3D Neutron Reflectometry on polyelectrolyte multilayers

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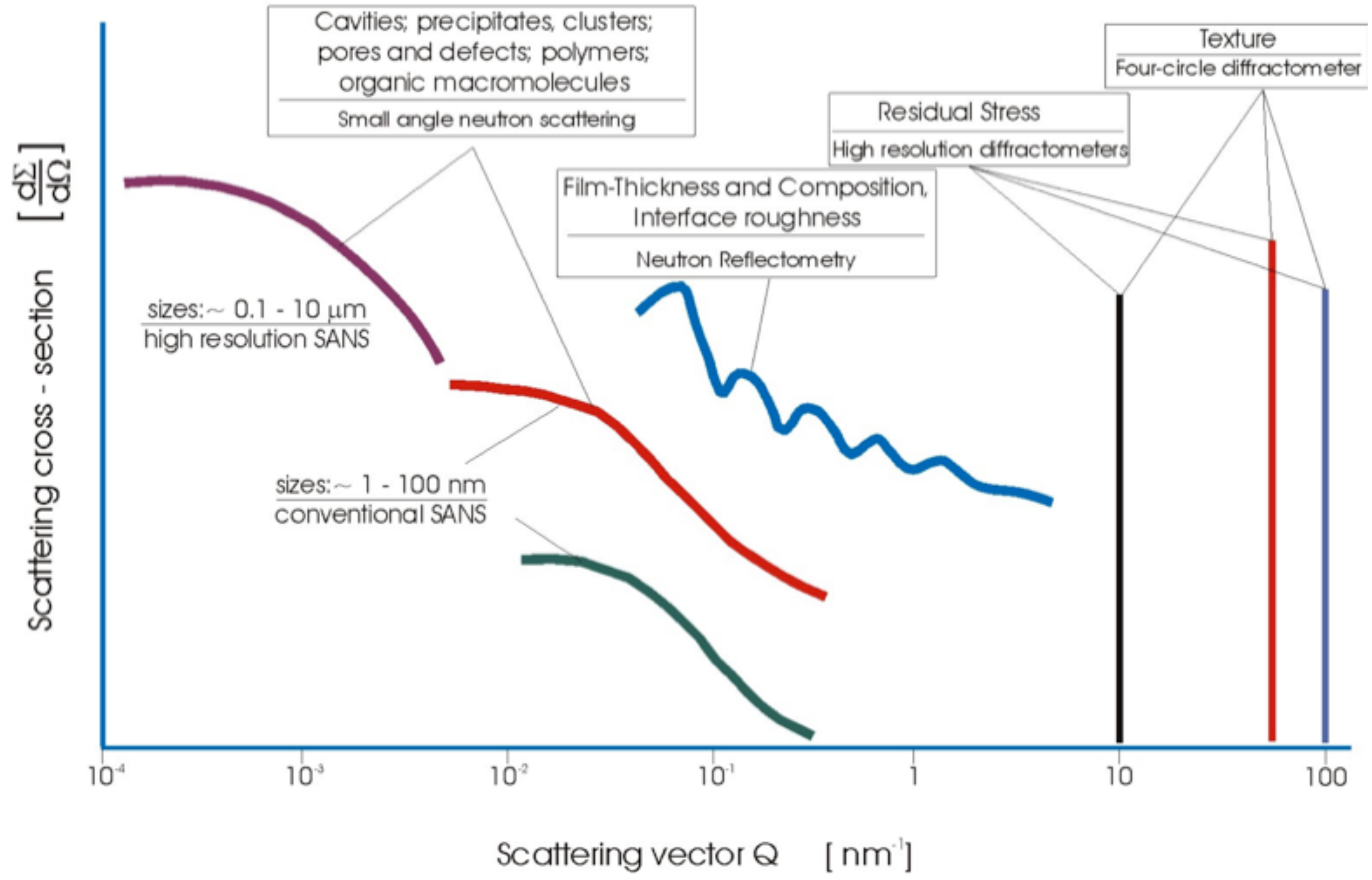
Outline

- Introduction into Reflectometry
- Polyelectrolyte multilayers (LbL)

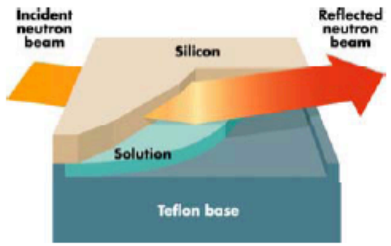
Schematic view of elastic neutron scattering spectra



Applications

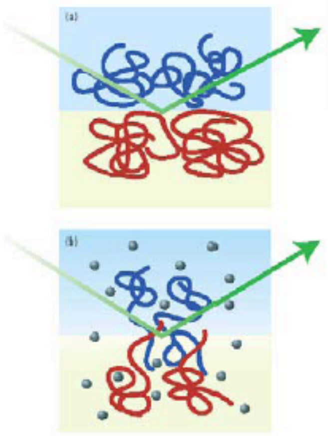
Kinetics

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



Model Devices

- Thin polymer films (finite size effects)
- Spin coating
- **Layer-by-Layer**

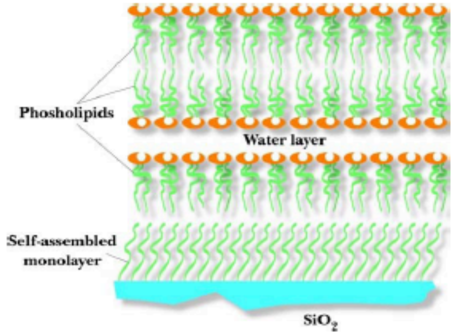


Surfactants

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

Electrochemistry

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



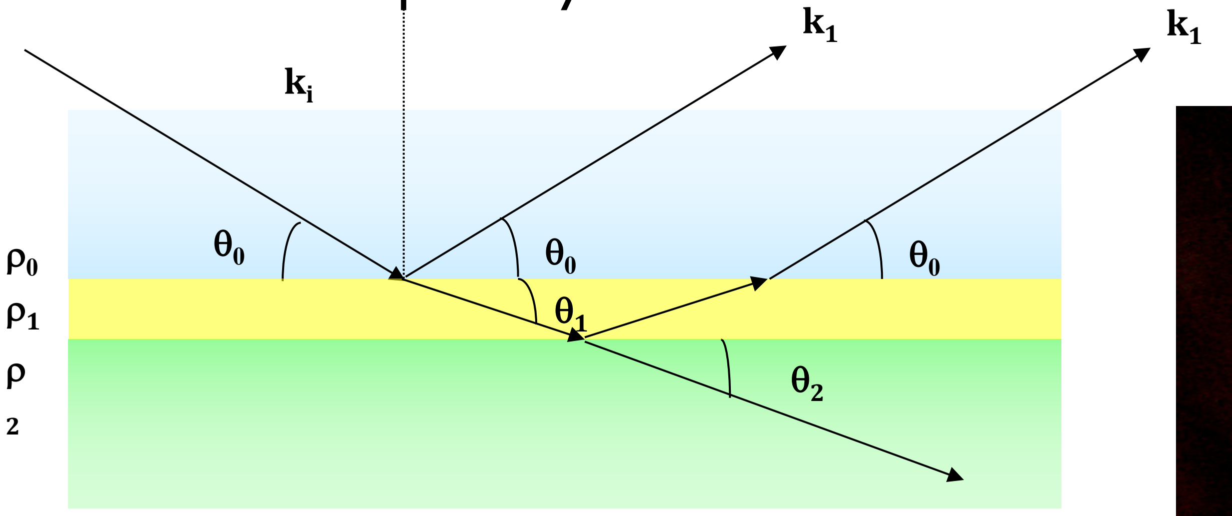
Biology

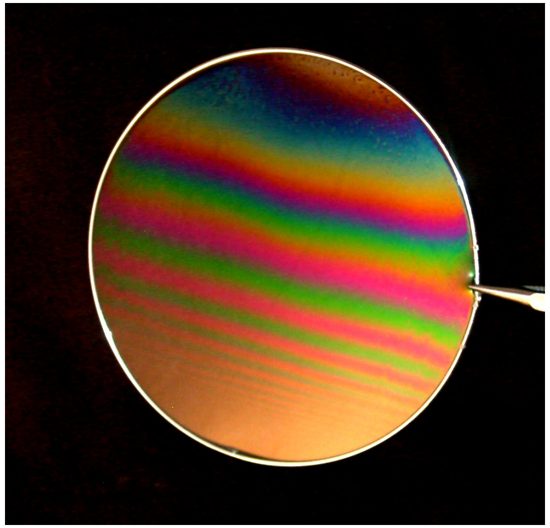
- Protein adsorption
- Biocompatible polymers
- Drug transport
- Anaesthesia mechanisms

Magentism: Magneitc multilayers, Thin magnetic films, Thin film magnetometry

Interference

The neutrons are partially reflected and transmitted:



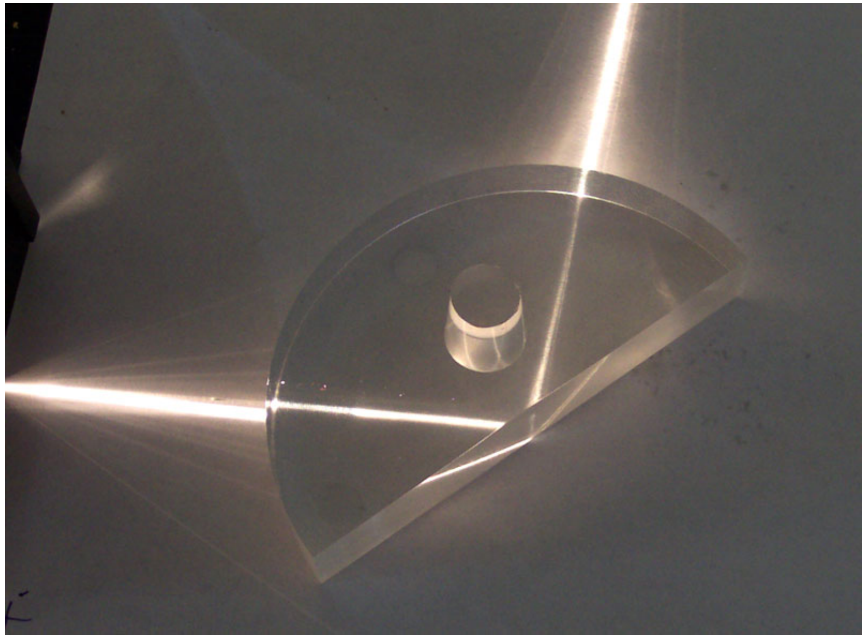


1675 - *Newton* realised that the colour of the light reflected by a thin film illuminated by a parallel beam of white light could be used to obtain a measure of the film thickness. Spectral colours develop as a result of interference between light reflected from the front and back surfaces of the film.

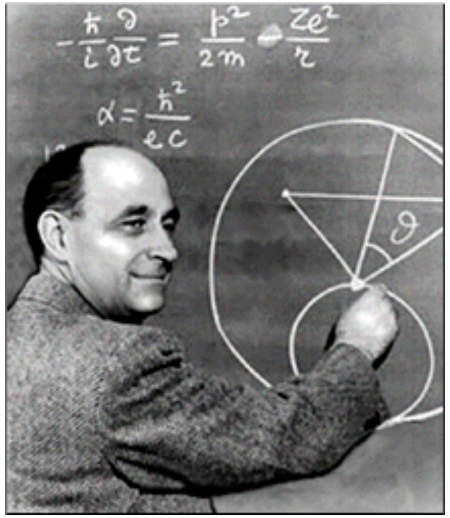
1931 - *H. Kiessig* measures the total external reflection of X-rays and the thickness interference oscillations named after him. (Ann. d. Physik **402**, 715)

Total Reflection

For both kinds of radiation the refractive index is a function of the scattering length density and wavelength.

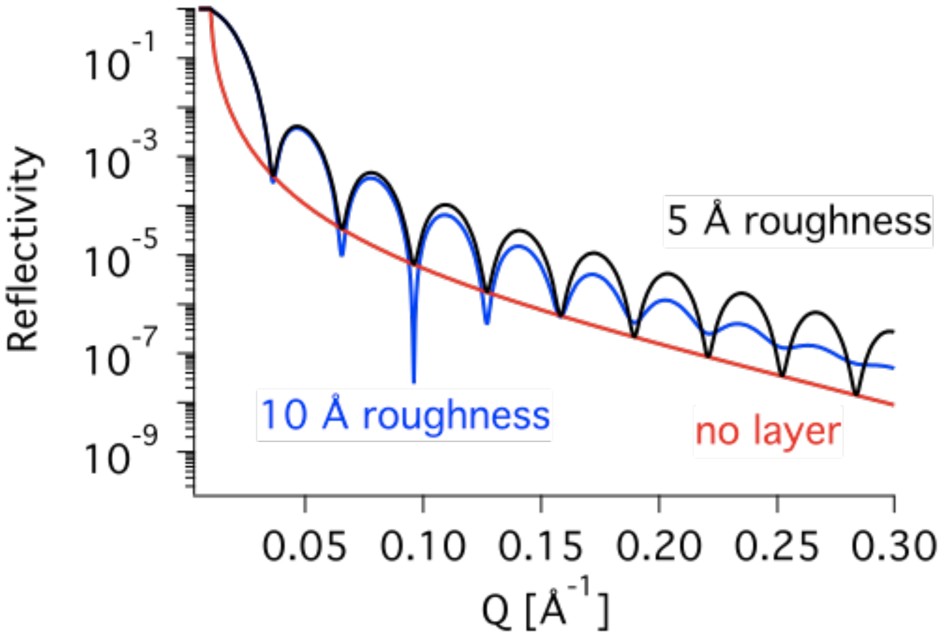


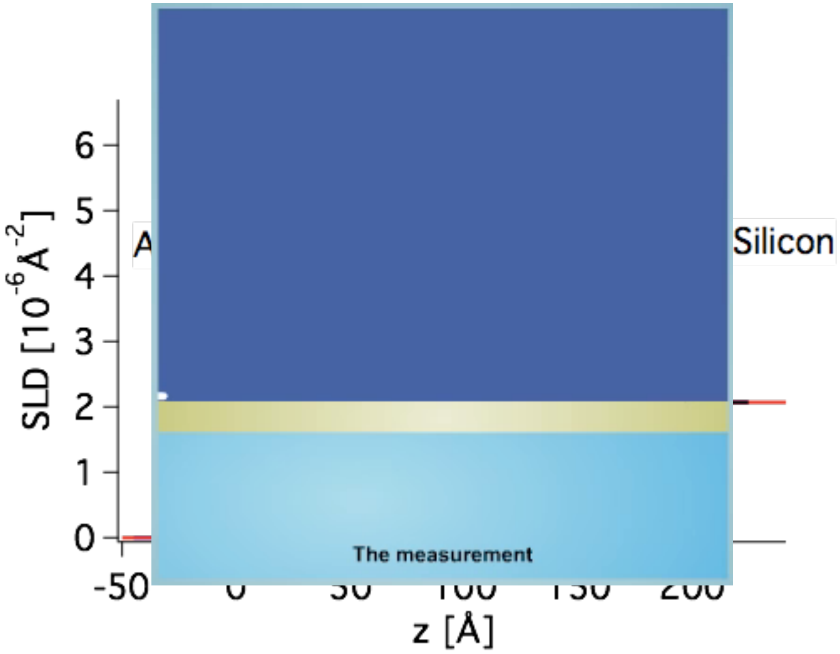
Total Reflection of neutrons was first observed in **1944** by Fermi and Zinn (Phys. Rev. 70, 103 (1946))



As with light, total reflection may occur when neutrons pass from a medium of higher refractive index to one of lower refractive index.

Reflectometry from stratified medium



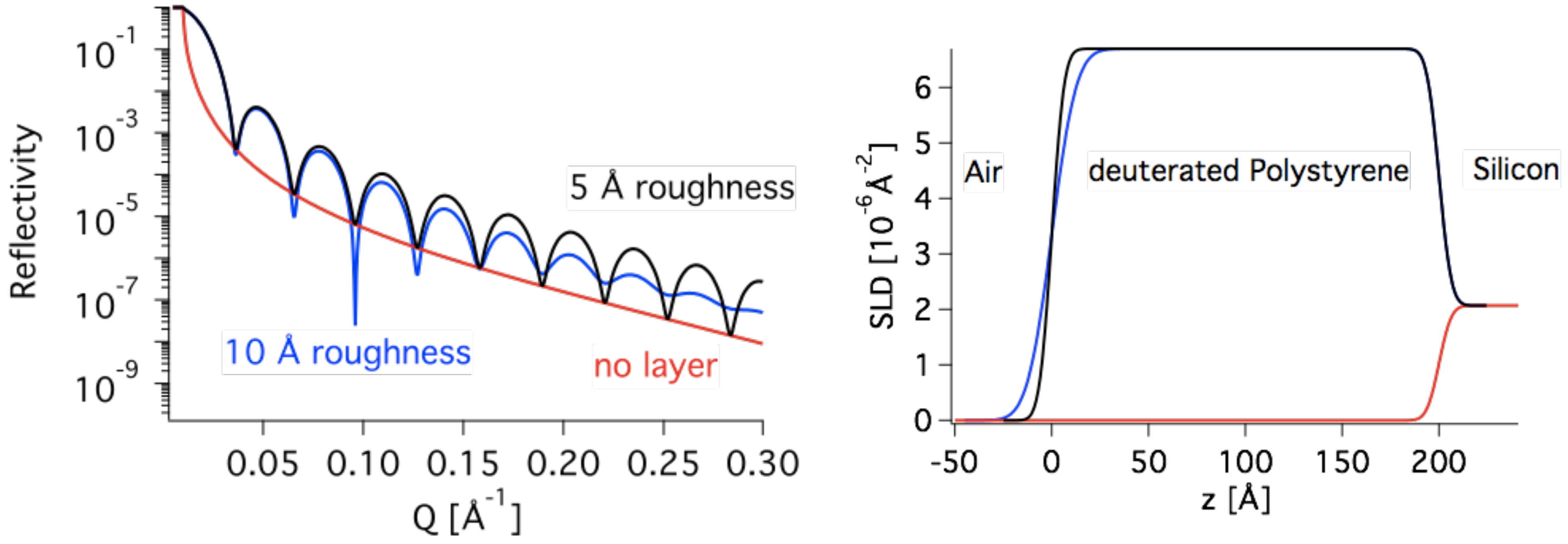


Roughness can be added from 1st Born calculation: $R(q_z) = R_F(q_z)\mathrm{e}^{-q_z^2\sigma^2}$

Recursively calculating the reflected and transmitted intensity via Fresnel adding the Debye-Waller roughness leads to the reflectivity of layered systems.

L.G. Parratt, Phys. Rev. **95**, 359 (1954).

Reflectometry from stratified medium



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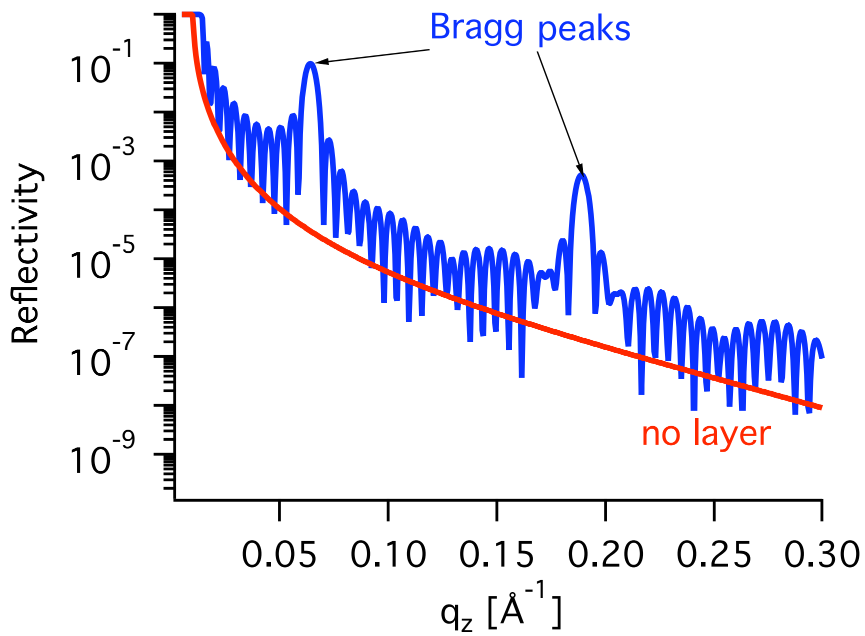
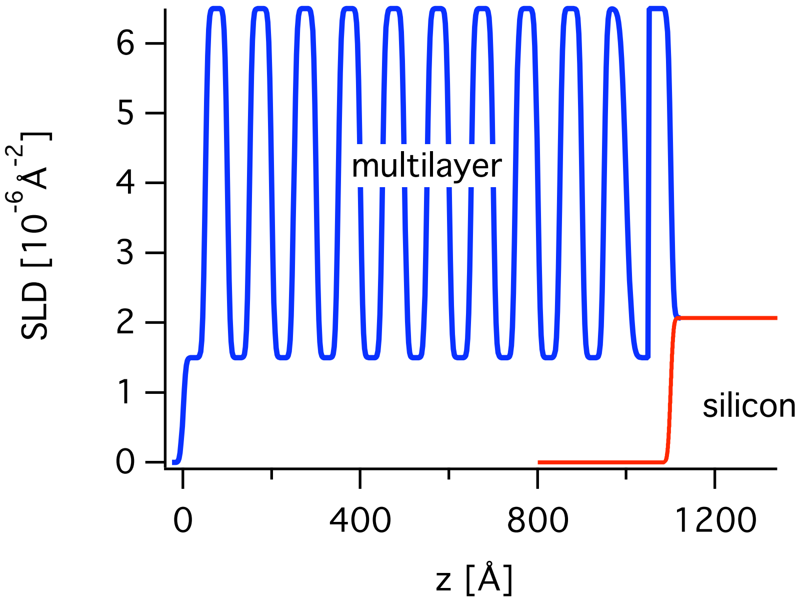
L.G. Parratt, Phys. Rev. **95**, 359 (1954).

Reflectometry from a multilayer





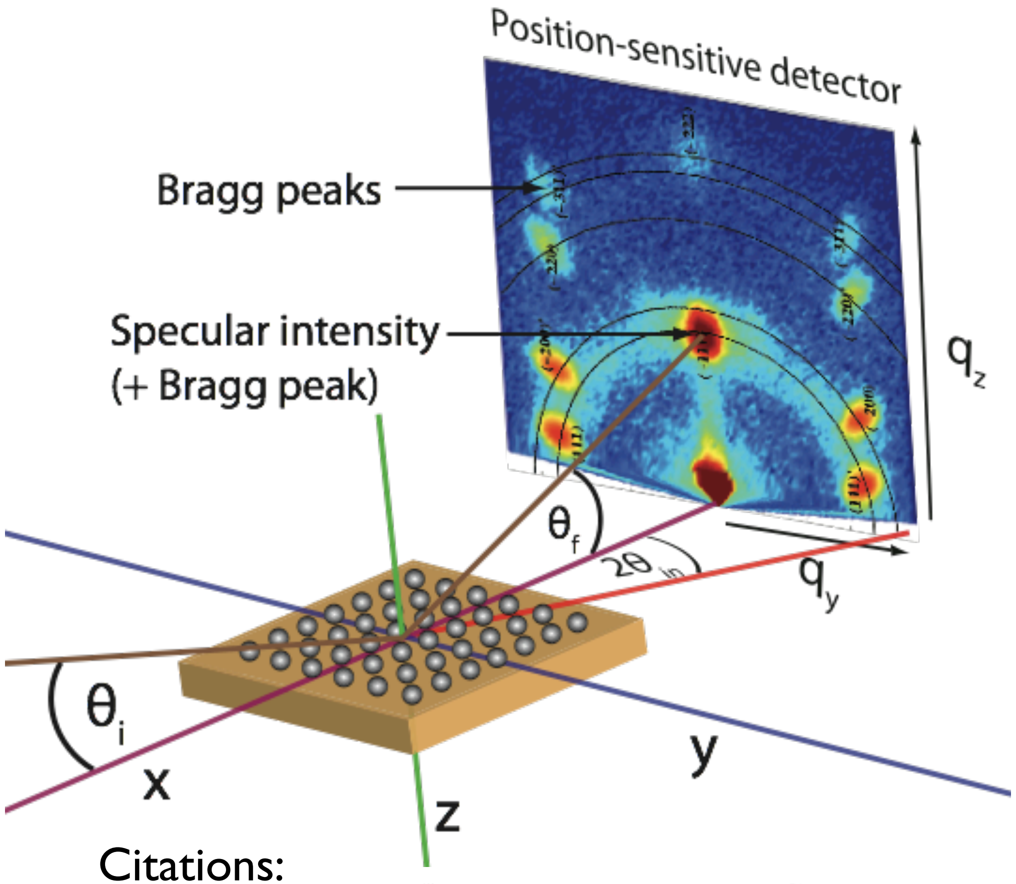
Closely related to Bragg condition in crystals, but slightly shifted by the critical edge.

$$q_z = \frac{2\pi n}{d}$$

Breagg peak order

layer pair thickness

Off-specular scattering (OSS) and GISANS



$$q_x = \frac{2\pi}{\lambda}(\cos\theta_f \cos 2\theta_{in} - \cos\theta_i)$$

$$q_y = \frac{2\pi}{\lambda}(\cos\theta_f \sin 2\theta_{in})$$

$$q_z = \frac{2\pi}{\lambda}(\sin\theta_i + \sin\theta_f)$$

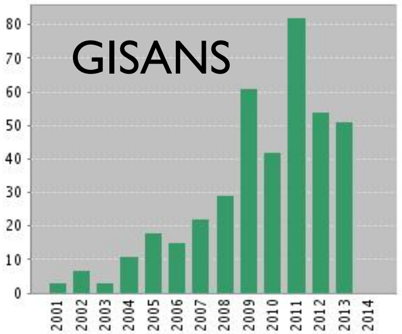
Accessible q-range:

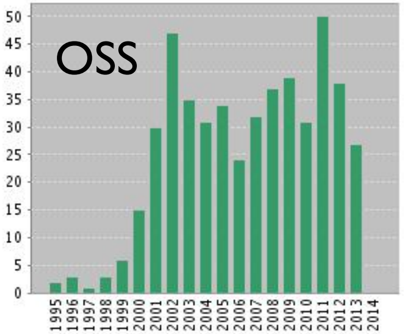
$$10^{-5}\,\text{Å}^{-1} \le q_x \le 10^{-3}\,\text{Å}^{-1} \equiv 1 - 100\,\mu m$$

$$10^{-3}\,\text{Å}^{-1} \le q_y \le 10\,\text{Å}^{-1} \equiv 1 - 10000\,\text{Å}$$

$$10^{-3}\,\text{Å}^{-1} \le q_z \le 1\,\text{Å}^{-1} \equiv 10 - 10000\,\text{Å}$$

Citations:





Polyelectrolyte multilayers
prepared by Layer-by-Layer (LbL)

Gero Decher, Christophe Higy and Giovanna Fragneto

UNIVERSITÉ DE STRASBOURG

cnrs

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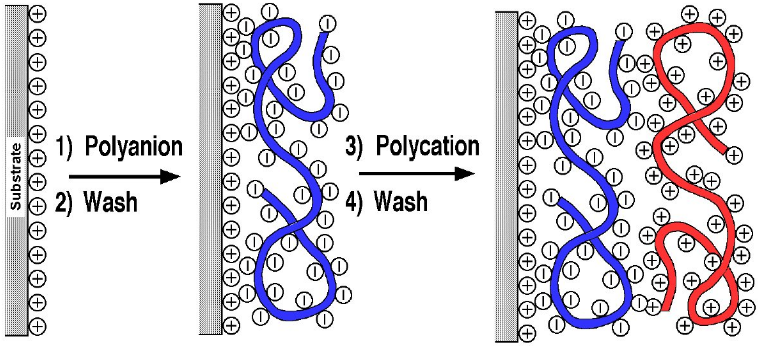
Polyelectrolyte multilayers (LbL)

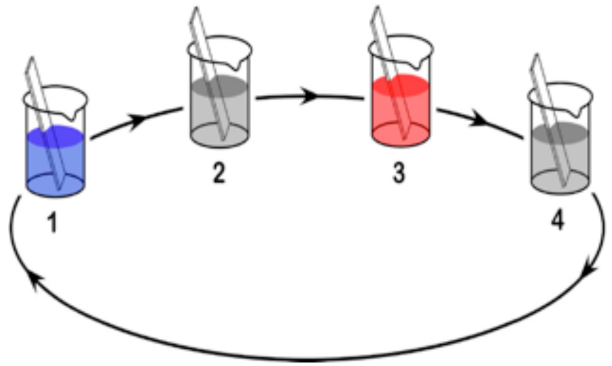
Layer-by-Layer method (LbL):



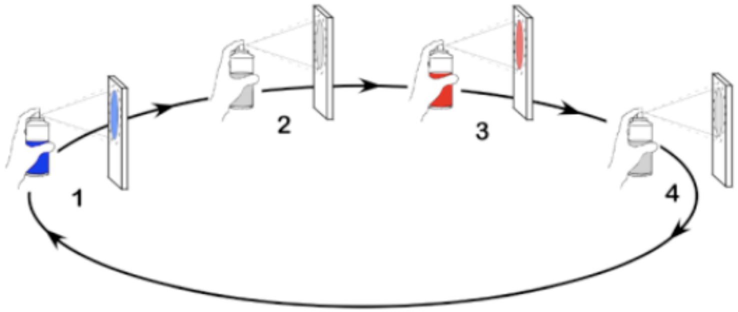
Decher, G., Science (1997) 277, 1232-1237.

- Easy and environment friendly production.
- General applicability to organic, polymeric inorganic and biological materials. (not limited to charges, also donor/acceptor, hydrogen bonding, covalent, smart recognition, hydrophilicity…)
- Scalable and largely substrate independent

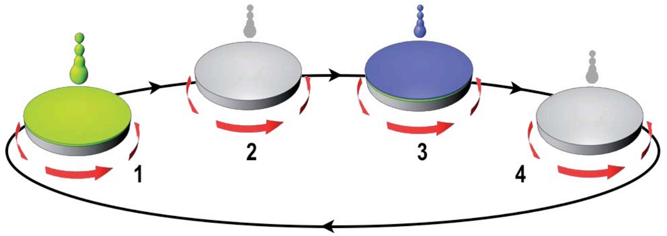
Dipping:



Spraying:



Spin-coating:



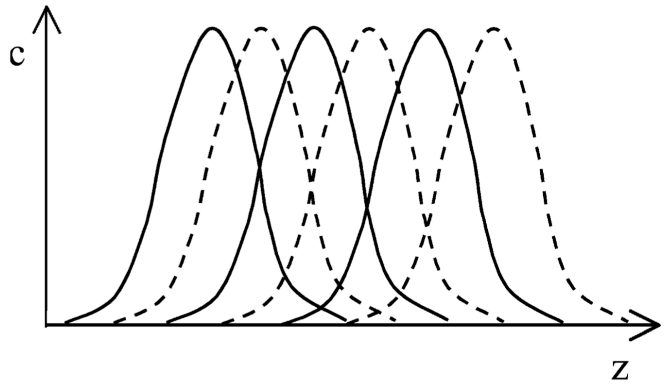
Polyelectrolyte multilayers (LbL)

Applications

- Antifouling or cell adhesive coatings [*Adv. Mater.* (2010) **22**, 441-467.]
- Filters (tunable salt/water permeability) [*J. Mem. Sci.* (2010) **349**, 268-278.]
  Microporous films [*Langmuir* (2000) **16**, 5017-5023.]
- Controlled drug release [*Angew. Chem.* (2005) **117**, 5213-5217.]
- Antireflection coatings [*Nature Mat.* (2002) **1**, 59-63.]
- Superhydrophobic coatings [*Nano Lett.* (2004) **4**, 1349-1353.]
- (Nano-)Sensors (pH, Temperature, (Biorelevant)-molecules etc.)
  [*Coll. Surf. A* (2007) **303**, 3-13; *Appl. Phys. Lett.* (2011) **98**, 73116.]
- Photovoltaics [*J. Am. Chem. Soc.* (1995) **171**, 12879.]
- Magnetotunable films [*Chem. Mater.* (2011) **23**, 3668–3675.]
- Lithography possible [*J. Am. Chem. Soc.* (2002) **124**, 2100–2101.]
- Protective Coatings [*Science* (1997) **277**, 1232-1237.]

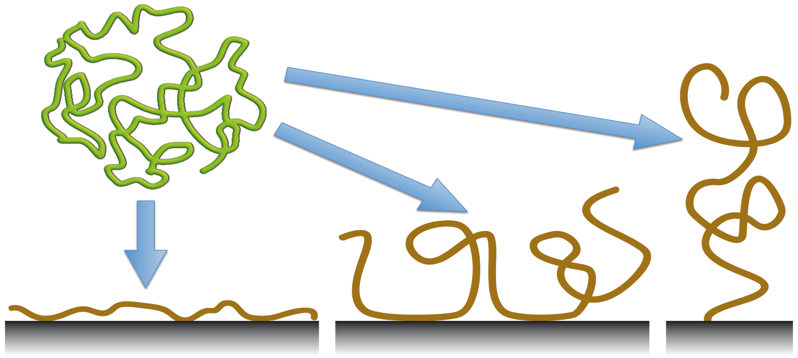
Polyelectrolyte multilayer (LbL)

Layer-by-Layer monomer profile:



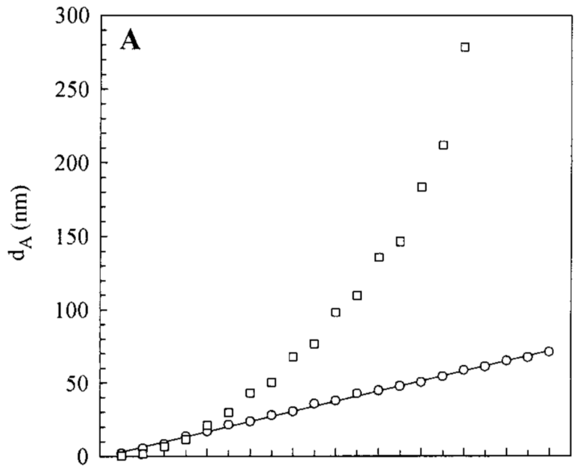
Decher, G., Science (1997) 277, 1232-1237.

Polymer Conformation:



Higy, C., PhD thesis, Strasbourg University (2015).

Linear vs. Exponential growth:



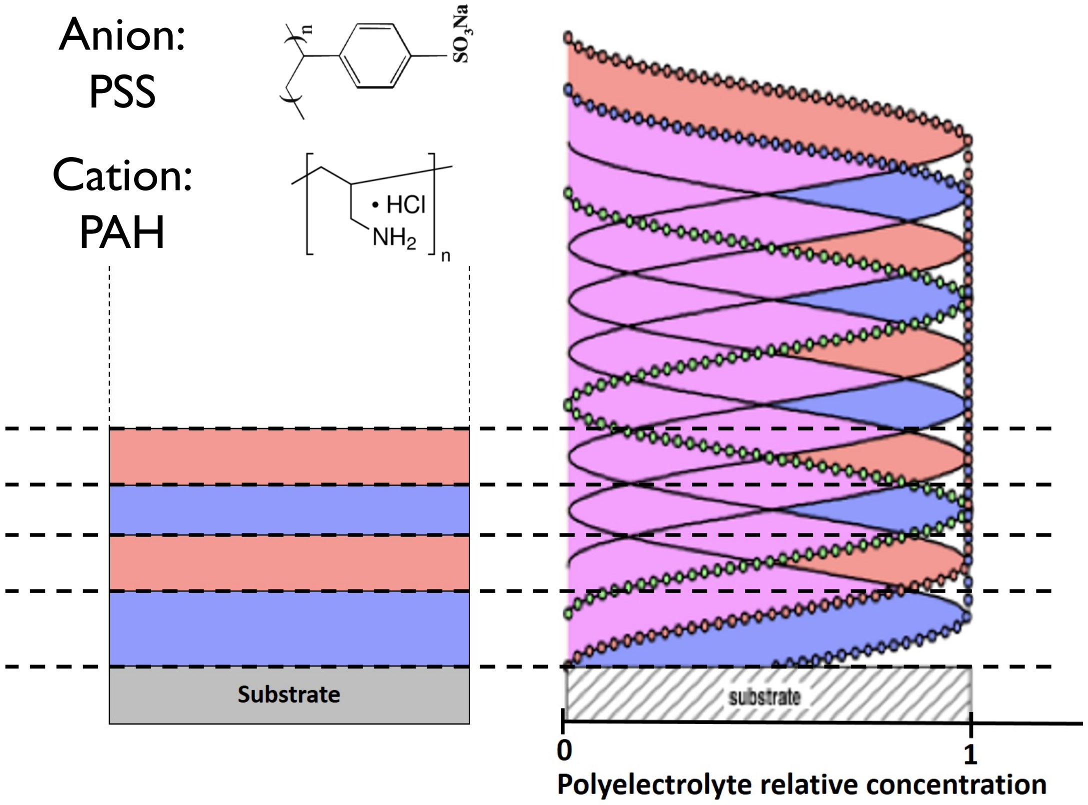
Lavalle, P. *et al.*, Macromolecules (2002) 35, 4458-4465.

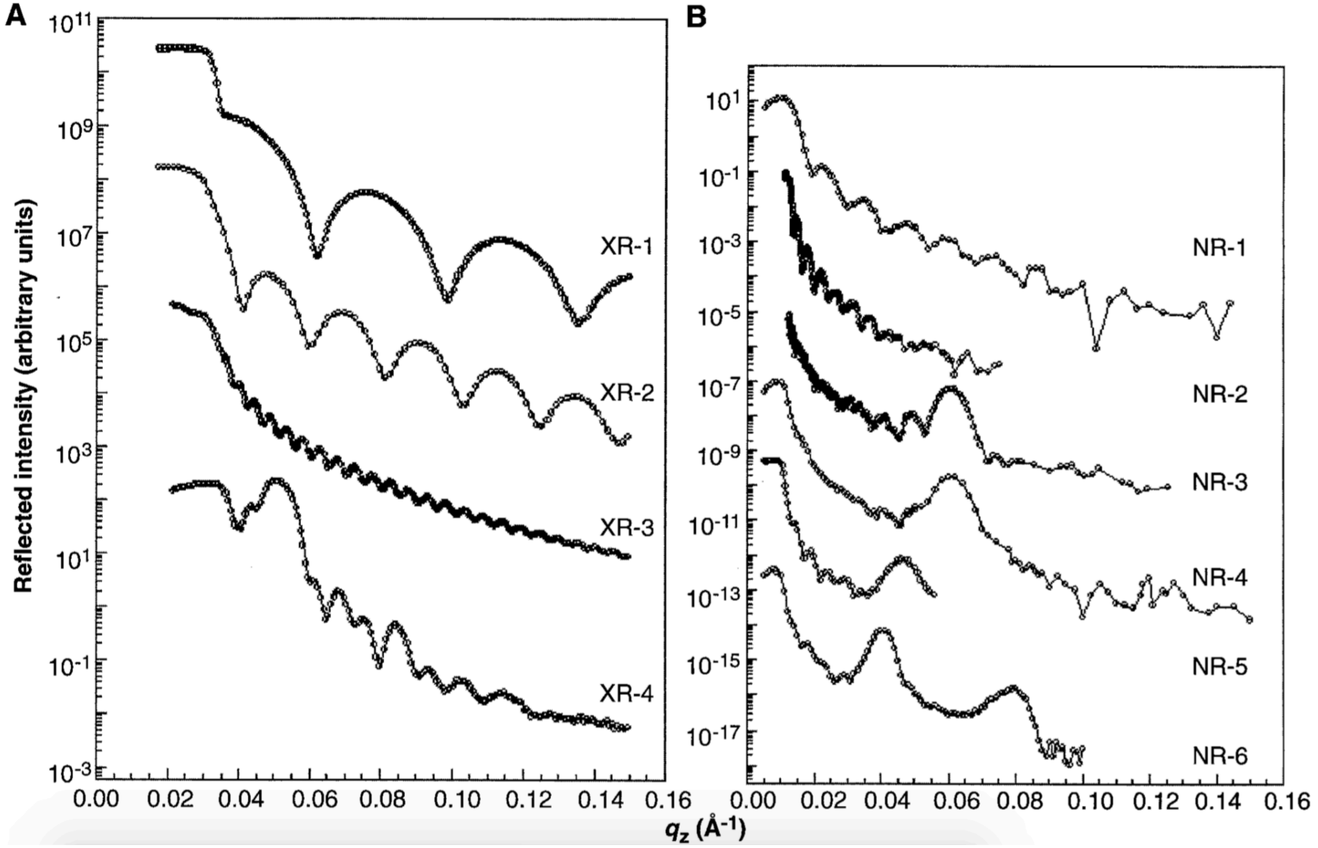
- It's a multilayer, but not crystalline (fuzzy layers)! Defects don't play a major role
- Internal interfaces are dominating the bulk growth (exponential growth, brush growth..)
- Highly non-equilibrium state (charges are balanced, but polymer coil is deformed)

Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

Out-of-plane structure:





Current understanding: Flat monomer density profile for both Cation and Anion! (No Bragg peaks visible if every polycation or anion marked)

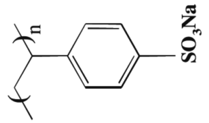
Decher, G., Science (1997) 277, 1232-1237.
Higy, C., PhD thesis, Strasbourg University (2015).

Polyelectrolyte multilayer (LbL)

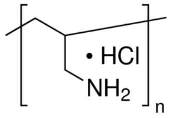
Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

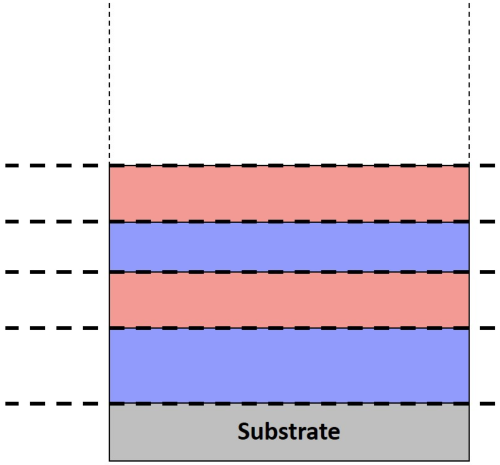
Out-of-plane structure:

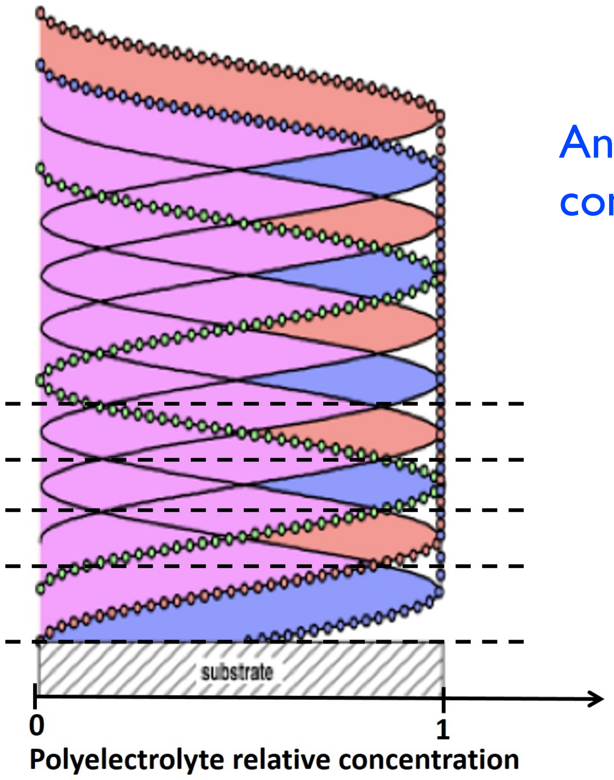
Anion: PSS



Cation: PAH

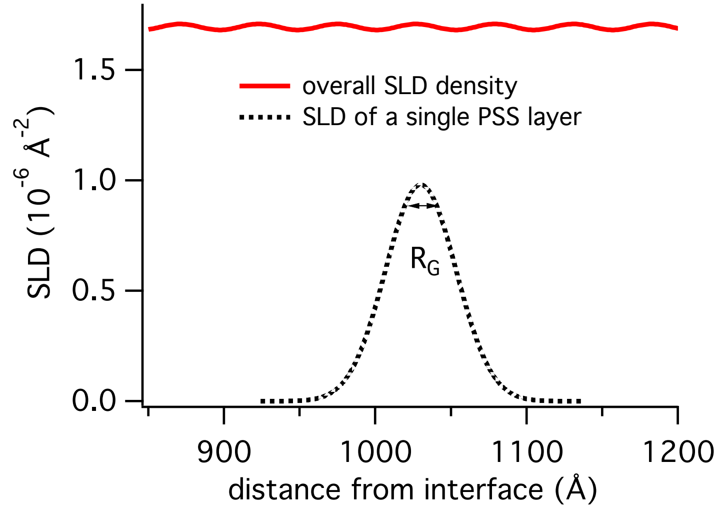


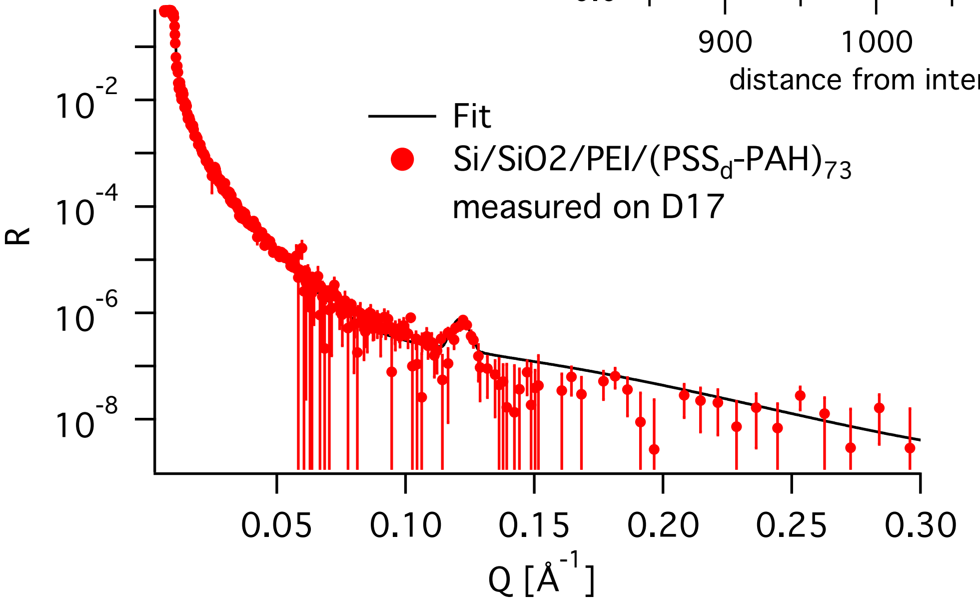




But with better instrument + more repetitions:

Anion denisty profile not completely flat!





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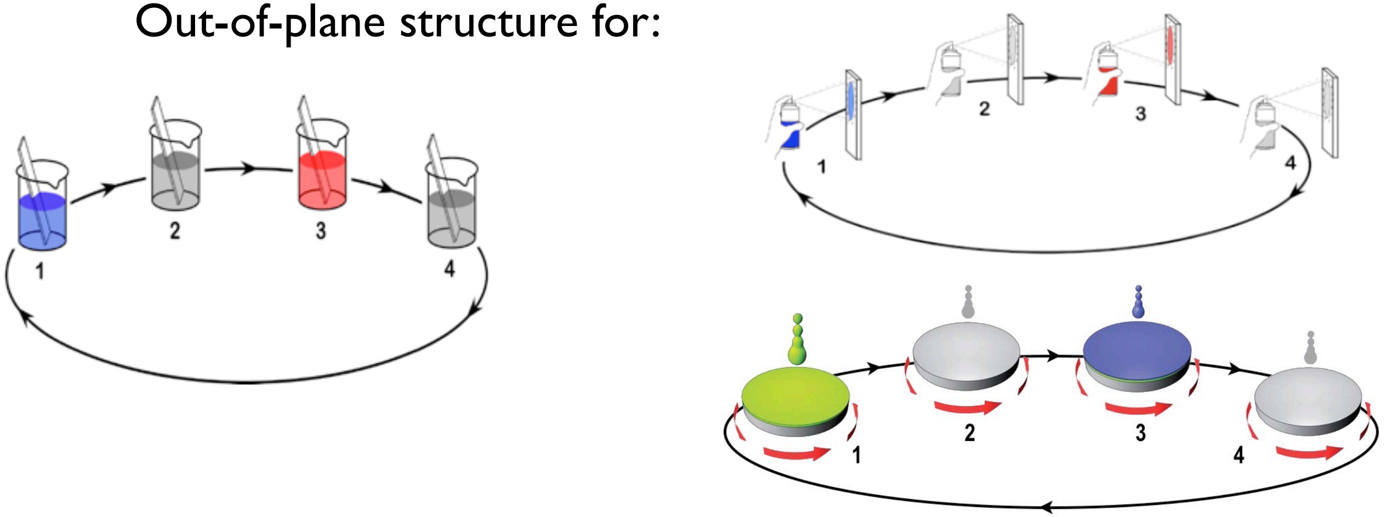
Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

Out-of-plane structure for:



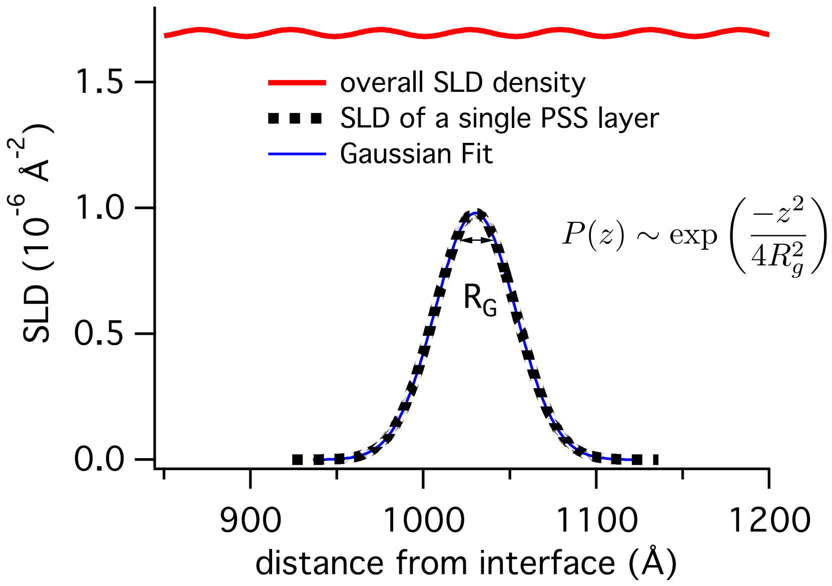
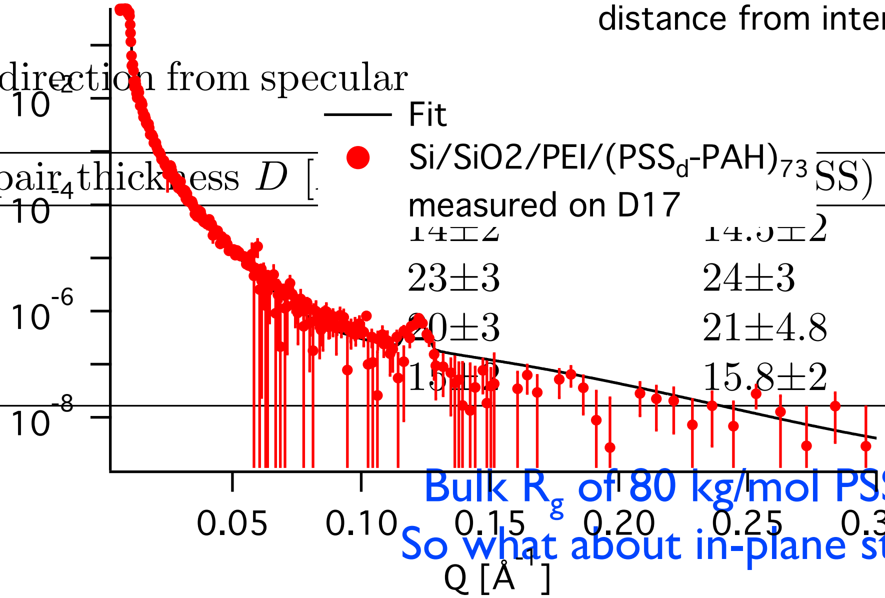


Table 1: Fitted radii of gyration of d-PSS in out-of-plane direction from specular neutron reflectometry

NaCl concentration [M]	Deposition method	Layer pair thickness D [	[illegible]	[illegible] SS) [Å]
0.5	Spraying	26±1	14±2	14.5±2
2	Dipping	52±1	23±3	24±3
2	Spraying	41±2	[illegible]0±3	21±4.8
2	Spin coating	34±2	15[illegible]	15.8±2



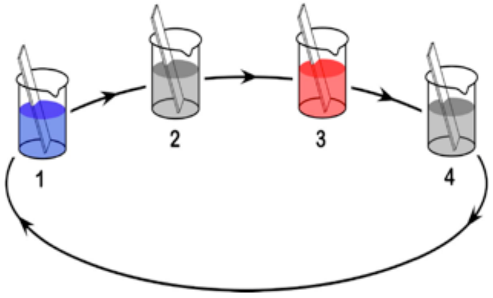
Thickness/R_g depends on deposition method:
Dipping > Spraying > Spin coating

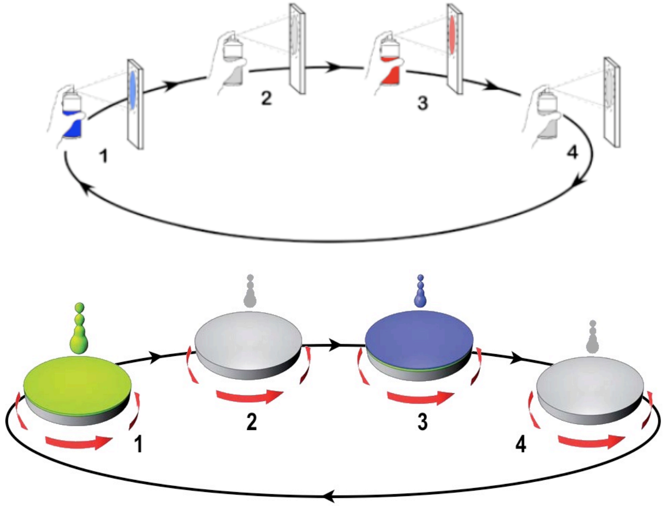
Bulk R_g of 80 kg/mol PSS: 9 nm!
So what about in-plane structure?

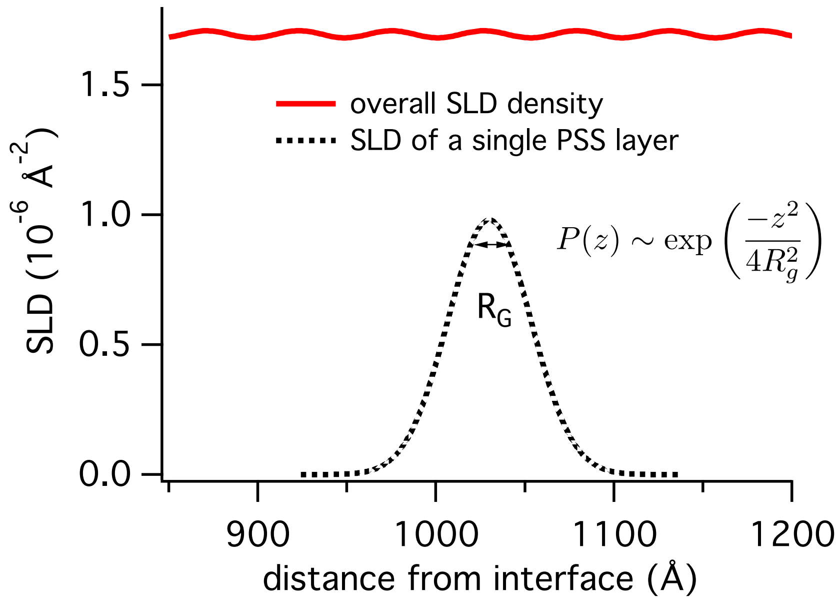
Polyelectrolyte multilayer (LbL)

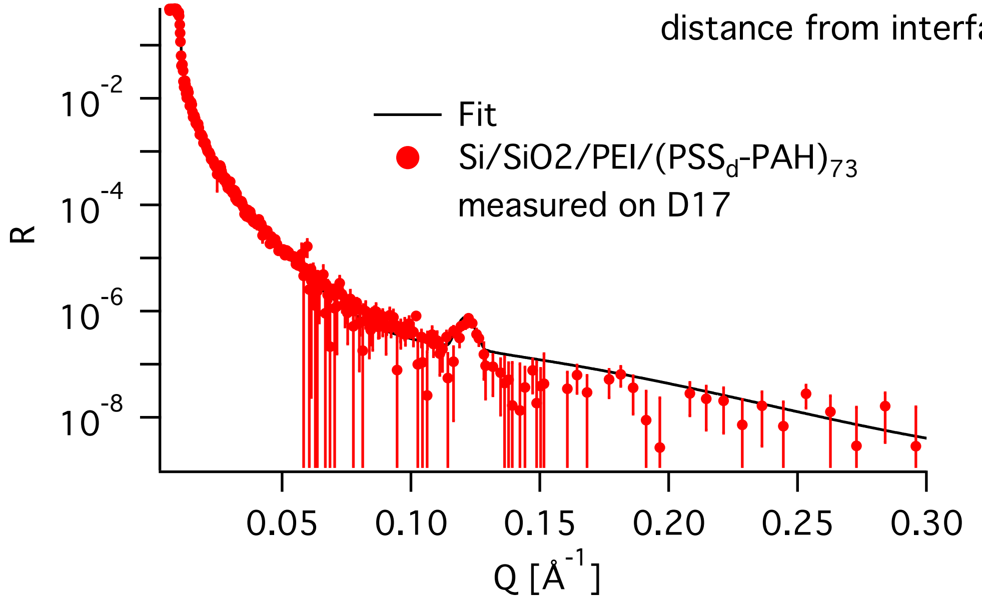
Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

Out-of-plane structure for:









Thickness/R_g depends on deposition method:
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Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

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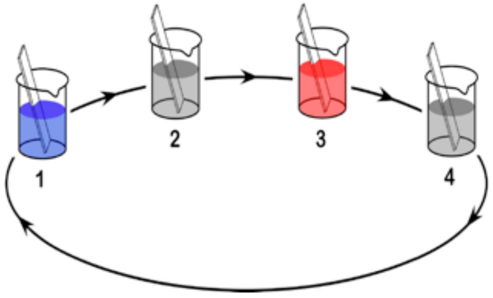

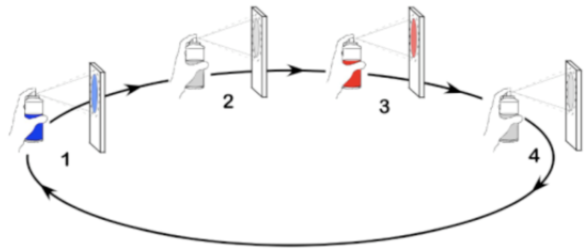

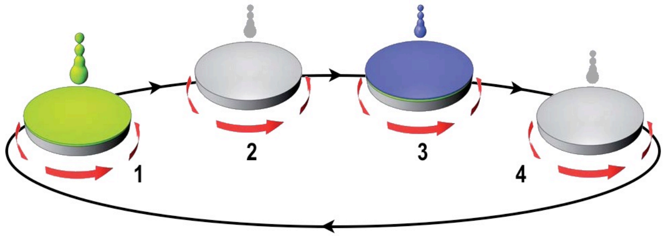

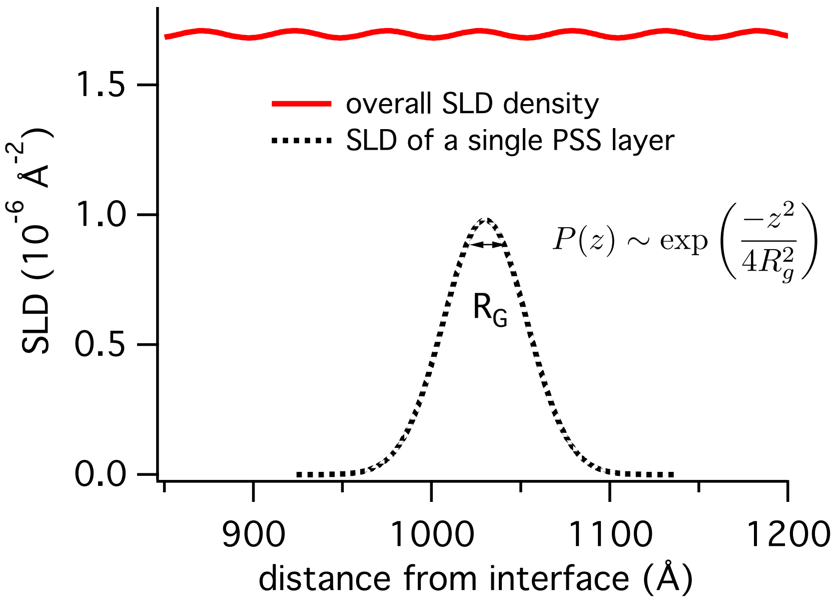

Table 1: Fitted radii of gyration of d-PSS in out-of-plane direction from specular neutron reflectometry

NaCl concentration [M]	Deposition method	Layer pair thickness D [Å]	roughness [Å]	R_{gz}(PSS) [Å]
0.5	Spraying	26±1	14±2	14.5±2
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Thickness/R_g depends on deposition method:

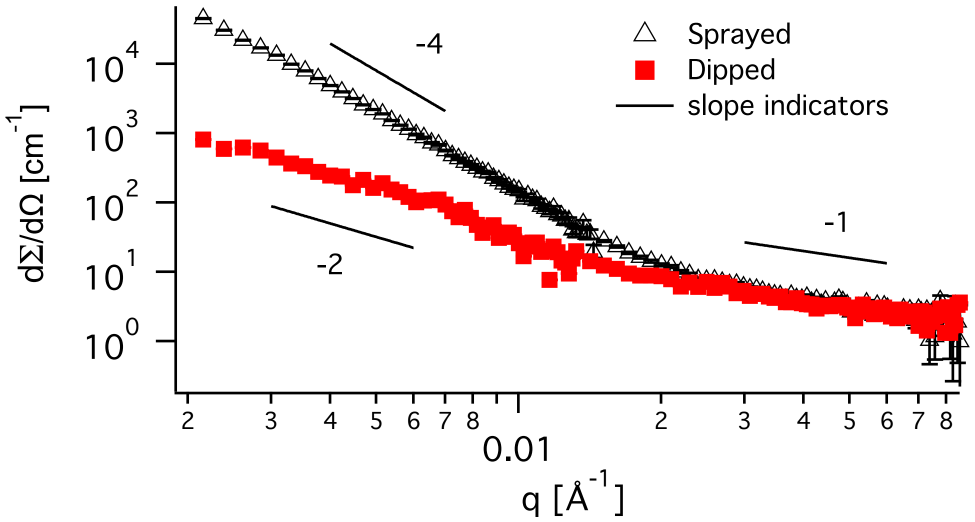
Dipping > Spraying > Spin coating

So what about in-plane structure?

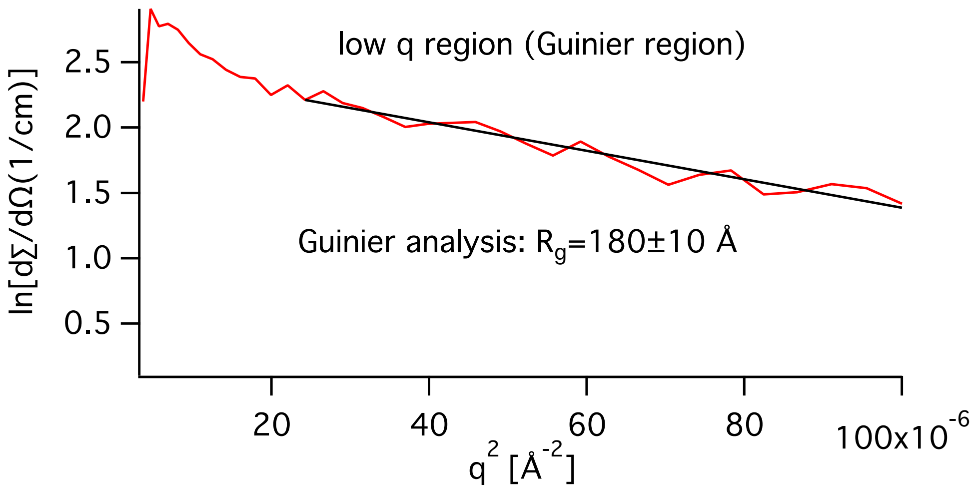
Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) ($PSS_{d/h}$)/ poly(allyl amine hydrochloride) (PAH)

Transmission SANS (D11):



Guinier analysis of Dipped Sample:



Observations:

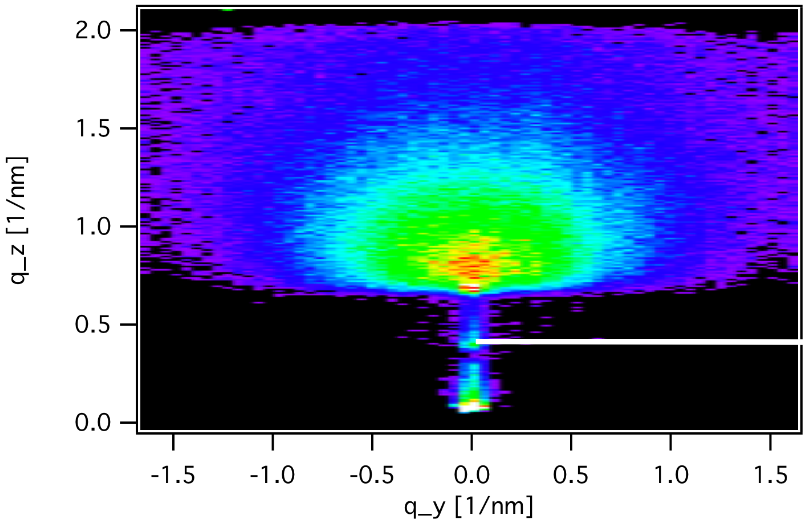
- At high q no change -> local structure is not influenced by the deposition method
- At low q Sprayed samples show surface fractal behavior, while dipped samples are more like Gaussian coils
- R_g of dipped sample: 18 nm in plane, versus 2.4 nm out of plane !

Bulk R_g in 2M Salt solution at 1 monM/L (from SANS): ~ 9 nm (-> volume roughly conserved)

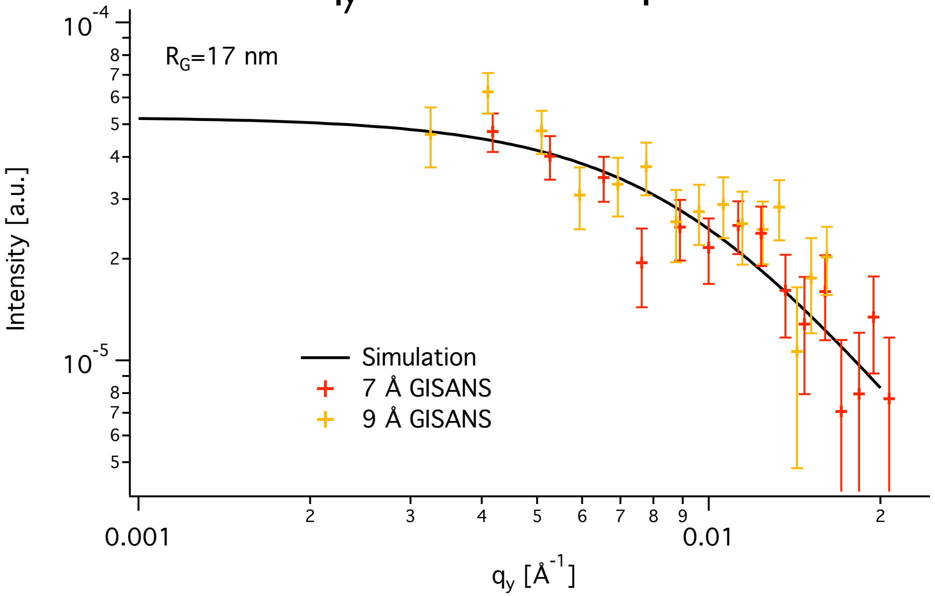
Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) ($PSS_{d/h}$)/ poly(allyl amine hydrochloride) (PAH)

GISANS on FIGARO:



q_y cut at Yoneda peak:



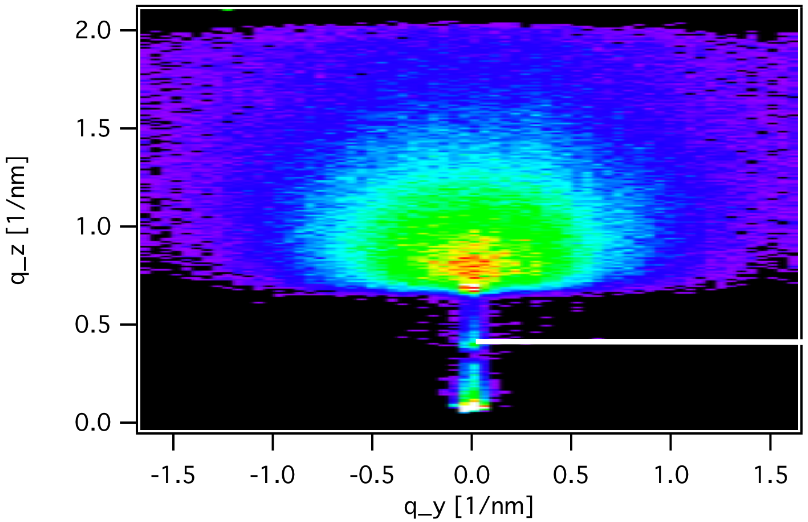
- Debye fit to GISANS curves at wavelengths of 0.7 nm and 0.9 nm reveals that the in-plane radius of gyration is 17 nm.

Higy, C., PhD thesis, Strasbourg University (2015).

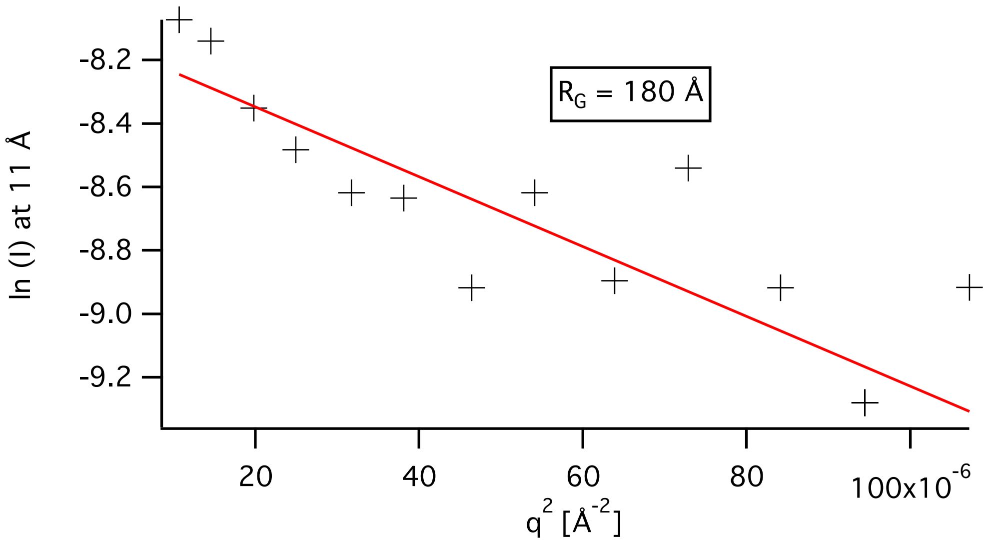
Polyelectrolyte multilayer (LbL)

Poly(styrenesulfonate) ($PSS_{d/h}$)/ poly(allyl amine hydrochloride) (PAH)

GISANS on FIGARO:



q_y cut at Yoneda peak (Guinier plot):



- GISANS with wavelength of 1.1 nm reveals the same in-plane radius of gyration as SANS: 18 nm. But counting time was 28h ! (Versus 6h on D11)

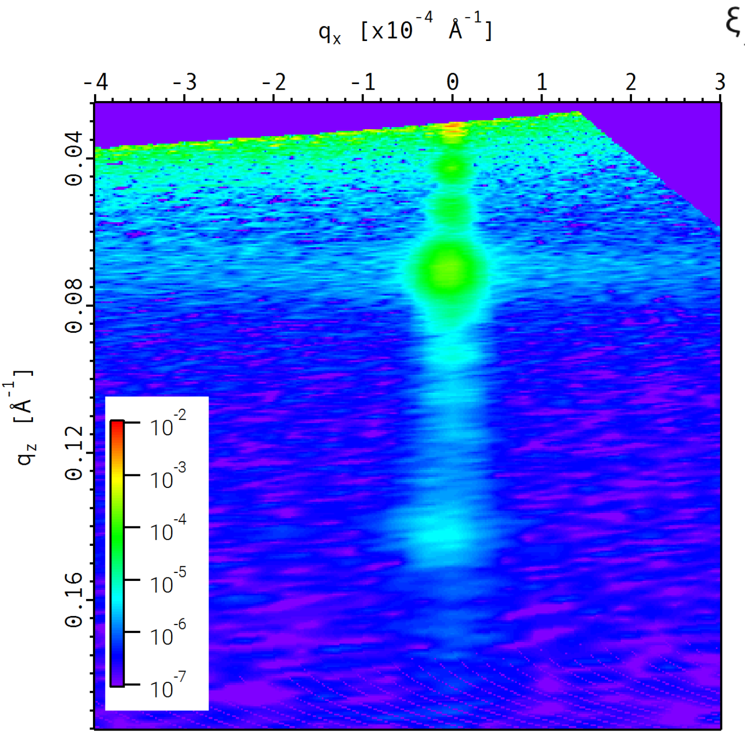
→ The combination of NR and (GI)SANS on polyelectrolyte multilayer films reveals the pancake like conformation of the polymer chains.

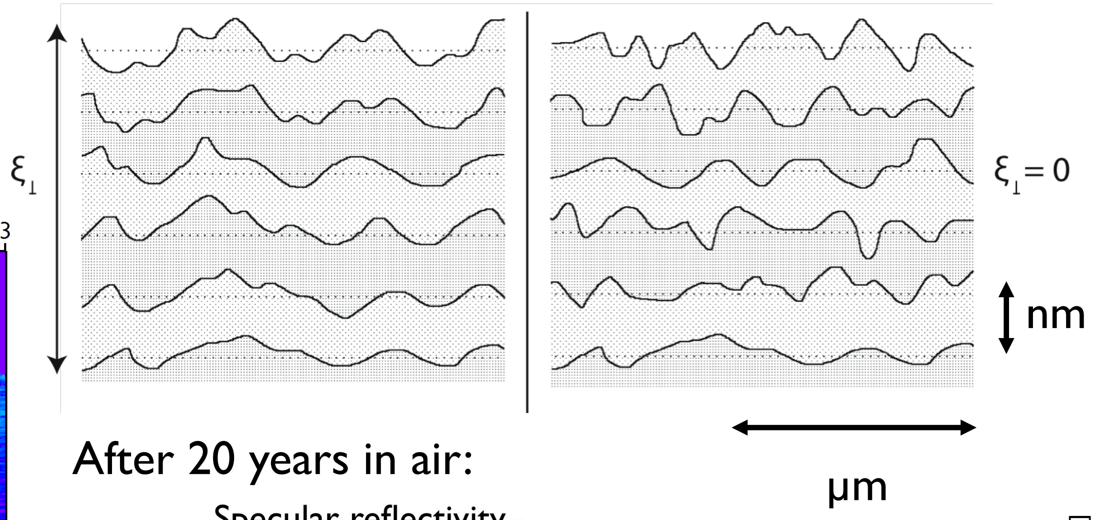
Higy, C., PhD thesis, Strasbourg University (2015).

Polyelectrolyte multilayer (LbL)

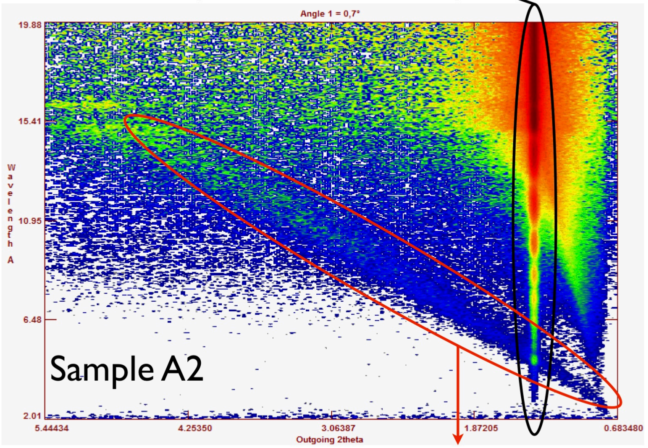
Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

OSS Dipped sample
$[(PSS_{h7}\text{-}PAH)_3\text{-}(PSS_{d7}\text{-}PAH)]_6$:

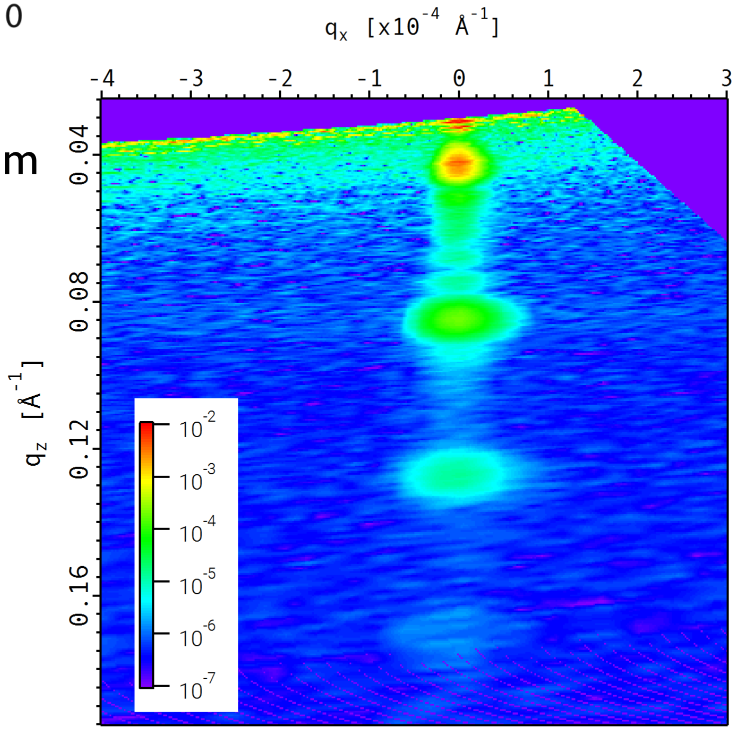




After 20 years in air:



OSS Sprayed sample
$[(PSS_{h7}\text{-}PAH)_5\text{-}(PSS_{d7}\text{-}PAH)]_6$:

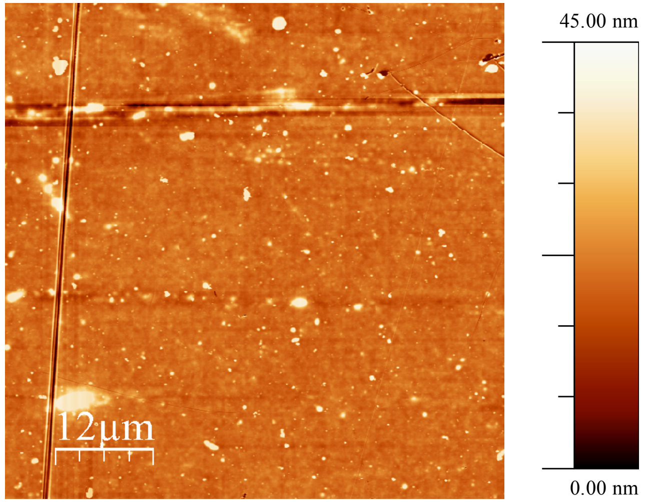


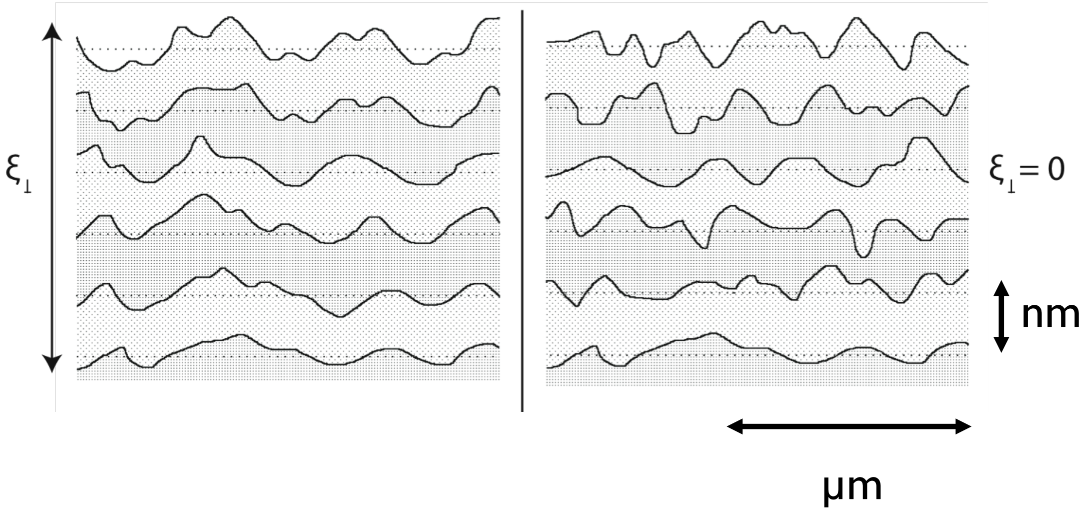
→ Dipped samples have better thickness correlation than sprayed samples.

Polyelectrolyte multilayer (LbL)

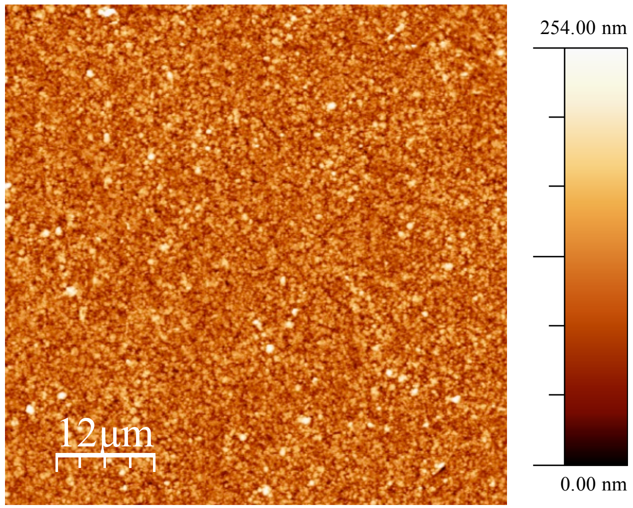
Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

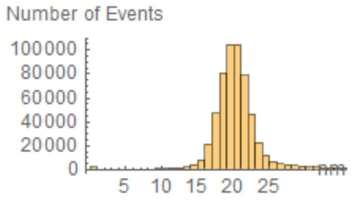
AFM Dipped sample (PSS$_{h7}$-PAH)$_{75}$:



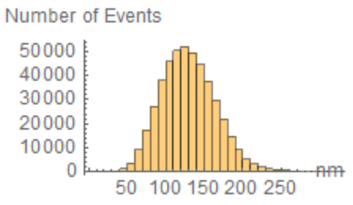


AFM Sprayed sample (PSS$_{h7}$-PAH)$_{80}$:



Roughness Analysis	
RMS (nm)	4.42189
Surface Skewness	1.69879
Surface Kurtosis	12.7312
Average Height (nm)	20.6606
Histogram	

Sprayed samples are more jagged than their dipped counterparts.

Roughness Analysis	
RMS (nm)	35.3482
Surface Skewness	0.547245
Surface Kurtosis	4.48527
Average Height (nm)	129.735
Histogram	

Conclusions

- By a **combination of specular and off-specular NR as well as (GI)SANS** one can measure the **3d conformation of polymer** coils in thin polymer films
- **LbL produced polyelectrolyte multilayers** were compared using three different preparation methods: **Dipping, Spraying and Spin-coating**.
- It turned out that **Spin-coating** produces the **least relaxed** films given the coil deformation from its unperturbed state in normal direction, **followed by spraying and dipping.**
- For the latter two examples **(GI)SANS confirmed the Gaussian like conformation of dipped** samples while the **sprayed once showed surface fractals**.
- **Off-specular scattering is suppressed for sprayed** samples corroborating **a less defined thickness correlation**

Thank you!