X-ray scattering for studying wood

Advanced Wood Science CHEM-E2170

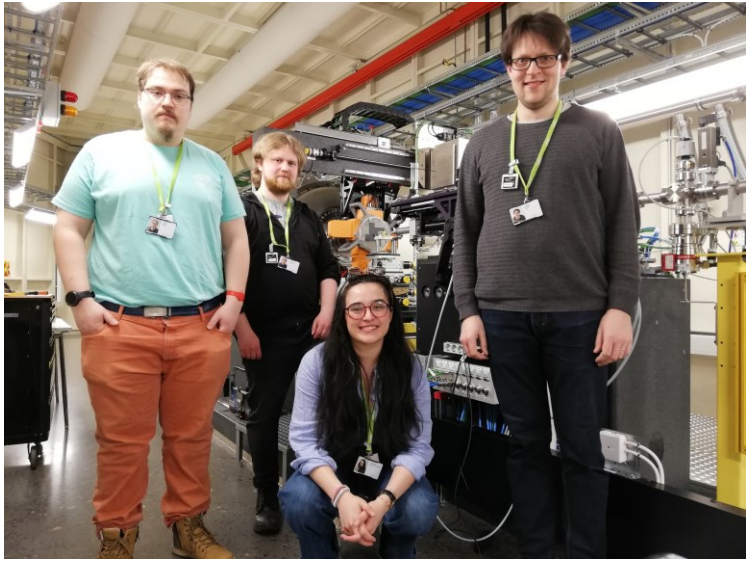
Aalto-universitetet
Högskolan för
kemiteknik

Paavo Penttilä

September 13, 2023

Teacher: *Paavo Penttilä*

- PhD from University of Helsinki, Department of Physics 2009–2013
  Thesis title: “Structural characterization of cellulosic materials using x-ray and neutron scattering”
- Postdocs at Kyoto University (2014–2016), Institut Laue-Langevin (2017–2018), Aalto University (2018–2021)
- Academy Research Fellow and leader of *Biobased Materials Structure* group 2021–



Group at ForMAX/MAX IV synchrotron, April 2023
(from the left: Aleksi, Patrik, Enriqueta, Paavo)

Learning objectives

After this week, you can…

- *describe* what information X-ray scattering can provide from wood materials
- *distinguish* between WAXS/XRD and SAXS in practice and regarding the information that can be obtained
- *summarize* the main strengths and weaknesses of X-ray scattering methods in characterizing wood materials
- *name* where X-ray scattering methods are available and how they can be accessed

We will get back to these questions at the end of the lecture

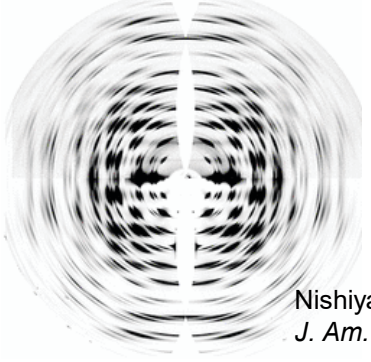
Introduction to the topic

What have we learned about wood by scattering methods?

- **Crystal structure of cellulose**
- **Structure of cellulose microfibril**
  Size, shape, molecular-level ordering
- **Packing of microfibrils into bundles**
  Packing distance between microfibrils, effects of moisture on fibril packing
- **Orientation of microfibrils**

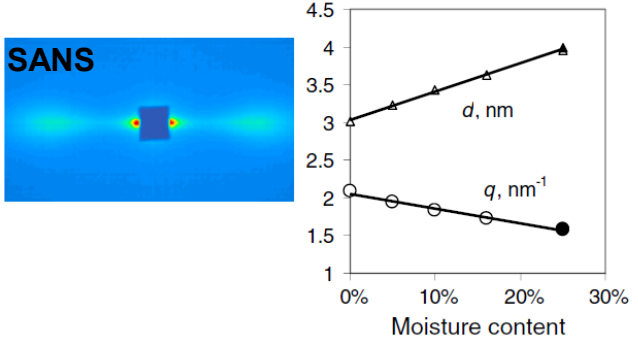
Structure inside "untouched" wood cell walls at different moisture states or in treated samples

Fiber diffraction pattern of cellulose I_β



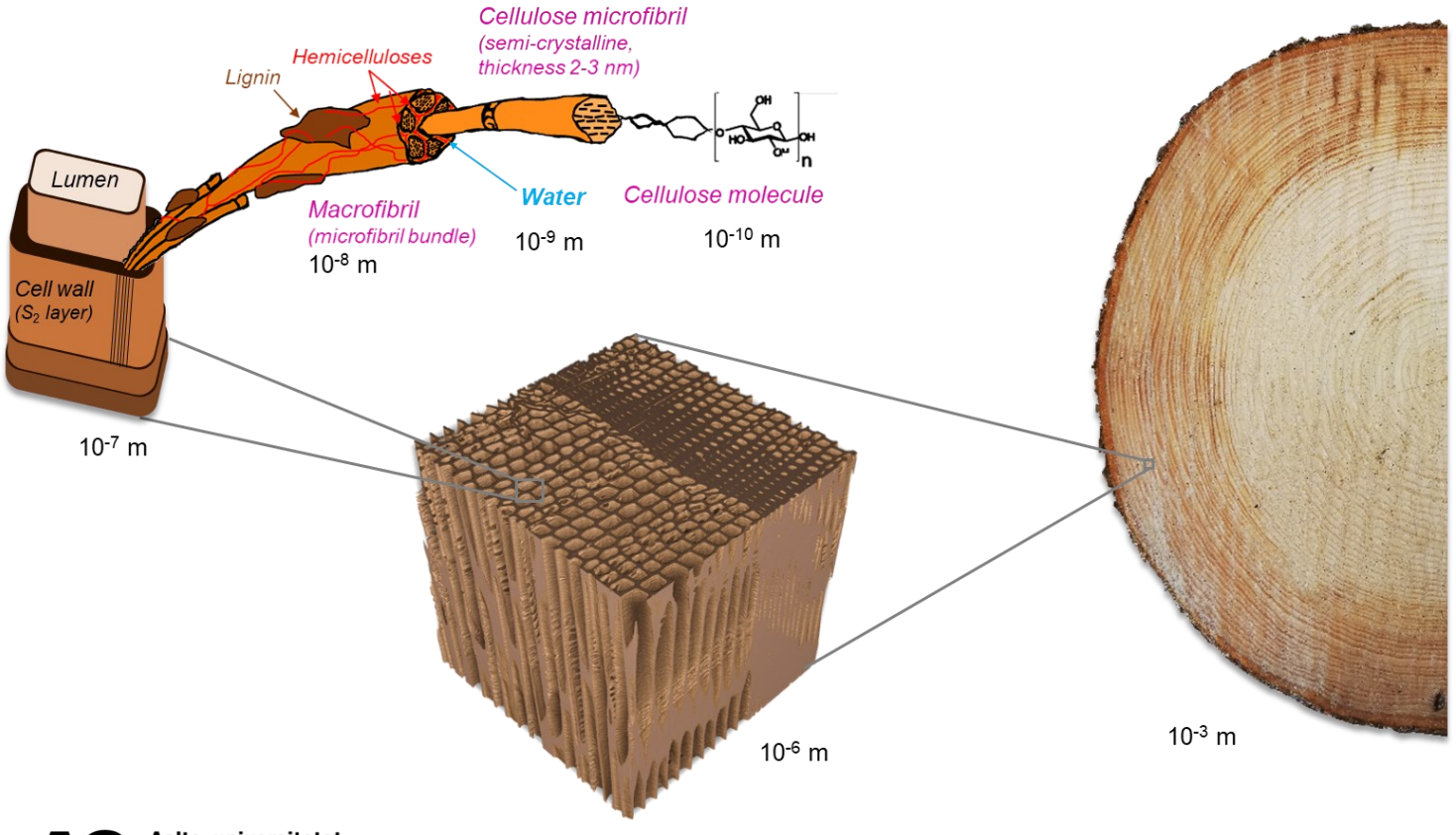
Nishiyama et al. (2002), *J. Am. Chem. Soc.*, 124:9074

Microfibril packing as a function of moisture content



Fernandes et al. (2011), *PNAS*, 108:E1195

Nanostructure of the wood cell wall



Electron tomography reconstruction of S_2 layer in spruce

Fernando et al. (2023), *Sci. Rep.*, 13:2350

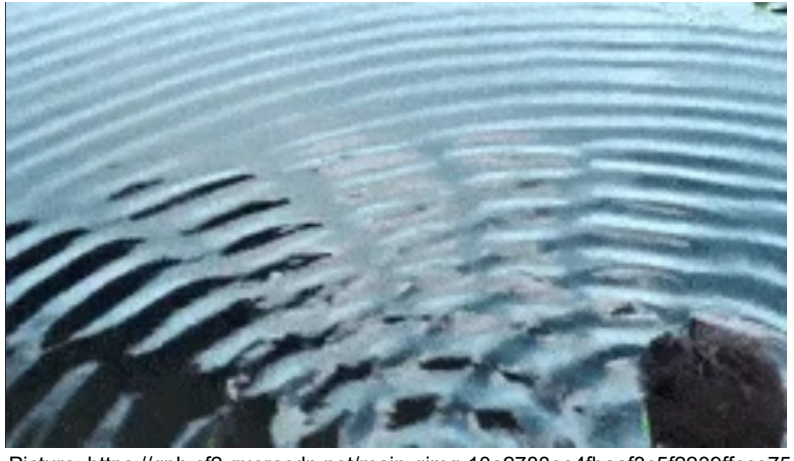
Aalto-universitetet
Högskolan för
kemiteknik

What happens when water is introduced into the wood cell wall?

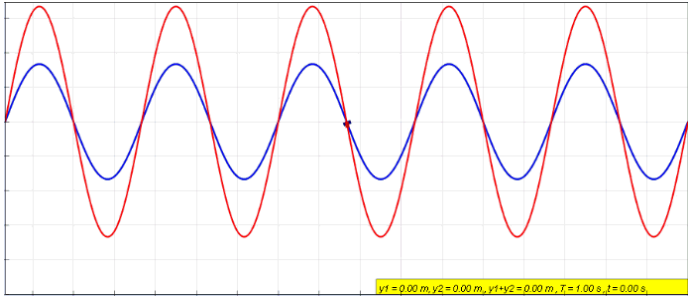
Basics of scattering techniques

Interference of waves

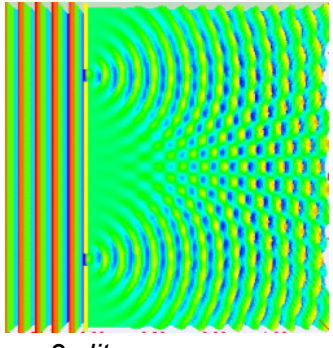
- Waves interfere with each other, leading to constructive or destructive interference
- Geometry and wavelength determine the interference pattern



Picture: https://qph.cf2.quoracdn.net/main-qimg-10a2788ee4fbaaf3c5f2239ffcce75ad
Full video: https://www.youtube.com/watch?v=Iuv6hY6zsd0, 4:29-5:39



Picture: https://commons.wikimedia.org/wiki/File:Waventerference.gif



Incoming wavefront

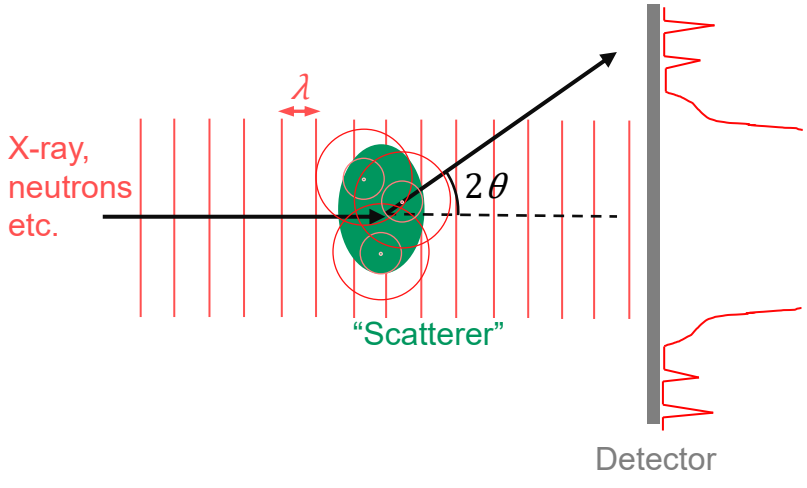
Interference pattern

2 slits

Picture: https://commons.wikimedia.org/wiki/File:Doubleslit3Dspectrum.gif

What is scattering?

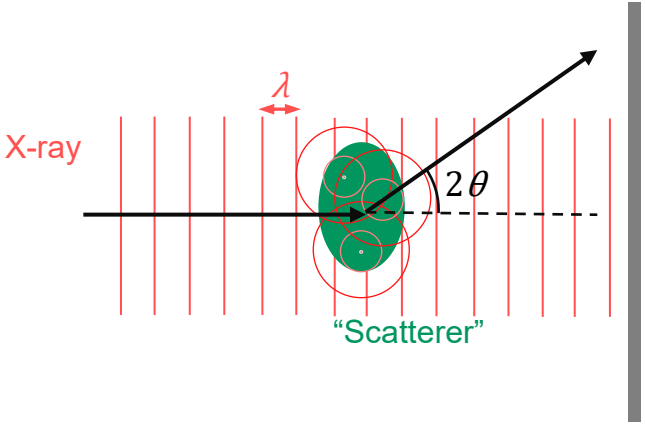
- Waves scattered by matter (*e.g.* particle) interfere with each other, producing a scattering/diffraction pattern that is observed
- Waves can be electromagnetic radiation (X-rays, visible light) or particles having wave character (neutrons, electrons)

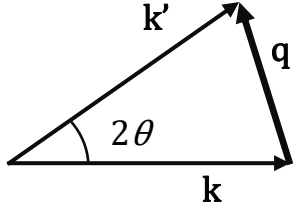


Scattering vector

Scattering is often described as a function *scattering vector* **q** and especially its magnitude *q* (unit Å^{-1} or nm^{-1}):

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





Scattering vector **q**:

$\mathbf{q} = \mathbf{k} - \mathbf{k'}$

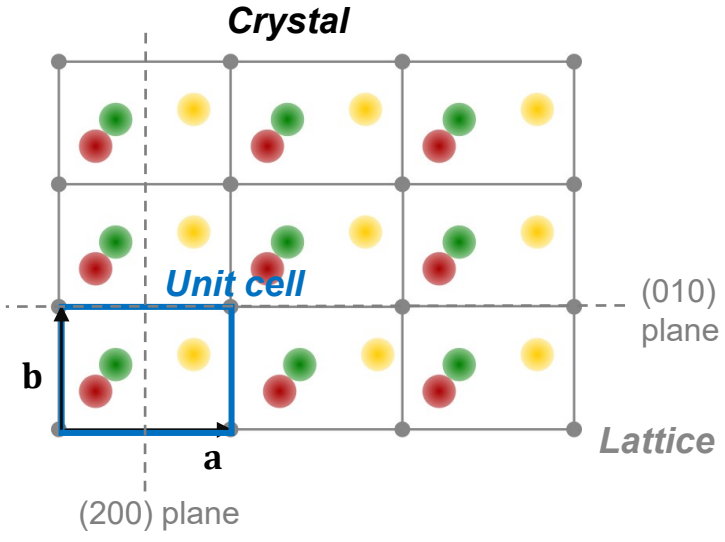
$|\mathbf{k}| = |\mathbf{k'}| = k = 2\pi/\lambda$ (elastic scattering)

$$q = |\mathbf{q}| = 2k\sin\theta = \frac{4\pi \sin\theta}{\lambda}$$

Why is it better to plot scattering intensities as a function of q (instead of 2θ)?

Diffraction by crystals

Crystalline material has long-range order of atoms/molecules



Which component in wood is crystalline (at least partially)?

Diffraction by crystals

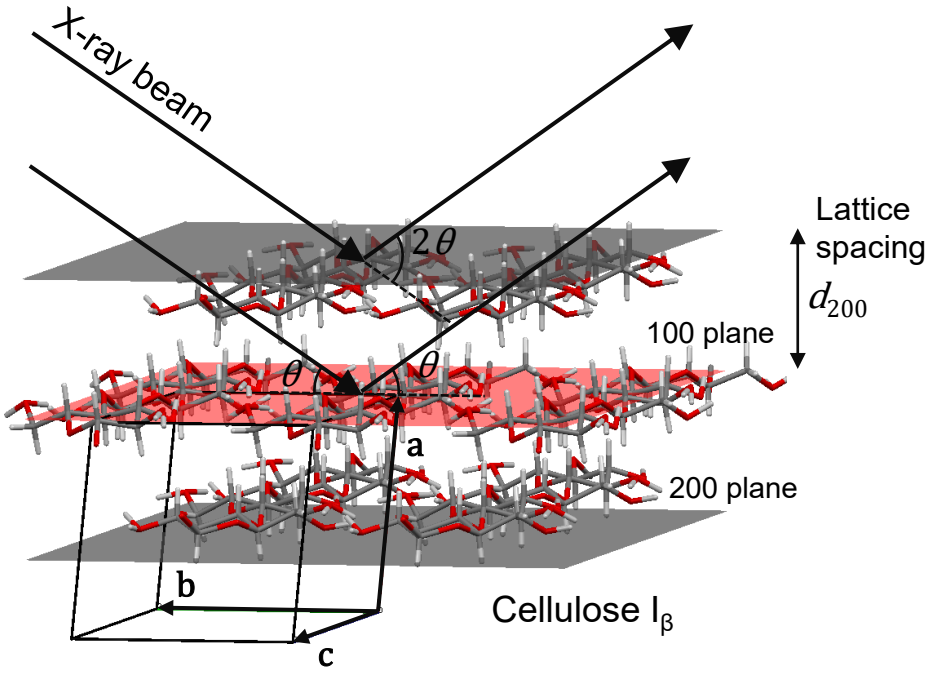
- Crystalline order leads to strong interference effects in scattering
- In a simplified view, diffraction can be thought as X-rays being reflected from the lattice planes
- The positions of the peaks follow **Bragg's law**:

$$2d \sin\theta = k\lambda$$

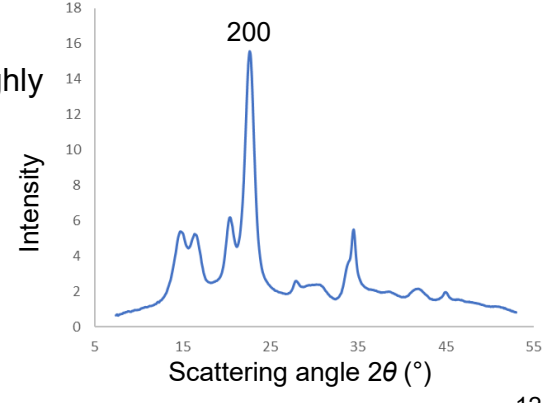
with $k = 1,2,3, \ldots$

or as a function of q:

$$d = 2\pi/q$$



Diffraction pattern of highly crystalline cellulose I_β (cotton filter paper)

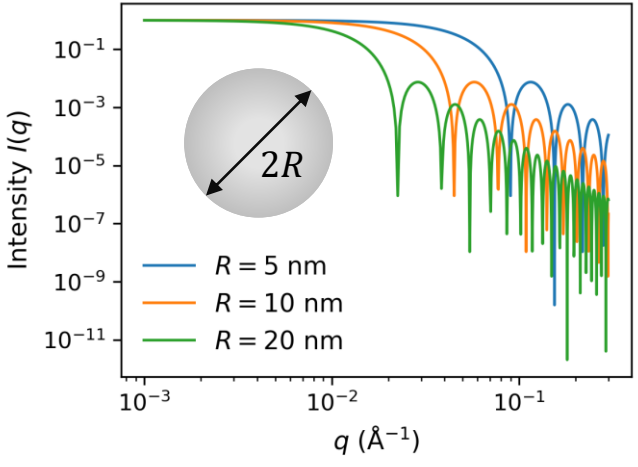


To which direction does a diffraction peak shift when its lattice spacing increases?

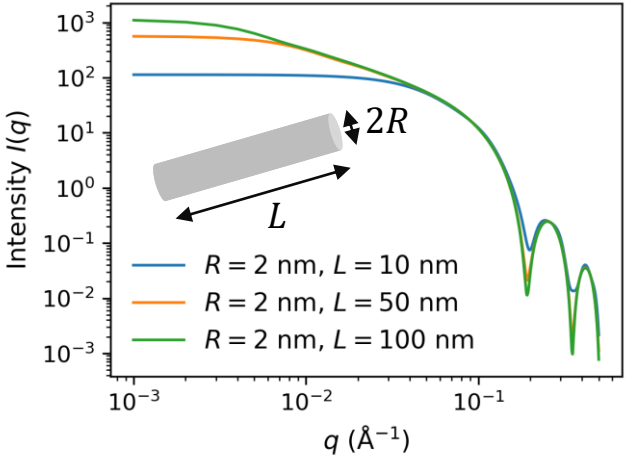
Scattering by weakly ordered materials

- Also non-crystalline materials scatter X-rays
- Structural information can be obtained from scattering patterns
- Especially at small scattering angles (2θ up to a few degrees), scattering can describe the nanoscale morphology

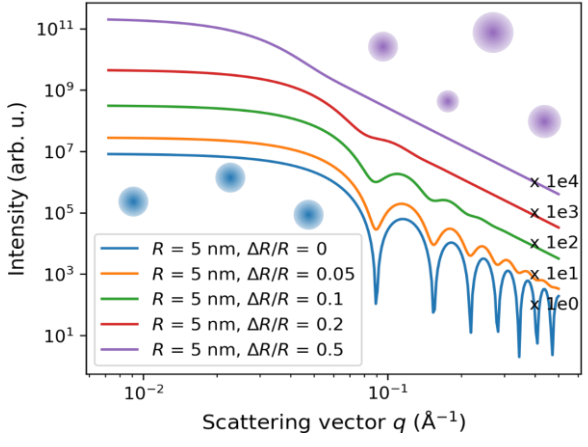
Spheres (radius *R*)



Cylinders (radius *R*, length *L*)



Spheres with polydisperse radius



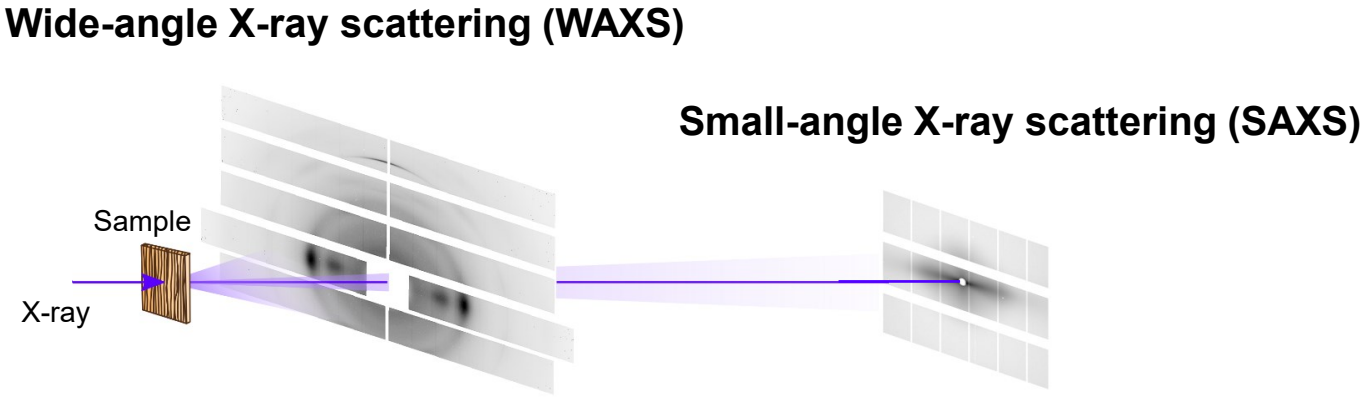
Polydispersity leads to loss of sharp features in scattered intensity

Aalto-universitetet
Högskolan för kemiteknik

Larger structures scatter at smaller angles (or smaller q)

Wide and small-angle scattering

- **Wide-angle scattering** for atomic-scale ordering (crystals)
- **Small-angle scattering** for structures in the nanoscale (> 1 nm), sensitive to spatial variation in scattering length density



Structure size vs. detector position

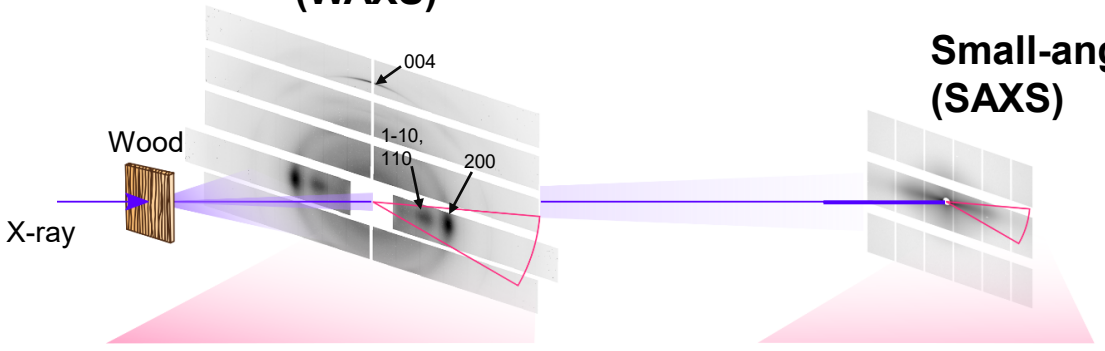
X-ray scattering from wood

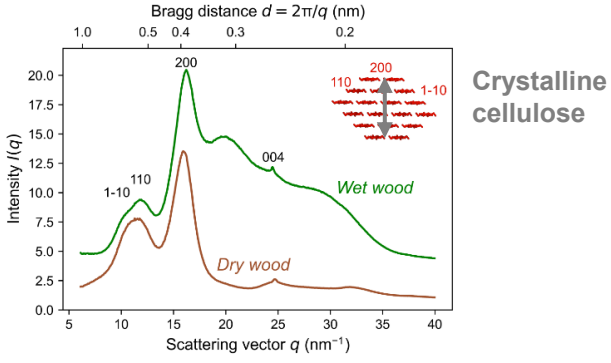
Aalto-universitetet
Högskolan för
kemiteknik

X-ray scattering from wood

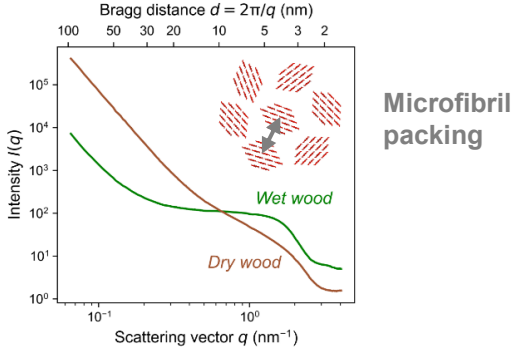
Wide-angle X-ray scattering (WAXS)

Small-angle X-ray scattering (SAXS)





Crystalline cellulose



Microfibril packing

- Lattice spacings
- Crystallite size

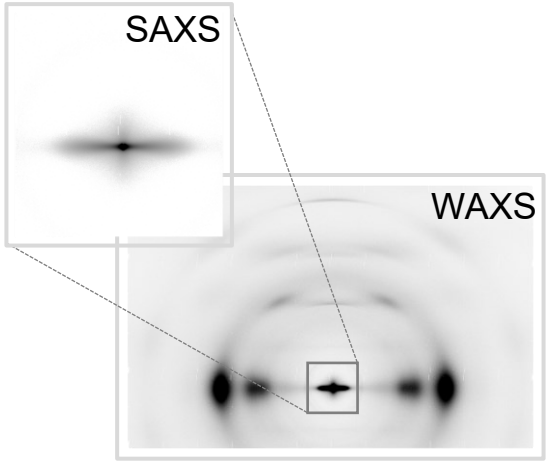
- Microfibril diameter
- Packing distance
- Orientation

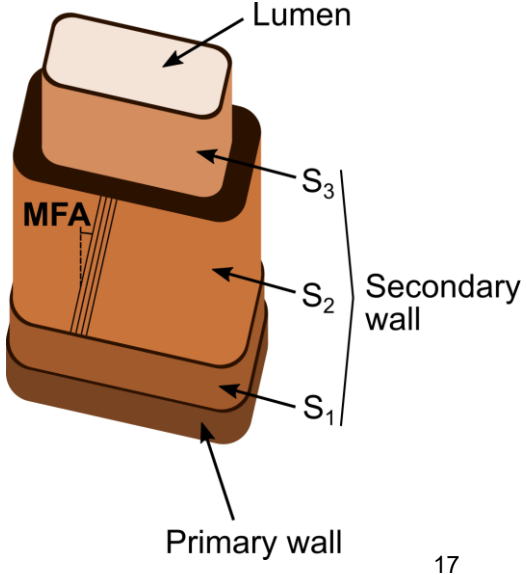
Aalto-universitetet
Högskolan för kemiteknik

Orientation

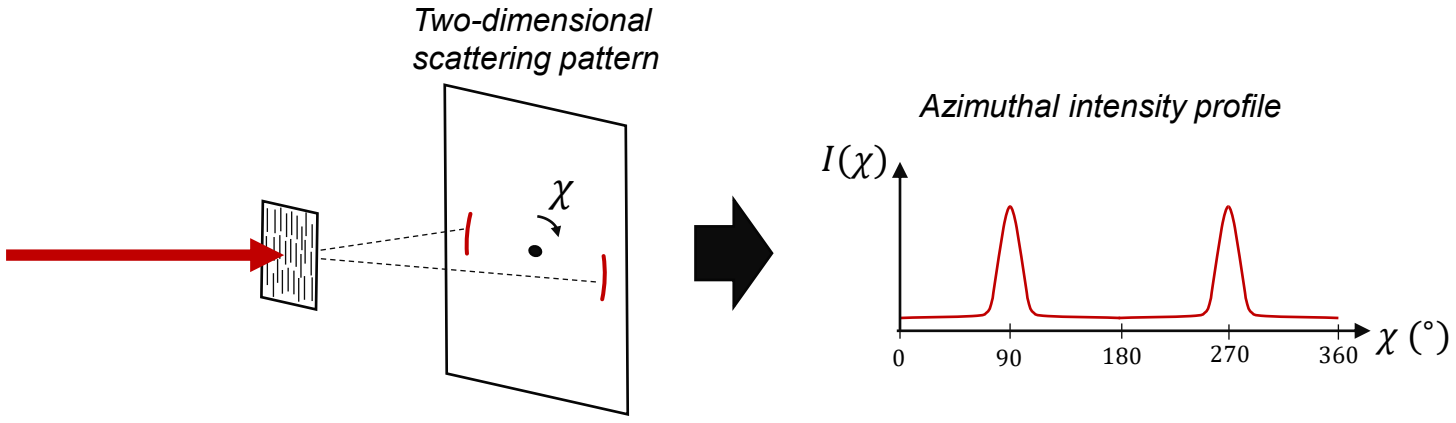
- Preferred orientation of structures (*e.g.* crystals) produces an oriented scattering pattern
- Scattering can be used to determine preferred orientation in a sample, both at the molecular level and in the nanoscale
- Microfibril angle (MFA) in wood can be analyzed from azimuthal intensity distribution (either WAXS or SAXS)

Why is the MFA important?

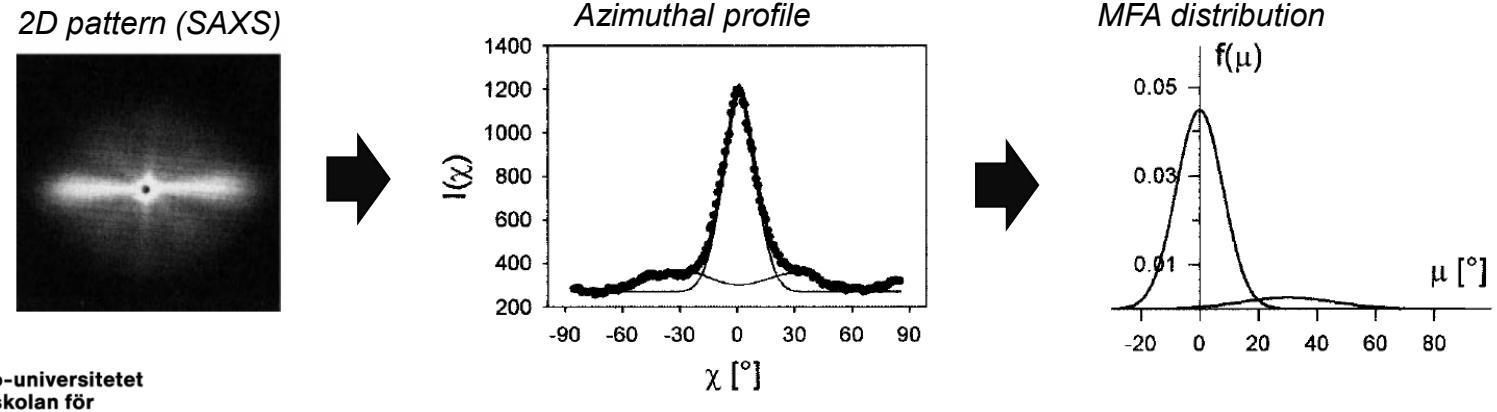




Analysis of microfibril angle



Example: MFA determination for beech wood



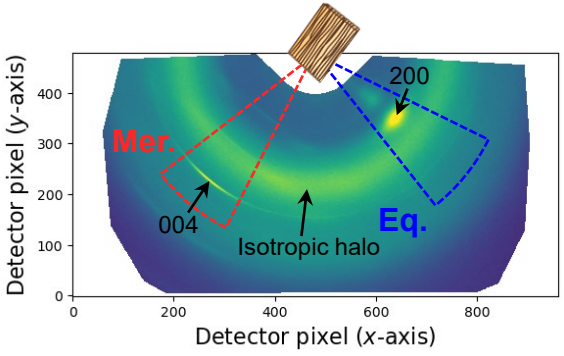
Lichtenegger et al. (1999), *J. Struct. Biol.*, 128:257

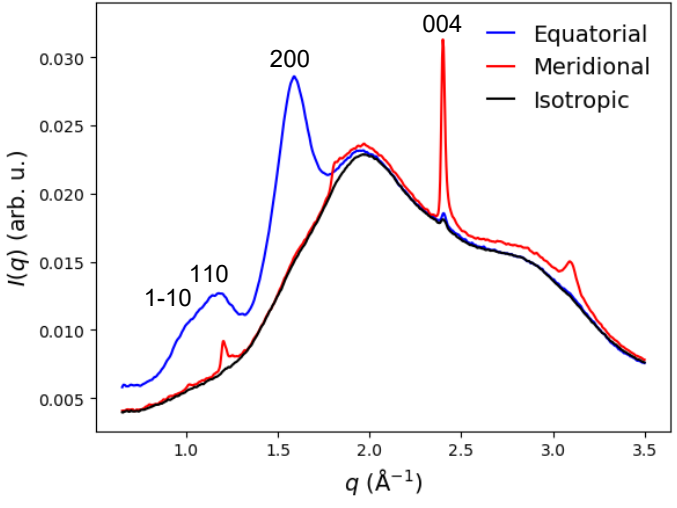
WAXS from wood samples

- Experimental scattering data contains contributions from all atoms that were on the path of the X-ray beam
- How to distinguish between scattering from (crystalline) cellulose and other components (hemicelluloses, lignin, water)?

General rule (can be discussed):
Crystals show diffraction peaks, non-crystalline material only broad halos

Spruce wood saturated with water





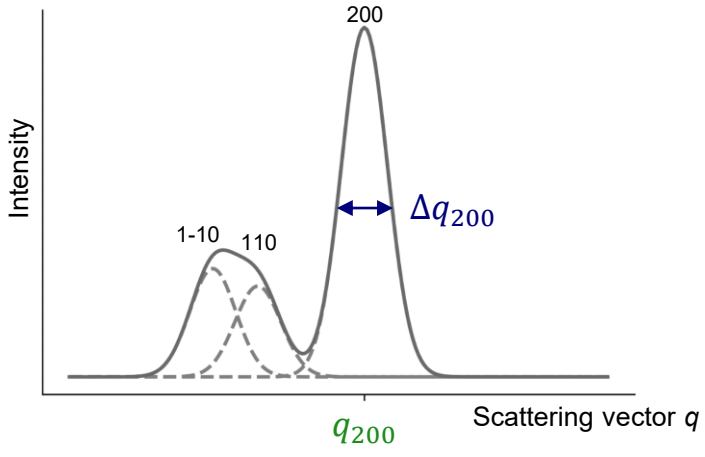
WAXS analysis of wood

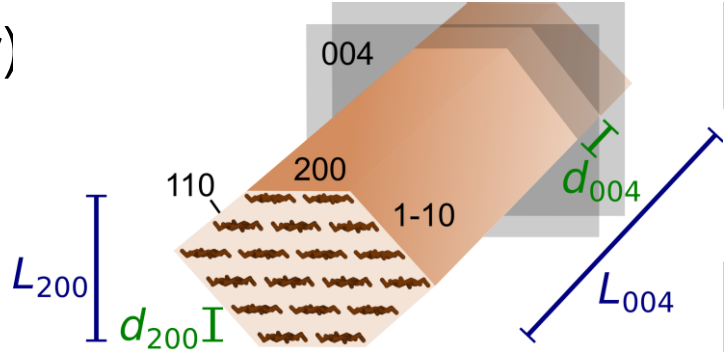
- Crystalline cellulose yields diffraction peaks corresponding to different directions in the crystal
- **Peak location** related to lattice spacing (distance between cellulose chains)

$$d_{hkl} = \frac{2\pi}{q_{hkl}}$$ (Bragg's law)

- **Peak width** related to *crystal size* (coherence length of crystalline order)

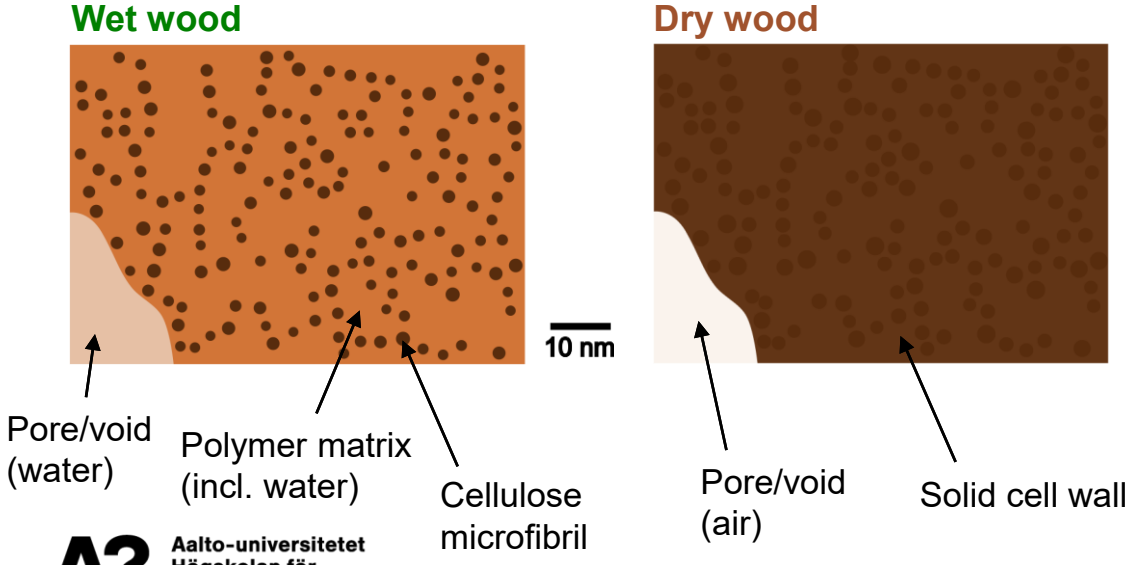
$$L_{hkl} = \frac{2\pi K}{\Delta q_{hkl}}$$ (Scherrer equation)

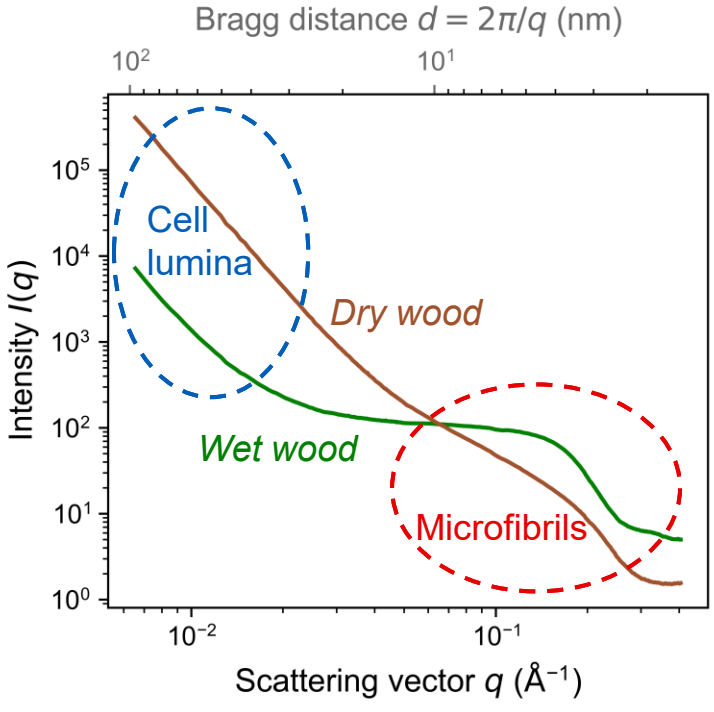




SAXS from wood samples

- SAXS senses spatial variations of density
- Different structures contribute to scattering at different *q*-values and under different moisture conditions



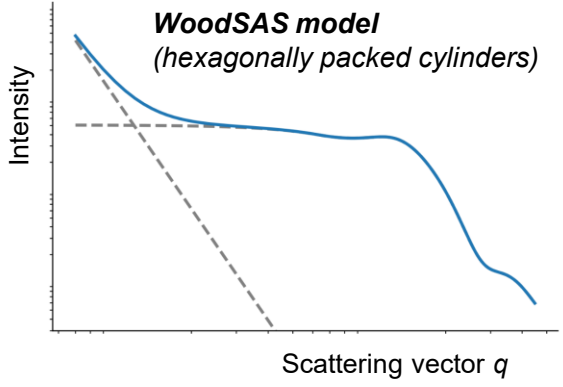


Aalto-universitetet
Högskolan för kemiteknik

SAXS analysis of wood

- Scattering from different levels of structural hierarchy can be separated
- Contributions from microfibril cross-section and packing intertwined, challenging to distinguish
- WoodSAS model aims to provide
  - distance between microfibrils
  - diameter of microfibrils

  (possible to interpret and fit the data also in other ways)



Microfibril diameter ~2.5 nm

Packing distance ~4 nm
in water-saturated wood,
~3 nm in dry wood

WoodSAS model: Penttilä et al. (2019), *J. Appl. Crystallogr.*, 2019

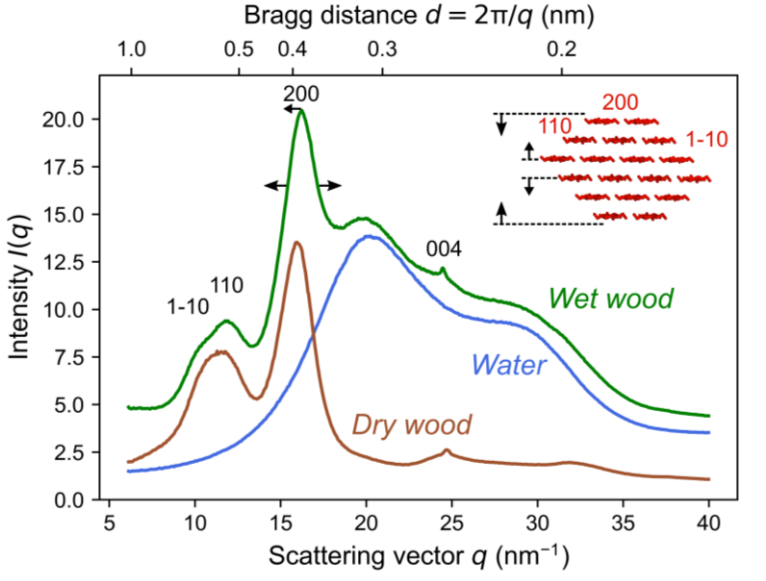
Example: Moisture interactions of wood studied with X-ray scattering

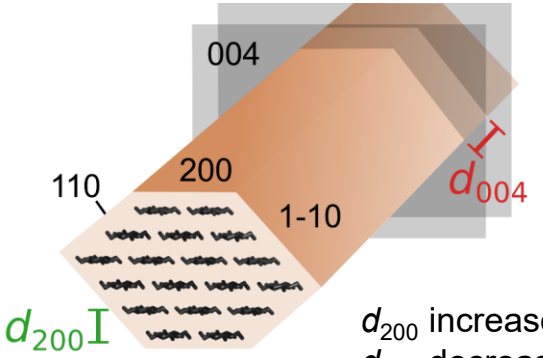
Water modifies the cell wall structure

- Wood nanostructure is sensitive to moisture, which explains *e.g.* swelling
- Diffraction peaks of cellulose shift and broaden with drying

e.g. Abe et al. (2005), *J. Wood. Sci.*, 51:334-338

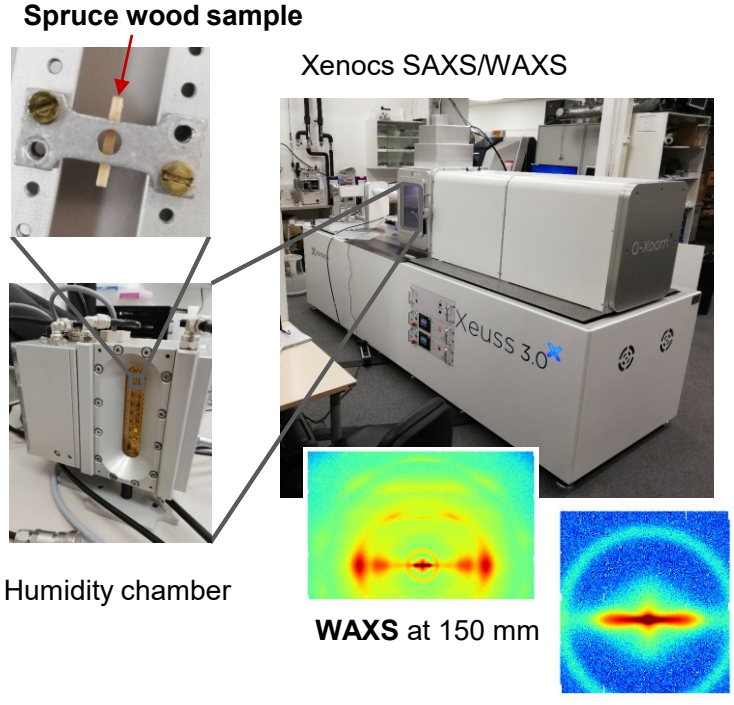
But why?

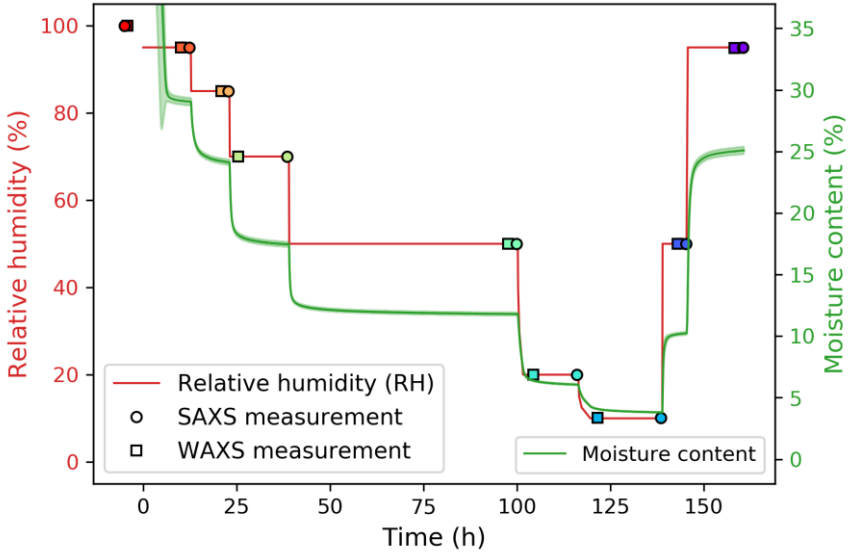




d_{200} increases and
d_{004} decreases with drying

X-ray scattering at controlled humidity





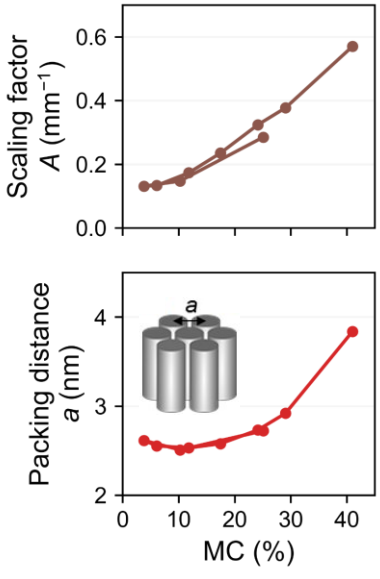
Humidity cycle in RH range 10–95%, moisture content (MC) determined using a gravimetric method

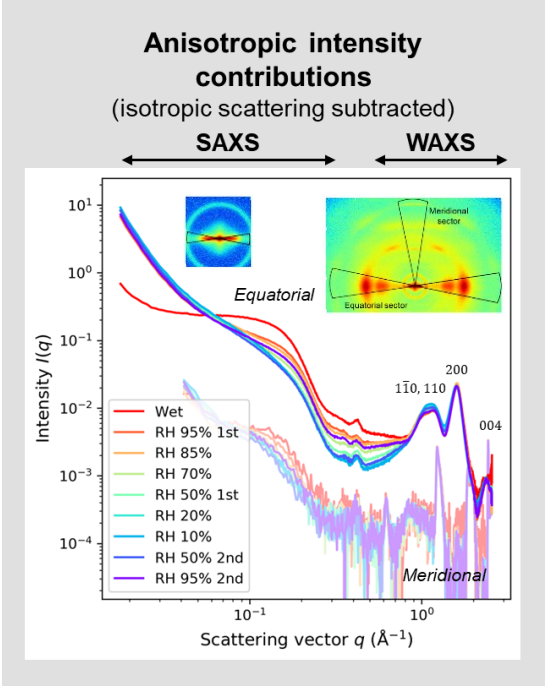
$$\mathrm{MC}\ (\%) = m_{\mathrm{water}}/m_{\mathrm{dry}}$$

Aalto-universitetet
Högskolan för kemiteknik

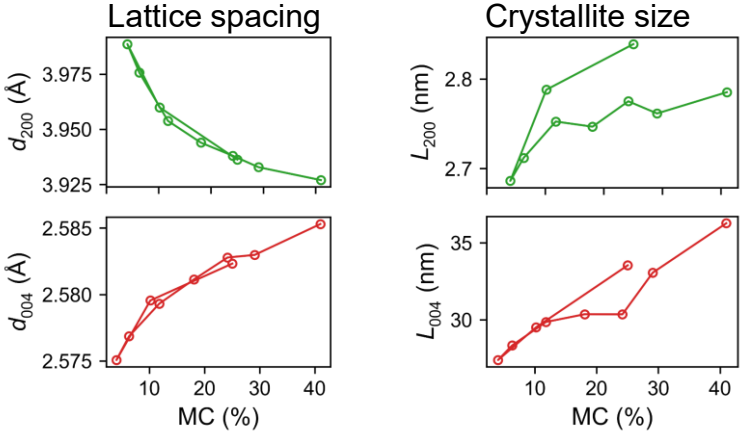
SAXS/WAXS at different moisture contents

Fibril bundles swell with increasing moisture content



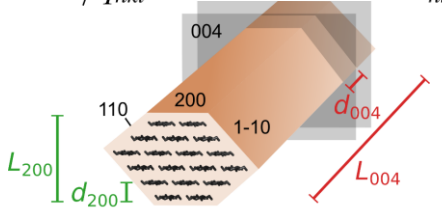


Peaks shift and broaden with drying



$$d_{hkl} = 2\pi / q_{hkl}$$

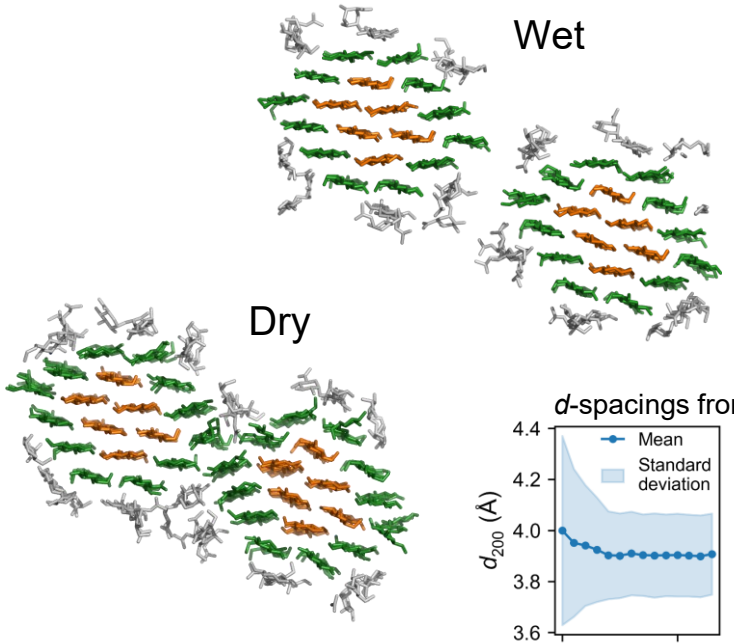
$$L_{hkl} = \frac{2\pi}{\Delta q_{hkl}}$$

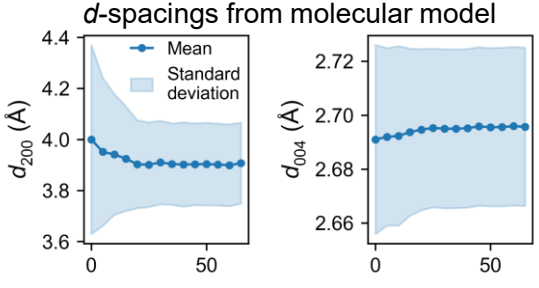


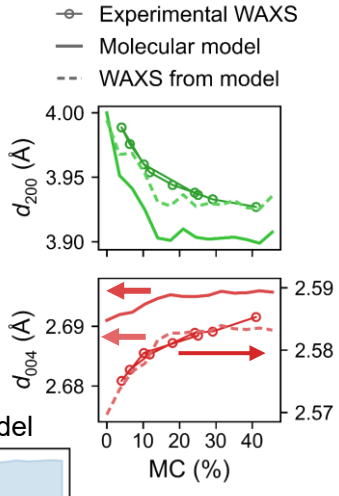
Paajanen et al. (2022), *Nano Letters*, 22:5143-5150

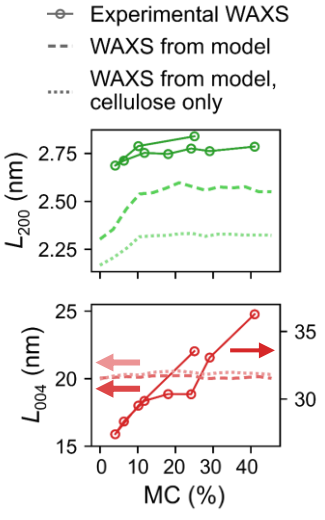
Modelling-assisted scattering analysis

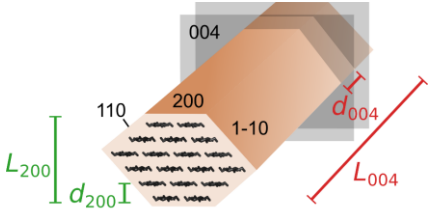
(collaboration with VTT Technical Research Centre of Finland)











Aggregation deforms crystals at low moisture contents

Paajanen et al. (2022), *Nano Letters*, 22:5143-5150

General aspects of X-ray scattering experiments

Aalto-universitetet
Högskolan för
kemiteknik

Strengths and weaknesses of scattering methods

Strengths

- Simple sample preparation, wet samples OK
- Average structure obtained efficiently
- Cover structures from molecular scale to ~10^2 nm
- *In situ* measurements as a function of time or in response to temperature, moisture, stress etc.

Weaknesses

- Averaging nature, no sensitivity to individual details
- Challenging data analysis

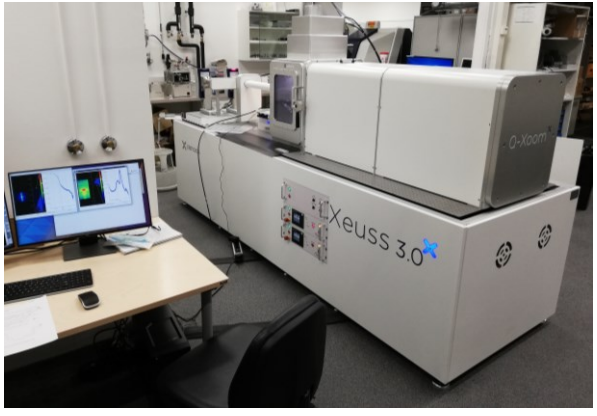
How do they compare to other methods you might use or know?

Where to measure X-ray scattering

- Laboratory X-ray scattering device (and some diffractometers) available at Aalto University

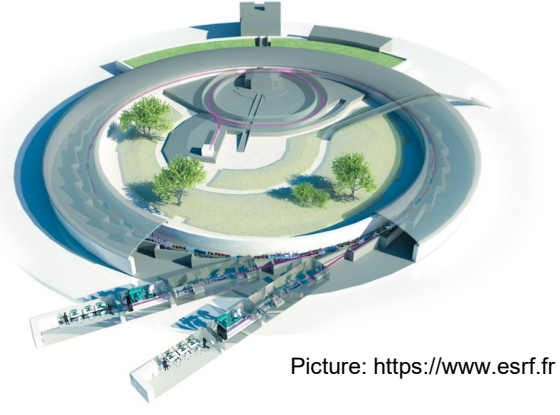
Demonstrations!

- For more complex (e.g. time-resolved experiments or scanning with small beam), beamtime at synchrotrons can be applied in bi-annual proposal rounds (or purchased)



Xenocs SAXS/WAXS in Nanotalo


MAX IV synchrotron in Lund, Sweden


Picture: https://www.esrf.fr

Summary

Summarizing questions

- What information can X-ray scattering provide from wood materials?
  Cellulose crystal structure, crystal/microfibril size, microfibril packing
- What is the difference between WAXS and SAXS in practice? Regarding the information that can be obtained?
  WAXS: small structures (~1 nm), SAXS: large structures (> 1 nm)
- What are the main strengths and weaknesses of X-ray scattering methods in characterizing wood materials?
  Averaging nature, requirement of assumptions, *in situ* possibilities
- Where are X-ray scattering methods available and how can they be accessed?
  Xenocs SAXS/WAXS at Aalto, synchrotrons abroad

X-ray scattering demonstrations

Teachers: Patrik Ahvenainen, Aleksi Zitting, Enriqueta Noriega Benitez

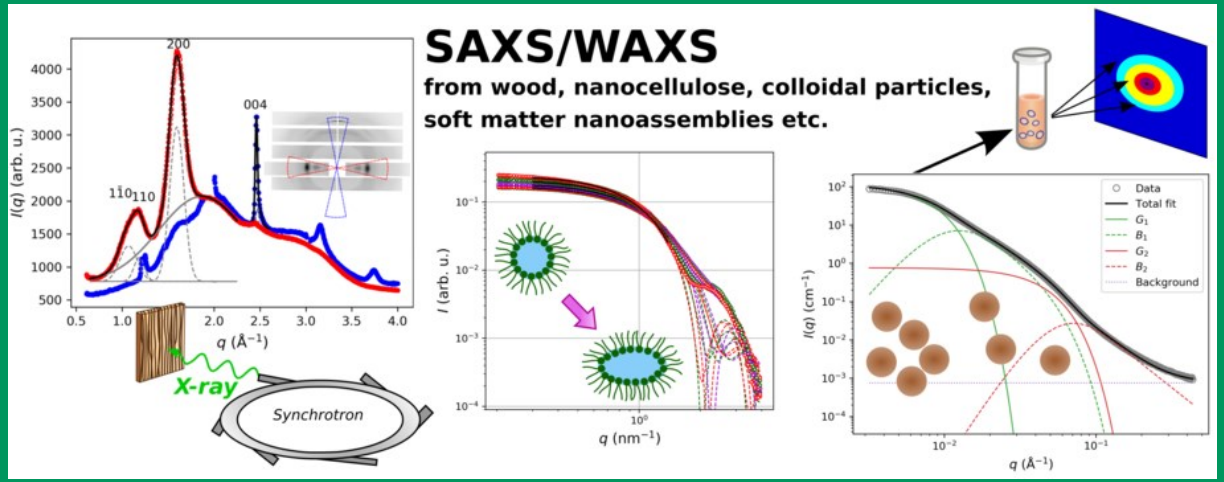
Place: Nanotalo building main entrance, Puumiehenkuja 2
(if needed, call Patrik: 050 4011904)

Groups:

Thu, Sept. 14, 13:30-15:30: Alenius, Kovalainen, Nguyen, Zhang

Fri, Sept. 15, 10:00-12:00: Heikkilä H., Kalac, Pham, Solene

Fri, Sept. 15, 13:30-15:30: Colb, Heikkilä M., Lucas



Interested to learn more?

"CHEM L-2300: X-ray scattering methods for structural analysis of bio-based materials" next time in April-June 2024 (period V)

Questions or comments?

Contact: paavo.penttila@aalto.fi

Aalto-universitetet
Högskolan för kemiteknik

Sources of pictures

All photos and pictures by Paavo Penttilä unless indicated otherwise.