Non-uniform hydration and odd-even effects in confined polyelectrolyte multilayers

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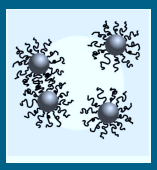
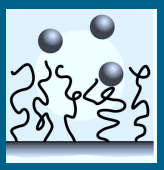
Why confinement?

Polymers at interfaces are a great way to tune inter-surface interactions.

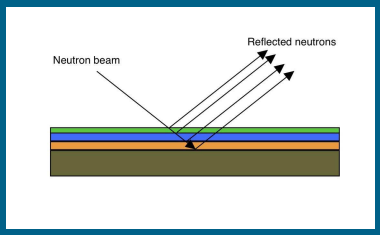




We want to measure the structure "in action"…
… that is to say under confinement.

Why neutron reflection?

Neutron reflection is an extremely powerful tool to study the structure of thin films



- Small wavelengths (1-20 Å)
- High penetration
- Contrast (isotopic substitution)
- Large footprint (5-40 cm^2)

Once upon a time…

1992-1997: Ali Zarbakhsh, Juliet Cox, Terence Cosgrove

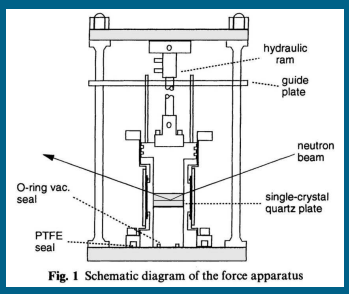


Fig. 1 Schematic diagram of the force apparatus

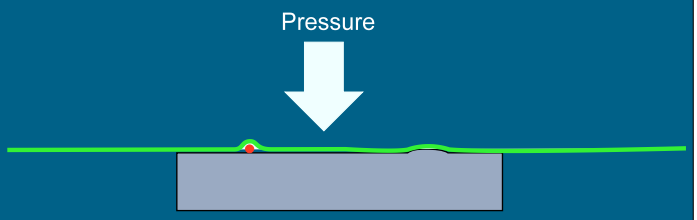
Once upon a time…

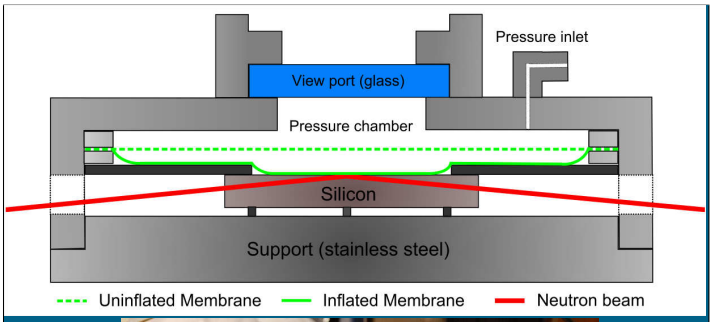
…the fairy tale had a scary ending:

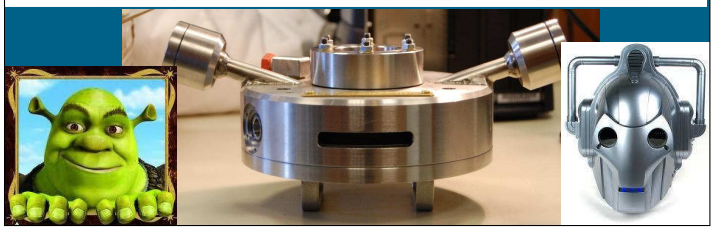
Dust and Waviness

With this approach no surfaces have come closer than about 100nm in distance

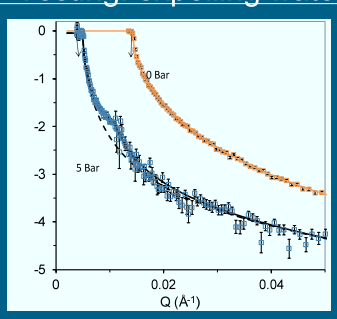
A new approach

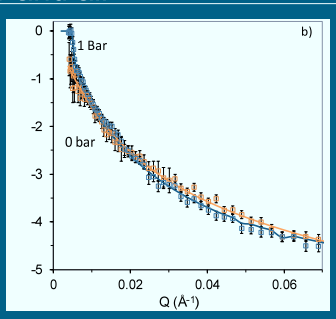






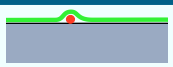
Testing: expelling water and air



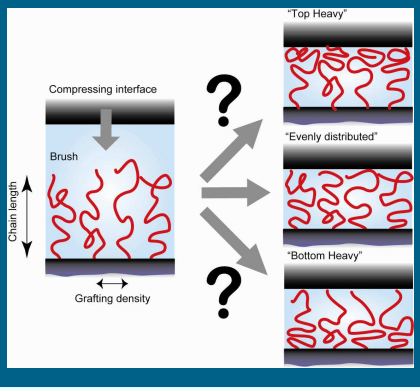


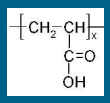
Si-D_2O to Si-Melinex
1% "mixed" signal

Si-Air to Si-Melinex
15% "mixed" signal



Polyelectrolyte brush under confinement

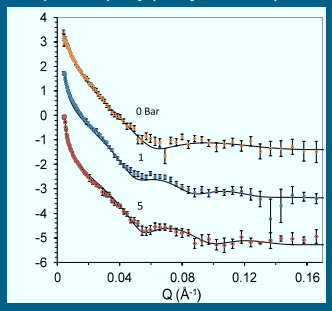


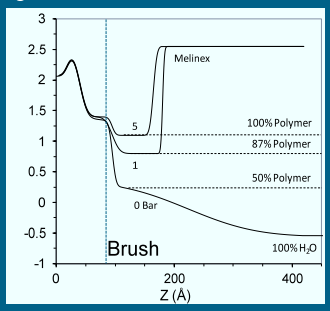


poly(acrylic acid)
x = 270
σ = 0.25 nm^{-2}
pK_a ~ 4.5

Polymer brushes

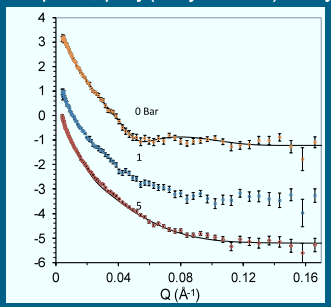
At pH 3, poly(acrylic acid) uncharged

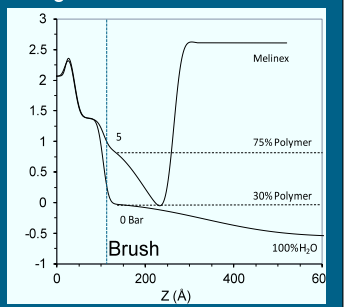




Polymer brushes

At pH 9, poly(acrylic acid) "fully" charged

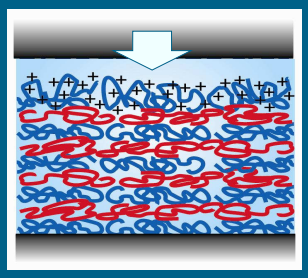




First conclusions

- molecular contact between substrate and flexible membrane is possible even at low pressures.
- dust particles remain a (small) problem
  - "mixed signals"
- poly(acrylic acid) brush can be confined and dehydrated, depending on pH
  - at pH 3, all solvent is removed at 5 bar
  - at pH 9, much more solvent remains and we find a "bottom-heavy" density profile

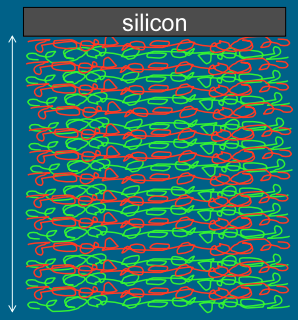
The structure of polyelectrolyte multilayers under confinement.



Polyelectrolyte multilayers

PAH:
poly(allylamine hydrochloride)
cationic, weakly charged

PSSA:
poly(styrene sulfonic acid)
anionic, strongly charged

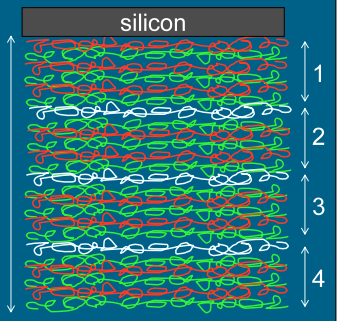


Polyelectrolyte multilayers

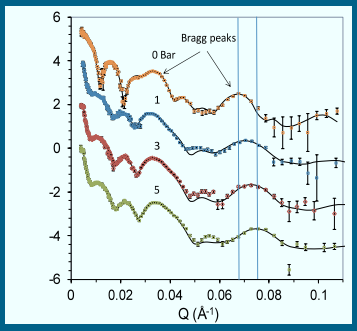
PAH:
poly(allylamine hydrochloride)
cationic, weakly charged

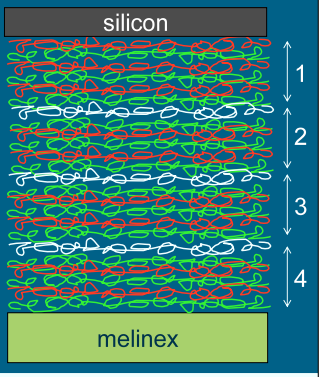
PSSA:
poly(styrene sulfonic acid)
anionic, strongly charged

d-PSSA:
d-poly(styrene sulfonic acid)
anionic, strongly charged
deuterated



Multilayer stack: 46 layers, PAH terminated





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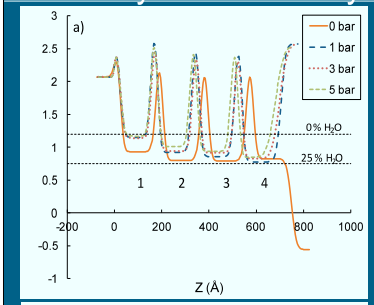
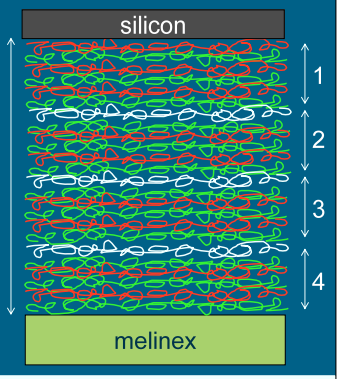


PAH Terminated

Block	0 Bar	1 Bar	3 Bar	5 Bar
1	15.3%	2.8%	3.5%	1.8%
2	22.9%	17.0%	14.9%	10.9%
3	23.4%	19.6%	16.3%	15.1%
4	21.4%	24.1%	21.2%	20.2%
Total Thickness (Å)	698	665	650	637
Avg. Hydration	20.8%	15.9%	14.0%	12.0%



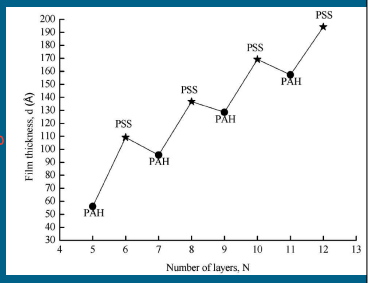
Non-uniform dehydration

- Inner layers (near silicon block) dehydrate first.
- Why?
  - water bound to polymer in outer layers?
  - polymer in outer layers more ionised?
  - different salt concentrations throughout layers?

Polyelectrolyte multilayers: “odd-even” effect

PAH:
poly(allylamine hydrochloride)
cationic, weakly charged

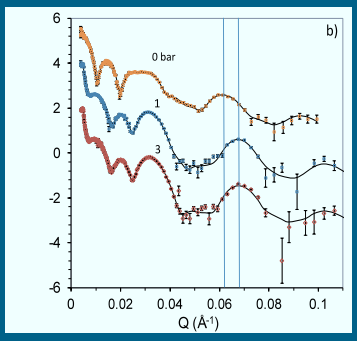
PSSA:
poly(styrene sulfonic acid)
anionic, strongly charged

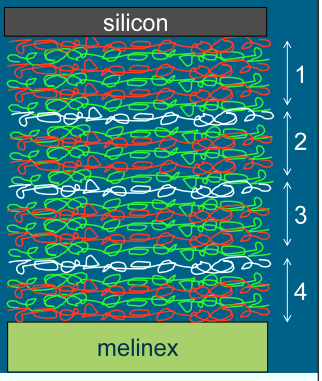


Odd-even effect explanations:
- swollen outer polymer layer when PSSA-terminated?
- ionisation difference → electric field difference?

Wong *et al.*, *Macromolecules*, **2004**, 37, 7285-7289. DOI: 10.1021/ma0351930

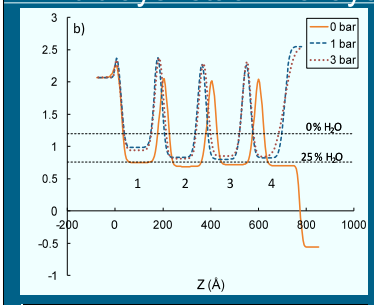
Multilayer stack: 45 layers, PSSA terminated



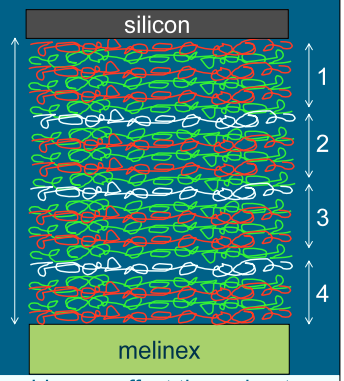


Fewer layers but thicker – “odd-even” effect

Multilayer stack: 45 layers, PSSA terminated



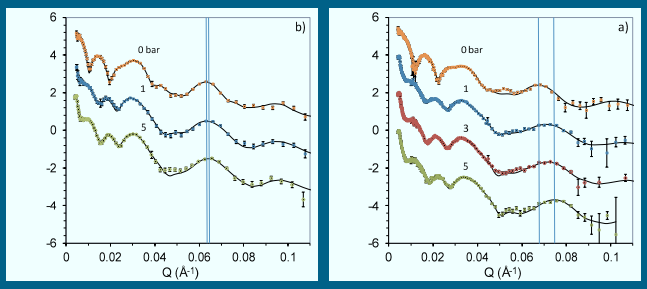
Block	0 bar	1 bar	3 bar
1	25.5%	12.1%	14.8%
2	29.1%	21.2%	22.3%
3	27.5%	22.6%	19.8%
4	28.3%	21.5%	20.7%
Total Thickness (Å)	757	687	687
Avg. Hydration	27.6%	19.4%	19.4%



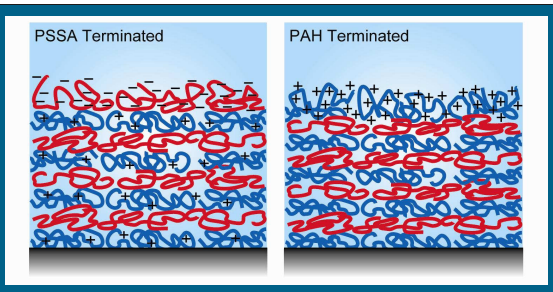
odd-even effect throughout (not just on surface)

Effect of ionic strength: 100 mM NaCl

PSSA-terminated **PAH-terminated**



PSSA-terminated layer less compressible:
• larger surface charge and stronger electric field throughout layer



For PSSA-terminated (strong electrolyte):
→ charge density on surface different
→ electric field higher throughout layer
→ more repulsive interactions
→ thicker layer
→ harder to compress

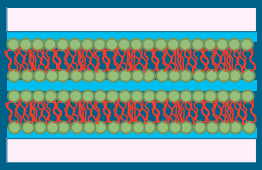
Schönhoff *et al.*, *Colloids Surf. A*, **2007**,14.

Conclusions

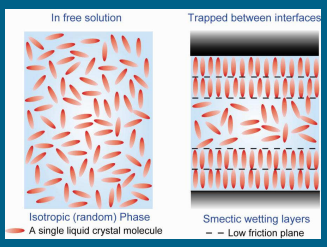
- Overall hydration decreases with increasing confinement
- Without confinement the multi-layer is not uniformly hydrated: more water in outer layers
- Confinement leads to more pronounced non-uniformity
  - inner layers ~completely dehydrated
- Odd-even effect persists throughout multilayer structure
  - it is **not** a surface swelling effect

Ongoing investigations

Lipid bilayer stacks



Liquid crystals



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  - Christy Kinane (ISIS)
- ISIS & ILL

EPSRC

MARIE CURIE ACTIONS