In-situ neutron reflectometry measurements of polyelectrolyte diffusion in Layer-by-Layer films in aqueous solution at ILL

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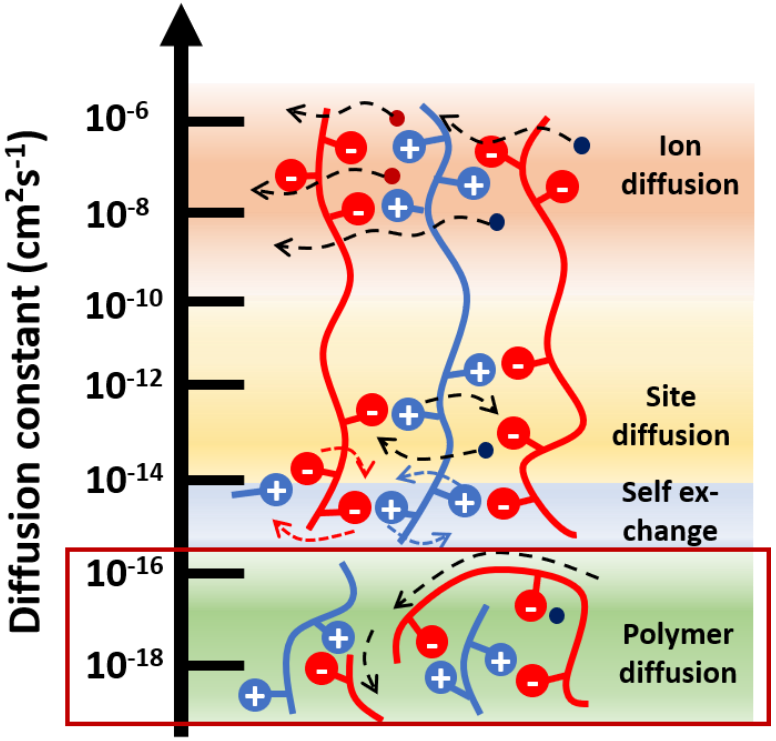
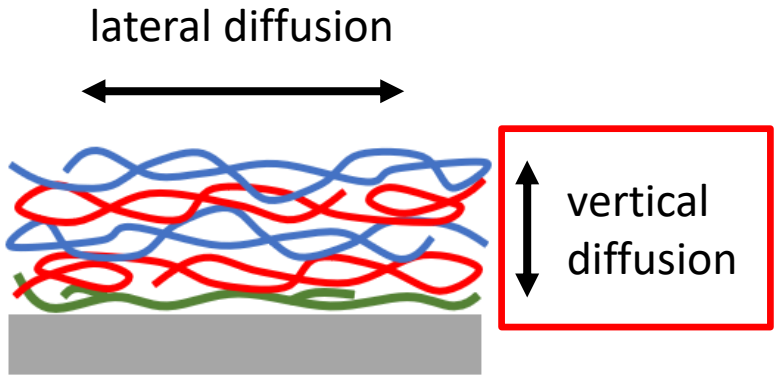
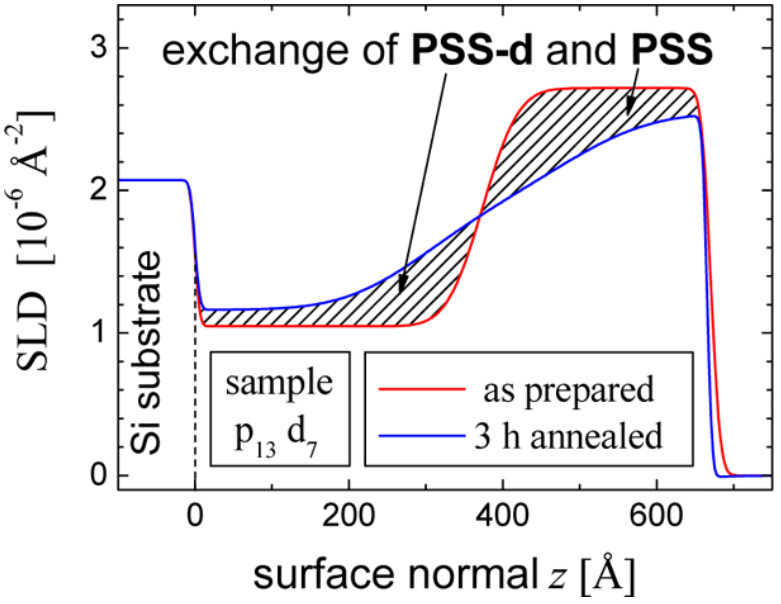
Vertical polyanion diffusion



scheme adapted from TOC image by Fares & Schlenoff 2017



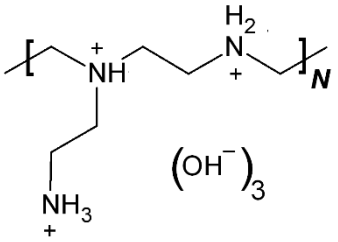


P. Nestler et al., Macromolecules, 2015

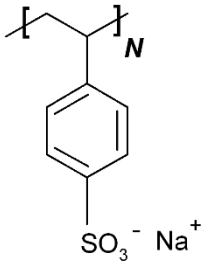
Polyelectrolyte multilayer (PEM)

Polyelectrolytes (PEs):

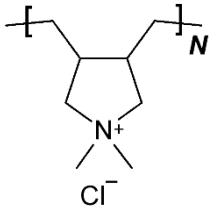
PEI



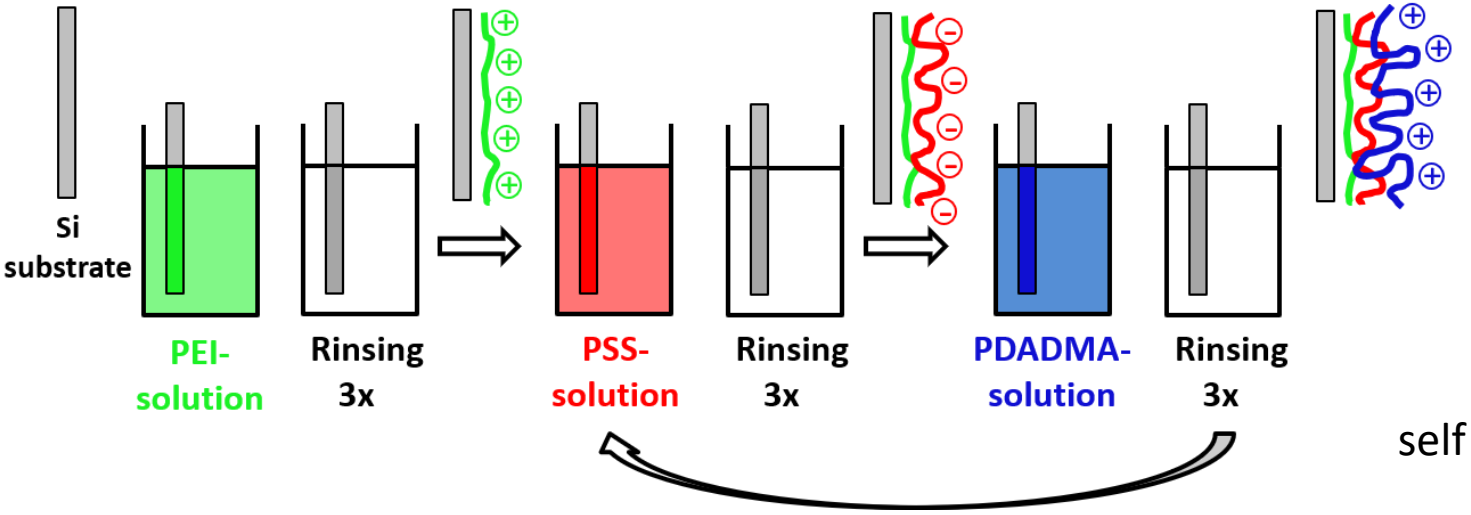
PSS



PDADMA

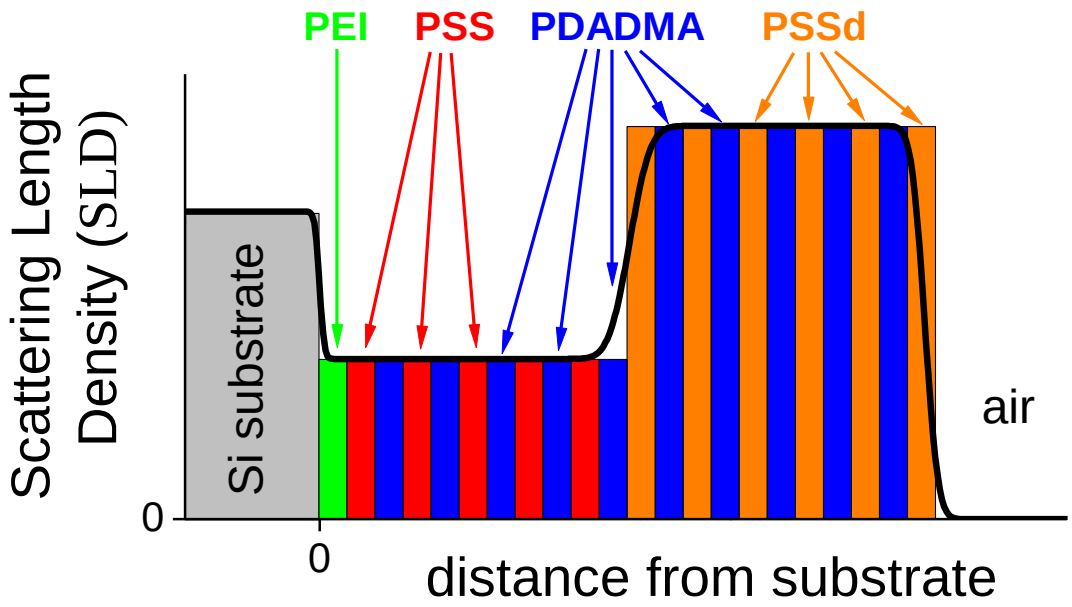


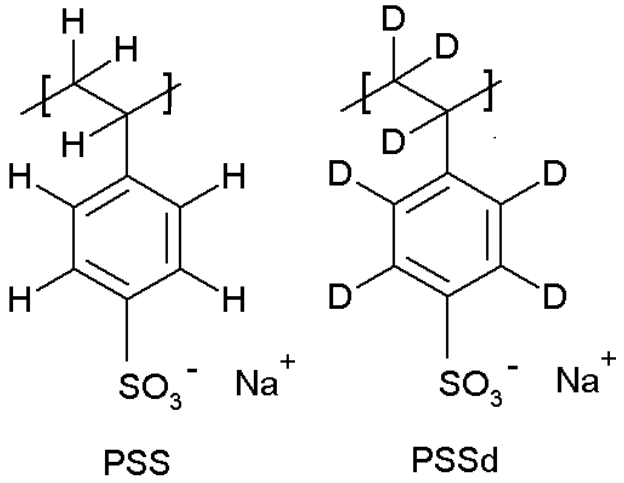
Polyelectrolyte multilayer (PEM) - Layer-by-Layer method:



adapted from Decher et al., Thin Solid Films, 1992, 210, 831-835

Approach: Slab Architecture





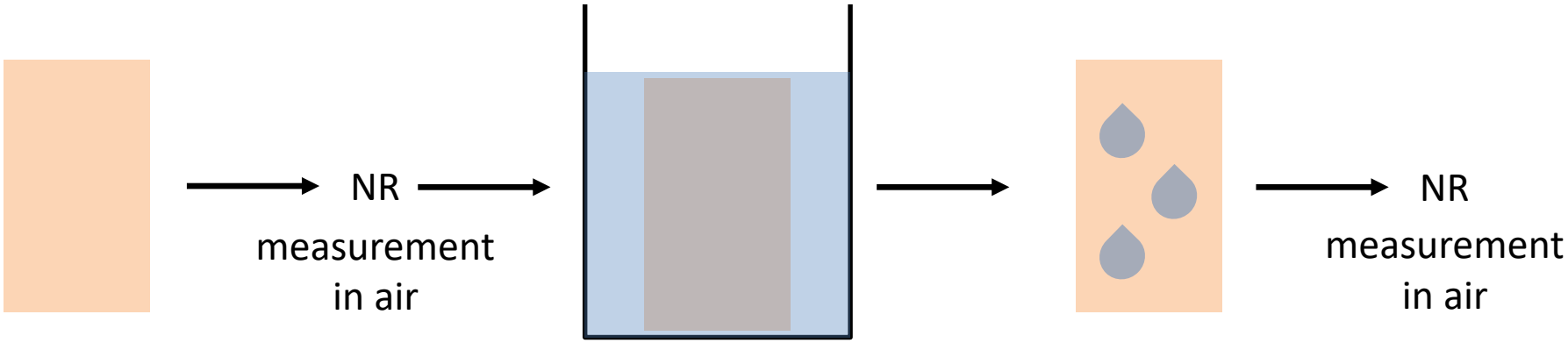
$$n = 1 - \frac{\lambda^2}{2\pi}\mathrm{SLD}$$

- slab architecture
- isotope labelling of PEM → protonated PSS and deuterated PSSd

n – refractive index
SLD – scattering length density
λ – wavelength of neutron wave

Motivation

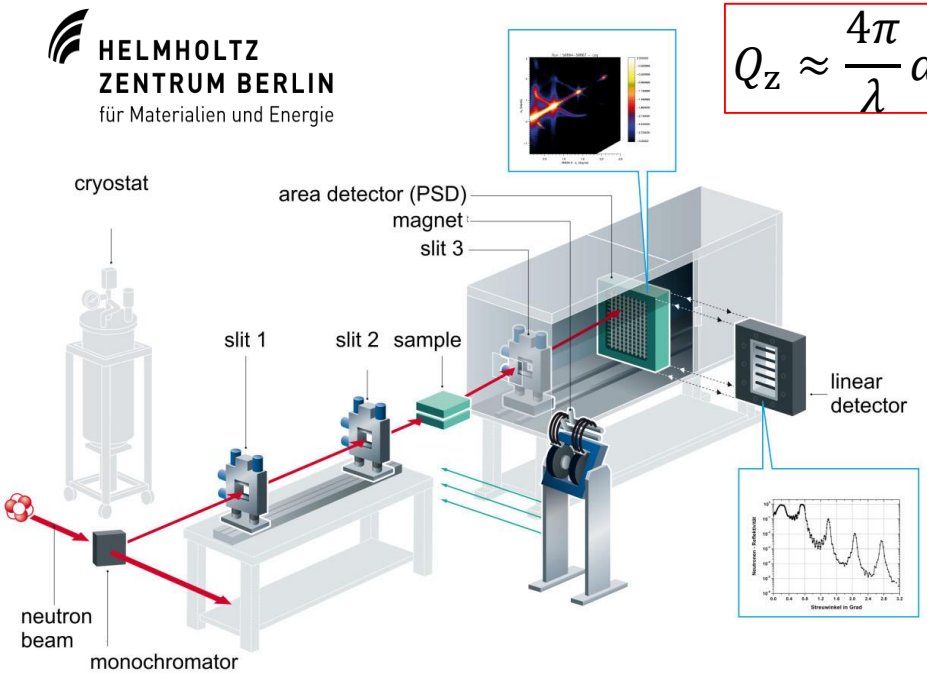
Up to now: snapshot experiments



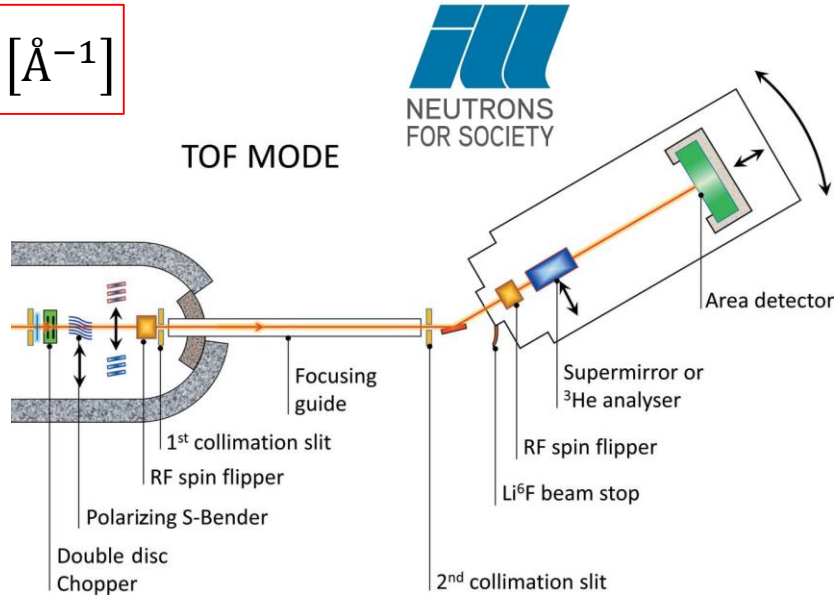
→ snapshot of the frozen-in polymer movement

→ our aim: in-situ studies of dynamics

V6 (snapshot) vs D17 (in-situu)



$$Q_z \approx \frac{4\pi}{\lambda}\alpha_{inc}\ [Å^{-1}]$$



Trapp, M. V6: The reflectometer at BER II. J. Large-Scale Res. Facil. JLSRF 2017, 3, 114

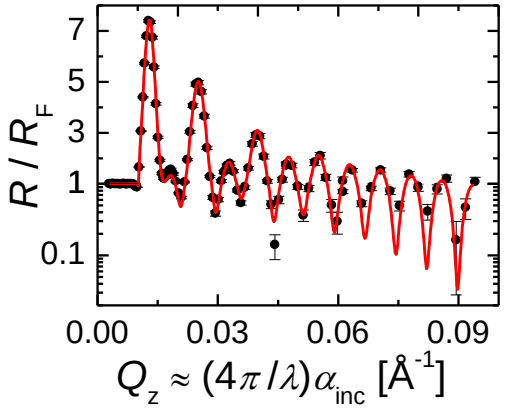
Saerbeck, T., Cubitt, R., Wildes, A., Manzin, G., Andersen, K. H., & Gutfreund, P., Journal of Applied Crystallography, 2018, 51, 249.

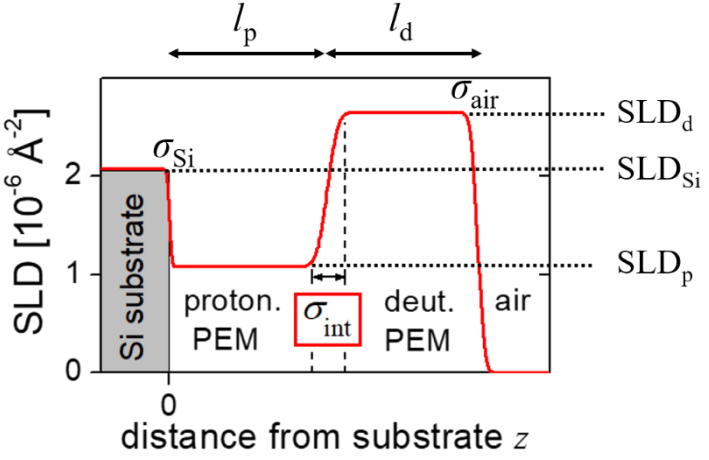
- λ = 4.66 Å, different α_{inc}
- to scan the entire Q_z range, 7-9 hours are required

- white neutron beam (2-27 Å), fixed α_{inc}
- scanning of the entire Q_z range within minutes

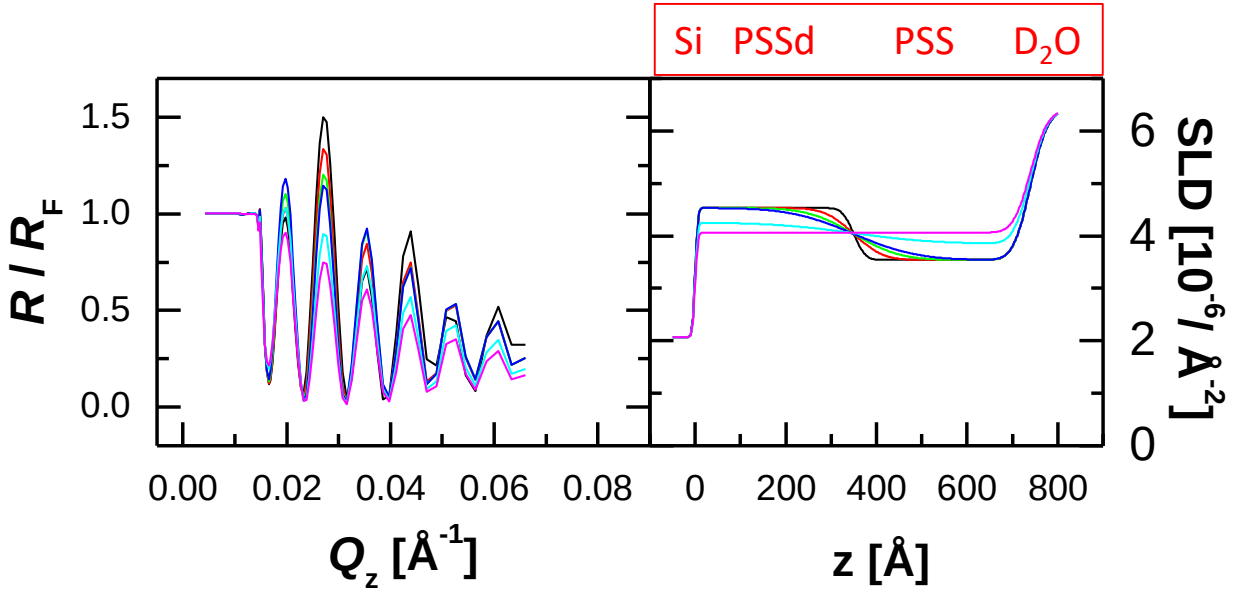
Approach: Slab Architecture

- snapshot: film setup for measurements air

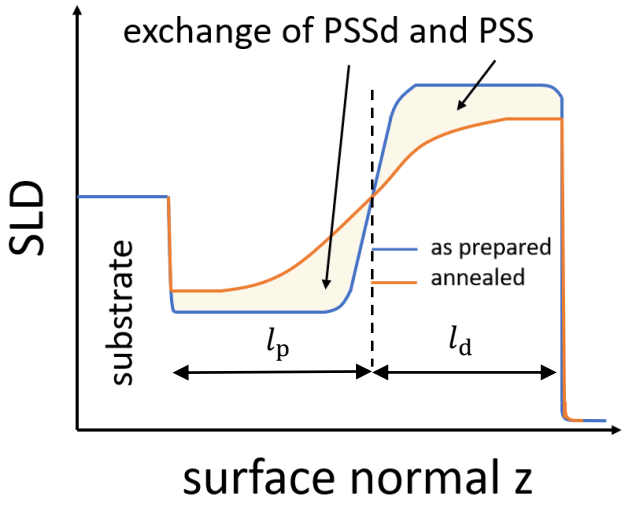




- simulation of PSS diffusion in PEMs annealed in D_2O solution containing 1 M NaCl
- the highest contrast was obtained by switching the slabs



Vertical polyanion diffusion



- Fick's Second Law $\frac{dc(z,t)}{dt} = D\frac{d^2c(z,t)}{dz^2}$
- width of internal interface :

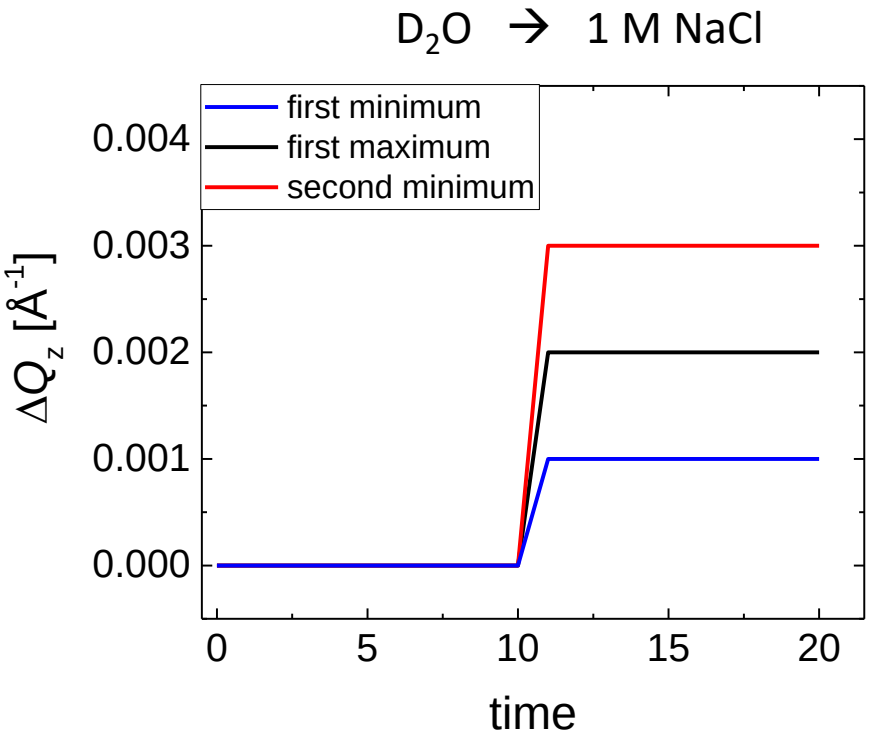
$$\sigma_{int} = \sqrt{2D_{PSS}t_{anneal} + \sigma_0^2}$$

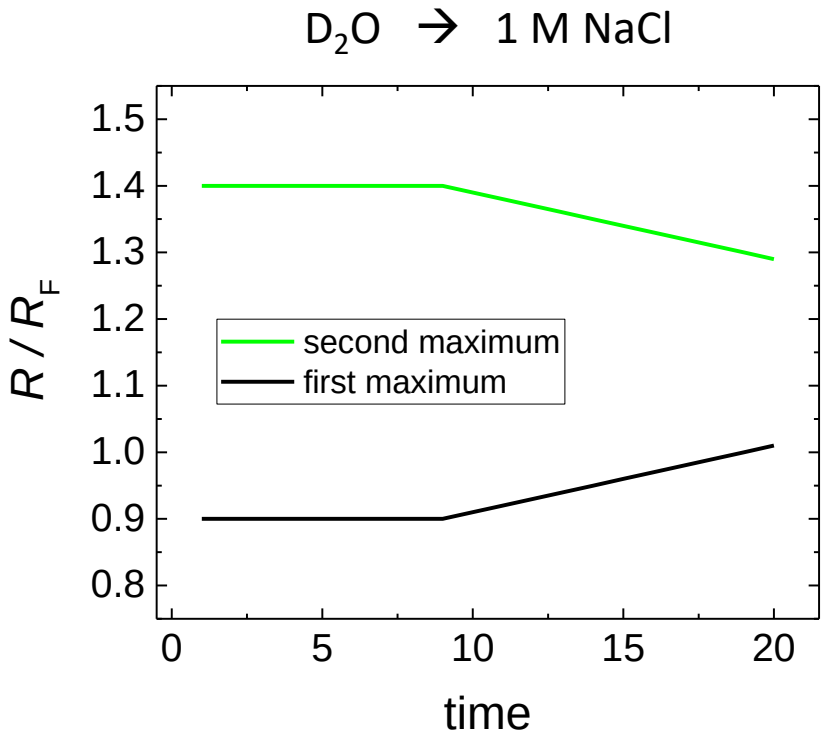
- one-dimensional solution:

$$c(z,t) = c_0\left[\Phi\left(\frac{z-l_p}{\tilde{\sigma}}\right) + \Phi\left(-\frac{z-l_p}{\tilde{\sigma}}\right) - \Phi\left(\frac{z-l_p-2l_d}{\tilde{\sigma}}\right)\right]$$

snapshot:	t_{anneal} = 0 → film as prepared
in-situ:	D_2O is exchanged against 1 M NaCl in D_2O t_{anneal} = 0 → ?

t_{anneal} = 0 → raw data





1. if the thickness of the multilayer changes, the Qz-position should shift
2. if the internal roughness between the slabs increases, the intensity of the first maximum (blue) should increase and the intensity of the second maximum (red) should decrease

→ If both changes correspond in time → t_{anneal} = 0

Summary

- it is possible to measure the dynamics in PEMs in-situ
- with the help of simulations, we have found the most suitable film setup for our studies

- by looking at the raw data, the starting point of the diffusion can be determined

➢ thus a check of the experiment is also possible during the measurement time

- the comparison with the snapshot experiments is not given yet

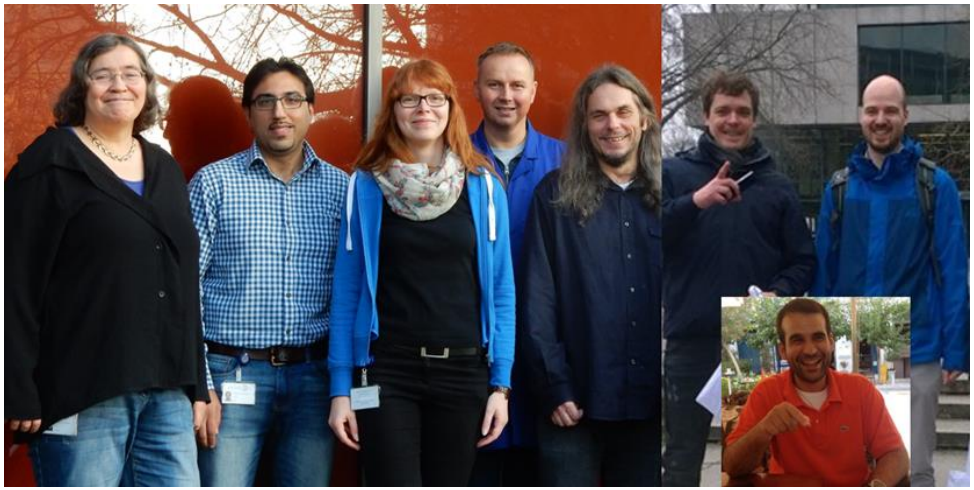
➢ further experiments are necessary for this

- the thickness increase of the films depends on the salt concentration in the solution

➢ further experiments are also planned (e.g. in-situ ellipsometry studies)

Thank you!

University Greifswald



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