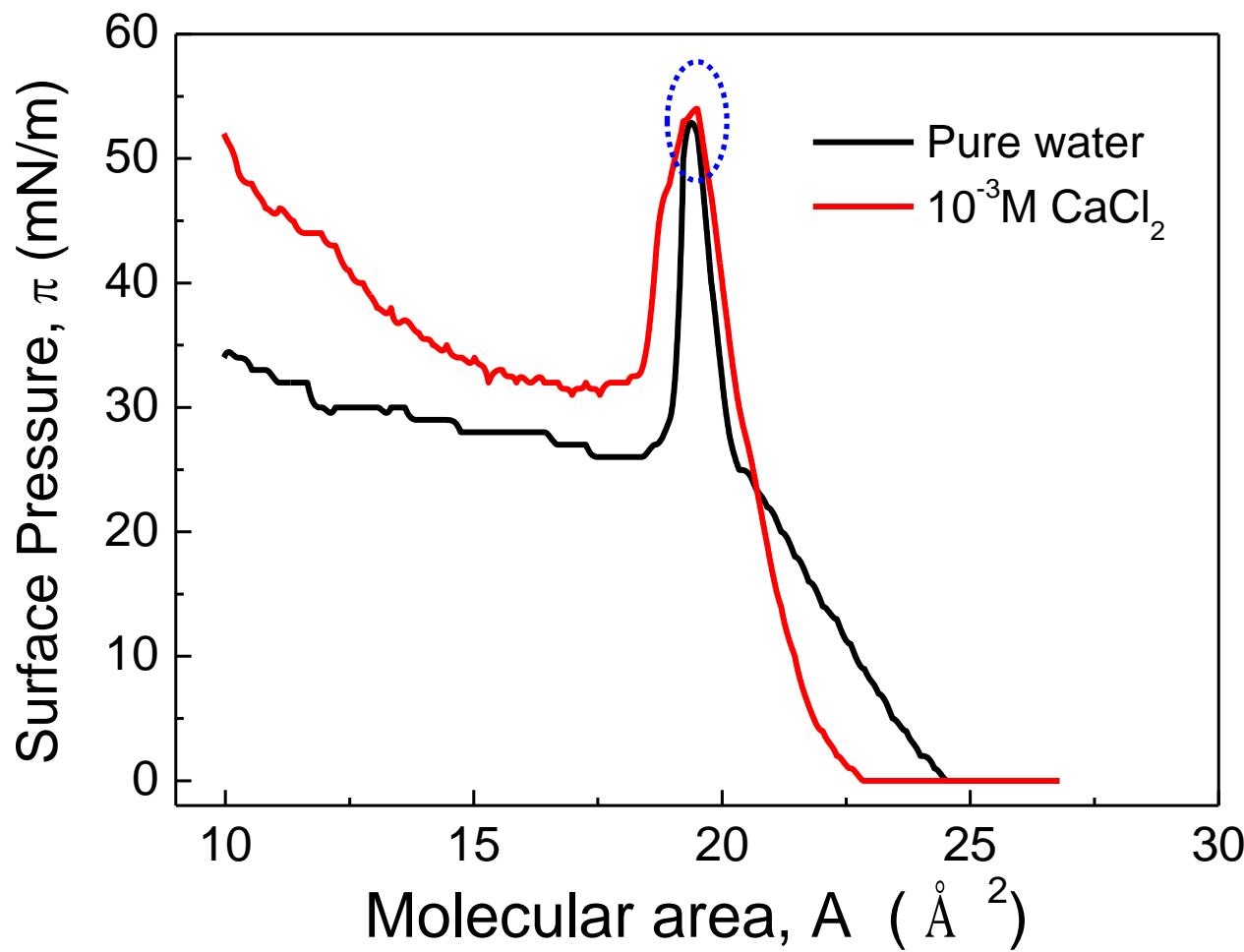


- 10⁻³ M CaCl₂ / at 20.5 Å²



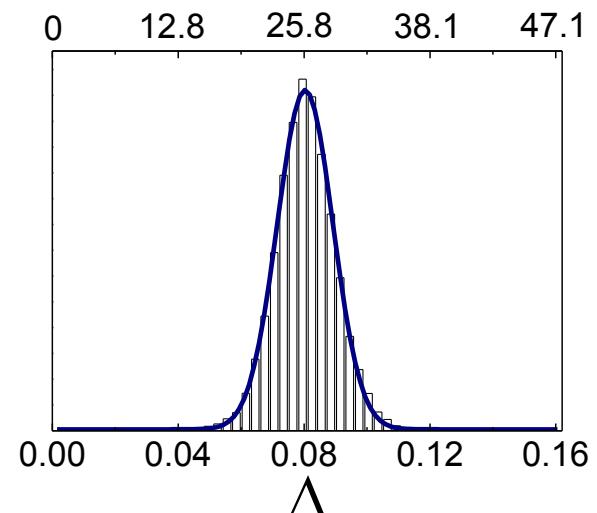
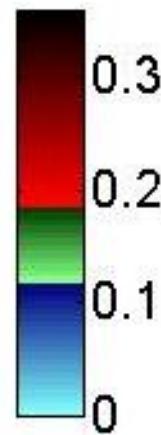
» untilted : $\Delta = 0.079$ ($d_s \sim 25.4$ Å)





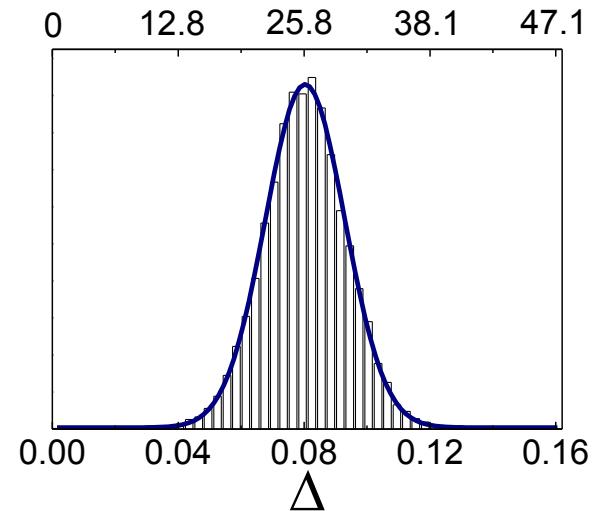
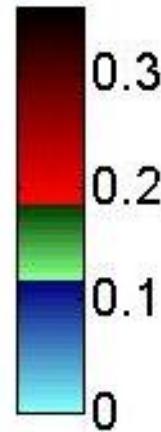
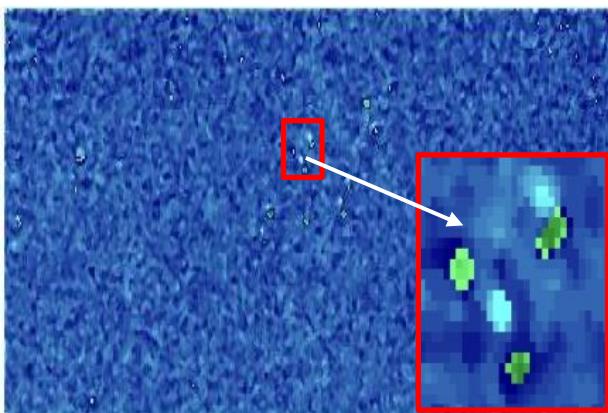
Experimental result - close-packed monolayer(A_0)/ Δ mapping

- Pure water / at 19.5 Å²



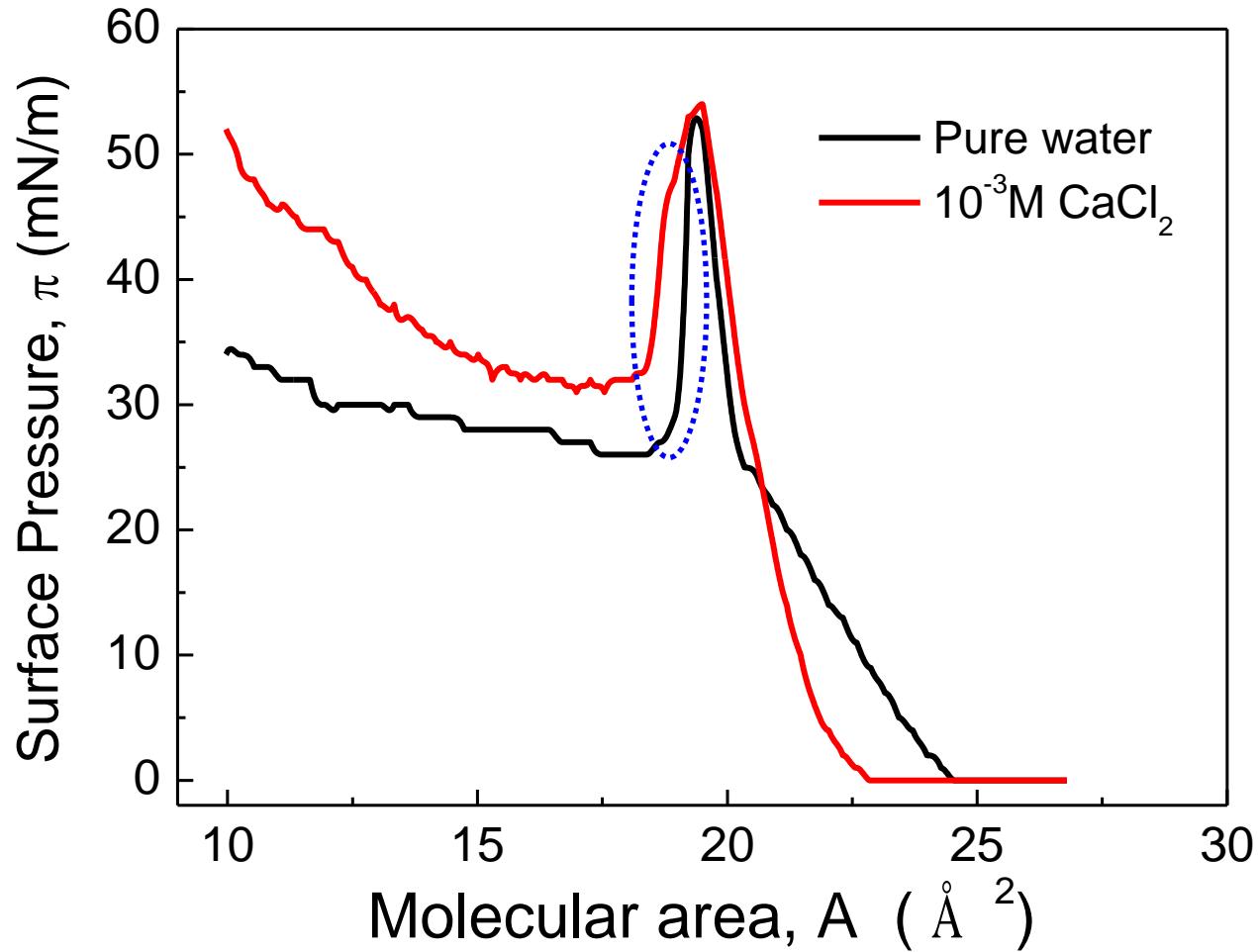
» close-packed monolayer : $\Delta = 0.080$ ($d_s \sim 25.8$ Å)

- 10⁻³ M CaCl₂ / at 19.5 Å²



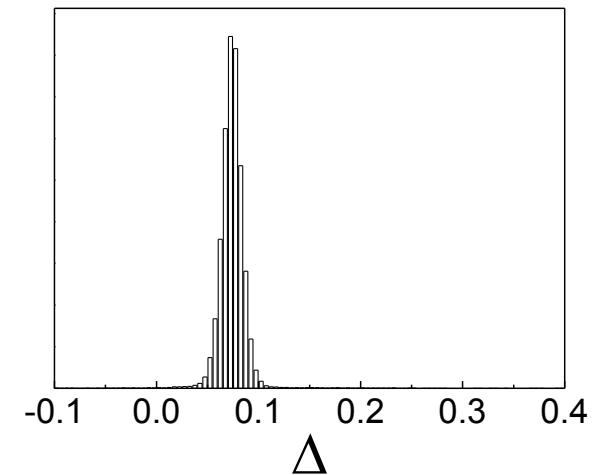
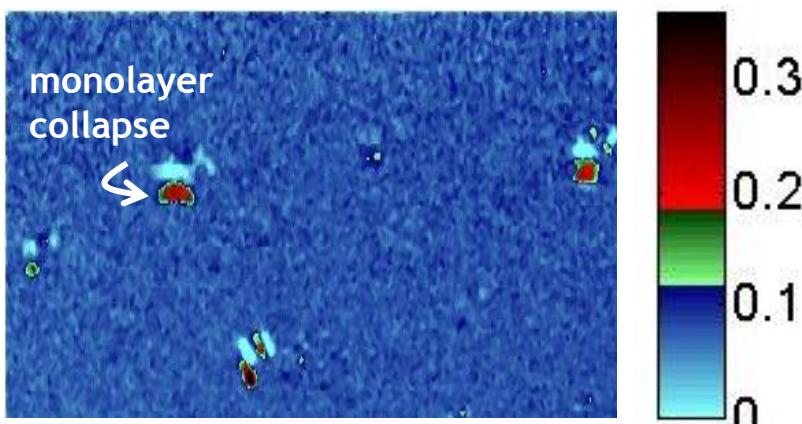
» close-packed monolayer : $\Delta = 0.080$ ($d_s \sim 25.8$ Å)

Monolayer collapse

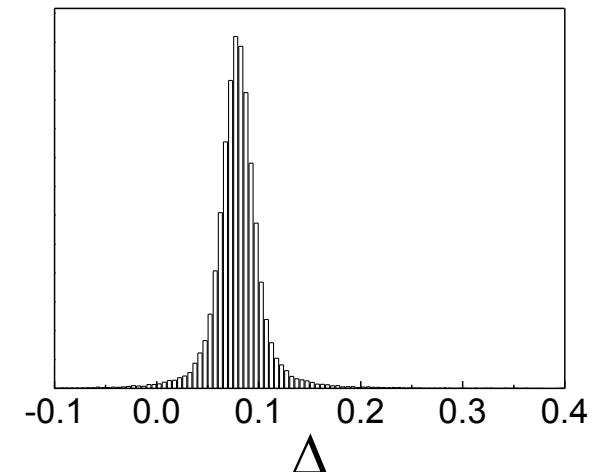
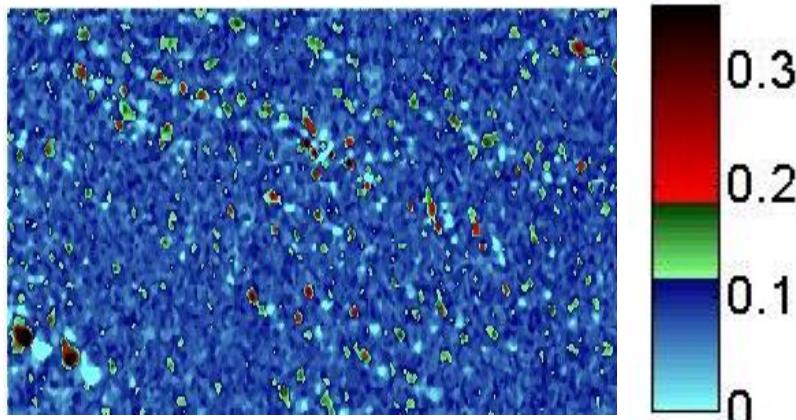


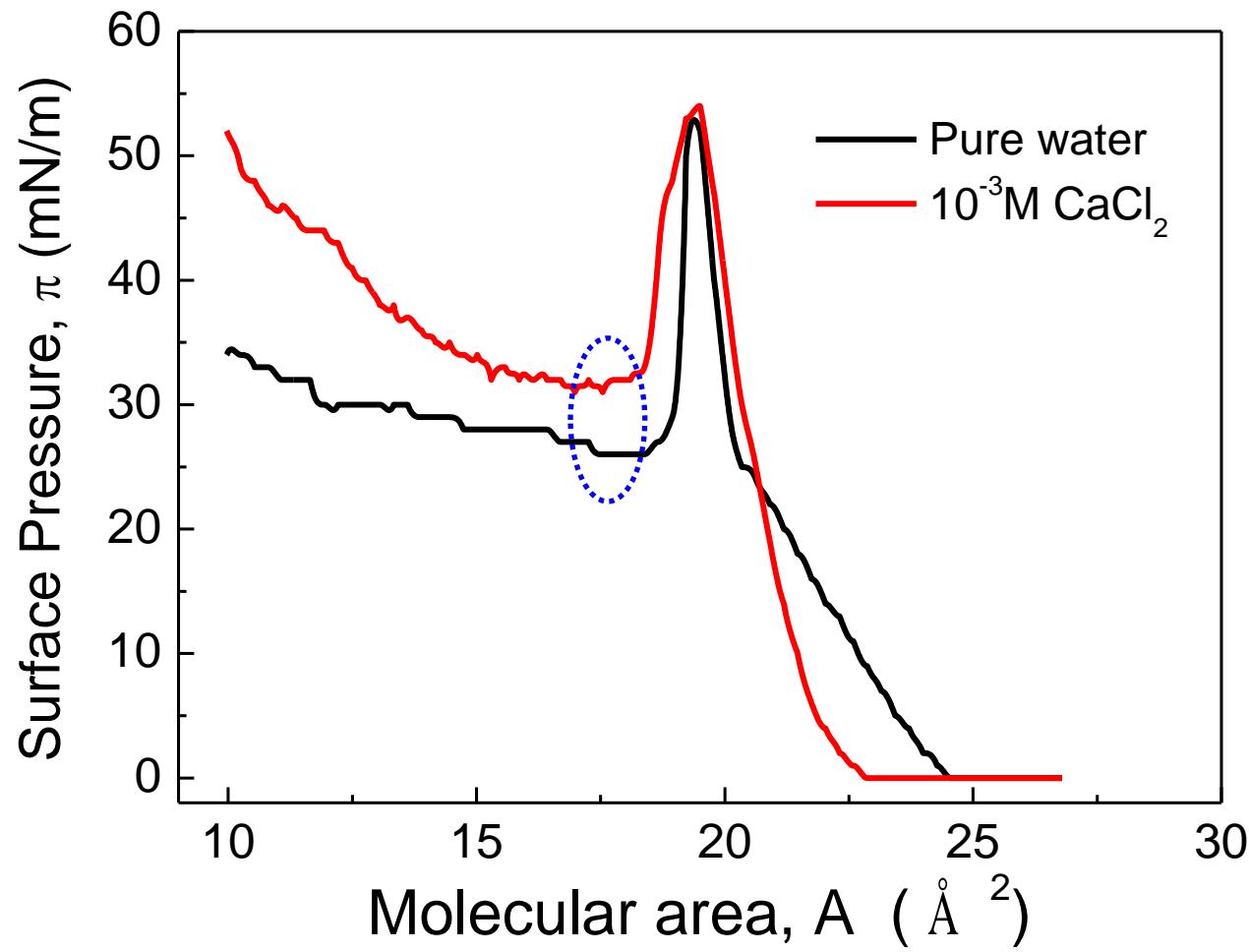
Experimental result - begin to collapse/ Δ mapping

- Pure water / at 18.5 Å²



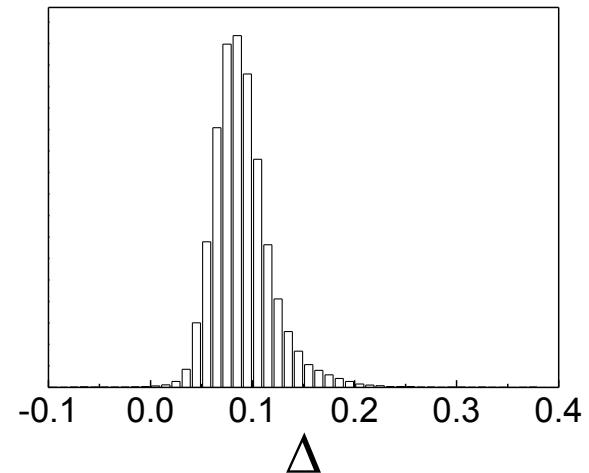
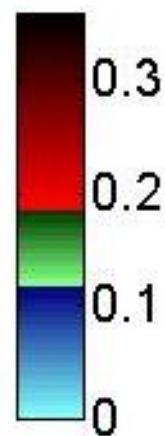
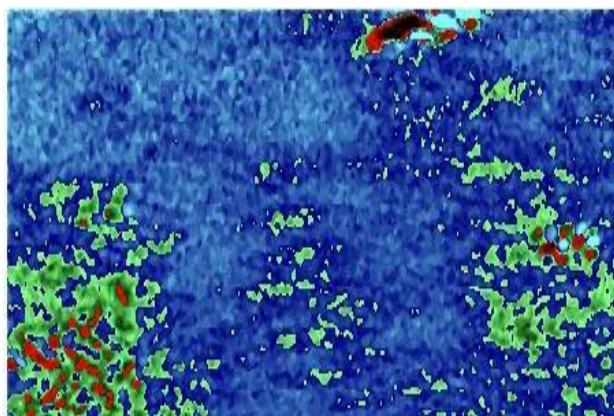
- 10⁻³ M CaCl₂ / at 18.5 Å²



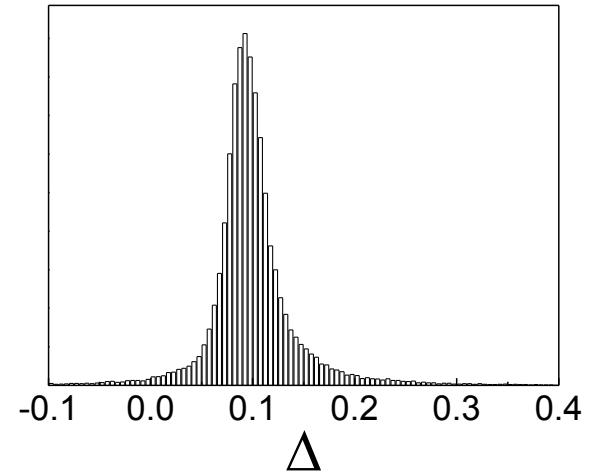
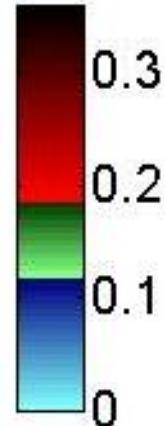
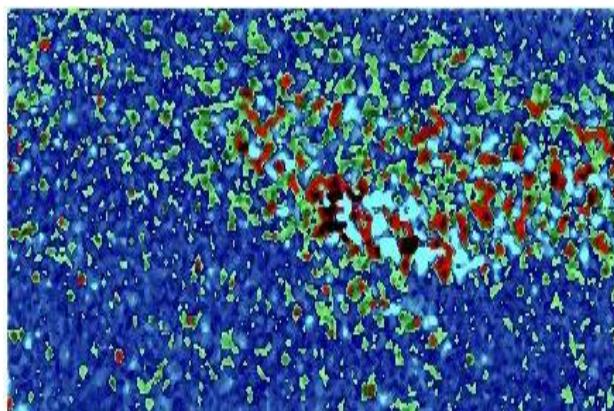


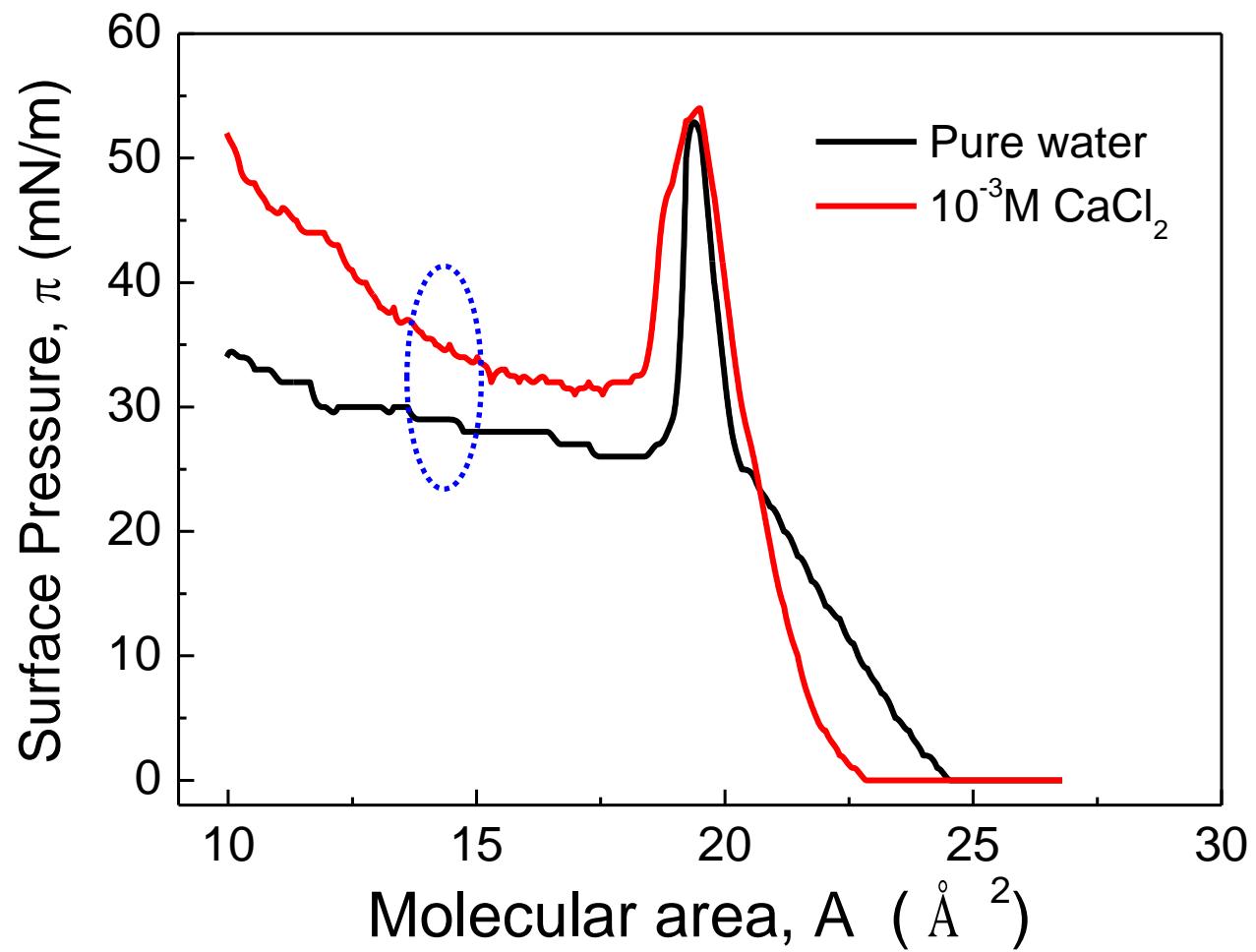
Experimental result - collapsed/ Δ mapping

- Pure water / at 17.1 Å²



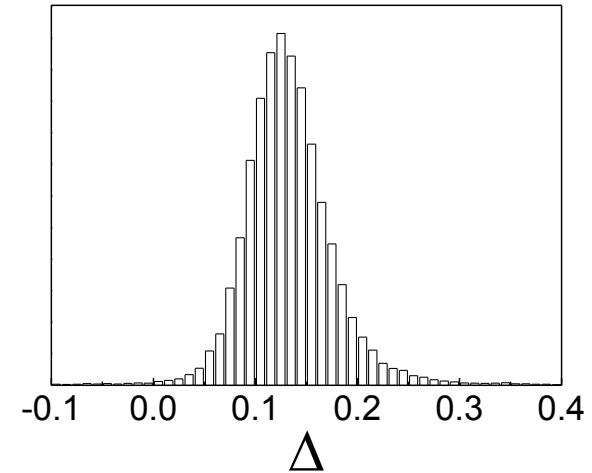
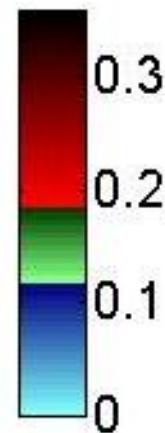
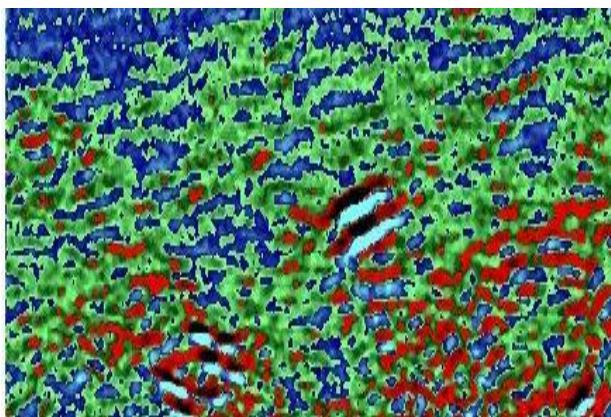
- 10⁻³ M CaCl₂ / at 17.5 Å²



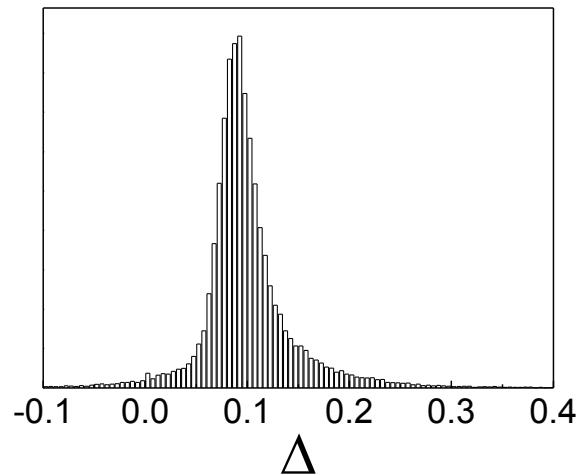
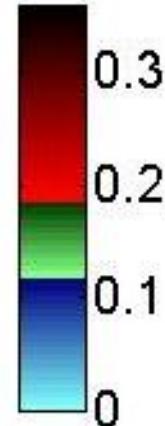
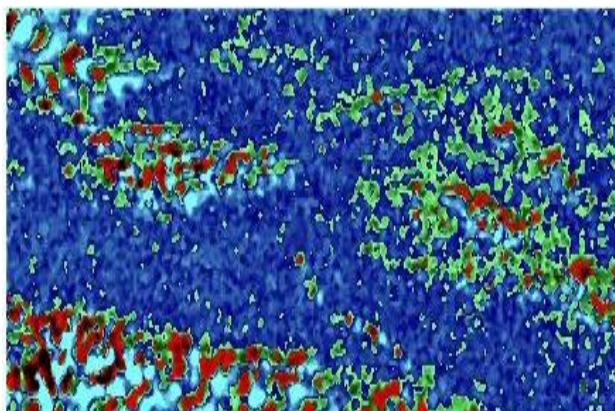


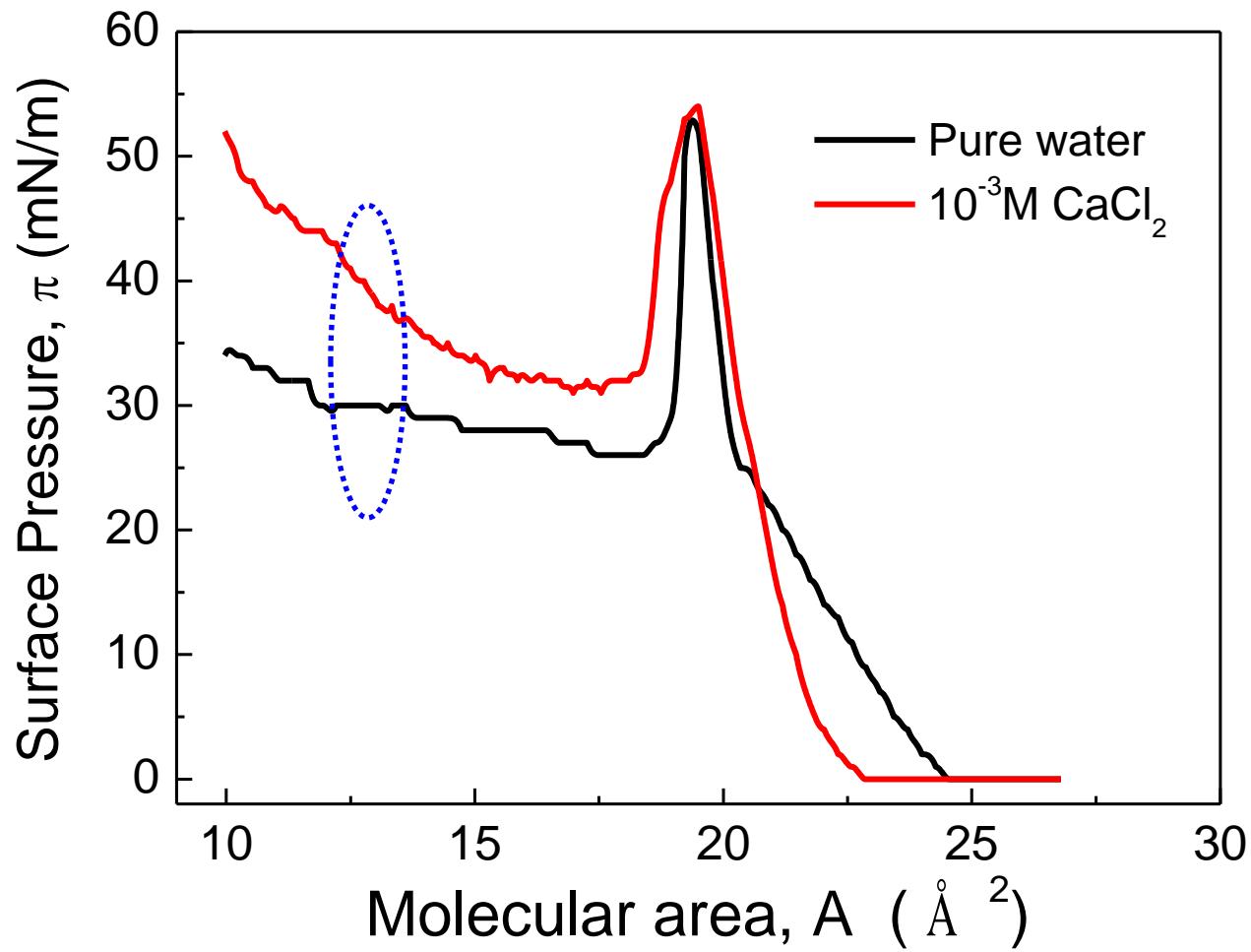
Experimental result - collapsed/ Δ mapping

- Pure water / at 14.5 Å²



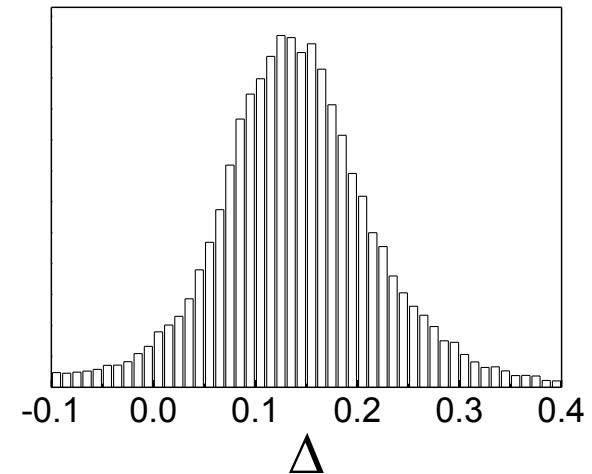
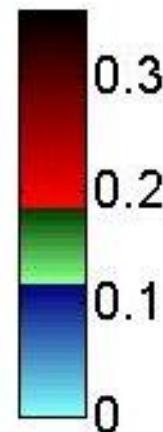
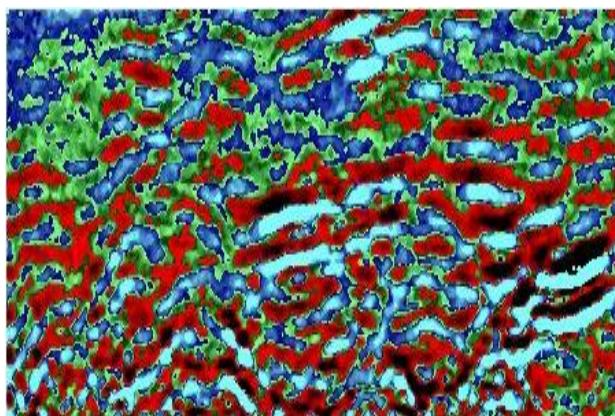
- 10⁻³ M CaCl₂ / at 13.5 Å²



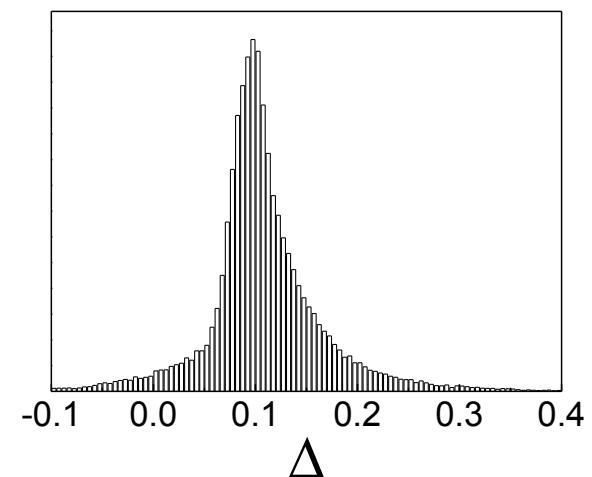
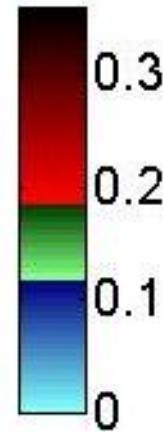
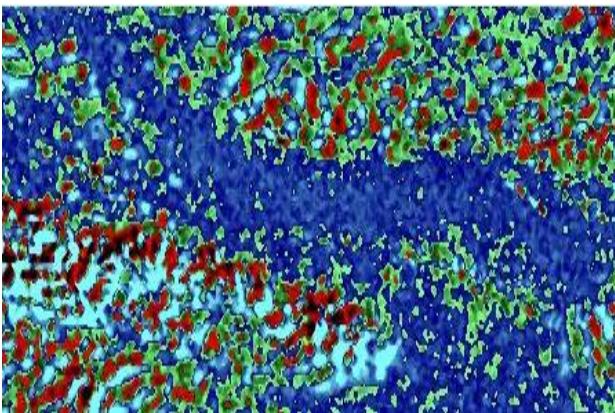


Experimental result - collapsed/ Δ mapping

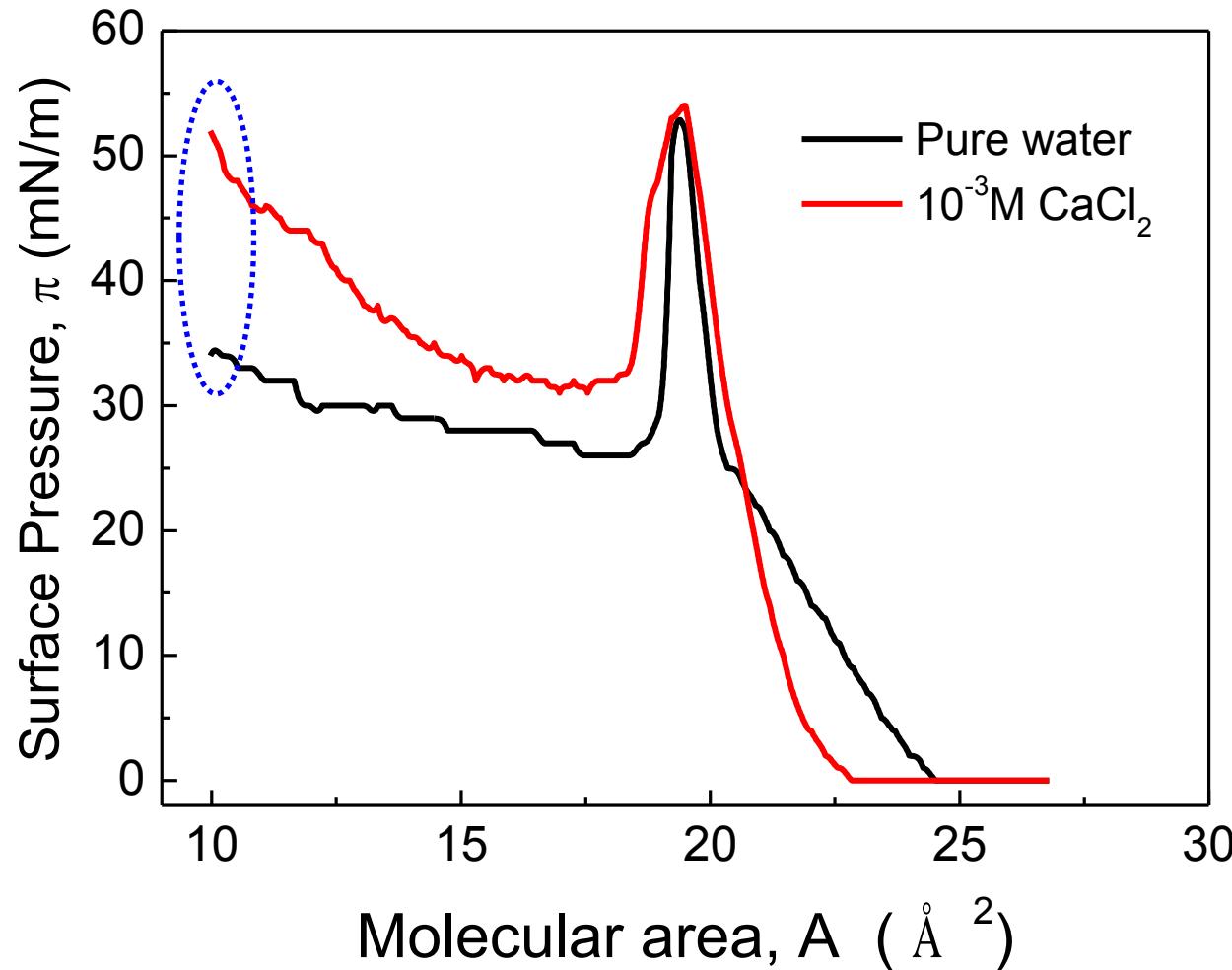
- Pure water / at 12.5 Å²



- 10⁻³ M CaCl₂ / at 12.3 Å²

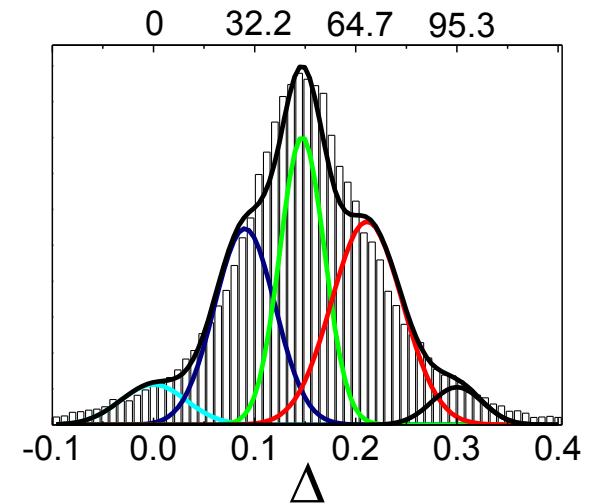
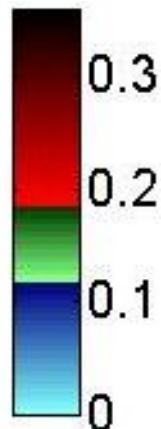
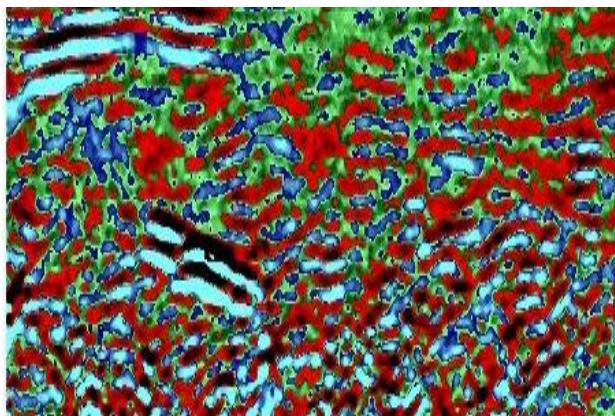


Final stage of the collapse process

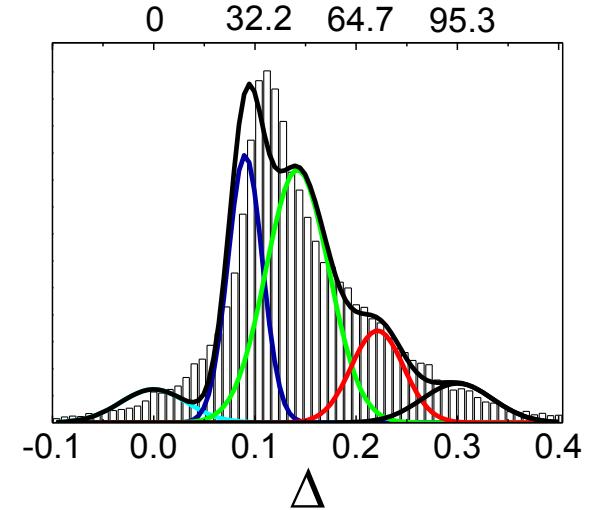
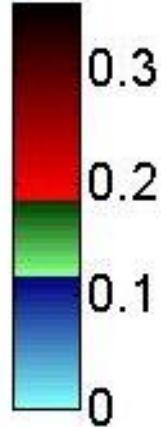
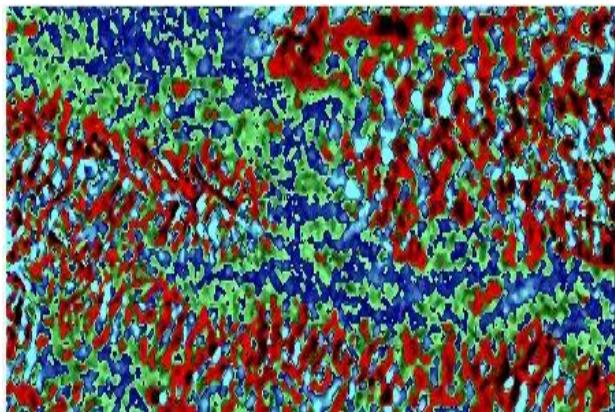


Experimental result - collapsed film ($A_0/2$)/ Δ mapping

- Pure water / at 9.5 \AA^2

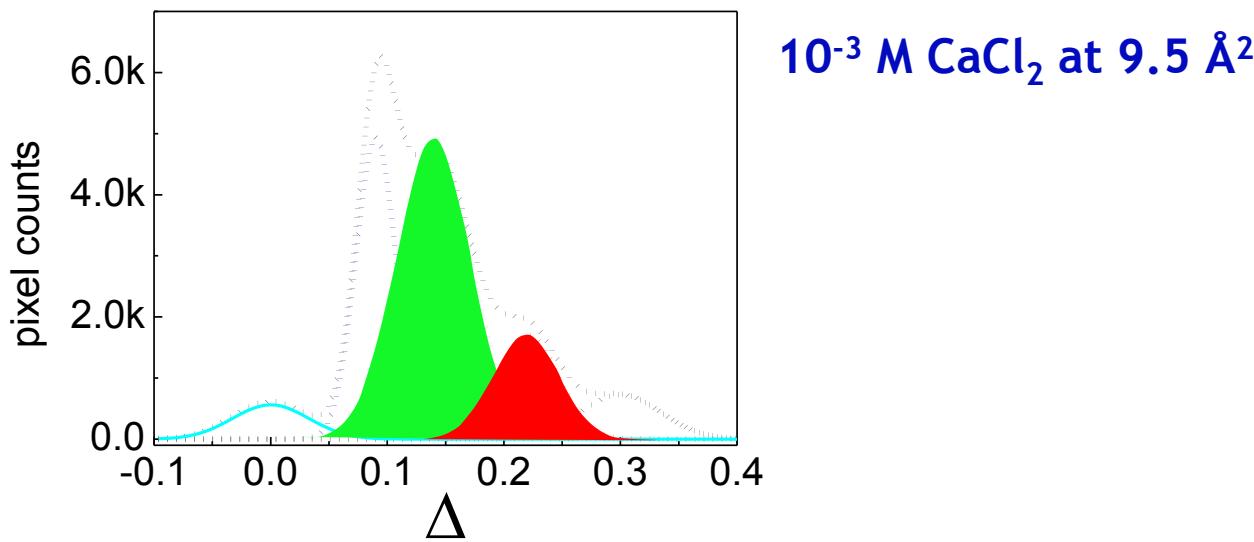
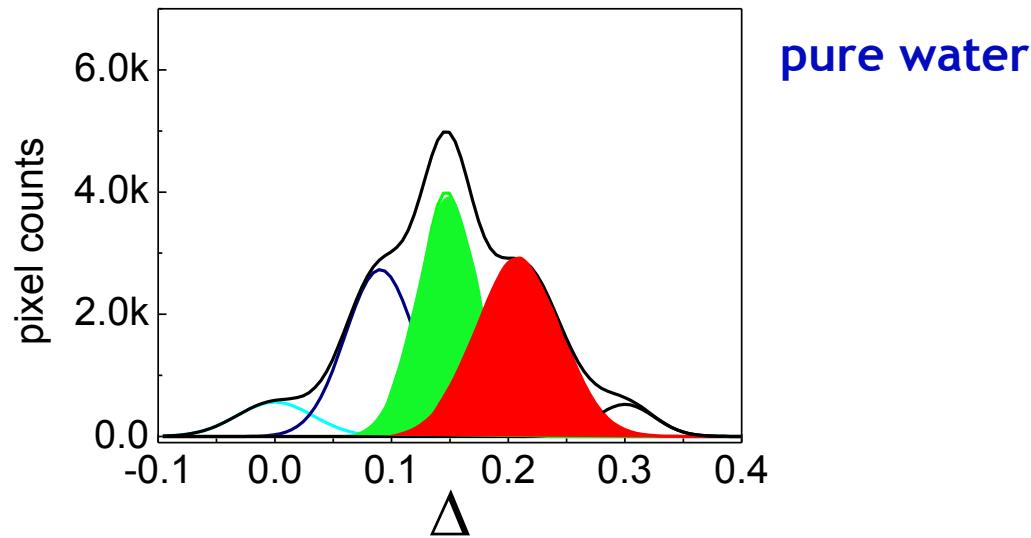


- 10^{-3} M CaCl_2 / at 9.5 \AA^2



Experimental result - collapsed film ($A_0/2$)/ Δ mapping

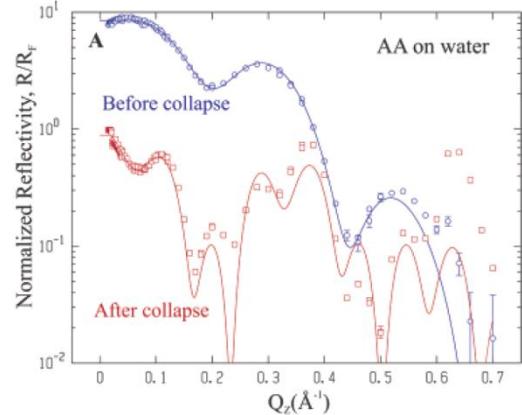
The fitted results from pure water (in solid lines) and 10^{-3} M CaCl_2 (in dotted lines) at 9.5 \AA^2



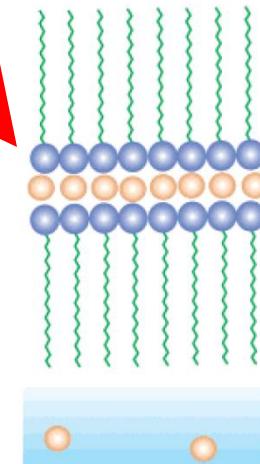
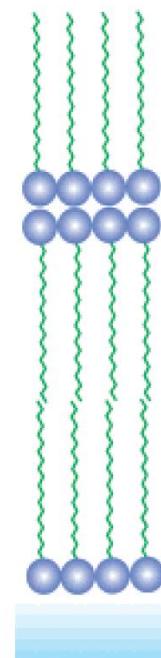
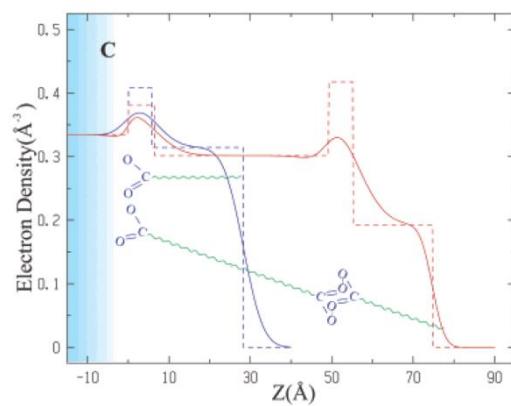
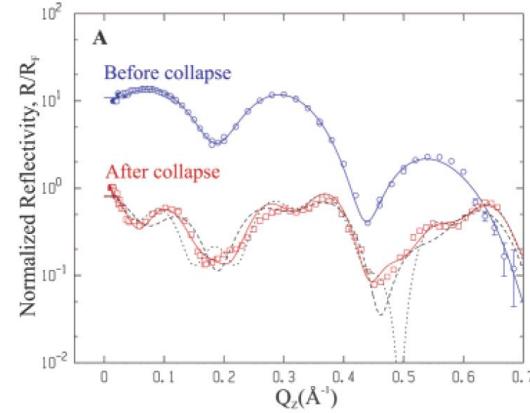
Collapse of the Langmuir monolayer

X-ray reflectivity

Fatty acid on pure water



Fatty acid on 1 mM CaCl_2 solution

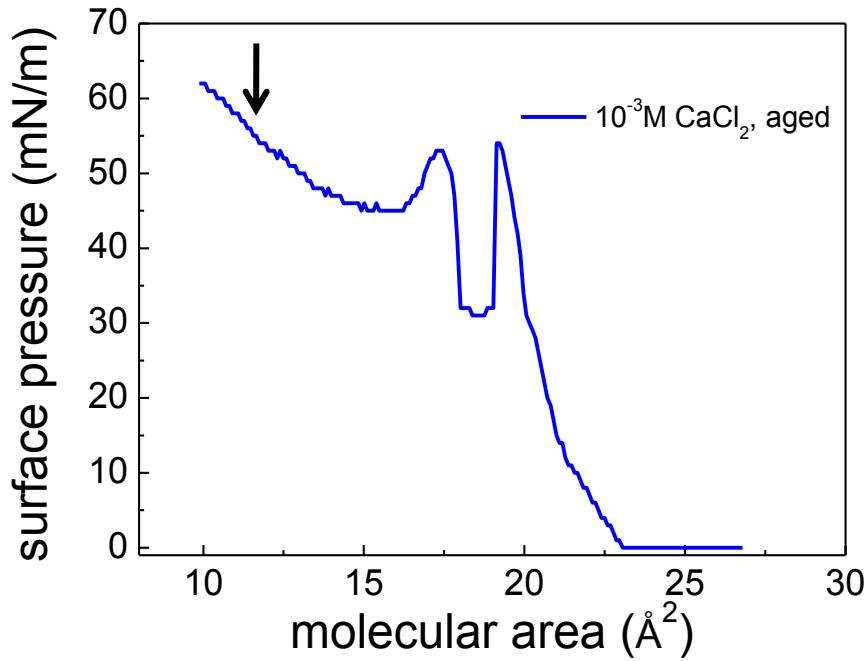


(Vaknin et al., Langmuir (2007))

Summary

1. *In-situ* Imaging ellipsometry was used to study the collapsed film of arachidic acid Langmuir monolayer.
2. Mono-, bi, and trilayers of AA were identified from the images.
3. The structure of the collapsed film changed with subphase salt concentration.
 - trilayer (thickness ~67.1 Å) preferred on water
 - bilayer (thickness ~45.4 Å) preferred on CaCl_2 solution

AA monolayer: aged and compressed again



- 10⁻³ M CaCl₂ / at 13.3 \AA^2

