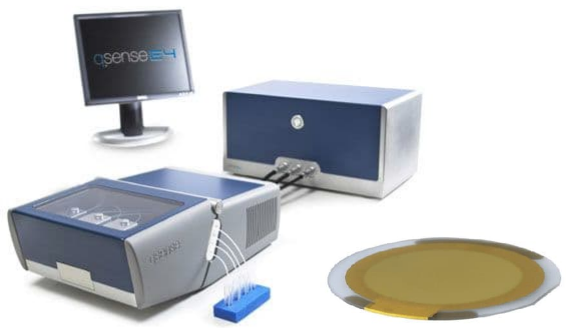

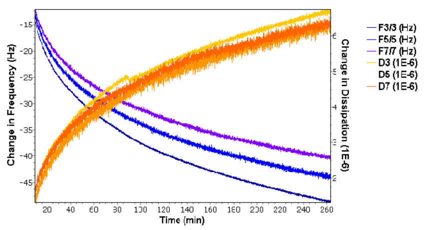

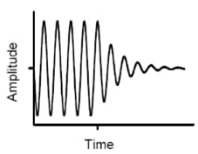

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Ultrathin films
CHEM-L2000

Quartz Crystal Microbalance with Dissipation Monitoring – QCM-D

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VTT Technical Research Centre of Finland
Docent in Bioproduct Technology at Aalto University

27 February, 2024

Aalto University
School of Science and Technology

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Learning objectives

- To understand why surface analysis is important
- To be aware of what an ultrathin film is
- To be aware of the distinction of a model surface
- To have knowledge of the common preparation techniques and analytical methods for ultrathin films

Aalto University
School of Chemical Technology

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Content of the Lecture

I Introduction of QCM-D method

II Interpretation of QCM-D data

III Ultrathin films (model surfaces) for wood-sourced components

IV Information gained with the QCM-D method
Solid-liquid interface: 1) Adsorption of hemicelluloses 2) Attachment of living cells
Solid-air interface: Water vapour sorption of cellulose nanofibrils

V Conclusions

3

INTRODUCTION TO QCM-D

4

QCM-D in thin film characterisation

- QCM-D measures mass changes with nanosensitivity due to
  - adsorption and desorption
  - dissolution and degradation
  - physical changes due to e.g. heat, UV or enzymatic treatments
  - physical changes due to e.g. swelling or vapour uptake
- Information on structural behaviour and viscoelastic properties of materials can be simultaneously achieved.
  - In situ and in real-time – kinetics
  - High resolution – very small mass changes can be detected
  - Highly selective
  - Does not require labelling – no artefacts
  - Can be used both in liquid and gas phase

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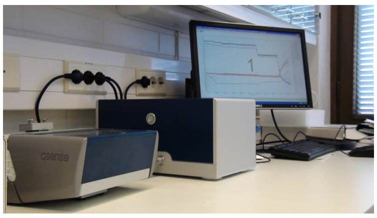
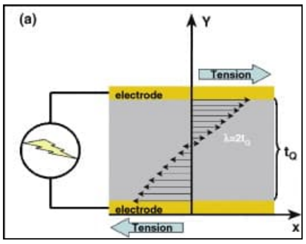
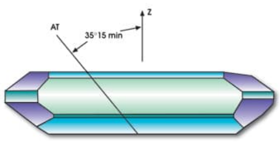
Quartz Crystal Microbalance with Dissipation monitoring (QCM-D)





- QCM is based on the piezoelectric effect: application of voltage results in mechanical deformation of the material
- AT-cut crystals which vibrate in thickness-shear mode: alternating voltage results in cyclical deformation leading to an oscillatory motion
  - AT-cut quartz crystal is cut from the quartz mineral at a 35.25° orientation to its optical axis
  - Alternating current causes mechanical vibration of the quartz in the MHz range



Rodahl, K.; Höök, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. *Rev. Sci. Instrum.* 1995, *66*, 3924.
Höök, F.; Rodahl, M.; Brzezinski, P.; Kasemo, B. *Langmuir* 1998, *14*, 7290.
Reviakine, I.; Johannsmann, D.; Richter, R.P. *Anal. Chem.* 2011, *83*, 8838-8848.
Ferreira, G. N. M.; da-Silva, A-C.; Tomé, B. *Trends in Biotechnology*. 2009, *27*, 689-697.

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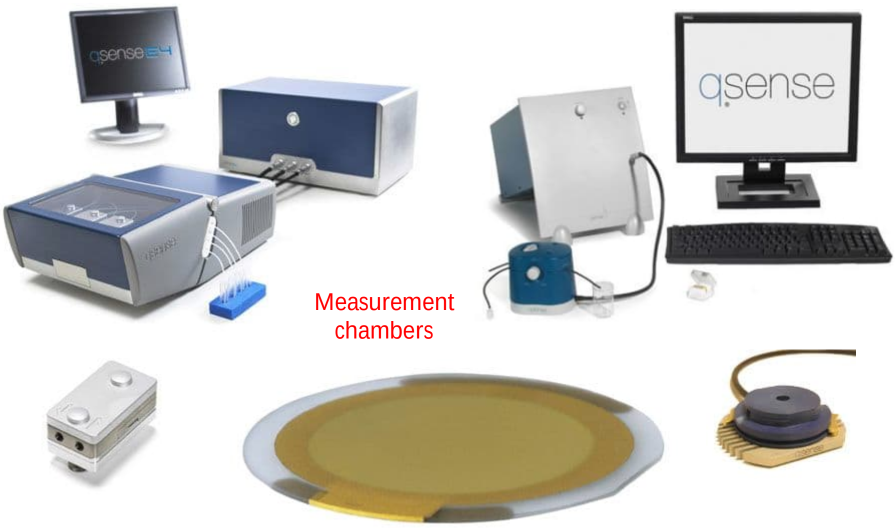
QCM-D – Different set-ups



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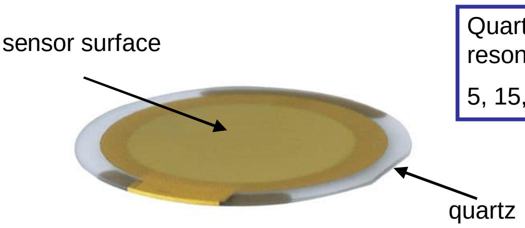
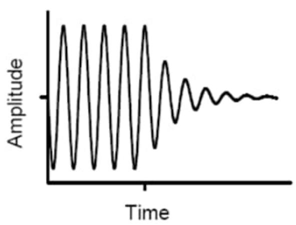
Main principle of QCM-D method



Quartz crystal oscillates at a resonant frequency

5, 15, 25, 35, 45, 55, and 65 MHz



- Negative/positive change in frequency (*Δf*) – mass increase/decrease on the crystal
- Change in dissipation (*Δ*D) during the adsorption process depends on the viscoelastic properties of the adsorbed layer
- Amplitude of the oscillation decays due to frictional losses in the crystal – dissipation of energy
  - soft – rigid layer
  - thick – thin layer
  - water bound in the layer structure

Adsorbed mass

$\Delta m = C\ \Delta f\ n^{-1}$

Dissipation

$D = \frac{E_{diss}}{2\pi E_{stor}}$

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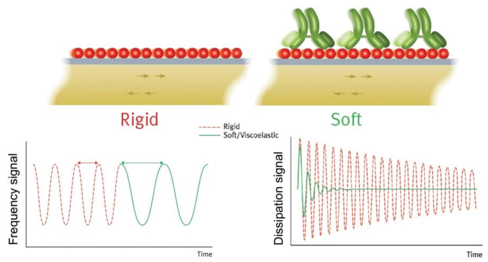
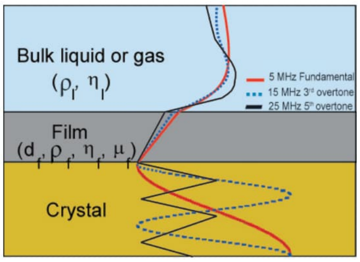
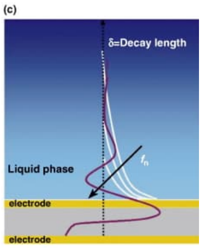
QCM-D working principle







- Frequency of the oscillating sensor crystal changes when the mass is increased on the sensor surface
- Energy dissipation occurs when the driving voltage is switched off and the energy of the oscillating crystal dissipates from the system
- Frictional losses lead to a damping of the oscillation with a decay rate of amplitude that depends on the viscoelastic properties of the material
- The amplitude and the decay length of the acoustic wave transmitted to the fluid decrease with increasing sensor resonance frequency or overtone

- Voigt based viscoelastic film model
  - Propagation and damping of acoustic waves in a uniform viscoelastic film in contact with a Newtonian bulk liquid

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INTERPRETATION OF QCM-D DATA

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Polyelectrolyte adsorption – Examples of rigid and viscoelastic layers

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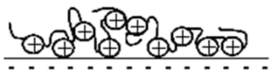

- High charge density
- Low ionic strength

→ Adsorbed amount is low, and the layer is thin

- Low charge density
- High ionic strength

→ Adsorbed amount is high, and the layer is thick

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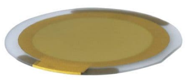

Interpretation of QCM-D data

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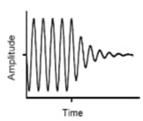
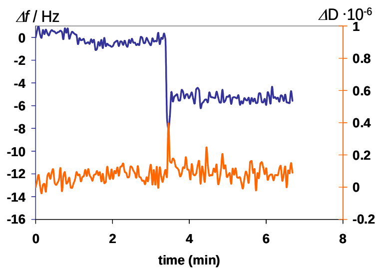
- Quartz crystal oscillates at a resonant frequency (5, 15, 25, 35, 45, 55, and 65 MHz)
- Change in frequency, Δf – change in mass on the crystal
  - When material adsorbs on the crystal surface the frequency decreases
  - Desorption is seen as frequency increase
  - $\Delta m = C \, \Delta f \, n^{-1}$
- Change in dissipation ΔD – The damping of the oscillation depends on the viscoelastic properties of the model film
  - soft – rigid
  - thick – thin layer
  - solvent bound in the adsorbed layer structure

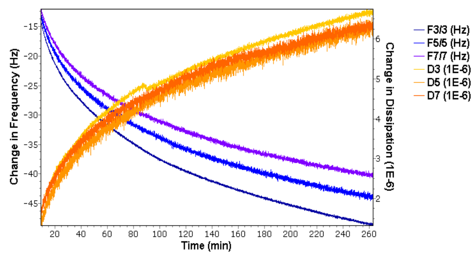
$$D = \frac{E_{diss}}{2\pi E_{stor}}$$



Fully elastic layer – Rigid material



Viscoelastic layer – Solid material deforms under stress



Tammelin, T., Merta, J., Johansson, L.-S. and Stenius, P. *Langmuir*, 2004, *20*, 10900.

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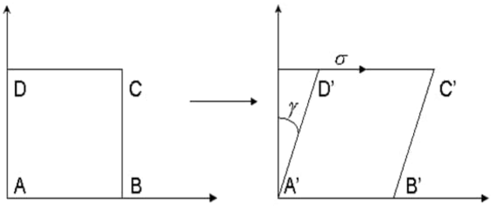
Hooke's law – Elastic part

$$\sigma = G\gamma$$

σ = tension

γ = strain

G = elastic modulus



- The amount by which a material body is deformed **(the strain)** is linearly related to the force causing the deformation **(the stress)**
- ⇨ Deforms under stress but regains its original shape and size when load is removed – **fully reversible** deformations
- ⇨ Time independent

Newton's law – Viscous part

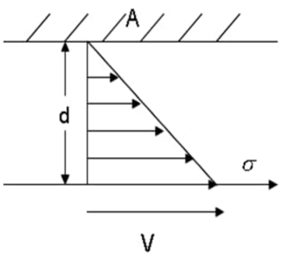
$$\sigma = \eta \frac{dV}{dt} = \eta\dot{\gamma}$$

σ = stress

η = viscosity

dV/dt = rate of strain

V/d = γ = shear rate

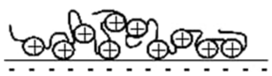


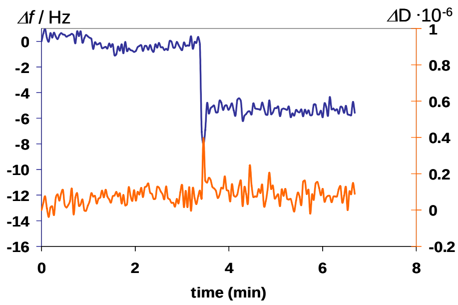
- Shear **stress produces flow** and the flow persists as long as the stress is applied
- Newtonian liquid which after being subjected to a deforming load does not recover its original shape and size when the load is removed
- Energy needed to produce flow transfers into heat
- Deformation is a linear function of time and is **fully irreversible**

Elastic layer - Rigid materials

- Materials which have only elastic properties
- The deformation of elastic material is reversible
- Quantitative data analysis
  - Adsorbed mass is low and evenly distributed
  - Low ΔD

$\Rightarrow$ Sauerbrey equation: $\Delta m = C\, \Delta f\, n^{-1}$





***C* = 17.7 ng/Hz cm^2**
for a 5 MHz quartz crystal

***n* = 1,3,5,7,…**
is the overtone number

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Viscoelastic materials

- In liquid, an adsorbed film may consist of a considerably high amount of water, which is sensed as a mass uptake by all QCMs. The amount of water may be 90% or 10% depending on the kind of molecule and the type of surface you are studying.
- By measuring several frequencies and the dissipation, it becomes possible to determine whether the adsorbed film is rigid or water-rich (soft) which is not possible by looking only at the frequency response.
- With QCM-D the kinetics of both structural changes and mass changes are obtained.

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Viscoelastic materials

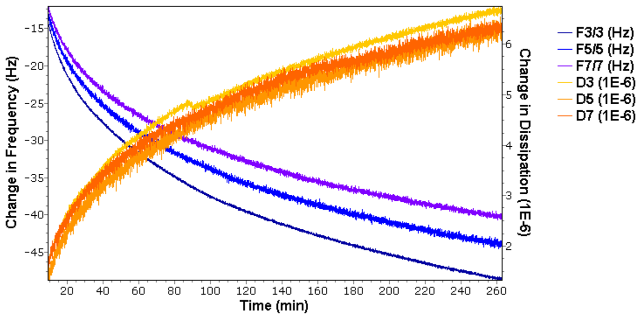
Polymers

- Rheological properties depend on
  - Shear rate
  - Molecular weight
  - Polymer structure (linear – branched)
  - Temperature

Viscoelastic materials

- Materials which have both elastic and viscous properties
- Solid material deforms under stress
  - Part of the deformation is reversible (elastic part)
  - Part of the deformation is irreversible (dissipates as heat)

- Quantitative data analysis
  - High ⊿D ⇒ **Viscoelastic modelling**



Barnes, H.A., Hutton, J.F. and Walters, K., *An Introduction to Rheology*, Rheology Series, 3, Elsevier, Amsterdam, 1989. Ferry, J.H., *Viscoelastic Properties of Polymers*, 3. ed., John Wiley & Sons, New York, 1980.

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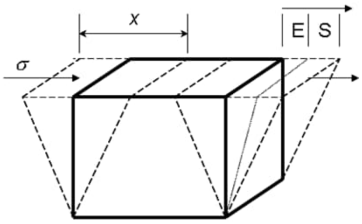
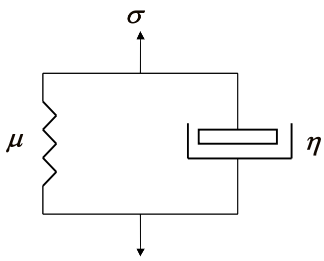
Voigt model for viscoelastic solid

- Adsorbed layer is described using a frequency dependent complex equation when layer is subjected to oscillating stress:

  G* = complex shear modulus = G' + iG" = $\mu_f + i2\pi f \eta_f$

- **G' (real part)** describes the adsorbed layers **ability to store energy**
  - elastic i.e. reversible deformation, storage modulus
- **G" (imaginary part)** describes the energy which **changes in to heat** (energy dissipation)
  - viscous i.e. irreversible deformation, loss modulus
- The larger G*, the stronger the structure





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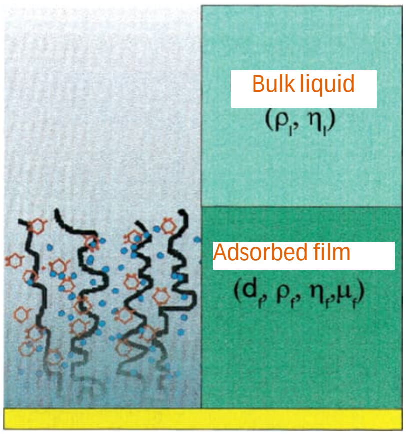
Interpretation of viscoelastic layers
QTools-modelling

- *Δf* and *Δ*D are interpreted as adsorbed mass and structural changes during the adsorption process
- **Known parameters**: viscosity (η_l) and density (ρ_l) of bulk liquid, *Δf* ja *Δ*D measured using several overtones
- **Estimated parameter**: Density of the adsorbed layer (ρ_f)
- **Modelled parameters**: Elastic modulus (μ_f), viscosity (η_f) and hydrodynamic thickness (d_f) of the adsorbed film
- **Preconditions:** The adsorbed film covers the sensor's entire active area, is homogeneous, and has a uniform thickness. The medium is a bulk Newtonian fluid, no slip conditions



Voinova et al. *Phys.Scr.* 59, 1999

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ULTRATHIN FILMS FOR WOOD-SOURCED COMPONENTS

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Background

Ultrathin films and model surfaces for wood-sourced components


Cotton fiber network

CELLULOSE FIBRES

- **Heterogeneous** in chemistry and morphology
- Large and rough

→

- Difficult to understand specific interactions
- Not suitable for QCM-D

THIN FILMS AND MODEL SURFACES

- Small amount of carefully characterized compound or compounds
- Evenly deposited on a flat substrate (QCM-D sensor)
- Well-defined
  - Chemical composition
  - Crystallinity
  - Thickness
  - Roughness

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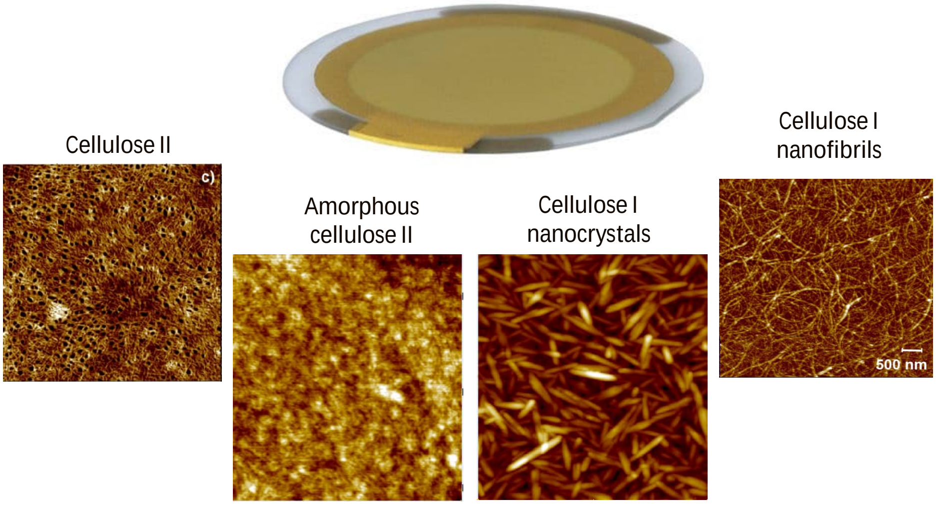
Ultrathin Films of Cellulose
Well-defined chemistry and morphology



Tammelin, T. et al. *Cellulose*, 2006, *13*, 519; Kontturi, E., Tammelin, T. and Österberg M. *Chem. Soc. Rev.* 2006, *35*, 1287; Kontturi, E. et al., *Langmuir,* 2007, *23*, 9674, Ahola, S. et al., *Biomacromolecules*, 2008, *9*, 1273. Eronen, P. et al., *J. Colloid Interface Sci*. **2011**, *373*, 84. Hakalahti et al., *Biomacromolecules*, 2017, *18*, 2951.

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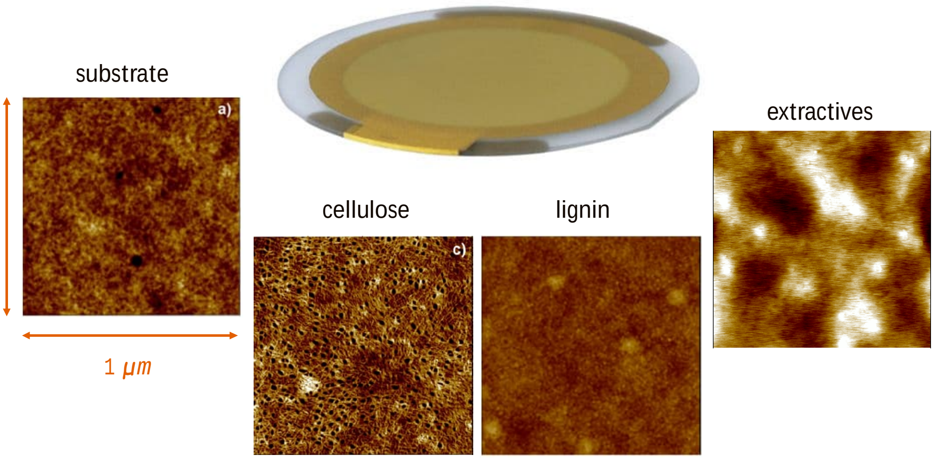
Model Surfaces for Main Fibre Components
Spruce Fibre



- Thin model surfaces prepared by spincoating or Langmuir-Schaefer technique

Tammelin et al. *Cellulose,* 2006, *13*, 519.Tammelin et al. *NPPRJ,* 2006, *21*, 444, Schaub et al. Adv.Mater. 1993, *5* , 919

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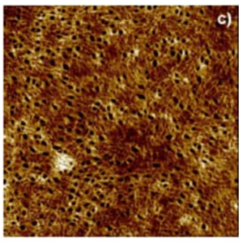
Examples of wood-based thin films and model surfaces

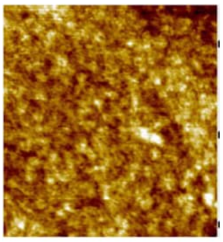
Regenerated cellulose made from TMSC

60% crystalline cellulose II



- Langmuir-Schaefer deposition
- Low negative charge

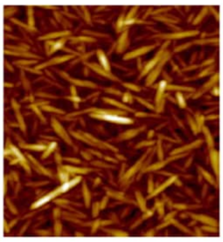
Amorphous cellulose



- Spin coating
- Low negative charge

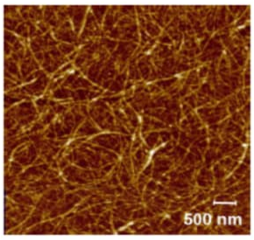
Cellulose I

CNC



- Spin coating
- Cellulose I with sulfate half-ester groups
- Strong negative charge

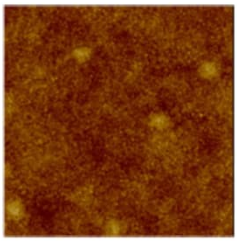
CNF



- Spin coating
- Cellulose I and thin layer of hemicelluloses
- Low negative charge

Other wood-based polymers

Lignin



- Spin coating
- Chemistry defined by the type of the dissolved lignin
- Less hydrophilic than cellulose

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INFORMATION GAINED USING QCM-D

ADSORPTION AT SOLID-LIQUID INTERFACE

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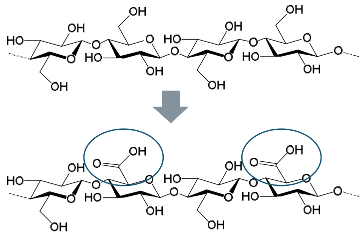
TEMPO-oxidized cellulose nanofibers (TCNF)

- Obtained from wood pulp via chemical pretreatment and mechanical disintegration
- Interesting properties:
  - Transparency
  - High mechanical strength
  - Tunable porosity
  - Non-toxicity, (biodegradability)
  - Unique water interactions: high hygroscopicity!

→ Hydrogels from all-polysaccharidic components



Saito et al. *Biomacromolecules* **2006** 7 (6), 1687-1691.

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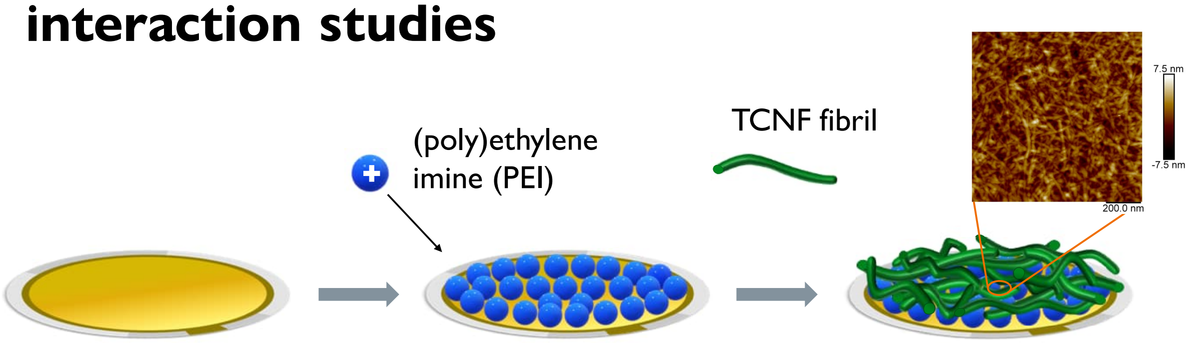
Preparation of model thin films for interaction studies



Au-coated sensors

Drop casting anchoring polymer ~30 min

Spincoating nanocellulose surfaces

+ Drying at 80° C to ensure fibril attachment

Methodology adapted from:

Eronen et al. *Carbohydr. Polym.* **2011**, *86*, 1281–1290.
Hakalahti et al. *Biomacromolecules* **2017**, *18*, 2951–2958.

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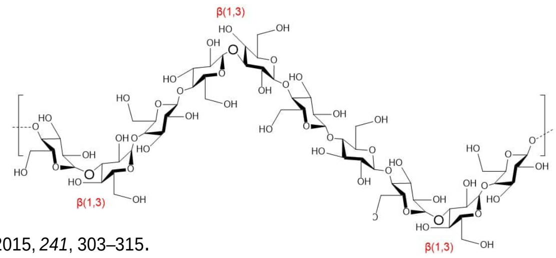
Mixed-linkage glucans (MLGs)

- 2.1 million tons of brewer's spent grain (BSG) are produced annually as industrial waste in Germany, the world's 5th largest producers beer.
- MLGs constitute around 0.02 – 0.11 wt% of rice husks and 1 wt% of BSG, counting up to roughly 1 300 – 8 800 tons and 21 000 tons of MLG per year being available from these two waste side streams alone. [1,2]
- Grass cell wall hemicellulose, e.g. cereals
- Flexible and water-soluble polymer with linear glucose backbone
  - β-(1,4)-linked cellotriosyl and cellotetraosyl units separated by interspersed β-(1,3)-linkages

  → Irregular shape

  - Longer (DP ≥ 5) segments approx. 10-20%



[1] P. Phuwadolpaisarn, *Molecules*, 2021, *26*, DOI:10.3390/molecules26216368.
[2] J. Steiner, S. Procopio and T. Becker, *European Food Research and Technology*, 2015, *241*, 303–315.

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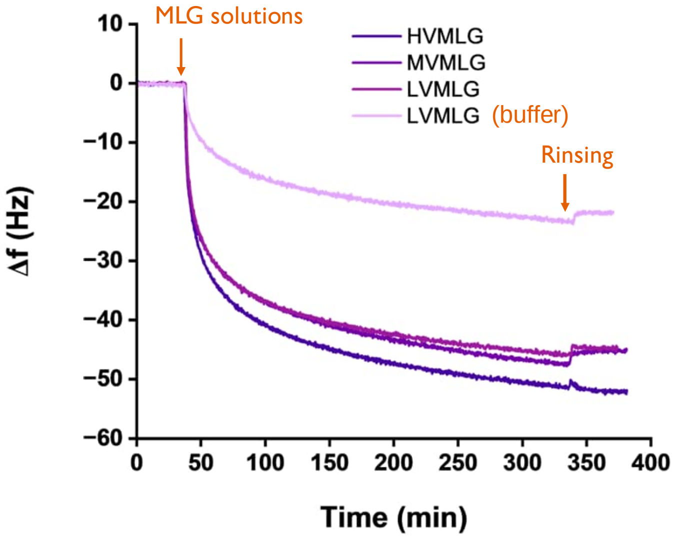
Adsorption of MLGs on TCNF

- 0.01 wt% MLG solutions adsorbed on TCNF thin films in water
  - LVMLG also in buffer (higher ionic strength)
- Irreversible adsorption
- M_w has little effect on adsorbed amount
  - Medium composition has bigger influence



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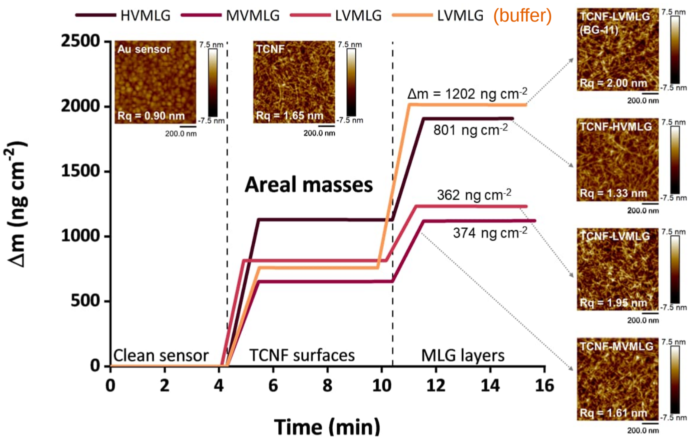
Dry areal masses of MLG layers

- Solid-air interface
  - Dry areal masses via Sauerbrey equation:

$$\Delta m = -C\,\frac{\Delta f}{n}$$

- Accumulation of higher mass on sensor with increasing M_w
- Adsorption increased in buffer
  - Specific ionic interactions



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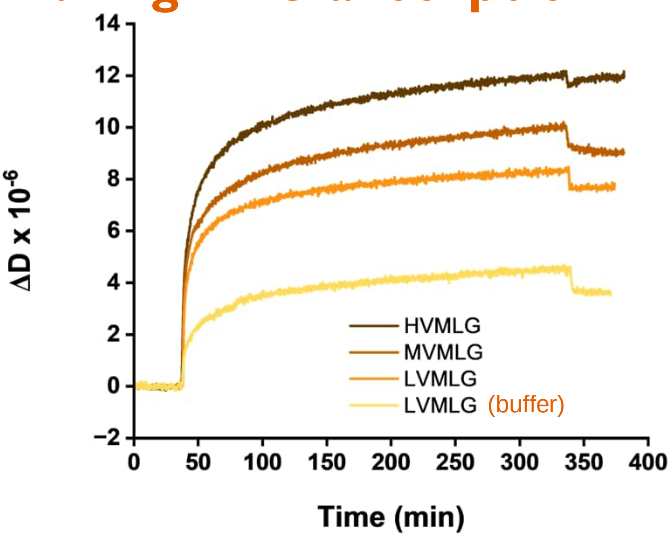
Dissipation changes during MLG adsorption

- ΔD increases with larger M_w

→ Larger M_w MLGs form softer layers and bind more water

- A more rigid LVMLG layer formed in presence of salts



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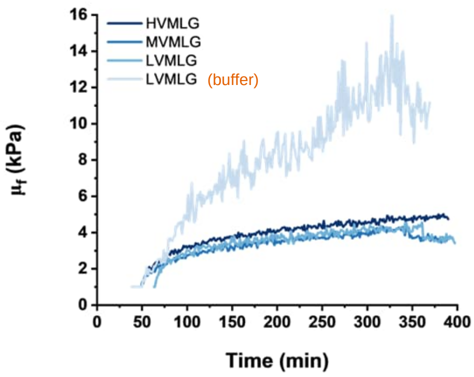
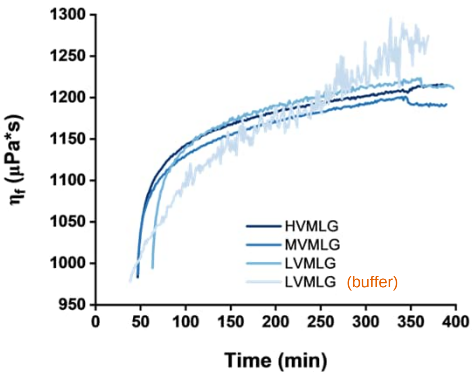
Viscoelastic properties of adsorbed MLG layers

- Modelled parameters: shear elastic modulus, shear viscosity, thickness
- Higher elastic modulus and viscosity in growth medium → stronger binding





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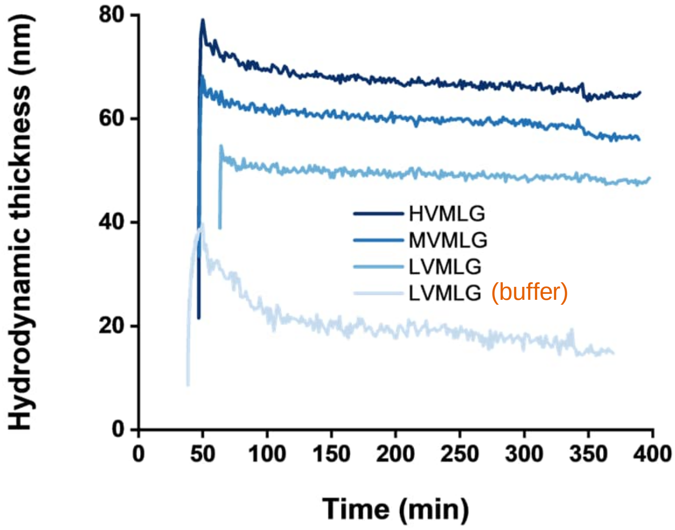
Hydrodynamic thicknesses

- Layer thickness increases with higher M_w
  - More bound water, softness increases
- Pronounced decrease in thickness when water is replaced with growth medium
  - Water not able to penetrate into the structure



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Summary of MLG properties

	M_w (kg/mol)	DP	Hydrodynamic diameter (nm)	Hydrohynamic thickness (nm)
LVMLG	179	994	35/220	50
• *in buffer*				20
MVMLG	238	1322	43/220	60
HVMLG	495	2750	75	70

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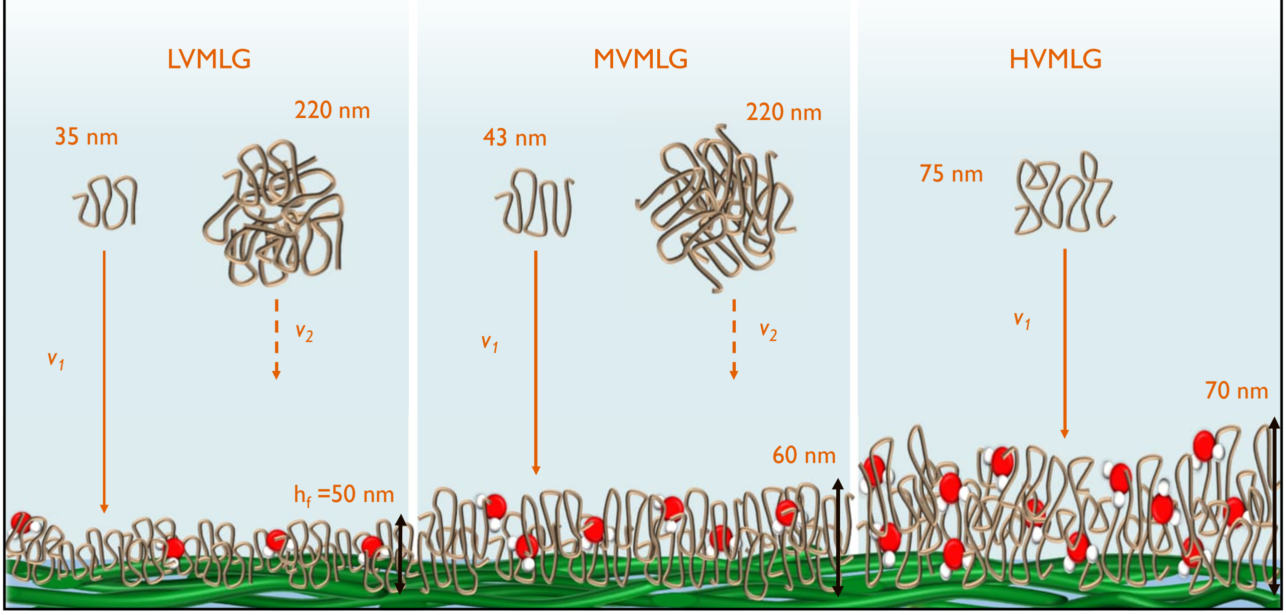
Effect of M_w on MLG adsorption



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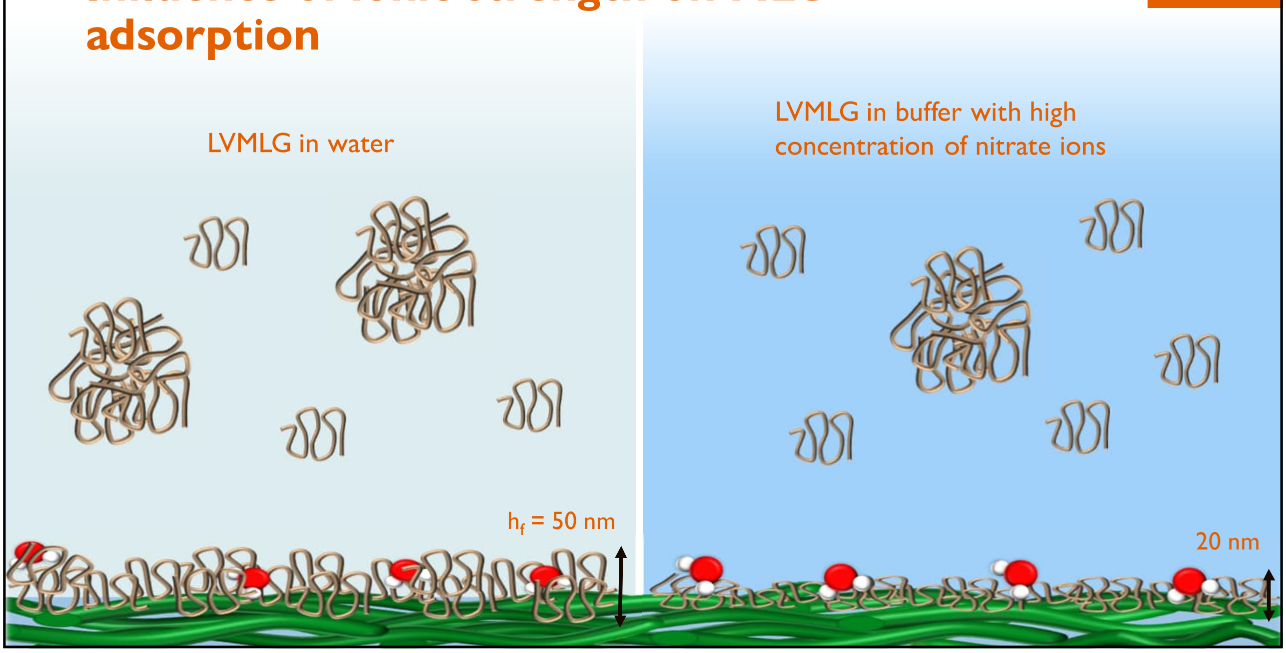
Influence of ionic strength on MLG adsorption



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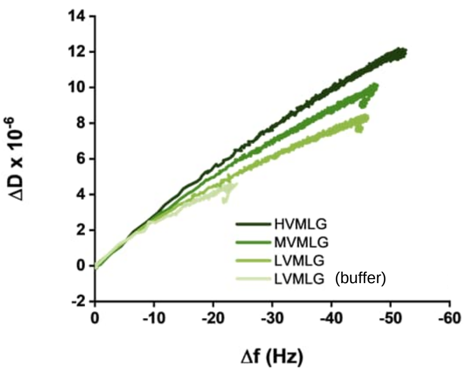
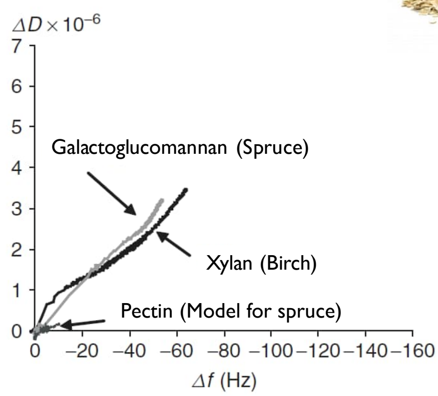
Adsorption of MLGs and wood hemicelluloses

- MLGs form far more dissipative layers than wood hemicelluloses
  - MLGs layers are soft, wood hemicellulose layers more rigid (Voigt model)





Virkkala T., Kosourov, S., Rissanen, V., Siitonen, V., Arola, S., Allahverdiyeva, Y., Tammelin, T. Bioinspired mechanically stable all-polysaccharide based scaffold for photosynthetic production. *J. Mater. Chem. B.* **2023**. DOI: 10.1039/D3TB00919J.

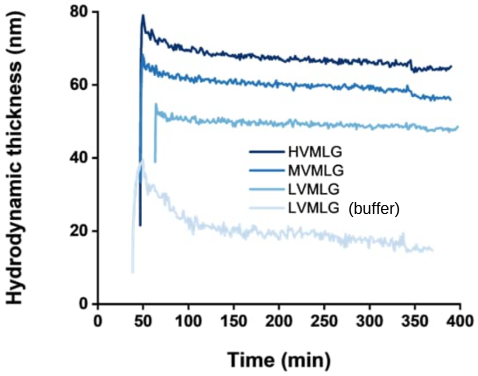
Tammelin, T., Paananen, A. and Österberg, M. Hemicelluloses at interfaces: Some aspects on the interactions *In: The Nanoscience and Technology of Renewable Biomaterials,* Lucia, A. L. and Rojas, O.J. (Eds), Wiley- Blackwell Publishing Ltd, West Sussex, UK, **2009**, 149-172.

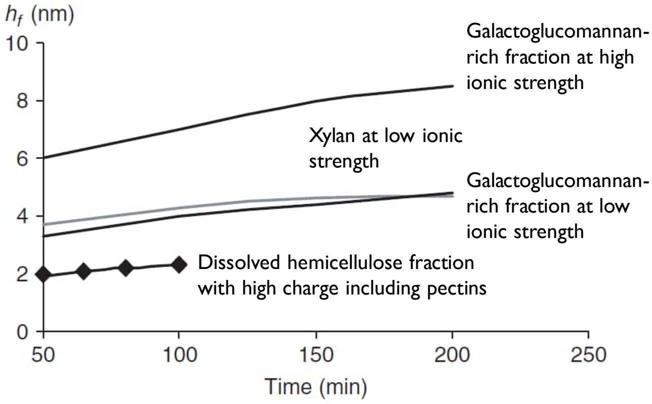
Tammelin et al. *Nord Pulp Paper Res J.* **2007**, *22*(1), 93 – 101.

38

Hydrodynamic thicknesses of MLG and wood hemicellulose layers

- MLG layer thicker than wood hemicellulose layers
  - Looser structure, more bound water





Tammelin, T., Paananen, A. and Österberg, M. Hemicelluloses at interfaces: Some aspects on the interactions *In: The Nanoscience and Technology of Renewable Biomaterials,* Lucia, A. L. and Rojas, O.J. (Eds), Wiley- Blackwell Publishing Ltd, West Sussex, UK, **2009**, 149-172.

Tammelin et al. *Nord Pulp Paper Res J.* **2007**, *22*(1), 93 – 101.

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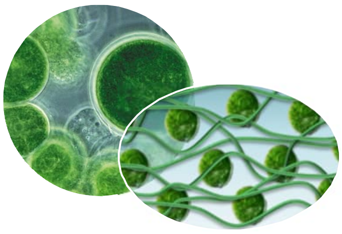

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Tools to investigate immobilisation mechanisms of living cells

- Photosynthetic microalgae cells immobilised in nanocellulose matrix
  - Construction of cell factories to produce e.g biofuels and other chemicals
  - Anionic cyanobacterial filaments
- Passive entrapment inside the nanocellulose network or strong attachment on the surface of nanofibrils?
  - Anionic TEMPO CNF network
  - TEMPO CNF cationised with polyethylene imine (PEI)

Jämsä, M. et al. *J. Mater.Chem.A.*, 2018, *6*, 5825-5835.

40

Cell immobilization via direct attachment

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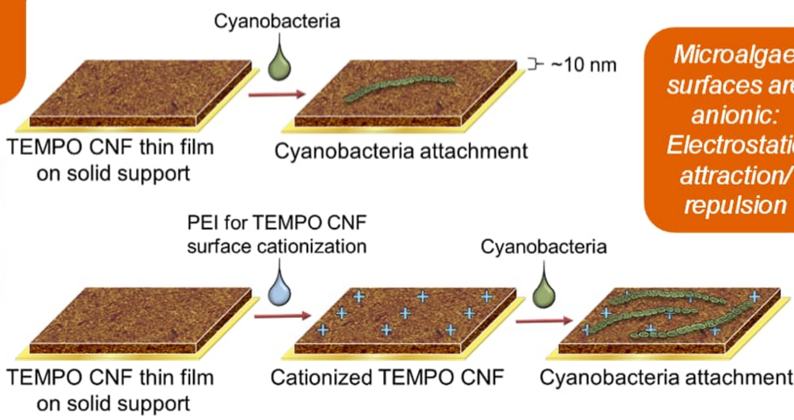
QCM-D Open Module: Real-time detection of surface interactions between TEMPO CNF films and cyanobacteria



Microalgae surfaces are anionic: Electrostatic attraction/ repulsion

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Cell immobilization via direct attachment

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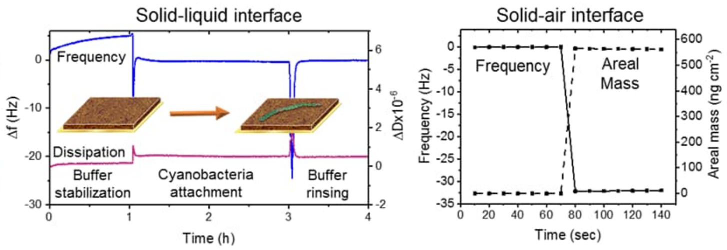
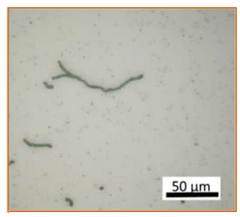
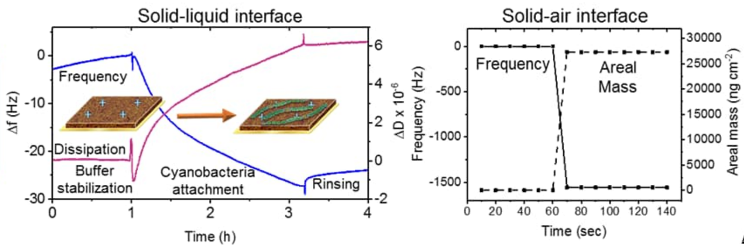
Anionic TEMPO CNF: Weak surface attachment

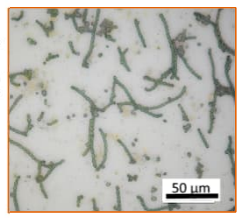




$\Delta m = 560 \pm 5$ ng cm^{-2}

Cationized TEMPO CNF: Strong surface attachment





$\Delta m = 34000 \pm 6600$ ng cm^{-2}

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INFORMATION GAINED USING QCM-D

WATER VAPOUR SORPTION AT SOLID-GAS INTERFACE

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How do these two methods complement each others?

Surface analytical approach

- Ultrathin film with well-defined composition and morphology (TEMPO-CNF, CNC)

Measurements as a function of RH%:

Spectroscopic Ellipsometry (SE)

- Optical method
- Changes in thickness and refractive index
- Supported ultrathin film
  → Δthickness ≈ Δvolume

➡ Thickness and volume isotherms

Quartz Crystal Microbalance (QCM-D)

- Acoustic method
- Changes in areal mass and dissipation of energy

➡ Mass isotherm

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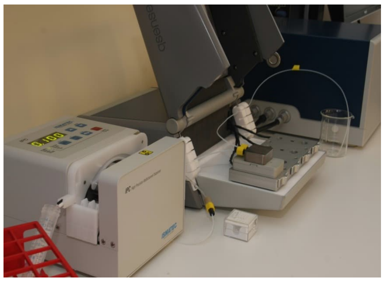
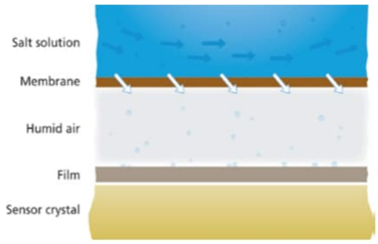
Water vapour uptake with QCM-D humidity module

- Change in frequency, Δf – change in mass on the crystal
  - Due to the film swelling and water vapour penetration the mass detected by the crystal increases → the frequency response decreases
  - $\Delta m = C \, \Delta f \, n^{-1}$
- Change in dissipation ΔD – The damping of the oscillation depends on the viscoelastic properties of the model film
  - solvent bound in the film structure generates softer and more mobile layer

Salt solution	Relative Humidity (%)
LiCl	11
$MgCl_2$	33
$Mg(NO_3)_2$	53
NaCl	75
K_2SO_4	97
pure milliQ H_2O	100





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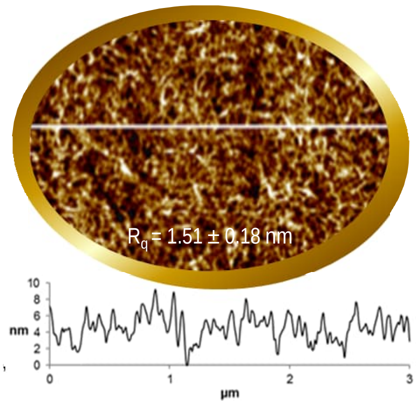
Ultrathin films of cellulose nanofibrils with well-known chemical composition and morphology

- TEMPO oxidized cellulose nanofibrils from bleached softwood pulp (charge 0.9 mmol/g)
  - Fibrillation with high pressure fluidizer
- Chemical composition by acid hydrolysis and HPLC
  - Hemicellulose content ~ 10 wt.-%
- Ultrathin films by spincoating
  - Au substrate
  - Fibrillar network, uniform fibril distribution, random orientation



Saito, T., Nishiyama, Y., Putaux, J., Vignon, M., & Isogai, A. (2006). *Biomacromolecules,* 7, 1687-1691.
Eronen, P., Laine, J., Ruokolainen, J., Österberg, M. (2011) J. *Colloid Interface Sci*, 373, 84-93.

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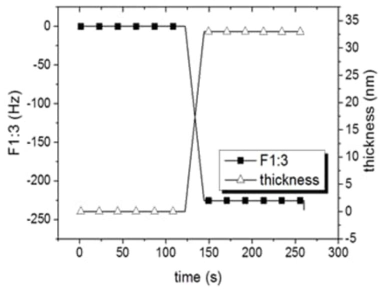
Initial Thickness of the Cellulose Film

Thickness determination by QCM-D



$$\Delta m = -\frac{C\Delta f}{n}$$

$$h = \frac{\Delta m_{Sauerbrey}}{\rho_{Assumed}}$$

- Frequency change measured in air before and after cellulose layer deposition
- Sauerbrey equation is valid to estimate the mass change
- Assuming the density values of the film, the thickness can be calculated

Peresin, S., Kammiovirta, K., Setälä, H. and Tammelin, T.*, Structural features and water interactions of etherified xylan thin films. *J Polym Environ.*, 2012, *20*, 895-904.

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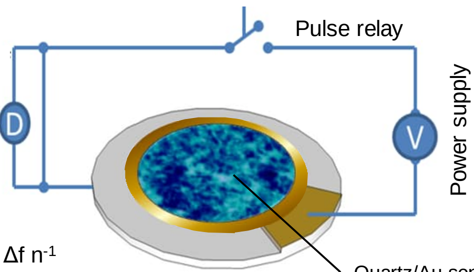
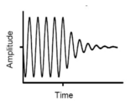
Mass uptake by QCM-D

$$D = \frac{E_{dissipation}}{2\pi E_{storage}}$$

- Quartz crystal sandwiched between two electrodes
- Measures the frequency and energy dissipation of the resonating crystal



Pulsed electric field (AC voltage) makes the quartz crystal oscillate at acoustic resonance frequency



$\Delta m = C\ \Delta f\ n^{-1}$

$D = \frac{E_{dissipation}}{2\pi E_{storage}}$

Quartz/Au sensor spincoated with TEMPO CNF and mounted to a QCM-D humidity chamber

In-situ data on

- the changes in areal mass due to binding of water molecules over a wide RH% range (RH 6-97%)
  → Mass isotherm
- **viscoelastic properties of the CNF layer** interacting with water vapor (amplitude of the oscillation decays due to frictional losses in the crystal – dissipation of energy)

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How to interpret QCM-D data during water vapour sorption and desorption

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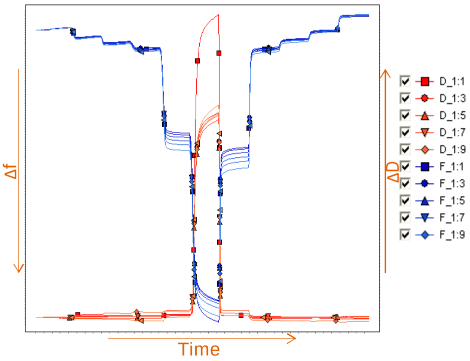
- The quartz crystal oscillate at specific frequencies when a current is applied across it.

- Change in frequency, Δf – change in mass on the crystal
  - When vapour adsorbs on the crystal surface the frequency decreases
  - Desorption is seen as frequency increase
  - $\Delta m = C\ \Delta f\ n^{-1}$
- Change in dissipation ΔD – The damping of the oscillation depends on the viscoelastic properties of the model film
  - soft – rigid
  - thick – thin layer
  - solvent bound in the layer structure

Example of QCM-D humidity module measurement



Steps indicate the gradually increasing and decreasing relative humidity (RH%) inside the measurement chamber

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Mass isotherm by QCM-D

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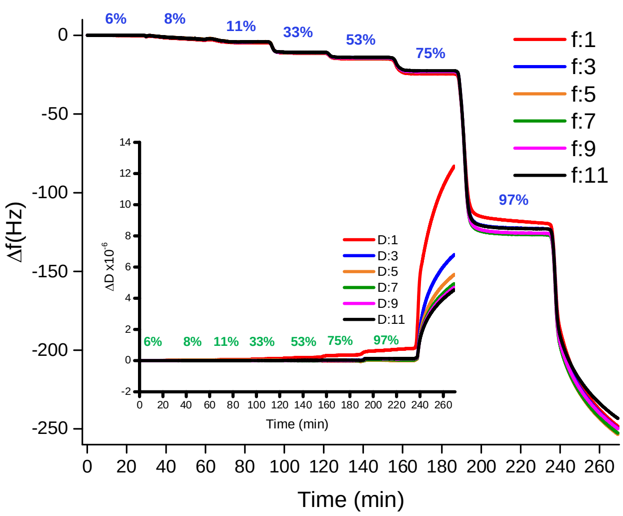
- Negative change in frequency due to water vapor uptake
- Minor dissipation response can be detected at RH > 75%
- TEMPO CNF layer shows viscoelastic behaviour at high relative humidity (75-97 RH%)

$$\Delta m = -C\frac{\Delta f}{n}$$



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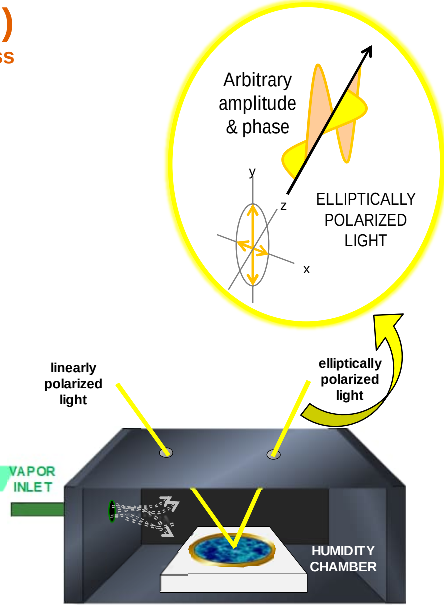
Spectroscopic Ellipsometry (SE)

Complementary technique to estimate thin film thickness

- Optical technique for determining film thickness and optical constants
- Measures the change in the state of polarization of light upon reflection
- Changes in thickness and refractive index as a function of RH% (RH 0-90%)
- Supported ultrathin film
  → Δthickness ≈ Δvolume

Thickness and volume isotherms



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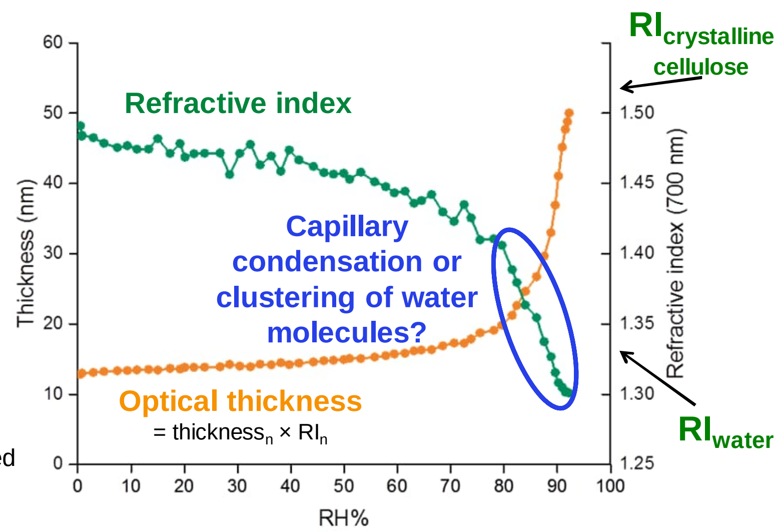
Thickness Isotherm by Spectroscopic Ellipsometry



How do you explain the difference in RI compared with RI of pure water?

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Thickness Isotherm by Spectroscopic Ellipsometry

Langmuir - Flory-Huggins – Clustering model

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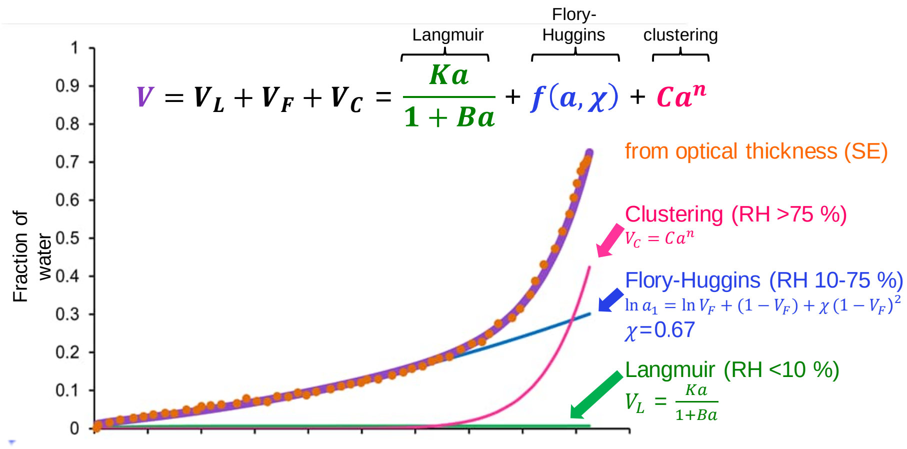

Hernandez, R., Giacin, J., Grulke, E. The, Journal of Membrane Science, 1992, 65, 187-199.

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Water Vapor Sorption described by a simple additive Langmuir/Flory-Huggins/Clustering model

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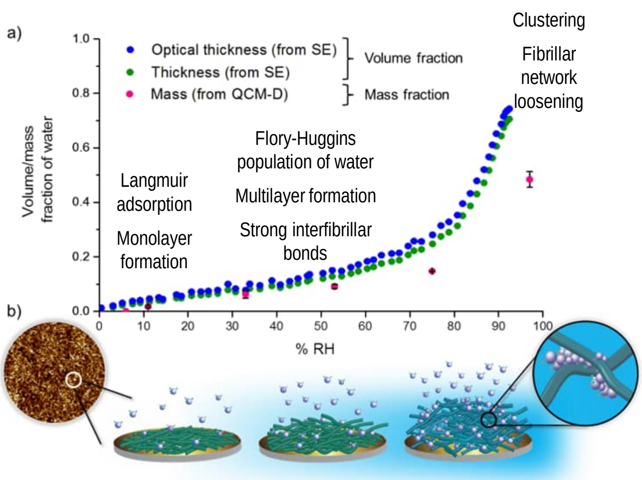

- Precise insight on the changes in the physical attributes of the moisture-sensitive nanocellulose films due to water vapor sorption
- Enables further evaluation of the sorption kinetics of water molecules

↓

- Diffusion and permeability coefficients of water vapor in CNF film can be determined
- Important parameters when considering the utilization of complex biobased materials in water sensitive applications

Water is a 4th main component in fibre cell wall?

Hakalahti, M.; Faustini, M.; Boissière, C.; Kontturi, E.; Tammelin, T. *Biomacromolecules*, **2017**, *18*, 2951-2958.

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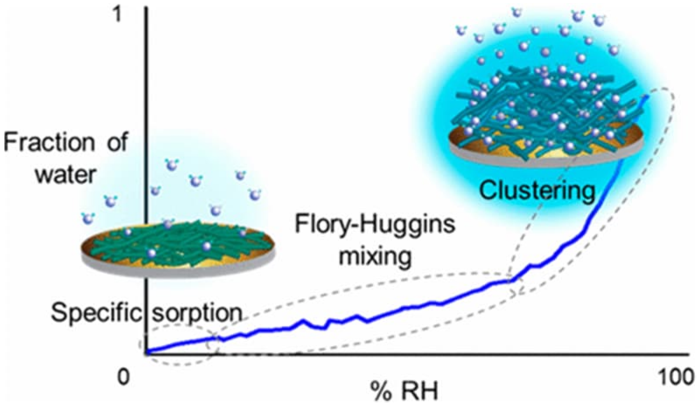
Nanofibre network swelling

Three specific regimes of water sorption with cellulose nanofibres



The data enables

- understanding on the mechanism of water vapour sorption at different conditions
- evaluating sorption kinetics
- determination of relevant materials parameters such as diffusion and permeability coefficients

Hakalahti, M.; Faustini, M.; Boissière, C.; Kontturi, E.; Tammelin, T. *Biomacromolecules*, **2017**, *18*, 2951-2958.

Hakalahti et al. *Biomacromolecules* **2017**, *18*, 2951.

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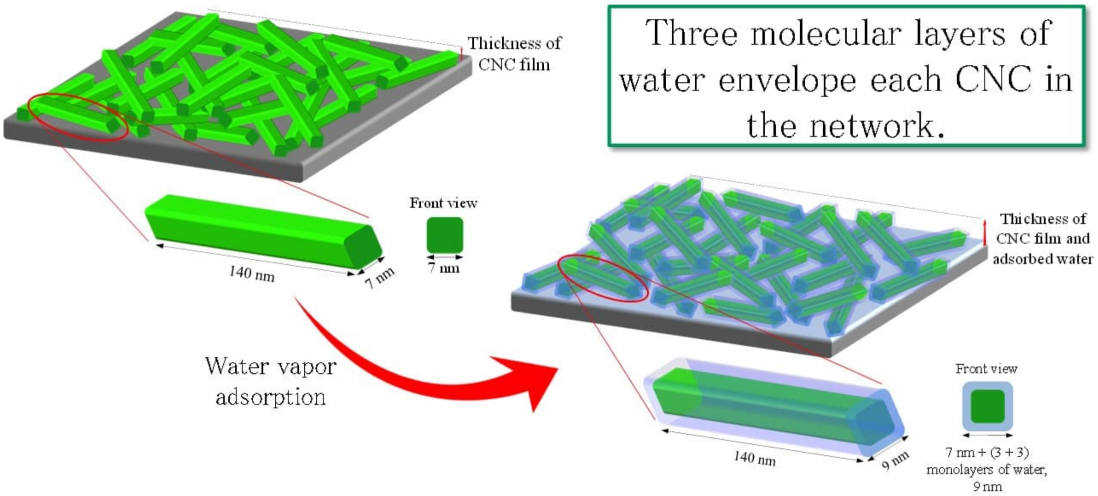
Nanocrystal network swells

Three molecular layers of water envelope each CNC in the network.



Niinivaara et al. *Langmuir* **2015**, *31*, 12170.

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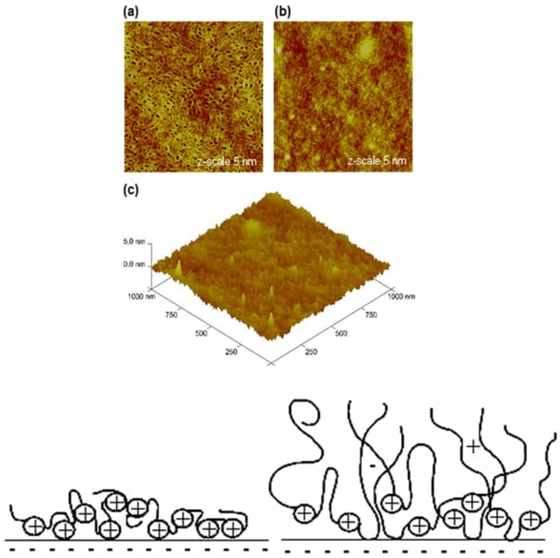
Conclusions

- By combining practical problems and macroscale phenomena with fundamental surface chemistry studies, the behaviour of the materials can be further clarified and understood
- The ultrathin model film approach and surface sensitive methods can effectively link the material behaviour at interfaces to the macroscale physical properties
- QCM-D method enables the usage of approach which link the material behaviour at interfaces to the macroscale physical properties
  - Affinity and interaction studies – controlled compatibility and film formation, essential parameters when considering e.g. strength enhancement of bioinspired (nano)composites or various immobilization strategies
  - Degradation and dissolution studies – enables e.g. the determination of the optimal usability of (modified) biopolymers (e.g. choice of solvents and other solvent parameters for example pH and ionic strength, hydrolysis)
  - Changes in material properties – Physical changes of biomaterial based films and coatings due to heat, UV or enzymatic treatments can be systematically studied.
  - Swelling and water vapour uptake studies – enables the investigations related to the barrier and membrane films and water interactions using the specific QCM-D humidity module



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