Cellulose Under Pressure For New Biopolymer Materials

By: Josh Devorkin

Mentors: Dr. Susana Teixeira and Dr. Yimin Mao

Outline

- *Background: Cellulose and Nanomaterials*
  - Cellulose is a natural polymer
  - Tempo-oxidation to extract nanofibers
  - Building block for new materials

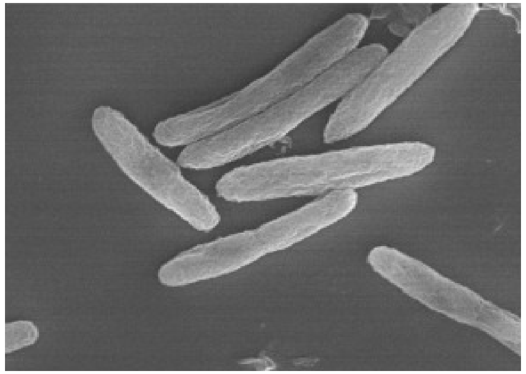
Goal:

Towards greener processing: can High hydrostatic pressure promote a more efficient oxidation reaction?

Assessing multi-characterization techniques to adequately probe the surface interactions and topography

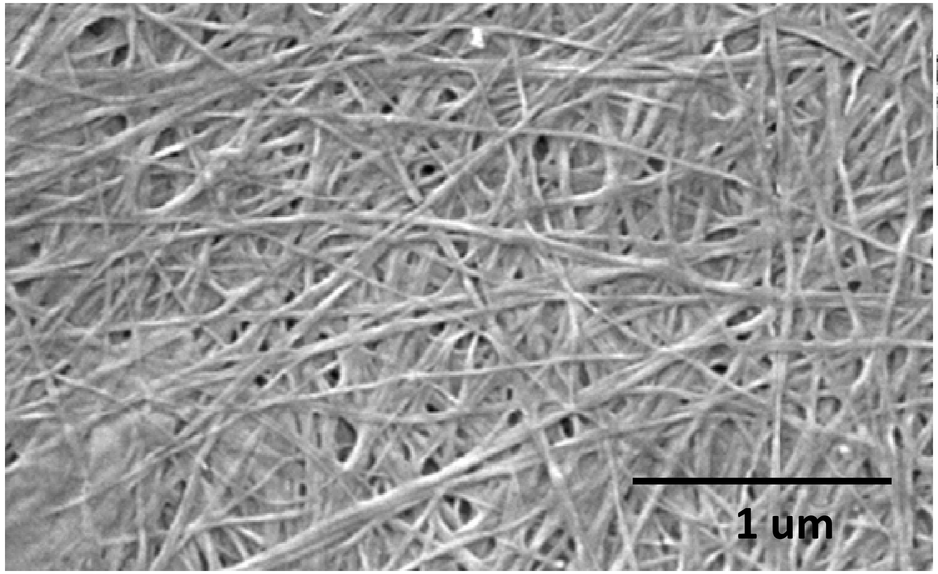
- *Results:* SANS, AFM, POM
- *Future work*

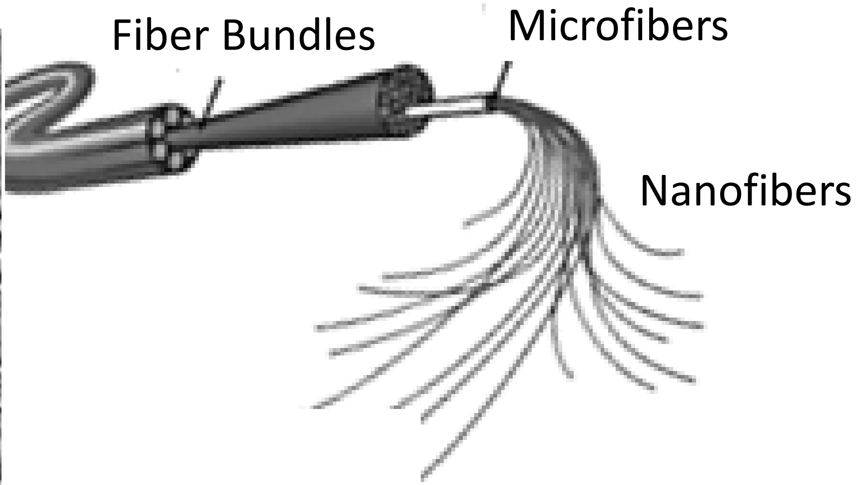
Cellulose as a building block for novel materials



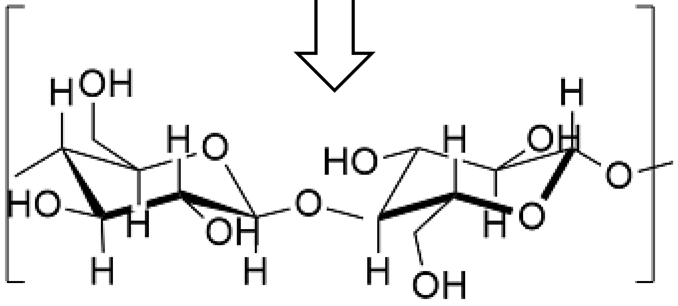
The abundance of cellulose gives rise for current and future novel applications

Fiber networks





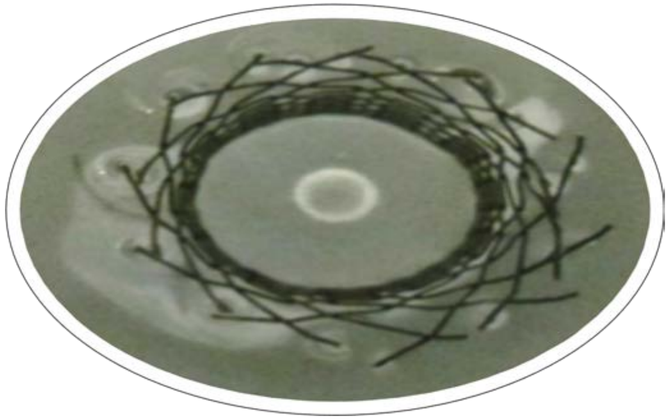
Complex Hierarchy structure rich in hydrogen bonding from the crystallization during biosynthesis



Adapted from T. Heinze et al.

Commercial Applications of Cellulose

Nanocomposites for lightweight durable materials



Coatings for Medical devices

- Drug delivery
- Antibacterial resistance
- Good biocompatibility and wear

High aspect ratio films to collect small dust particles

New lightweight, durable material for 3-D printing

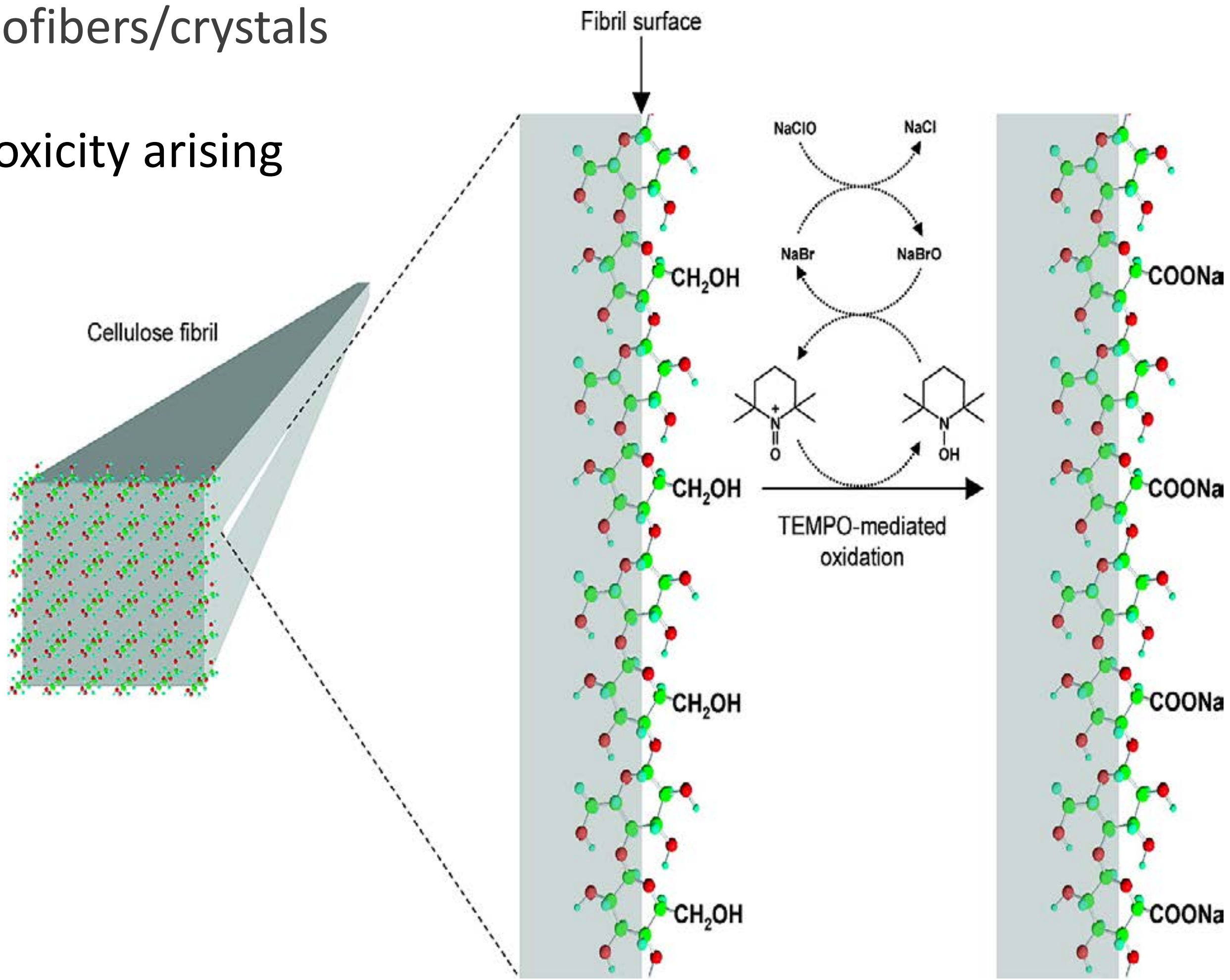
Paper industry

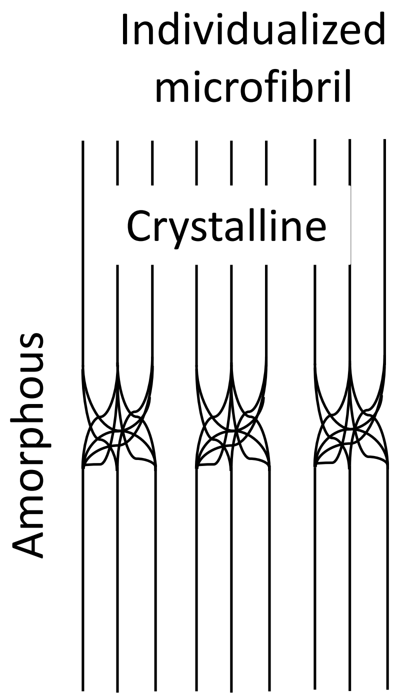
TEMPO-mediated oxidation for processing of cellulose

- Tempo treatment attacks the C6 primary hydroxyls on the surface of the individual cellulose microfibers
- Oxidation into carboxyl groups creates an electrostatic repulsion in water leading to the disintegration of the cellulose nanofibers/crystals

Major drawback is the price and toxicity arising from the use of TEMPO

Motivation: *New methods to extract cellulose nanofibers using green chemistry to reduce the use of chemicals*





Adapted from Okita et al.

High hydrostatic pressure as a probing tool

- Emerging as a useful tool for probing changes in the structure and functional properties of polymers
- Pressure does not introduce other agents into the system, helps aid with green chemistry
- Samples/ Applications
  - Solutions of soft matter polymers
  - Proteins, lipids, polysaccharides
  - Pressure assisted self aggregation
  - Cellulose processing

Hypothesis: High pressure to aid in the oxidation of cellulose through the TEMPO-reaction to dissociate cellulose nanofibers

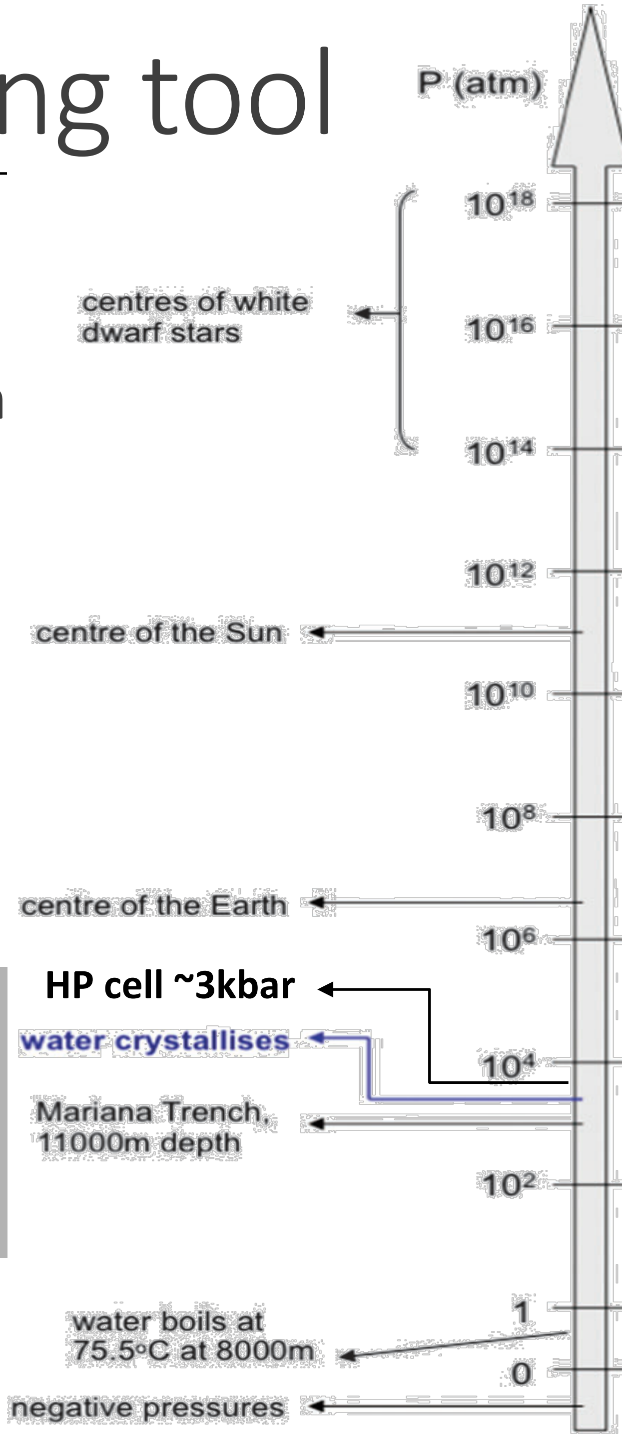
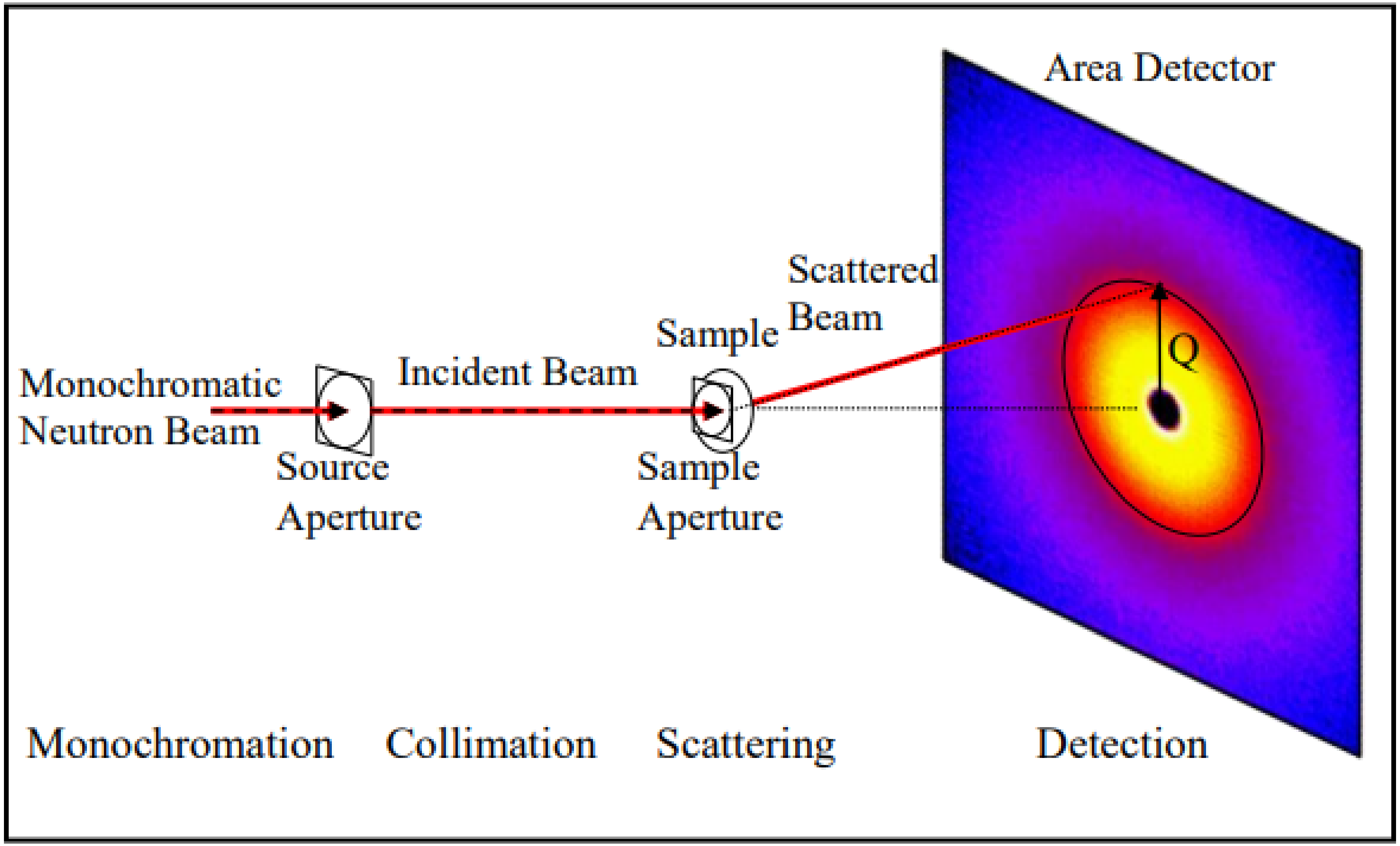


Image from: Meersman & McMillan, 2014. Chem. Comm. 50, 766-765

What neutrons can do

- Structure, conformation of biomaterials ⟹ Function and behavior



Reciprocal space

↓

Real space

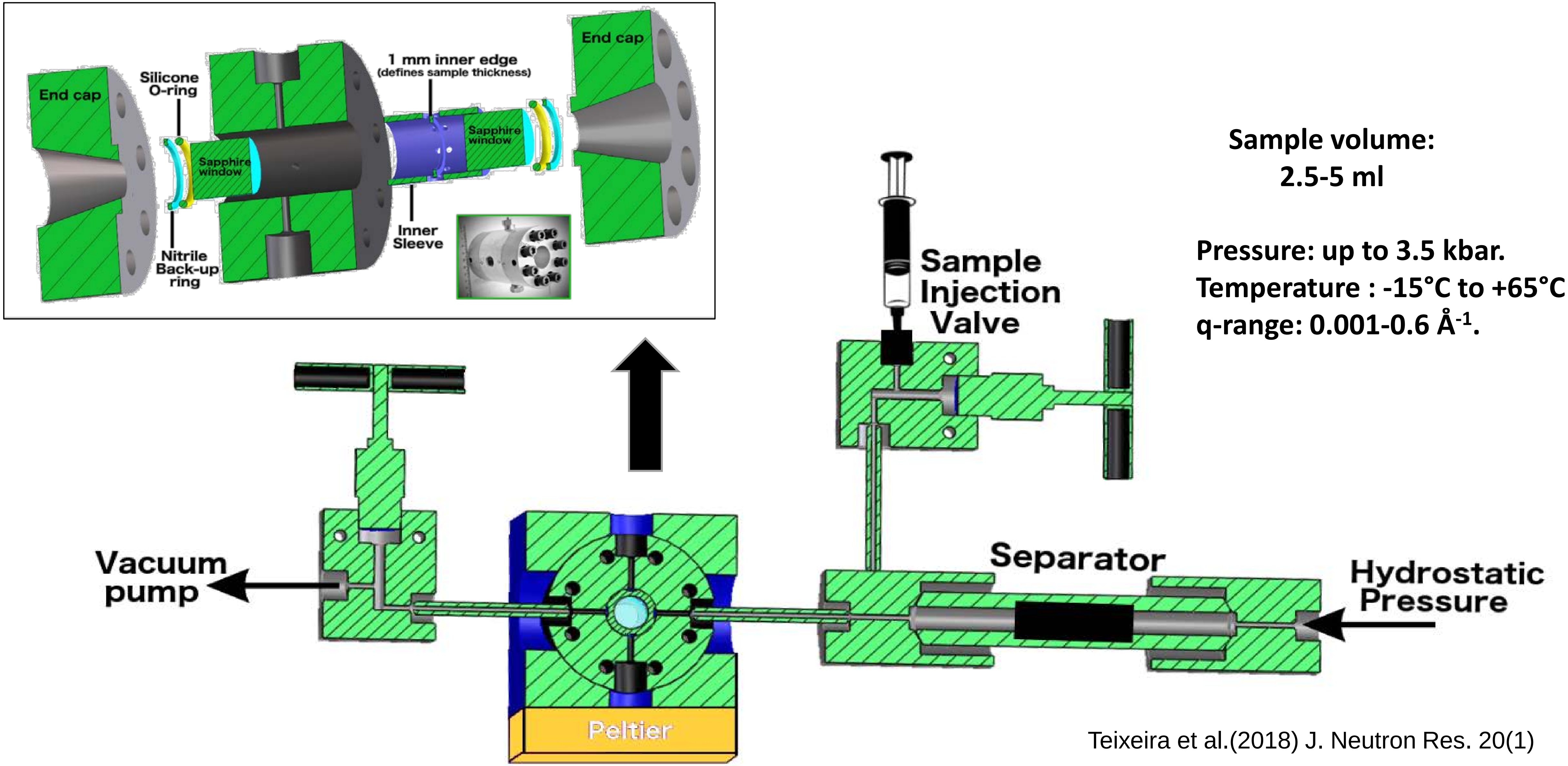
Scattering variable q

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

λ: *neutron wavelength*
θ: *scattering angle*

$0.001\ \dot{A}^{-1} < q < .45\ \dot{A}^{-1}$

HP- SANS System At The NCNR

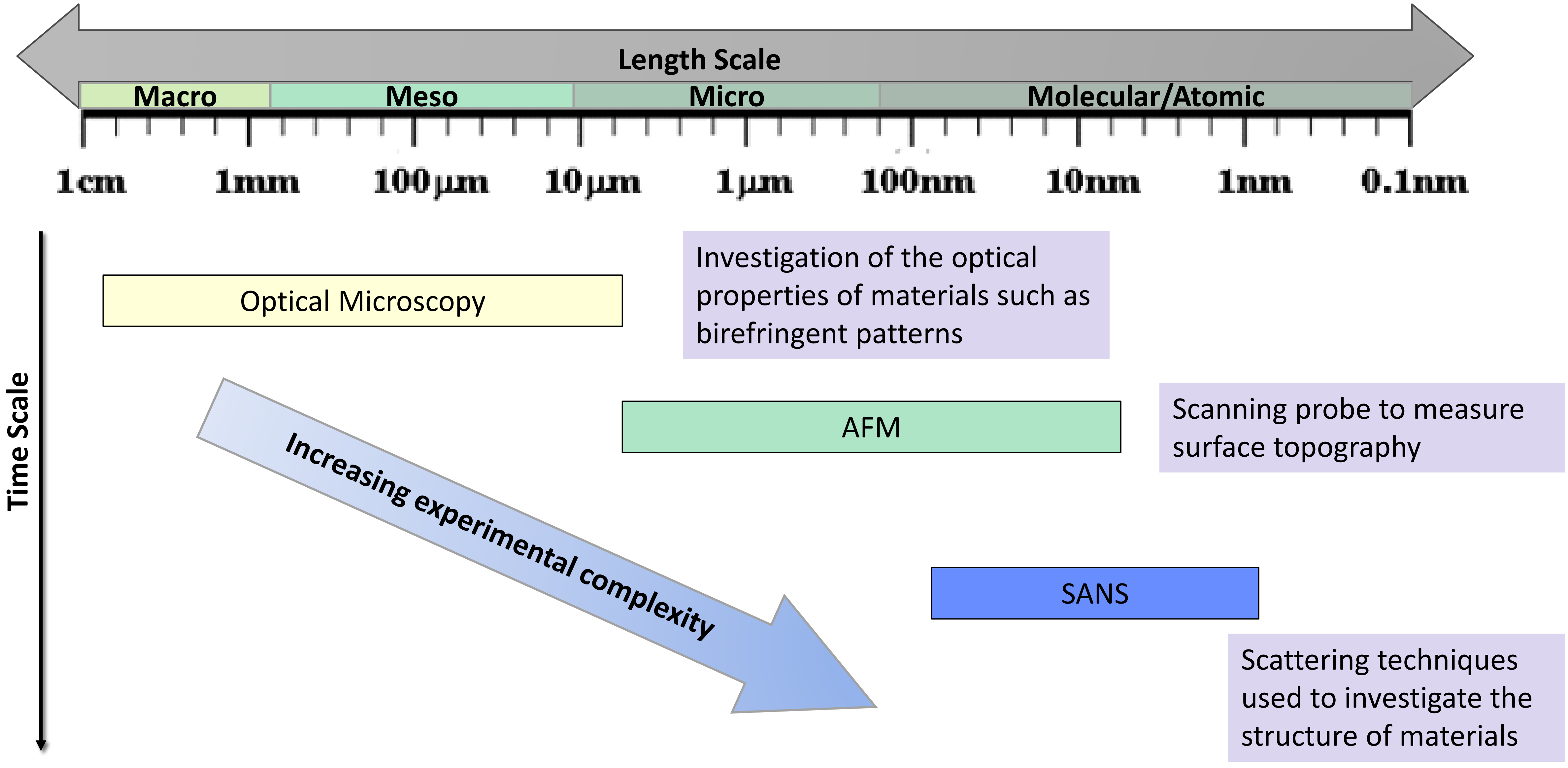


Sample volume:
2.5-5 ml

Pressure: up to 3.5 kbar.
Temperature : -15°C to +65°C
q-range: 0.001-0.6 Å^{-1}.

Teixeira et al.(2018) J. Neutron Res. 20(1)

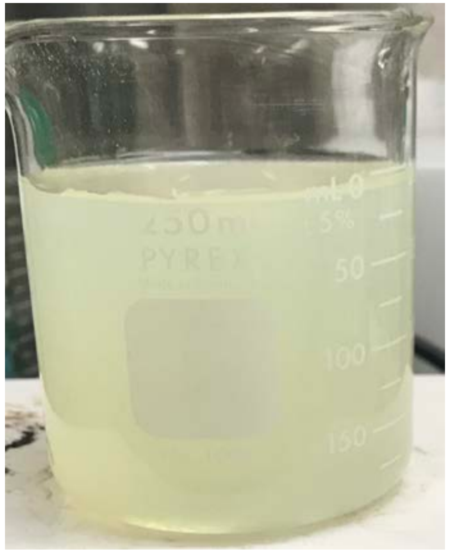
Multiscale characterization of cellulose



Recipe for extraction of nanofibers

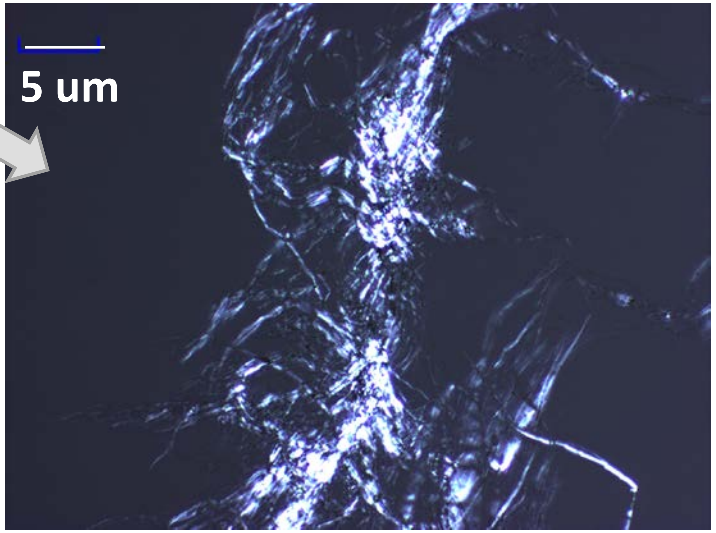
1) Pristine bacteria Cellulose

2) Homogenizer

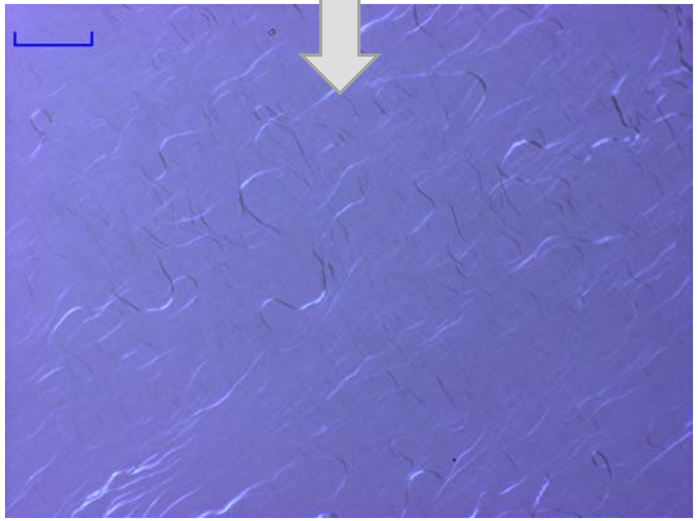


3) TEMPO treatment

4) Viscous gel solution at 1.5 wt%



After Tempo treatment



POM images taken at UMD facilities

Simulated scattering curves using Sasview

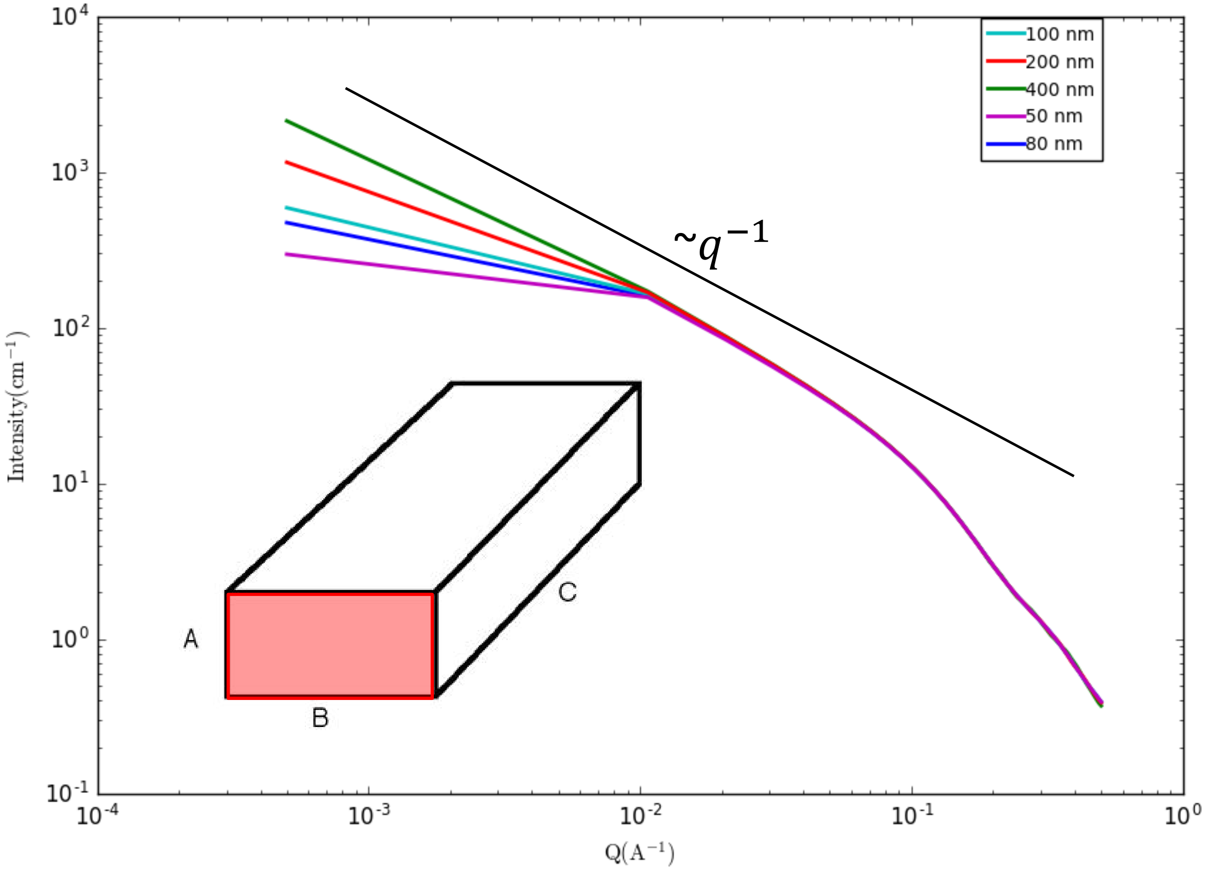


Figure 1: Calculated 1-D curves using the parallelepiped model with different lengths (c). Cross section width b and thickness a are fixed at 3 and 30 nm.

Data fitted with a parallelepiped model with a uniform scattering length density

Assumption:

1. Rod-like particles due to the crystallographic packing
2. L is very long in the micron scale which SANS cannot probe with our configurations
3. b>a due to crystallographic packing of cellulose chains

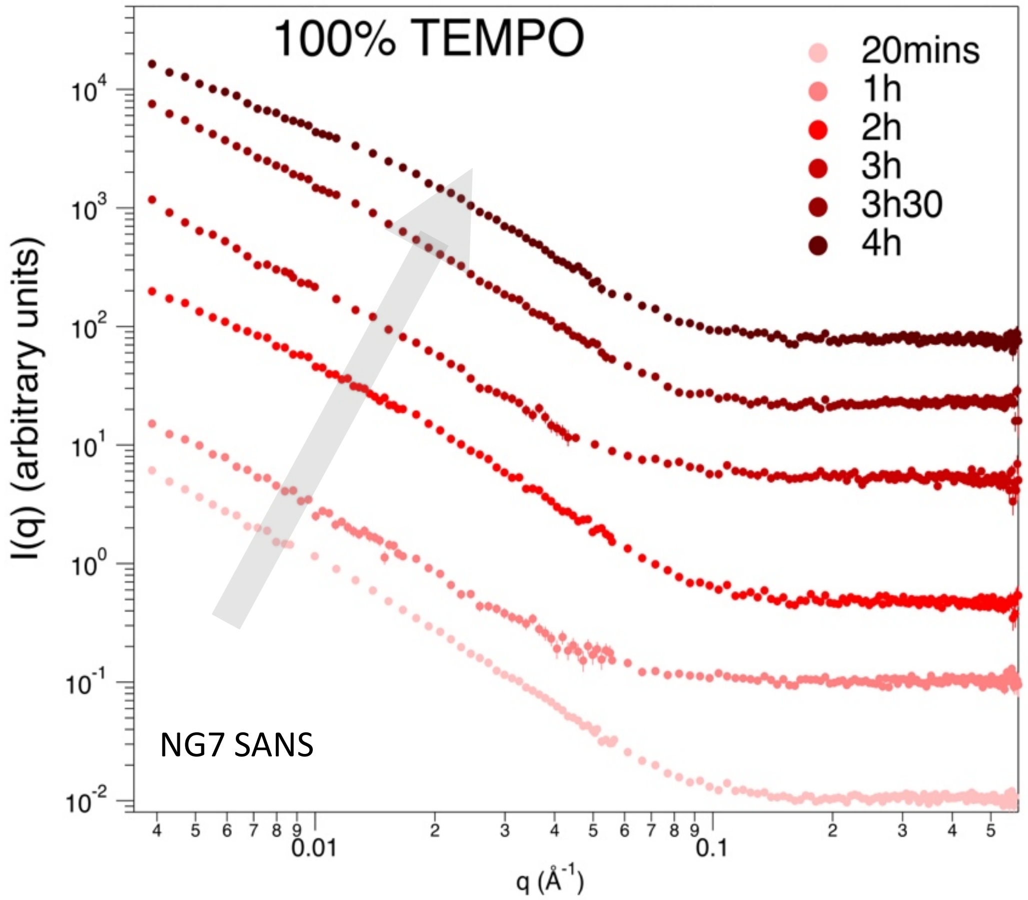
$$\mathrm{I(q)} = \frac{\mathrm{Scale}}{\mathrm{V}} (\Delta\rho.\mathrm{V})^2 < \mathrm{P(q)} > + \text{Background}$$

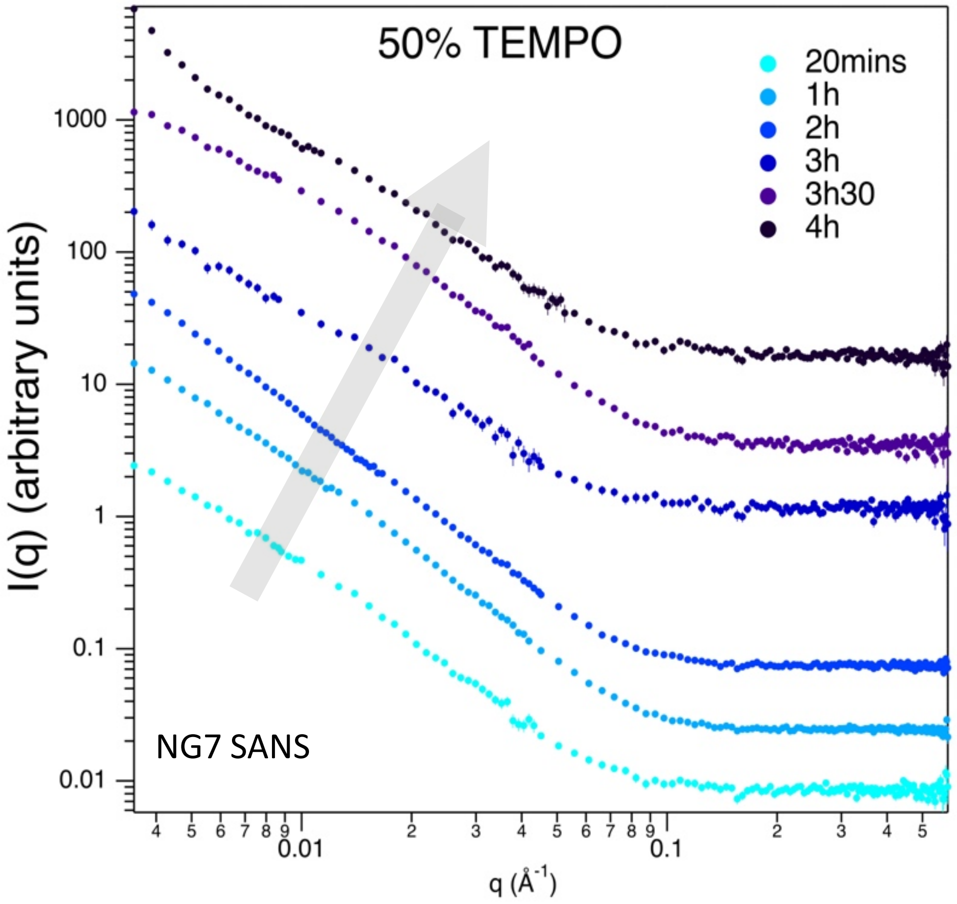
$\mathrm{I(q)}$- Measured intensity

P(q)- Form factor to derive a/b

Guinier region shown for low q at 50nm.

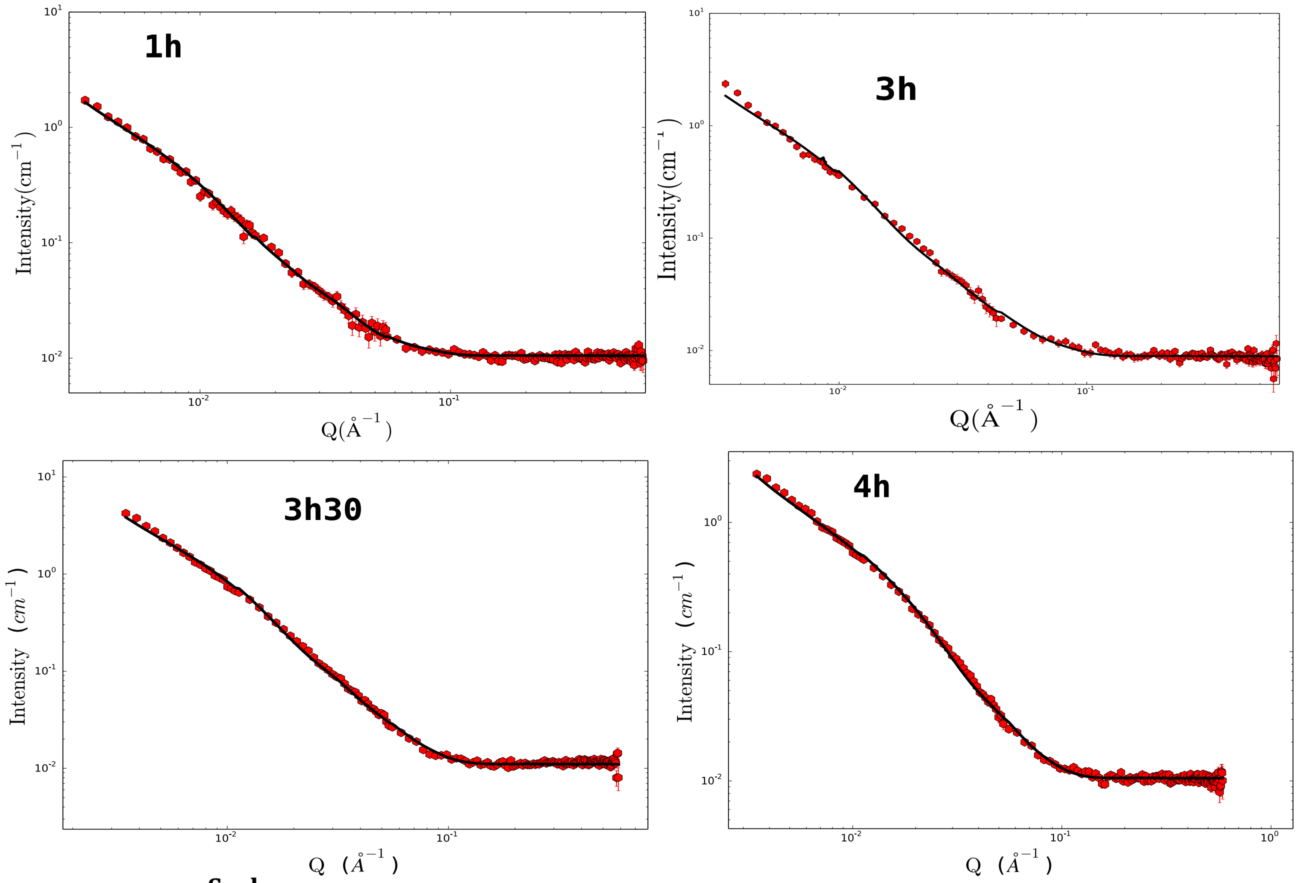
Ex-situ SANS data on Flask TEMPO oxidation (RT, 1am)





Samples were collected on aliquots taken from the reaction mixture after quenching with ethanol, centrifuging and washing.

Ex-situ Fitting of Reaction (100% TEMPO) vs Time



$$\mathbf{I(q)} = \frac{\mathbf{Scale}}{\mathbf{V}} (\mathbf{\Delta\rho . V})^2 < \mathbf{P(q)} > + \textbf{Background}$$

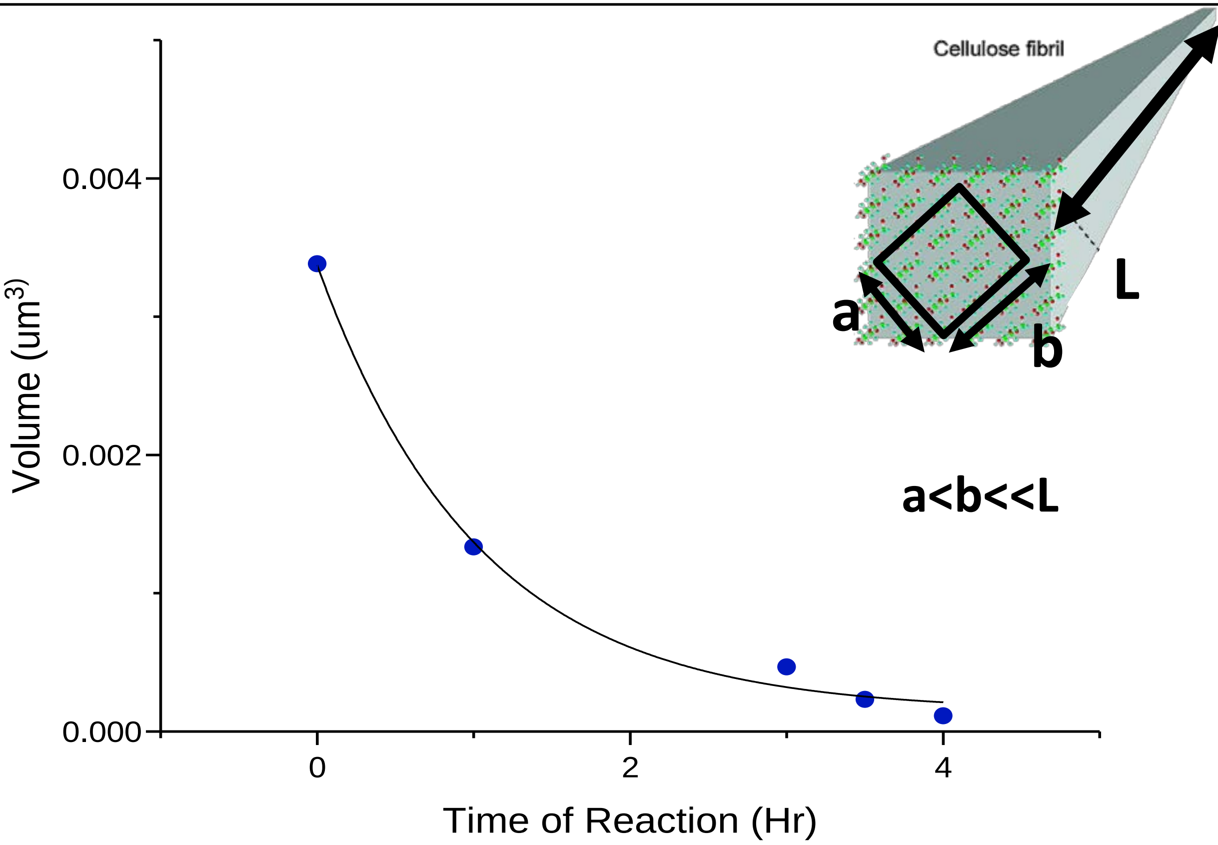
Cellulose SLD:
(1.65±0.2)x10^{-6} Å^{-2}

Parallelepiped model

Nayuk & Huber, *Z. Phys. Chem.*, 226 (2012) 837-854

Mao et al., J. Phys. Chem. B (2017), 121, 1340−1351

SASVIEW fits: *http://www.sasview.org/*

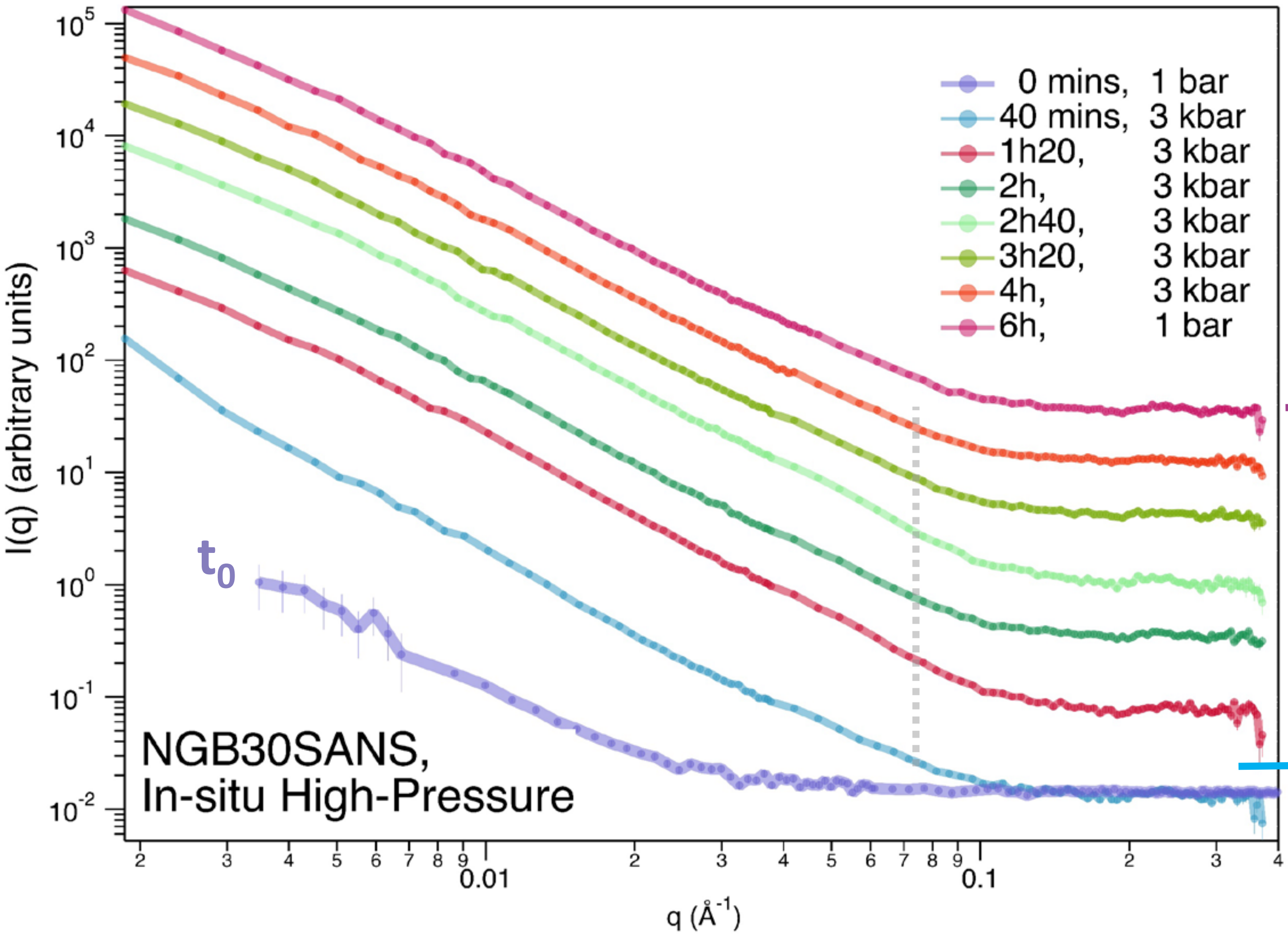


a<b<<L

Reaction time	a (nm)	b (nm)
1h	4.6 ± 0.3	38 ± 1.4
3h	4.1 ± 0.3	37 ± 1.3
3h30	3.9 ± 0.1	32 ± 0.5
4h	3.9 ± 0.1	19 ± 0.3

In-situ High pressure at 3kbar

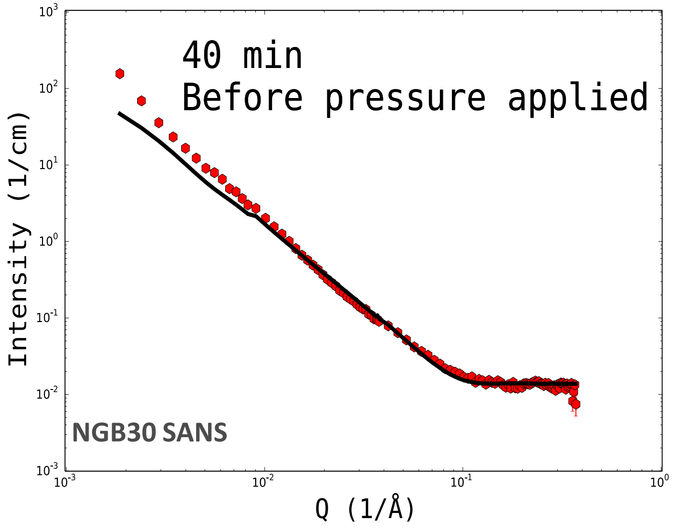
Due to the complexity of the mixture (ex-situ data came from samples that were filtered and washed) the fits are more difficult. In the first 40 mins the presence of the long fibers still dominates the signal (upturn at low-q)

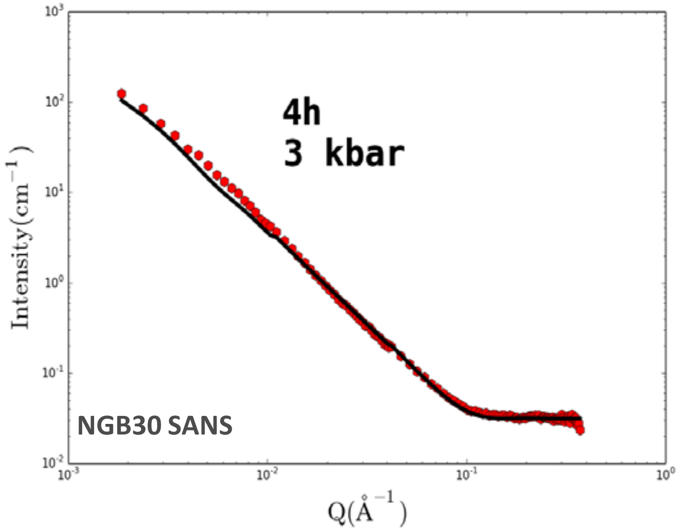


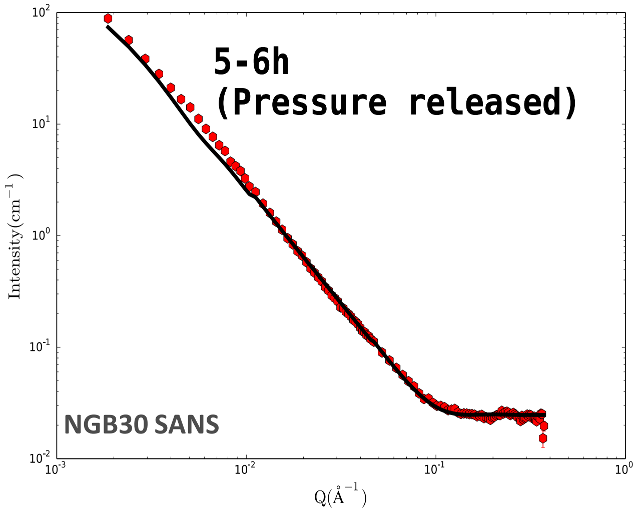
Pressure release
(relaxation monitored for 2h)

In the first 40 mins the presence of the long fibers still dominates the signal (upturn at low-q)

In-situ Reaction (50% TEMPO) Under High Pressure





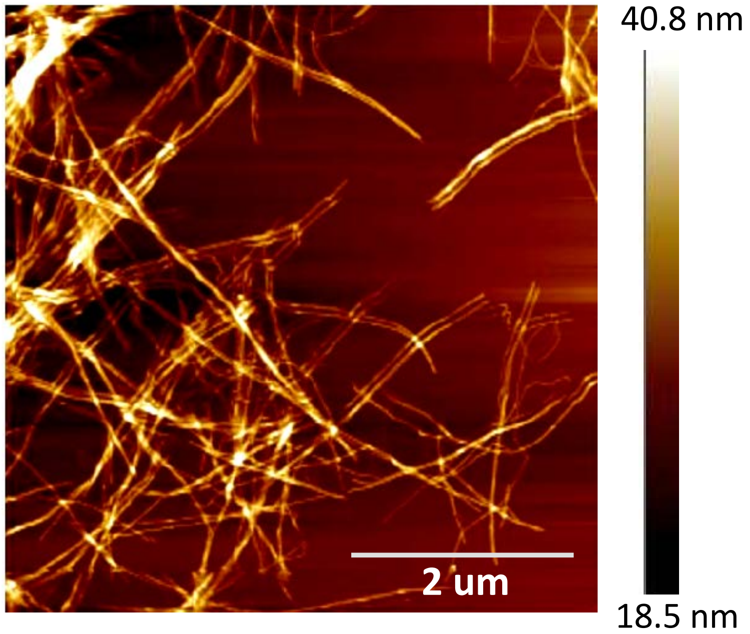


Reaction time	a (nm)	b (nm)	P (kbar)
40min	5.0 ± 0.06	180 ± 33	0.001
1h20	4.5 ± 0.02	151 ± 12	3
2h	4.4 ± 0.03	152 ± 10	3
2h40	4.4 ± 0.01	151 ± 10	3
3h20	4.3 ± 0.03	137 ± 8	3
4h	4.2 ± 0.03	128 ± 7	3
5-6h	4.3 ± .02	128 ± 8	0.001

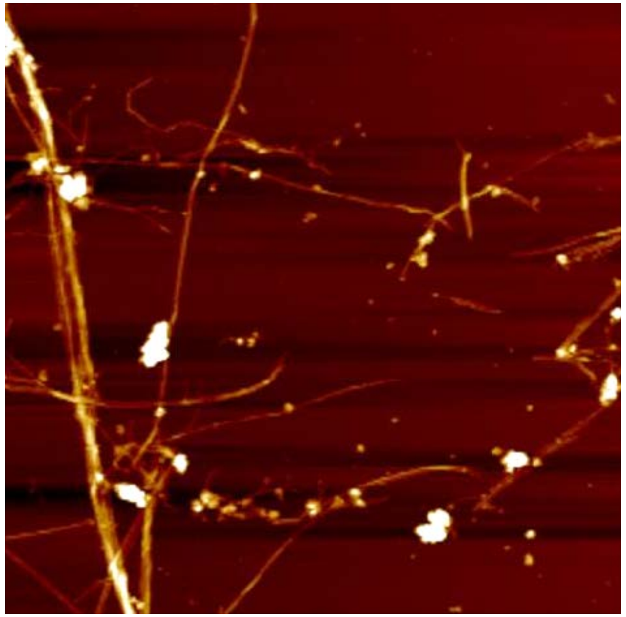
Pressurized

De-pressurized

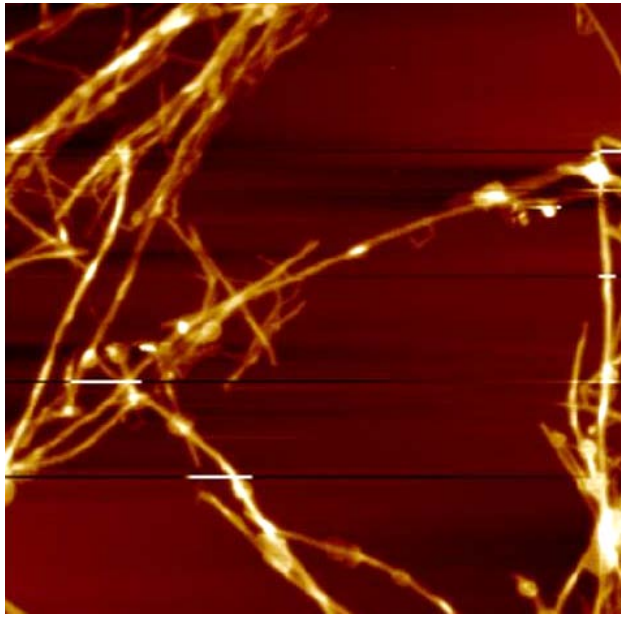
Atomic Force Microscopy



No pressure Tempo Reaction

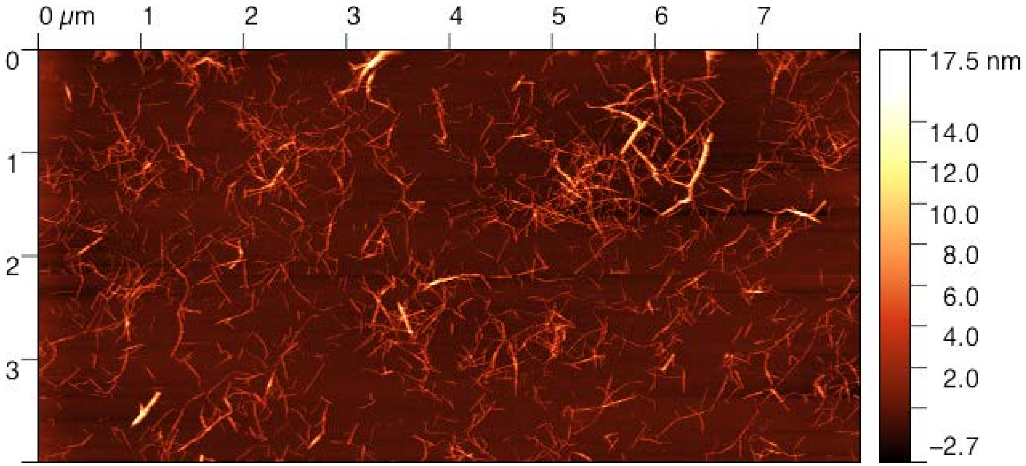


HP_3kbar_4hr



HP_3kbar_3hr
Half amount of TEMPO

Wood pulp courtesy of D. Henderson research group at UMD



- Complementary technique to SANS data
- Confirms the dissociation of bundles of fibers to individual nanofibers

Conclusions and Future work

- High pressure was able to alter the Tempo-oxidation reaction
- Dissociate nanofibers under high pressure using half the amount of reagents
- Produced long fibers able to form viscous gel solutions at low weight percentages

- Cross link individual nanofibers to create a hydrogel
- Alter surface properties, to create a biocompatible, antimicrobial wound dressing

Acknowledgements

NGB30 SANS instrument

Sample environment team at the NCNR

Surf organizers: Joe Dura, Julie Borchers

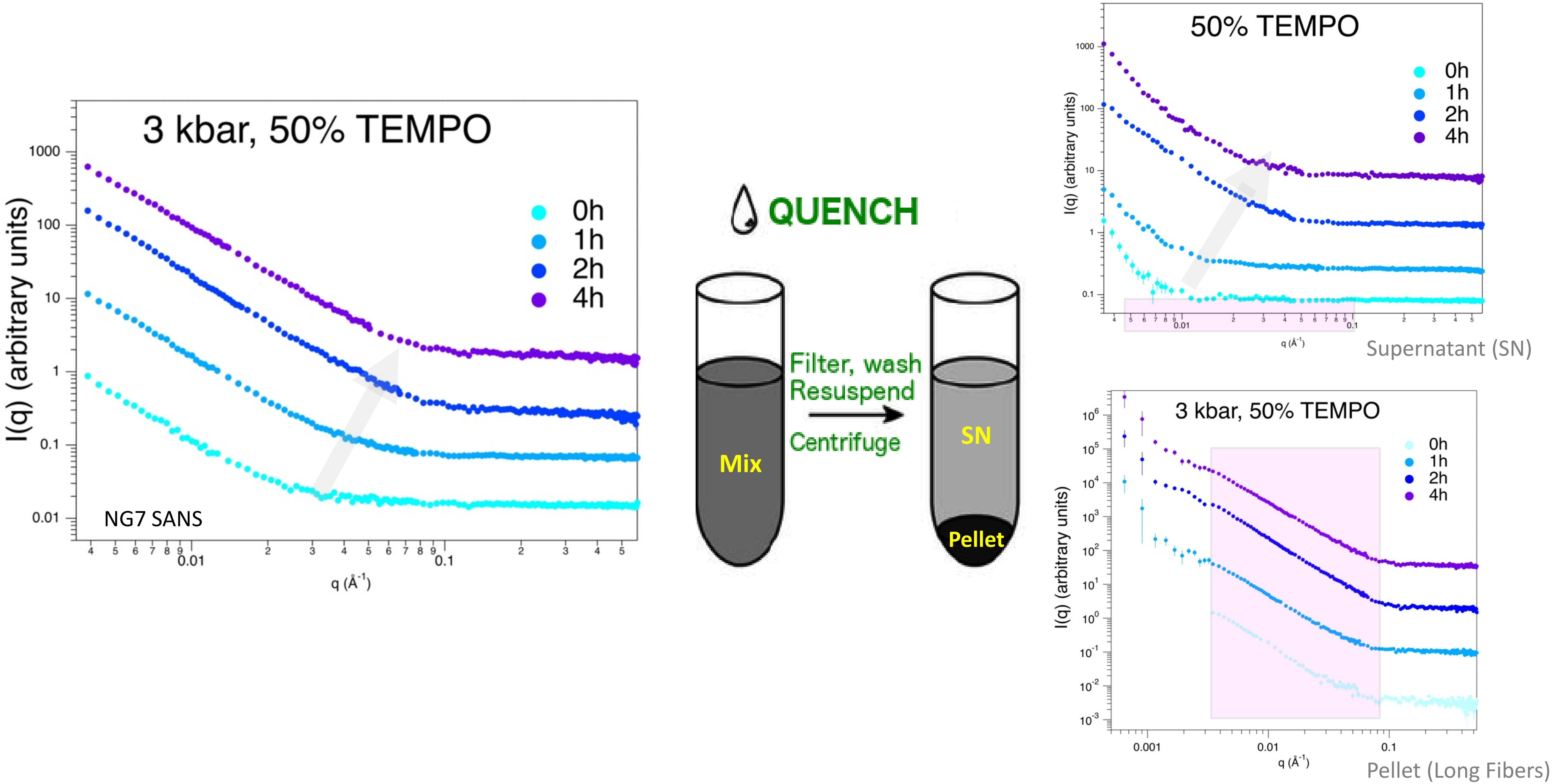
Mentors: Dr. Susana Teixeira and Dr.Yimin Mao

This work benefited from the use of the SasView application, originally developed under NSF award DMR-0520547.

CHRNS CENTER FOR HIGH RESOLUTION NEUTRON SCATTERING NIST

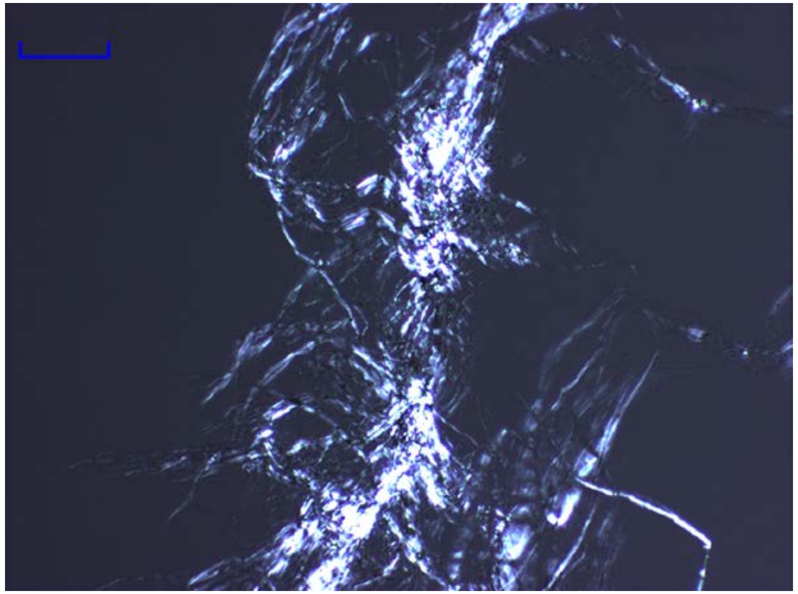
NIST National Institute of Standards and Technology U.S. Department of Commerce

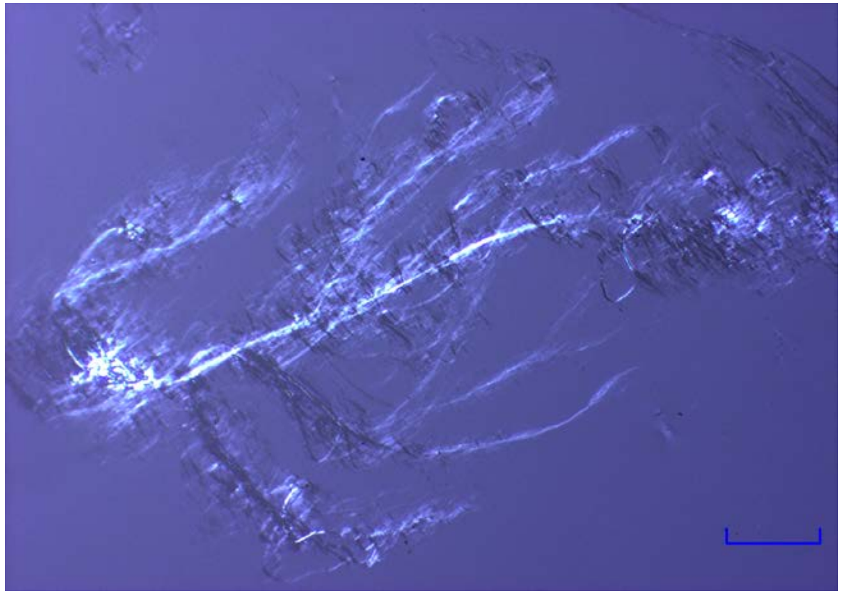
Testing Ex-situ sampling effects on HP-cell TEMPO oxidation



Polarized Optical Microscopy

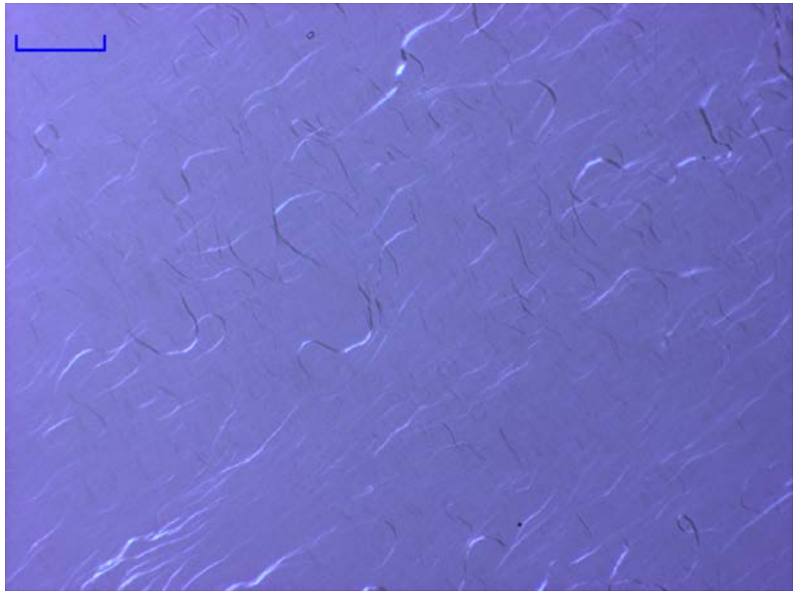
Control _ No tempo

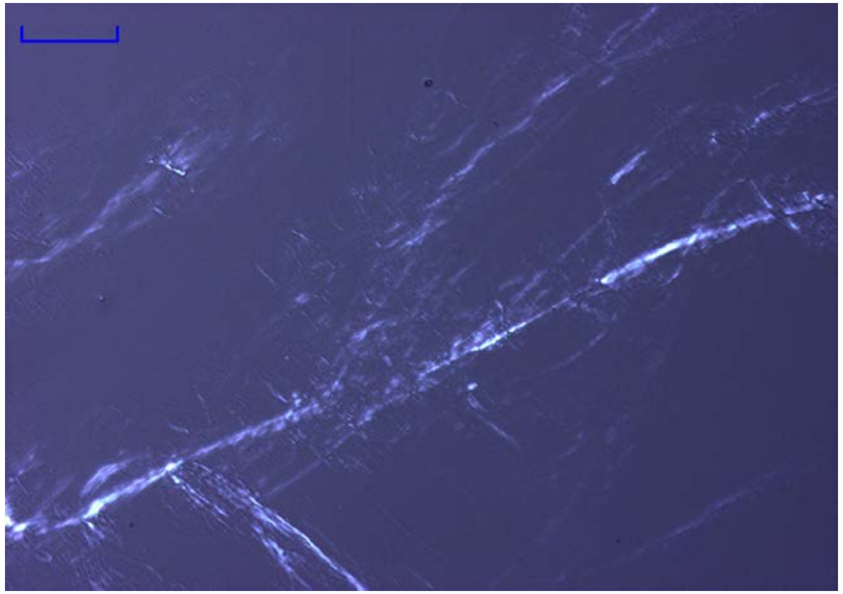




High pressure_ 3kbar

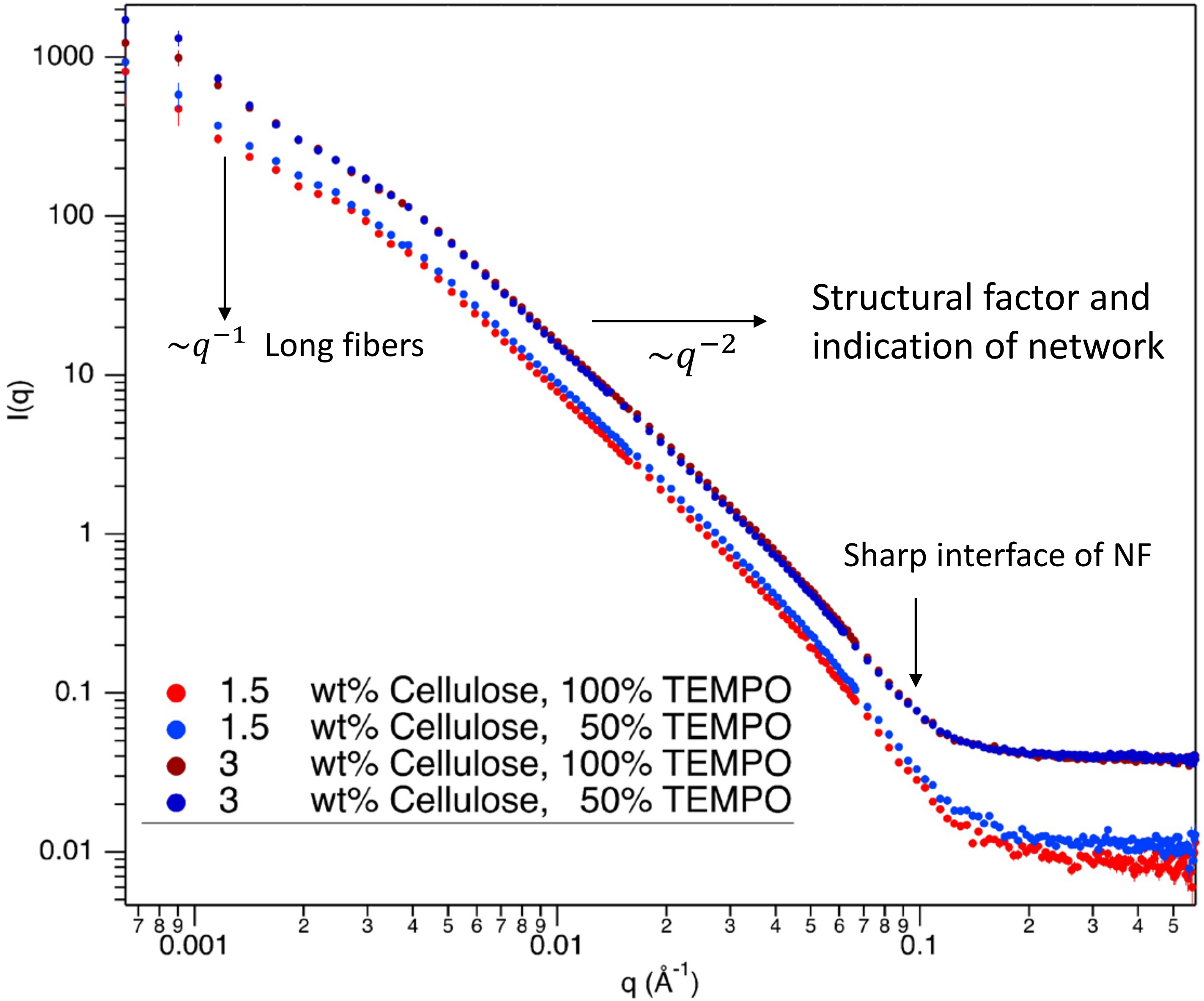
Tempo

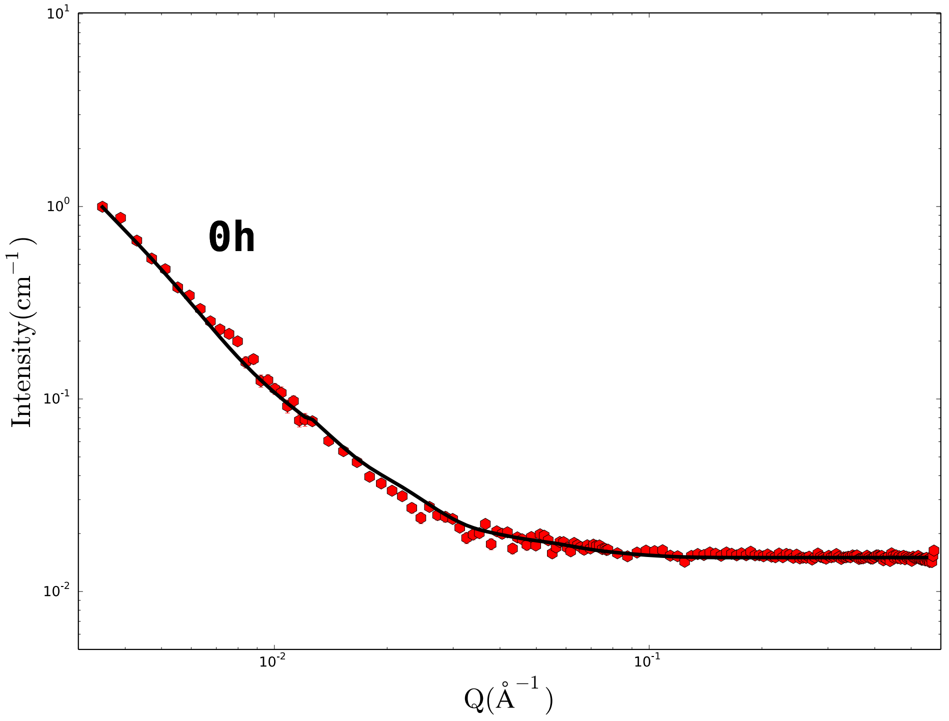




POM images taken at UMD facilities

Effects of Tempo reaction





Reaction time	a (nm)	b (nm)	c (nm)	Chi2/ #points	# points
0h	3.3 ± 0.3	84 ± 4.8	12200 ± 684	1.66	174
1h	4.6 ± 0.3	38 ± 1.4	7632 ± 709	0.86	178
3h	4.1 ± 0.3	37 ± 1.3	3075 ± 686	1.21	161
3h30	3.9 ± 0.1	32 ± 0.5	1858 ± 460	1.95	168
4h	3.9 ± 0.1	19 ± 0.3	1536 ± 157	1.22	167

Ex-Situ investigation for time dependence of TEMPO reaction

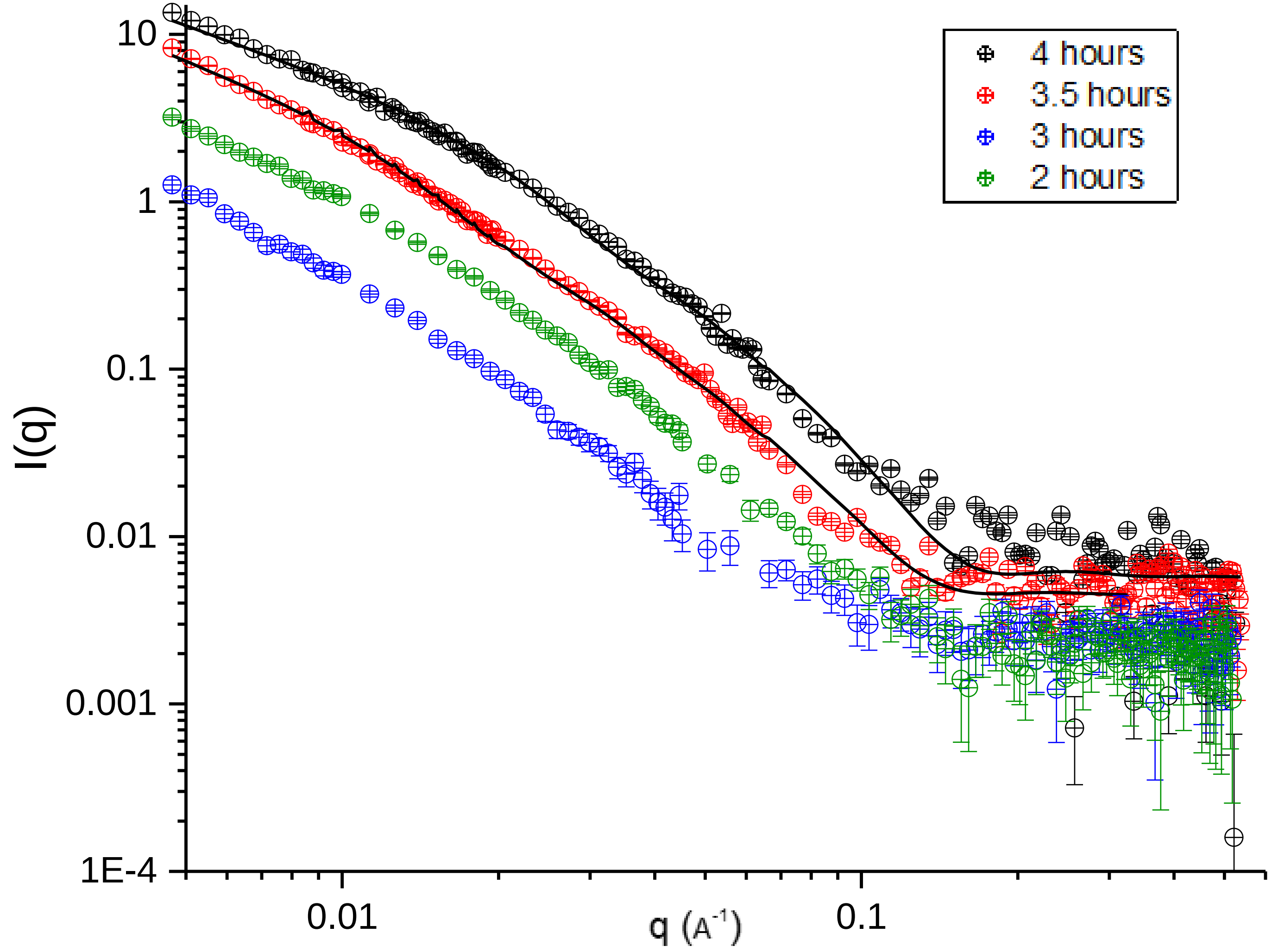


Figure 2: Scattering profiles of the time dependency of TEMPO-oxidation. 4 hour and 3.5 hour curves were offset to better illustrate the fitting

Fibers cross-section size inversely related to the reaction time

Dissociation of NF's after 4 hour of TEMPO-oxidation

Cross-section dimensions derived from SANS methods (one STD in parentheses)

Time	a (nm)	b (nm)
4hr	3.3271 (0.2201)	19.227 (0.2112)
3.5hr	3.4949 (0.1566)	30.877 (2.96)
3hr	4.7012 (1.198)	33.220 (7.8)