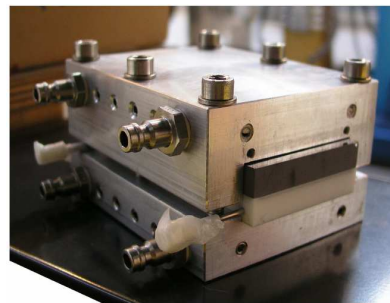


Probing hidden films

with
neutron reflectometry



08. 06. 2016

TU Clausthal, Germany

experiments

Ursula Bengaard Hansen
Wolfgang Kreuzpaintner
Saumya Mukherjee
Birgit Wiedemann
Wolfgang Gruber
Harald Schmidt
Florian Strauß
Erwin Hüger
Artur Glavic
Bujar Jerliu
Sina Mayr
...

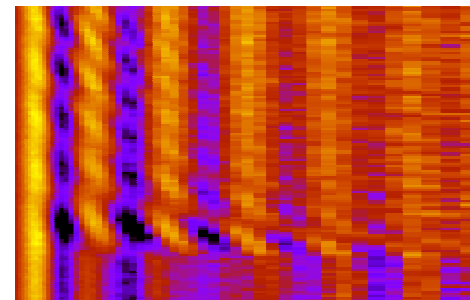
simulations

Emanouela Rantsiou
Tobias Panzner
Panos Korelis
Uwe Filges

ideas / discussions

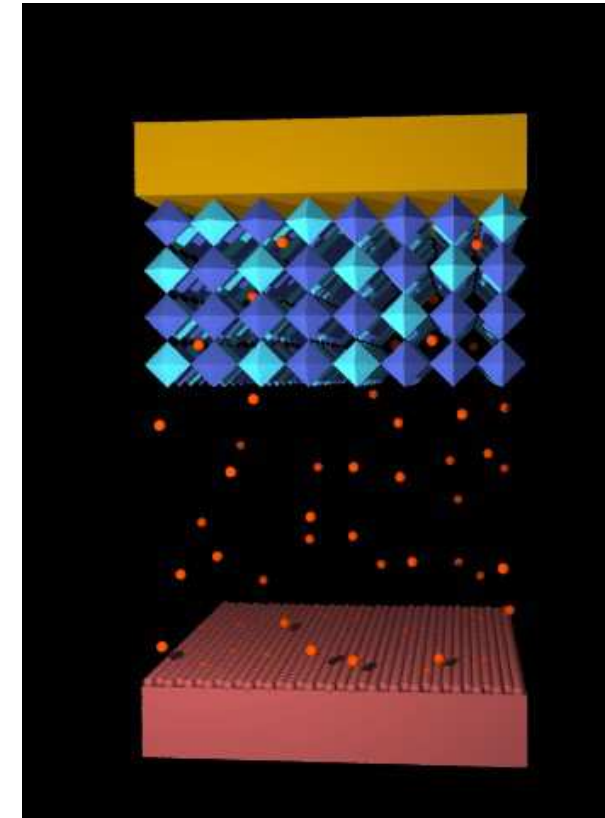
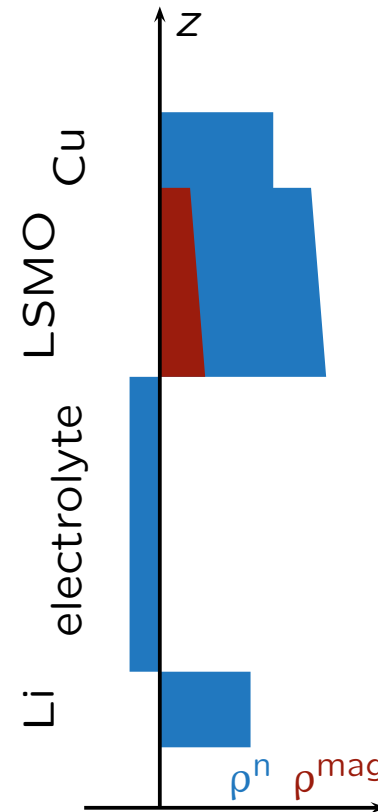
Marité Cardenas
Rob Dalgliesh
Frédéric Ott
Phil Bentley
Bob Cubitt
Peter Böni
Uwe Stuhr
...

- intro
- reflectometry
 - general introduction
 - the neutron
- neutron reflectometry
 - the next generation
- experimental examples
 - Li diffusion in Si
 - in-situ film growth
 - strain-induced magnetism
 - in-operando Li battery
- the future
 - projects for Amor
 - instrumentation
 - conceptual challenges



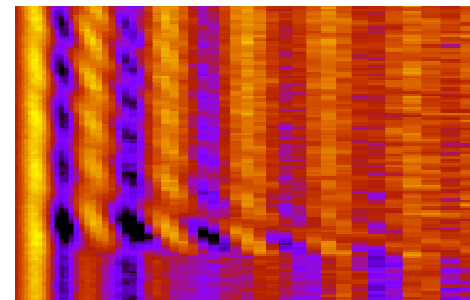
features of **neutron reflectometry**

- depth-profile of chemical composition
- depth-profile of magnetic induction
- near surfaces: $\rightarrow 0.5 \mu\text{m}$
- flat samples: $\rightarrow 30 \text{ \AA}$
- sample sizes: $3 \text{ mm}^2 \rightarrow 30 \text{ cm}^2$
- measurement time: $1 \text{ min} \rightarrow 1 \text{ day}$
- high penetration depth: $\rightarrow 10 \text{ cm}$



alternative / complementary to: XR, resonant x-ray techniques, SIMS, TEM, ...

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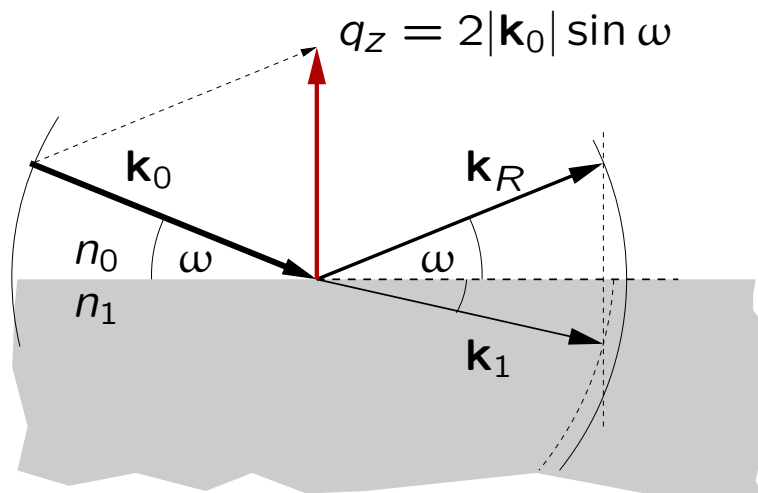


analogy to visible light

flat surfaces partly reflect light
→ picture of the boot

some media also transmit light
→ ground below the water

parallel interfaces
→ colourful soap bubbles



$$|\mathbf{k}| = 2\pi/\lambda$$

n = index of refraction

reflected intensity of a multilayer

$$R(q_z) \approx |\mathcal{F}[\rho(z)]_{q_z}|^2$$

⇒ all phase information is lost

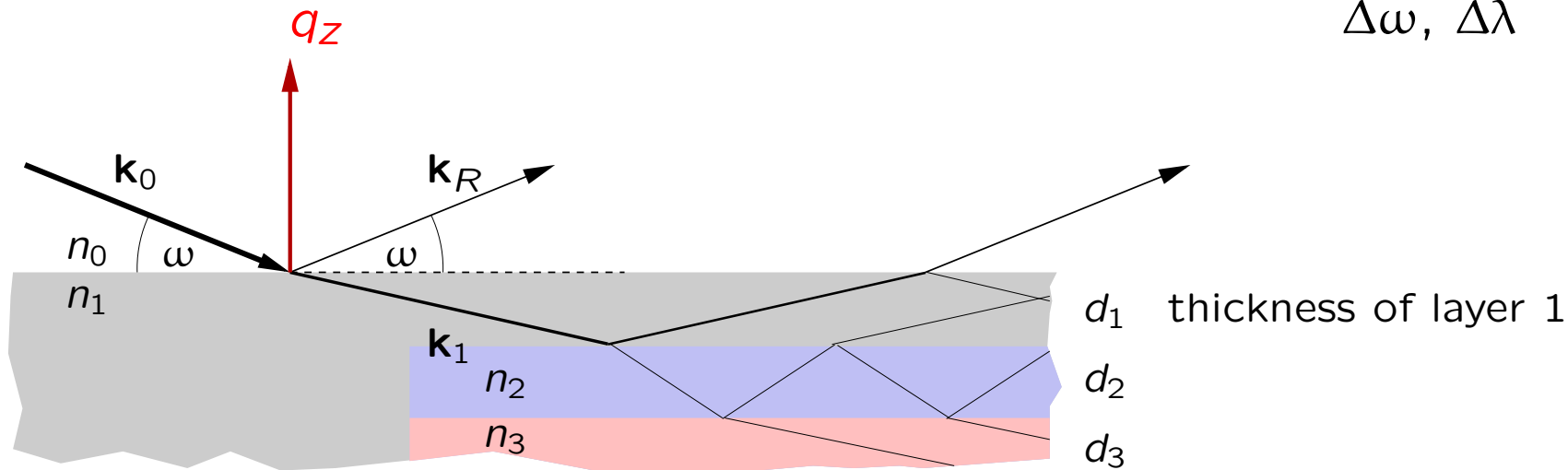
⇒ one way road:

⇒ calculation of $R(q_z)$ using a model
and
comparison to measured curve(s)

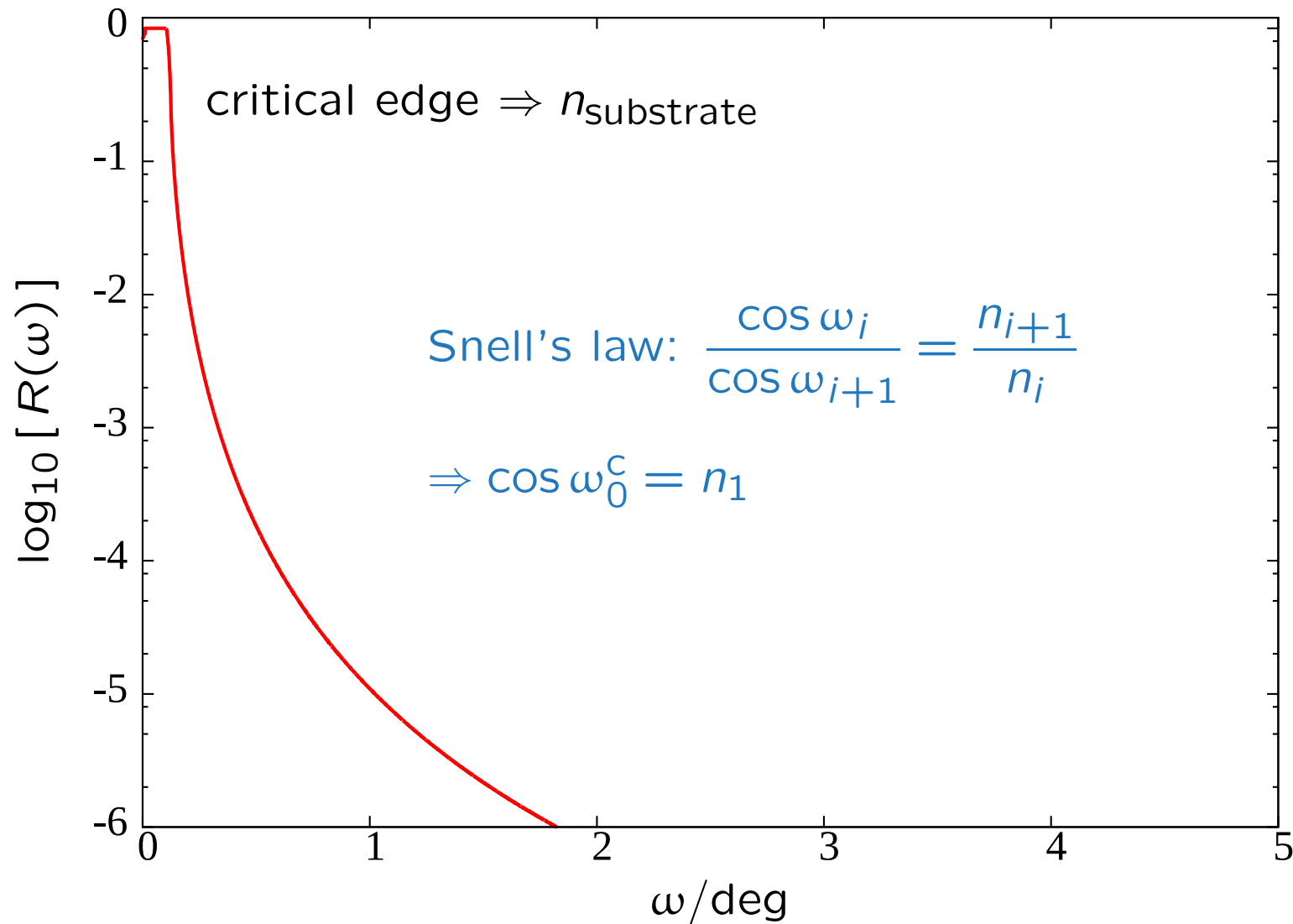
real effects

to be taken into account:

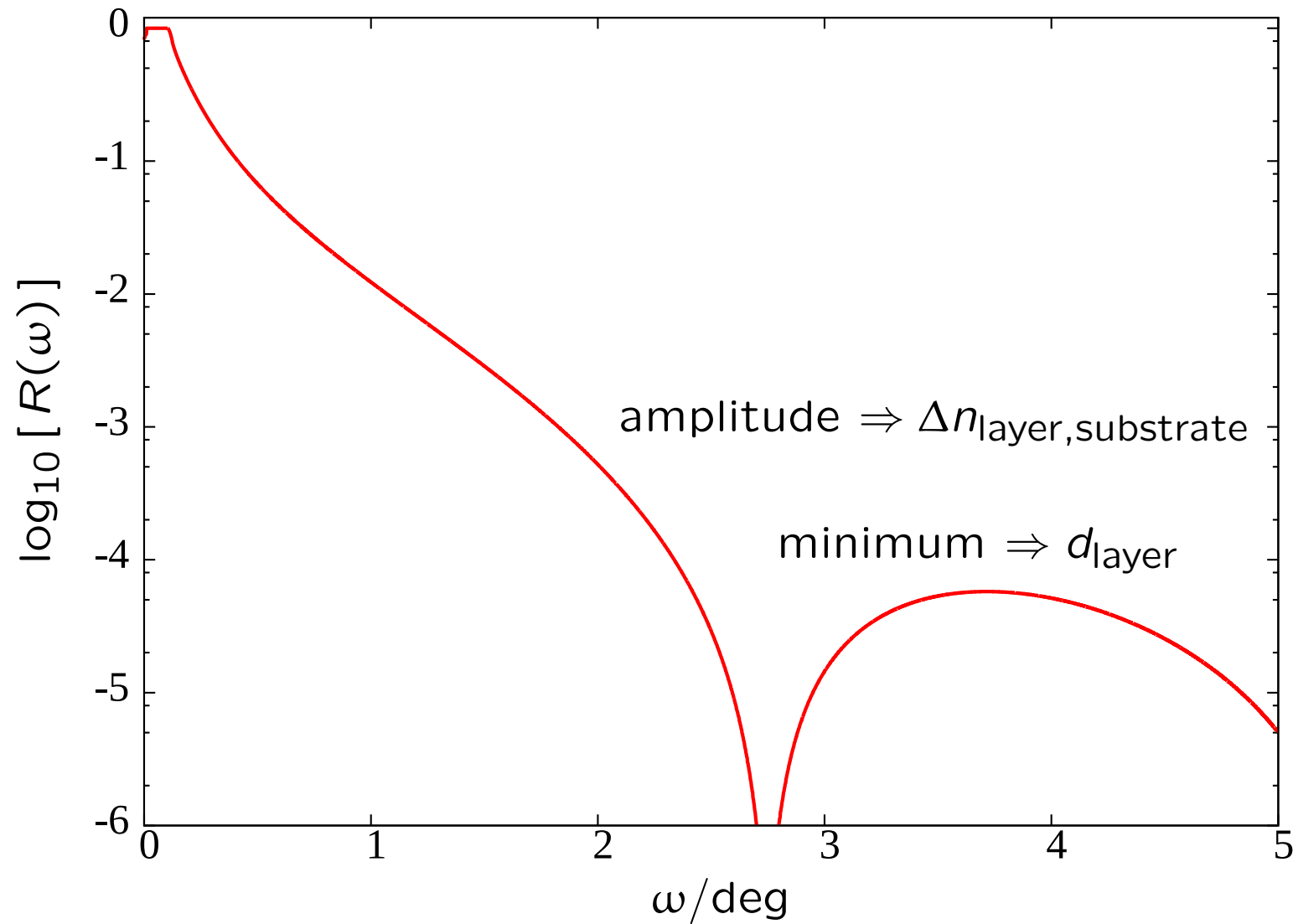
- non-sharp interfaces
- inhomogeneous layers
- illumination of the sample
- resolution of the set-up
 $\Delta\omega, \Delta\lambda$



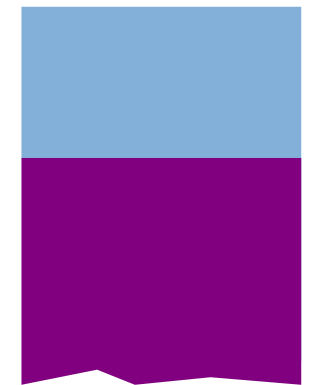
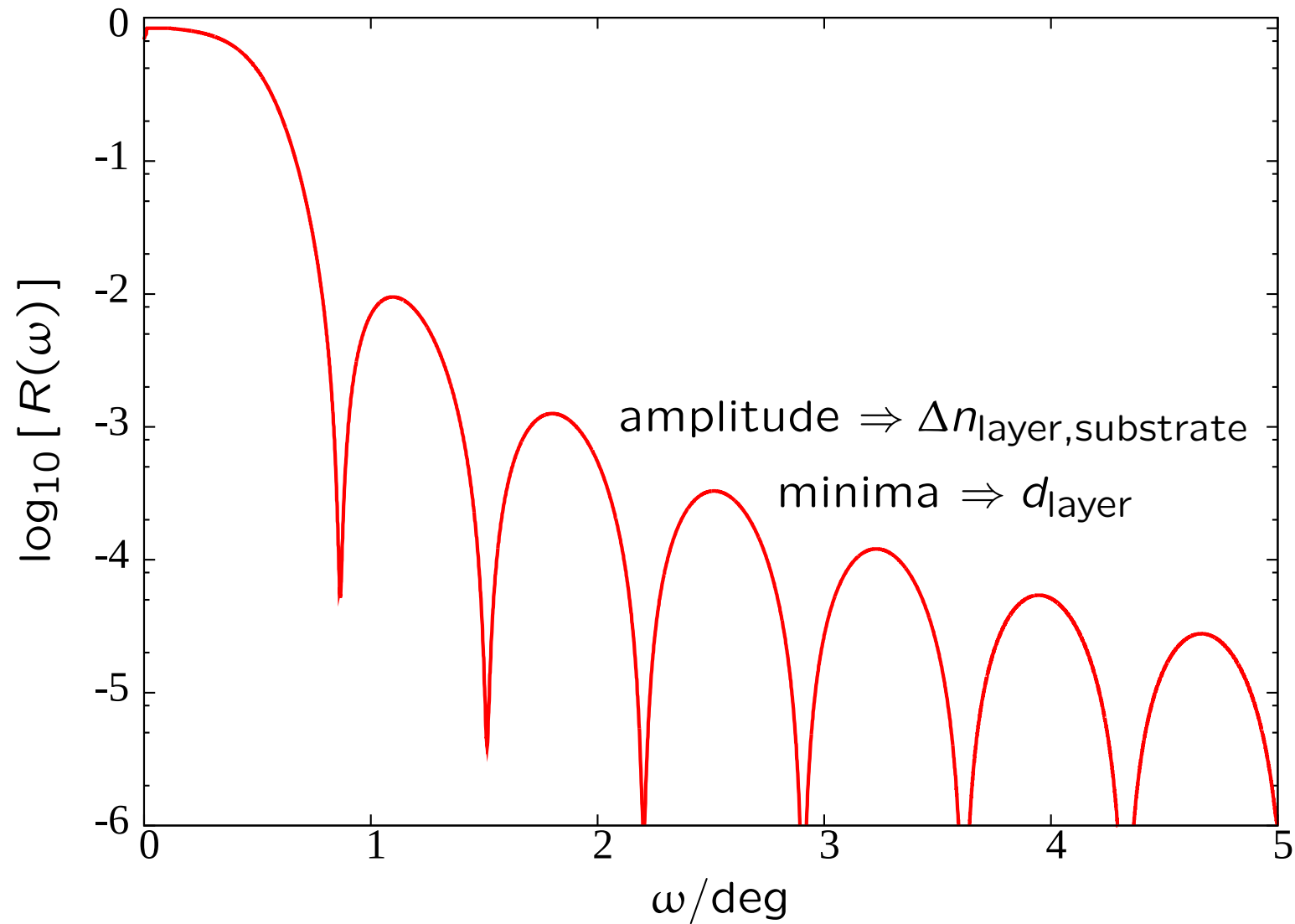
simulated reflectivity of a surface



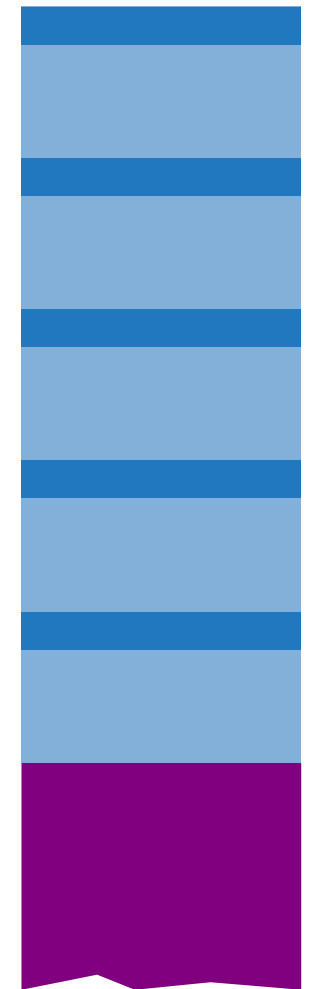
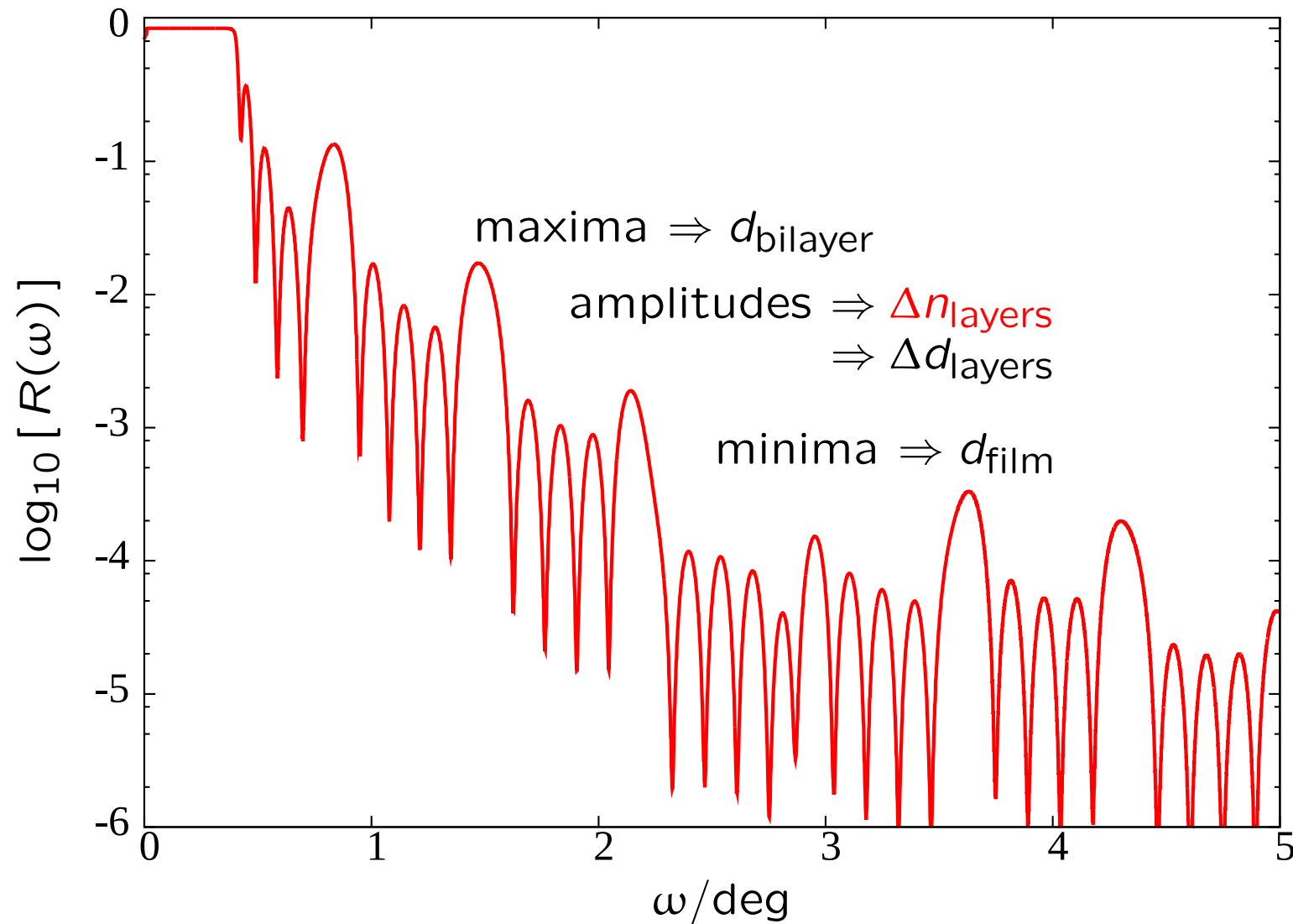
simulated reflectivity of a thin layer



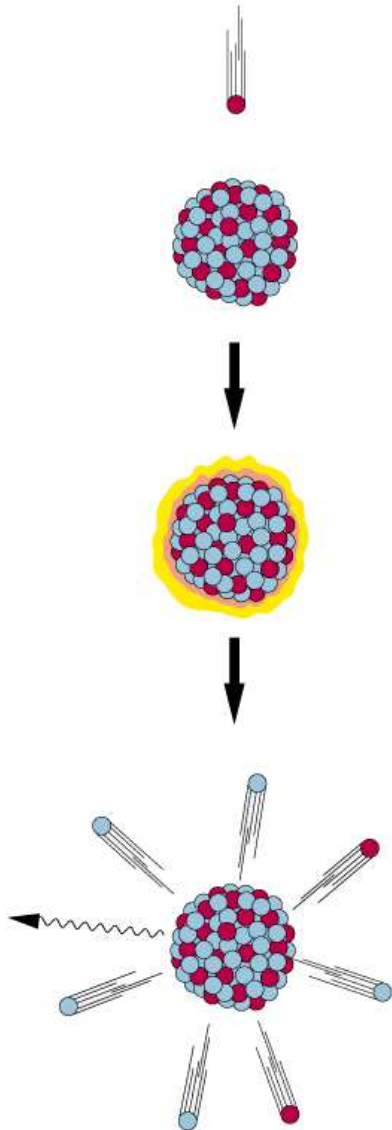
simulated reflectivity of a thick layer



simulated reflectivity of a periodic multilayer



... with neutrons



- building unit of atomic nuclei
- $\approx$ mass of a **proton**
 $\Rightarrow$ collision with nuclei
- no charge
 $\Rightarrow$ no interaction with electrons / charges
- spin $1/2$
 $\Rightarrow$ magnetic moment
 $\Rightarrow$ interaction with magnetic fields
- De-Broglie wavelength $\approx 1 \dots 20 \text{ \AA}$
 $\Rightarrow$ atomic / crystallographic dimensions
 $\Rightarrow$ energy of phonons
- interaction with nuclei
 $\Rightarrow$ *random* sensitivity across the PSE
 $\Rightarrow$ isotope-sensitive

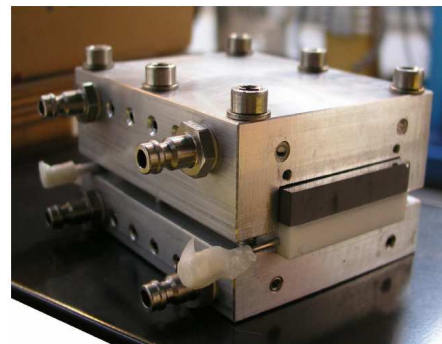
some numbers

probed depth $100 \text{ nm} \rightarrow 1 \text{ }\mu\text{m}$ (less for absorbers)

depth resolution $0.2 \text{ nm} \rightarrow 400 \text{ nm}$ strongly model dependent
 t and δ might be correlated

lateral coherence $1 \text{ }\mu\text{m} \rightarrow 100 \text{ }\mu\text{m}$ averaging laterally over all
microstructures

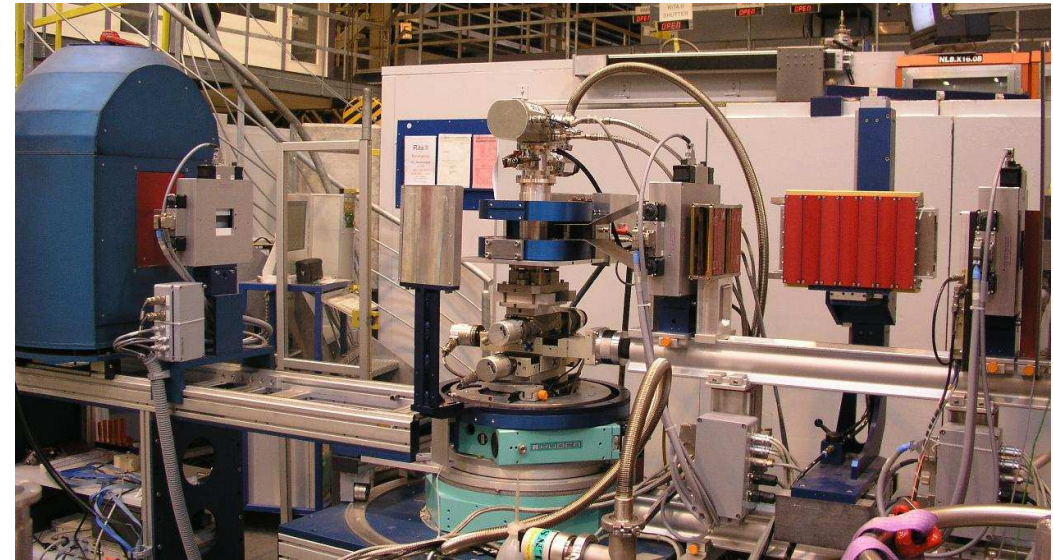
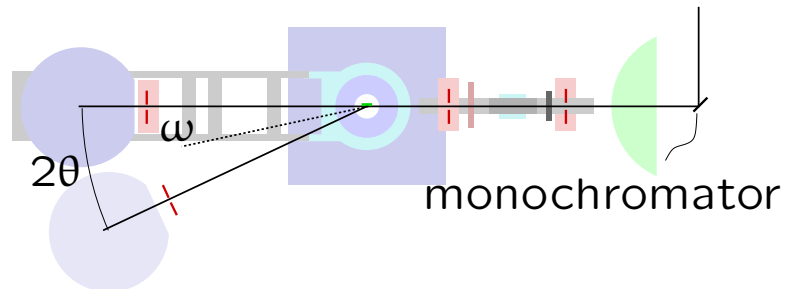
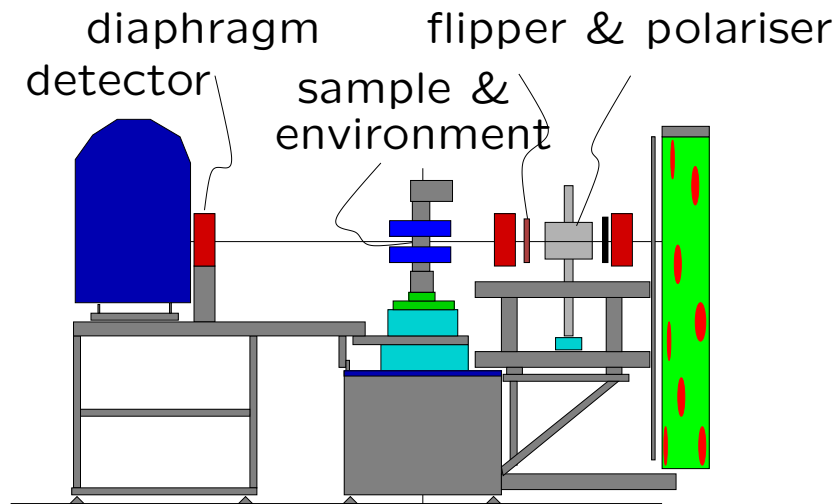
penetration depth $\rightarrow 10 \text{ cm}$



equipment

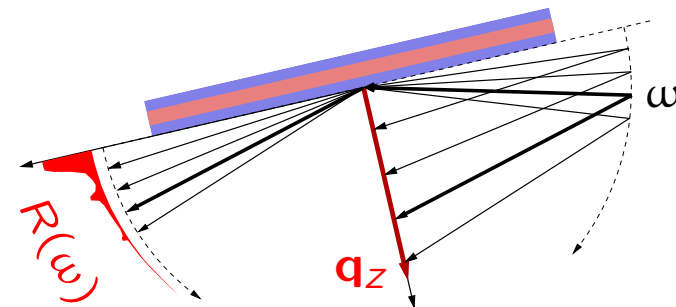
neutron reflectometer

e.g. Morpheus at SINQ



angle-dispersive set-up

$$q_z = 4\pi \frac{\sin \omega}{\lambda}$$



equipment

sample environment

e.g. cooling with a
closed cycle refrigerator

$$8\text{ K} < T < 300\text{ K}$$

application of an external magnetic field with
Helmholtz coils $-1000\text{ Oe} < H < 1000\text{ Oe}$

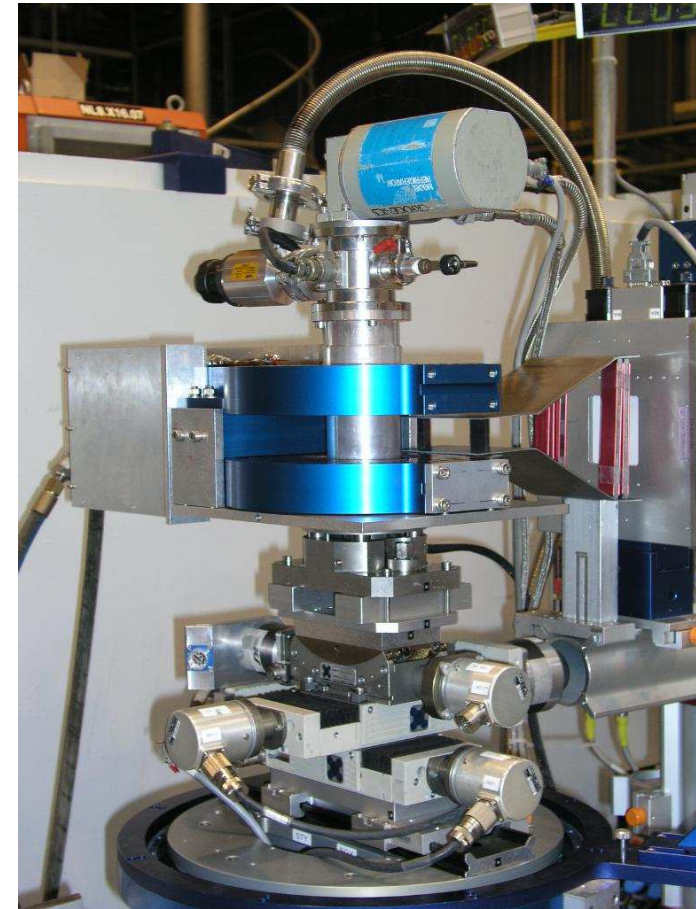
tilt- and translation stages
for alignment

ω rotation stage



sample

within
sample-holder



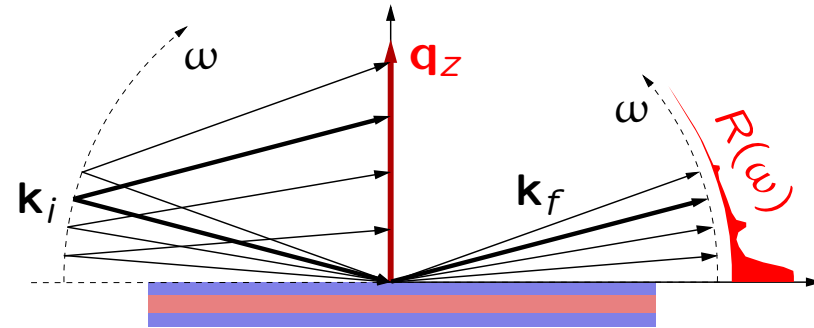
data acquisition

typical quantities:

angular range $0^\circ \dots 10^\circ$

λ range $3 \text{ \AA} \dots 15 \text{ \AA}$

measurement time 10 min ... 12h

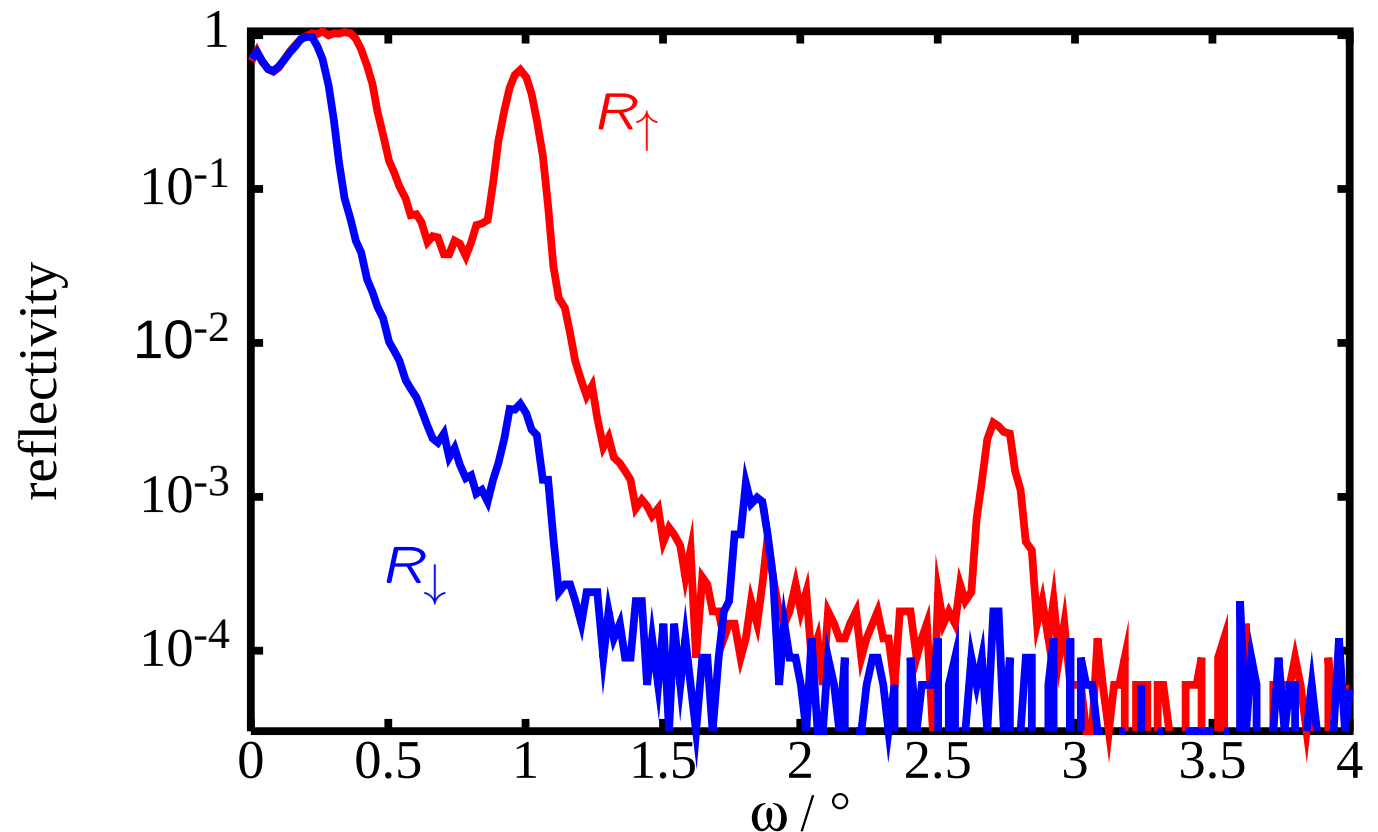


example:

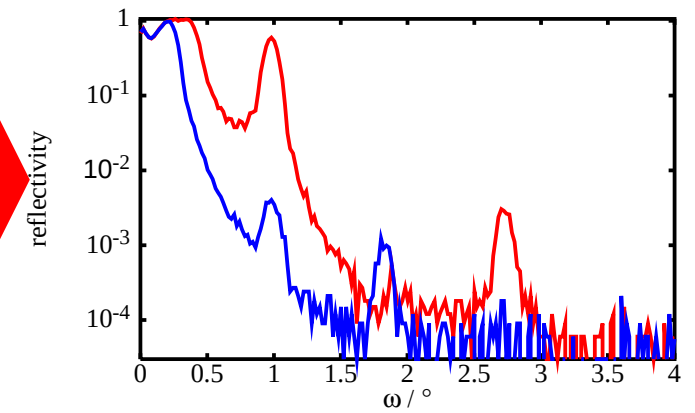
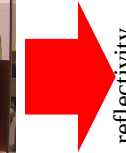
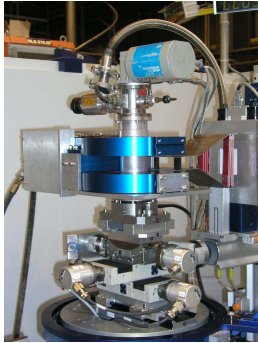
Fe/Si multilayer on glass

polarised neutrons

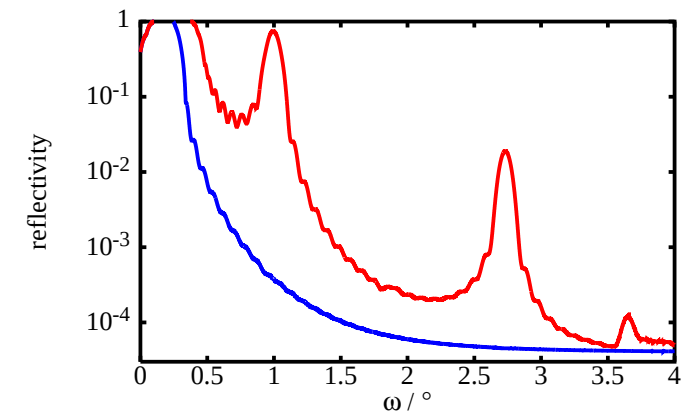
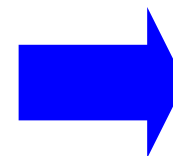
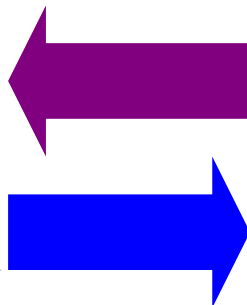
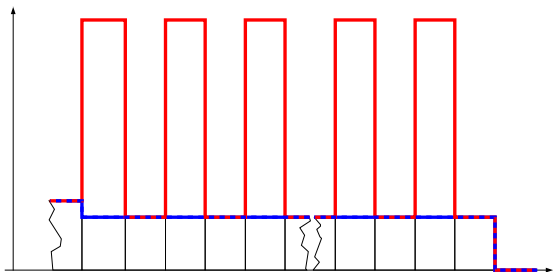
1h per spin state



data acquisition and interpretation



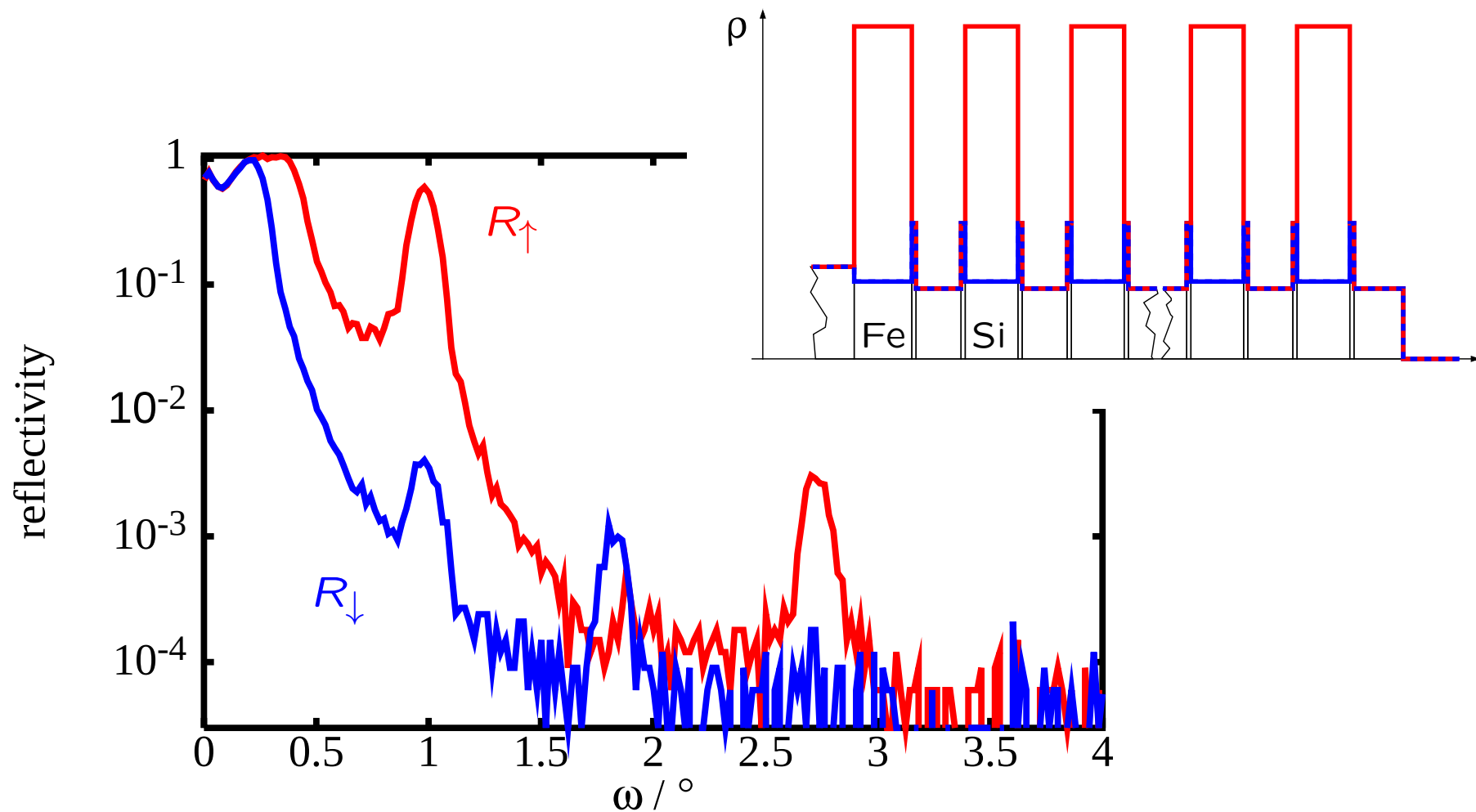
?



data acquisition and interpretation

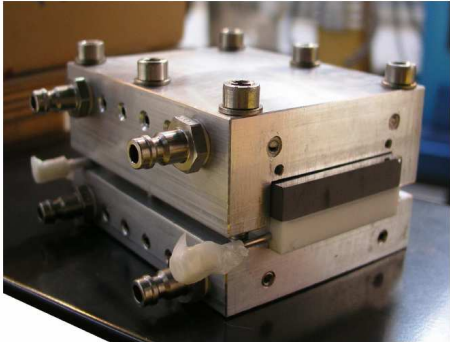
Fe/Si multilayer

interdiffusion leads to 5 Å thin magnetically dead Fe : Si layers

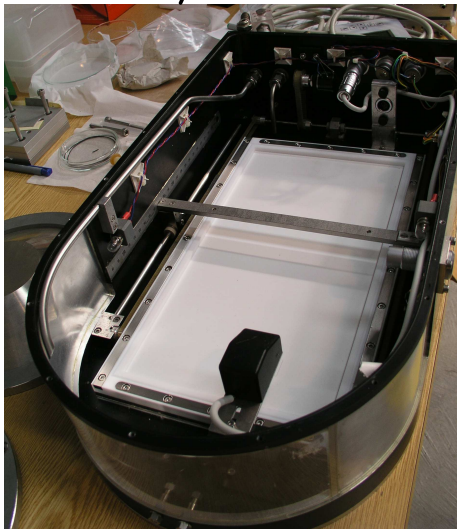


typical scientific questions

adsorption at ...
solid/water

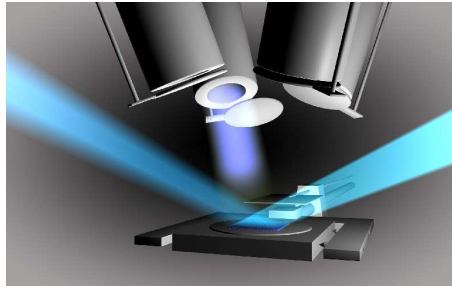


air/water

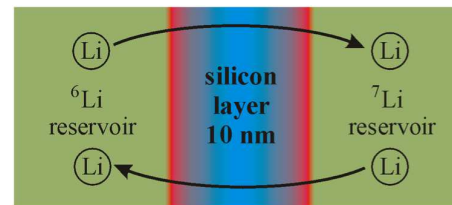


... interfaces

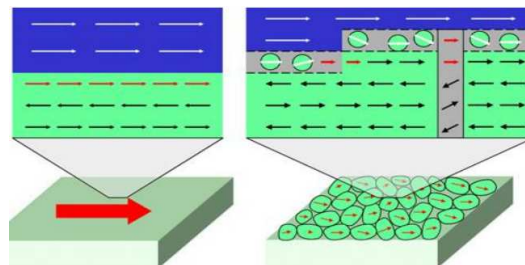
growth
mechanisms



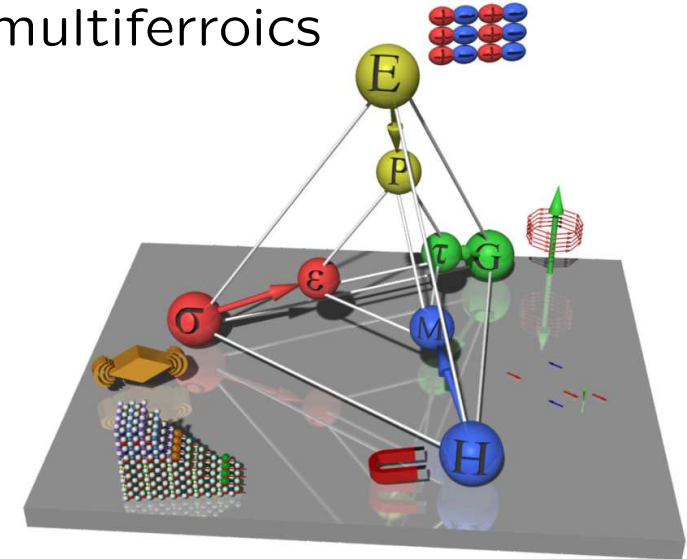
diffusion



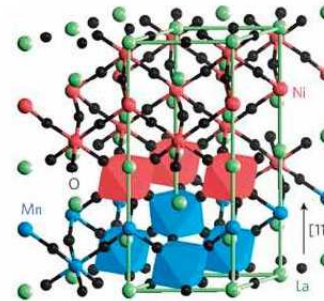
exchange bias



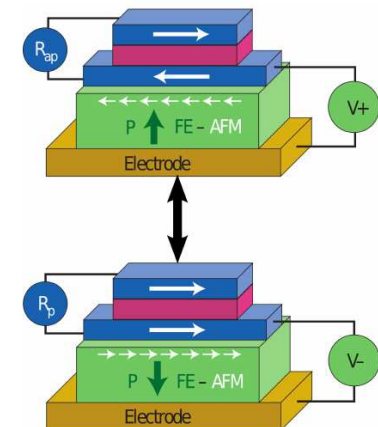
multiferroics



interface
magnetism



spintronics



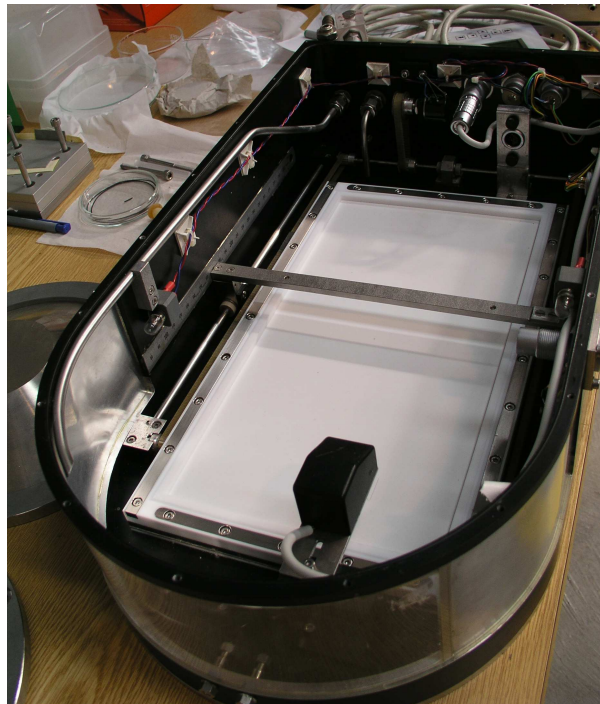
liquid/gas interface

compression of self-organising polyglycerol-ester films

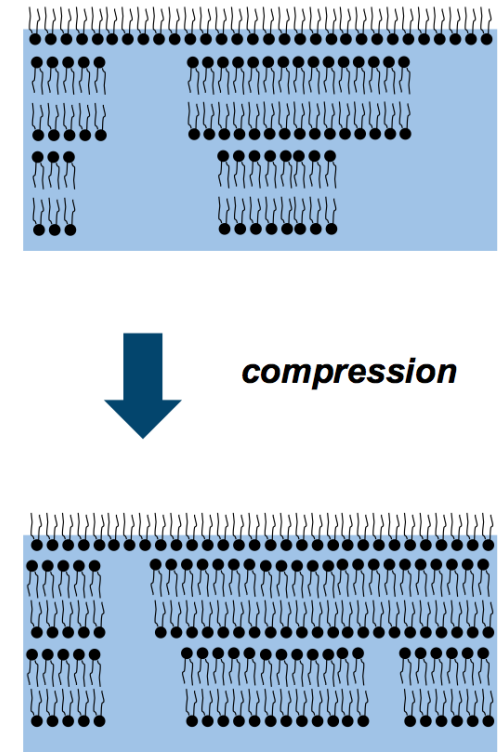
model-system for

foams used for stabilising food products

e.g. yogurt



trough to investigate
membranes at the
liquid/air interface



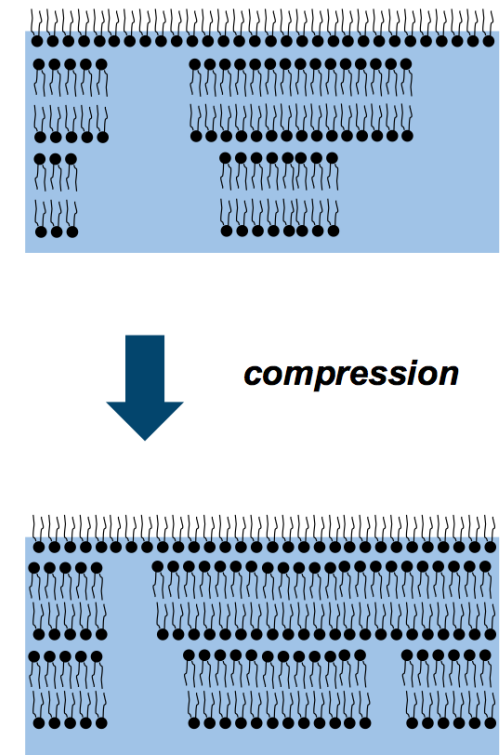
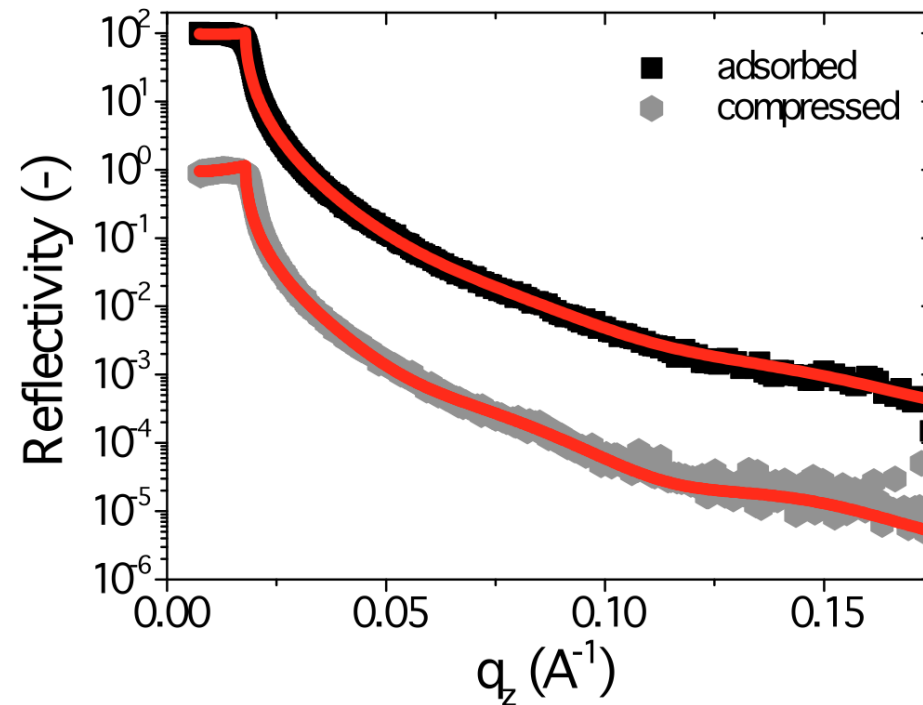
liquid/gas interface

compression of self-organising polyglycerol-ester films

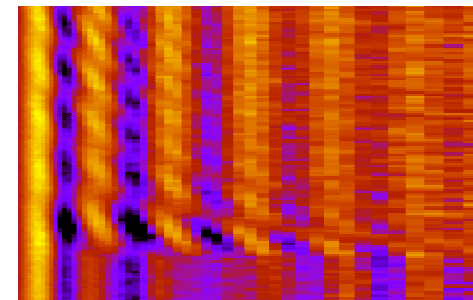
H₂O substituted by D₂O

⇒ strong contrast between solvent and film (essentially [CH₂]_n)

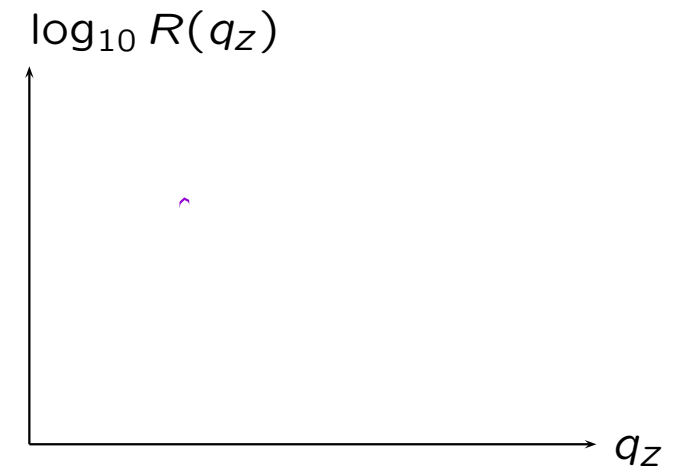
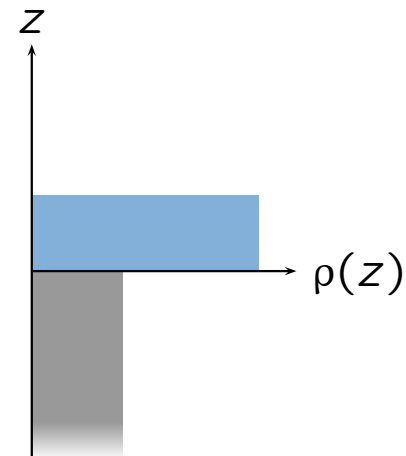
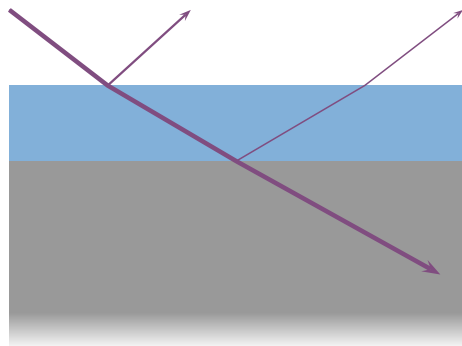
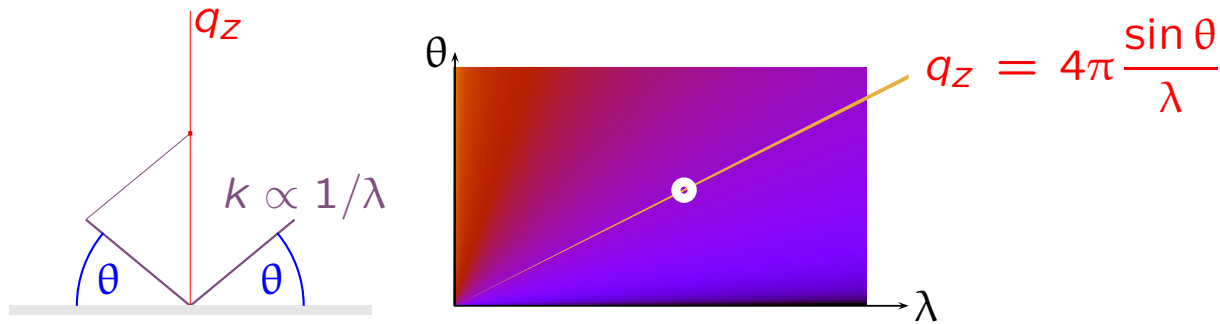
⇒ *high* critical edge



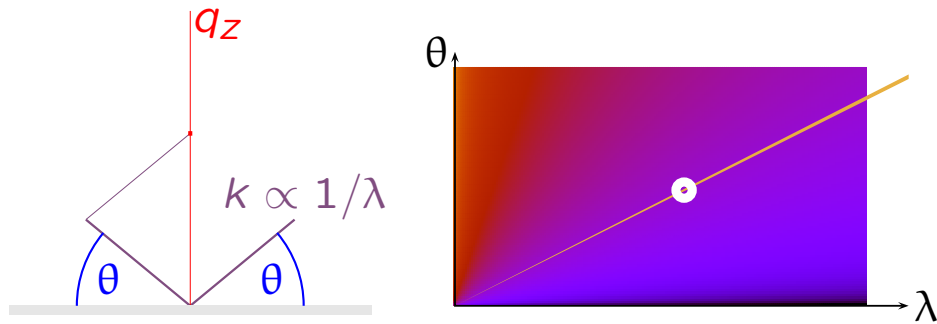
- intro
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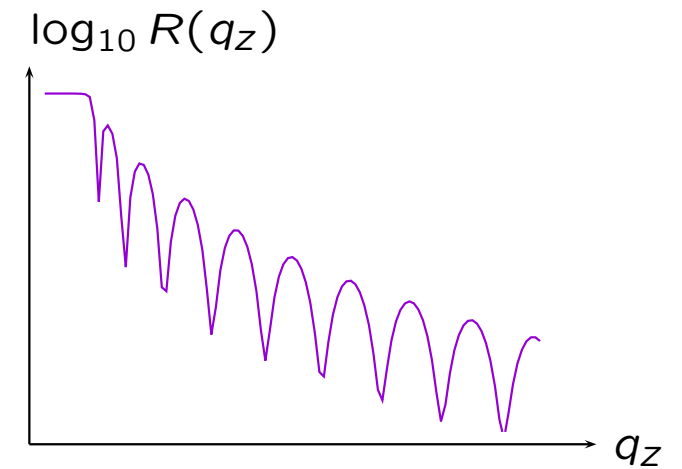
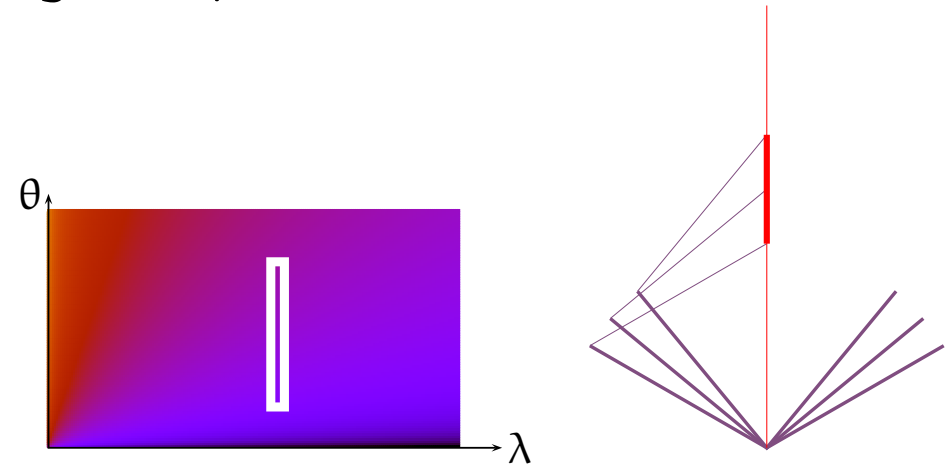
specular reflectometry



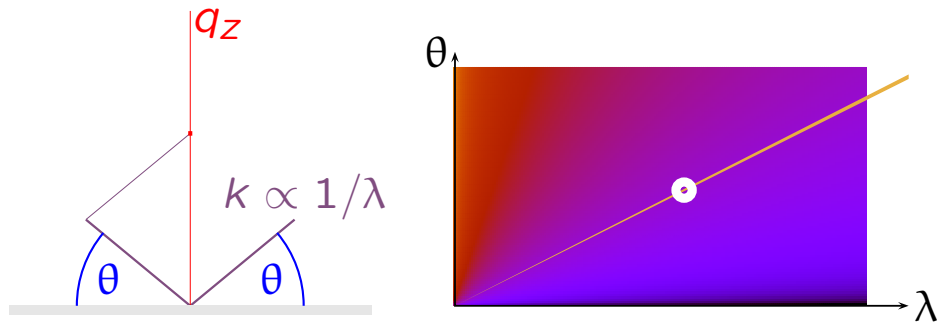
specular reflectometry



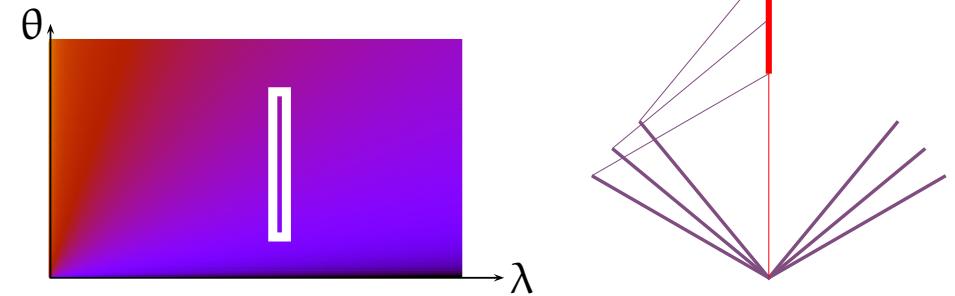
angle-dispersive



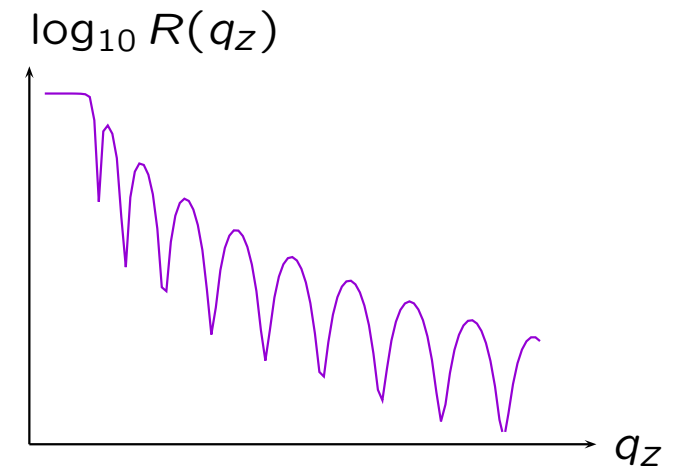
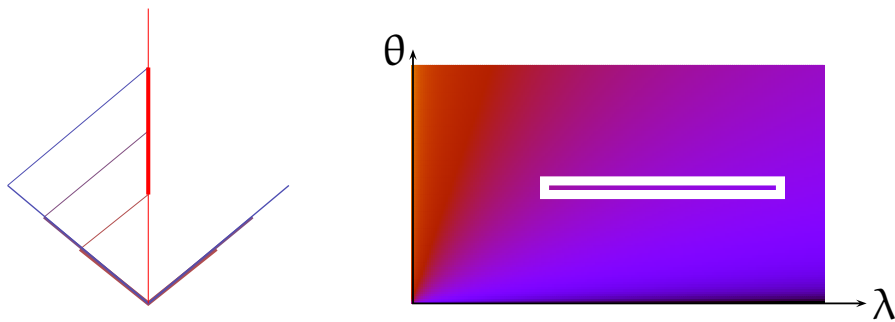
specular reflectometry



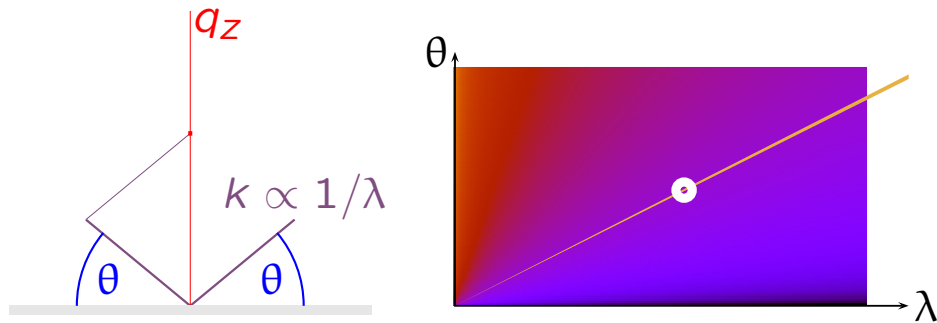
angle-dispersive



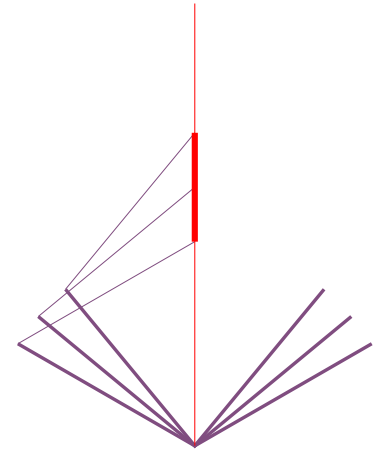
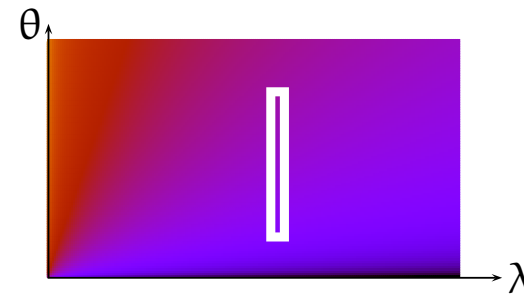
energy-dispersive



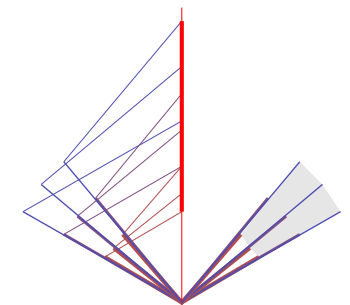
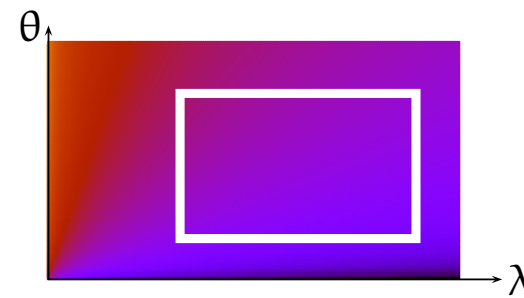
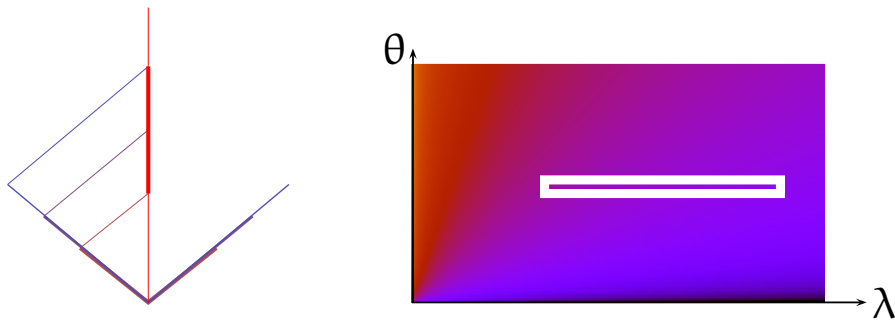
specular reflectometry



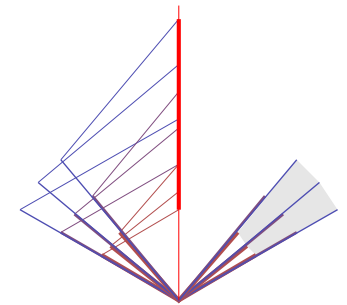
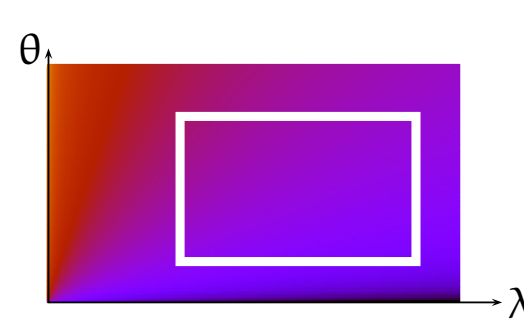
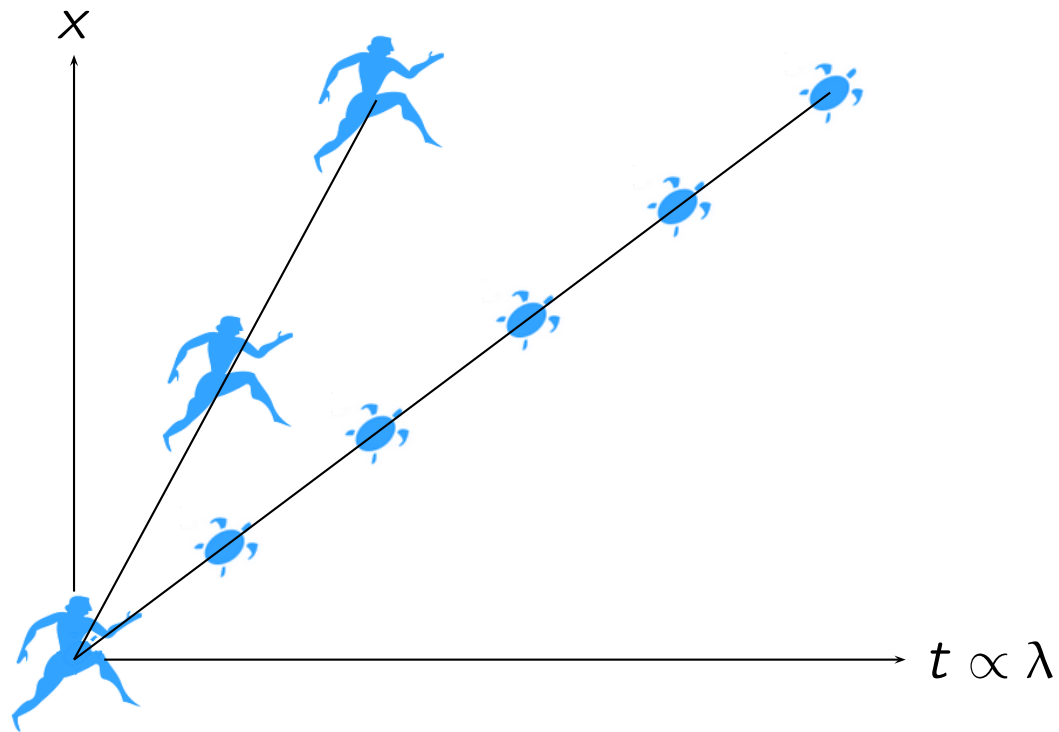
angle-dispersive



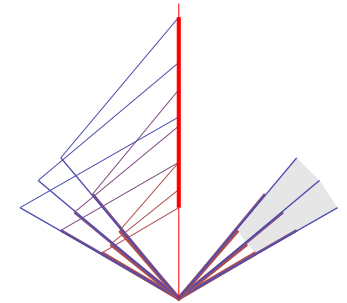
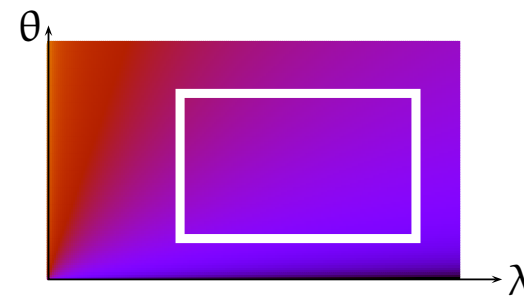
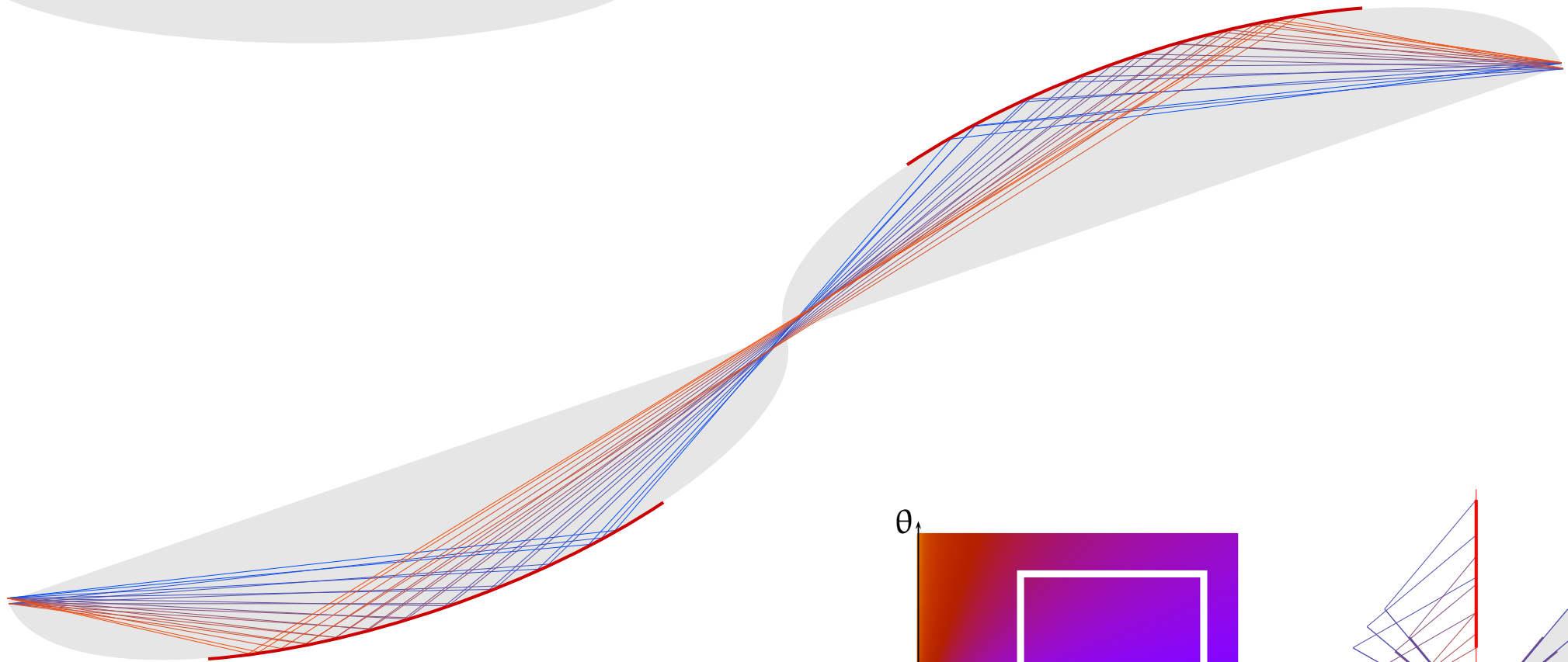
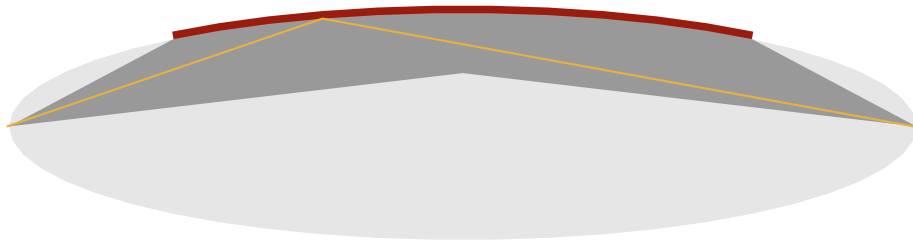
energy-dispersive



λ -dispersion by time-of-flight



ω -dispersion by focusing



the **Selene** guide

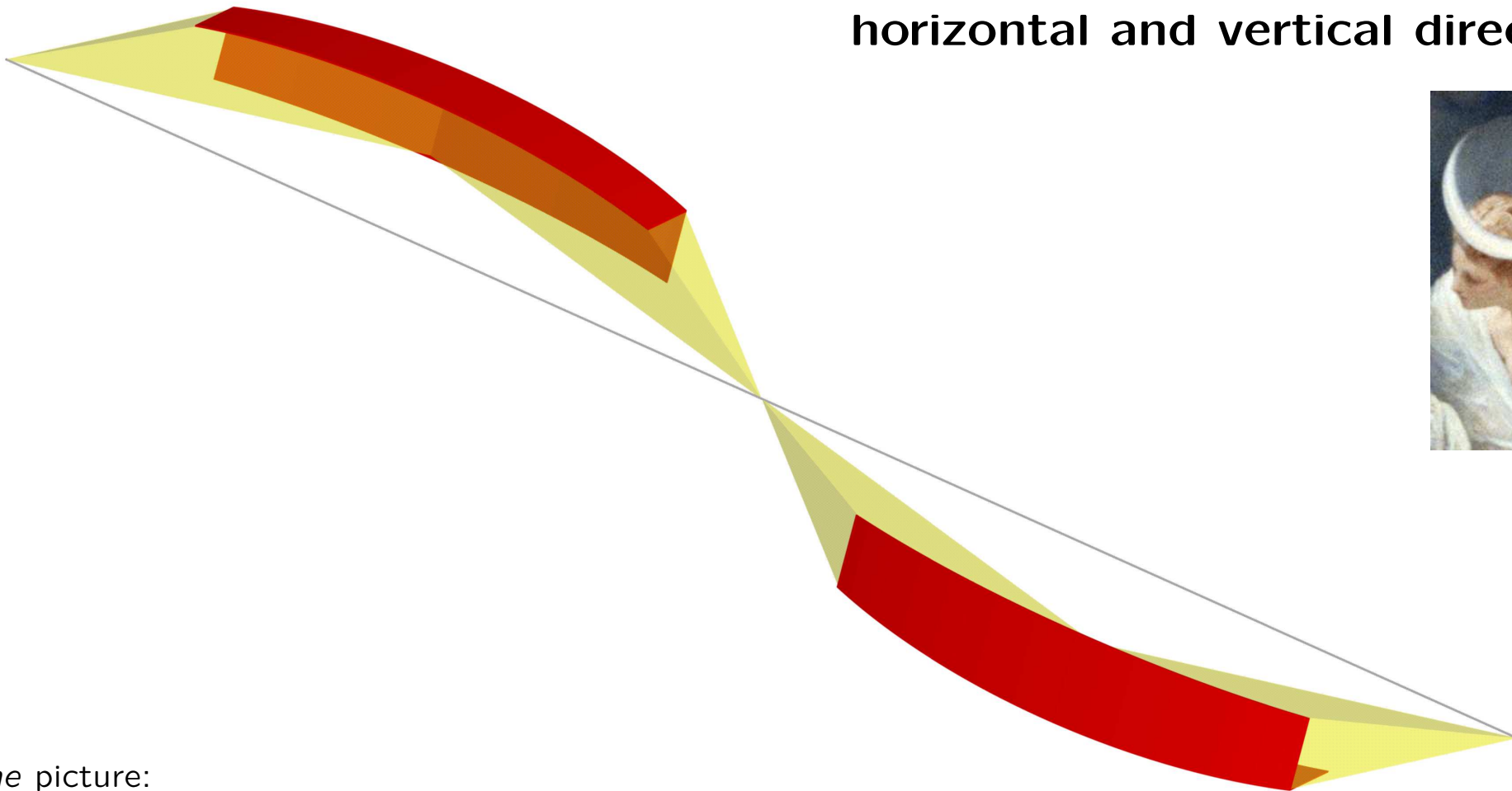
point-to-point focusing

with

2 subsequent elliptical reflectors

for

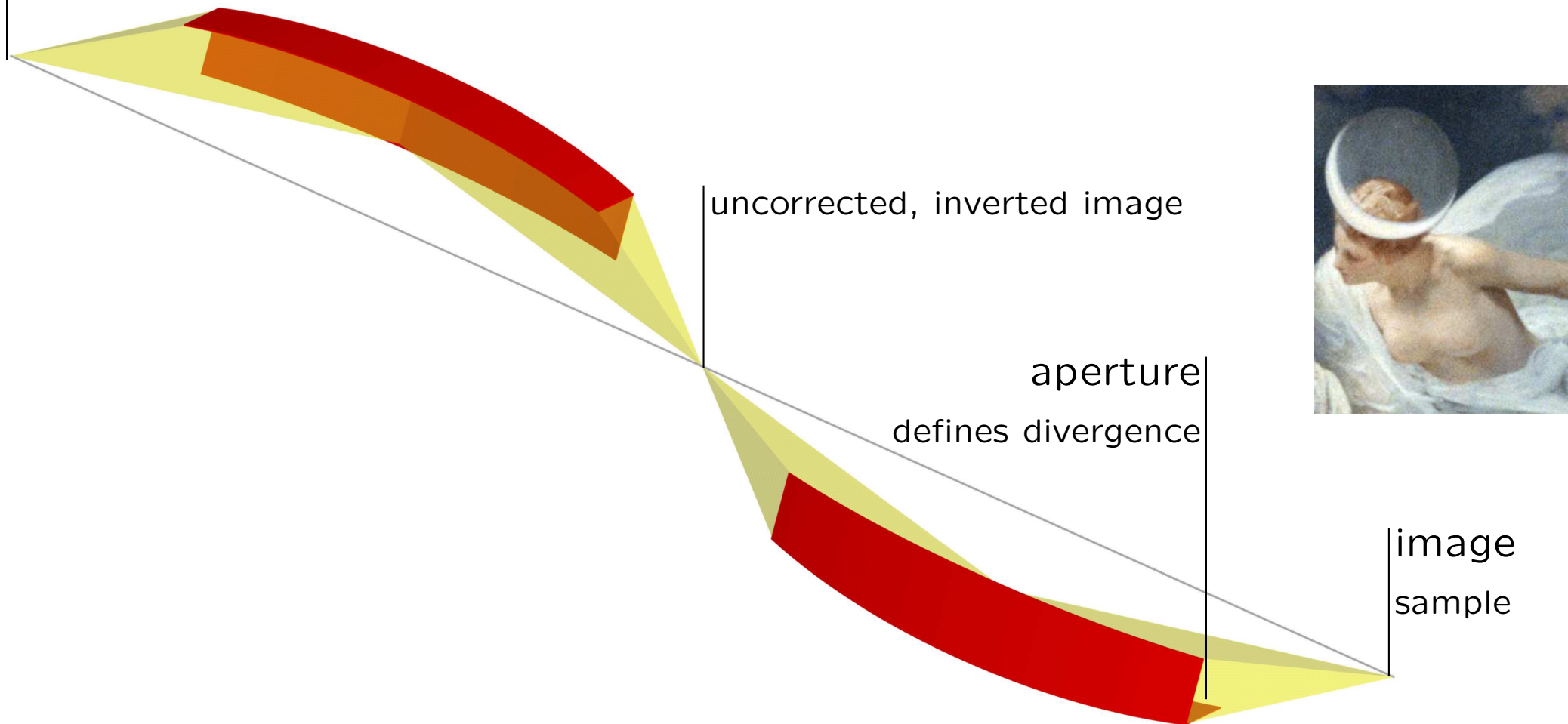
horizontal and vertical direction



Selene picture:
ceiling painting in the Ny Carlsberg Glyptotek, København

the *Selene* guide

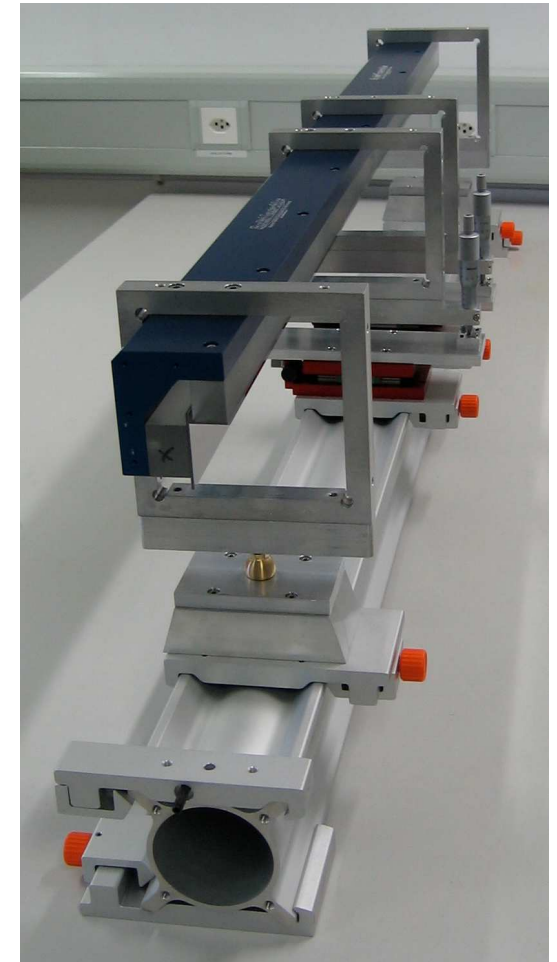
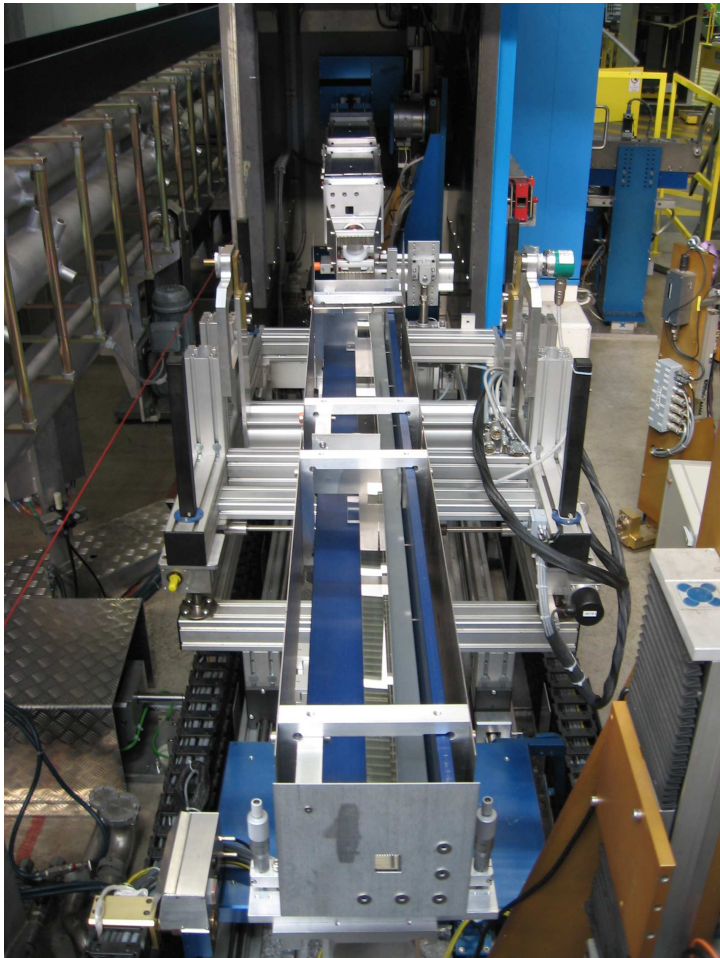
light-field-diaphragm
control of footprint



the **Selene** guide demonstrator

on Amor@PSI

- total length = 4 m
- max spot size $\approx 2 \times 2 \text{ mm}^2$
- divergence $\approx 1.8^\circ \times 1.8^\circ$



the **Selene** guide demonstrator on Amor@PSI

slit = virtual source

polariser

1st segment

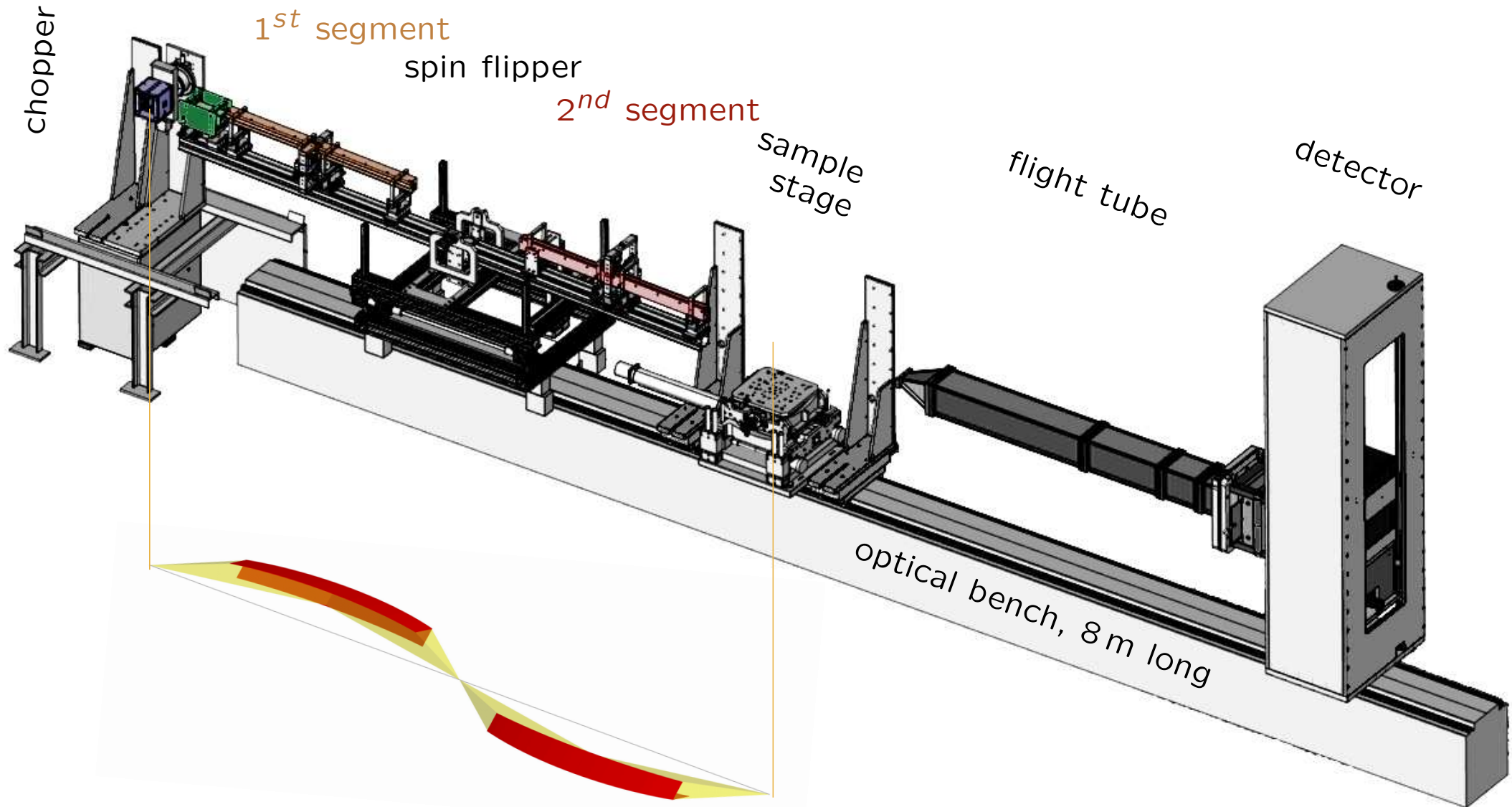
spin flipper

2nd segment

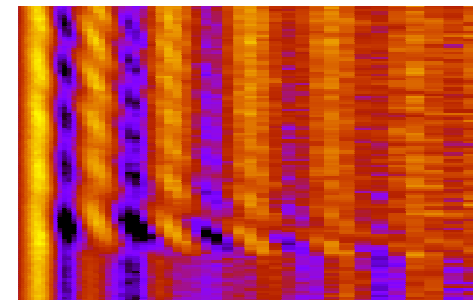
sample stage

flight tube

detector



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Li transport through thin silicon films

in-situ study in cooperation with E. Hüger, F. Strauß and H. Schmidt, TU Clausthal

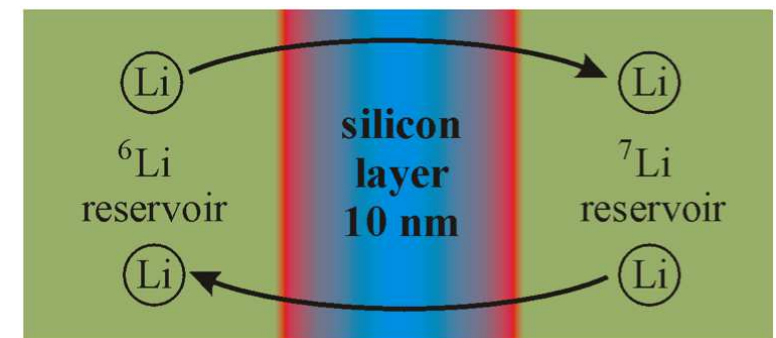
technological motivation:

- Si layers can be used in Li batteries to prevent oxidation of the electrodes
- Si films can be used as electrodes in Li batteries

⇒ How fast does Li diffuse through thin amorphous Si films?

⇒ What is the solubility of Li in Si?

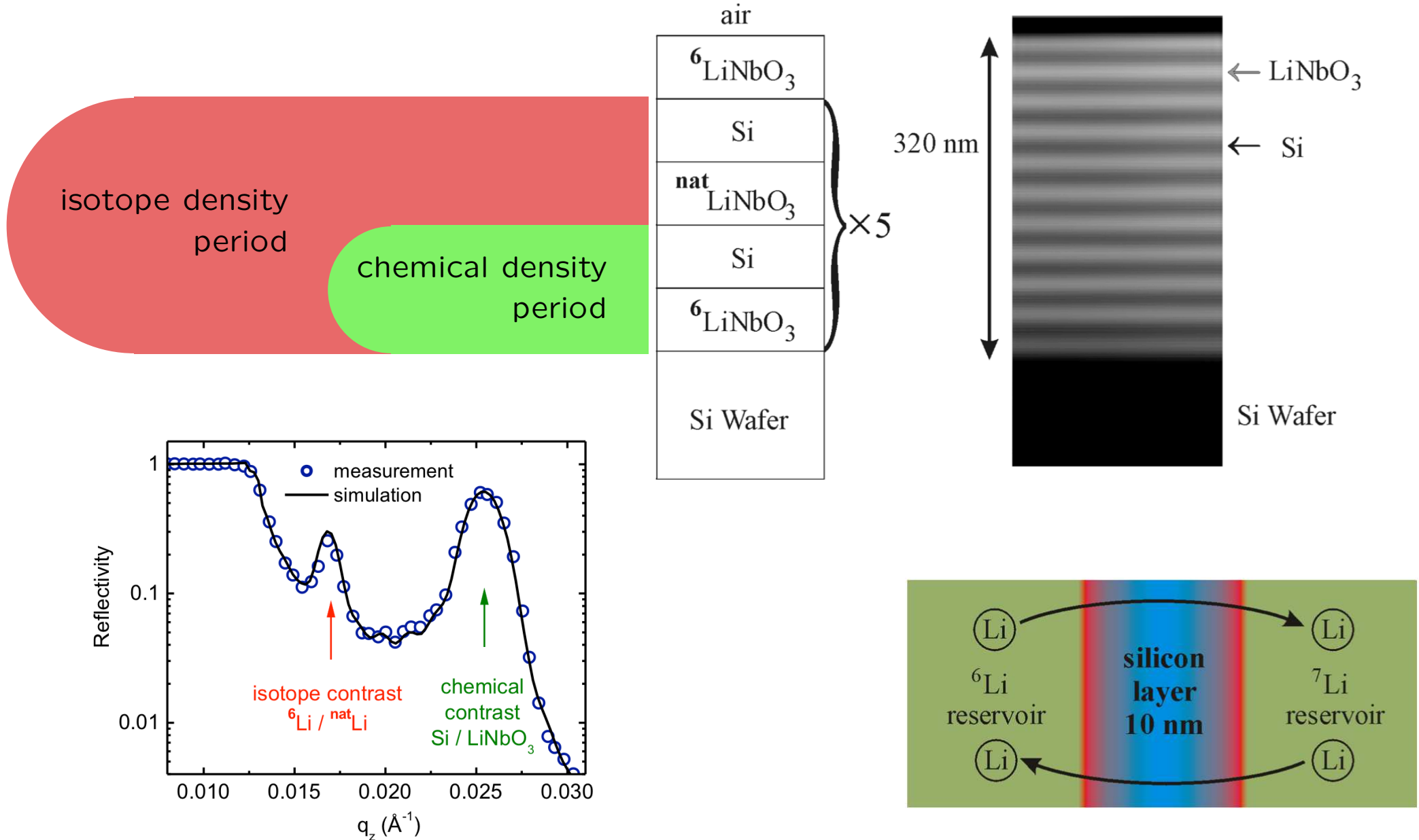
⇒ What is the influence of the Si:O:Li interface layer?



E. Hüger, *et al.*, Nano Letters 13 (2013) 1237.

Li transport | the sample

multilayer structure using the different densities of ^6Li and ^7Li



Li transport | experimental set-up

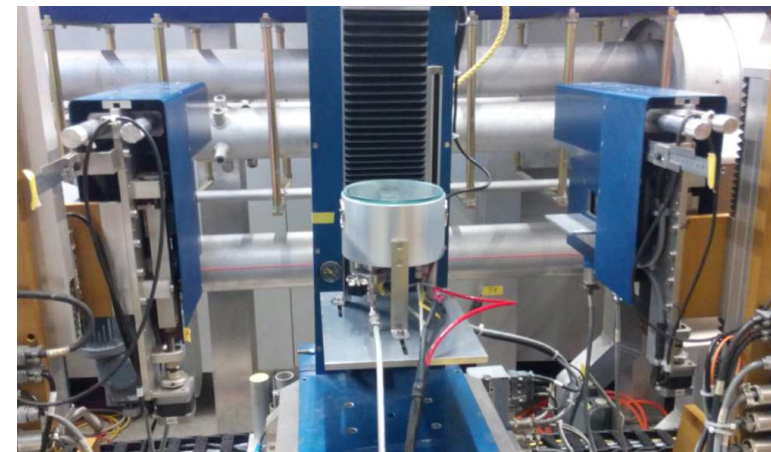
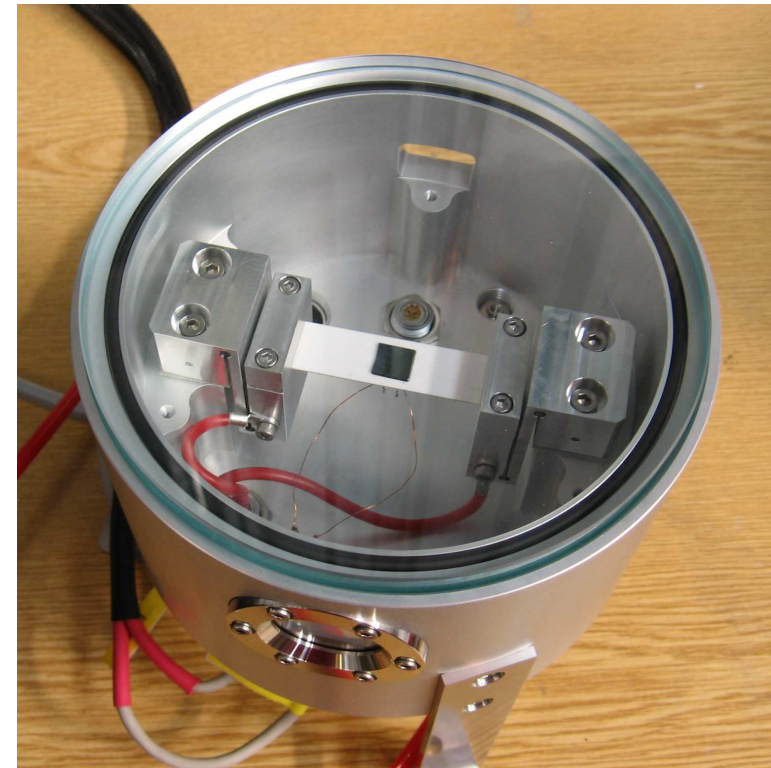
in-situ furnace

- $T \in [25^\circ\text{C}, 500^\circ\text{C}]$
- $\dot{T} = 50 \text{ Ks}^{-1}$ for heating
- $\dot{T} = 12 \text{ Ks}^{-1}$ for cooling

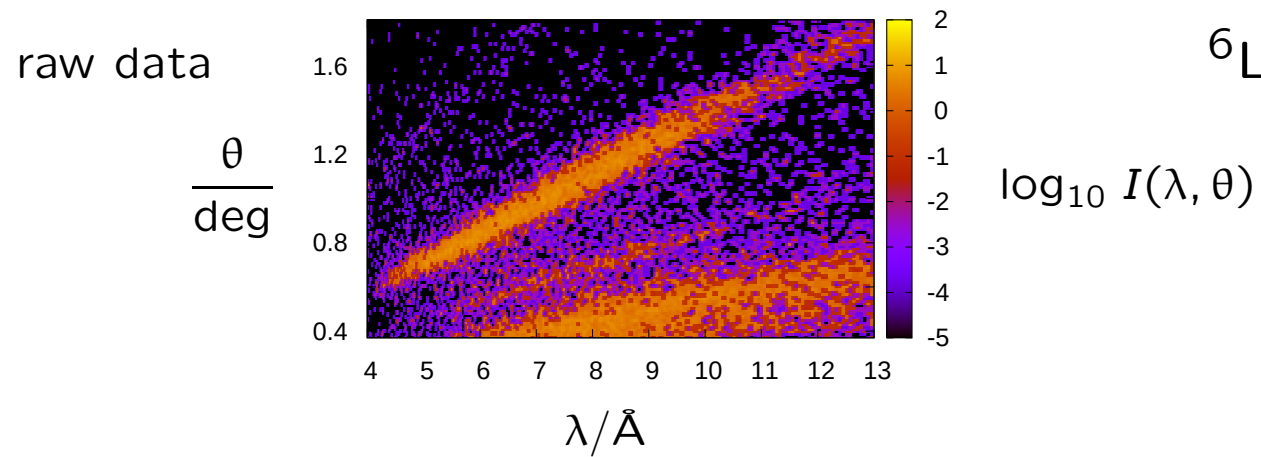
here: $T = 240^\circ\text{C}$

time-structure

- interval
(measurements at RT in between annealing periods)
- **continuous measurement**

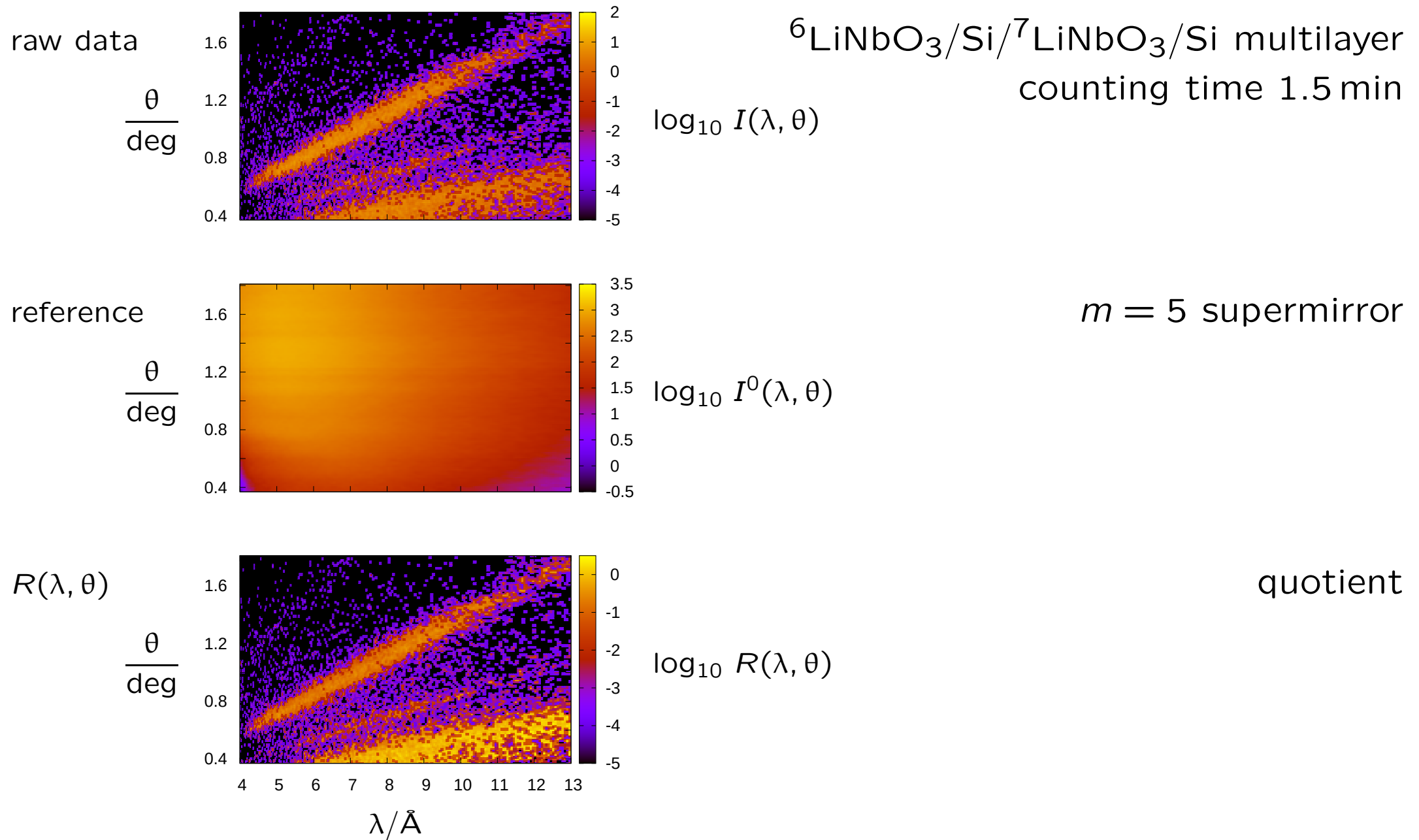


Li transport | measurements

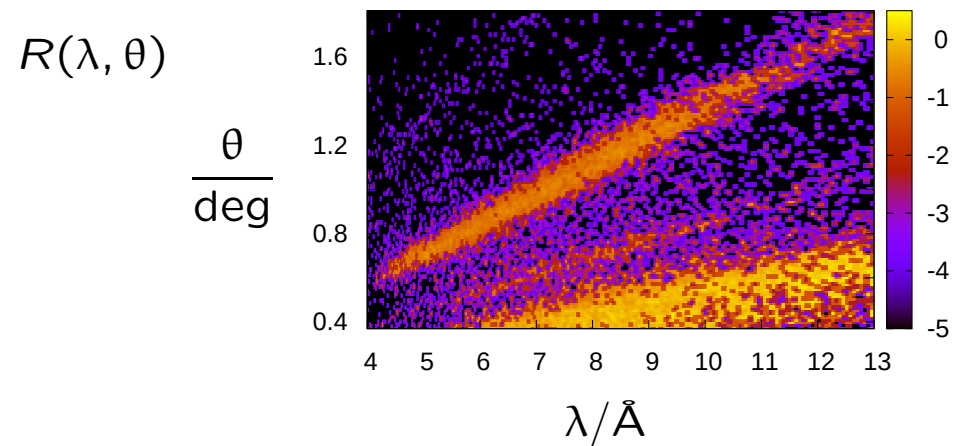
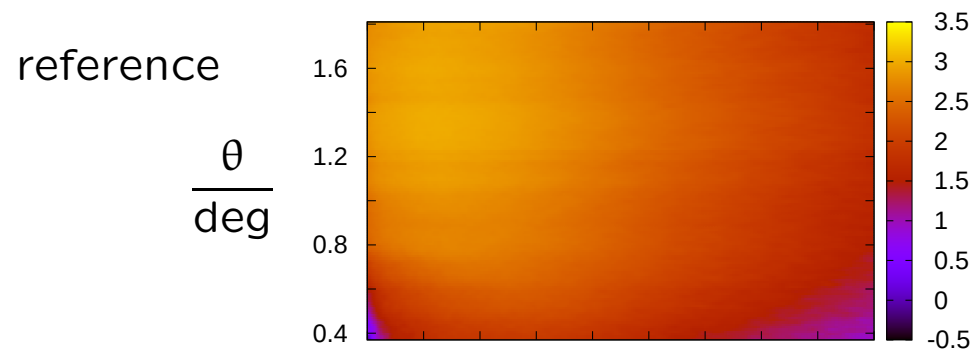
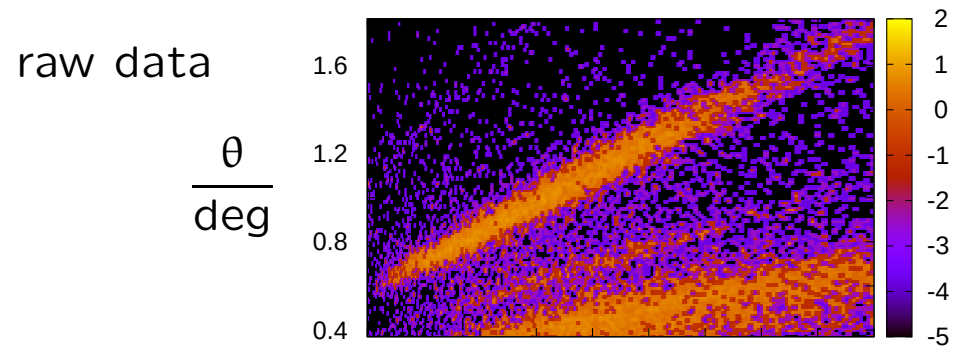


${}^6\text{LiNbO}_3/\text{Si}/{}^7\text{LiNbO}_3/\text{Si}$ multilayer
counting time 1.5 min

Li transport | measurements & data reduction

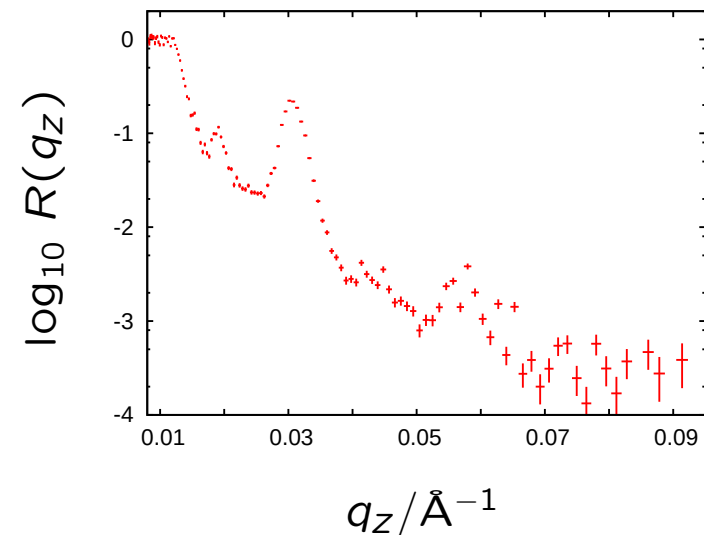


Li transport | measurements & data reduction



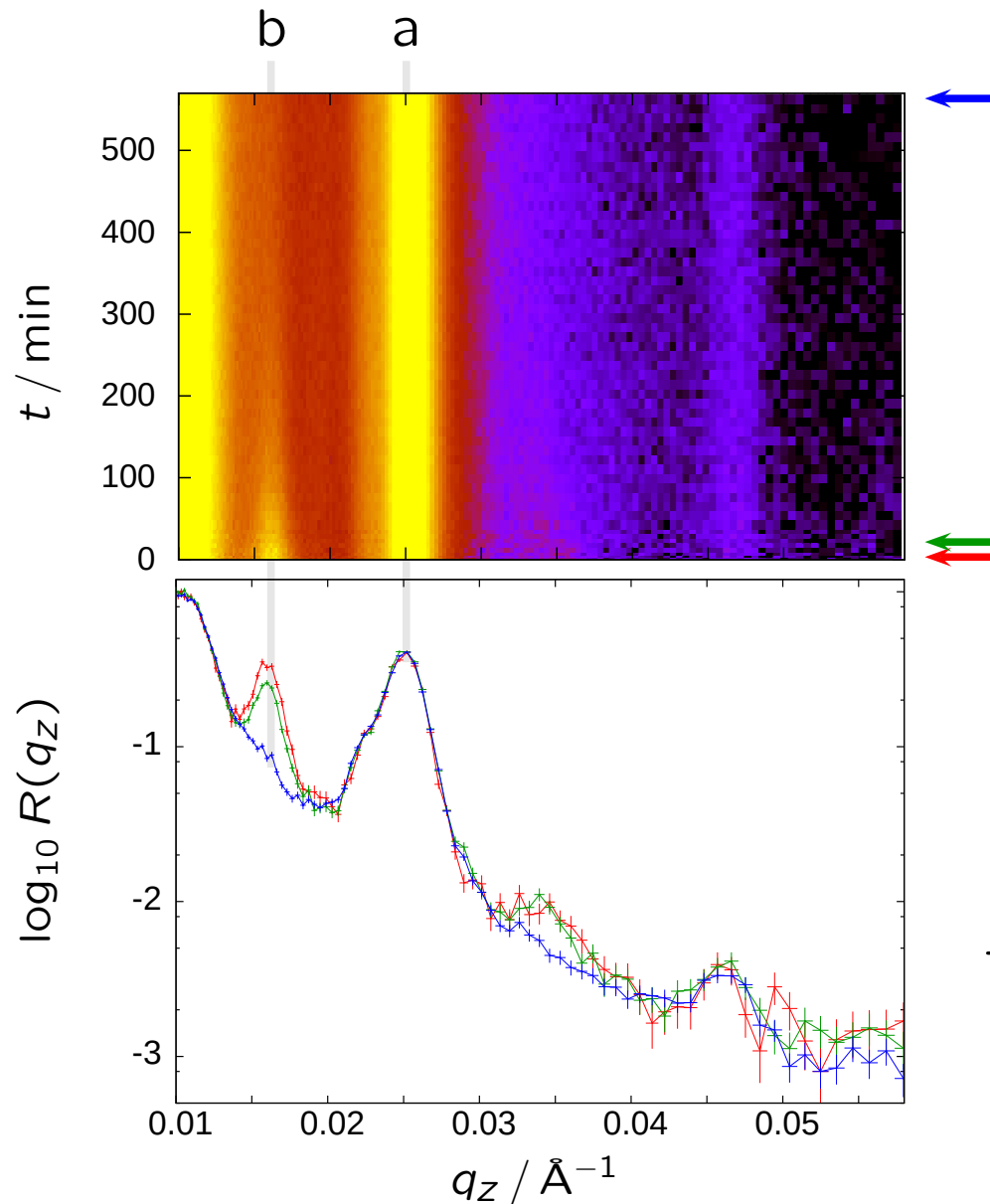
averaging
along q_z

${}^6\text{LiNbO}_3/\text{Si}/{}^7\text{LiNbO}_3/\text{Si}$ multilayer
counting time 1.5 min



Li transport | reflectivity curves

measurements on a ${}^6\text{Li}_3\text{NbO}_4/\text{Si}/{}^7\text{Li}_3\text{NbO}_4/\text{Si}$ multilayer



annealing at $T = 240^\circ\text{C}$

(a) ml is chemically stable

(b) Li contrast is vanishing

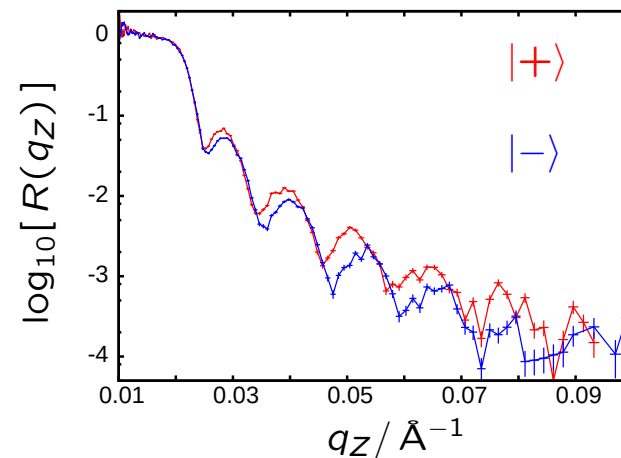
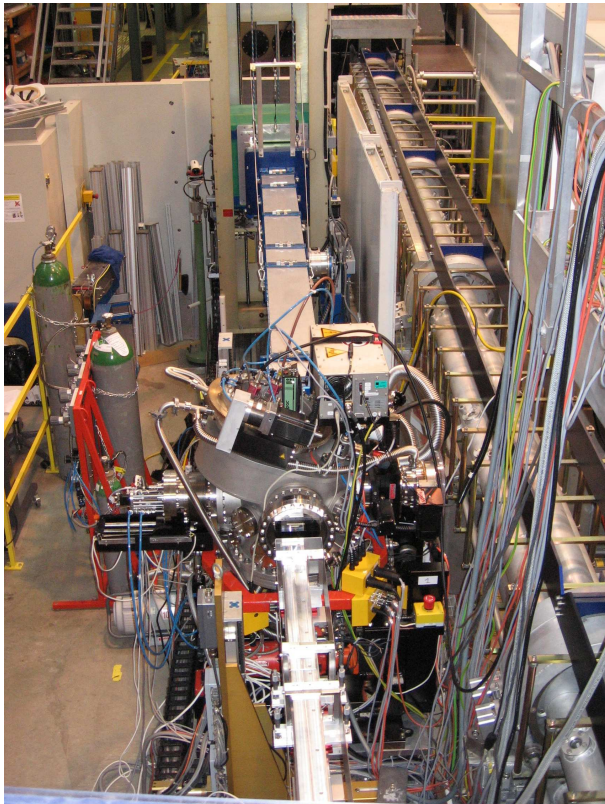
$t =$ 0 $\rightarrow$ 3 min
 18 $\rightarrow$ 24 min
 558 $\rightarrow$ 570 min

quasi in-situ reflectometry during sample growth

sample: Si/Cu(50 nm)/Fe(0 ... 20 layers)

by B. Wiedemann, S. Mayr, W. Kreuzpaintner, TU Munich

sputter chamber on Amor



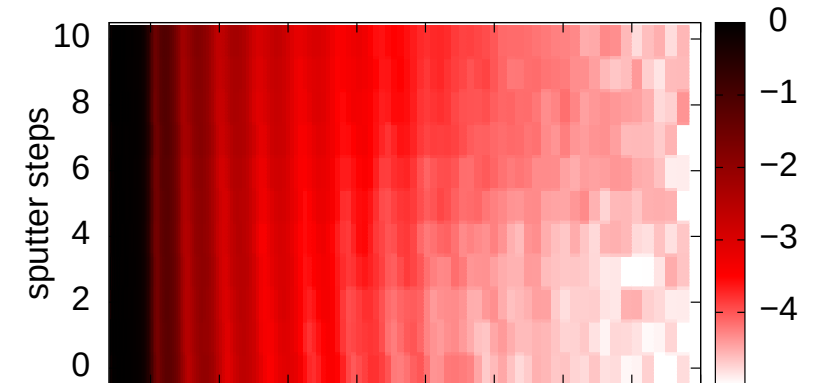
counting time per spin
state = 10 min

quasi in-situ reflectometry during sample growth

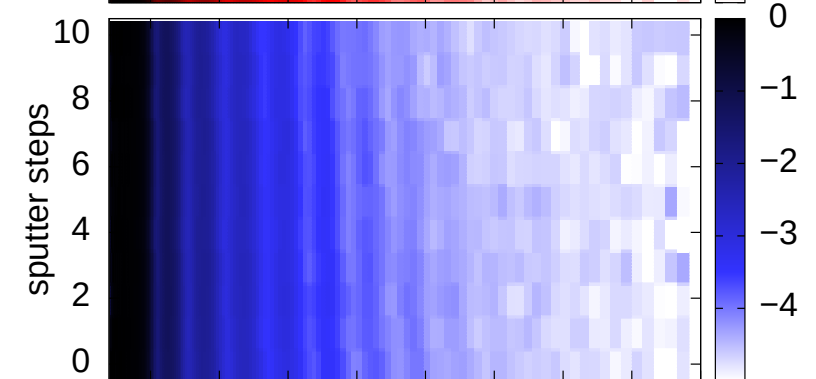
sample: Si/Cu(50 nm)/Fe(0 ... 20 layers)

sputter steps	growth	structure	moment/ μ_B
1	island	fcc	3.3
2			
3			
4			
5	layer-by-layer	fcc	1.2
6			
7			
8			
9			
10			
11		bcc	2.0

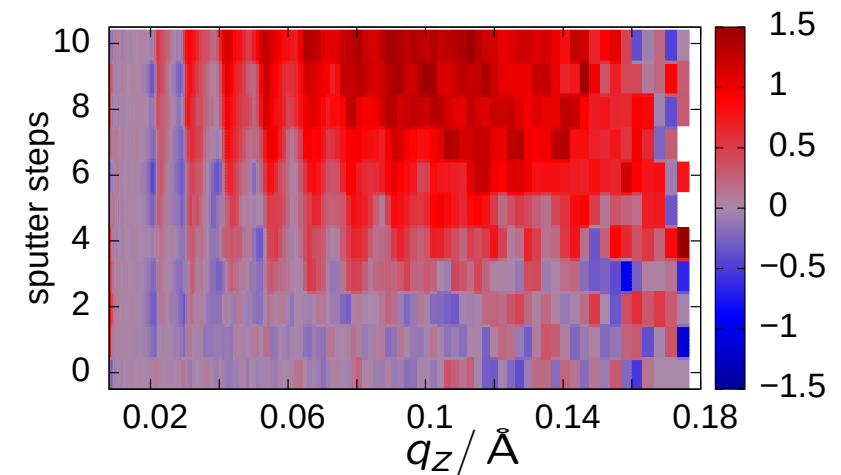
$$\log_{10} R^{|\rightarrow\rangle}(q_z)$$



$$\log_{10} R^{|\rightarrow\rangle}(q_z)$$



$$\frac{R^{|\rightarrow\rangle} - R^{|\leftarrow\rangle}}{R^{|\rightarrow\rangle} + R^{|\leftarrow\rangle}}$$



strain-induced ferromagnetism

sample:

- LuMnO_3
- ferroelectric
- antiferromagnetic

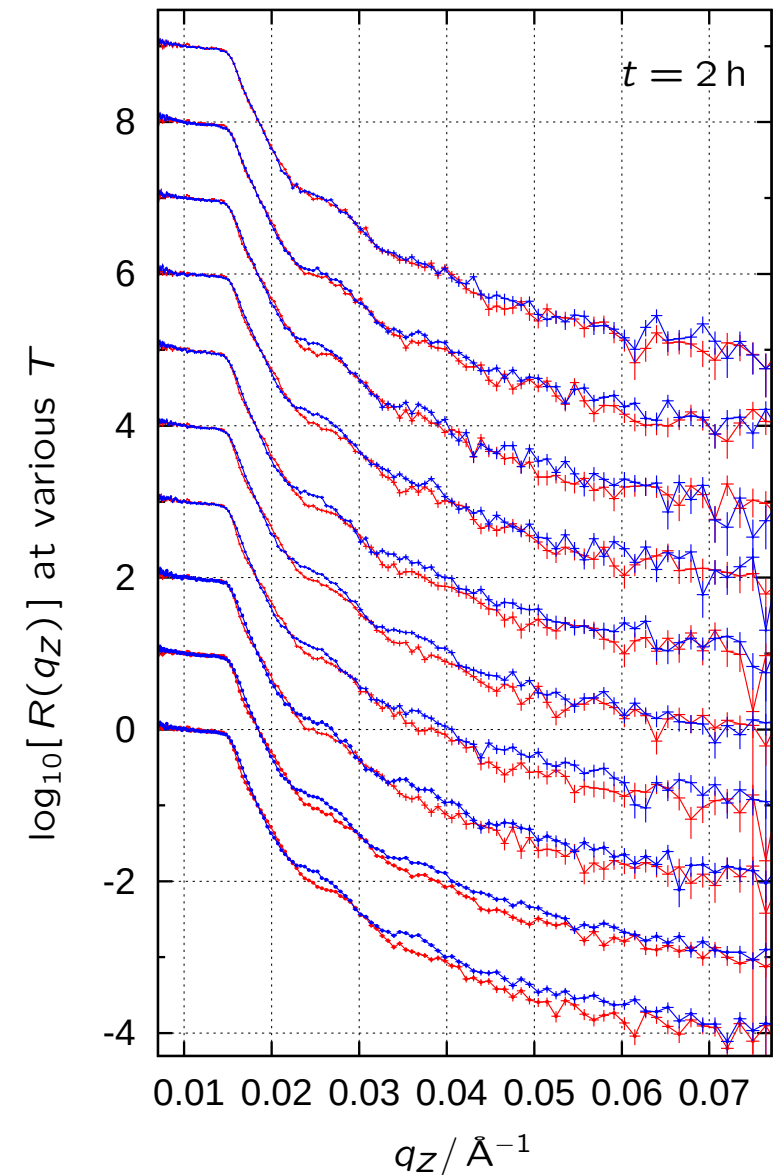
film (20...50 nm) on YAlO_3 substrate:

- strained at interface
- induced ferromagnetism

⇒ manipulation of magnetic state
by electric polarisation



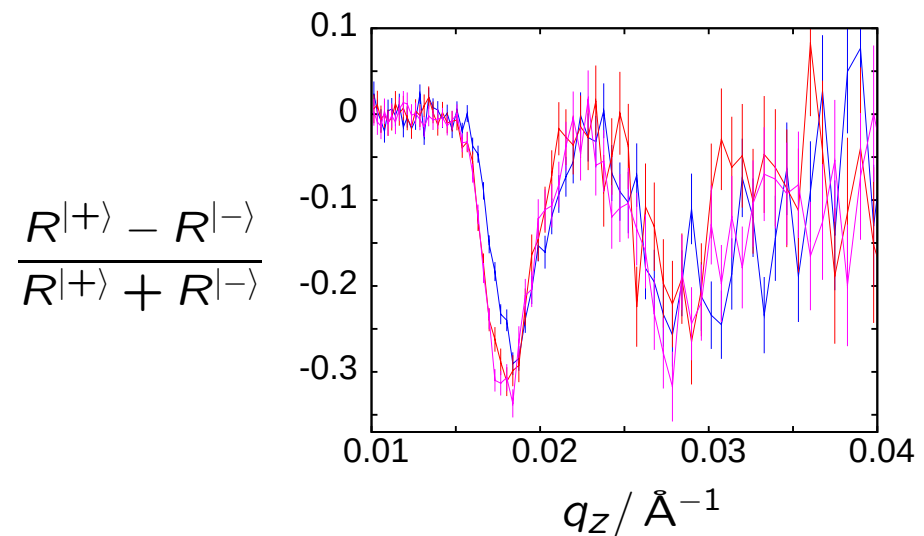
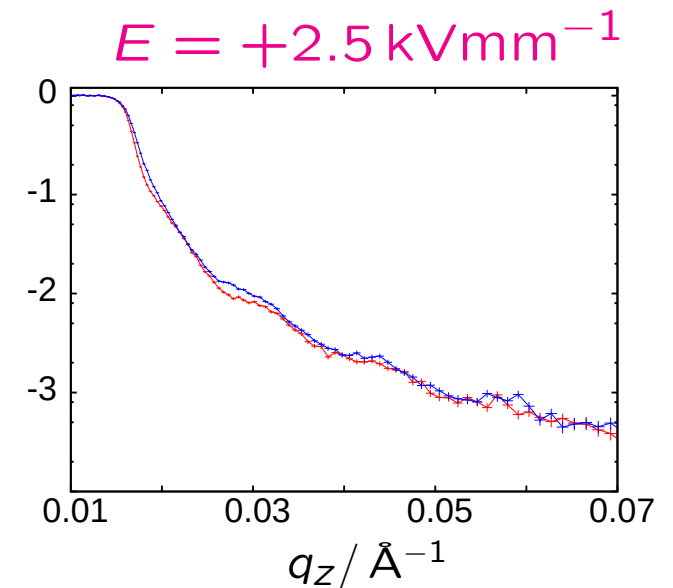
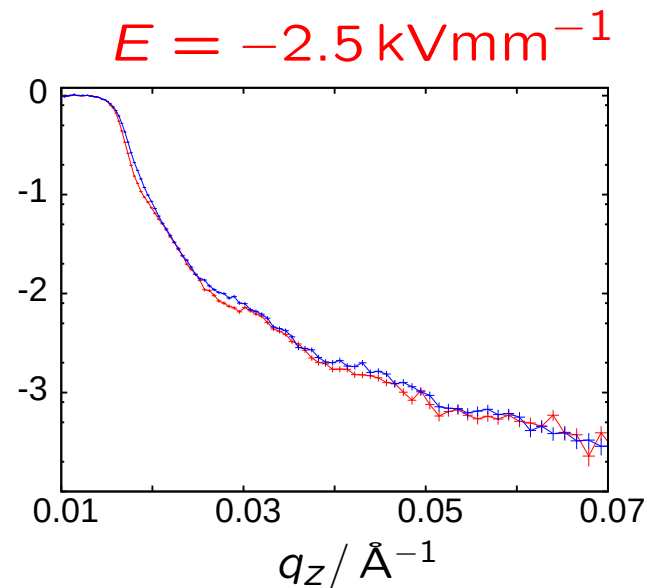
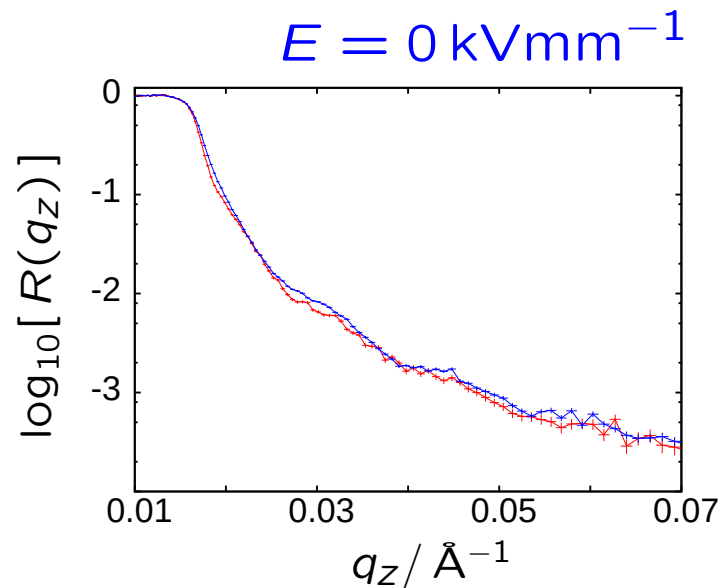
S. Mukherjee, J. Stahn, C. Niedermayer



strain-induced ferromagnetism

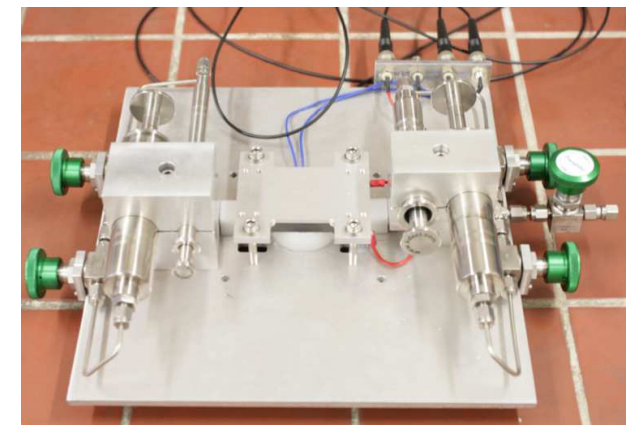
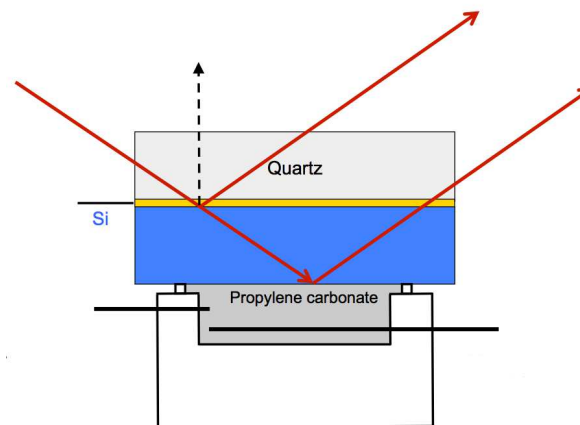
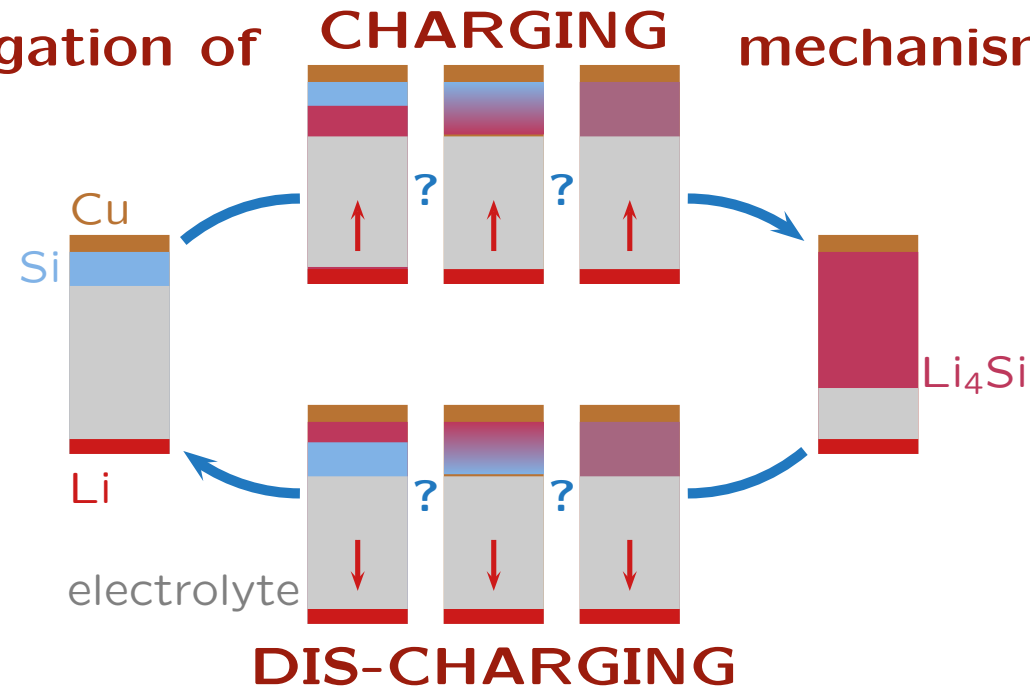
last week's measurements:

$$T = 10 \text{ K}, \quad H = 4 \text{ T}, \quad p = 10^{-10} \text{ bar}$$



in-operando battery studies

H. Schmidt, E. Hüger, B. Jerliu

In-operando investigation of **CHARGING** mechanism in Si/Li batteries

in-operando battery studies

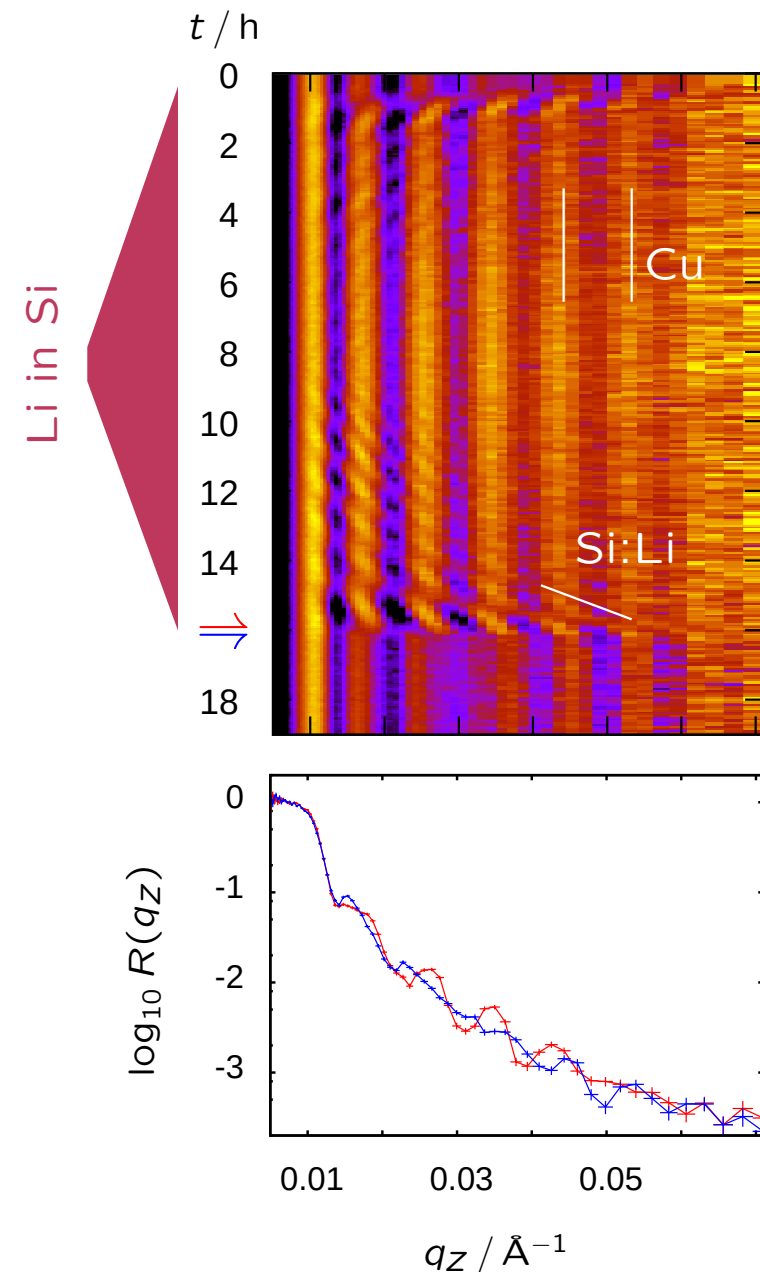
- Cu contact $\Rightarrow$ oscillations
- Si electrode $\Rightarrow$ adds phase factor
- Li in Si $\Rightarrow$ swelling
 - $\Rightarrow$ phase shift
 - $\Rightarrow$ density change
 - $\Rightarrow$ contrast variation

time-resolution: 1...6 min

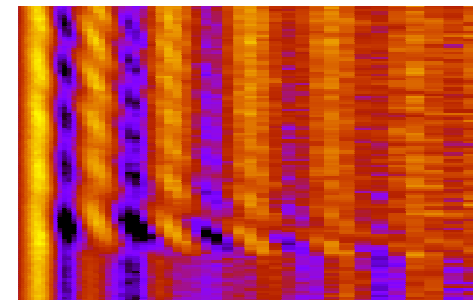
≈ 400 measurements per cycle

≈ 4000 measurements per beamtime

$\Rightarrow$ new data analysis strategy required

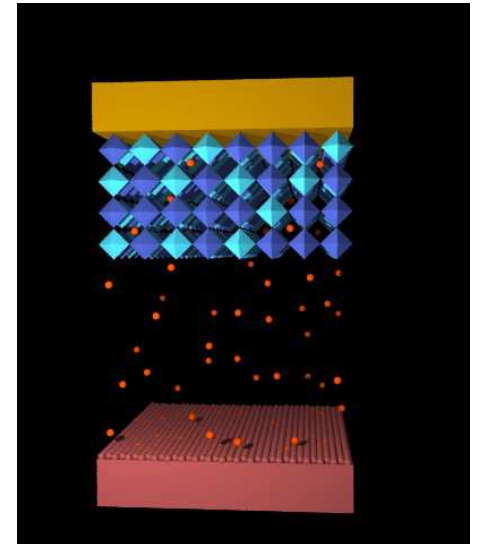
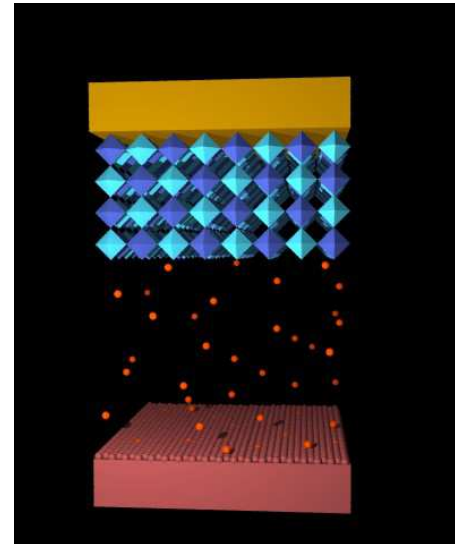


- intro
- reflectometry
 - general introduction
 - the neutron
- neutron reflectometry
 - the next generation
- experimental examples
 - Li diffusion in Si
 - in-situ film growth
 - strain-induced magnetism
 - in-operando Li battery
- the future
 - projects for Amor
 - instrumentation
 - conceptual challenges



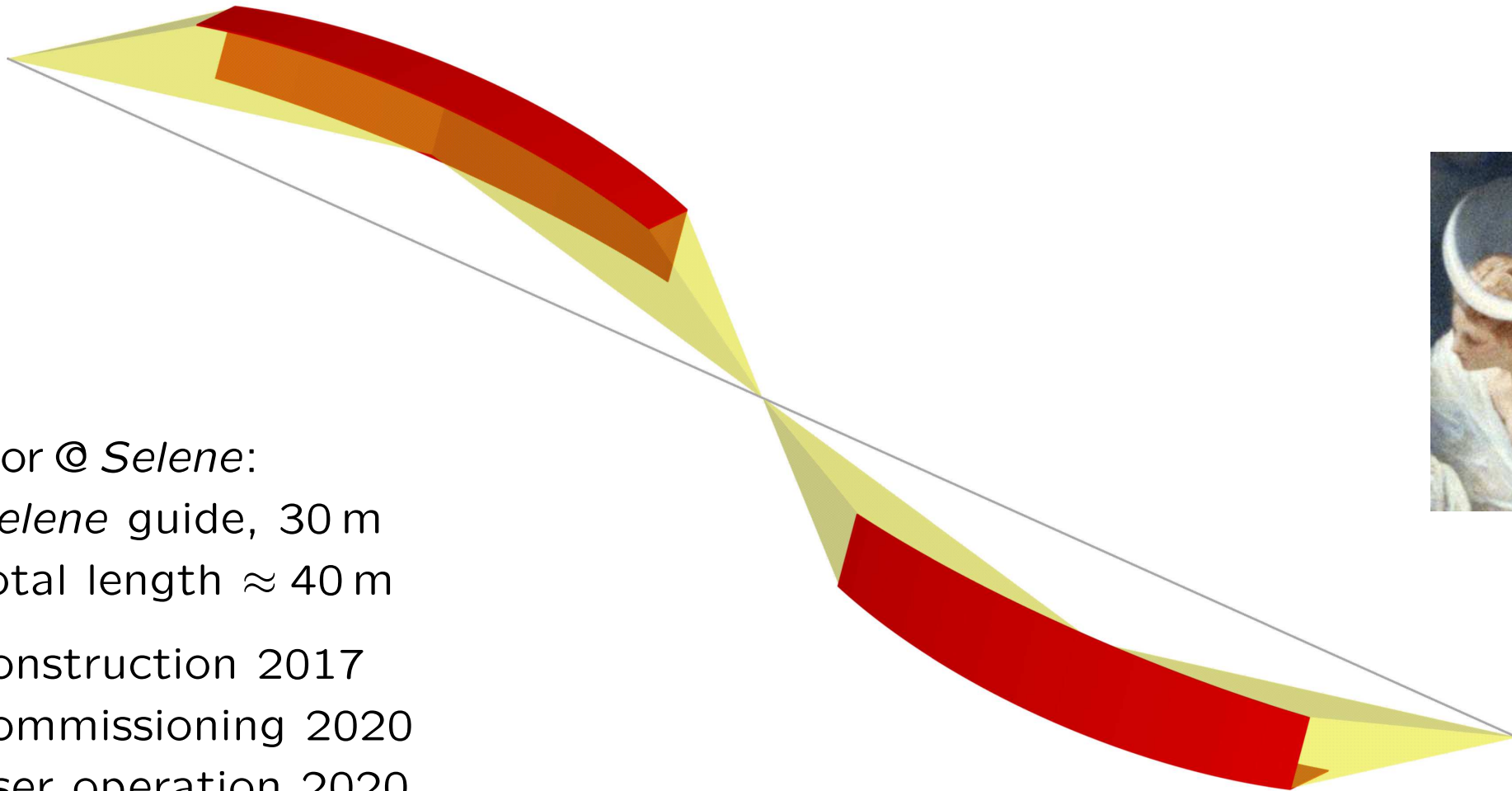
projects for Amor

- smaller electrochemical cell
 - lower background
 - less absorption
 - extension to fundamental research:
 - e.g. switching of FM by Li intercalation
- ⇒ low T and high H needed



- spin-analysis
 - switching of magnetic domains

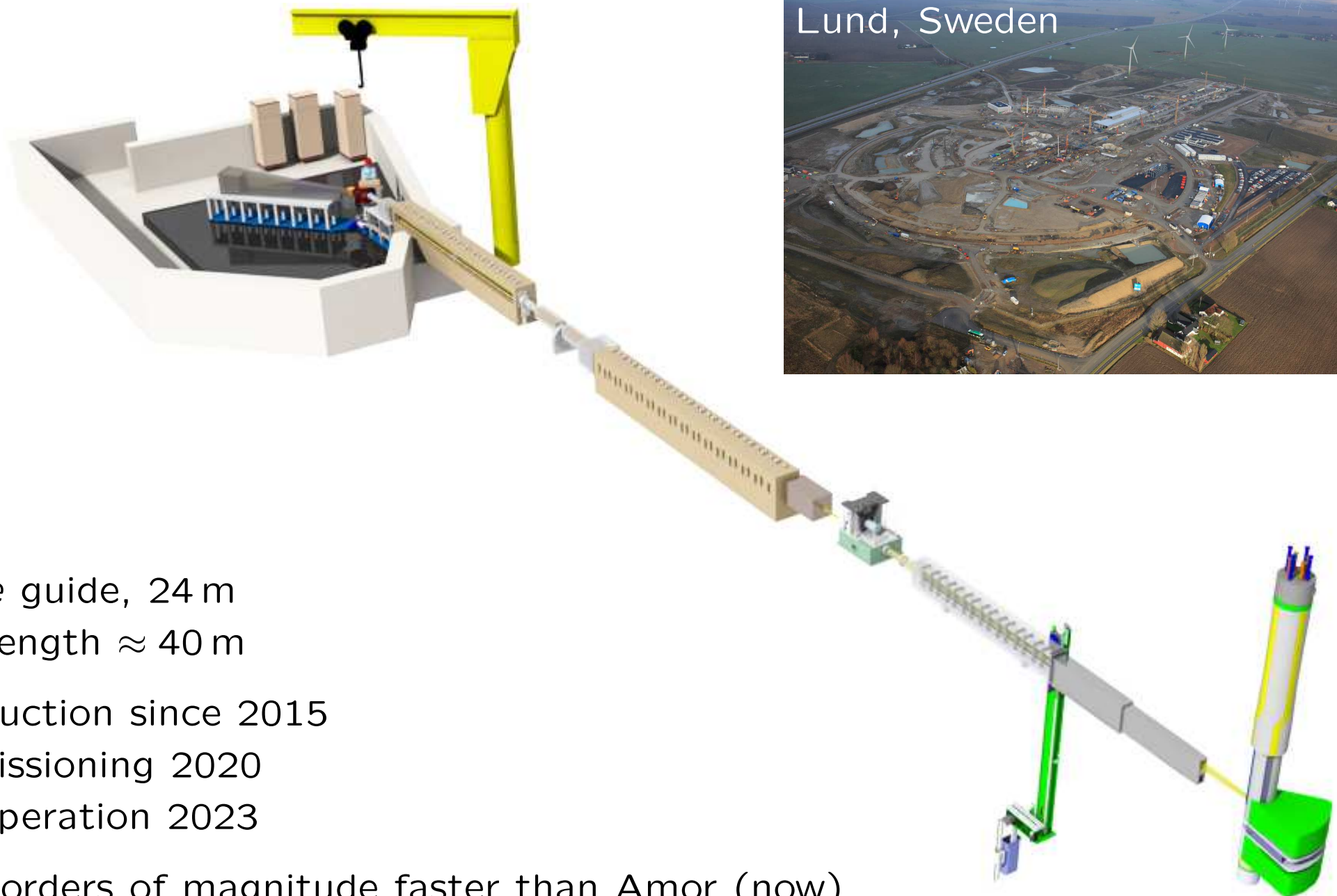
Amor upgrade with **Selene** guide



Amor @ *Selene*:

- *Selene* guide, 30 m
- total length $\approx$ 40 m
- construction 2017
- commissioning 2020
- user operation 2020
- 1...2 orders of magnitude faster than Amor (now)

Estia at the ESS



European Spallation Source
Lund, Sweden

Estia:

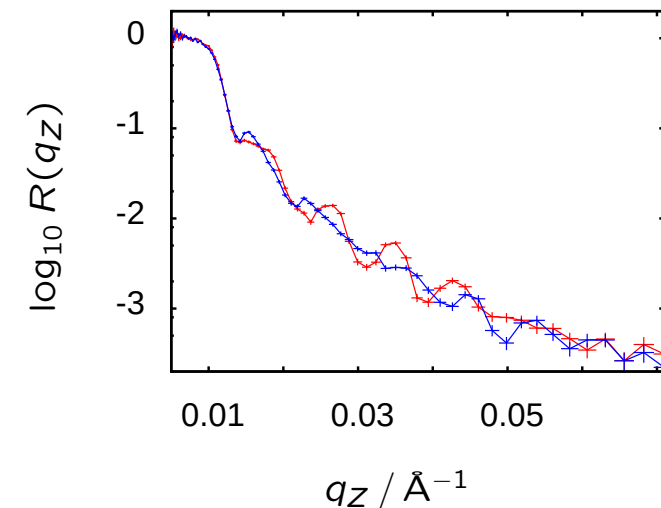
- *Selene* guide, 24 m
- total length ≈ 40 m
- construction since 2015
- commissioning 2020
- user operation 2023
- 3...4 orders of magnitude faster than Amor (now)

concepts and software

we are working on:

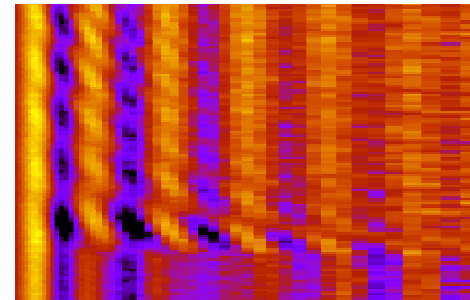
- better instrument control
- faster and reliable alignment
- automatising of data reduction
- new concepts of data interpretation

Amor	15 min
D17@ILL	6 min
Amor + prototype	< 3 min
Amor with <i>Selene</i> guide	10 sec
<i>Estia</i>	< 0.1 sec



Thank you!

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reflectometry, in general

J. Daillant, A. Gibaud: *X-ray and Neutron Reflectivity*
Lect. Notes Phys. 770 (Springer 2009)

U. Pietsch, V. Holý, T. Baumbach: *High-Resolution X-Ray Scattering*
(Springer 2004)

... on magnetic systems

F. Ott: *Neutron scattering on magnetic surfaces*
C. R. Physique **8**, 763-776 (2007)

focusing reflectometry

J. Stahn, A. Glavic: *Focusing neutron reflectometry*
N.I.M. A **821**, 44-54 (2016)

this talk

https://www.psi.ch/lens-kur/JochenStahnEN/stahn_2016_t1.pdf