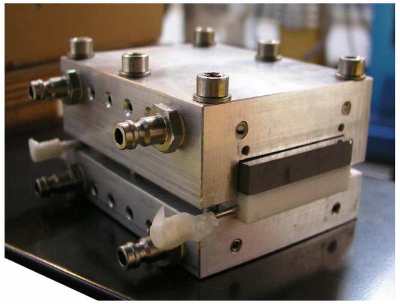
PAUL SCHERRER INSTITUT

Laboratory for Neutron Scattering and Imaging

Jochen Stahn

Probing hidden films

with
neutron reflectometry



08. 06. 2016

TU Clausthal, Germany

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experiments

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outline

- intro

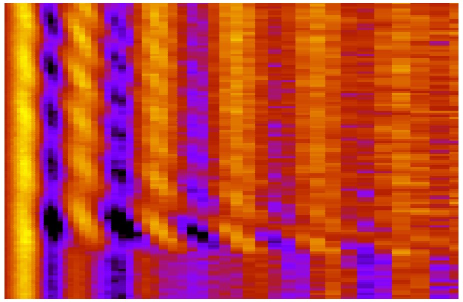
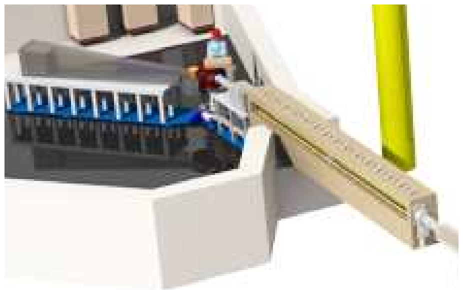
- reflectometry
  - general introduction
  - the neutron

- neutron reflectometry
  - the next generation

- experimental examples
  - → Li diffusion in Si
  - → in-situ film growth
  - → strain-induced magnetism
  - → in-operando Li battery

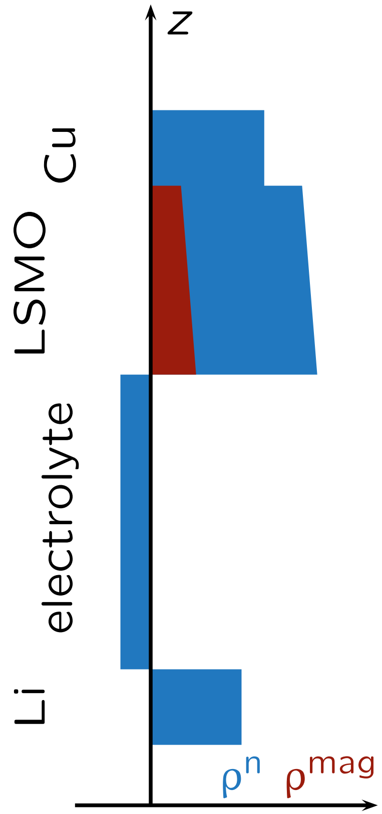
- the future
  - → projects for Amor
  - → instrumentation
  - → conceptual challenges

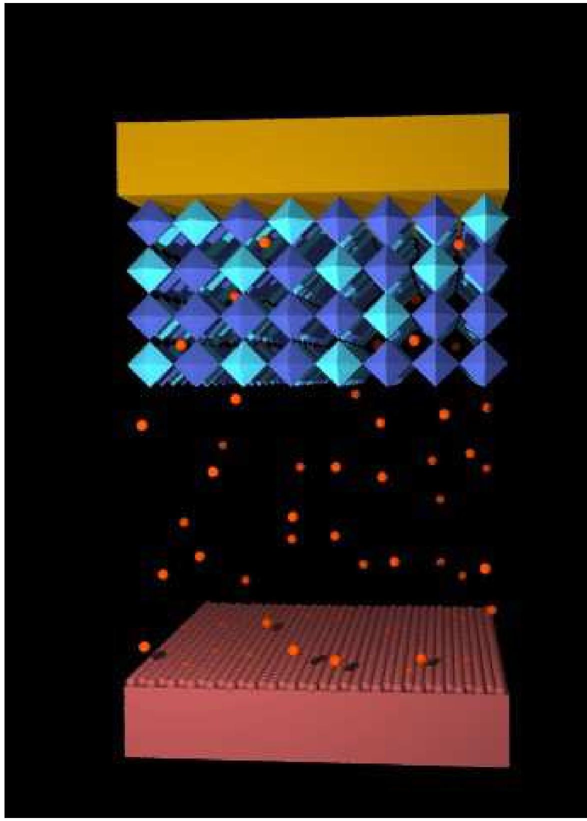


features of **neutron reflectometry**

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





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

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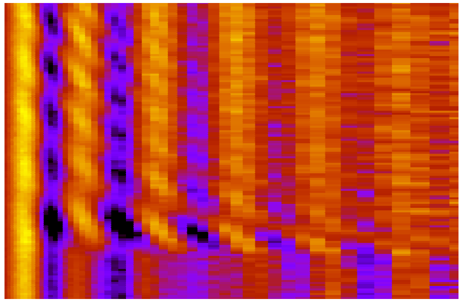
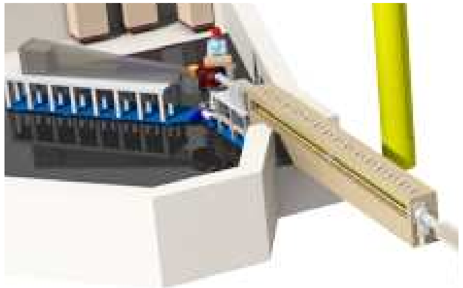
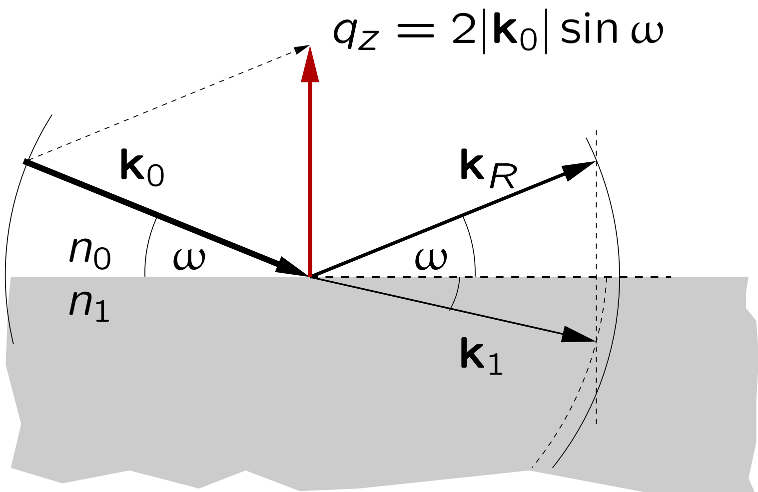



analogy to visible light

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

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

$\Rightarrow$ all phase information is lost

$\Rightarrow$ one way road:

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

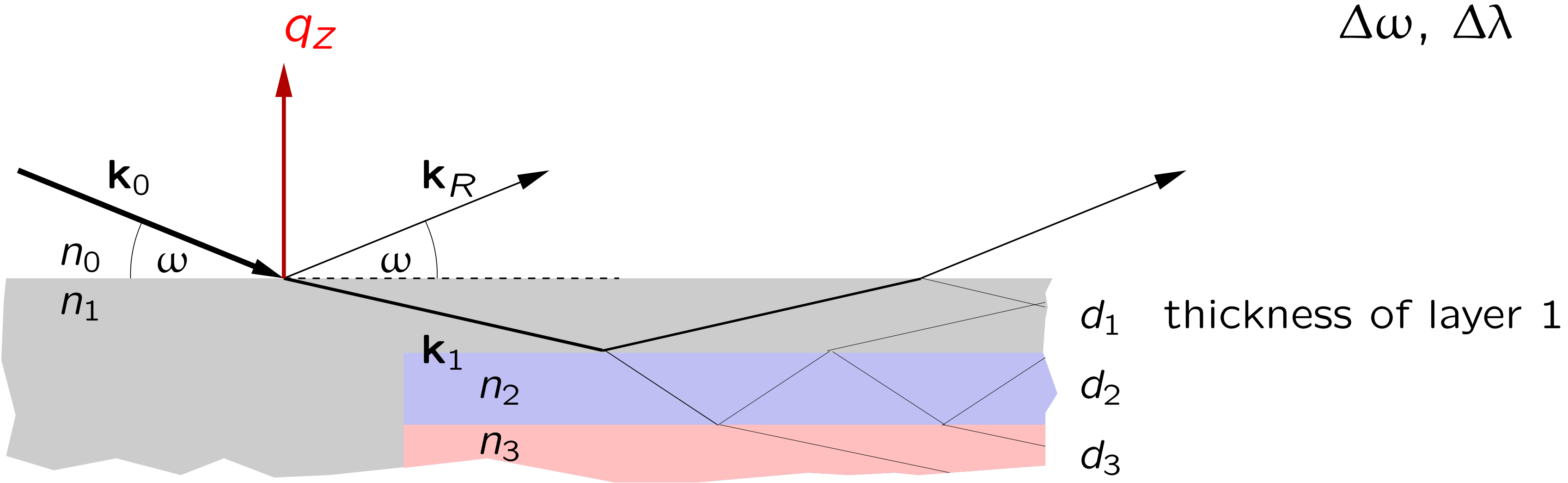
real effects
to be taken into account:

– non-sharp interfaces

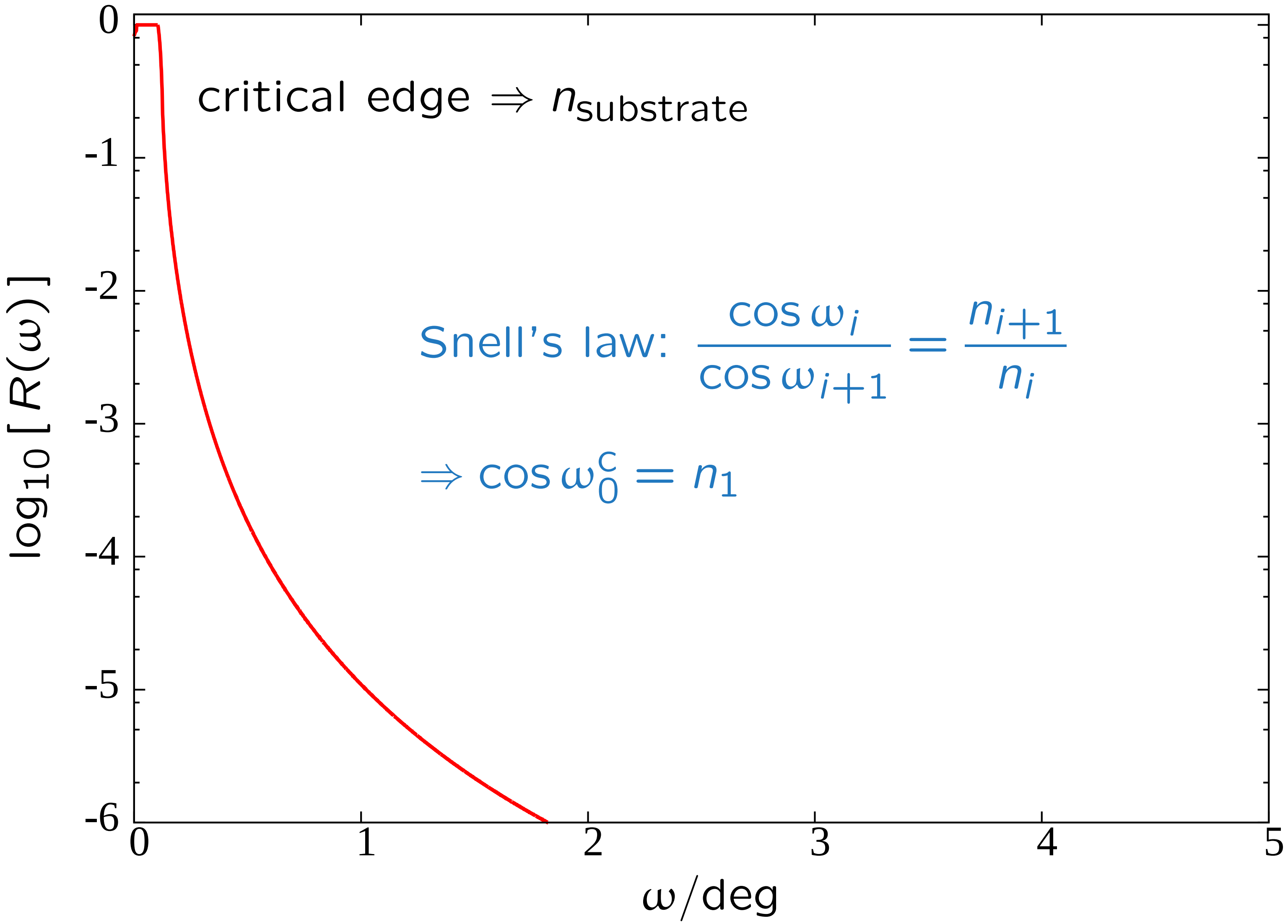
– inhomogeneous layers

– illumination of the sample

– resolution of the set-up
$\Delta\omega$, $\Delta\lambda$



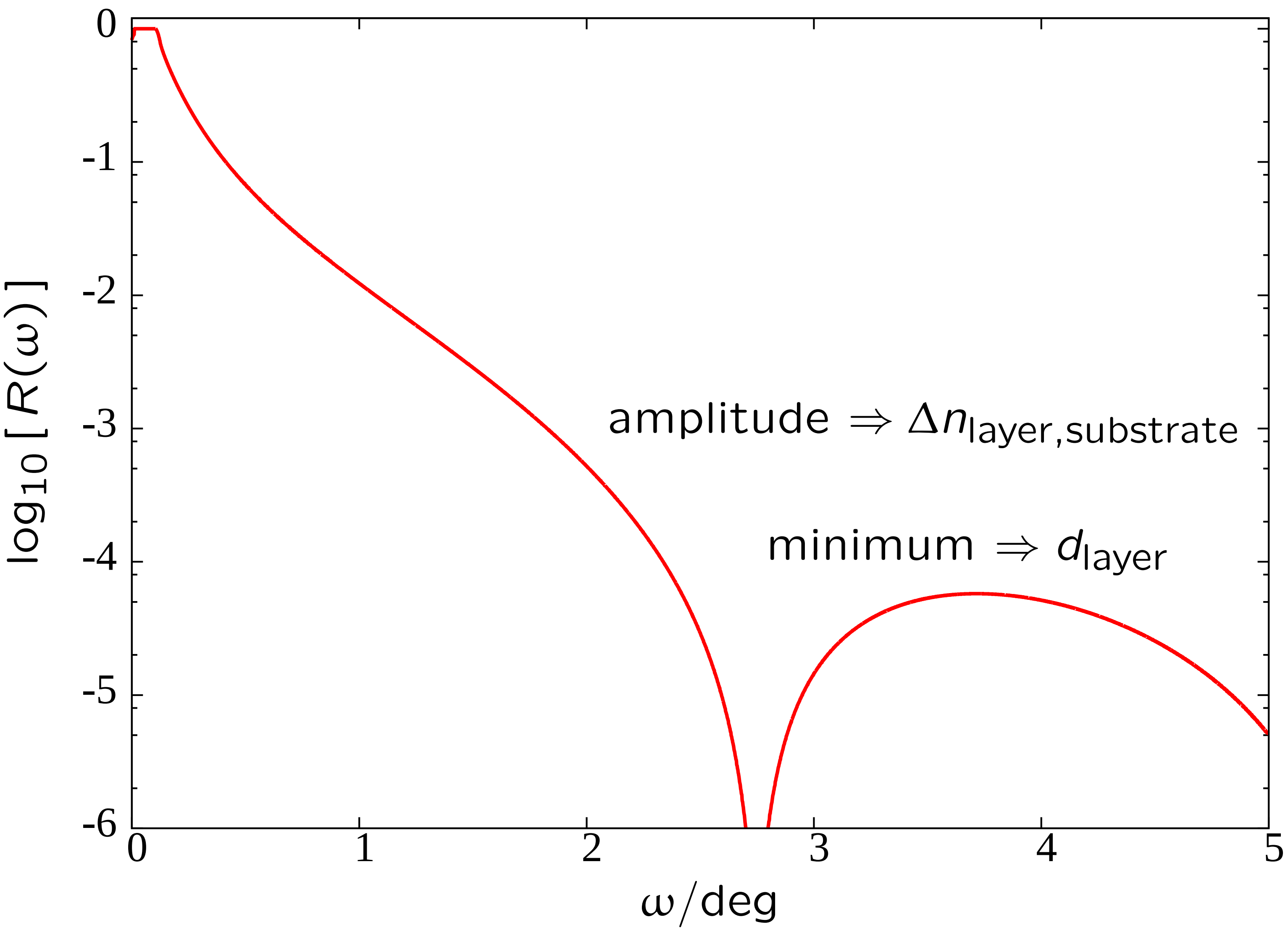
simulated reflectivity of a surface



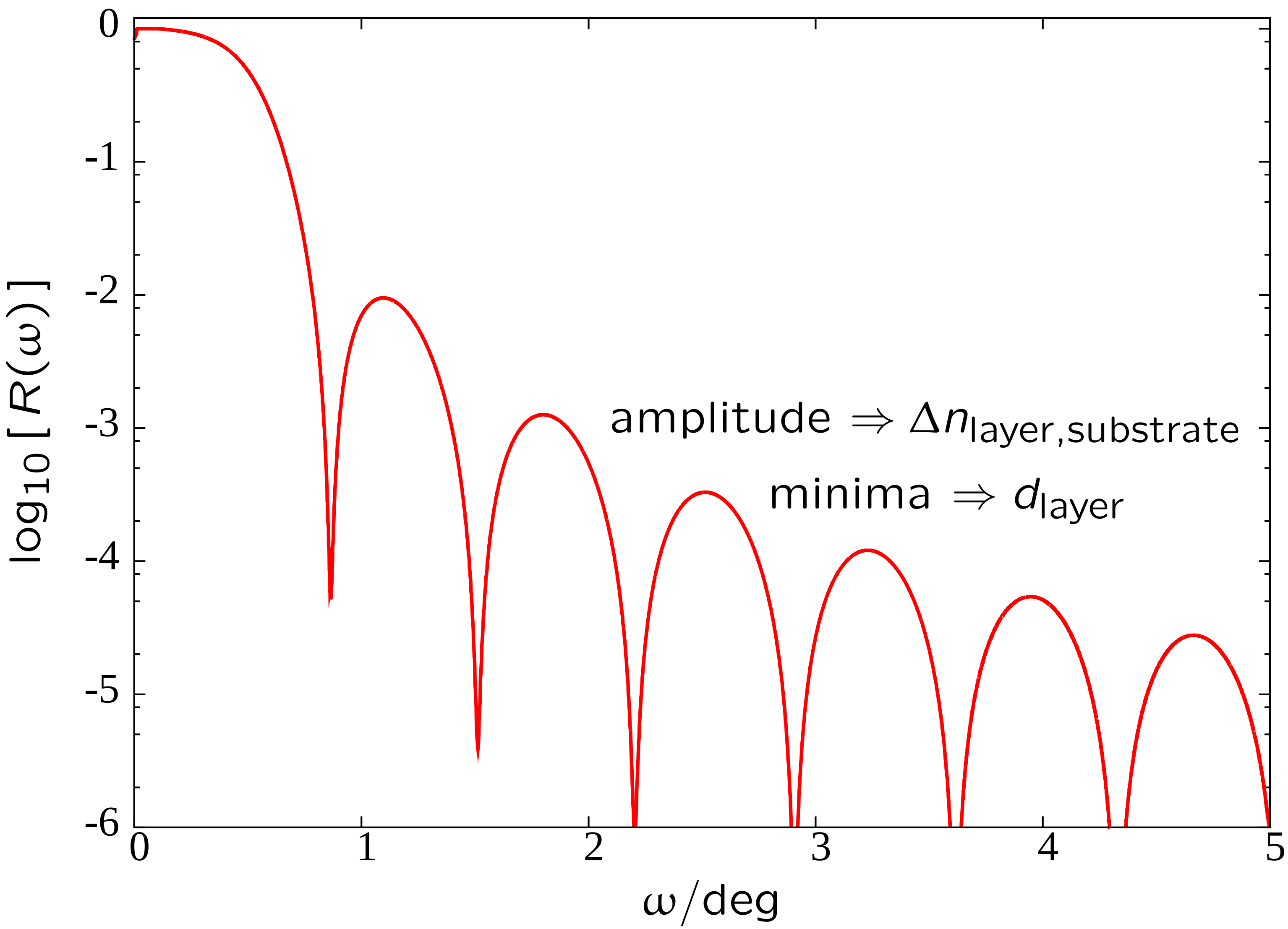
Snell's law: $\dfrac{\cos\omega_i}{\cos\omega_{i+1}} = \dfrac{n_{i+1}}{n_i}$

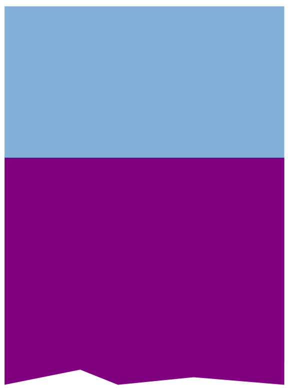
$\Rightarrow \cos\omega_0^{c} = n_1$

simulated reflectivity of a thin layer

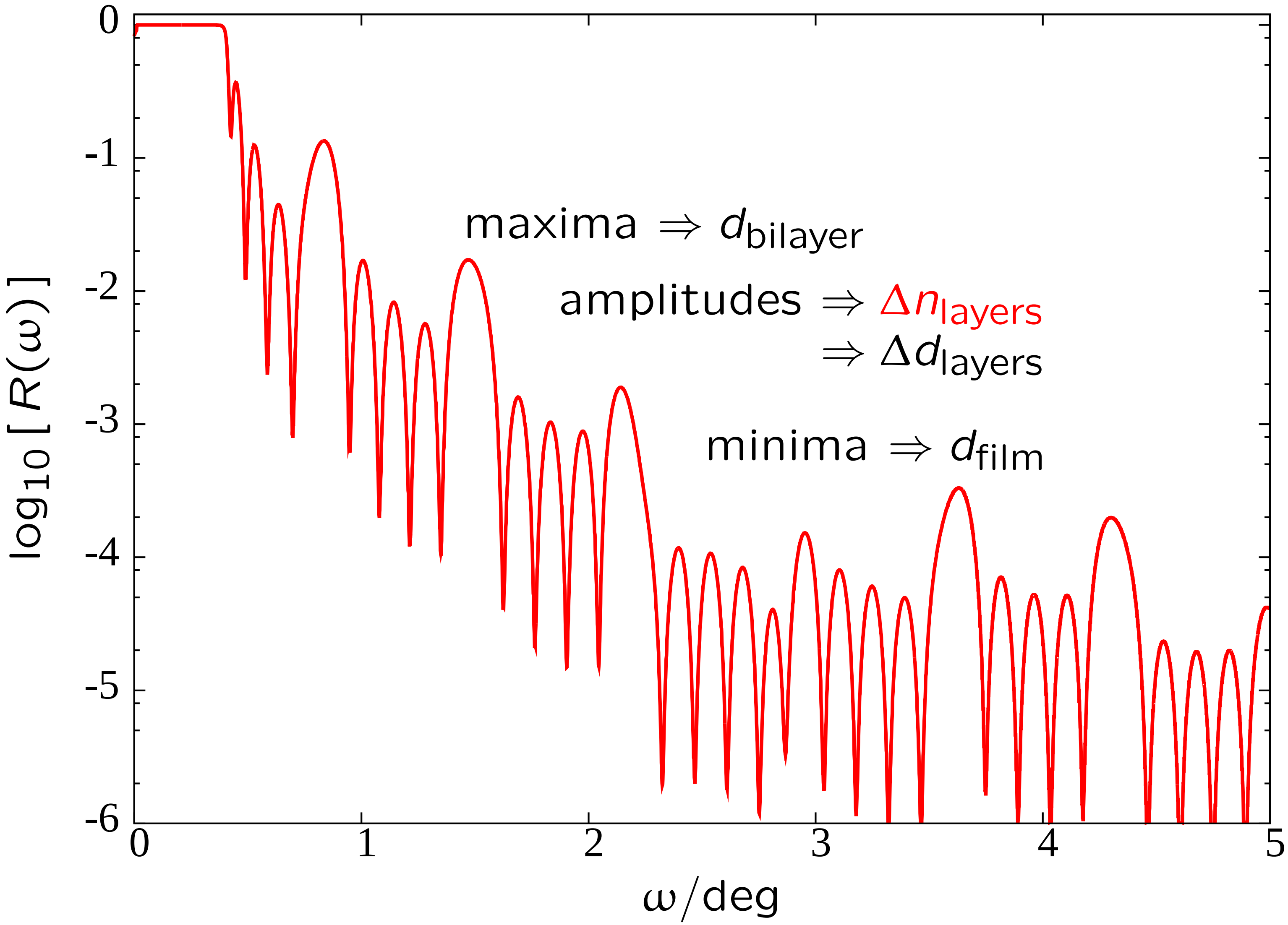


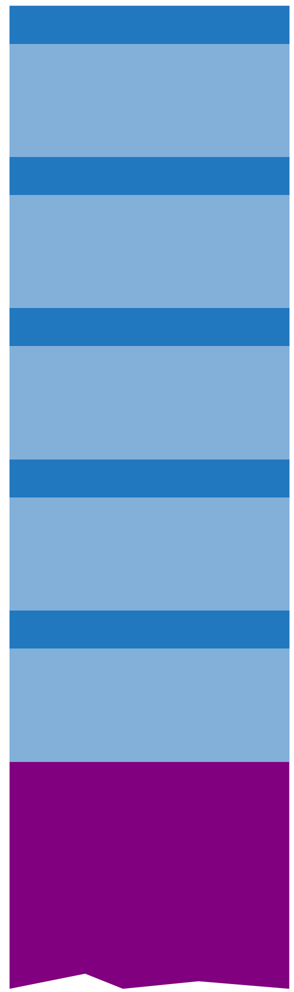
simulated reflectivity of a thick layer



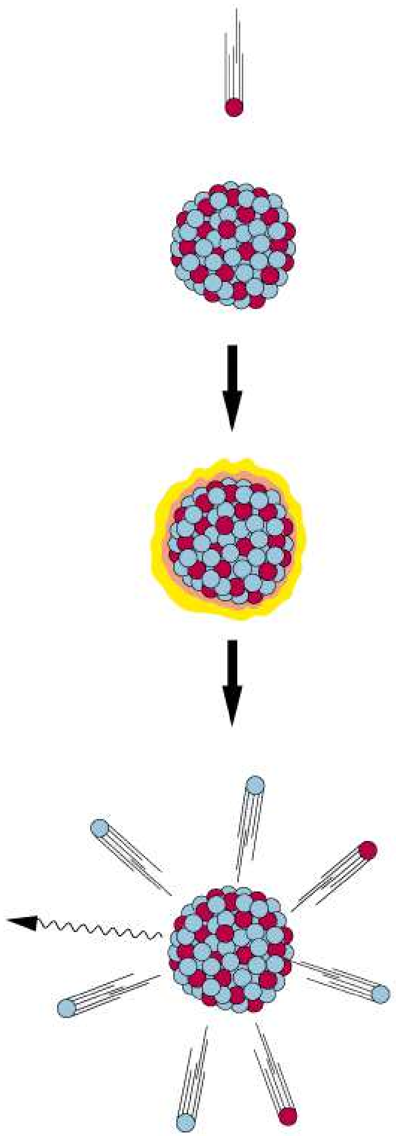


simulated reflectivity of a periodic multilayer



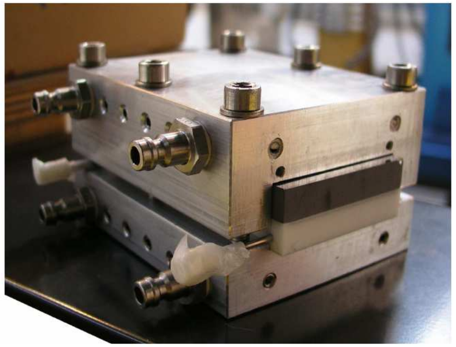


. . . with neutrons



- building unit of atomic nuclei
- ≈ mass of a proton
  ⇒ collision with nuclei
- no charge
  ⇒ no interaction with electrons / charges
- spin 1/2
  ⇒ magnetic moment
  ⇒ interaction with magnetic fields
- De-Broglie wavelength ≈ 1 . . . 20 Å
  ⇒ atomic / crystallographic dimensions
  ⇒ energy of phonons
- interaction with nuclei
  ⇒ *random* sensitivity across the PSE
  ⇒ isotope-sensitive

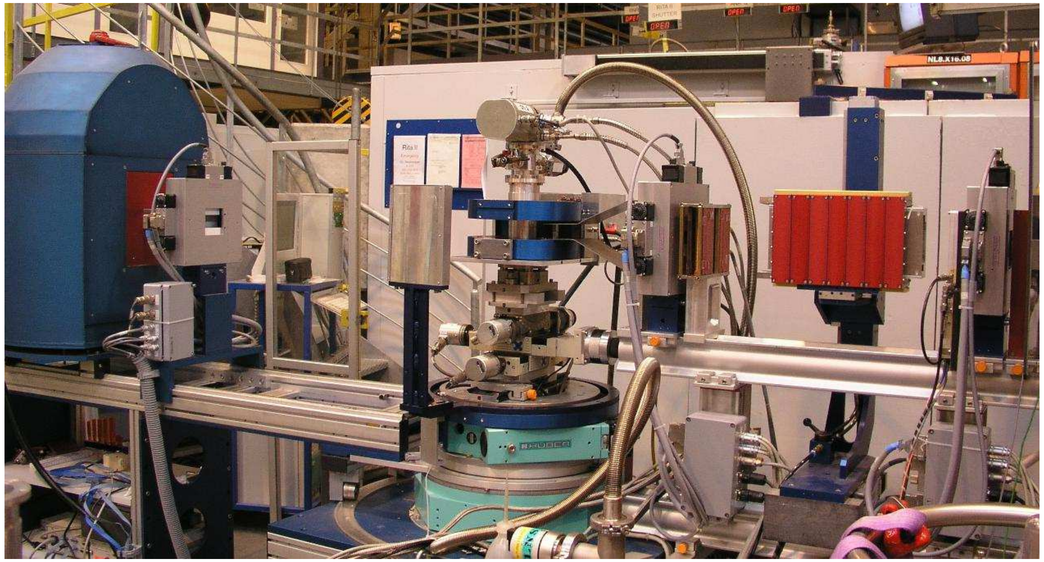
some numbers

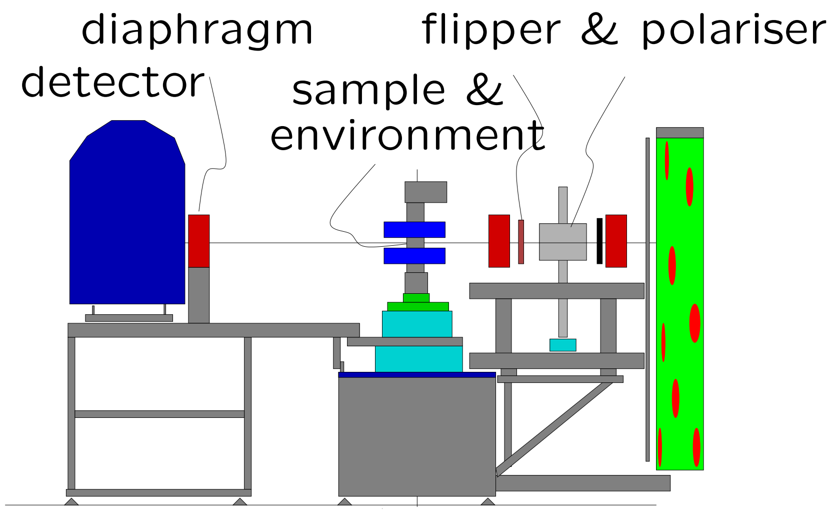
probed depth	100 nm → 1 μm	(less for absorbers)
depth resolution	0.2 nm → 400 nm	strongly model dependent *t* and δ might be correlated
lateral coherence	1 μm → 100 μm	averaging laterally over all *microstructures*
penetration depth	→ 10 cm	

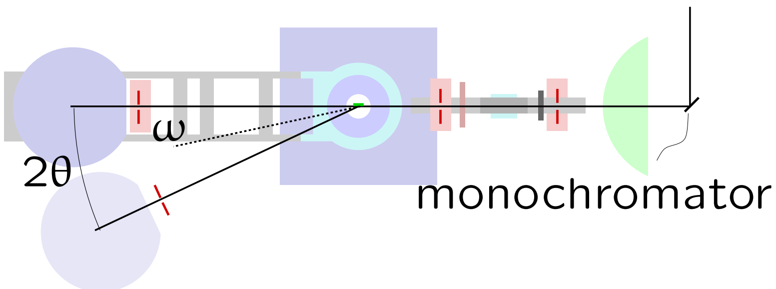
equipment

neutron reflectometer

e.g. Morpheus at SINQ

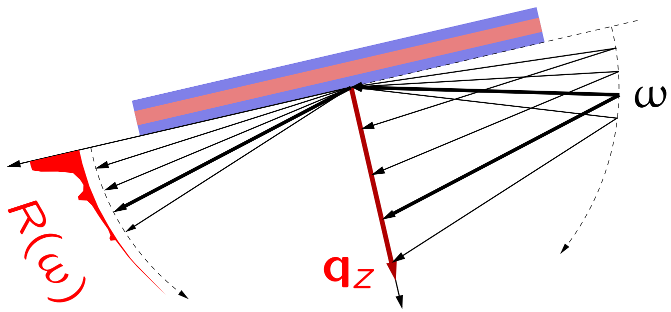






angle-dispersive set-up

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



equipment

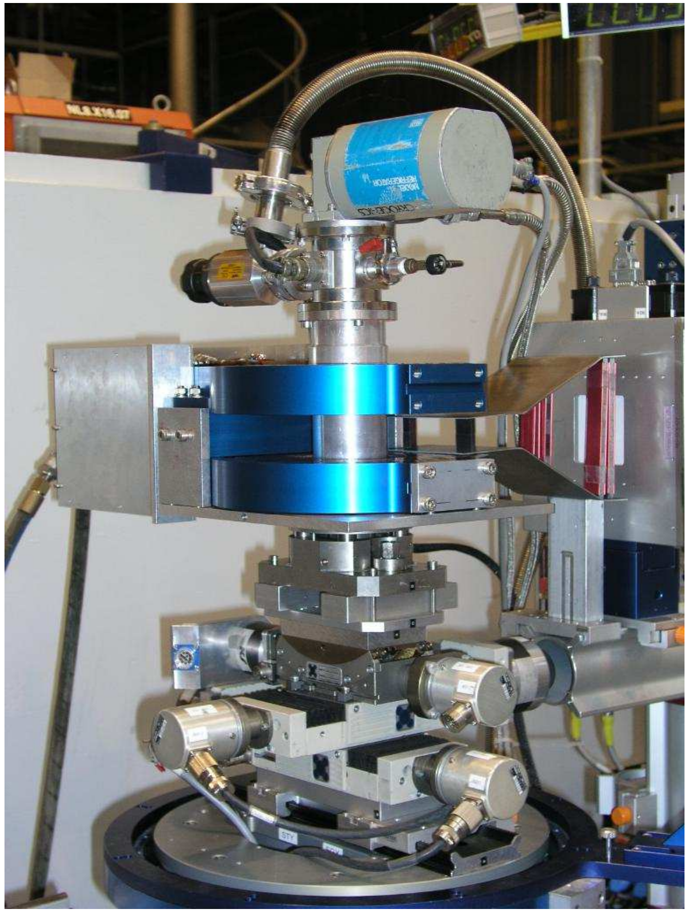
sample environment

e.g. cooling with a

closed cycle refrigerator $8\,\mathrm{K} < T < 300\,\mathrm{K}$

application of an external magnetic field with

Helmholtz coils $-1000\,\mathrm{Oe} < H < 1000\,\mathrm{Oe}$



tilt- and translation stages
for alignment

ω rotation stage

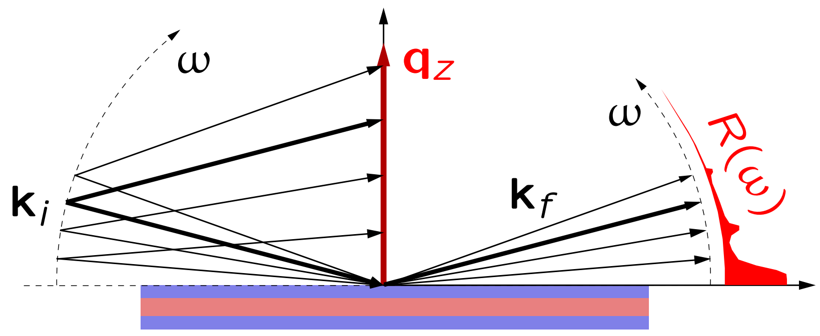
sample

within
sample-holder

data acquisition

typical quantities:

angular range	$0^\circ \dots 10^\circ$
λ range	$3\,Å \dots 15\,Å$
measurement time	10 min ... 12h

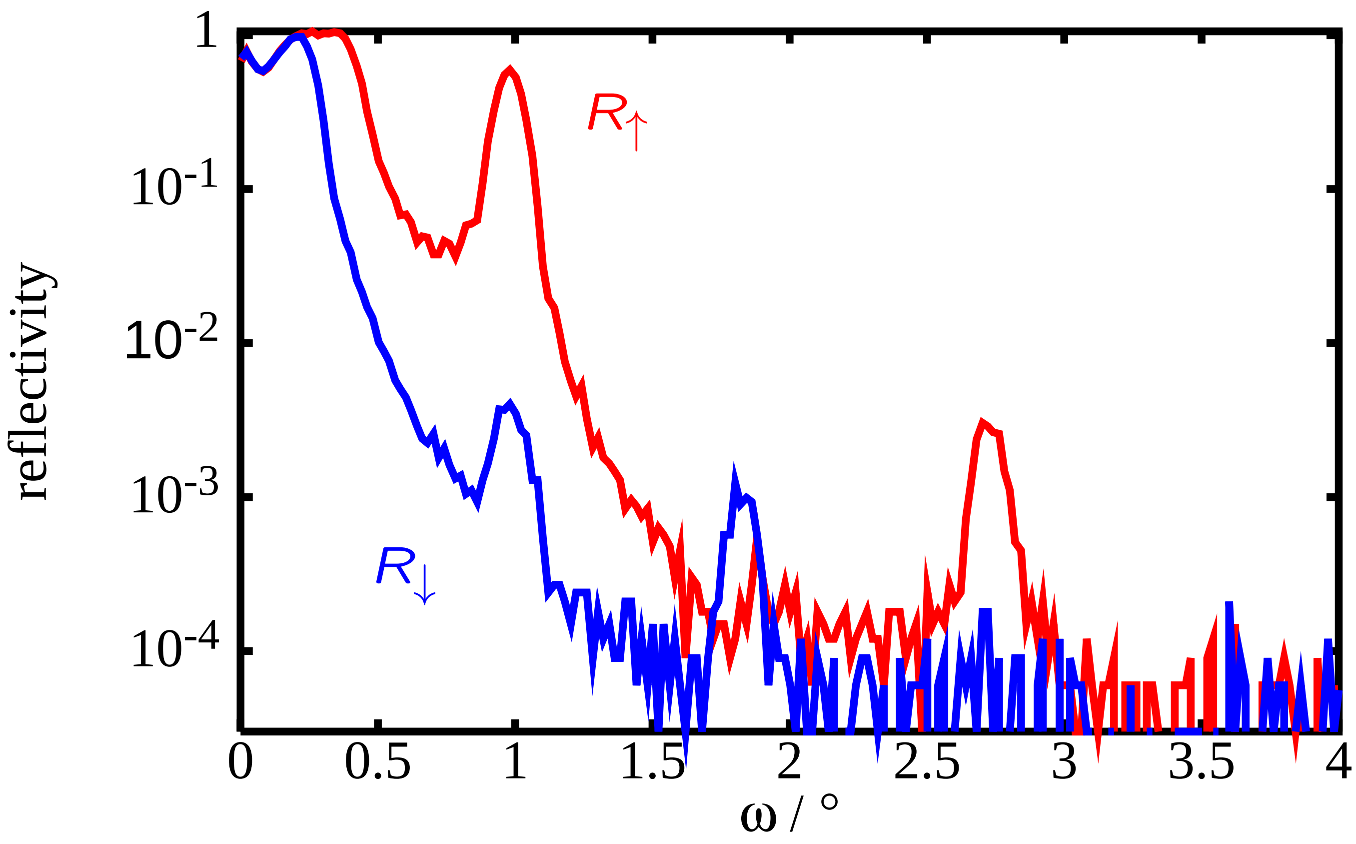


example:

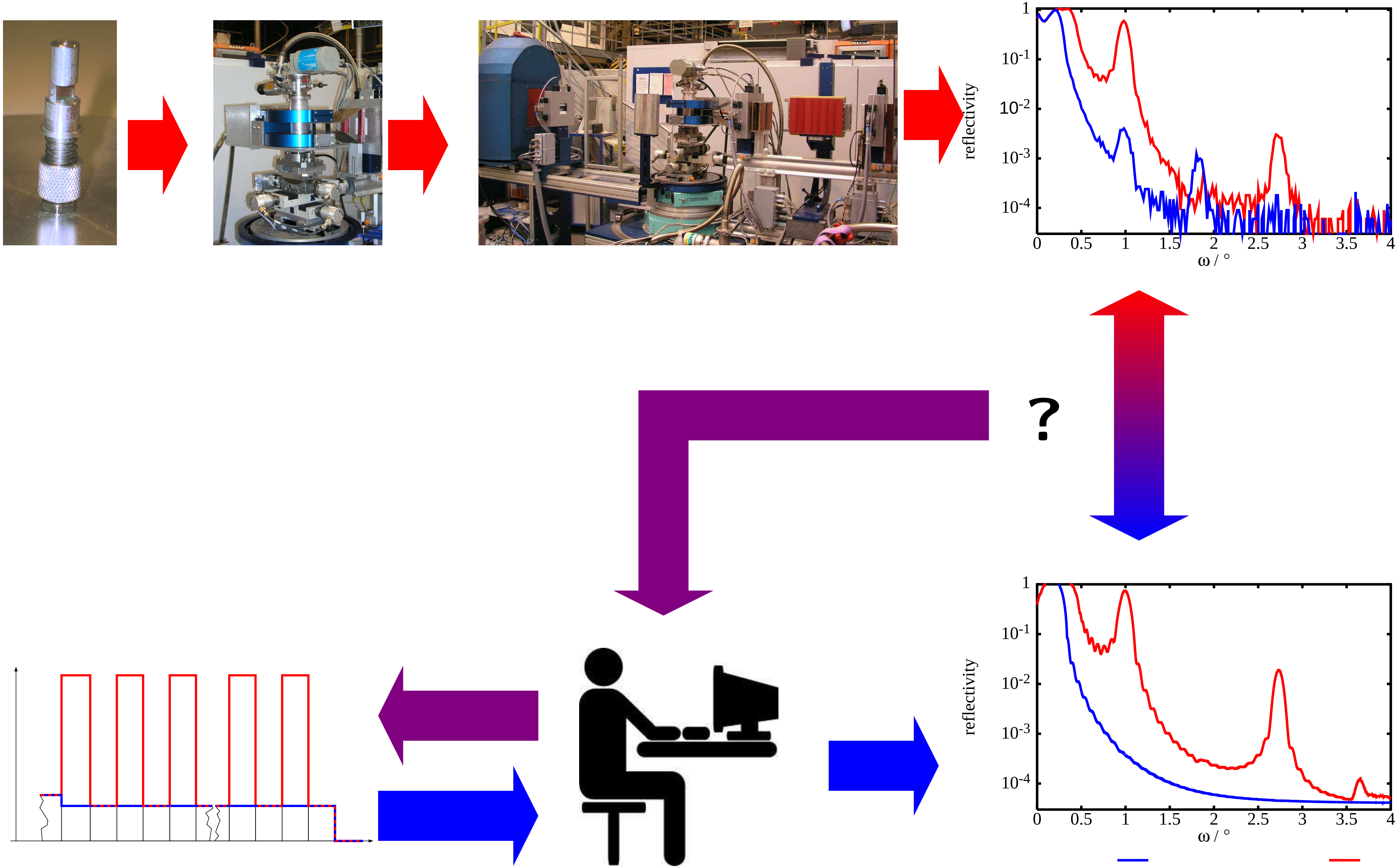
Fe/Si multilayer on glass

polarised neutrons

1h per spin state



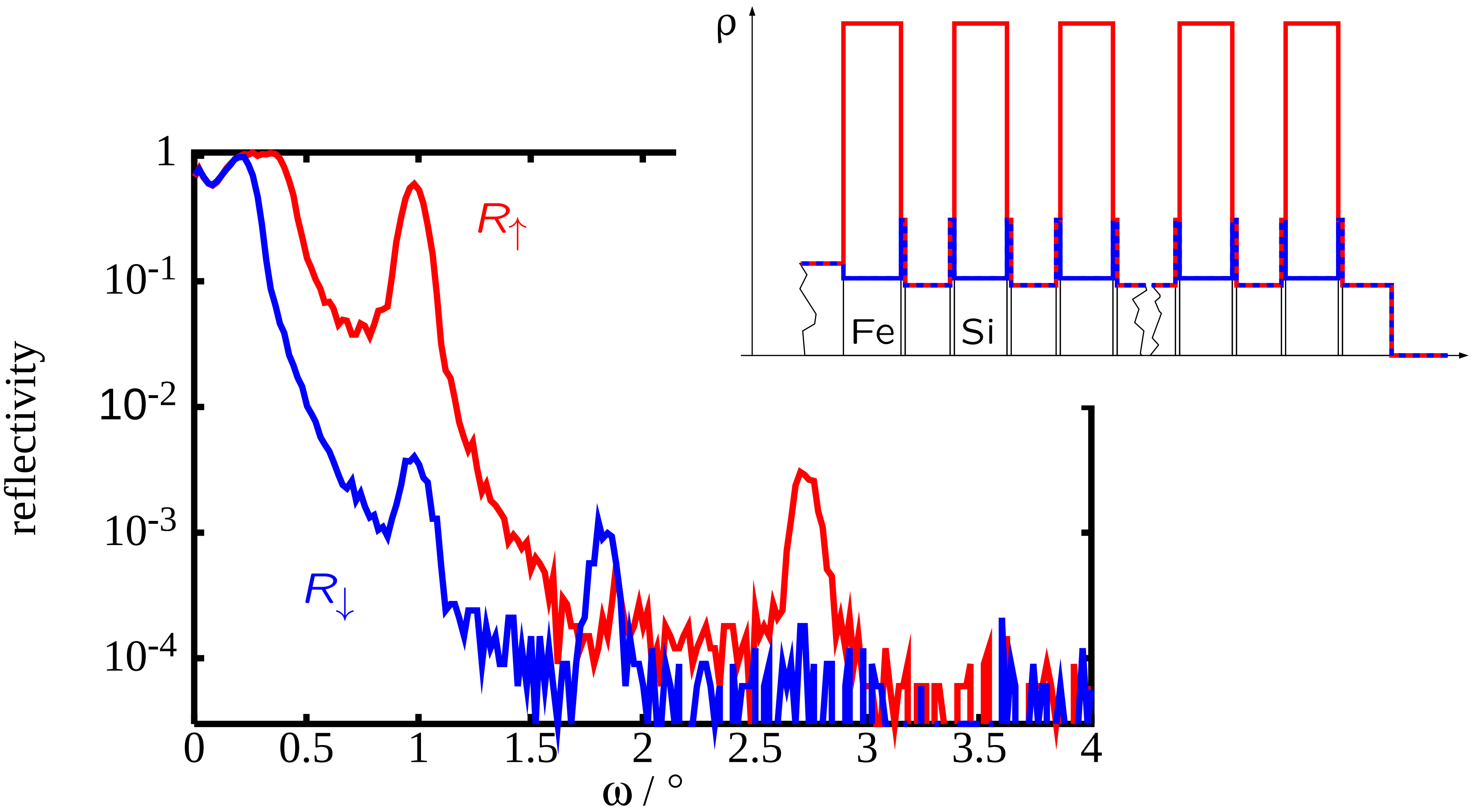
data acquisition and interpretation



data acquisition and interpretation

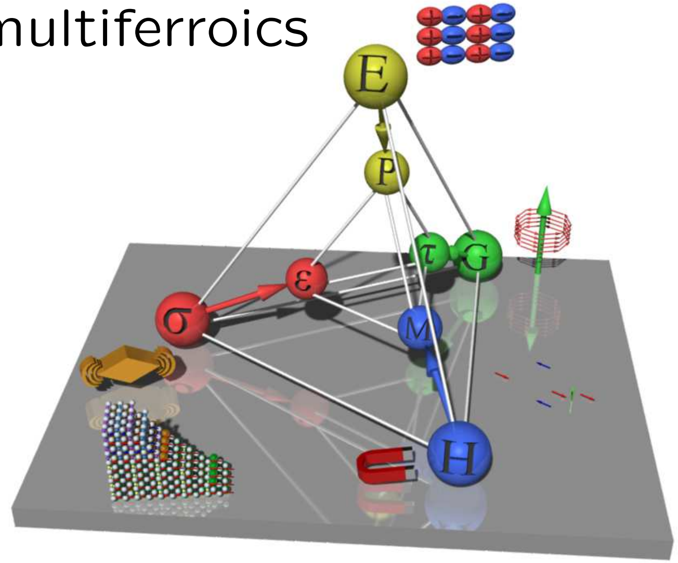
Fe/Si multilayer

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

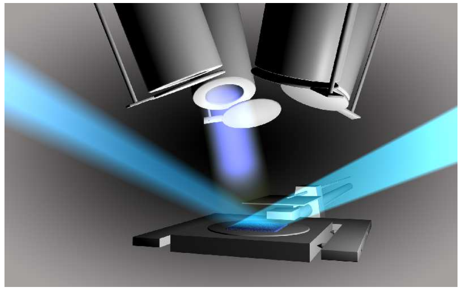


typical scientific questions

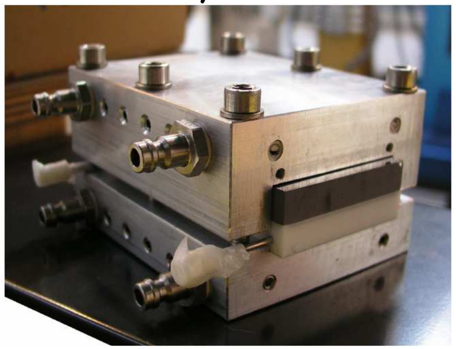
multiferroics



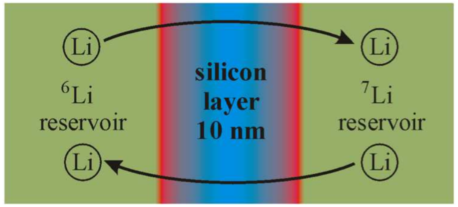
growth
mechanisms



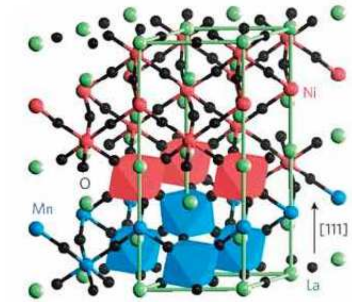
adsorption at ...
solid/water



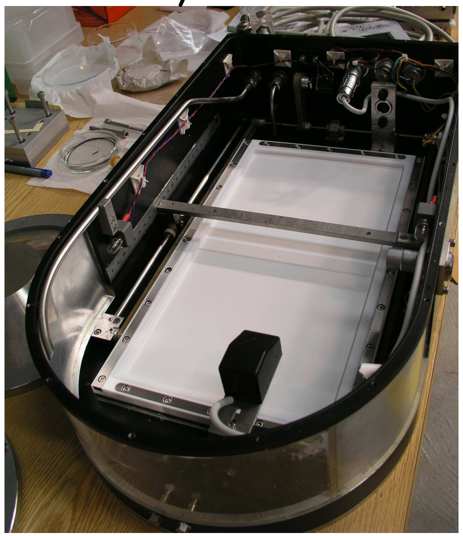
diffusion



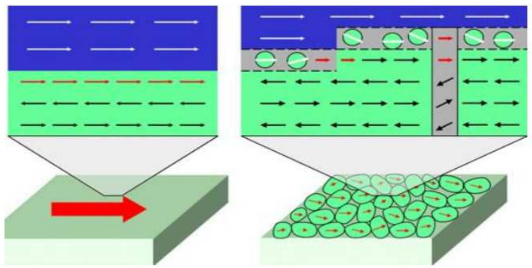
interface
magnetism



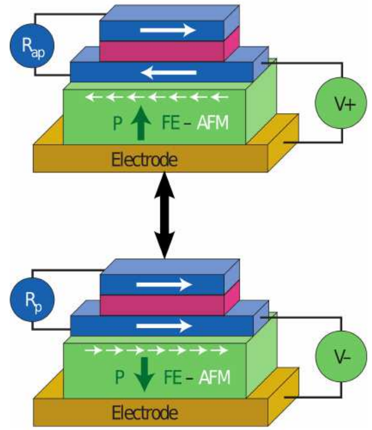
air/water



exchange bias



spintronics

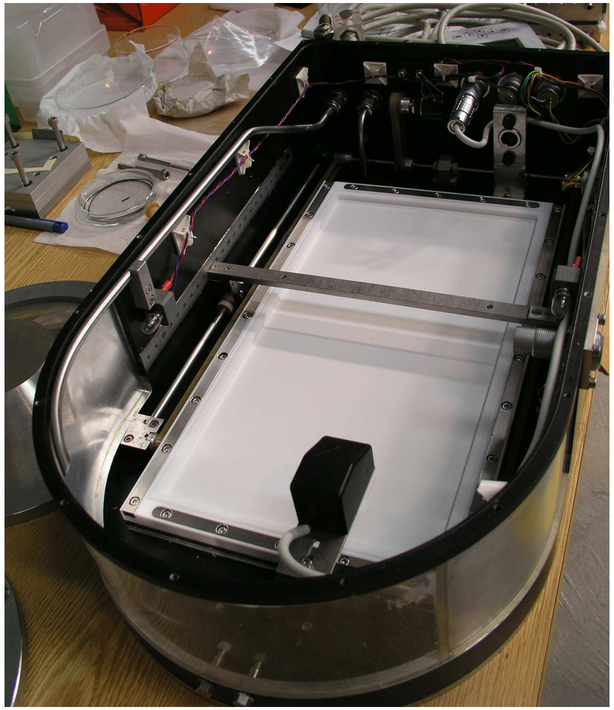


... interfaces

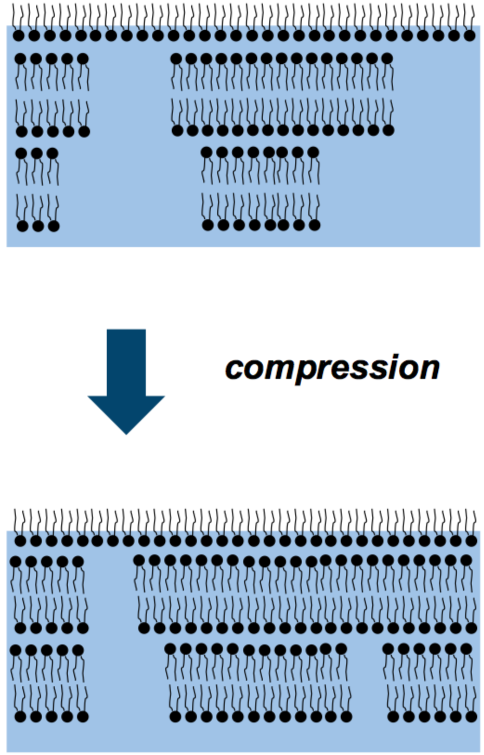
liquid/gas interface

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



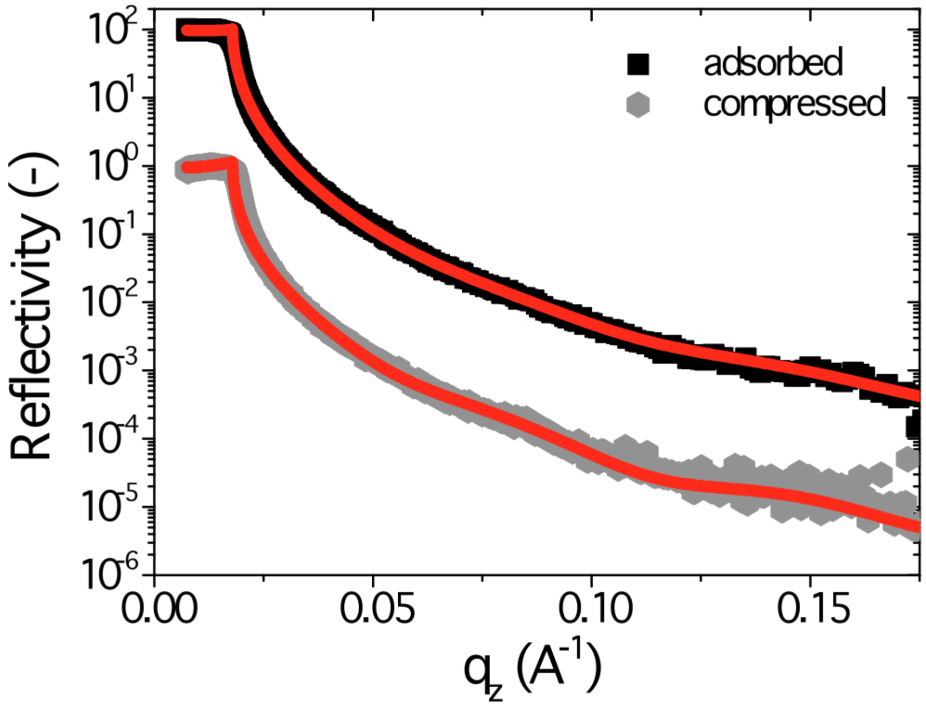
liquid/gas interface

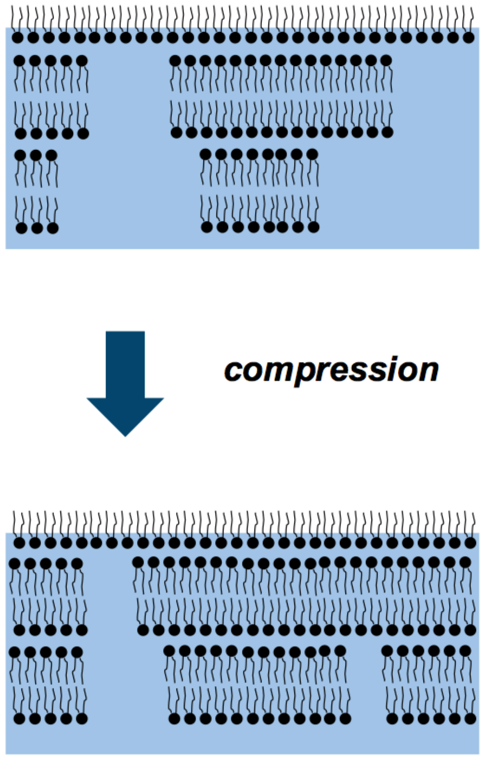
compression of self-organising polyglycerol-ester films

H_2O substituted by D_2O

⇒ strong contrast between solvent and film (essentially $[CH_2]_n$)

⇒ *high* critical edge





C. Curschellas, IACIS, Sendai, 2012

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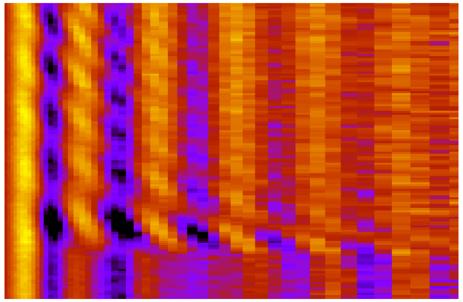
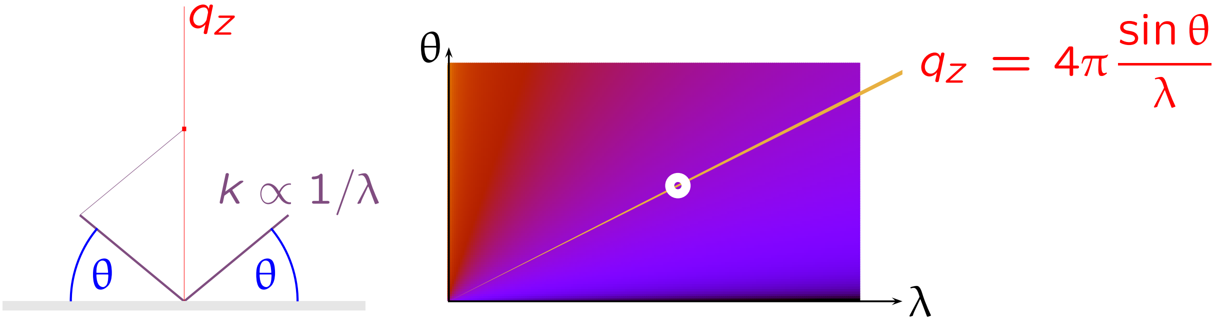
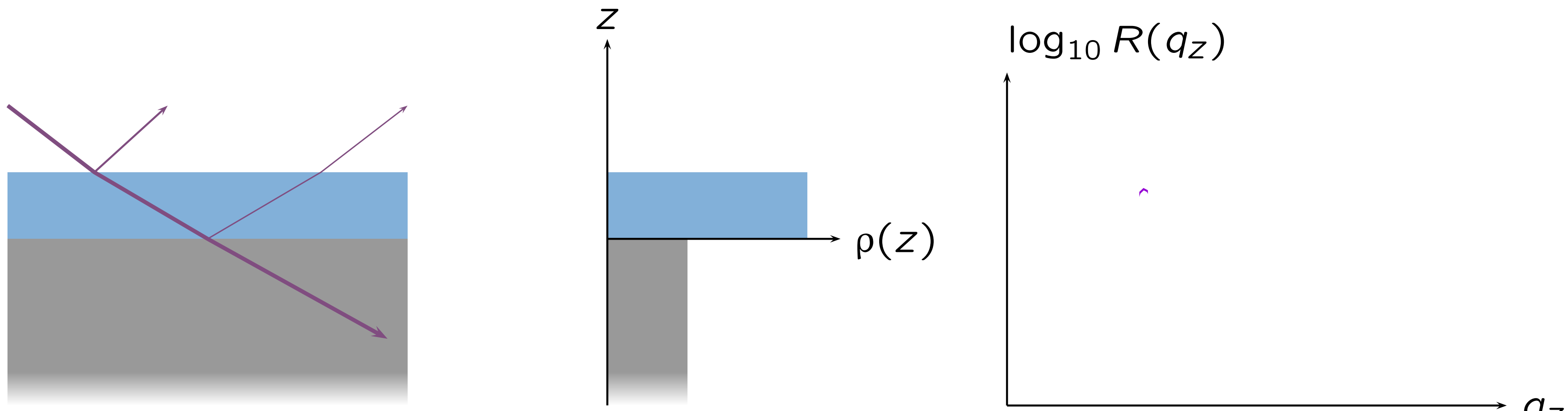
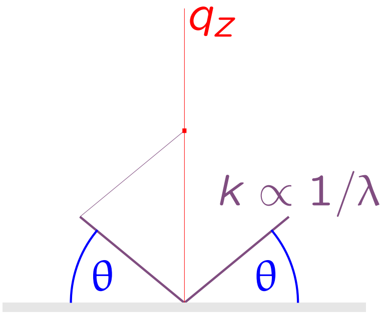


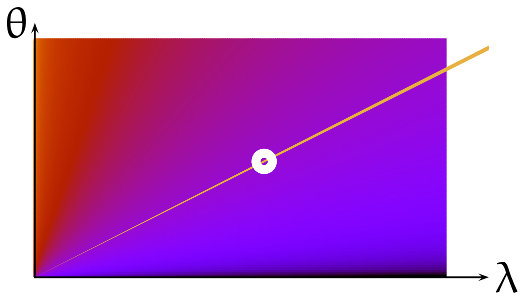

specular reflectometry



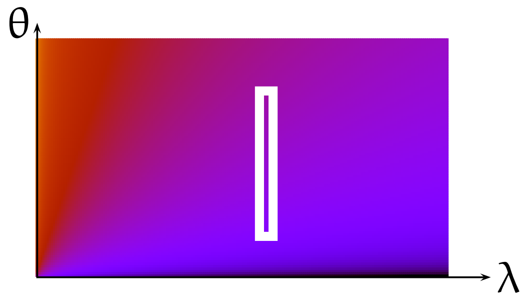


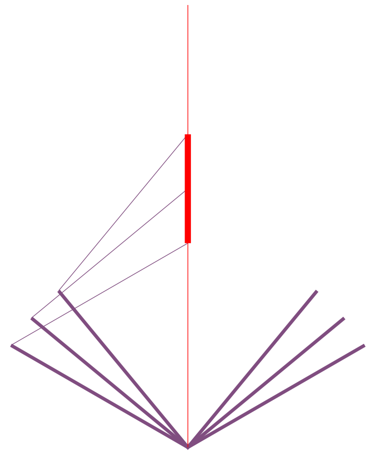
specular reflectometry

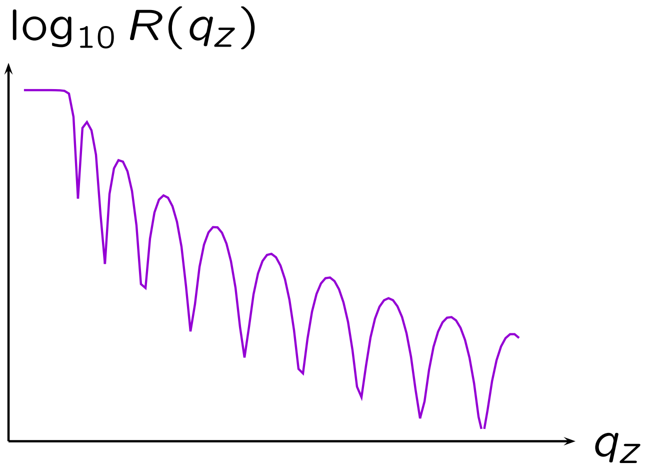




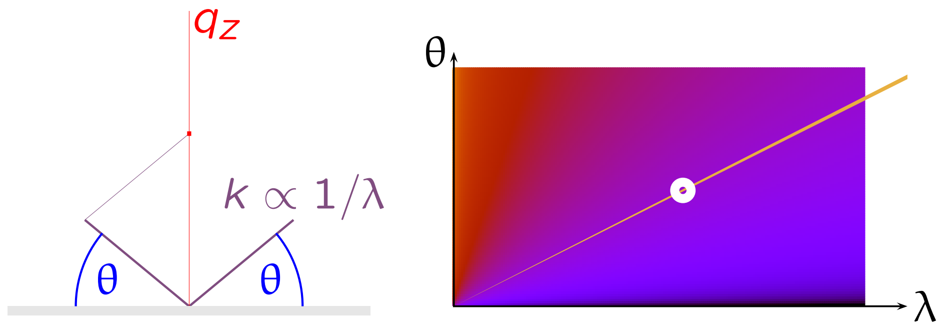
angle-dispersive







specular reflectometry



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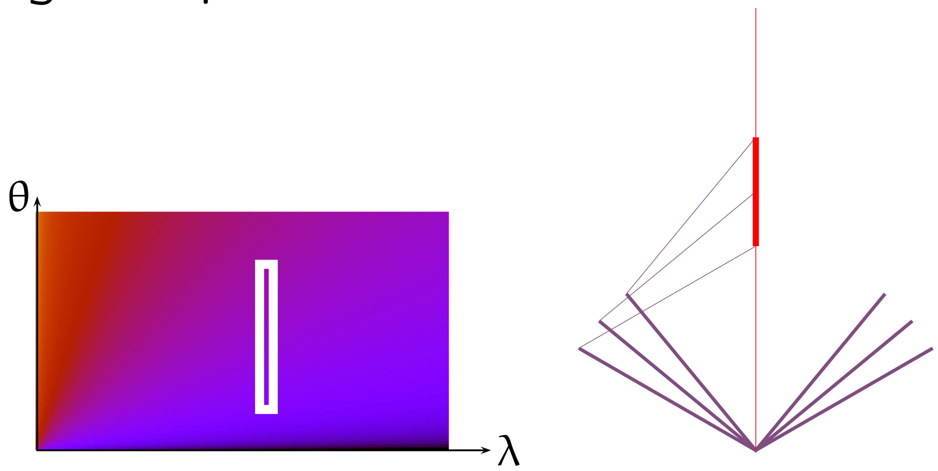
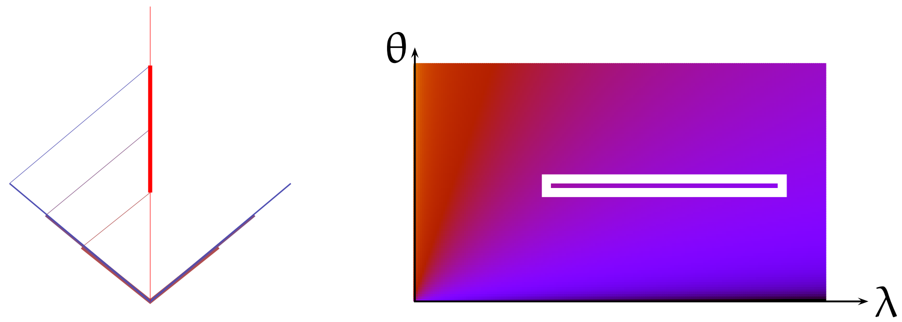
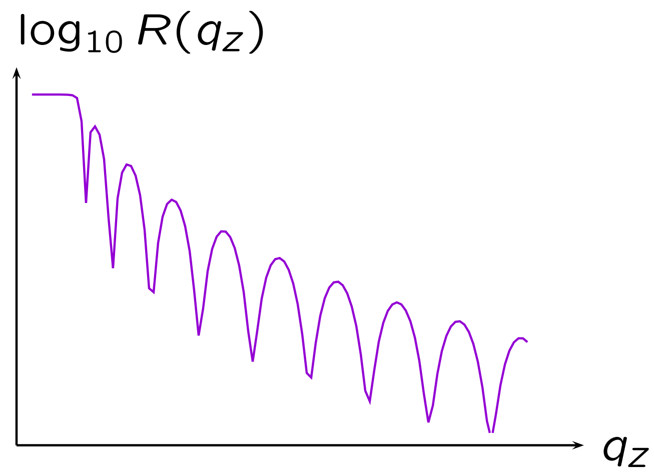


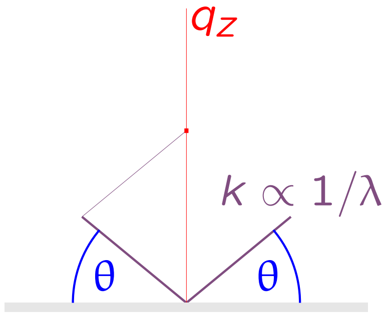
energy-dispersive

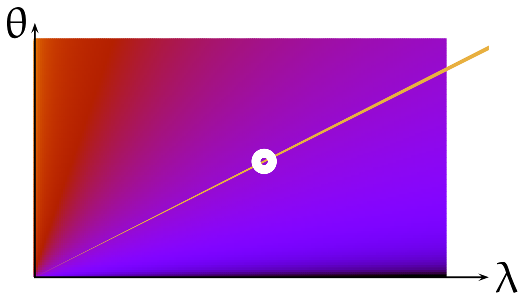


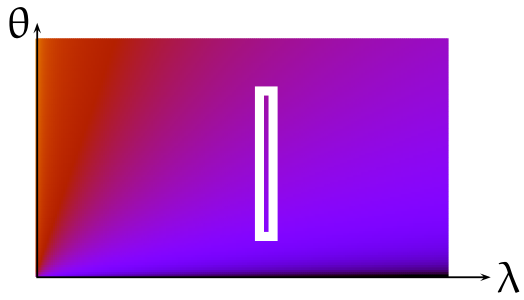


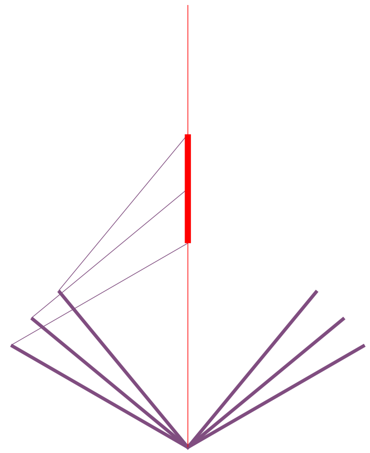
specular reflectometry

angle-dispersive

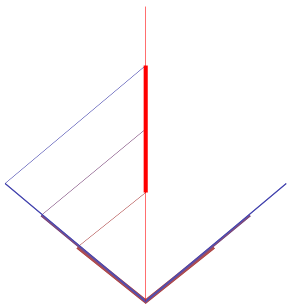


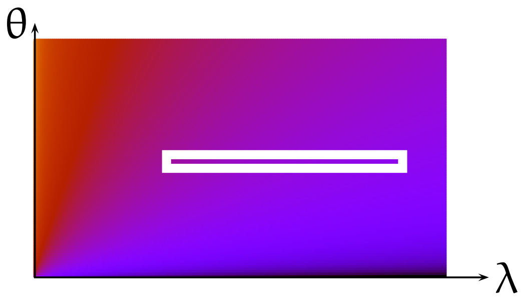


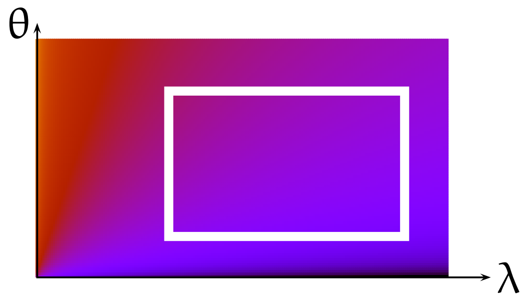


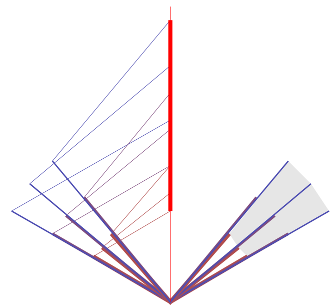


energy-dispersive

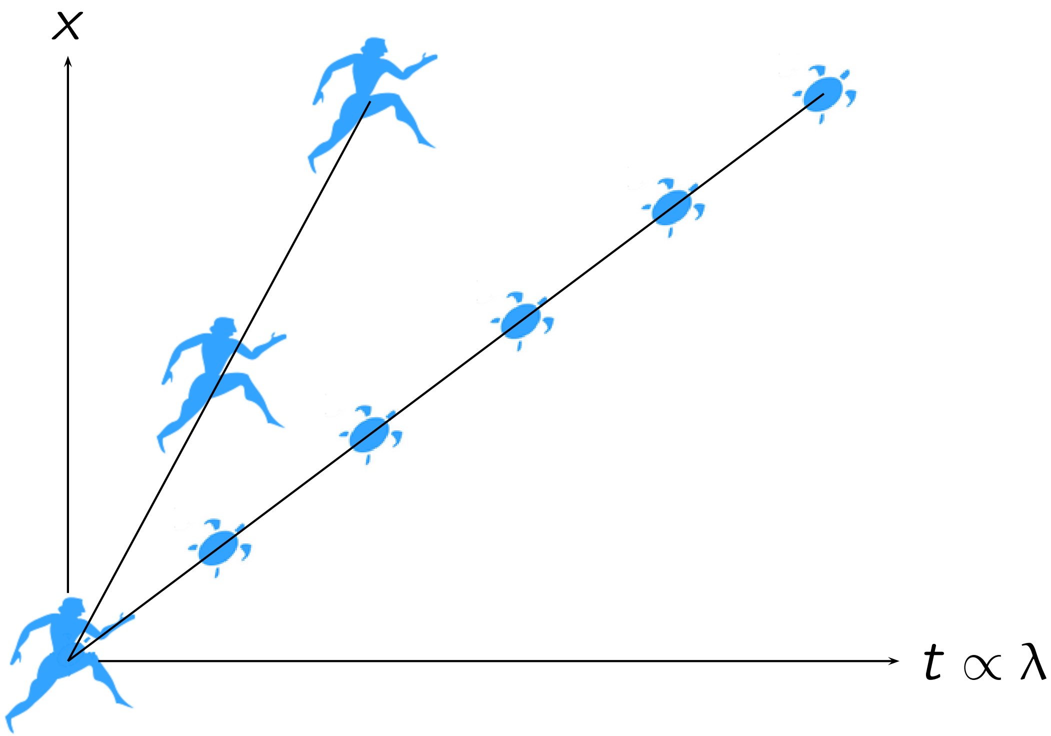


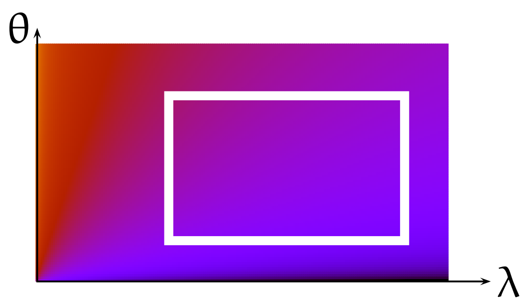


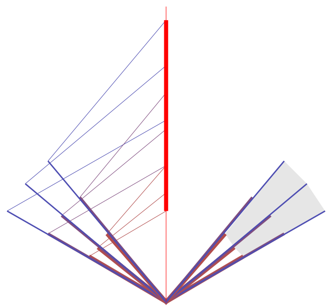




λ-dispersion by time-of-flight

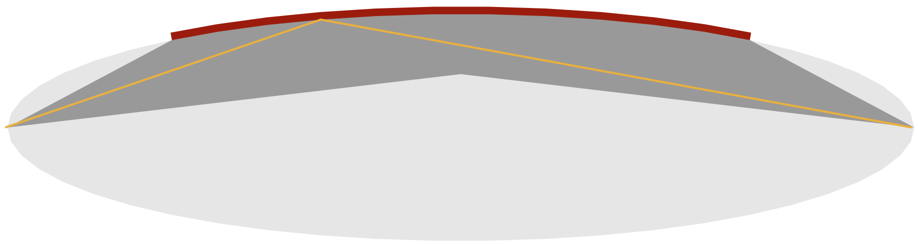


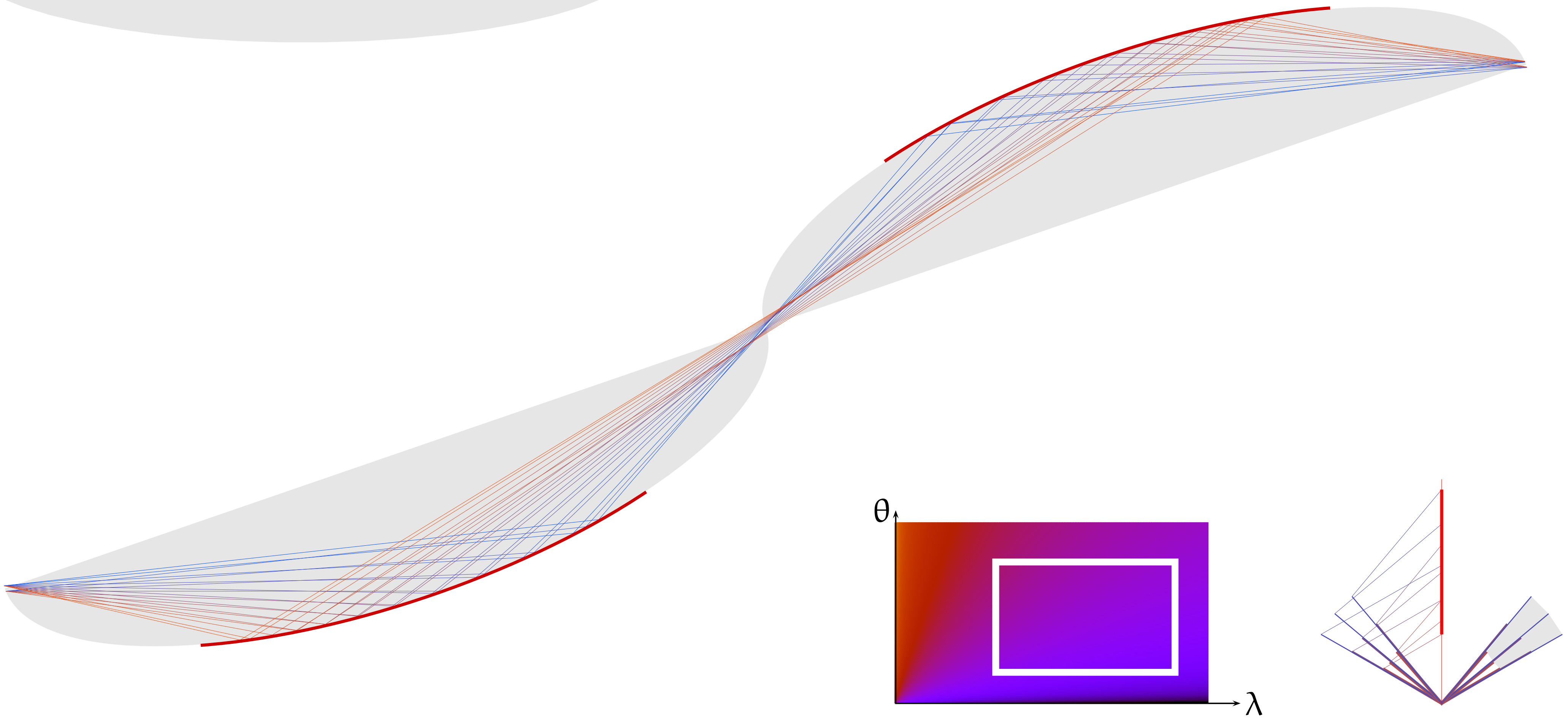




focusing reflectometry

ω-dispersion by focusing





the ***Selene*** guide

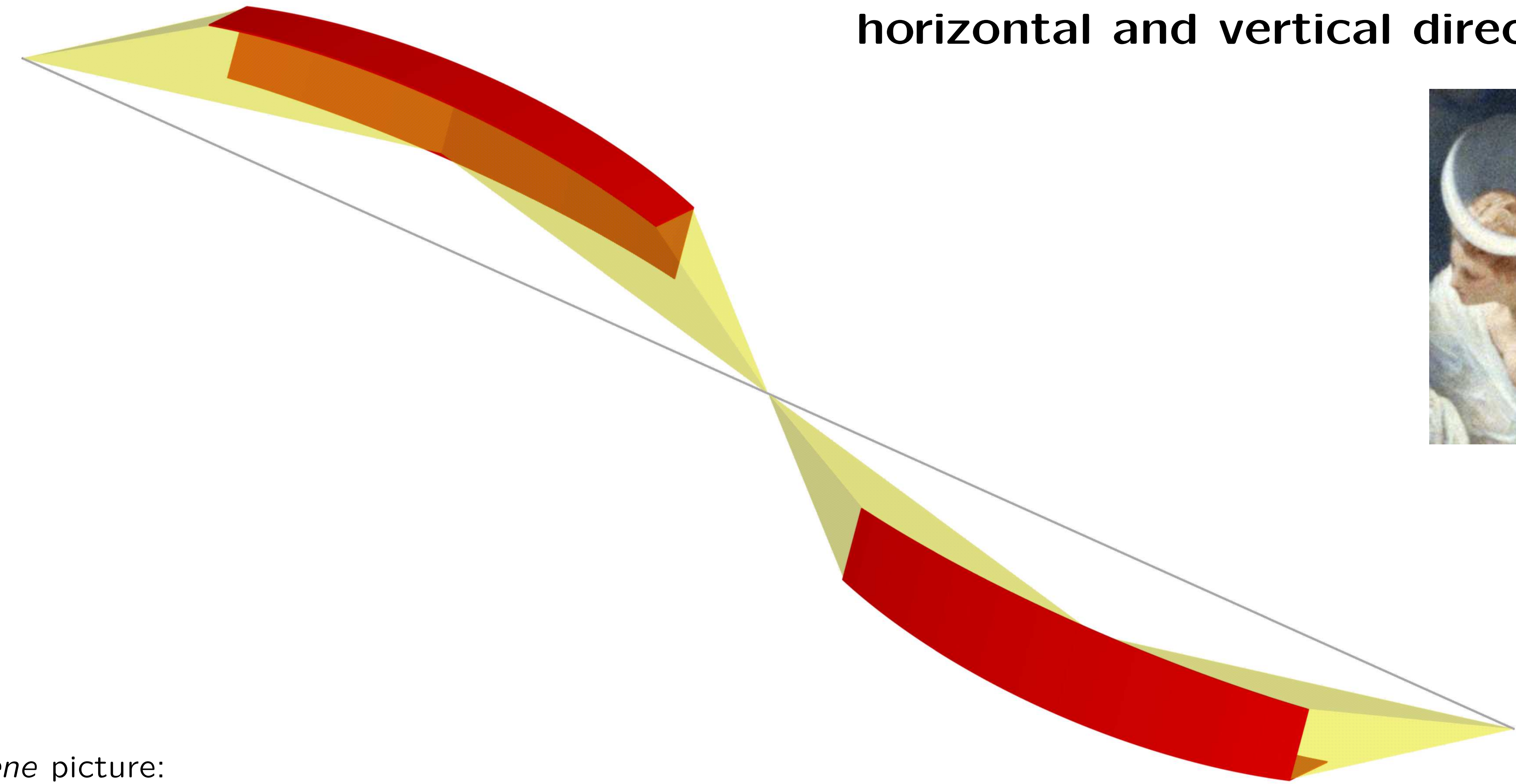
point-to-point focusing

with

2 subsequent elliptical reflectors

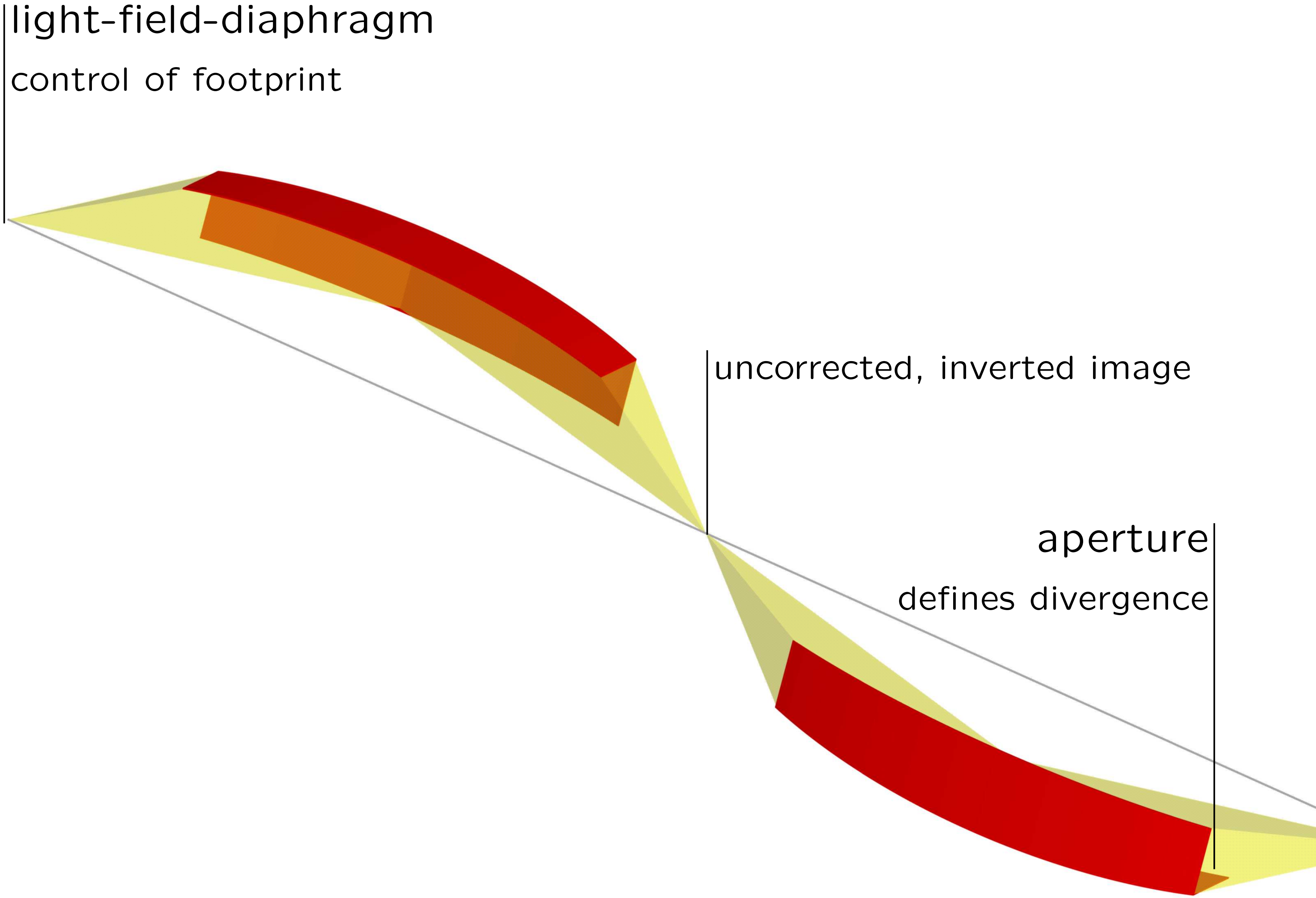
for

horizontal and vertical direction



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

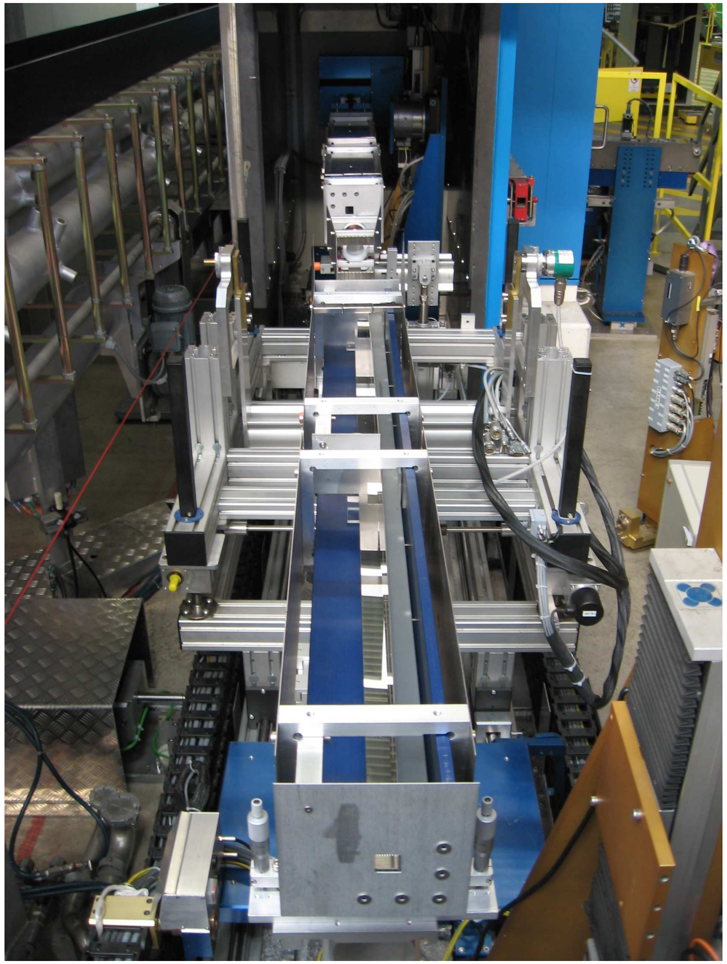
the *Selene* guide

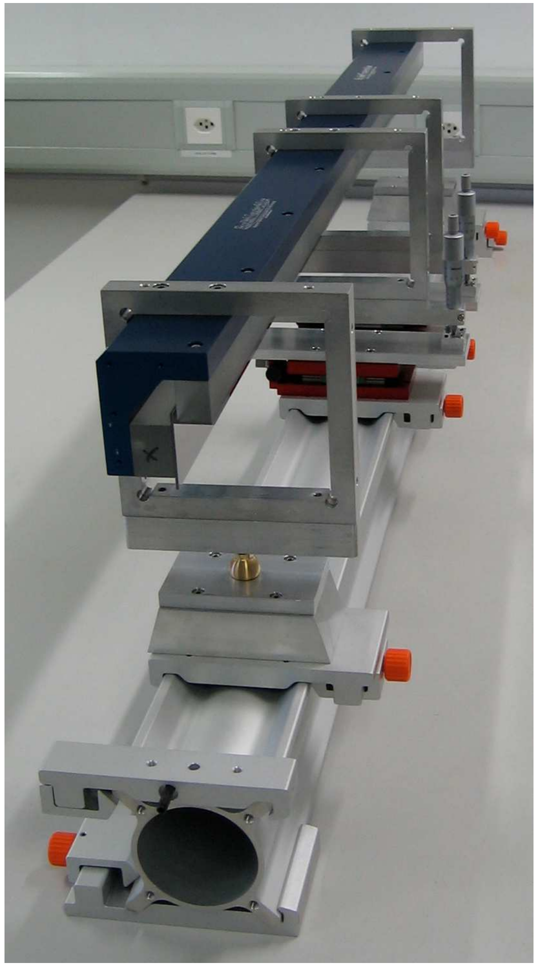


the ***Selene*** guide demonstrator

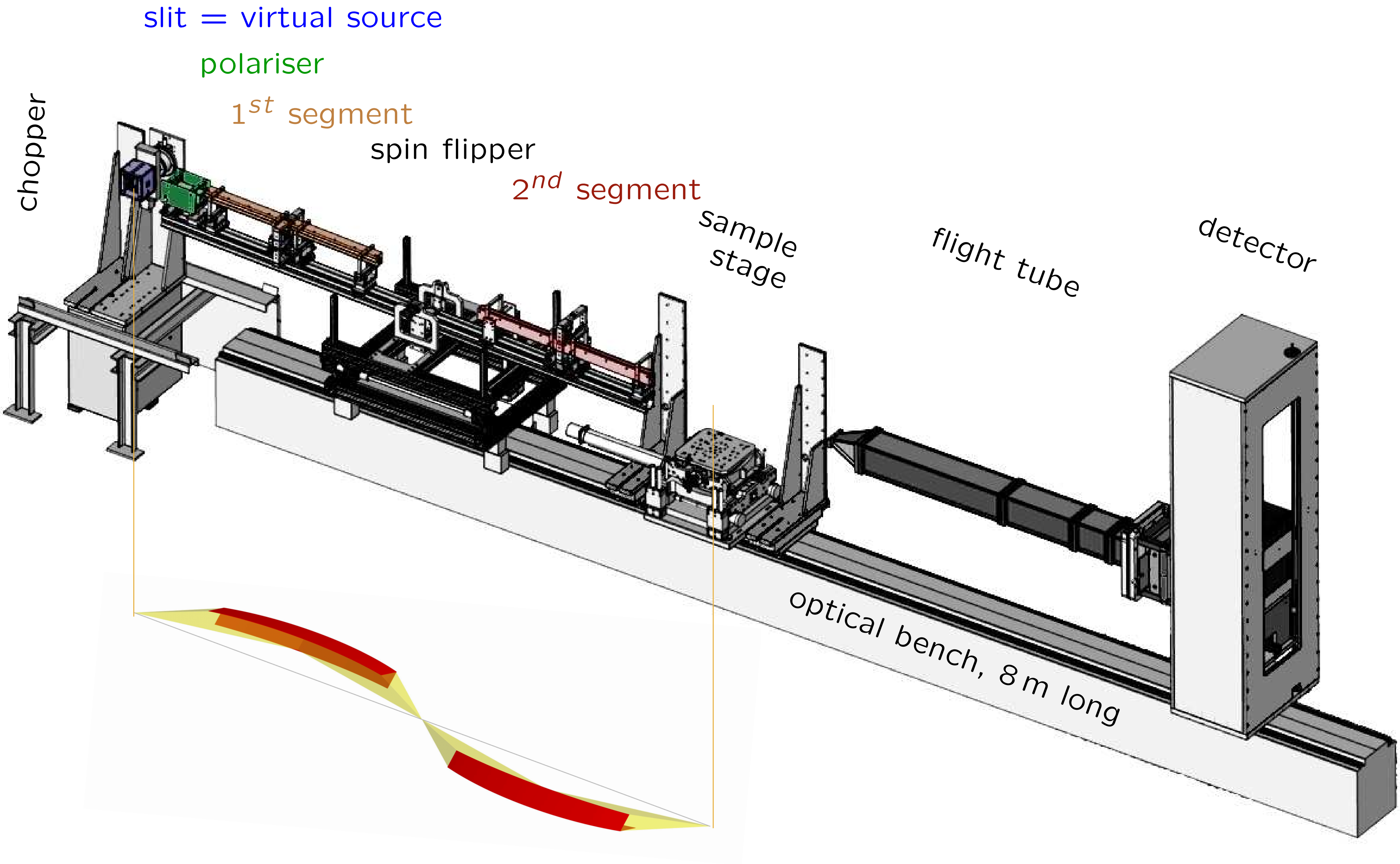
on Amor@PSI

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





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



- intro
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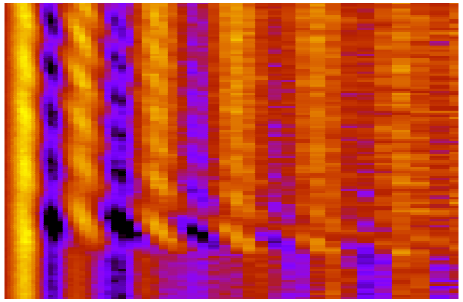
  - → conceptual challenges



Li transport through thin silicon films

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

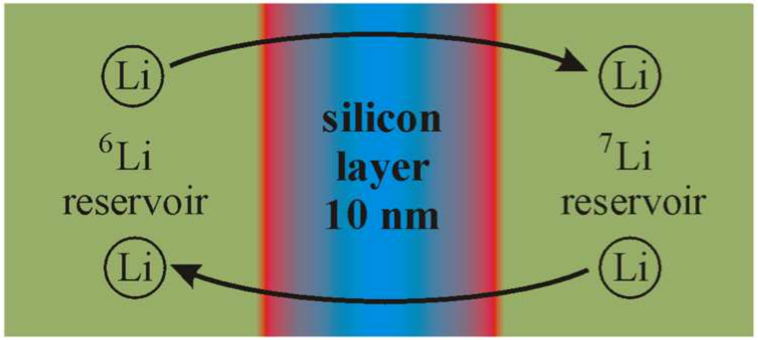
technological motivation:

- 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?

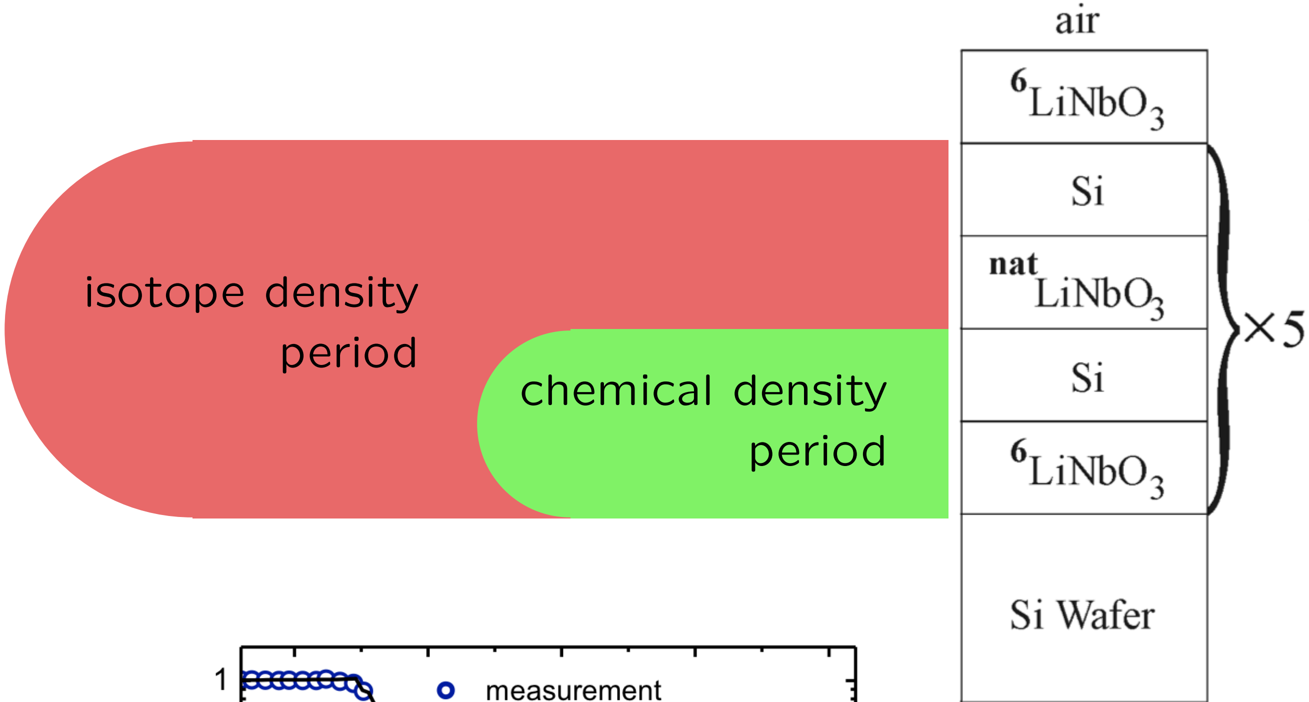
⇒ What is the influence of the Si:O:Li interface layer?

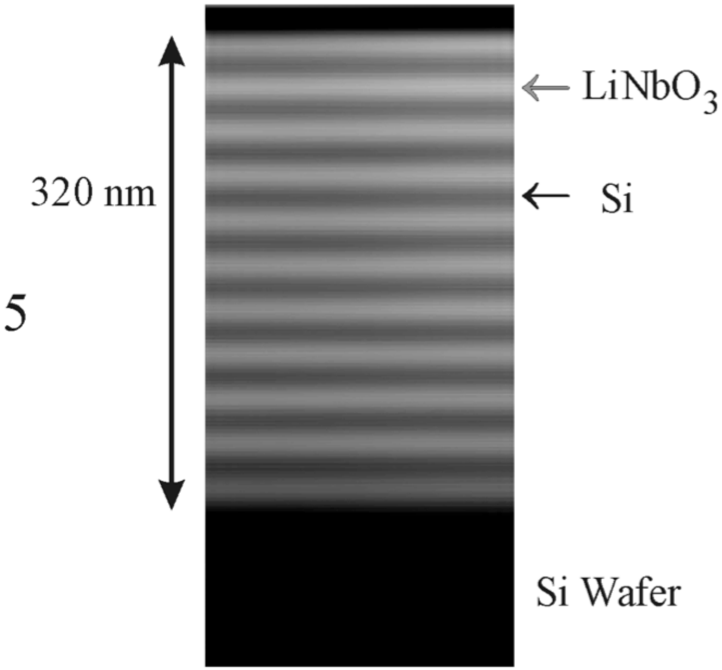


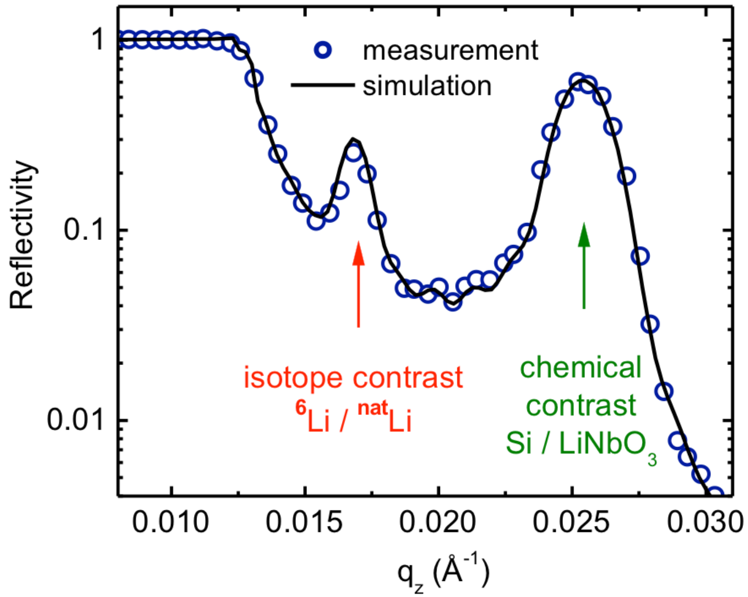
E. Hüger, *et al.*, Nano Letters 13 (2013) 1237.

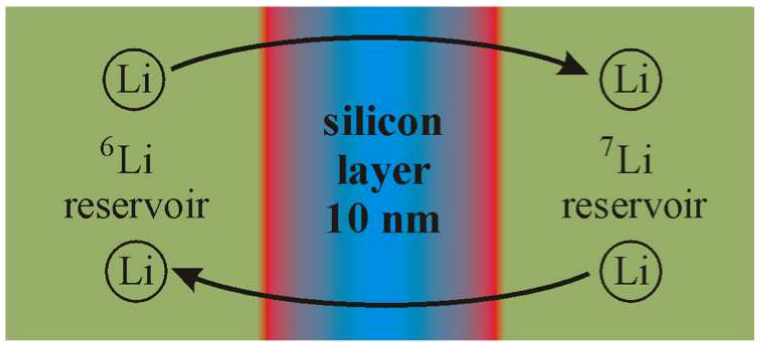
Li transport | the sample

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





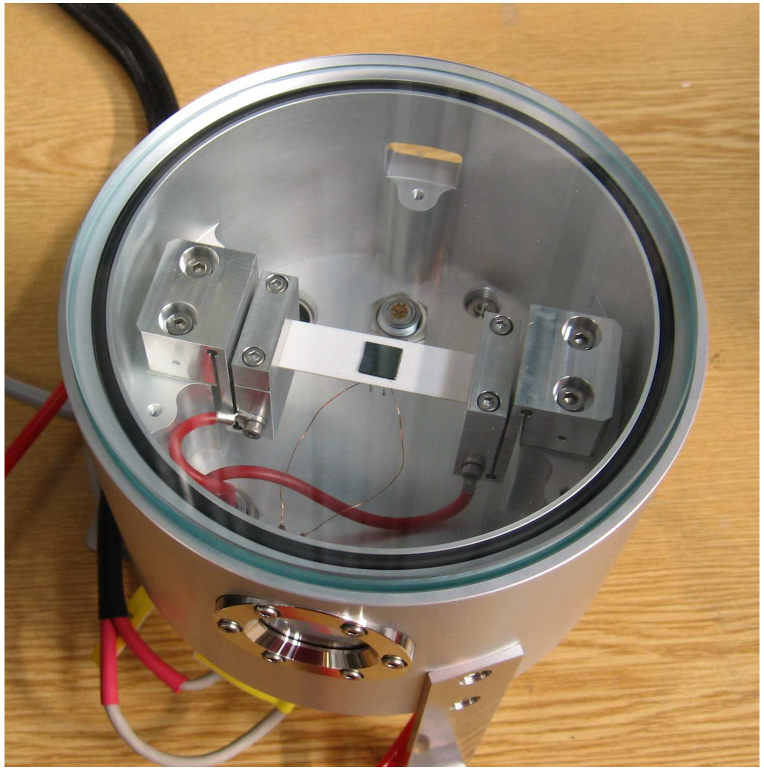




Li transport | experimental set-up

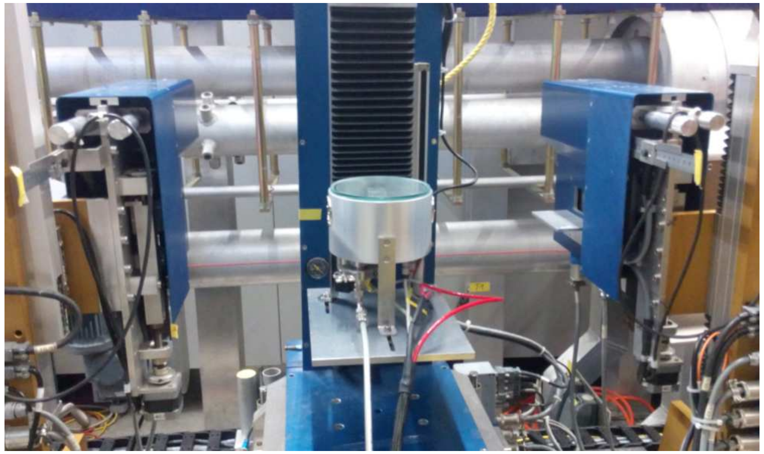
in-situ furnace

- $T \in [25^\circ\mathrm{C}, 500^\circ\mathrm{C}]$ here: $T = 240^\circ\mathrm{C}$
- $\dot{T} = 50\,\mathrm{Ks}^{-1}$ for heating
- $\dot{T} = 12\,\mathrm{Ks}^{-1}$ for cooling



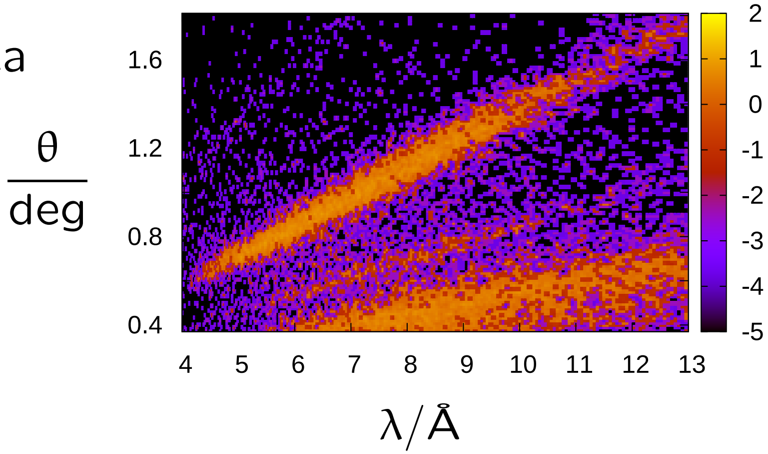
time-structure

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



Li transport | measurements

raw data



$\log_{10} I(\lambda, \theta)$

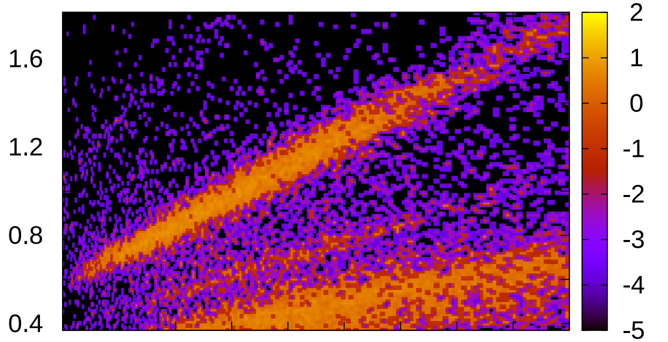
$^6LiNbO_3/Si/^7LiNbO_3/Si$ multilayer

counting time 1.5 min

Li transport | measurements & data reduction

raw data

θ / deg

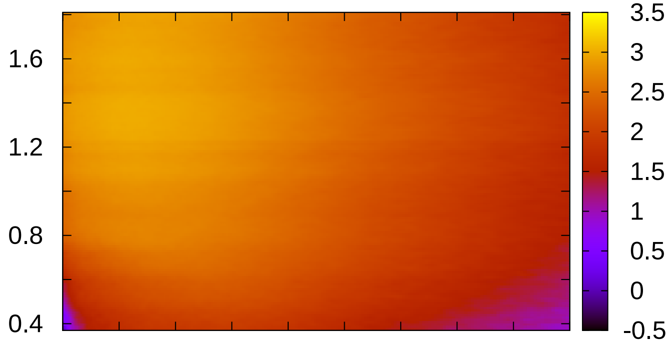


$\log_{10} I(\lambda, \theta)$

$^{6}LiNbO_3/Si/^{7}LiNbO_3/Si$ multilayer
counting time 1.5 min

reference

θ / deg

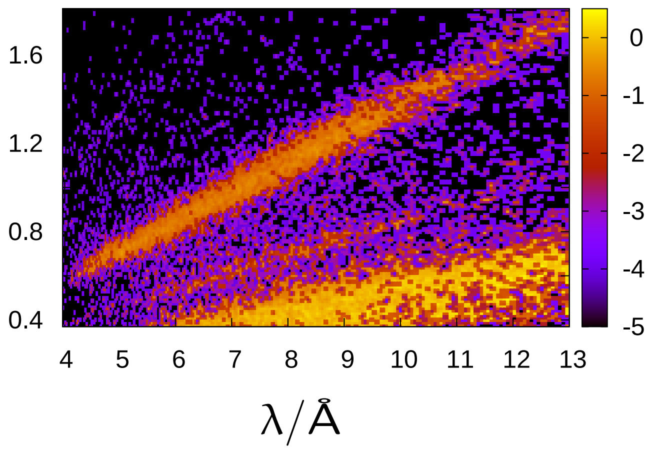


$\log_{10} I^{0}(\lambda, \theta)$

$m = 5$ supermirror

$R(\lambda, \theta)$

θ / deg



$\log_{10} R(\lambda, \theta)$

quotient

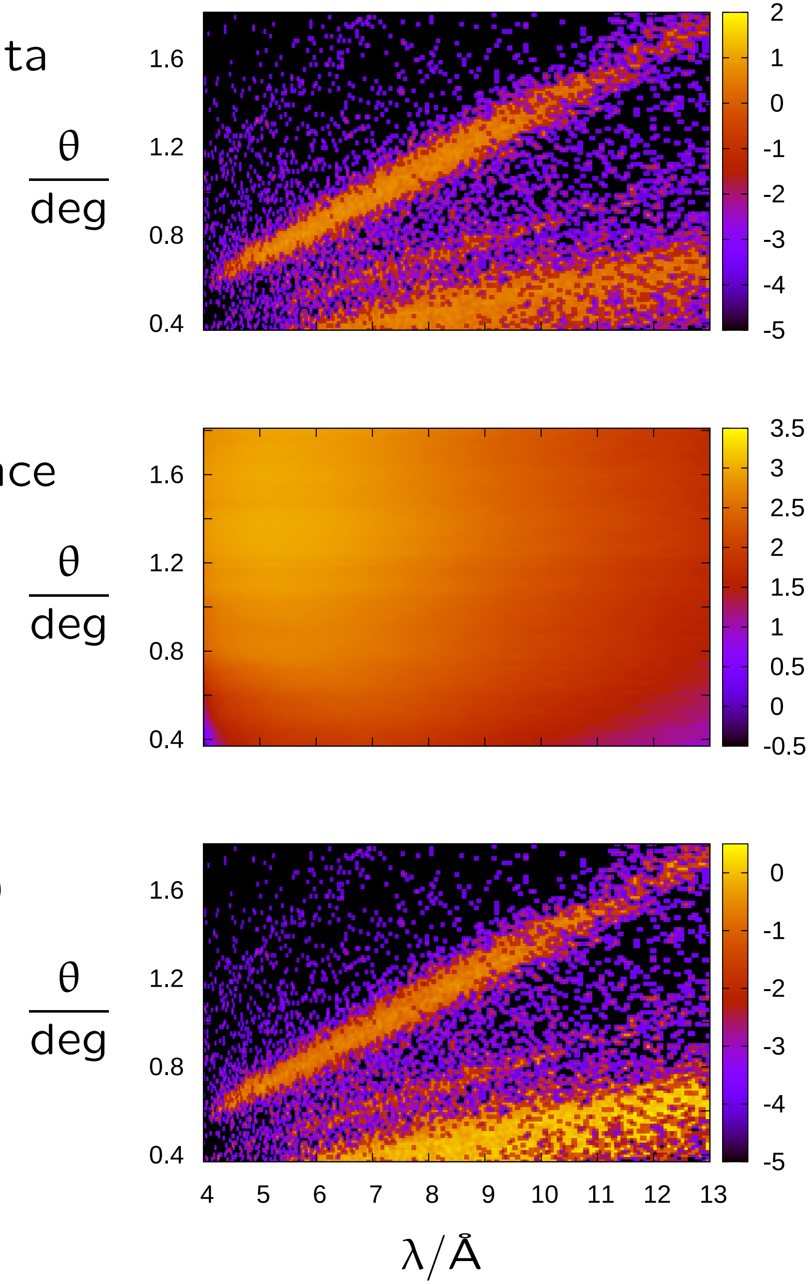
Li transport | measurements & data reduction

$^{6}LiNbO_3/Si/^{7}LiNbO_3/Si$ multilayer
counting time 1.5 min

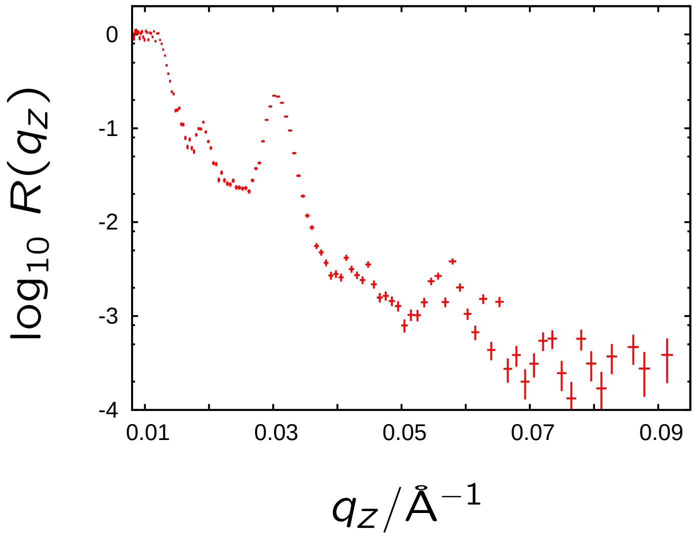
raw data

reference

$R(\lambda, \theta)$

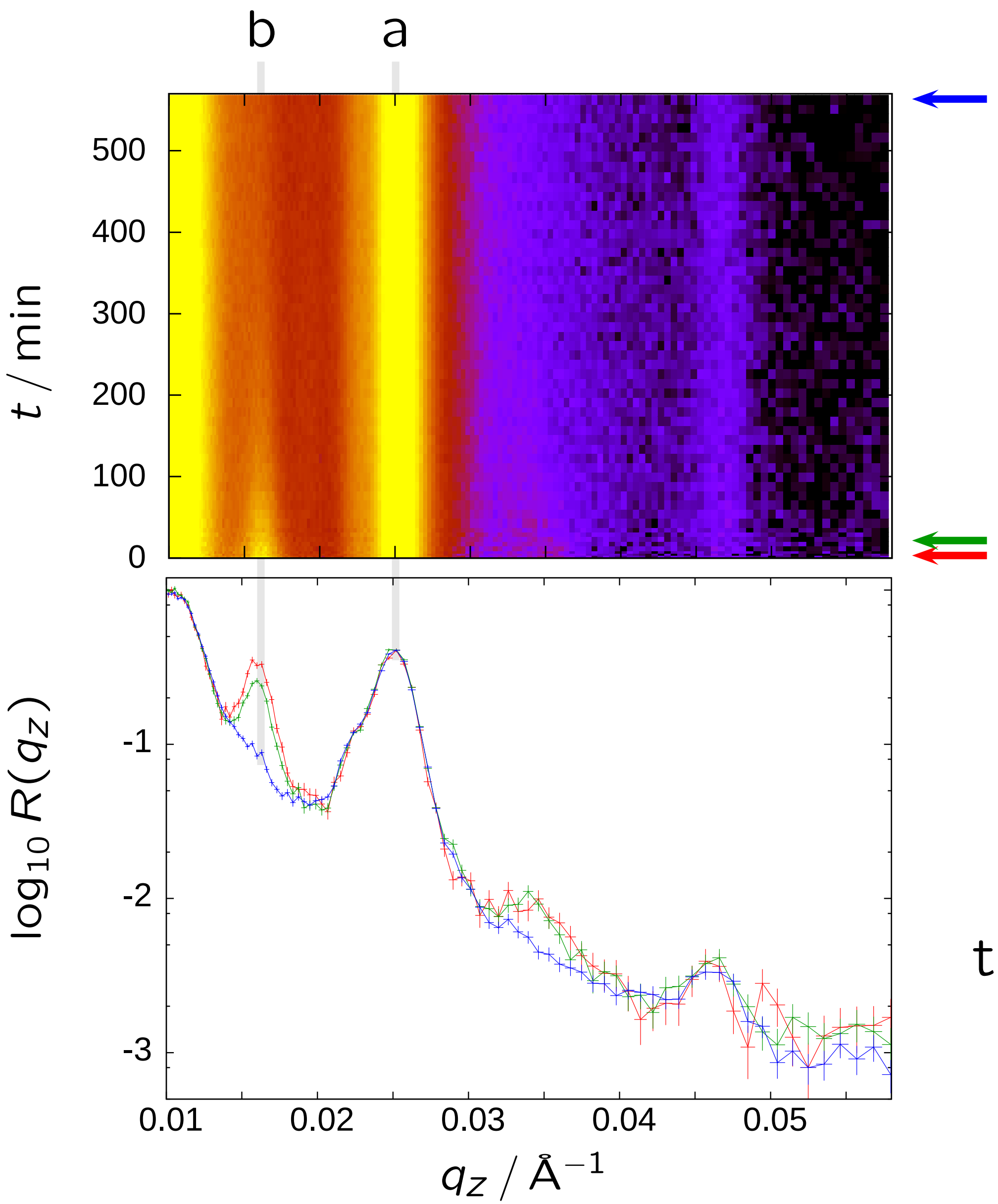


averaging along q_z



Li transport | reflectivity curves

measurements on a $^{6}Li_3NbO_4/Si/^{7}Li_3NbO_4/Si$ multilayer



annealing at $T = 240°C$

(a) ml is chemically stable

(b) Li contrast is vanishing

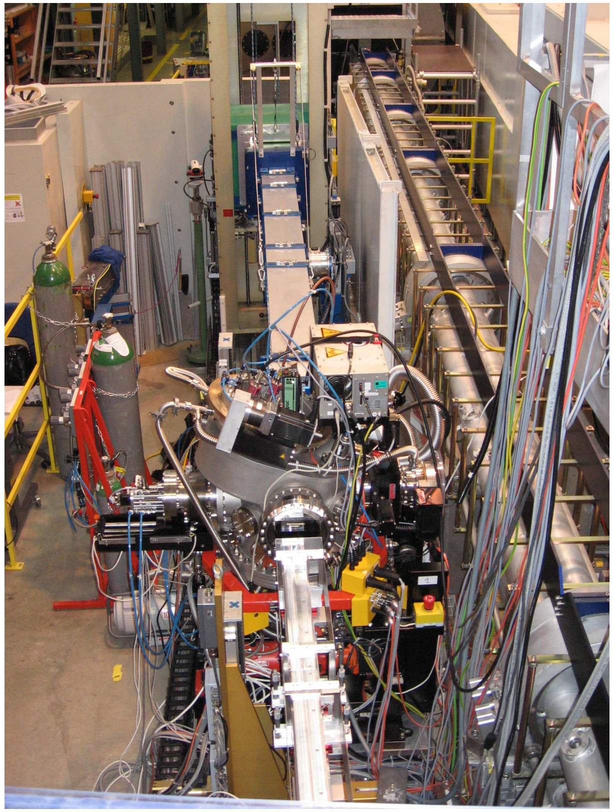
t = 0 → 3 min
18 → 24 min
558 → 570 min

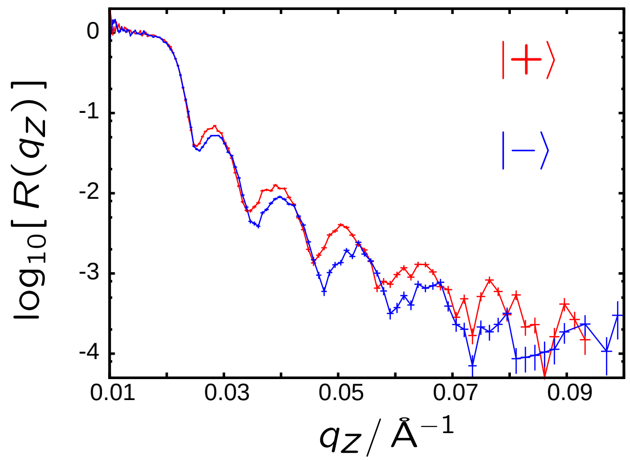
quasi in-situ reflectometry during sample growth

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)

<table>
<tr><th>sputter steps</th><th>growth</th><th>structure</th><th>moment/μ_B</th></tr>
<tr><td>1</td><td rowspan="4">island</td><td rowspan="9">fcc</td><td rowspan="4">3.3</td></tr>
<tr><td>2</td></tr>
<tr><td>3</td></tr>
<tr><td>4</td></tr>
<tr><td>5</td><td rowspan="7">layer-by-layer</td><td rowspan="5">1.2</td></tr>
<tr><td>6</td></tr>
<tr><td>7</td></tr>
<tr><td>8</td></tr>
<tr><td>9</td></tr>
<tr><td>10</td><td rowspan="2">bcc</td><td rowspan="2">2.0</td></tr>
<tr><td>11</td></tr>
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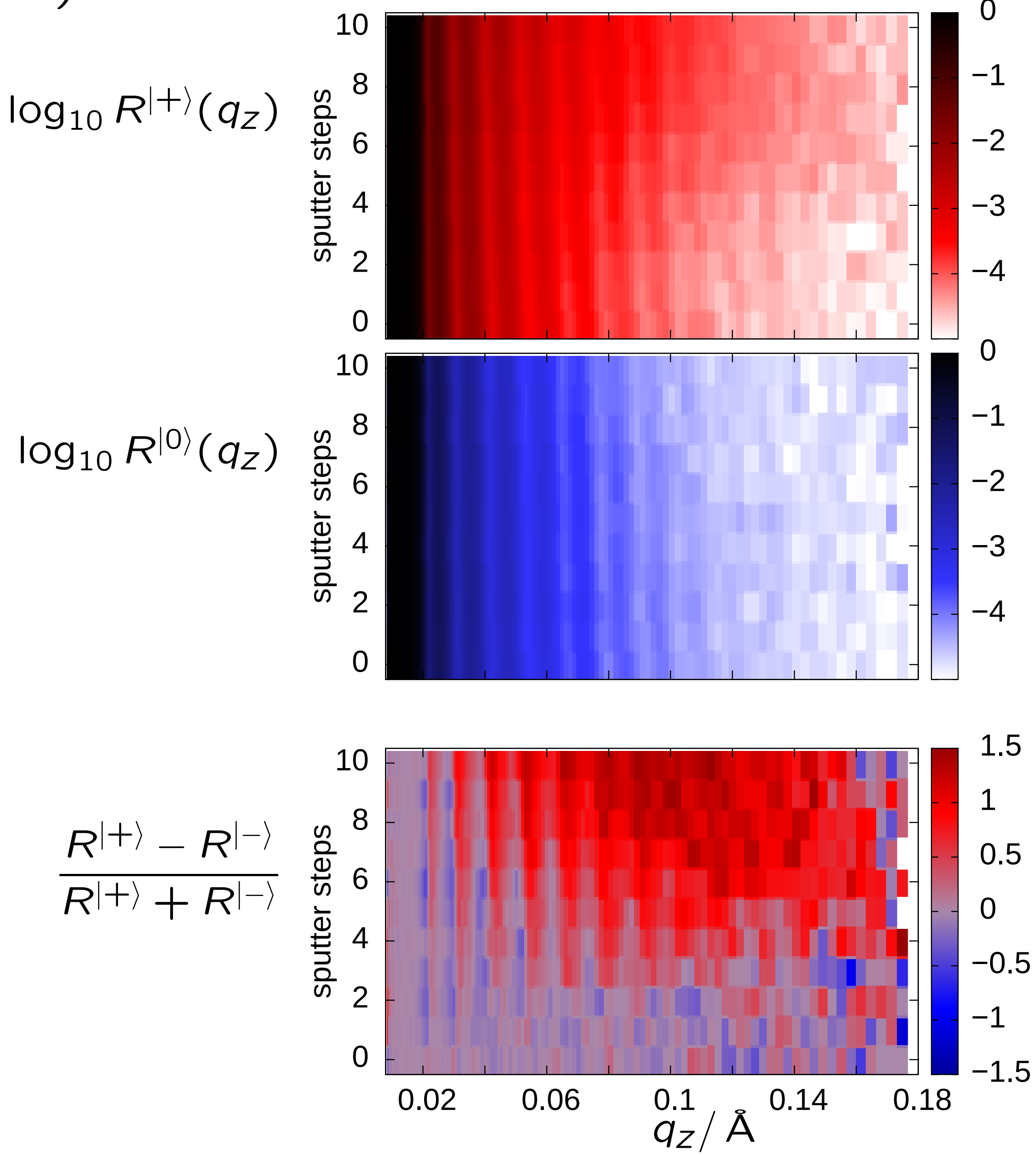


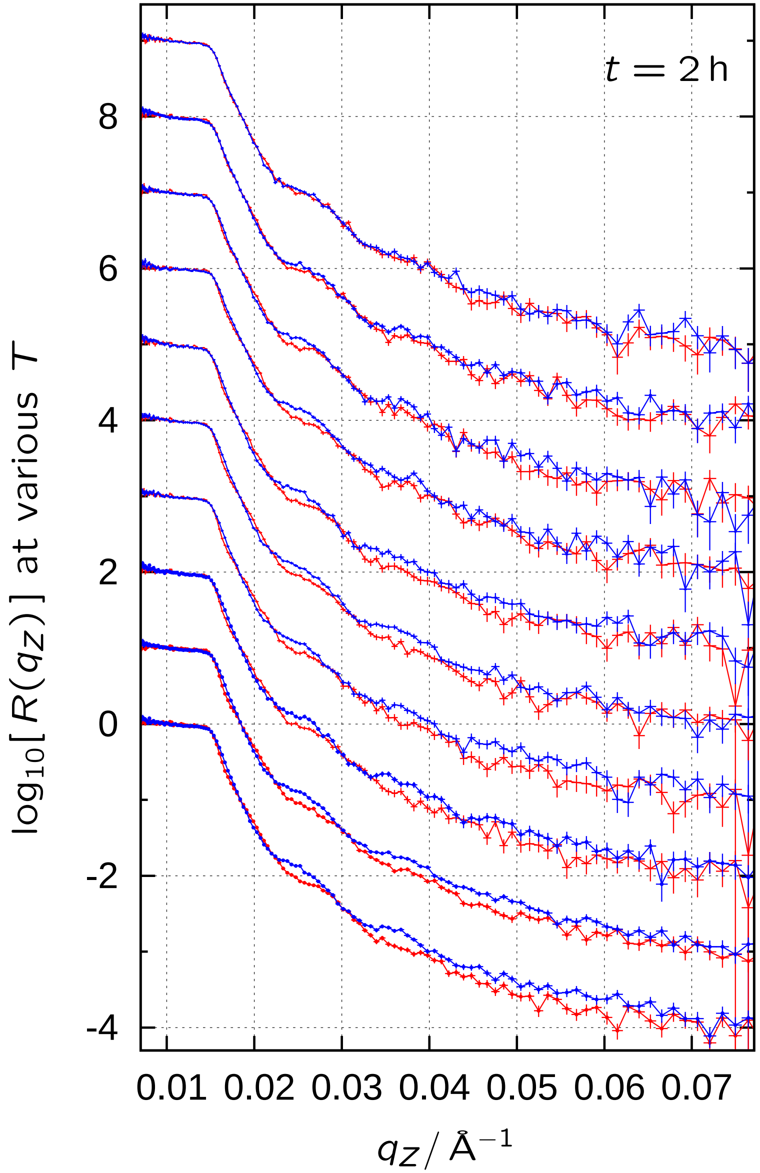
strain-induced ferromagnetism

S. Mukherjee, J. Stahn, C. Niedermayer

sample:
- $LuMnO_3$
- ferroelectric
- antiferromagnetic

film (20 . . . 50 nm) on $YAlO_3$ substrate:
- strained at interface
- induced ferromagnetism

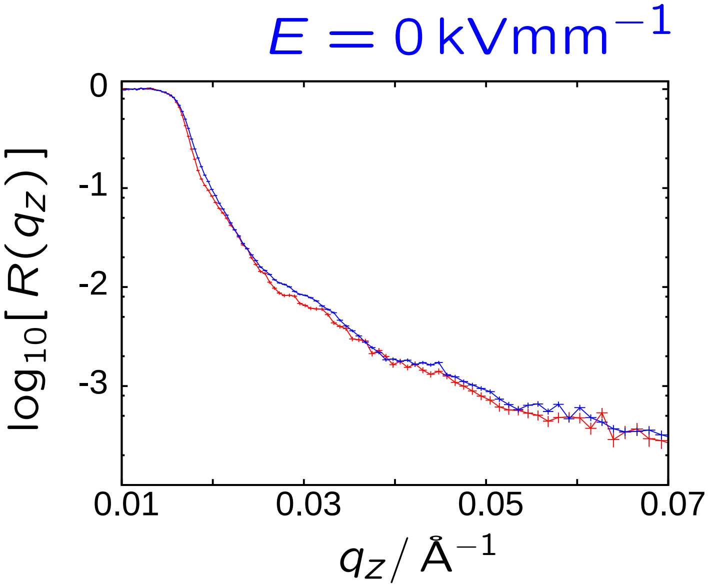
⇒ manipulation of magnetic state
by electric polarisation

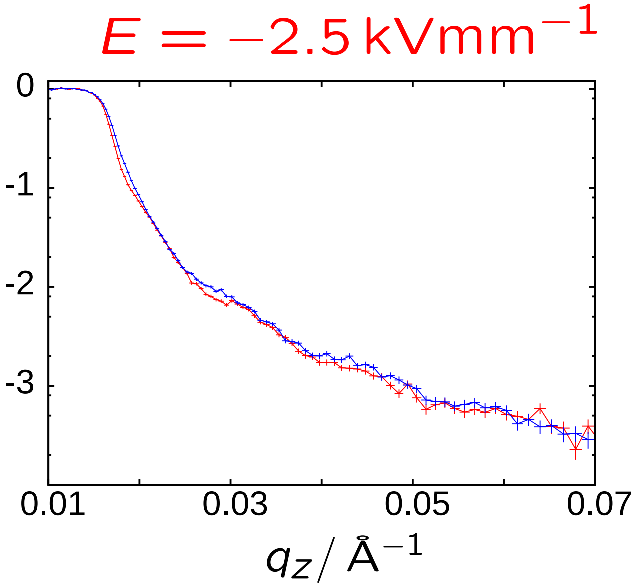


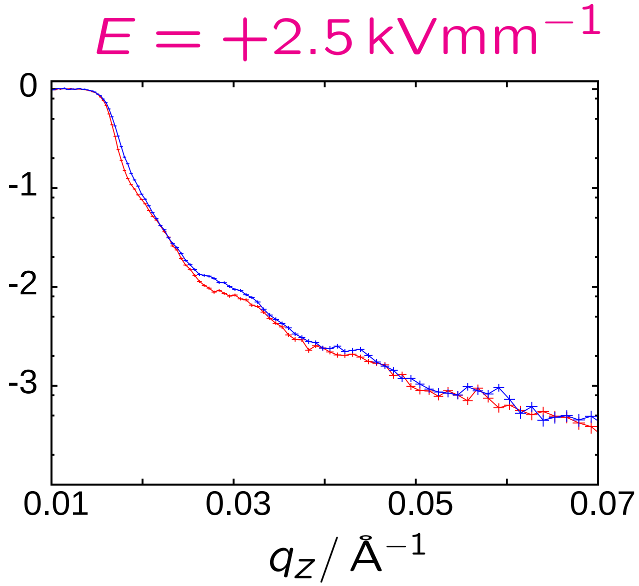
strain-induced ferromagnetism

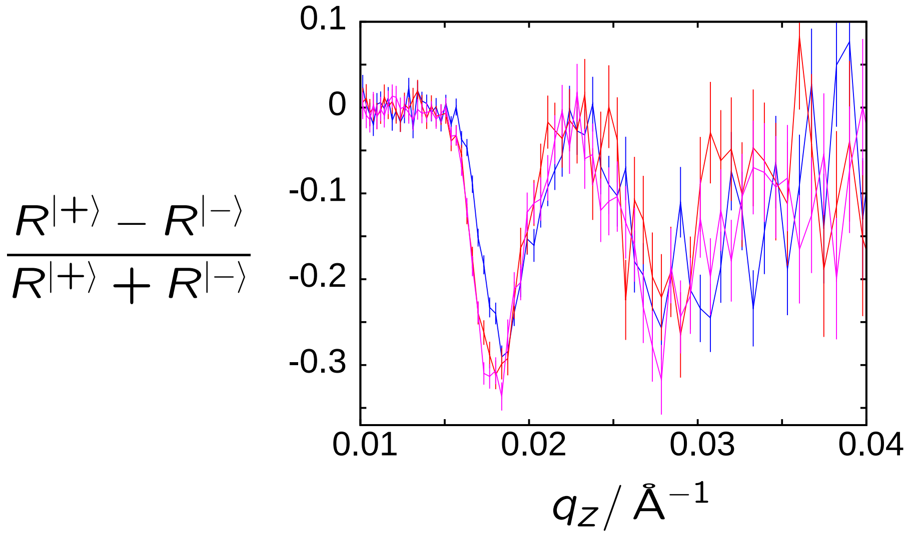
last week's measurements:

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





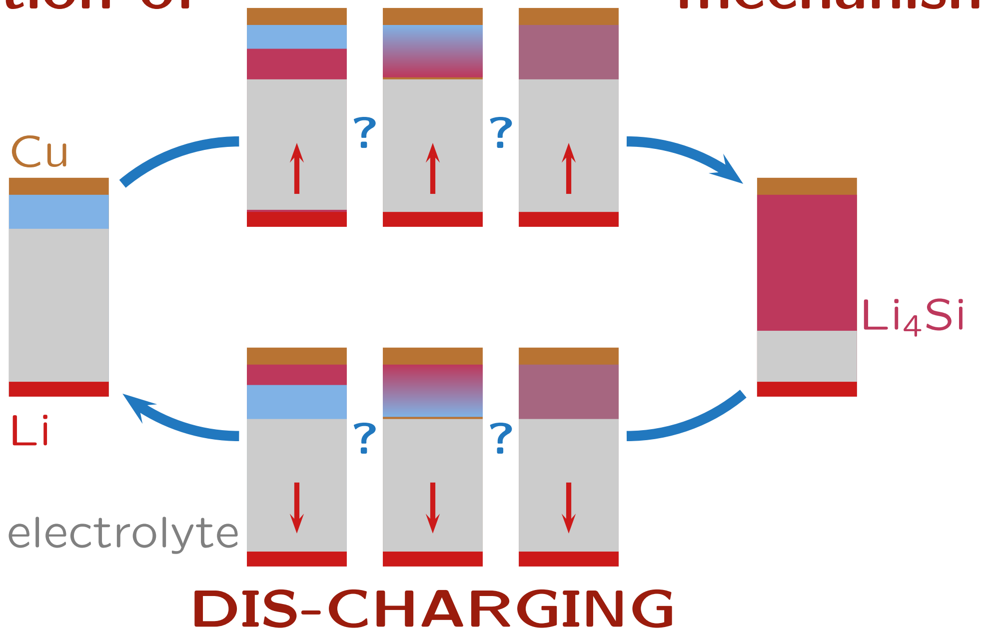


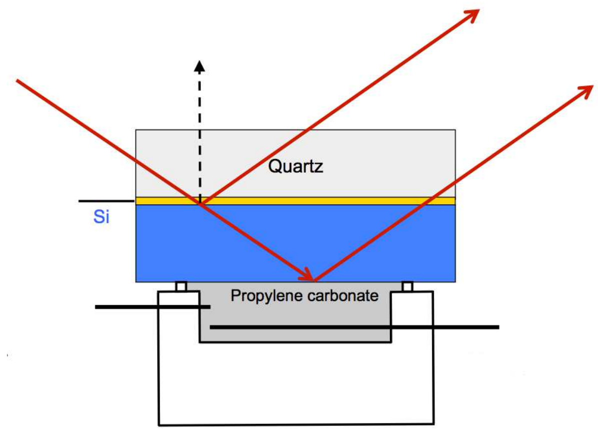


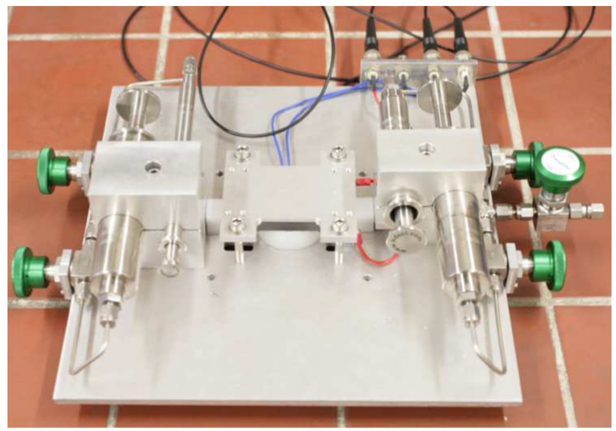
in-operando battery studies

H. Schmidt, E. Hüger, B. Jerliu

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







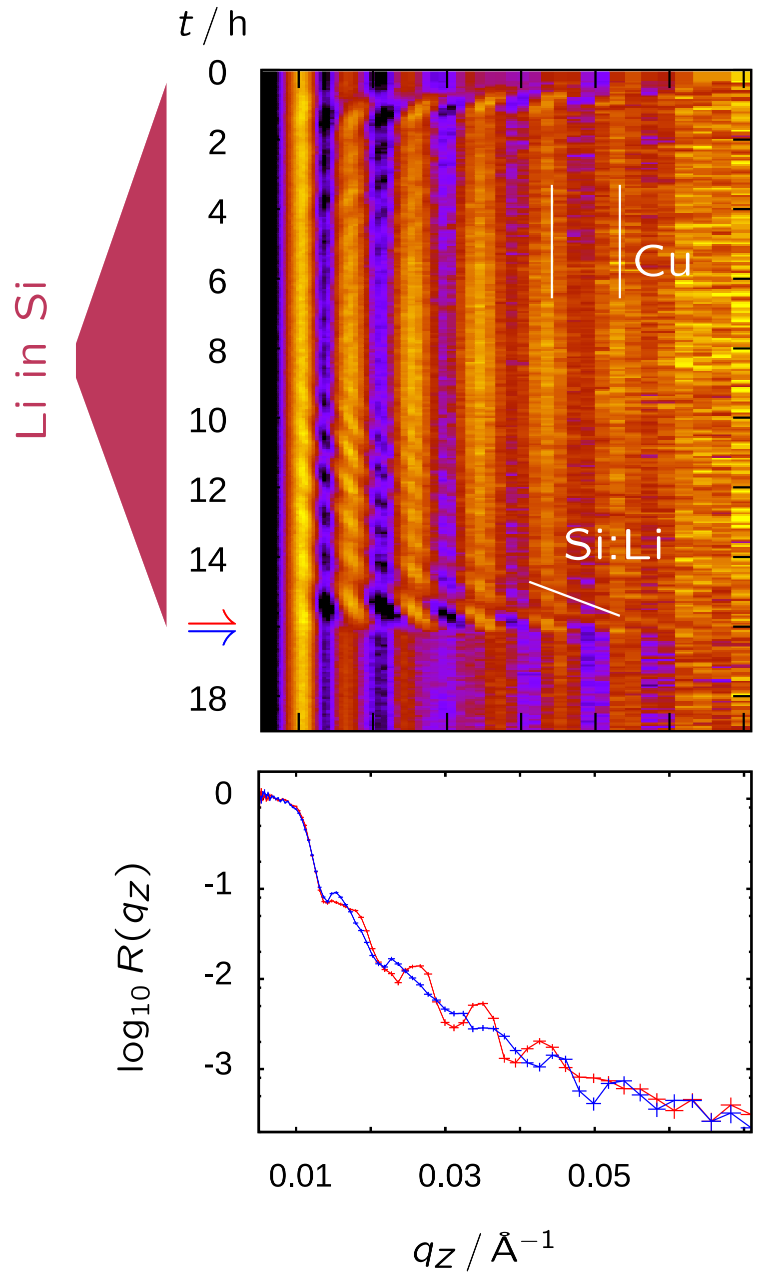
in-operando battery studies

Cu contact ⇒ oscillations

Si electrode ⇒ adds phase factor

Li in Si ⇒ swelling
⇒ phase shift

⇒ density change
⇒ contrast variation



time-resolution: 1 . . . 6 min

≈ 400 measurements per cycle

≈ 4000 measurements per beamtime

⇒ new data analysis strategy required

outline

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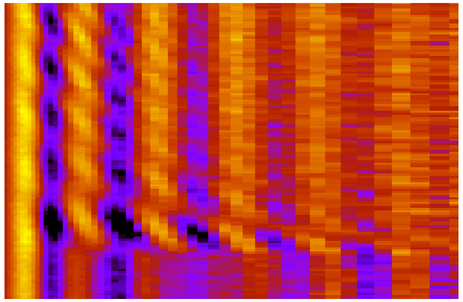
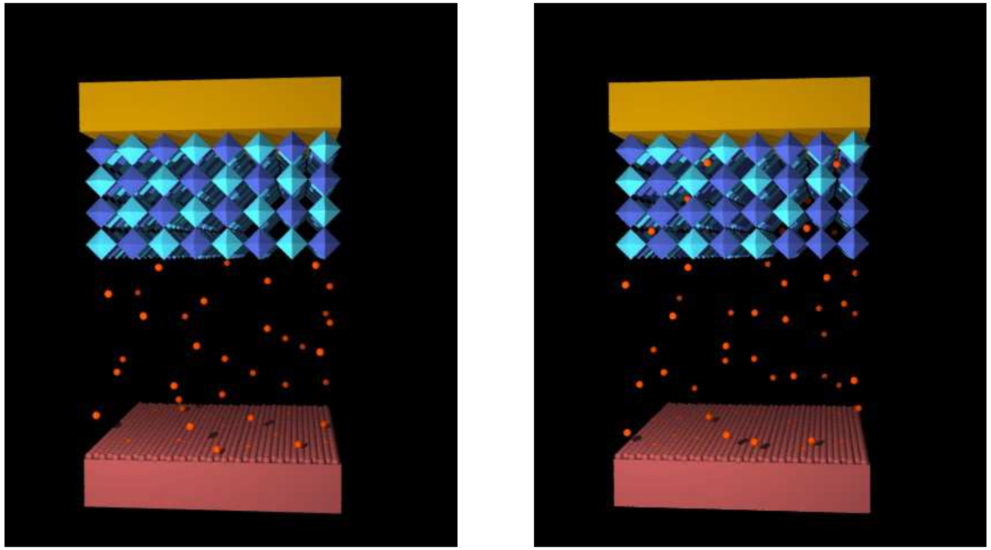


projects for Amor

- smaller electrochemical cell
  - lower background
  - less absorption
  - extension to fundamental research:

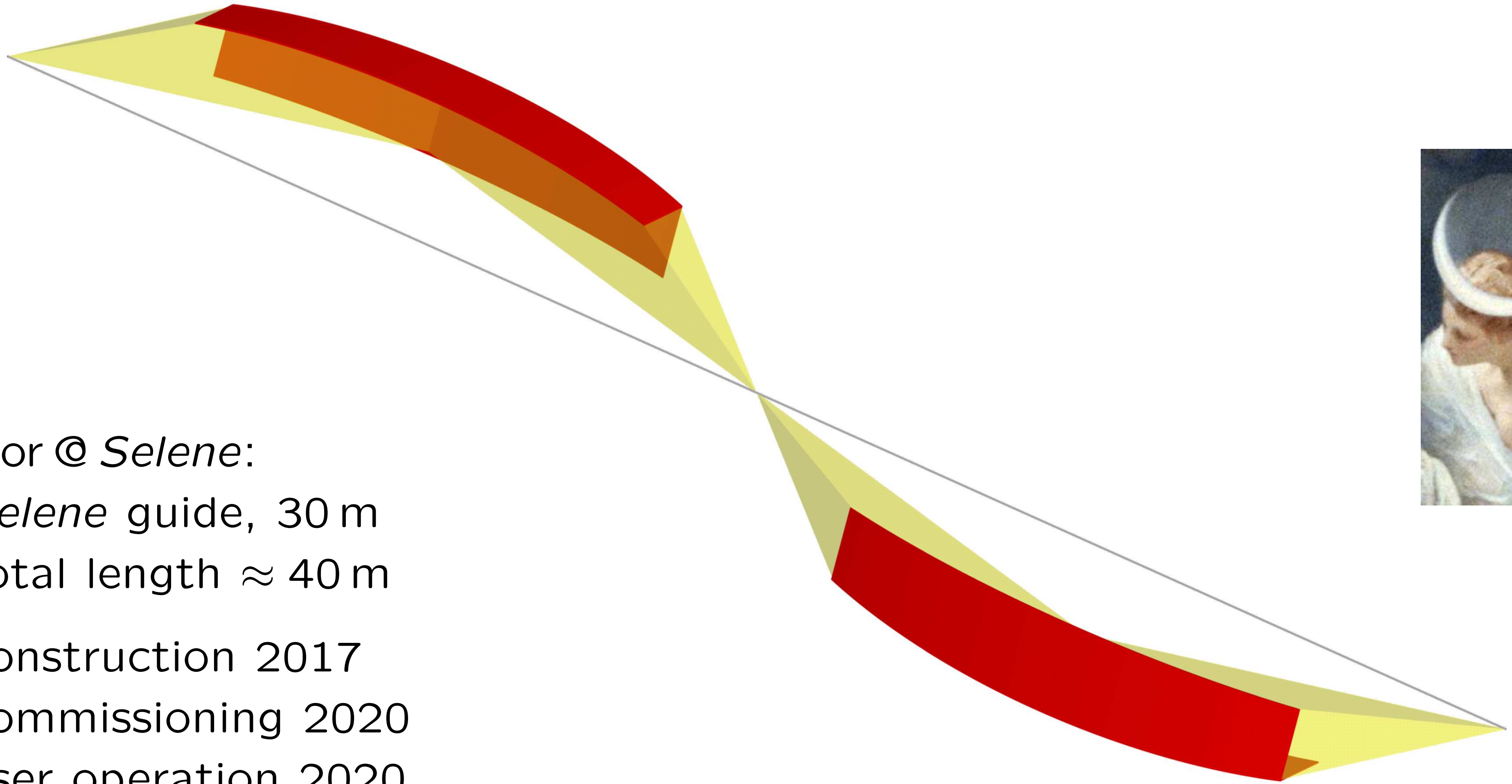
    e.g. switching of FM by Li intercalation

    $\Rightarrow$ low T and high **H** needed



- spin-analysis
  - switching of magnetic domains

Amor upgrade with ***Selene*** guide



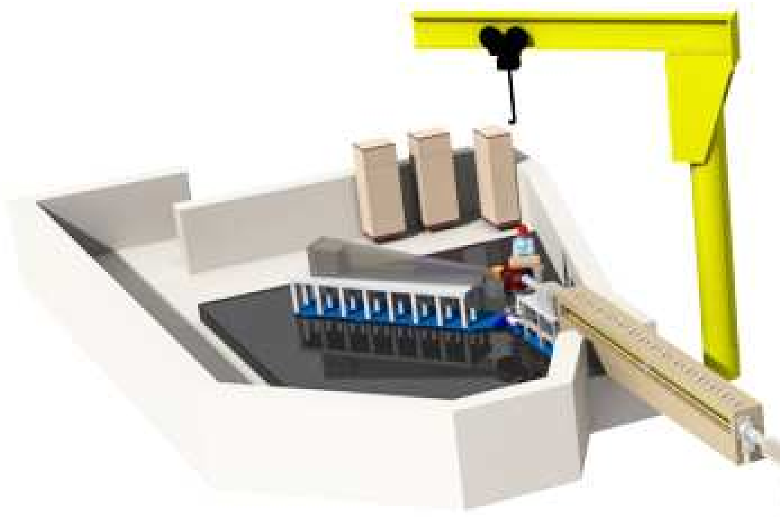
Amor @ *Selene*:

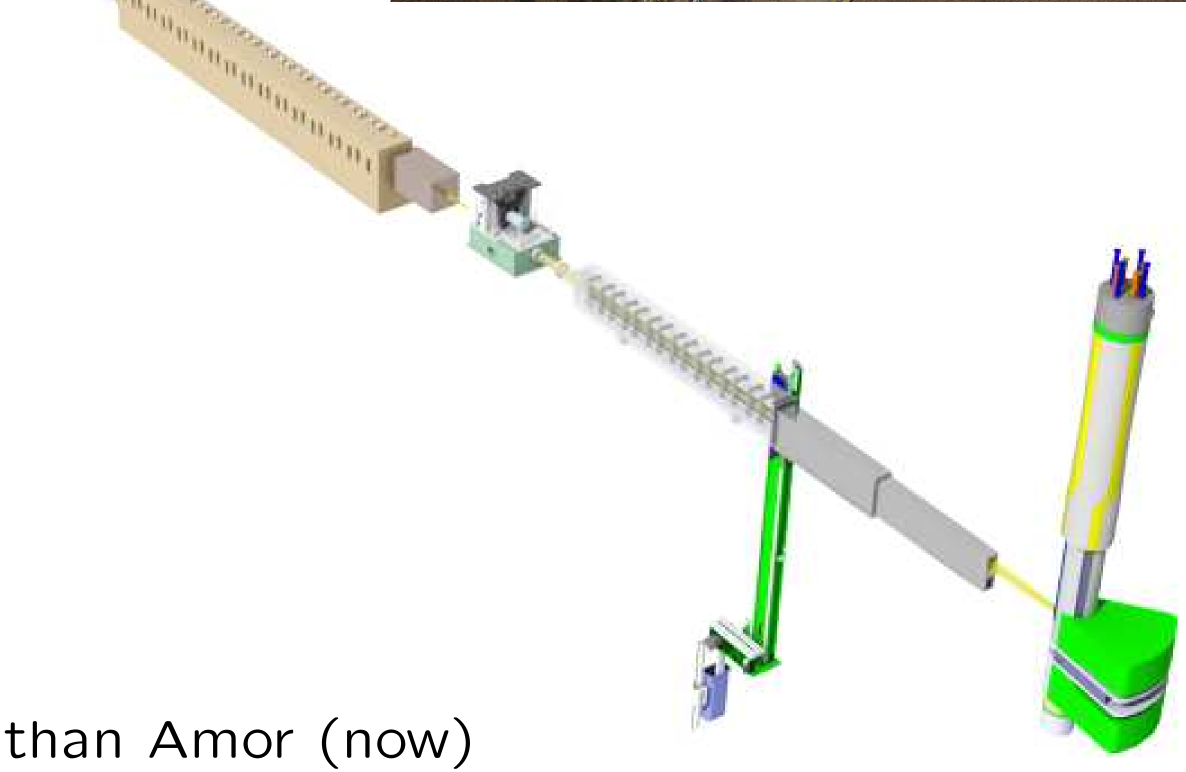
- *Selene* guide, 30 m
- total length ≈ 40 m

- construction 2017
- commissioning 2020
- user operation 2020

- 1 . . . 2 orders of magnitude faster than Amor (now)

Estia at the ESS





European Spallation Source

Estia:

- *Selene* guide, 24 m
- total length ≈ 40 m

- construction since 2015
- commissioning 2020
- user operation 2023

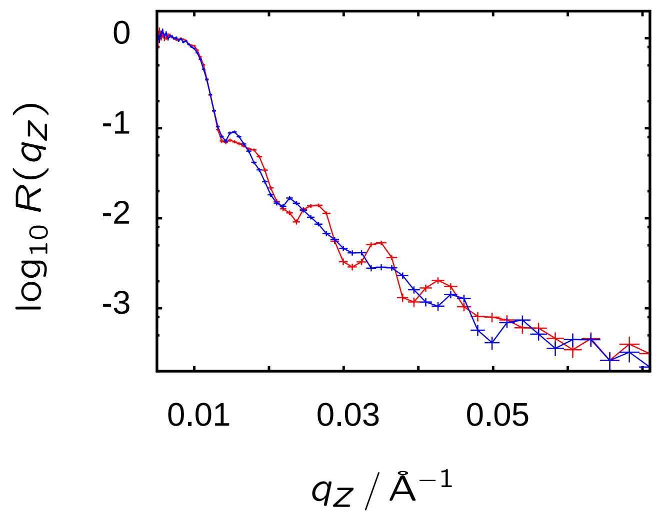
- 3 . . . 4 orders of magnitude faster than Amor (now)

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 *Selene* guide	10 sec
Estia	$<$ 0.1 sec



Thank you!

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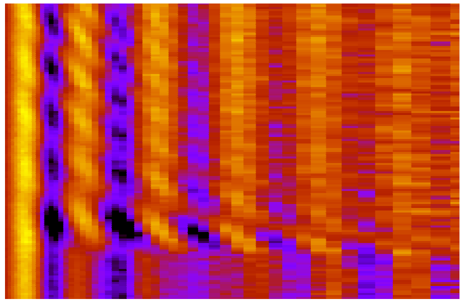

references

reflectometry, in general

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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/lns-kur/JochenStahnEN/stahn_2016_t1.pdf`