Neutron Reflectometry for Energy

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D17 (Polarised) Neutron Reflectometer @ ILL
Thin Film Magnetism Research

Overview

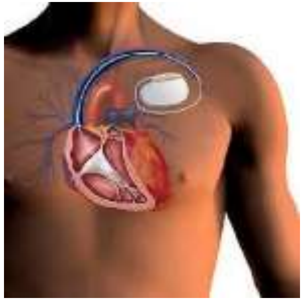
- Energy research and neutrons / reflectometry:
  - Probing **interface** structure and composition **deep** inside a material
- Reflectometry on batteries
  - Working principle of batteries
  - The solid electrolyte interphase (SEI)
  - In-operando Si-anode Li-ion batteries: Volume expansion, SEI, cycling
- Reflectometry and hydrogen sensing/storage
- Reflectometry on solar-cells

Energy Research ? = Light Elements

- Li-Batteries
- Hydrogen Fuel Cells
- Solar-Cells: Organic/inorganic compounds
- Compact structures with high capacity
- Safe, flexible, reliable, fast-charging



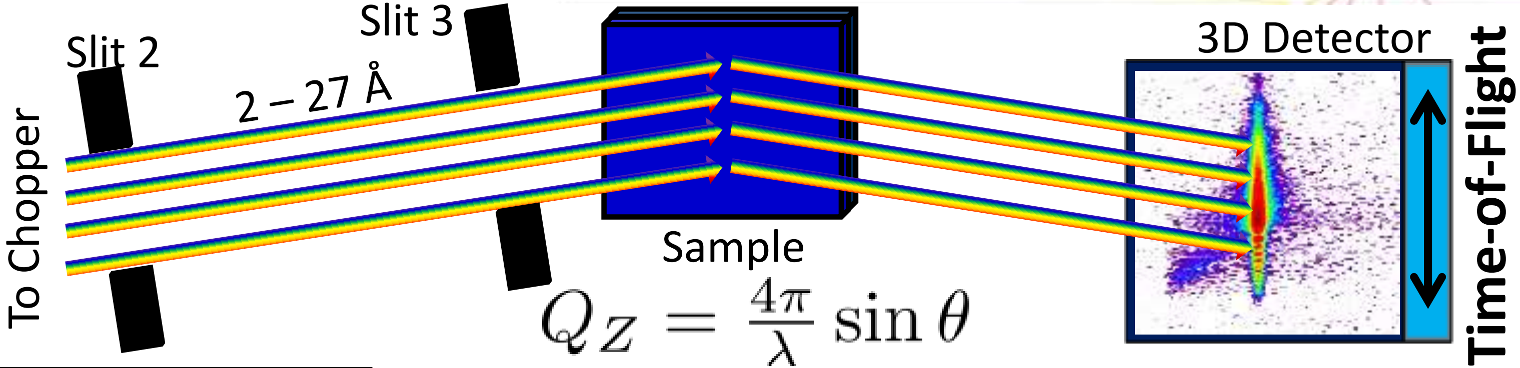


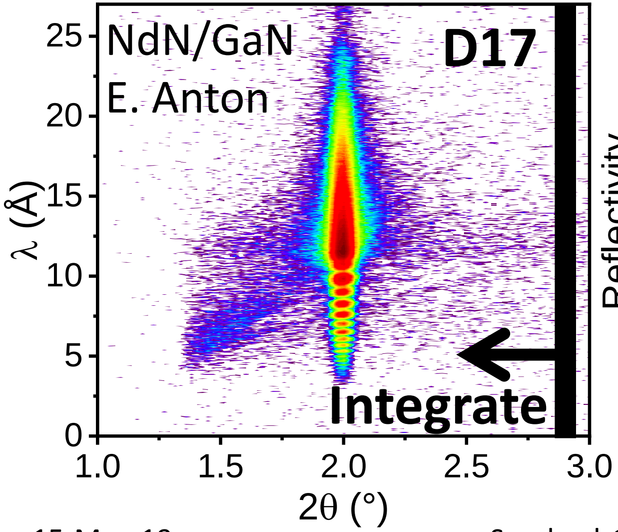
The Benefits of Neutrons:

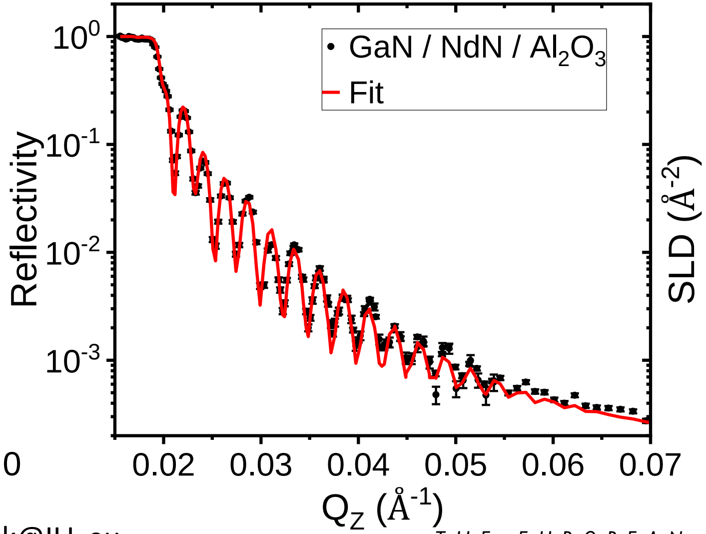
- Neutrons
  - are not photons, electrons,…
    No electrical charge, no acceleration, no Coulomb interaction
  - have the right **wavelength/energy**
  - have **nuclear** and **magnetic** interactions with matter
  - are **non-destructive**
  - have a **high penetration depth**
  - See **light elements**
  - Distinguish **isotopes** & **neighbouring atoms** in periodic table
  - See microscopic, nanoscopic and atomic **magnets**

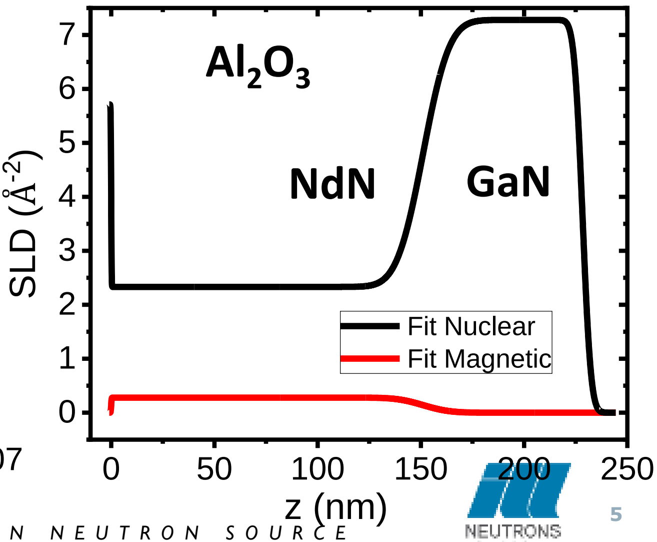
Time-of-Flight on 2D Detector



$$Q_Z = \frac{4\pi}{\lambda} \sin\theta$$







The ILL Reflectometers:

Figaro

- Time-of-flight
- Horizontal sample
- Reflection Up+Down
- Flexible resolution

D17

- Time-of-flight
- Monochromatic
- Vertical sample
- Polarized
- Flexible resolution

SuperAdam

- Monochromatic
- Vertical sample
- Polarized
- High resolution or high intensity

- Science: Soft matter, biology, biophysics/biochemistry, electrochemistry, materials science, magnetism, instrumentation

The Potentials (Elastic)

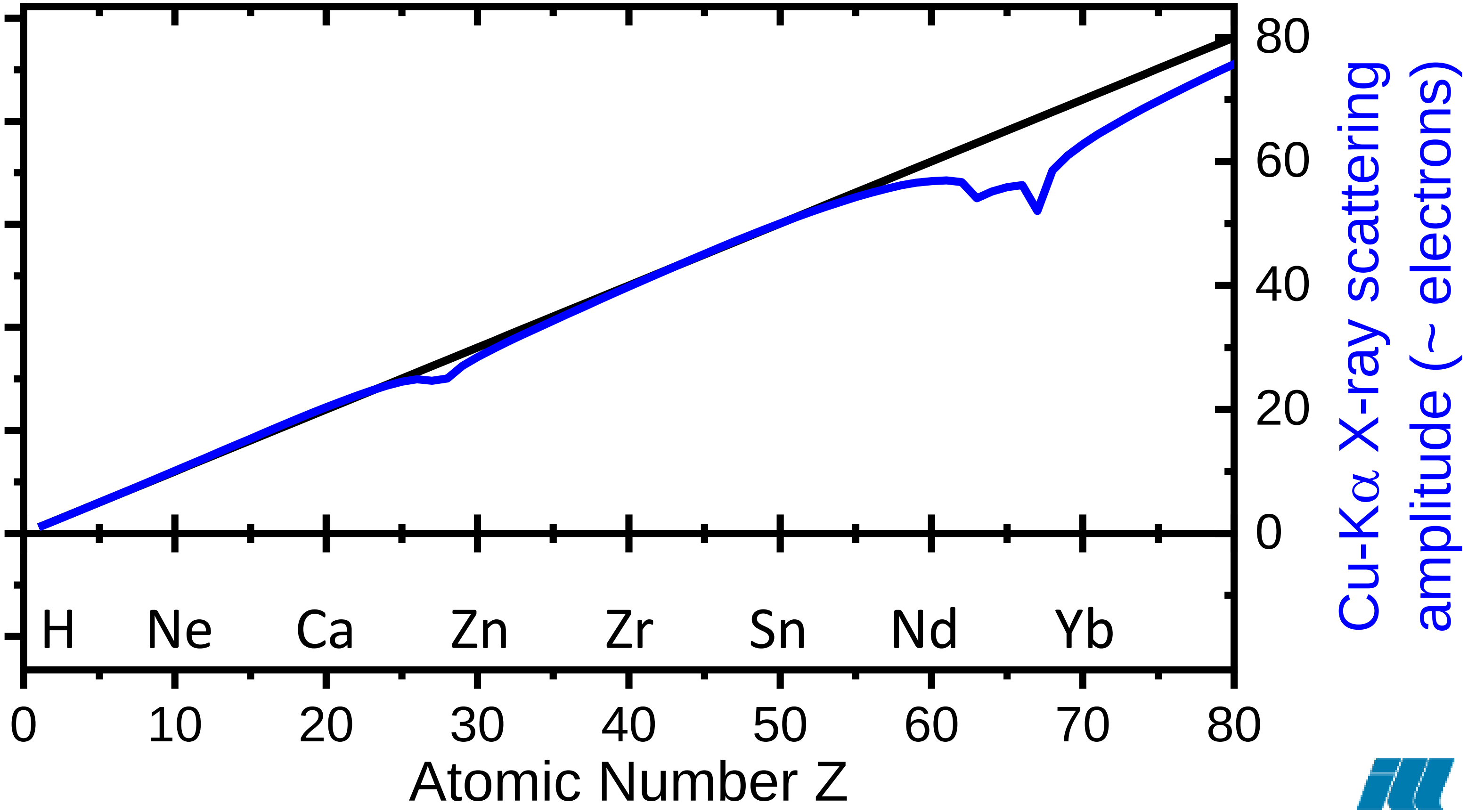
- Fermi Pseudo Potential:
- $$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b_n \delta(\mathbf{r})$$
- $$\hat{V}(z) = \frac{2\pi\hbar^2}{m_n} N b_n$$

- Magnetic (Zeeman) Potential:
- $$\hat{V}_{MAG} = -\vec{\mu}_n \cdot \vec{B}(\vec{r})$$
- $$\vec{\mu}_n = -\gamma \mu_N \vec{\boldsymbol{\sigma}}$$
- $$\mathbf{B} = \mathbf{B_0} + \mu_0 \mathbf{M}$$

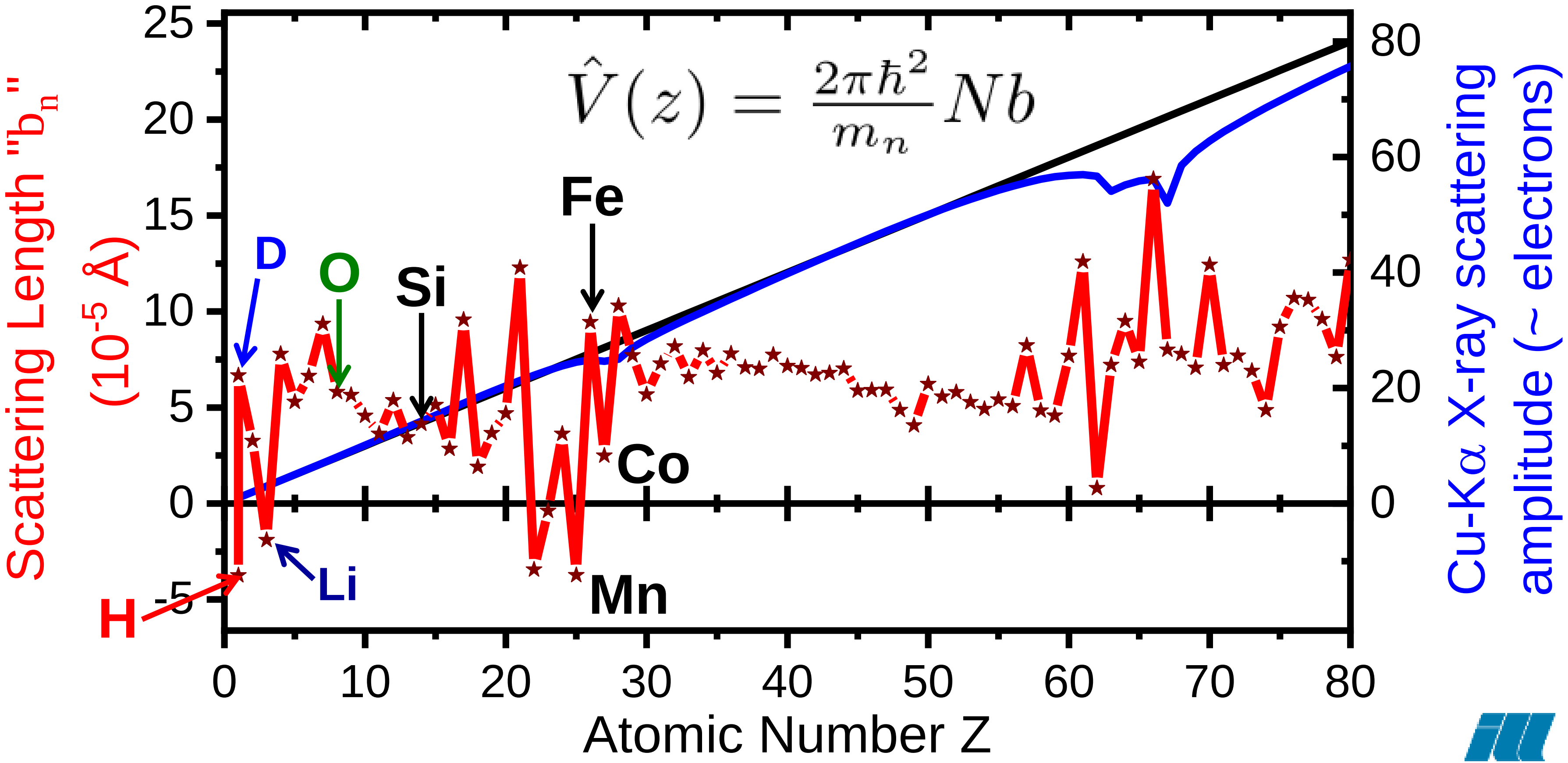
$$\hat{V}_{\pm}(z) = \frac{2\pi\hbar^2}{m_n} N(b_n \pm b_m)$$

- N: Number Density (atoms/cm^3)
- m_n: Neutron Mass
- b_n: Nuclear Scattering Length
- $\boldsymbol{b}_m$: Magnetic Scattering Length

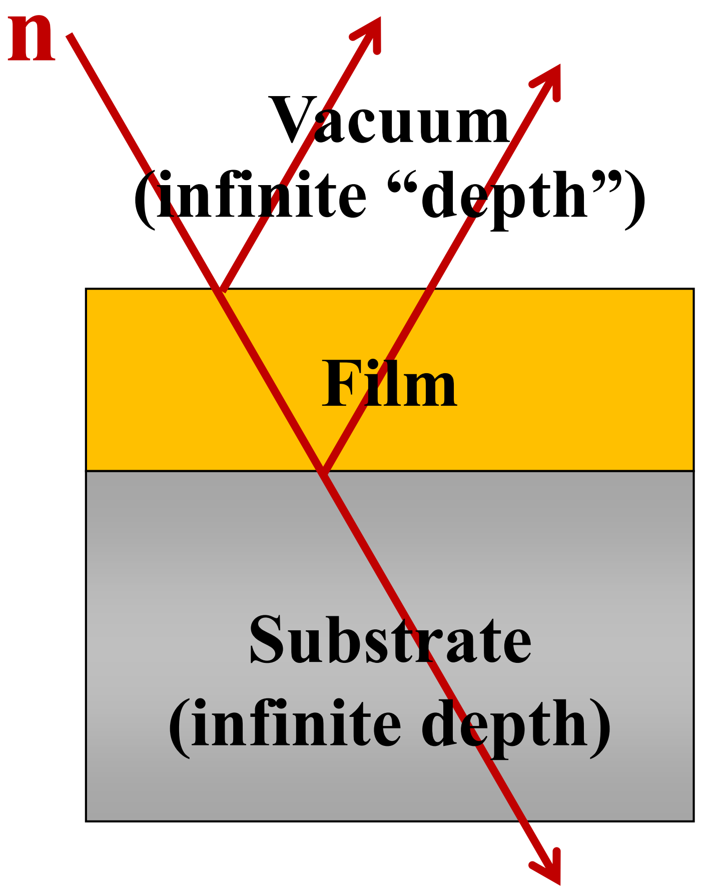
Neutron vs. X-ray Contrast

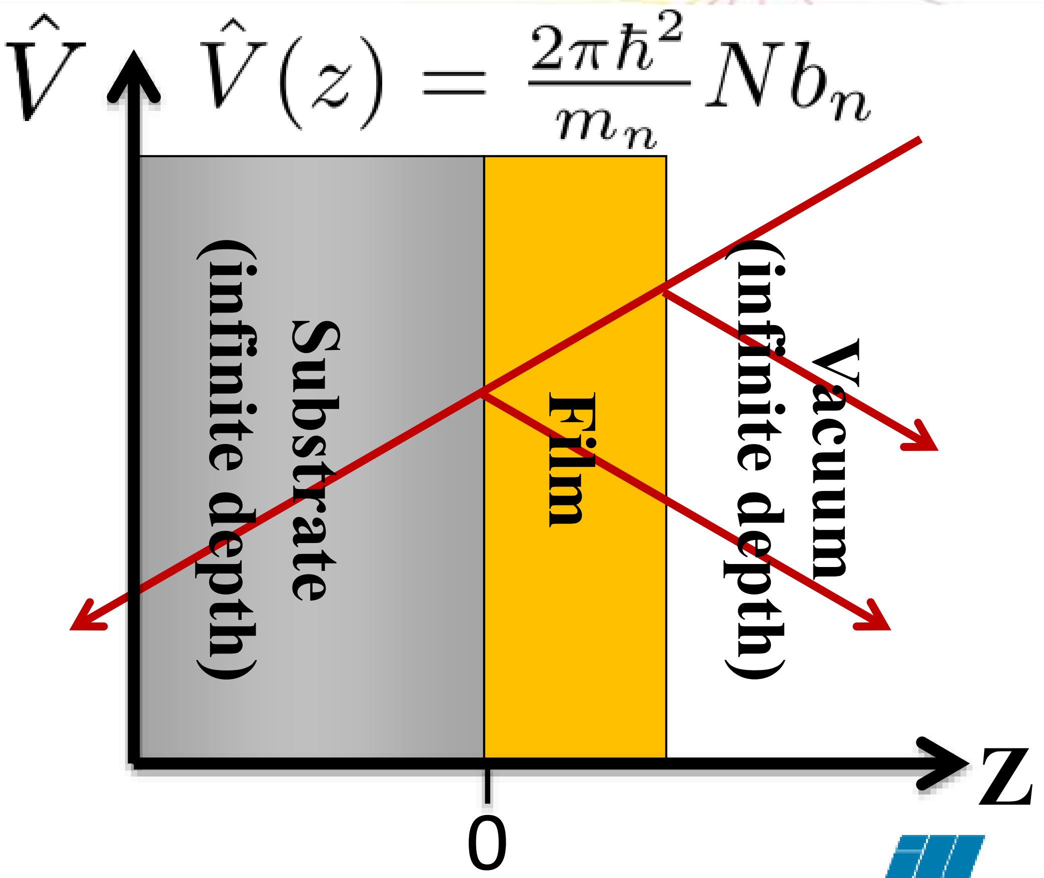


Neutron vs. X-ray Contrast



Reflectometry as 1D Problem: The SLD





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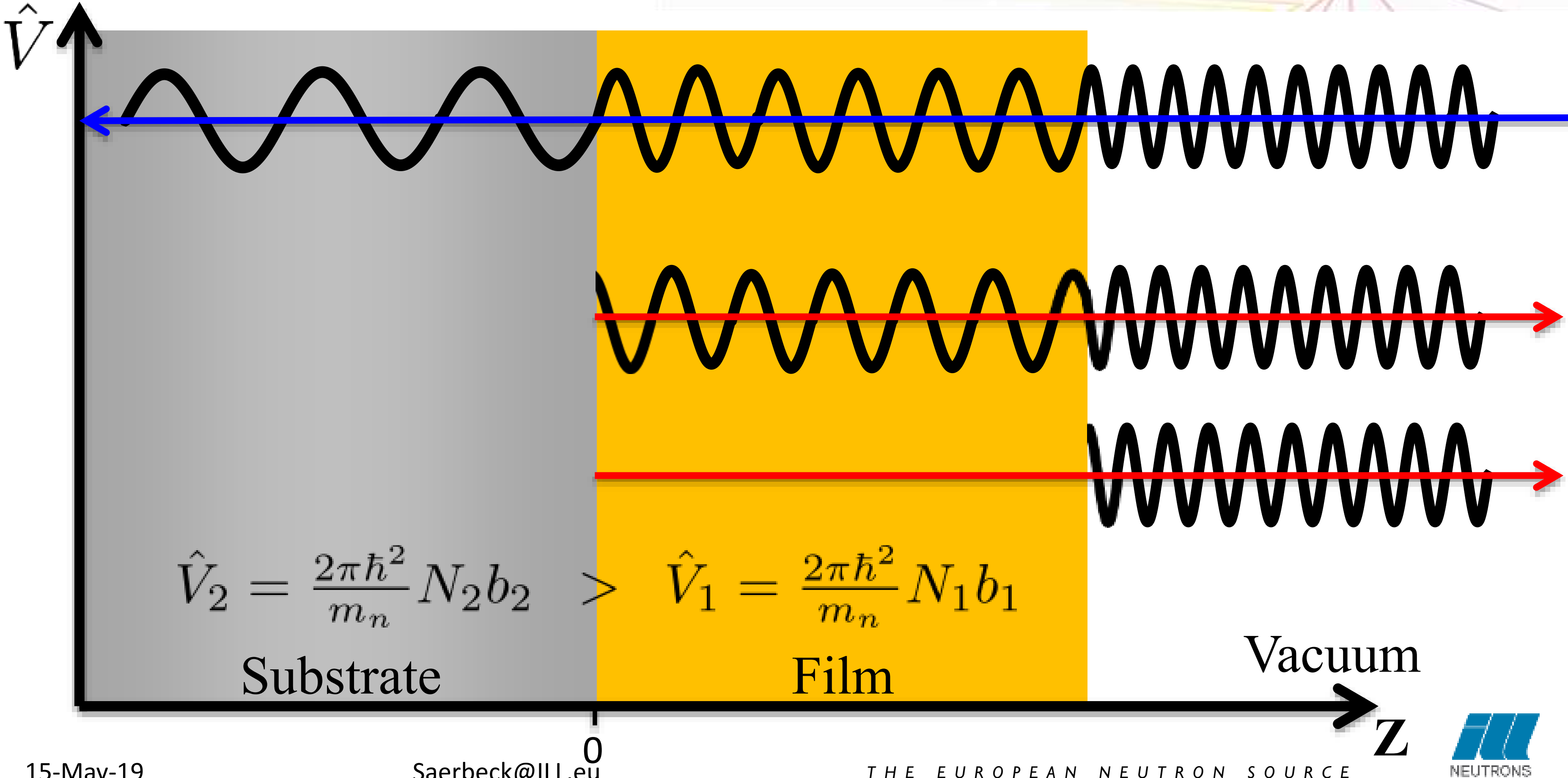
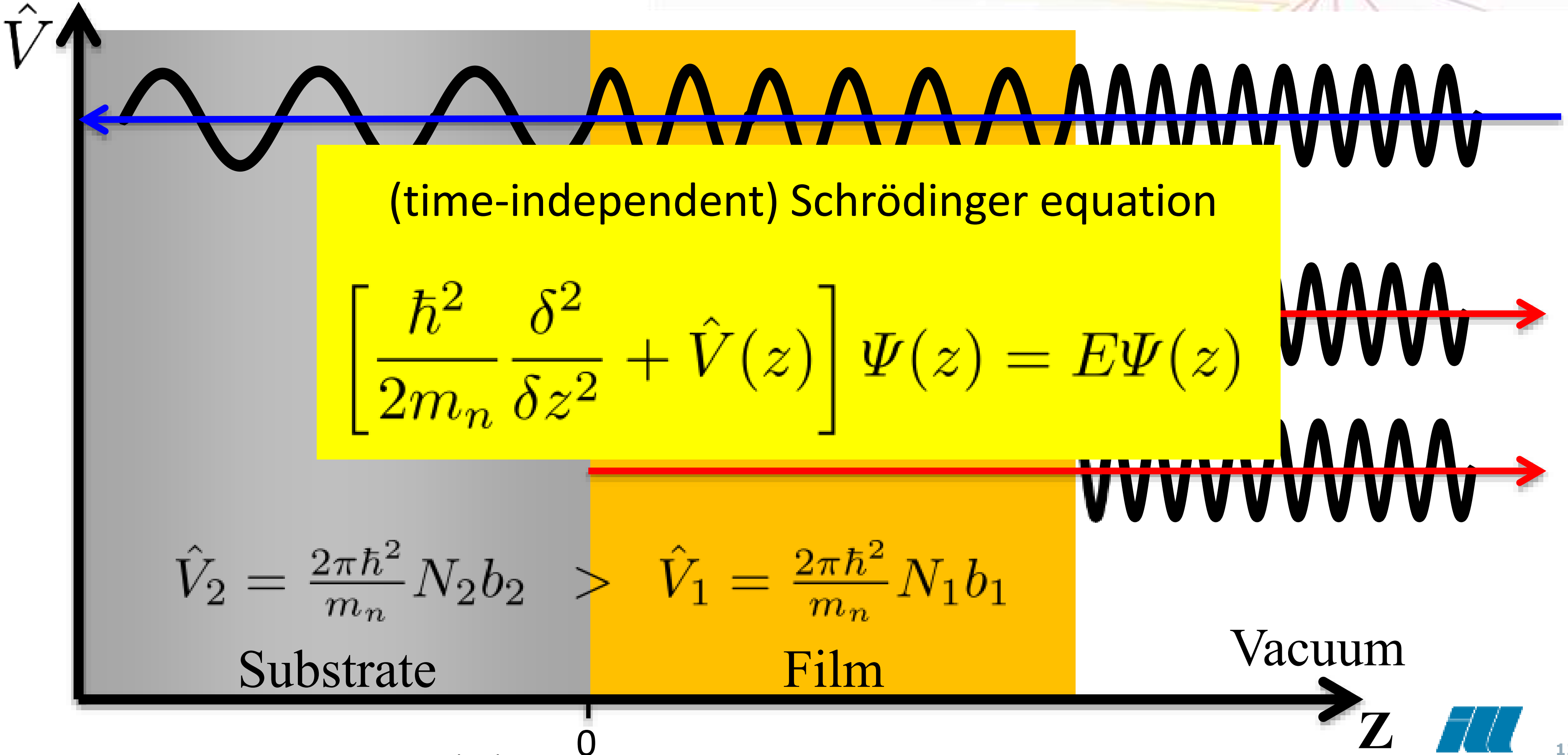


Reflectometry as 1D Problem: The SLD



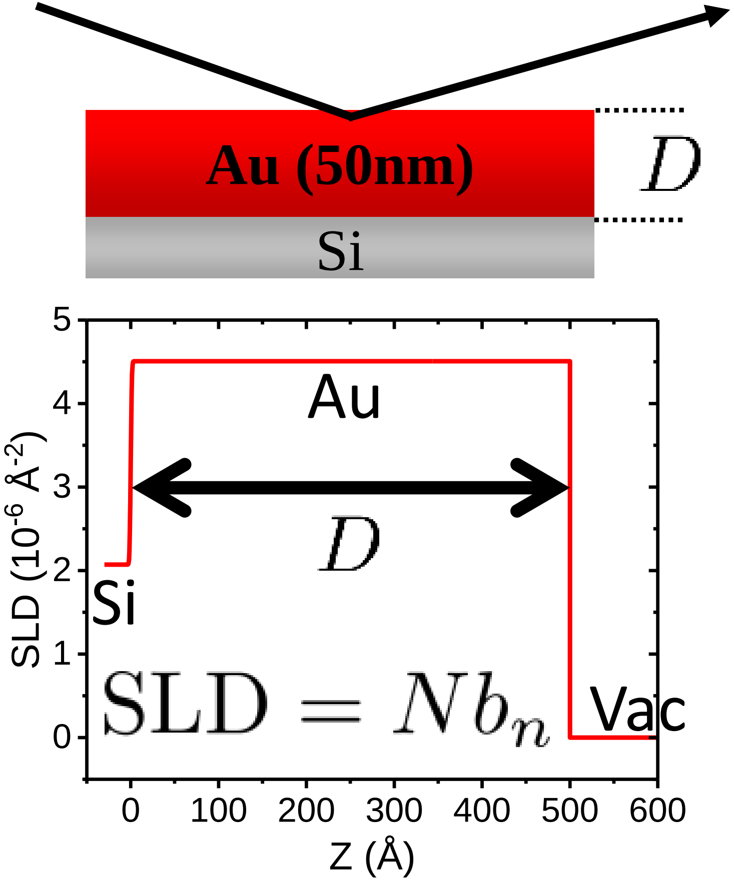
(time-independent) Schrödinger equation

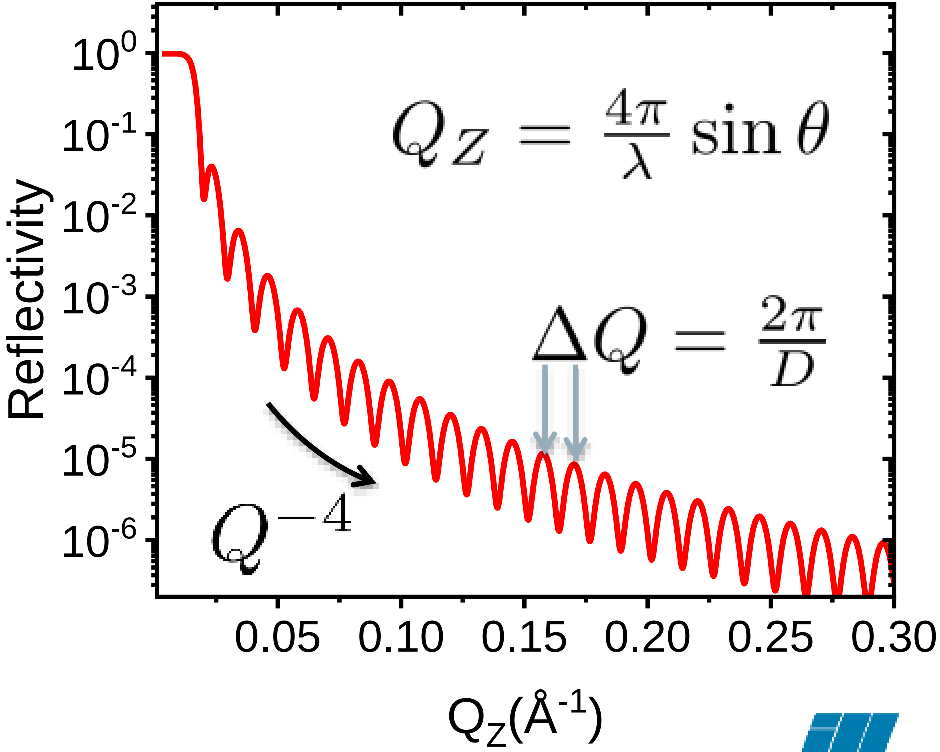
$$\left[\frac{\hbar^2}{2m_n}\frac{\delta^2}{\delta z^2}+\hat{V}(z)\right]\Psi(z)=E\Psi(z)$$

$$\hat{V}_2=\frac{2\pi\hbar^2}{m_n}N_2b_2 \quad > \quad \hat{V}_1=\frac{2\pi\hbar^2}{m_n}N_1b_1$$

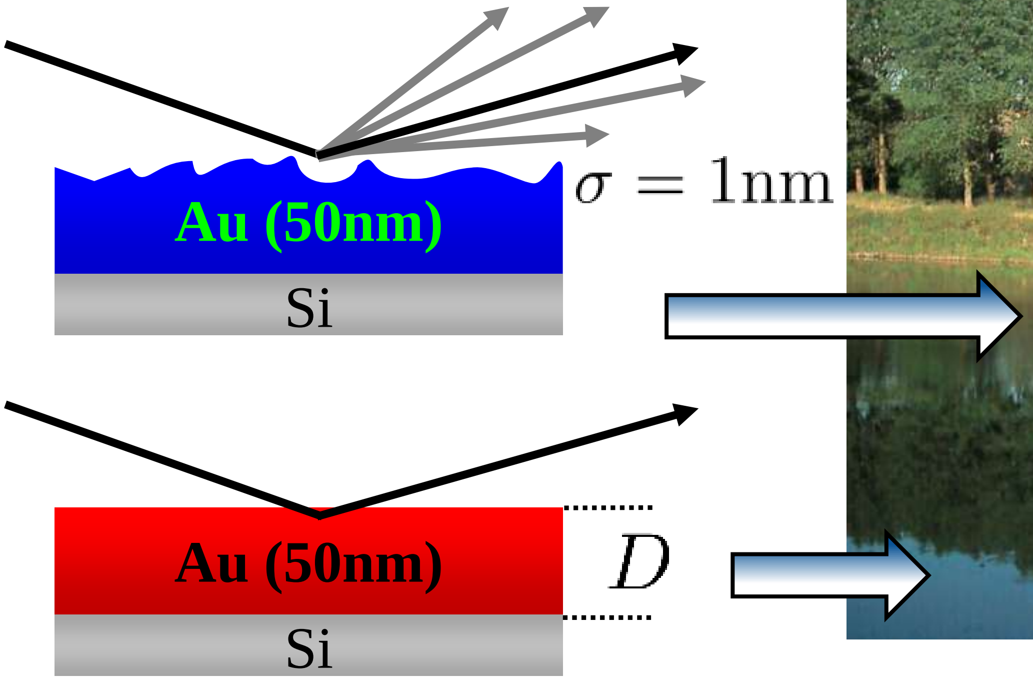
Reflection from Thin Film

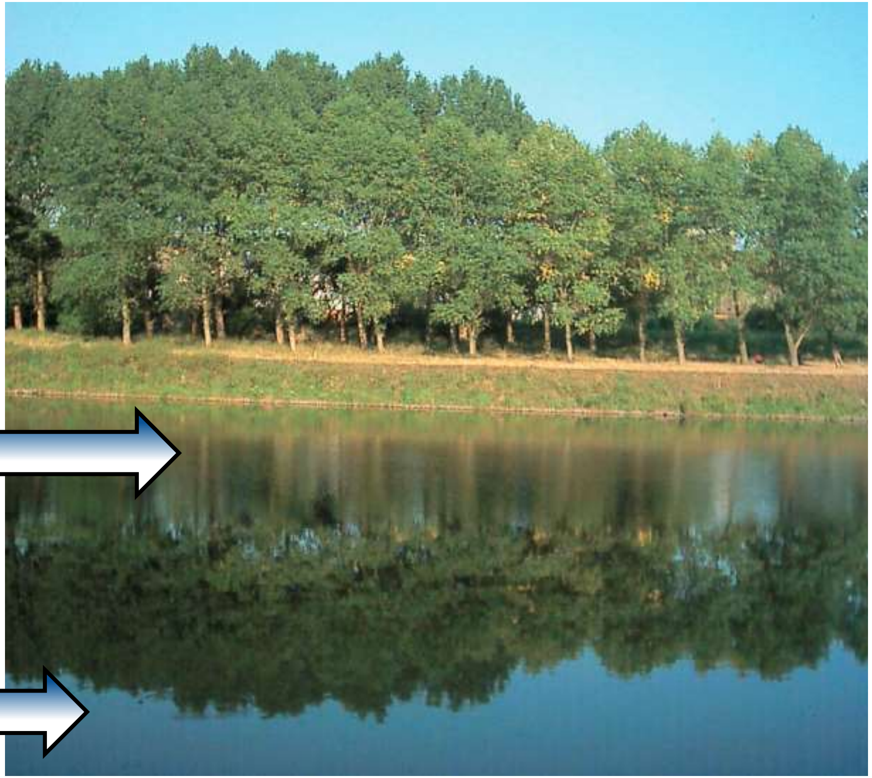
$$\hat{V}(z) = \frac{2\pi\hbar^2}{m_n} N b_n(z)$$



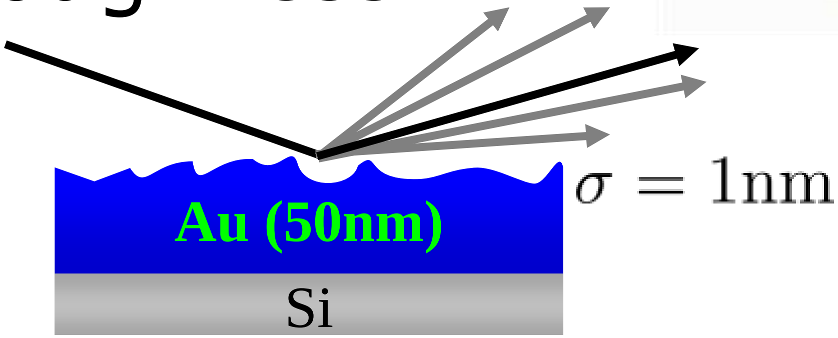


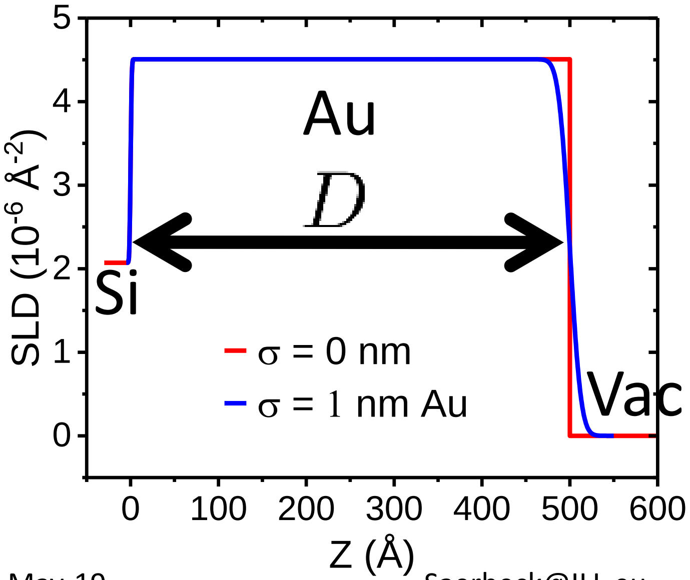
Roughness

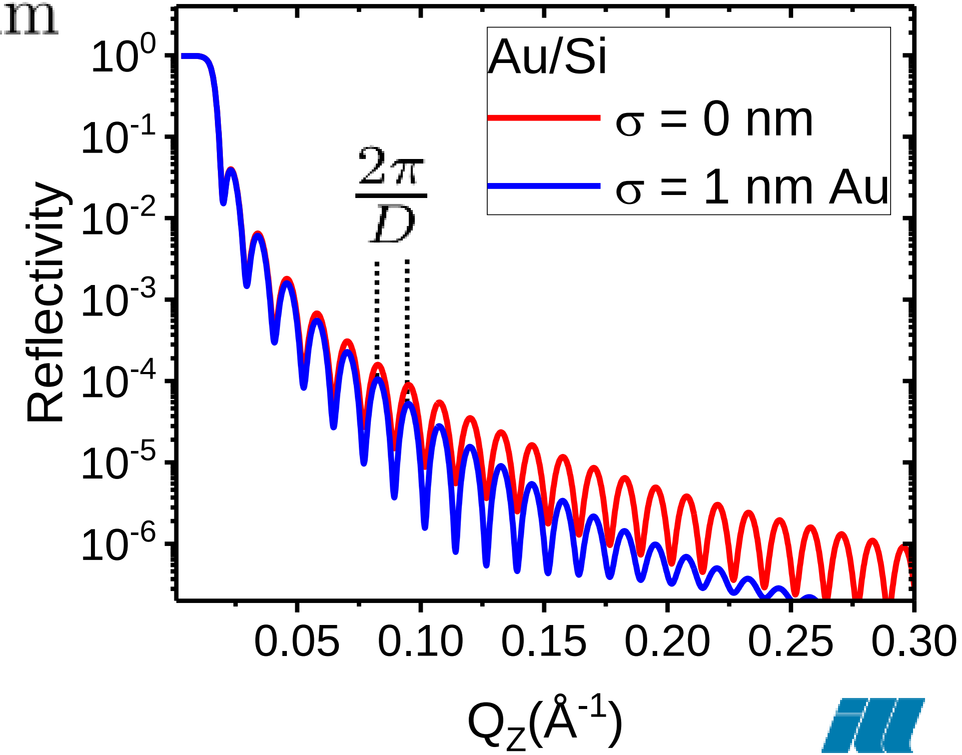




Roughness







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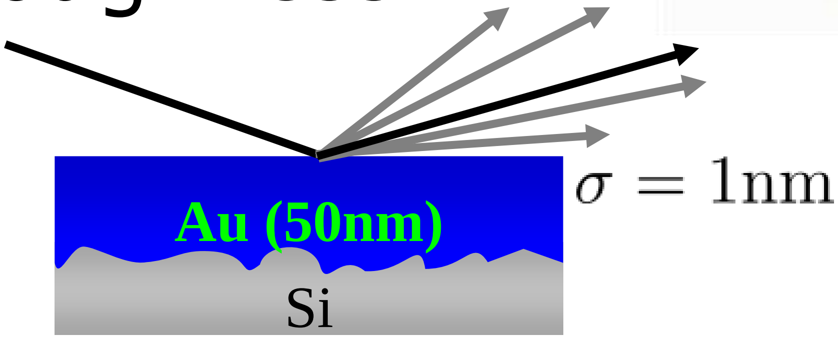
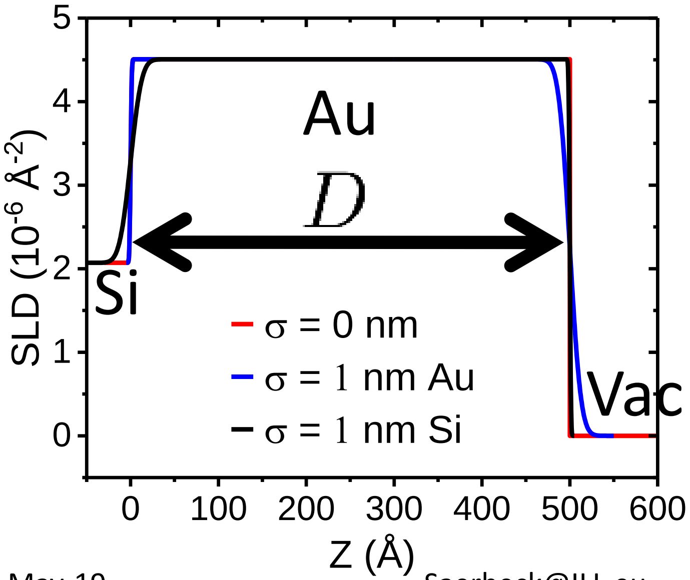
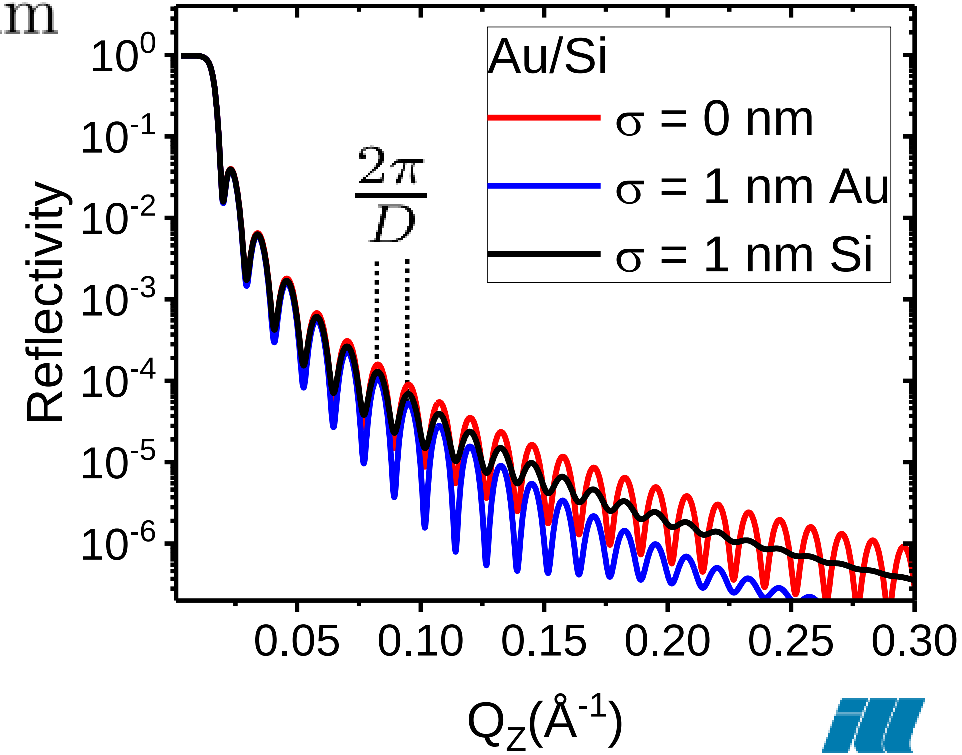
Roughness



Au (50nm)
Si
$\sigma = 1\text{nm}$

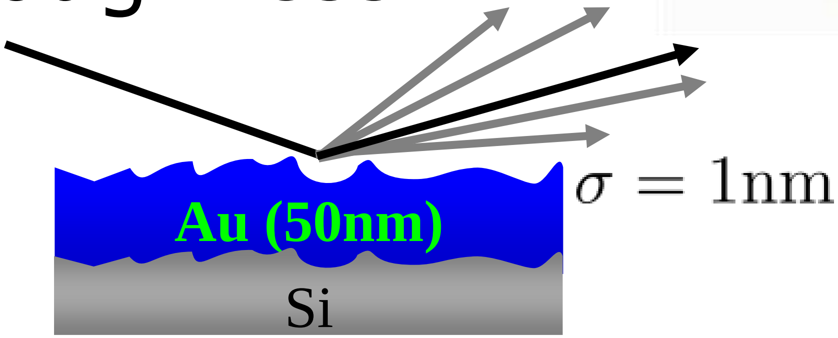


Au
D
Si
Vac
σ = 0 nm
σ = 1 nm Au
σ = 1 nm Si
SLD (10^{-6} Å^{-2})
Z (Å)
0
1
2
3
4
5
0
100
200
300
400
500
600

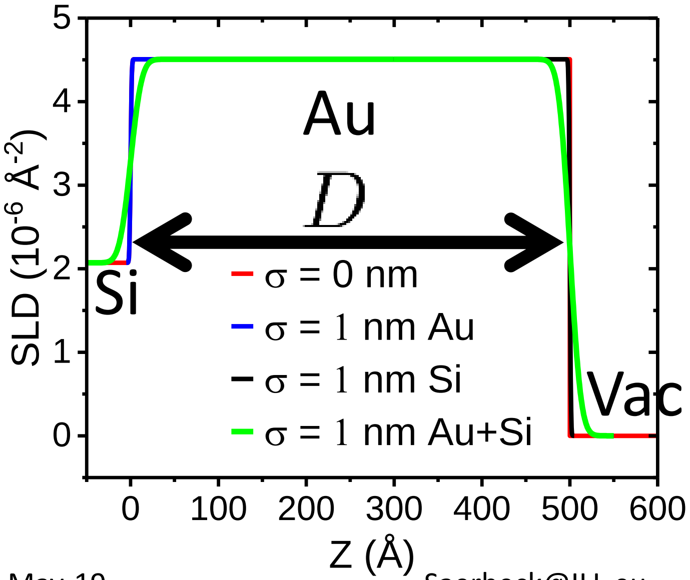


Au/Si
σ = 0 nm
σ = 1 nm Au
σ = 1 nm Si
$\frac{2\pi}{D}$
Reflectivity
Q_Z(Å^{-1})
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
0.05
0.10
0.15
0.20
0.25
0.30

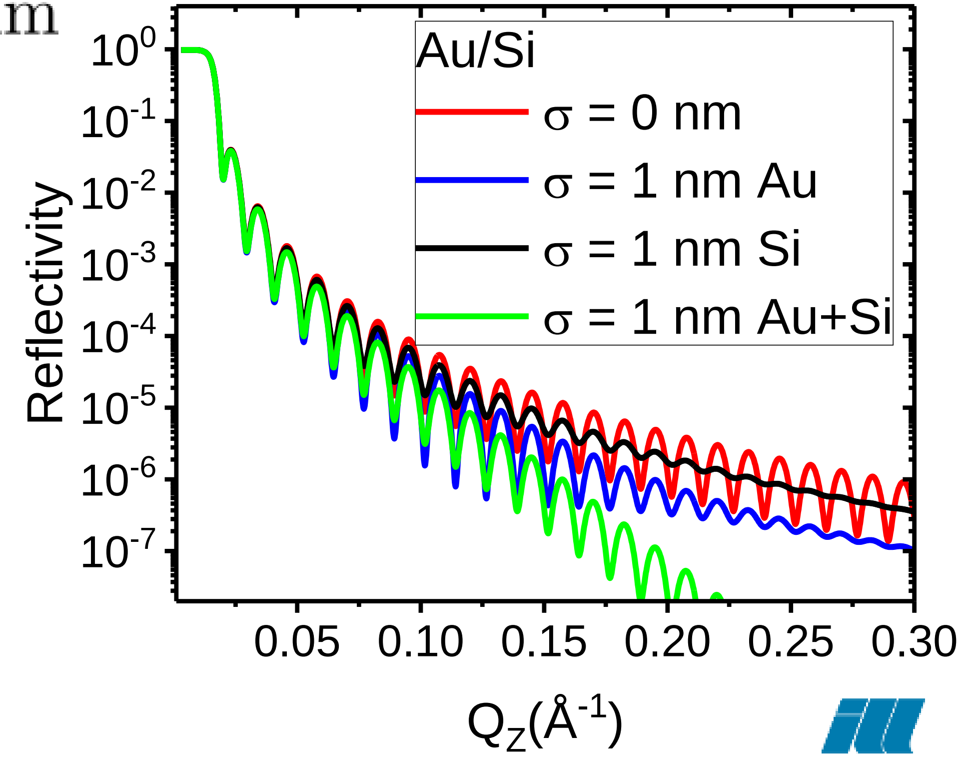
Roughness



Au (50nm)
Si
σ = 1nm

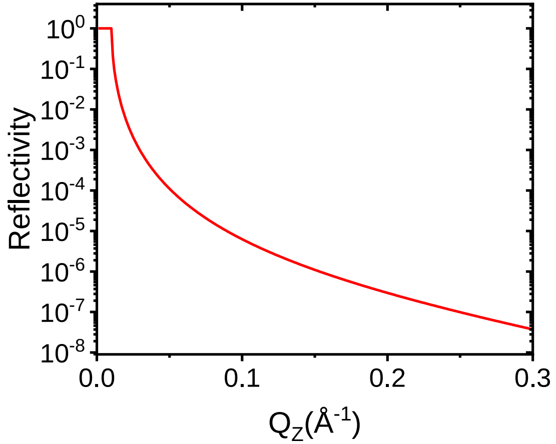


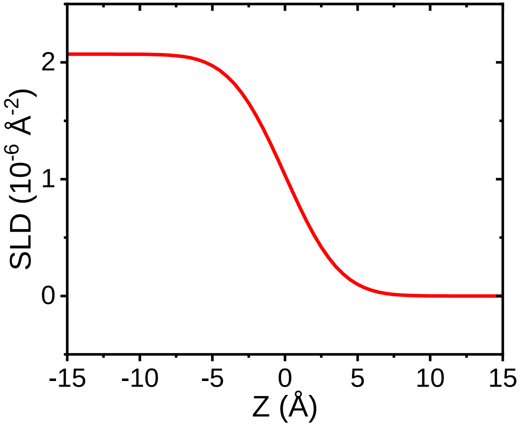
Au
D
Si
Vac
σ = 0 nm
σ = 1 nm Au
σ = 1 nm Si
σ = 1 nm Au+Si
SLD (10⁻⁶ Å⁻²)
Z (Å)



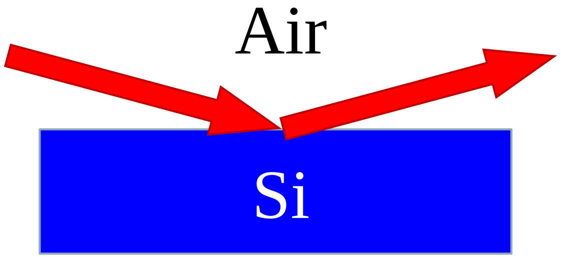
Au/Si
σ = 0 nm
σ = 1 nm Au
σ = 1 nm Si
σ = 1 nm Au+Si
Reflectivity
Q_Z(Å⁻¹)

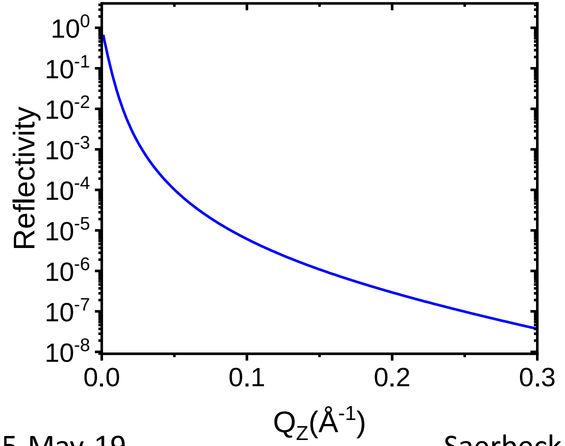
Medium 1 ↔ Medium 2

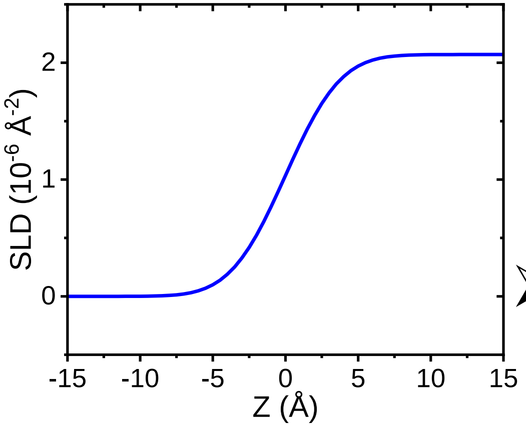




- ➢ High depth penetration…

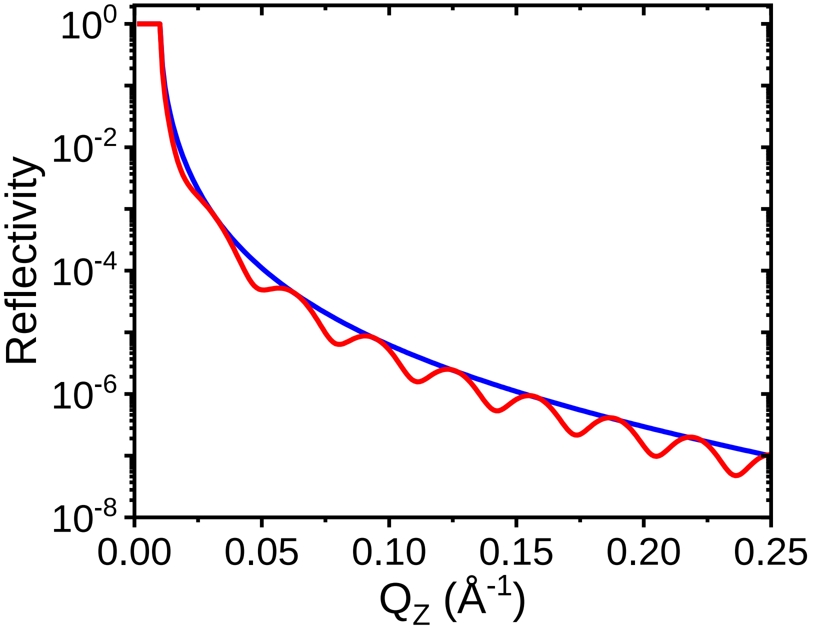




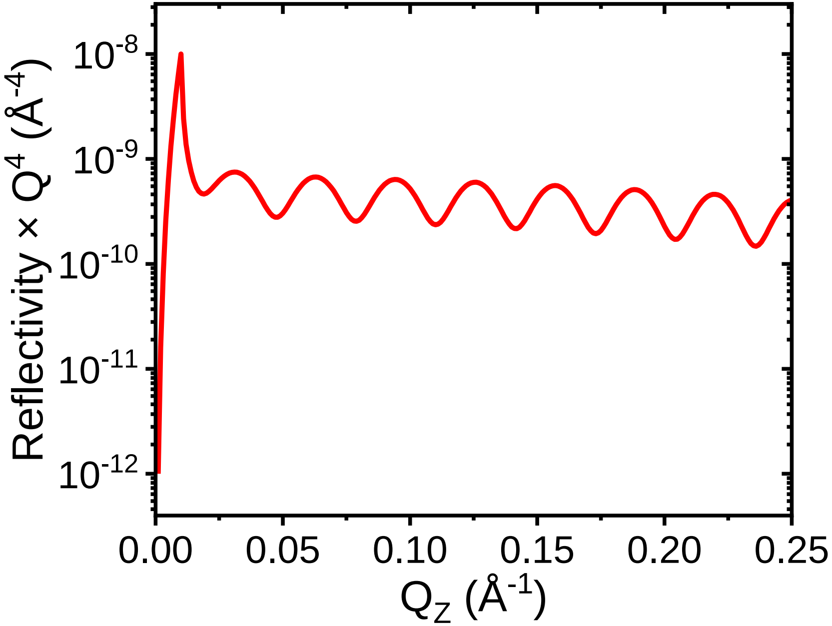


- ➢ Enables complex sample + experiment design

Don't be confused: R or RQ^4



⇔



- Shows normalization
- Highlights total reflection
- Accentuates low-Q region

- No normalization visible
- Highlights weak oscillations
- Accentuates high-Q region

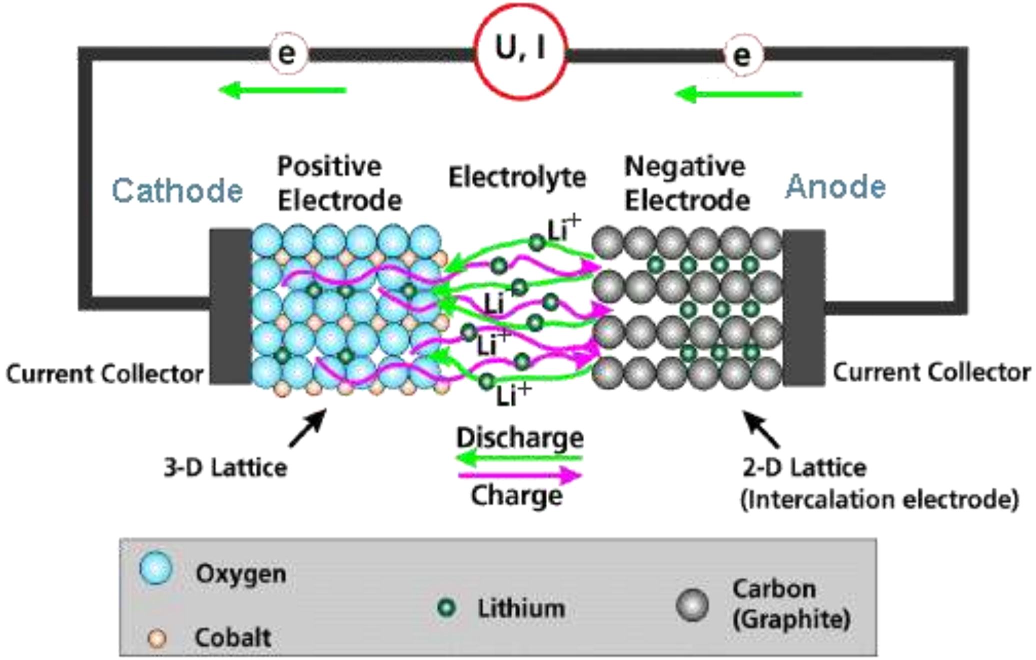
Li-ion batteries: portable, flexible, ever-lasting

IoT, MEMS, CMOS memories, Medical implantable	Smart cards, Skin patch, RFID	Wearables, E-textile, Medical device	Smartphone, Tablet, Power tool, Toy	Transport	Large-scale energy storage
Capacity range →					
1 mAh	10 mAh	100 mAh	1 Ah	100 Ah	> 1 kAh
Important features					
• Rechargeable • Small footprint, many micro-batteries • Long life time • Rapid discharge • Tend to incorporate with energy harvesting	• Can be both disposable and rechargeable • Laminar and thin, some with special form factor • Relatively low power • Cost sensitive	• High energy density for small volume • Long working hours • Flexible, stretchable or thin, some with special form factor	• Light-weight and small volume • Long working hours • Some with special form factors • High power	• Safe • Reliable • High power • High capacity	• Cost advantage • Long life time • Reliable • High capacity
					
Technology Status					
Small volume production	Available, mostly customized	Prototypes available	Research to prototype	Research	Very early stage

drkeithkantor.com

Source: IDTechEx Flexible, Printed and Thin Film Batteries 2019-2029
https://www.idtechex.com/en/research-report/flexible-printed-and-thin-film-batteries-2019-2029/634

Li-ion batteries

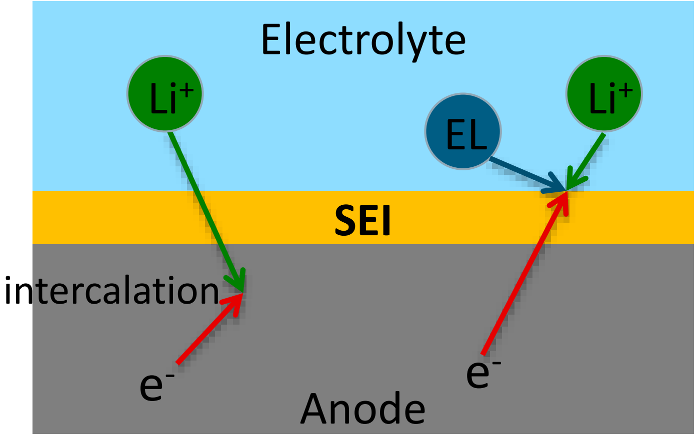


https://www.tf.uni-kiel.de

C. Liu *et al.*, Advanced Materials **22**, E28 (2010).

- Cathode (positive)
  - Li-containing metal oxides:
    $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$…
- Electrolyte:
  - e^- insulating ionic conductor
- Anode (negative)
  - Insertion: Graphite, TiO_2
  - Conversion: M_aX_b
    M = Mn, Fe, Co... X = O, S, F...
  - Alloying: Si, Sn…

The Solid Electrolyte Interphase (SEI)



- Left: Normal battery operation
- Right: Formation of SEI
  - Electrolyte decomposes by reduction

⇒ Electronically insulating layer

- Made from inorganic and organic/polymeric species
- Passivation of surface
  ⇒ prevents electrolyte consumption
- Prevents exfoliation of graphite
- Suppresses Li dendrite formation

- SEI is important for stability, long-term cycling and safety of battery
- A “bad” SEI can lead to electrolyte consumption, capacity fading and limited cycle life
- Depending on material and electrolyte

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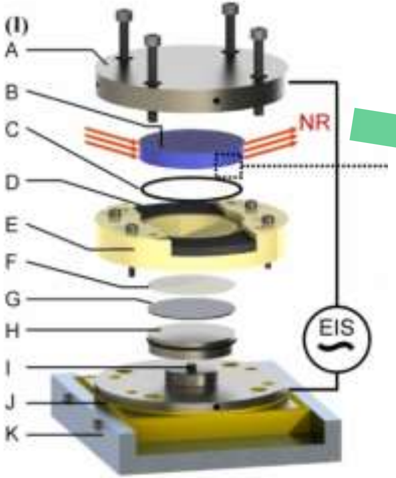
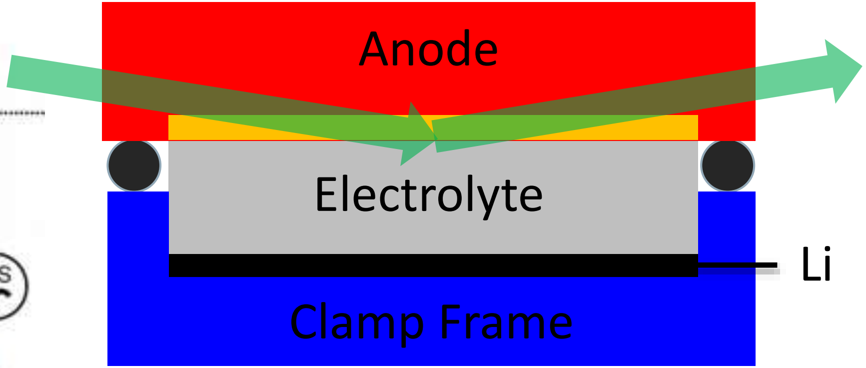
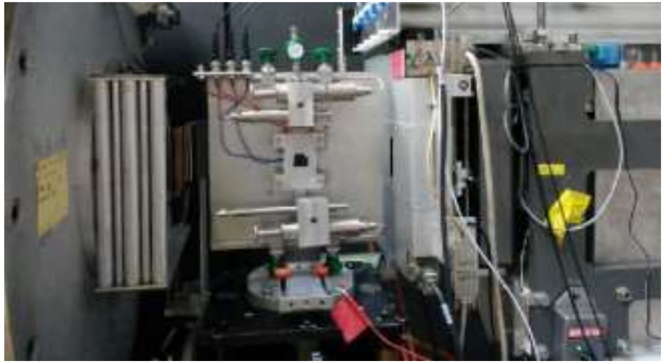
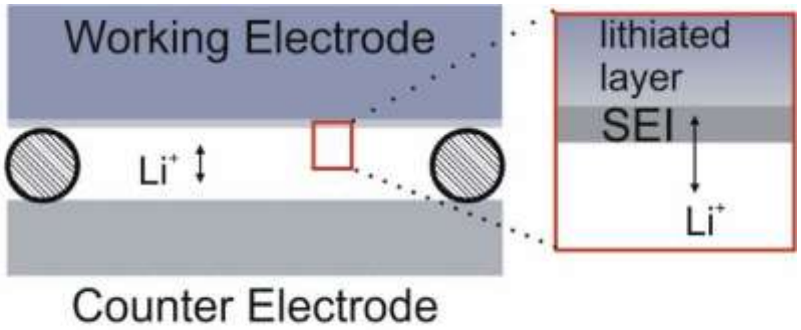
NR on In-Operando Model Batteries



Si absorption coefficient ~ 0.004 mm^{-1}

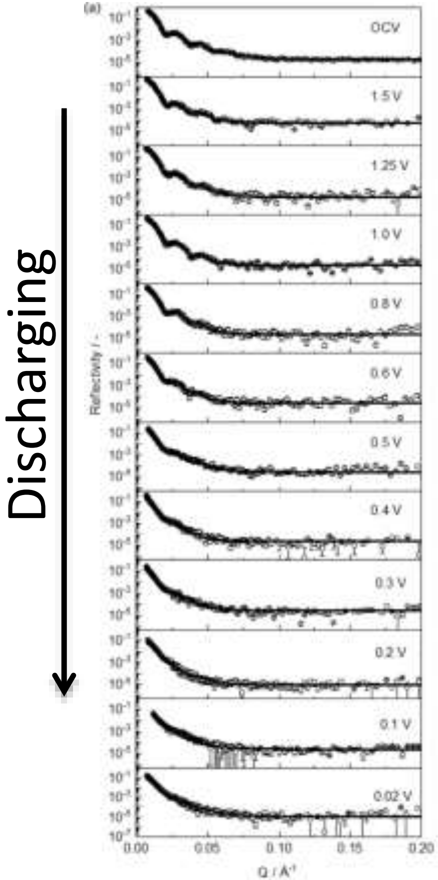




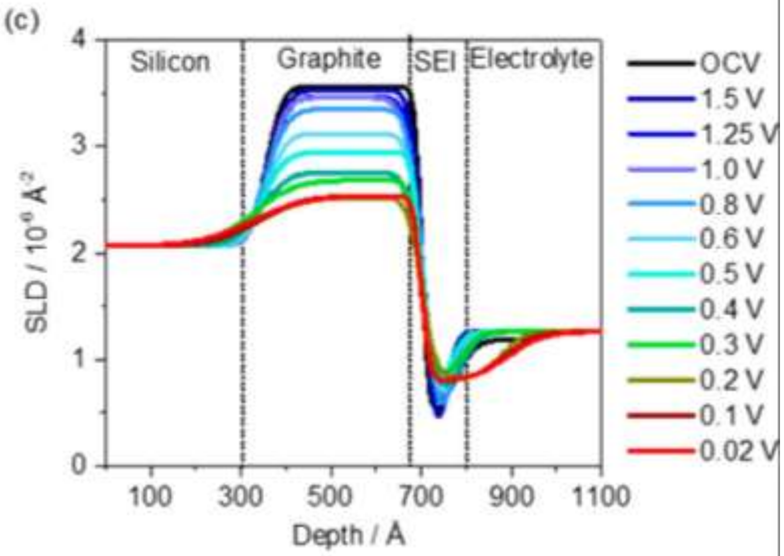


- ➢ Working in-operando conditions
- ➢ In-situ elec. impedance spectroscopy
- ➢ In-situ cell cycling

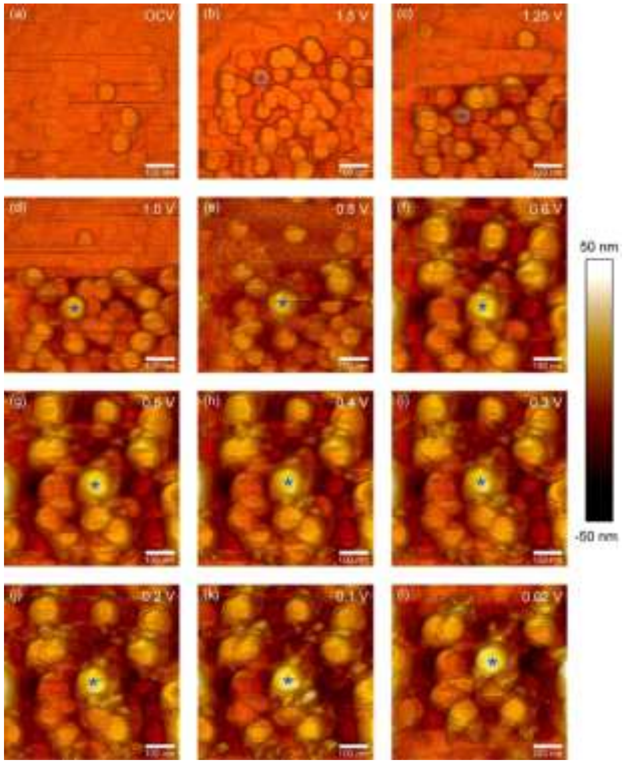
The SEI on Carbon Electrodes



- ➢ Lithiation of 30 nm carbon on Si
- ➢ Development of SEI
- SLD change – Li uptake
- 2 growth modes



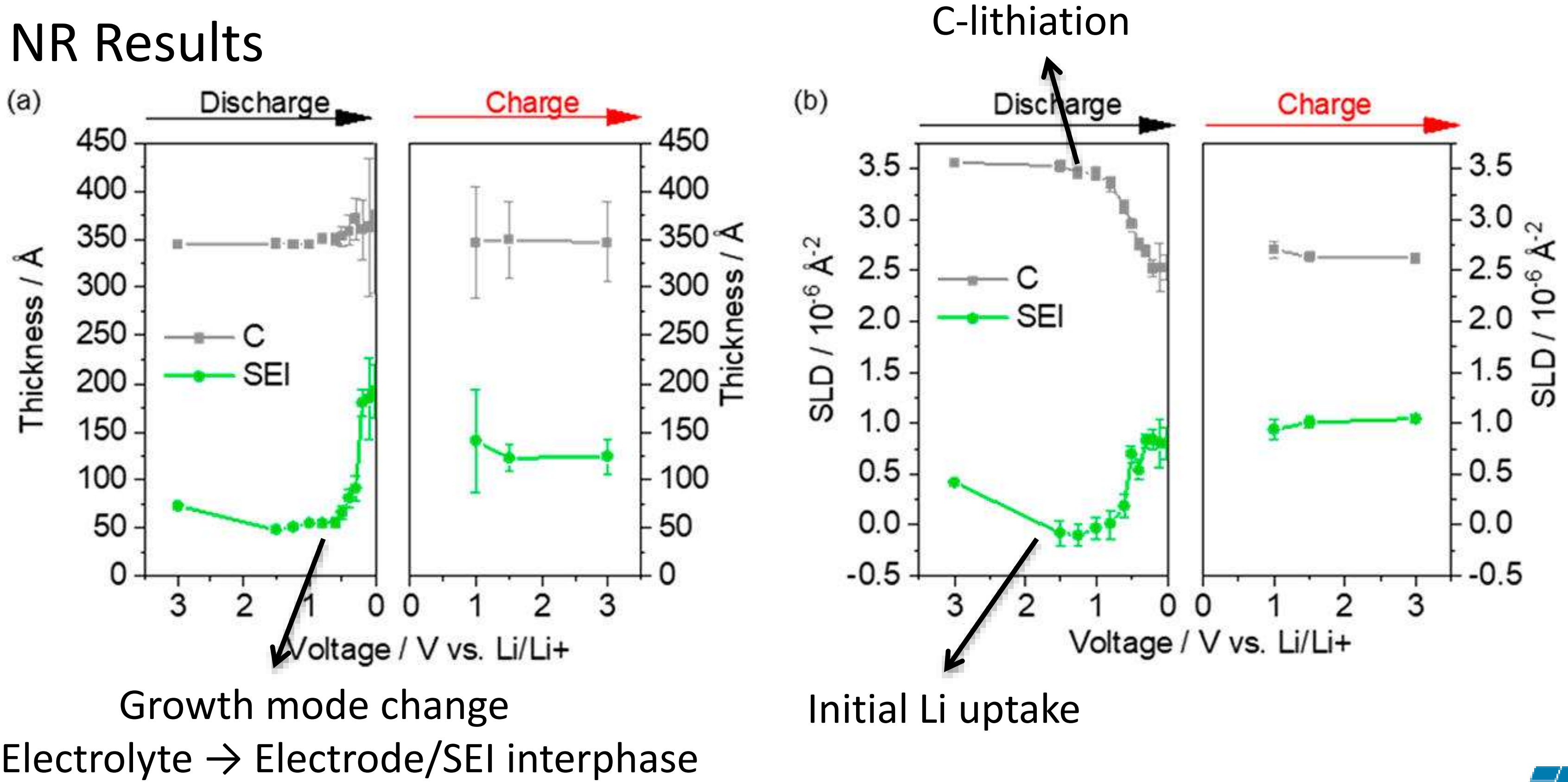
In-situ AFM



M. Steinhauer, *et al.*, ACS Applied Materials & Interfaces **9**, 35794 (2017).

The SEI on Carbon Electrodes

- NR Results



M. Steinhauer, *et al.*, ACS Applied Materials & Interfaces **9**, 35794 (2017).

Li-ion batteries: The case for Si

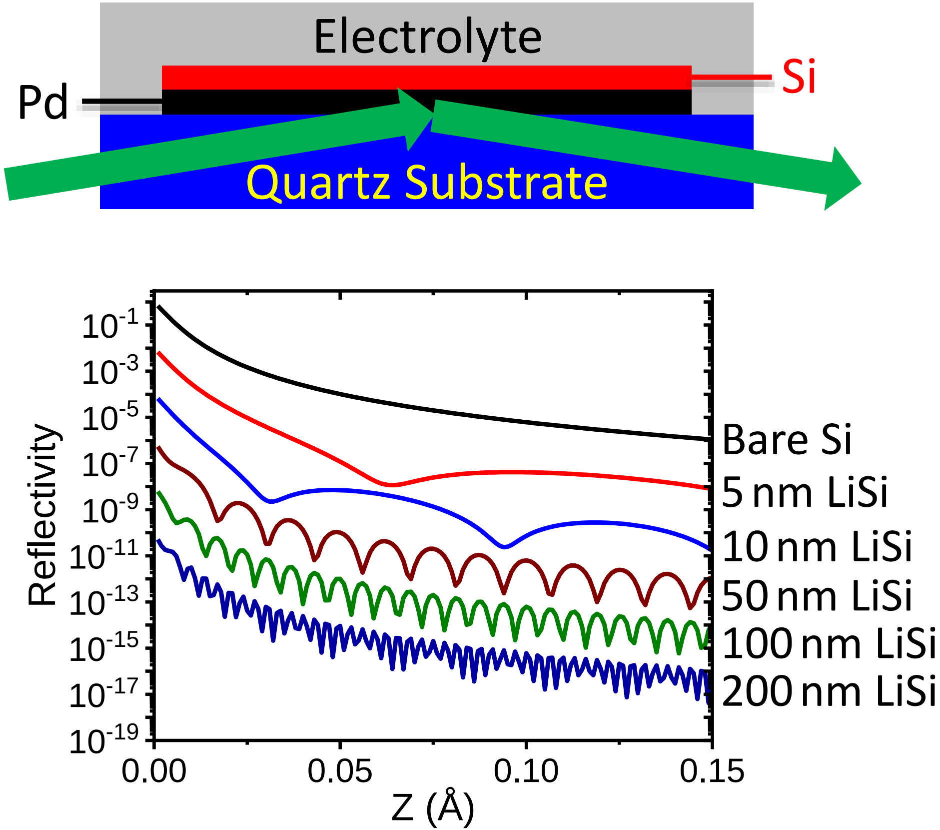
Anode material	Specific capacity (mAh/g)	Volume change
Li	3862	-
$Li_{13}Sn_5$	990	252%
$Li_{22}Si_5$	4200	320%
Li_9Al_4	2235	604%
LiC_6	372	10%

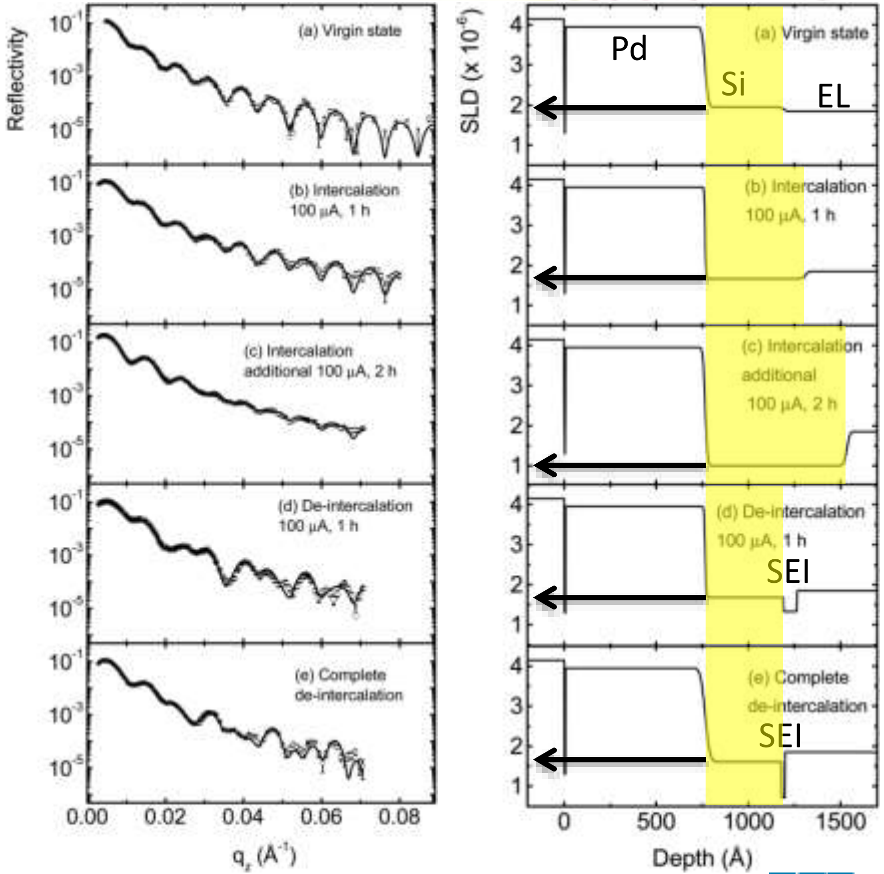
- ➢ Great theoretical capacity
  - ○ Graphite: 372 mAh/g
- ➢ Formation of SEI:
  chemistry and uniformity of SEI mediates stability, safety, cycling rate, and lifetime
- ➢ Naturally abundant and cheap

BUT

- ➢ Enormous volume change
- ➢ Narrow reaction front
- ⇒ Mechanical stress
- ⇒ Retardation of reaction front
- ⇒ Fragmentation of Si
- ⇒ Poor cycling stability
- ➢ Slow and irreversible charge/discharge processes
- ➢ Strong capacity fading
- ➢ Loss of Coulombic efficiency
- ➢ Delithiation ⇒ amorphous Si

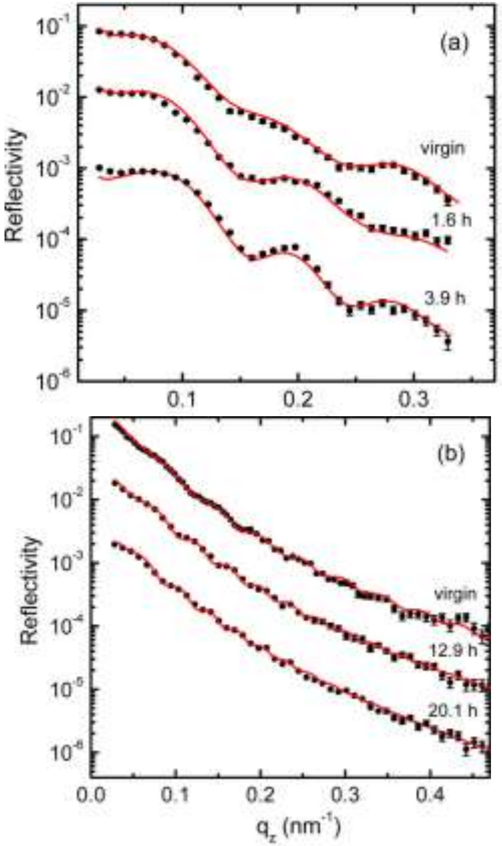
Li incorporation and Volume expansion



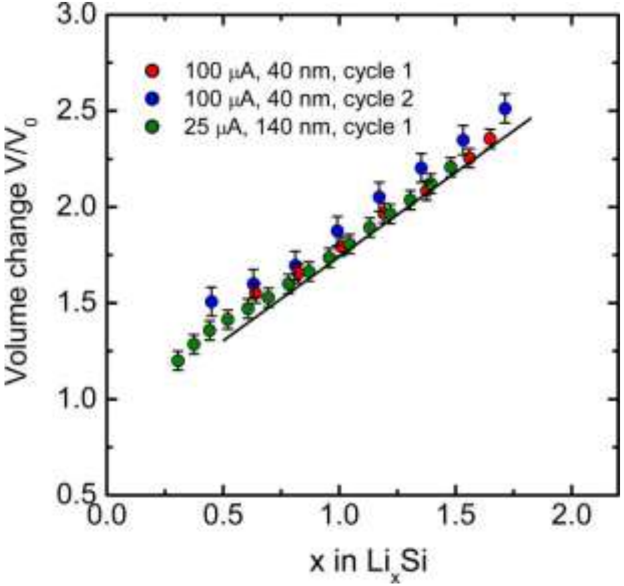


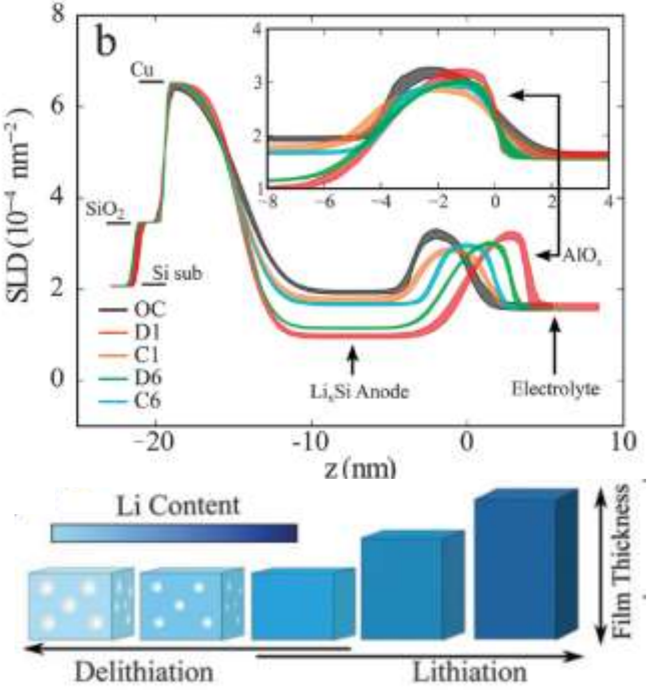
B. Jerliu *et al.*, Physical Chemistry Chemical Physics **15**, 7777 (2013).
B. Jerliu *et al.*, The Journal of Physical Chemistry C **118**, 9395 (2014).

Li Incorporation and Volume Expansion



- ➢ Linear volume increase with Li incorporation

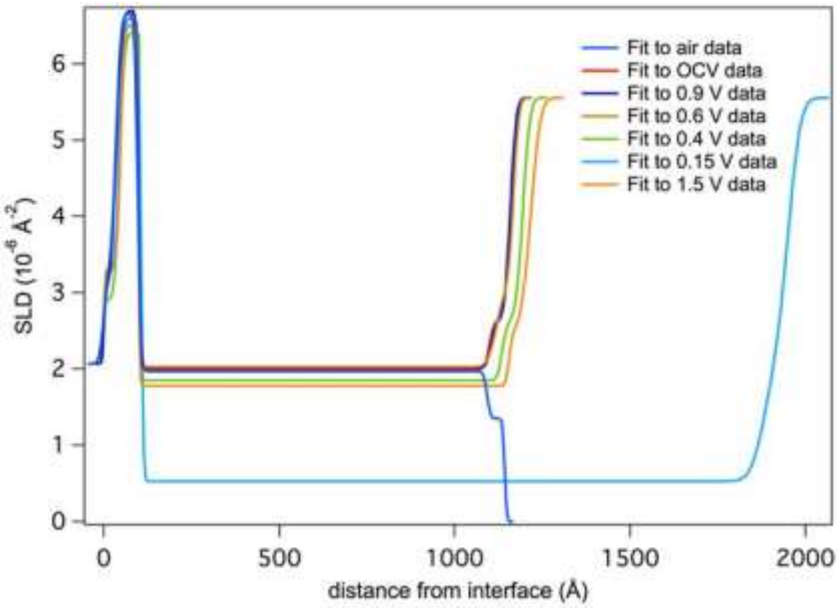


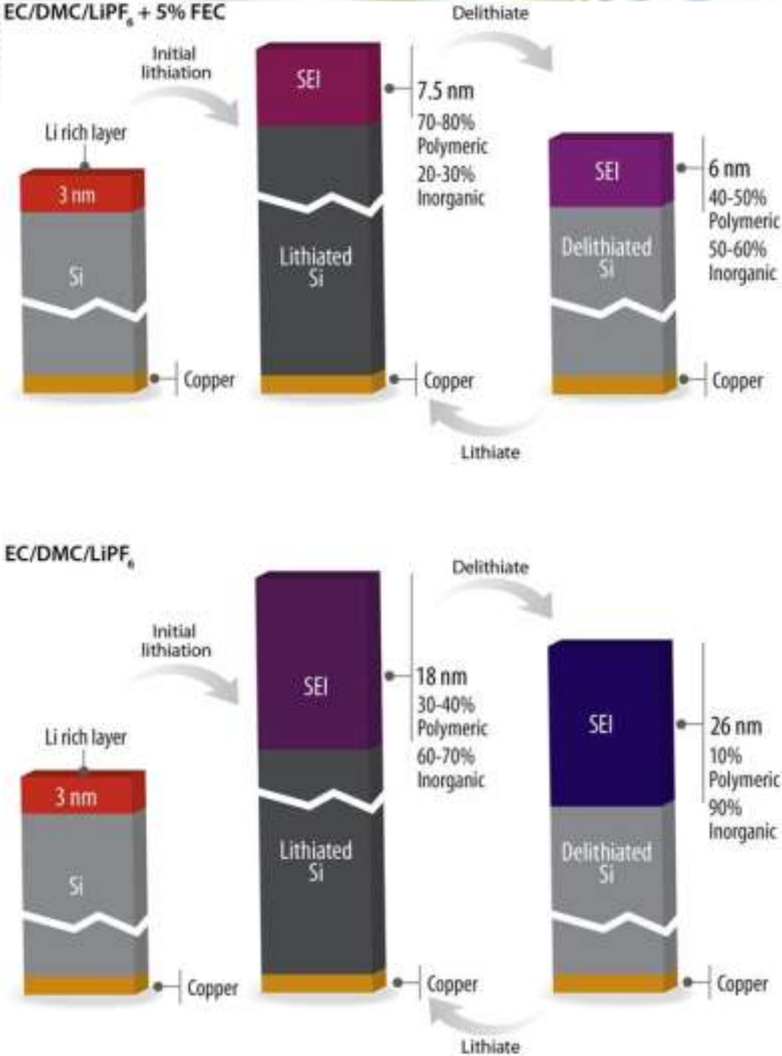


B. Jerliu *et al.*, Physical Chemistry Chemical Physics **15**, 7777 (2013).
B. Jerliu *et al.*, The Journal of Physical Chemistry C **118**, 9395 (2014).
S. C. DeCaluwe *et al.*, Physical Chemistry Chemical Physics **17**, 11301 (2015).

The SEI on Si Electrodes

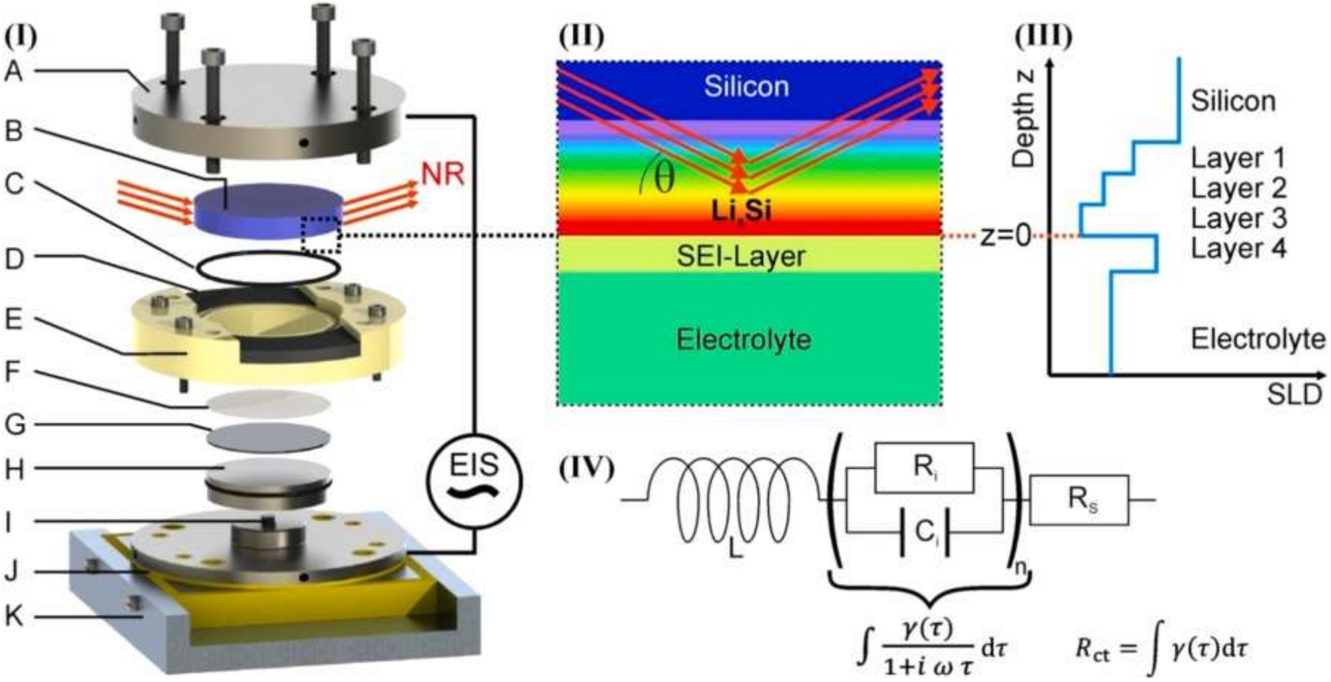
- SEI formation not self-terminating
- Consumption of electrochemically active Si
- Fluorinated ethylene carbonate additive improves cycleability





G. M. Veith *et al.*, Chemical Communications **50**, 3081 (2014).
G. M. Veith *et al.*, Scientific Reports **7**, 6326 (2017).

Time Resolved Discharging/Charging



First lithiation

⇒ c-Si → a-Li_xSi

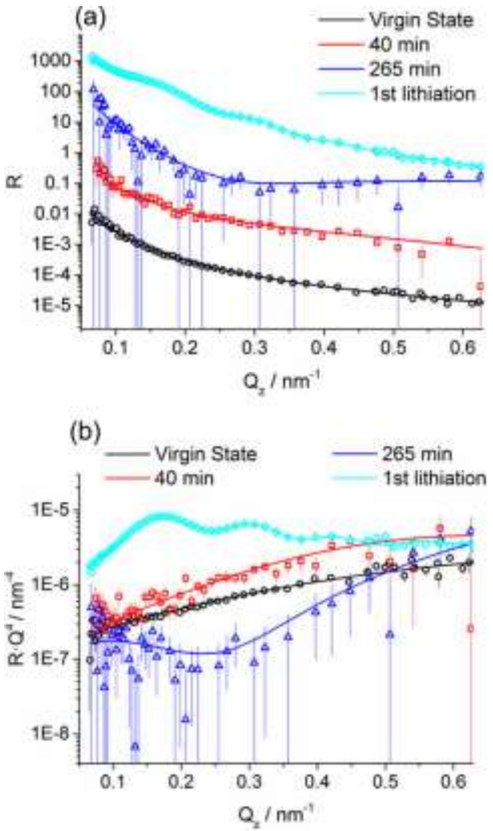
First delithiation

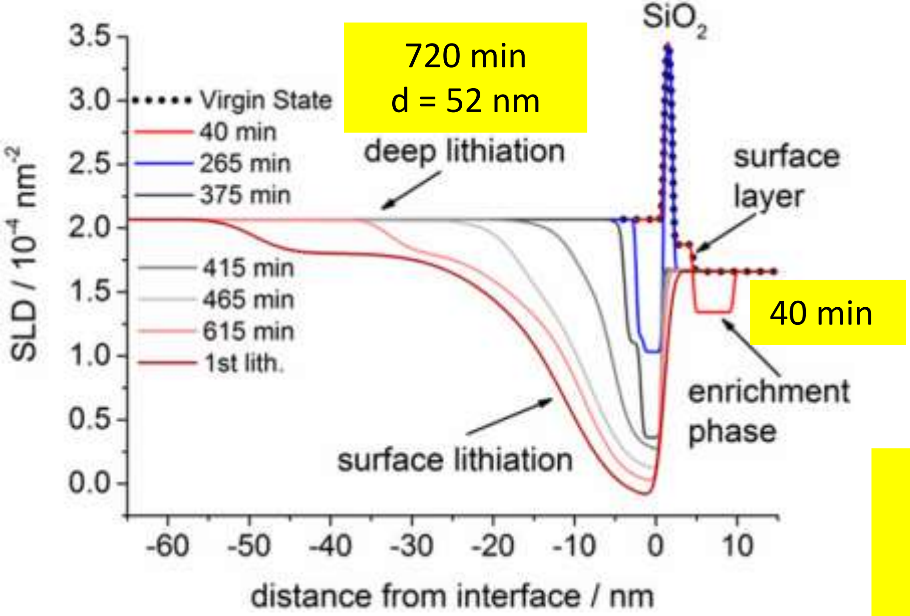
⇒ a-LixSi → a-Si + SEI

Second lithiation

⇒ a-Si → a-Li_xSi + ….

First Lithiation of c-Si





$$SLD = \frac{b_{Si} + x \cdot b_{Li}}{x \cdot \Delta V + V_{Si}}$$

$$b_{Si} = 4.15 \cdot 10^{-5} \text{Å}$$

$$b_{Li} = -1.9 \cdot 10^{-5} \text{Å}$$

$$V_{a-Si} = 21.3 \text{Å}^3$$

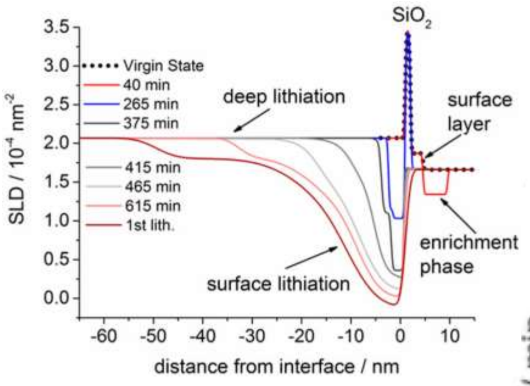
$$\Delta V = 14.7 \text{Å}^3$$

$\Rightarrow$ Calculate Li_xSi:

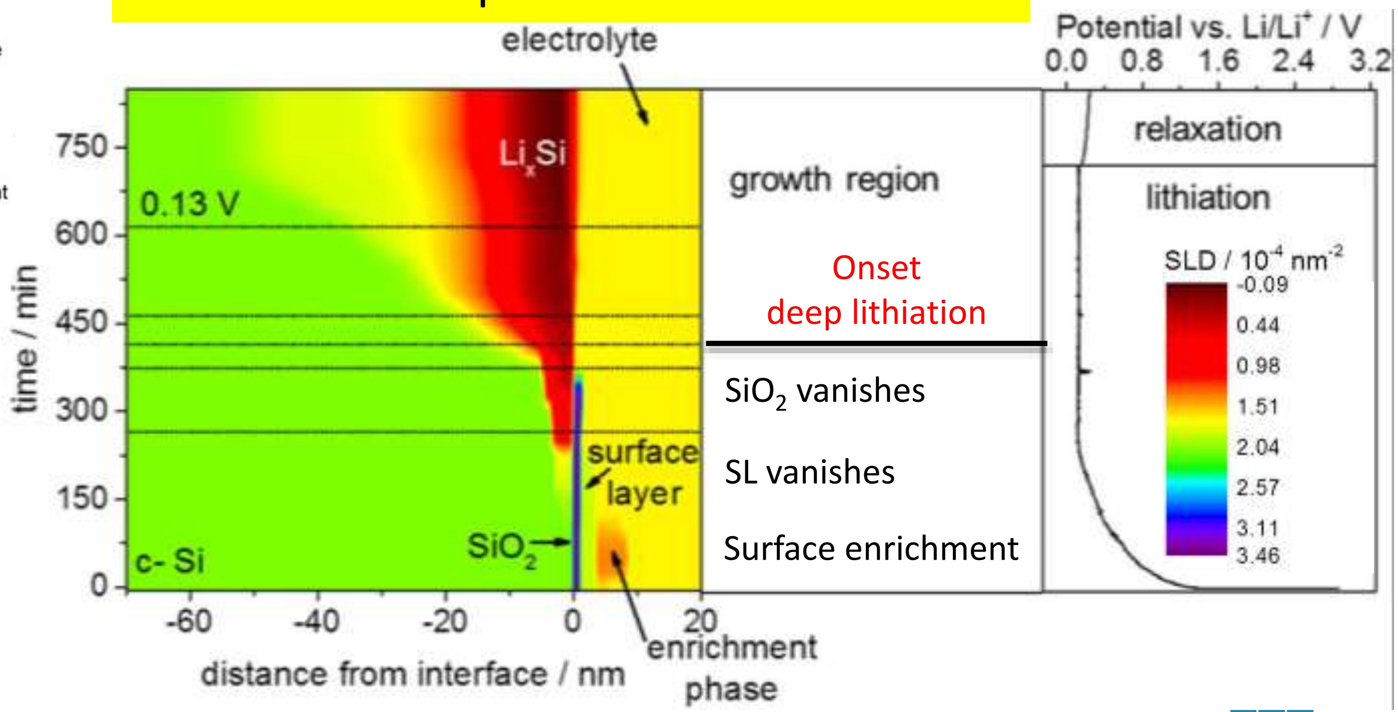
$$x = \frac{b_{Si} - SLD \cdot V_{Si}}{SLD \cdot \Delta V - b_{Li}}$$

Kinetic process of Si-lithiation

- 5 min reflectivity measurements during cycling (25 µA; 2 µA/cm²)



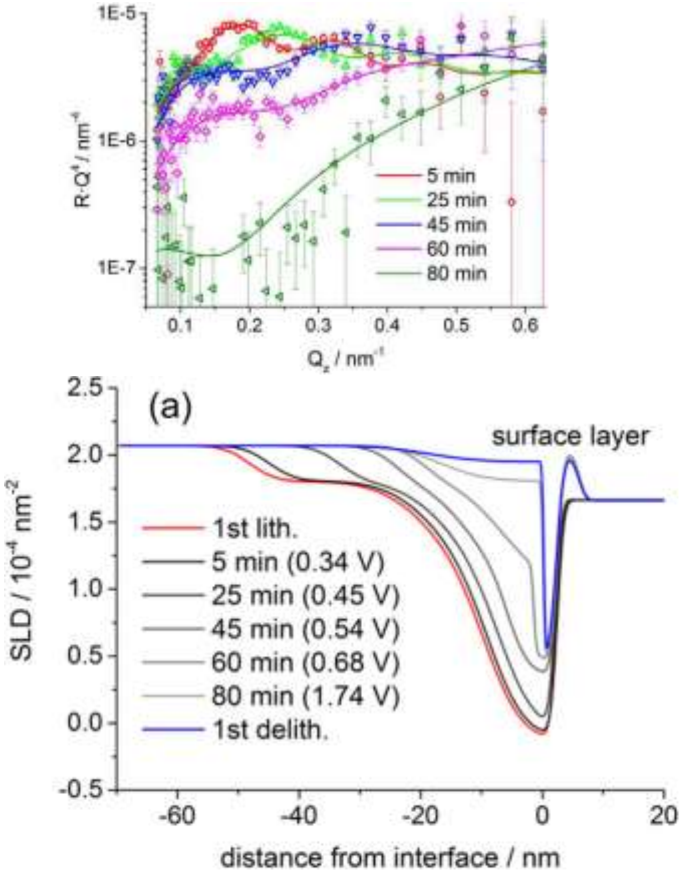
- SLD contour plot of distance vs. time

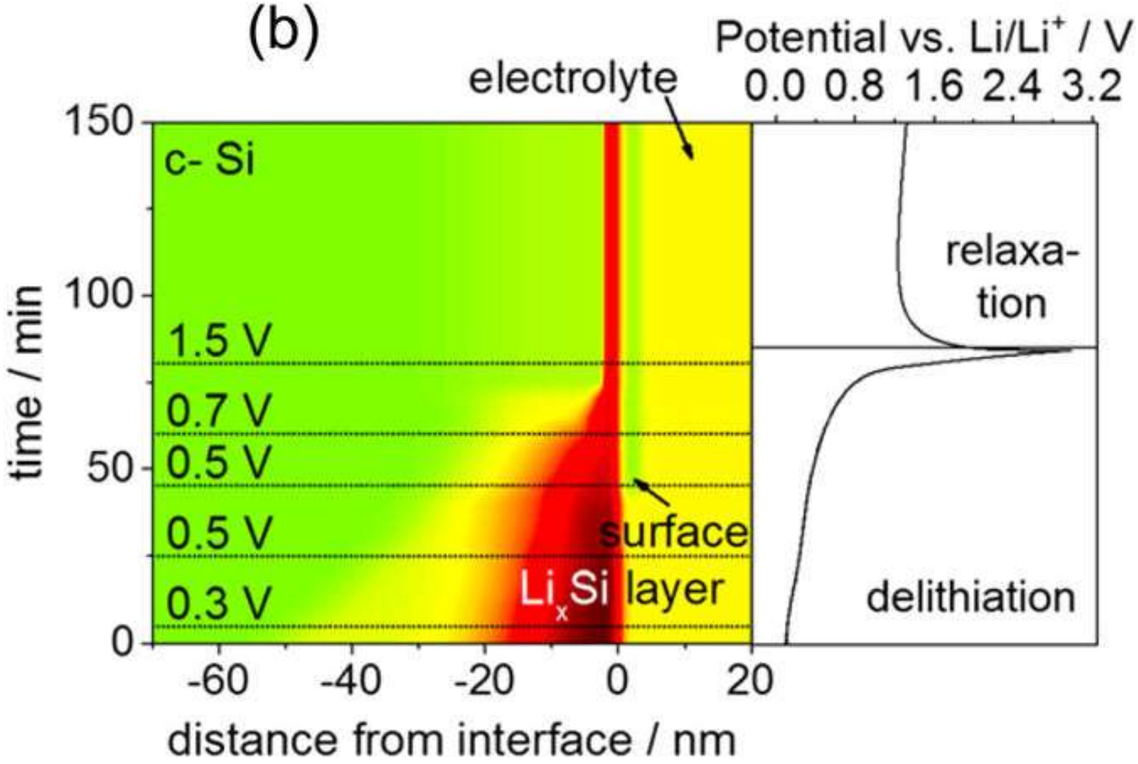


- Start: 4 regions = Si + SiO_2 + SL + EL
- SL = surface layer
- EL = electrolyte

 B.-K. Seidlhofer *et al.*, ACS Nano **10**, 7458 (2016).

Kinetic process of Si-delithiation



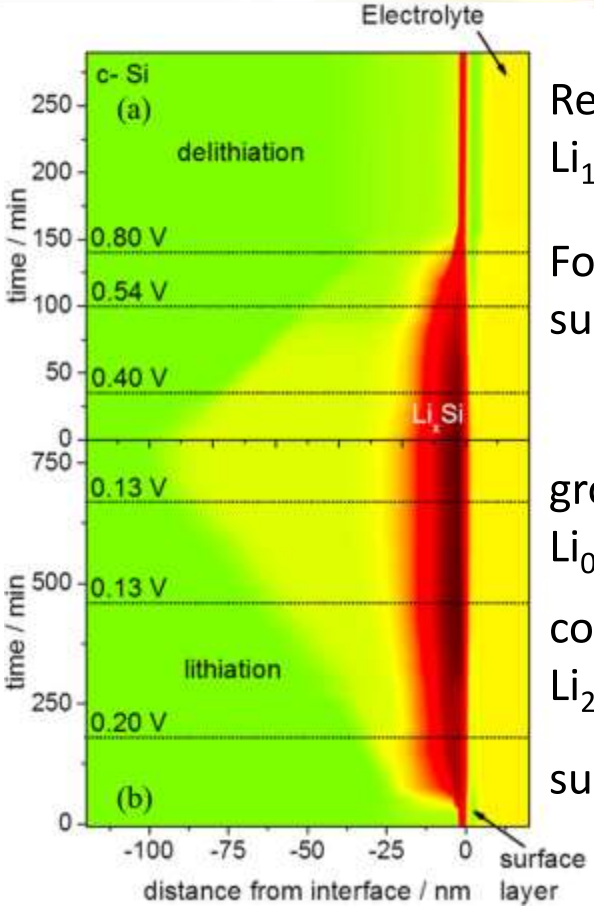


 B.-K. Seidlhofer *et al.*, ACS Nano **10**, 7458 (2016).

2^{nd} lithiation/delithiation cycle

- **First lithiation:**
  - Enrichment phase in electrolyte
  - Consumption of surface layer
  - Strong lithiation in skin region of Si: $Li_{2.5}Si$ ~ 3 – 5 nm
  - Weaker lithiation in region towards bulk: $Li_{0.1}Si$ ~ 50 nm

- **First delithiation:**
  - Deacrease of thickness and Li content in Si: $Li_{0.05}Si$ ~ 20 nm
  - Remaining Li in skin region: $Li_{1.1}Si$ ~ 3 nm
  - Thin surface layer: SEI ~ 2 – 5 nm



Remnant 3 nm $Li_{1.1}Si$ region

Formation of 5.4 nm surface layer

growing 76 nm $Li_{0.1}Si$ region

constant 18 nm $Li_{2.5}Si$ region

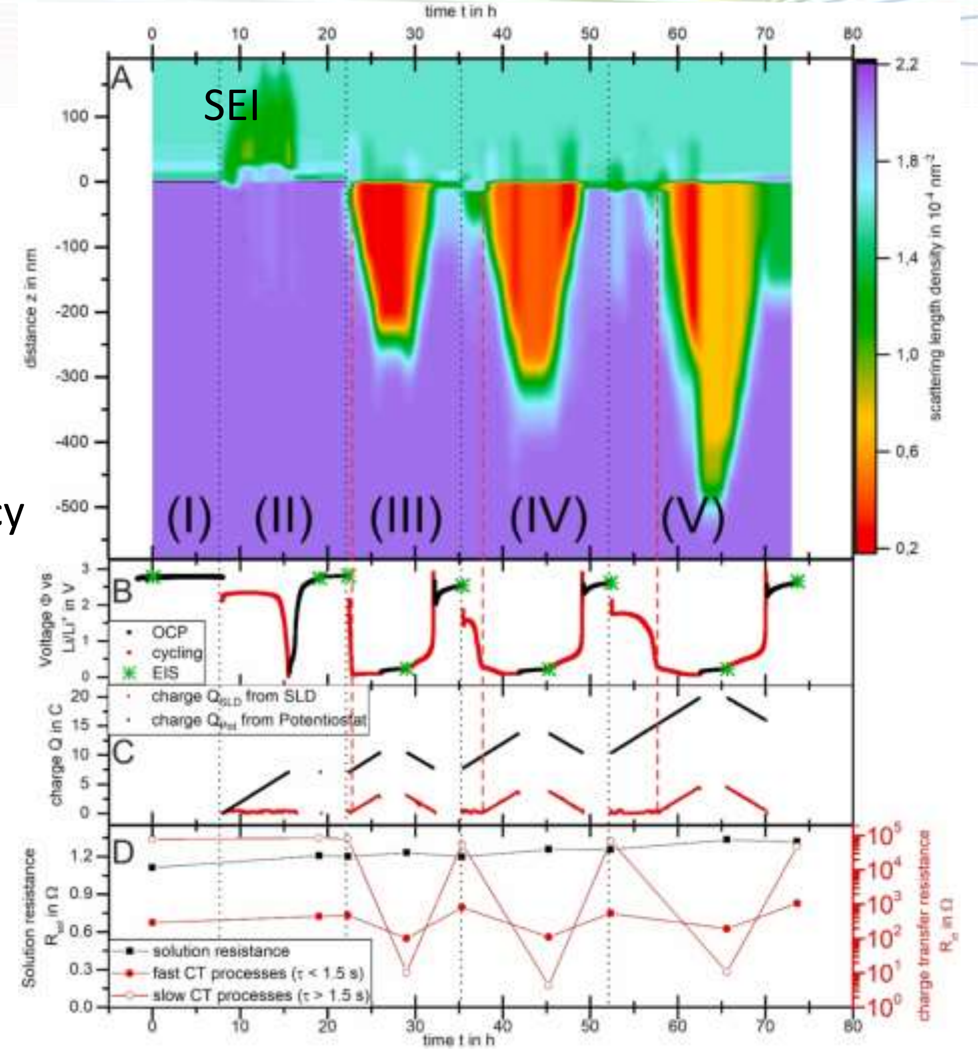
surface layer 3.6 nm

B.-K. Seidlhofer *et al.*, ACS Nano **10**, 7458 (2016).

Battery Cycling

- ➢ 5 min reflectivity measurements
- ➢ cycling (250 μA; 20 μA/cm²)

- ➢ Initial SEI inhibits lithiation
- ➢ Side reactions → loss of Coulombic efficiency
- ➢ Formation and dissolution of surface layer
- ➢ Bilayer SEI structure
- ➢ Progressing lithiation front + depth

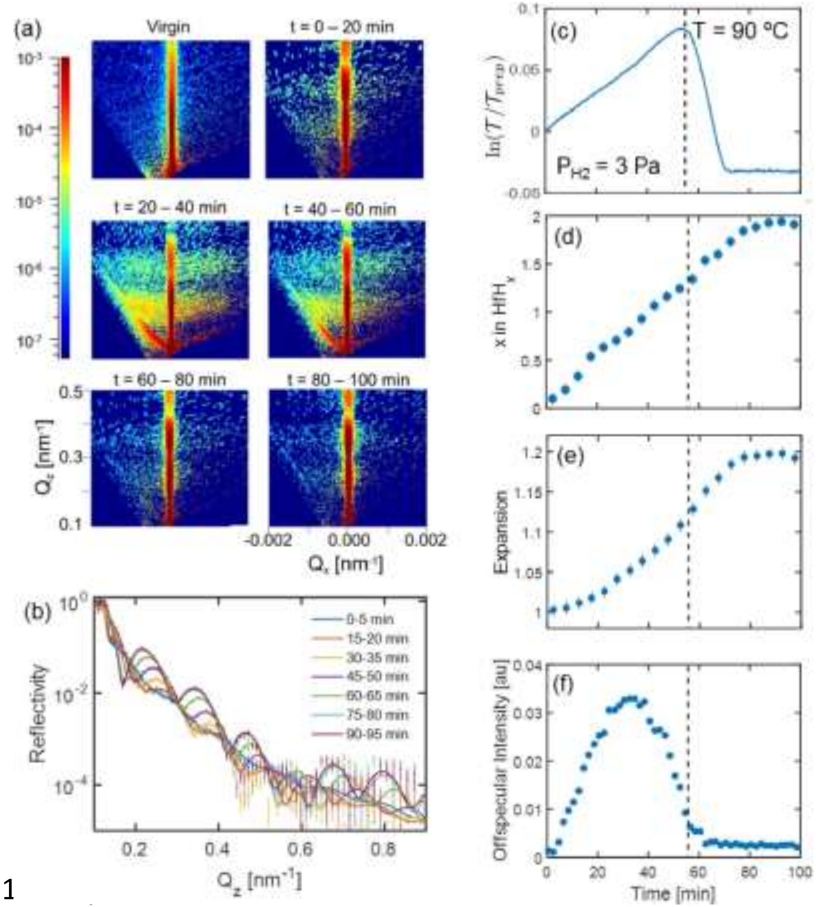


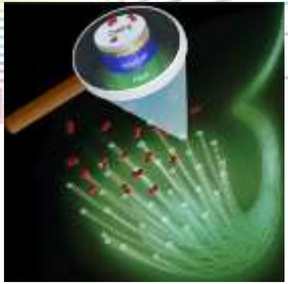
A. Ronneburg *et al.*,
Energy Storage Materials **18**, 182 (2019).

Summary Li-Batteries

- Volume expansion of Si + Li ~ 310%
- Two lithiation regimes: depending on current density
  - Strong surface lithiation
  - Lower lithium content deeper in bulk
- Roughness of propagation front ~ 10 nm
- Second lithiation proceeds easier and with modified kinetics
- SEI forms and dissolves during lithiation and delithiation
- Remanent lithiated Si

Hydrogen in Metals





- Hydrogen uptake in Hf
- Fast and efficient detection of hydrogen
- Optical readout: No electrical current
- Change in optical properties with H
- Pd: non-linear response + hysteresis
- Hf: hcp – fct phase transformation
- Homogeneous increase of H in depth
- Lateral inhomogeneities
- Remaining H content in $HfH_{1.43}$ and fcc phase

C. Boelsma *et al.*, Nature Communications **8**, 15718 (2017).
L. J. Bannenberg *et al.*, Sensors and Actuators B: Chemical **283**, 538 (2019).

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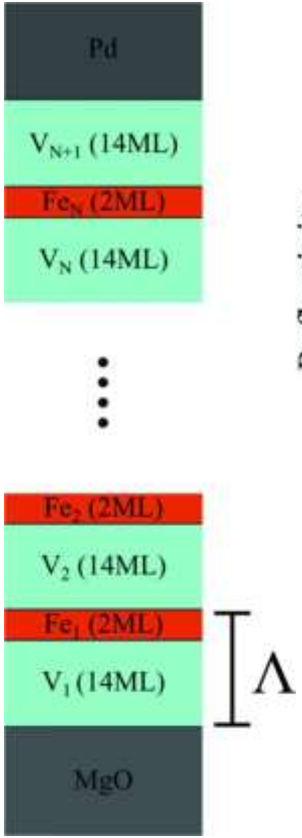
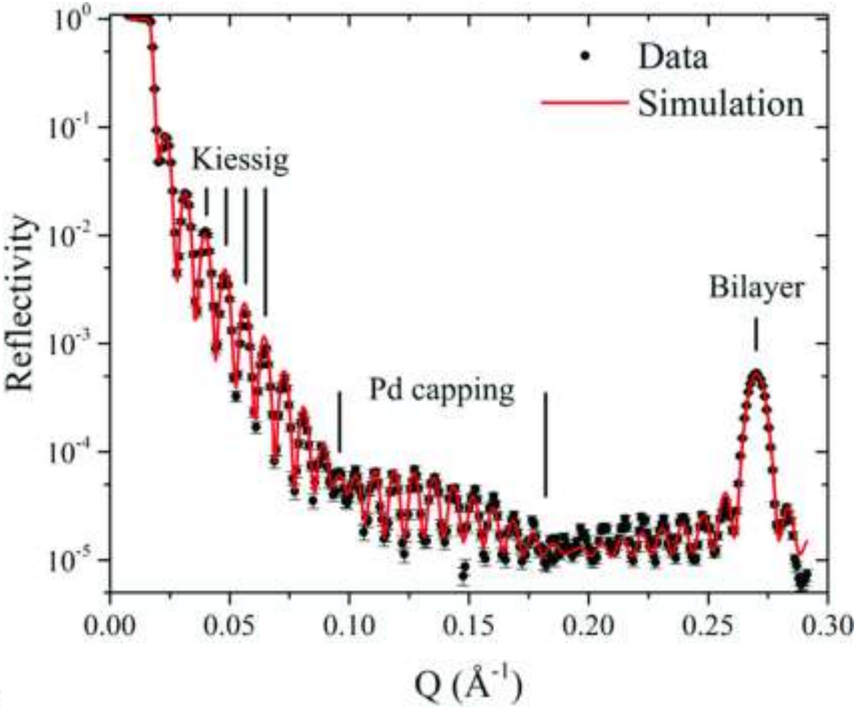
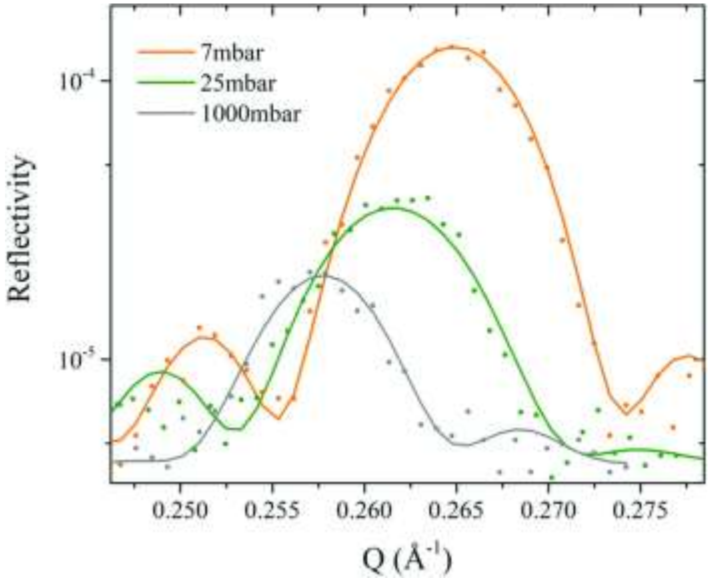
Hydrogen diffusion in V





- ➢ V thickness increase with H



- ➢ Dissociation of H at Pd surface
- ➢ Diffusion into multilayer (V)

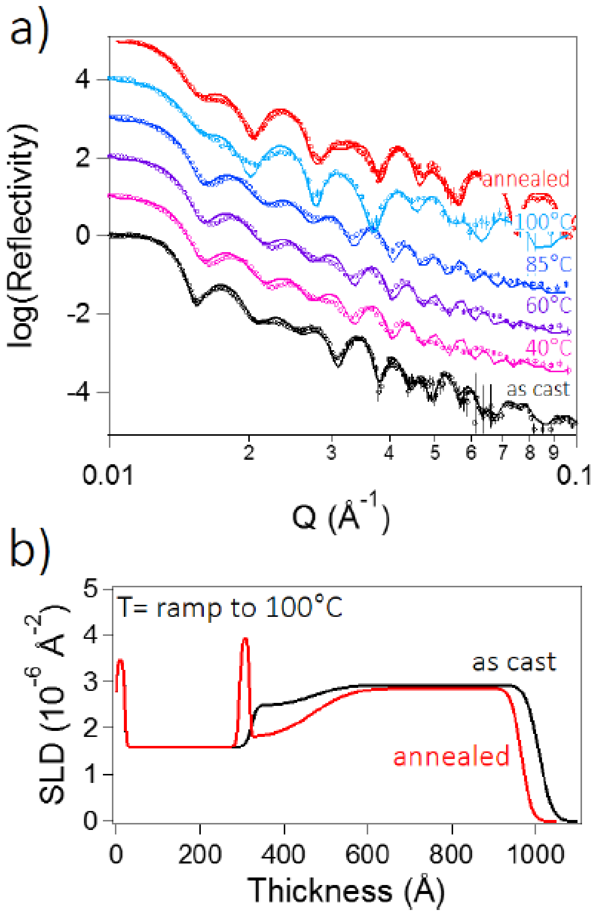
S. A. Droulias *et al.*, Journal of Applied Crystallography **51**, 1556 (2018).

Thermal/Stress Stability of Solar Cells

- Si/PEDOT:PSS/PS:PCMB
- Light causes fullerene dimerization
- Stress causes dedimerization
- Evolution of composition with annealing
- No change until glass transition T_g

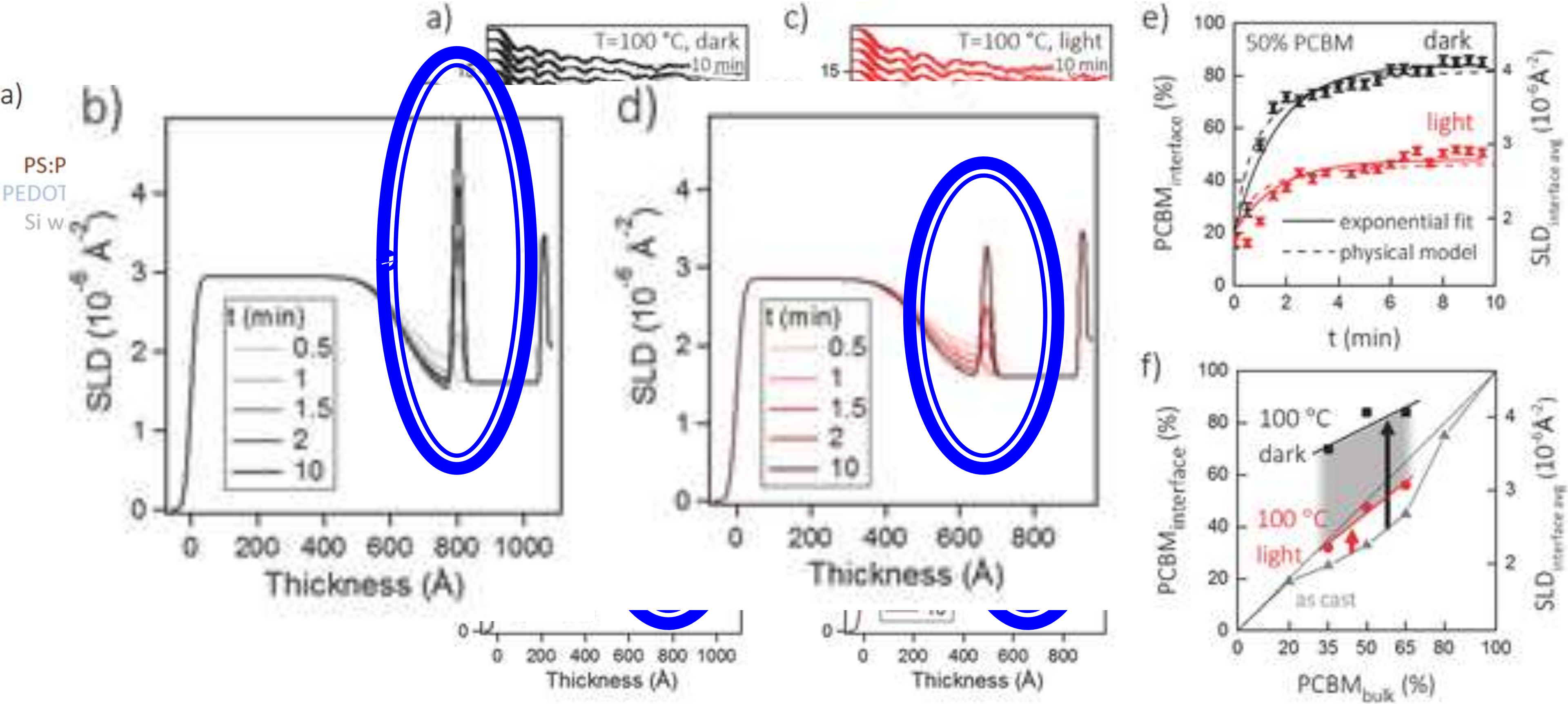
⇒ 2-3 nm PCMB enriched interface

- Time resolved measurements…



S. Pont *et al.*, Advanced Functional Materials **28**, 1802520 (2018).

Thermal/Stress Stability of Solar Cells



15-May-19 S. Pont *et al.*, Advanced Functional Materials **28**, 1802520 (2018).

Summary + Outlook

- Neutron reflectometry enables insight into processes deeply buried in layered structures
- Volume expansion, surface lithiation, bulk lithiation, roughness, SEI
- Under in-operando and in-situ conditions
- Time-resolved neutron reflectometry enables monitoring kinetic processes
- Further upgrades in instruments enable faster measurements of irreversible processes
- Work on more realistic battery cells

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