Nanoscale wood-water interactions studied with small-angle neutron scattering

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1. Wood structure and scattering

2. *In situ* SANS drying of wood

3. *In situ* SANS of water exchange in cell wall

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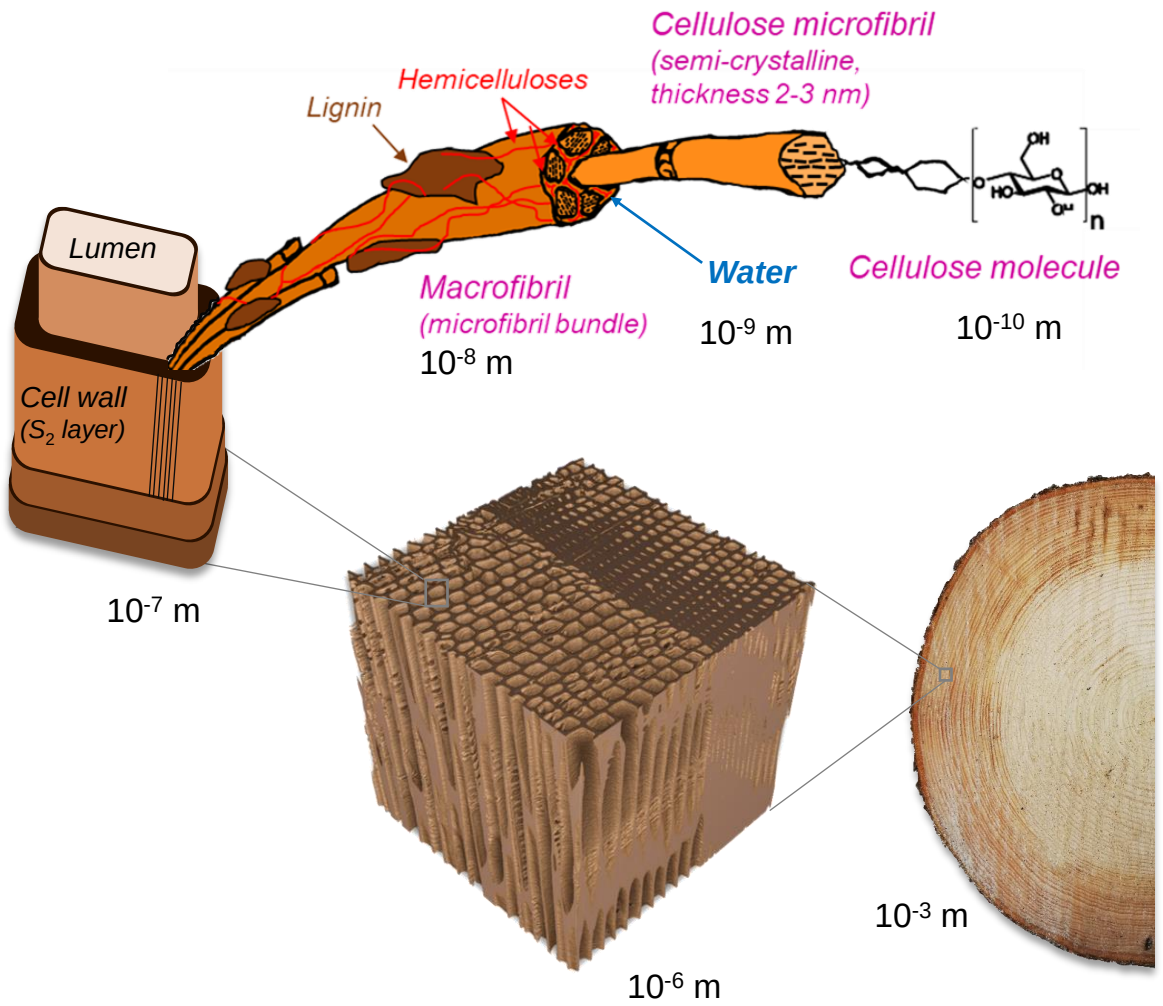
Wood nanostructure and its role

- Hierarchical natural material
- Material properties closely related to cell wall structure
- New applications utilize the nanoscale building blocks of wood cell walls
- Water interactions important



Color from wood. Researchers: B. Tardy, K. Klockars, N. Yau. Photo: V. Azovskaya

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Wood(-based) samples for scattering

- Hierarchical multicomponent systems
- Anisotropic, low degree of order
- Structural heterogeneity
- Sensitivity to environment (*e.g.* humidity)

Representative average in a single exposure, non-destructive sample preparation

Opportunities for *in situ* experiments

Small-angle scattering analysis of wood

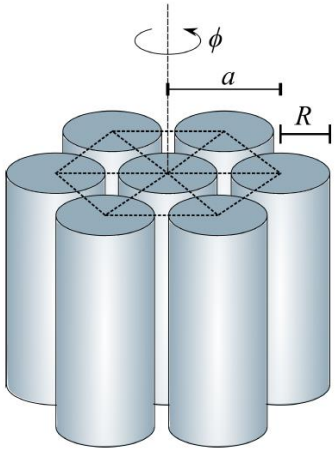
WoodSAS model

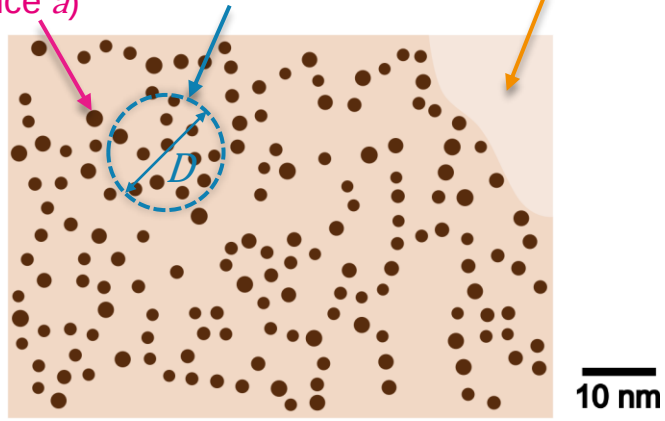
$$I(q) = AI_{cyl,hex,eq,mod}(q) + Be^{-q^2/(2\sigma^2)} + Cq^{-\alpha}$$

Microfibrils (hexagonally packed cylinders, diameter $2R$, distance a)

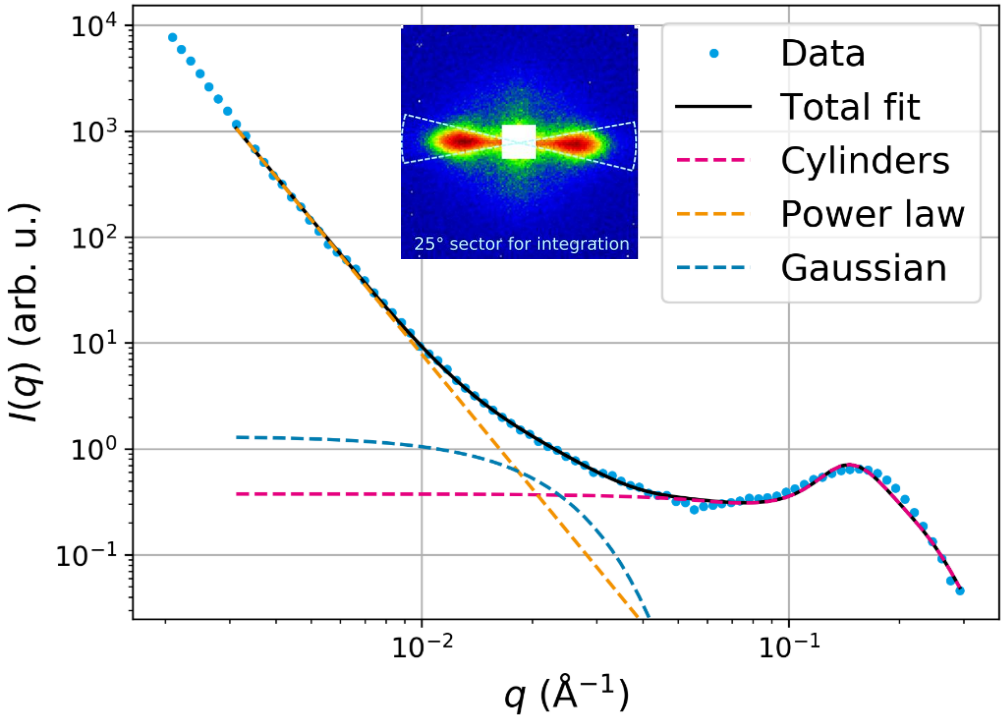
SANS: Microfibril bundles (diameter $D = 2\sqrt{2}/\sigma$)

Large pores/ cell lumina





Equatorial, anisotropic SANS intensity of pine wood in D_2O



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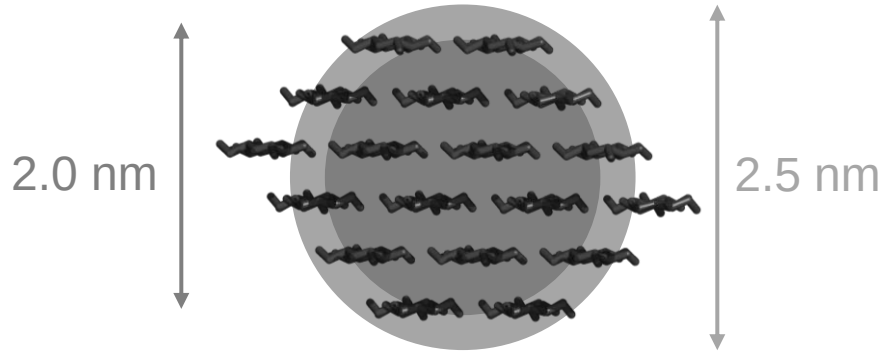
Penttilä et al. (2019), *J. Appl. Crystallogr.*, 52:369
Model available at http://marketplace.sasview.org/

Microfibrils according to WoodSAS

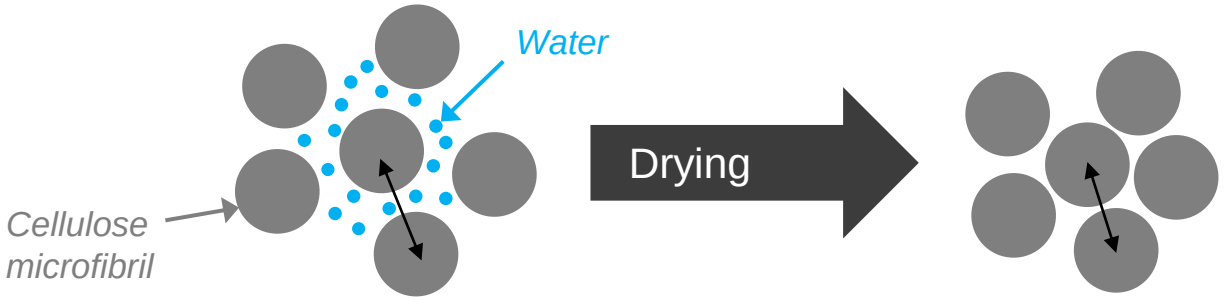
- Diameter of microfibrils:

  2.0 nm (D_2O), **2.3 nm** (H_2O) based on SANS
  2.5 nm based on SAXS



18-chain cellulose crystal

- Microfibril packing distance:



Wet: **3–4 nm**

Dry: **2–3 nm**

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Penttilä et al. (2019), *J. Appl. Crystallogr.*, 52:369-377
Penttilä et al. (2020), *Cellulose*, 27:71-87
Penttilä et al. (2021), *Cellulose*, 28:11231-11245

Other references:
Jakob et al. (1996), *Macromol.*, 29:8435-8440
Fernandes et al. (2011), PNAS, 108:E1195-E1203
Plaza et al. (2016), Cellulose, 23:1593-1607

Microfibril bundles in WoodSAS model

- Diameter of microfibril bundles

$$I(q) = AI_{cyl}(q, \bar{R}, \Delta R, a, \Delta a) + Be^{-q^2/(2\sigma^2)} + Cq^{-\alpha}$$

Microfibrils (hexagonally packed cylinders)

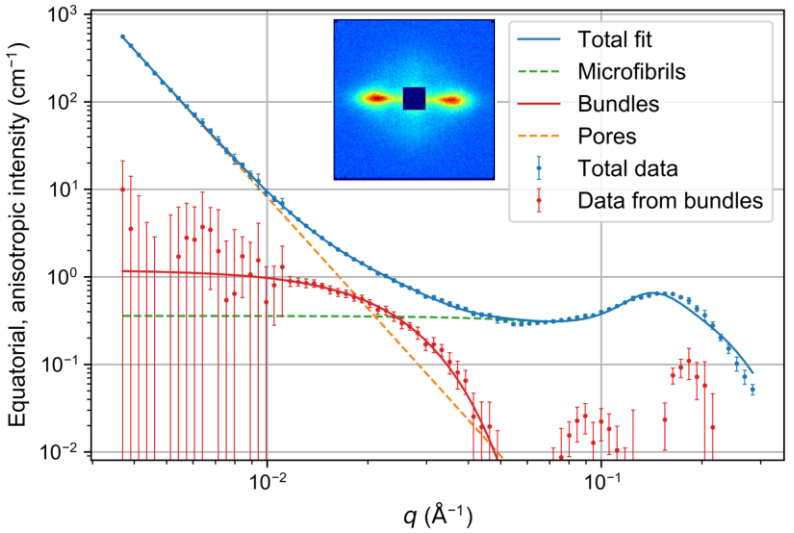
Microfibril bundles (SANS)

Large pores/ lumina

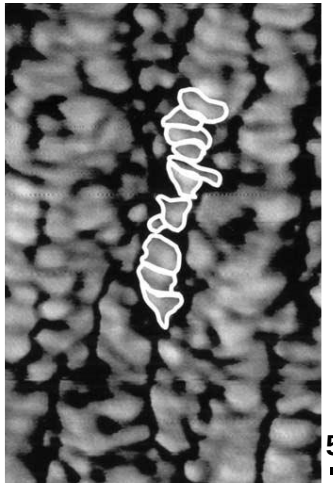
$$\text{Bundle diameter} = \frac{2\sqrt{2}}{\sigma}$$

(assuming Guinier law and circular cross-section)

Pine wood in D_2O



- Variation with species and moisture
  - Wet softwoods 16–19 nm
  - Wet hardwoods 11–14 nm
  - Smaller (8–12 nm) in dry softwood



AFM
Mean bundle width in spruce 18 nm

Fahlén & Salmén (2003), *J. Mat. Sci.*, 38:119-126

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Penttilä et al. (2020), *Sci. Rep.*, 10:20844

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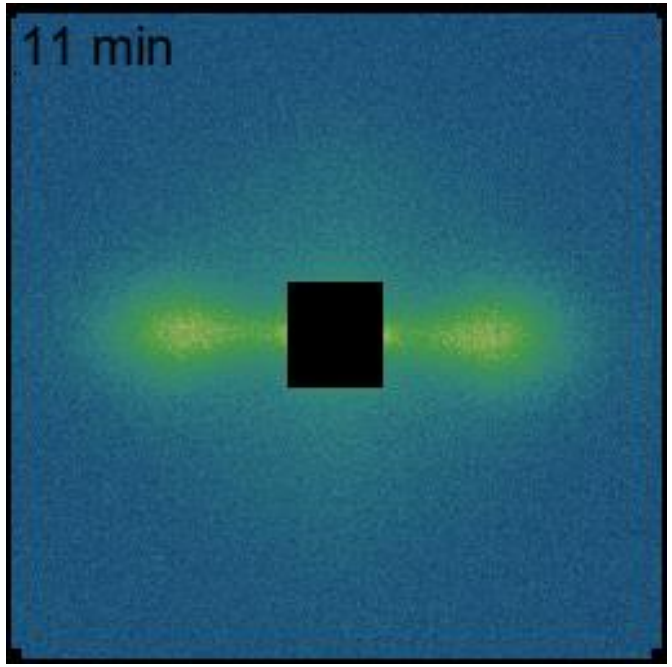
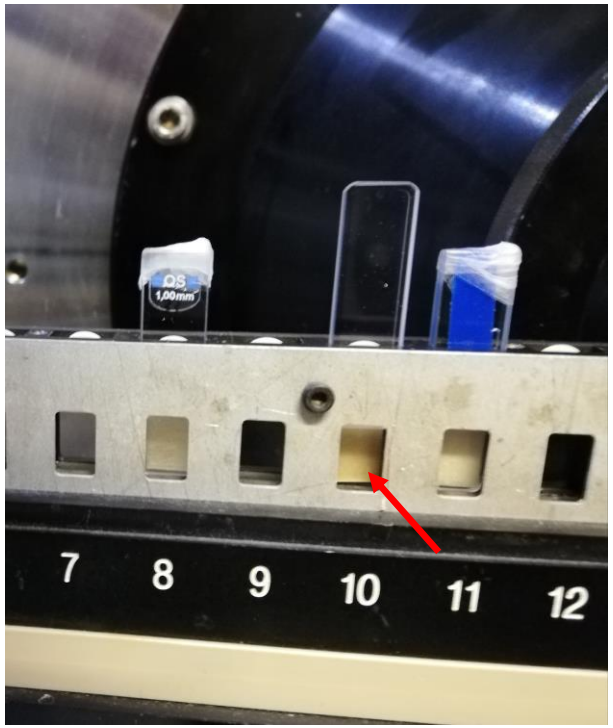
SANS measurement of drying wood

- Time-resolved SANS experiment of D_2O-saturated wood drying in the neutron beam
- Data collected at sample-to-detector distance 1.5 m with time resolution down to 5 min



D11/ILL



T = 24°C,
RH = 26%

Zitting et al. (2021) *Cellulose*, 28:10765

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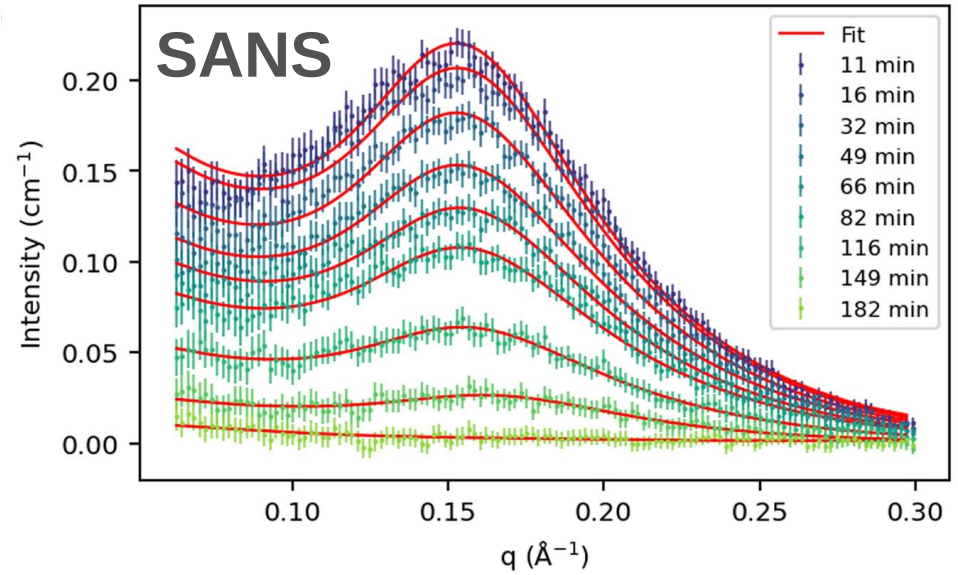
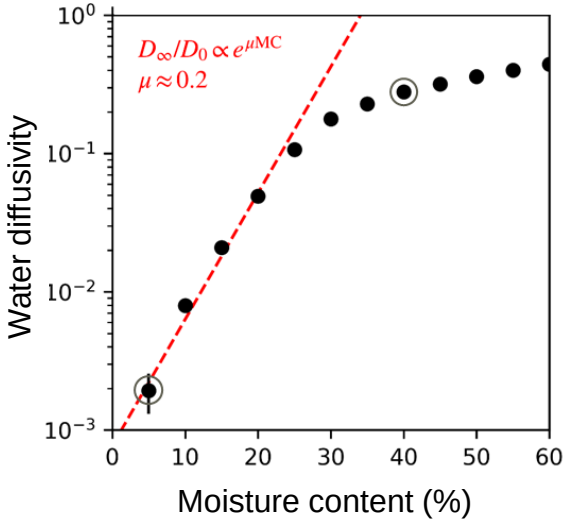
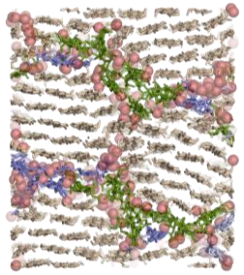
Microfibril bundles deswell with drying

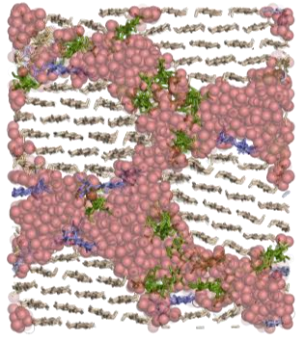
- Microfibrils pack closer as water is removed from between them
- Molecular models reproduced deswelling and showed its implications on water diffusion



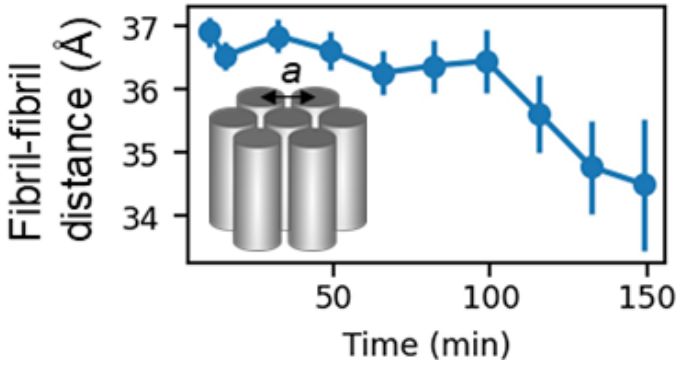




MC 5%



MC 40%



Analysis with WoodSAS model

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Zitting et al. (2021) *Cellulose*, 28:10765

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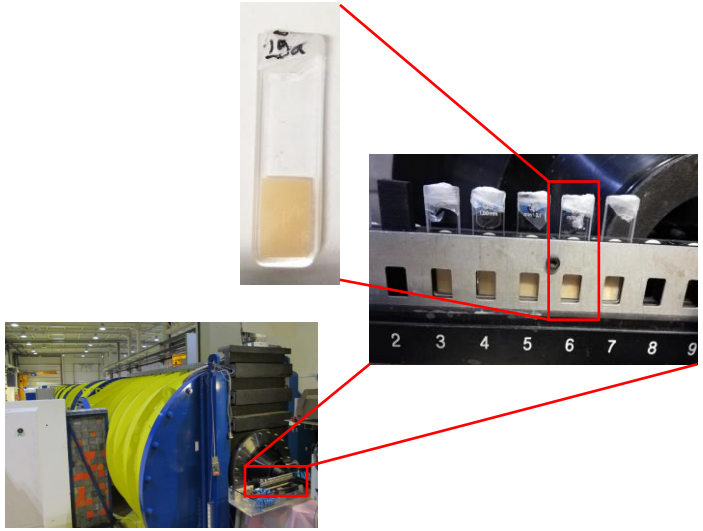
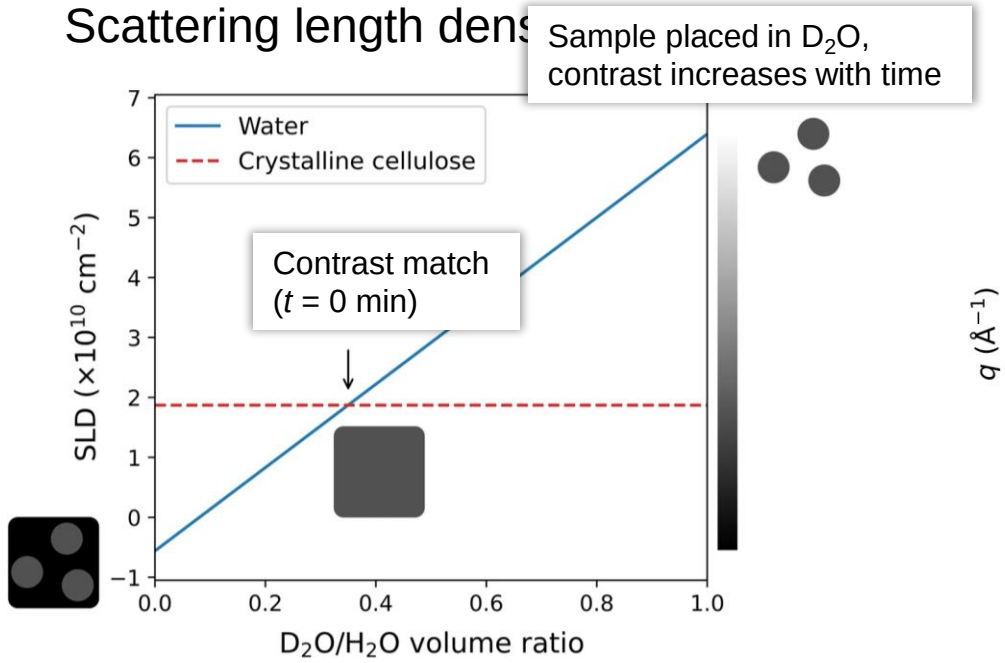
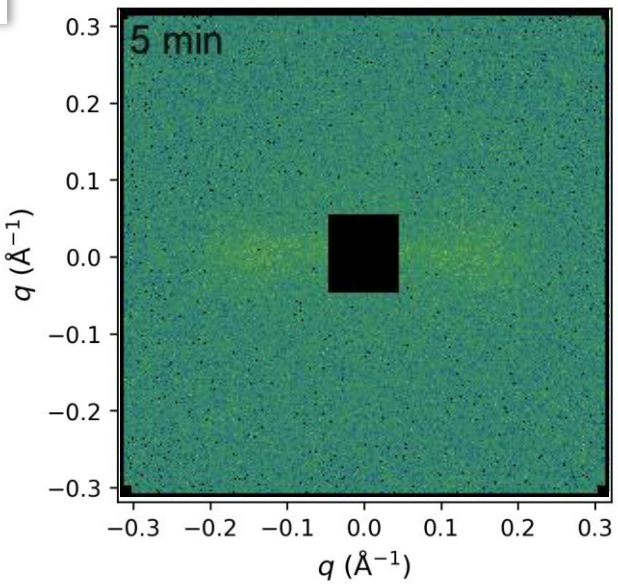
Water accessibility studied with time-resolved SANS



D11, ILL





Exposure time ≥30 s

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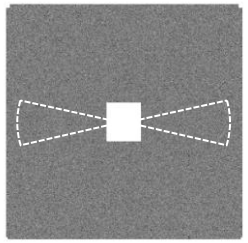
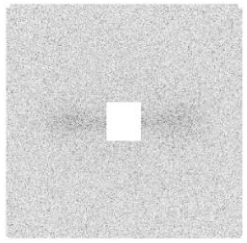
Penttilä et al. (2021), *Cellulose*, 28:11231-11245

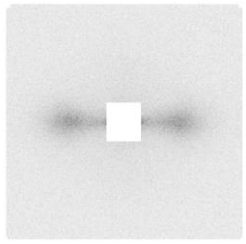
Water accessibility studied with time-resolved SANS



Equilibrated in
65% H_2O/35% D_2O

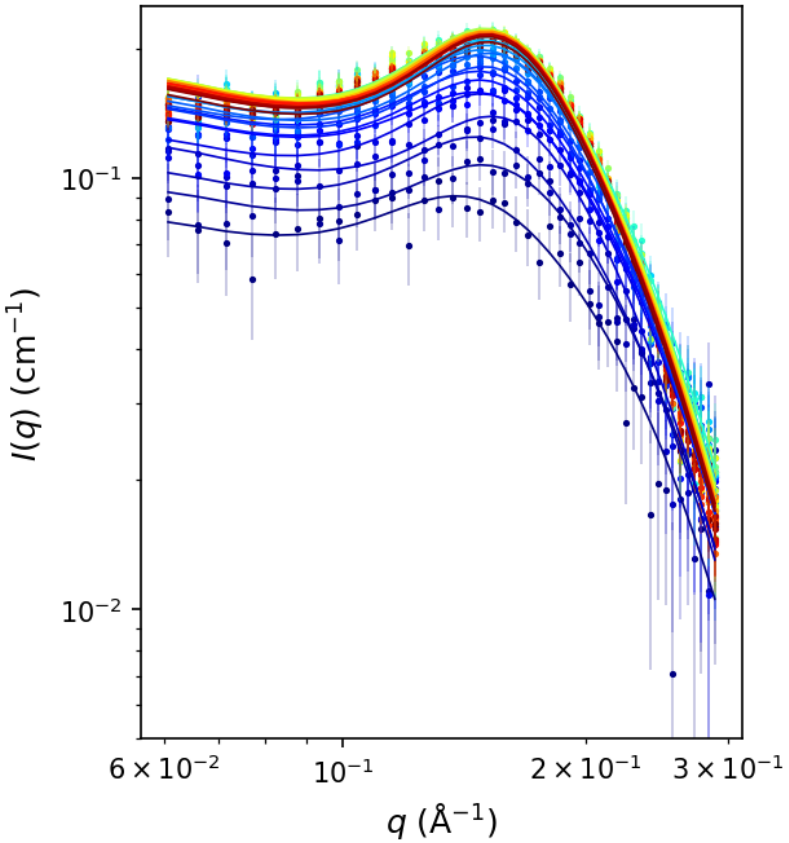


5 min after immersing
in 100% D_2O



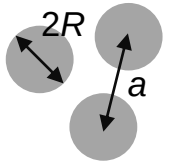
30 h after immersing
in 100% D_2O

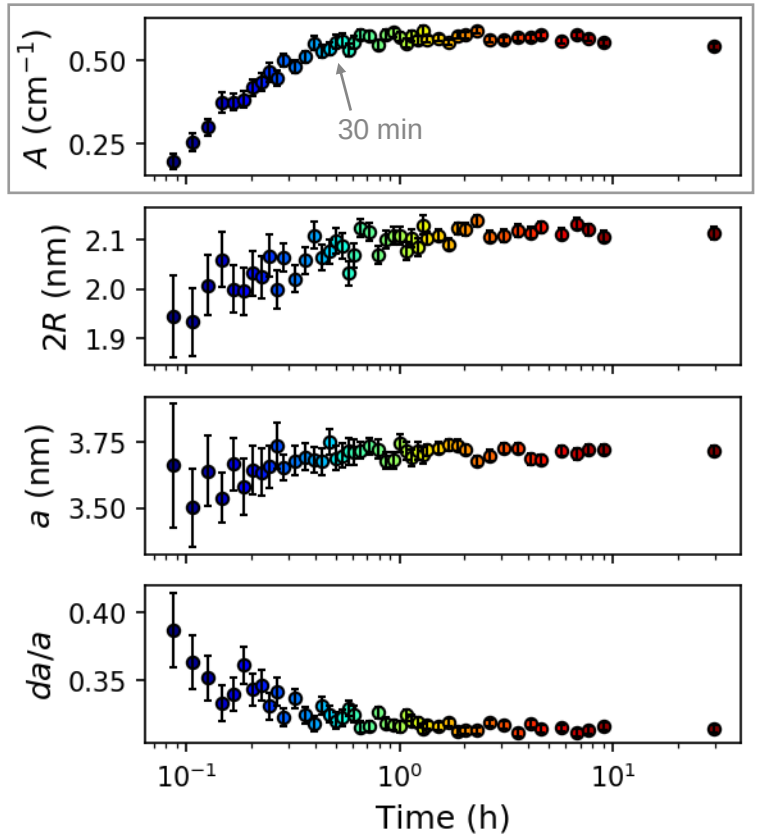
Equatorial, anisotropic SANS intensity



Fits with microfibril term of WoodSAS model

$$I(q) = A I_{cyl}(q, \bar{R}, \Delta R, a, \Delta a)$$





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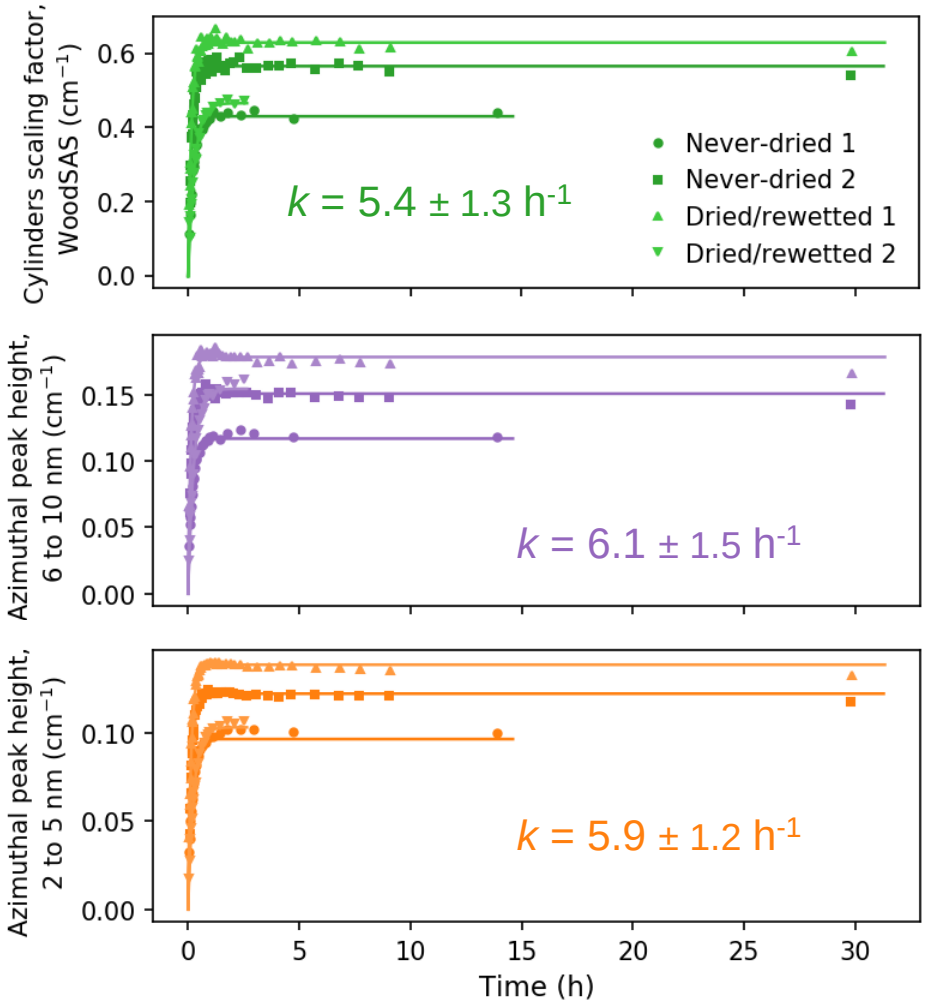
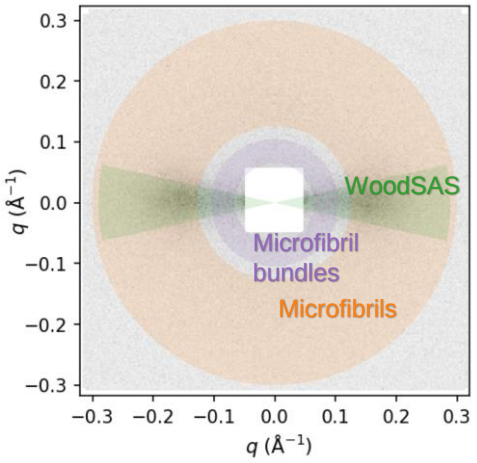
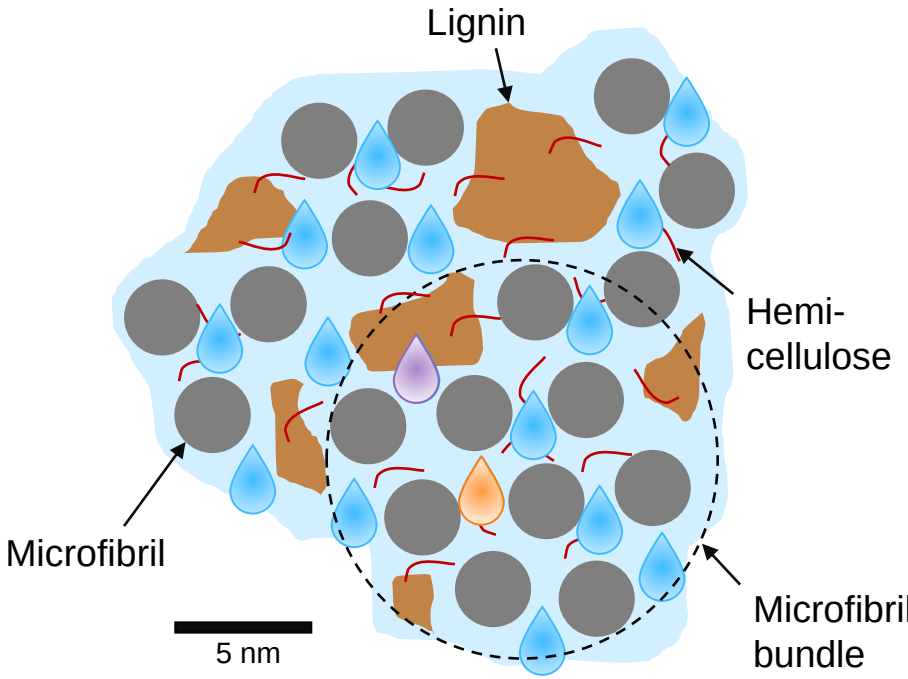
Penttilä et al. (2021), *Cellulose*, 28:11231-11245

Exchange of interfibrillar water







- All water exchanged within first ~30 min
- No clear difference in exchange rate of water “inside and outside of microfibril bundles”

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$$f(t) = f_\infty(1 - e^{-kt})$$

Penttilä et al. (2021), *Cellulose*, 28:11231-11245

Conclusions

Conclusions

- SANS provides powerful tools to characterize wood nanostructure and its interactions with moisture
- Water diffusion within the hierarchical cell wall structure was studied using *in situ* SANS

Thank you

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