Atomic Force Microscopy (AFM) Part I

CHEM-L2000

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Lectures on AFM

Part I
- Principles and practice
- Imaging of native materials, including nanocellulose

Part II
- Surface force measurements on ultrathin films

Part III
- Quantification and special applications

Learning objectives of the current lecture

After this lecture, you will be able to
- Understand the principles behind scanning probe microscopies, especially AFM

- Tell the difference between main operating and imaging modes of AFM

- Possess a clear picture on the instrumentation of tapping mode AFM

- Be aware of the main advantages and limitations of AFM

- Give examples of applying AFM on native (soft) materials, including various nanocellulosic materials

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Outline

(1) Scanning probe microscopies in general

(2) Principle of AFM

(3) Tapping mode / Peak force tapping

(4) Experimental aspects of AFM

(5) Native materials by AFM

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Terminology

- AFM belongs to the family of Scanning Probe Microscopies (SPM)

- The first SPM introduced was Scanning Tunnelling Microscopy (STM)

- Other SPM techniques: Scanning Near-field Optical Microscopy (SNOM), Magnetic Force Microscopy (MFM), or Scanning Thermal Microscopy (SThM), among many others

- AFM is often referred to as Scanning Force Microscopy (SFM)

- AFM is by far the most common of the SPM techniques

Basic principle of all SPM techniques

- unlike optical or electron microscopy, SPM is *not* based on electromagnetic waves

- Instead, a probe scans across the surface

- Probe consists of a cantilever and a very sharp tip

- The tip interacts with the surface

- The cantilever deflects

- The deflections in the cantilever are recorded
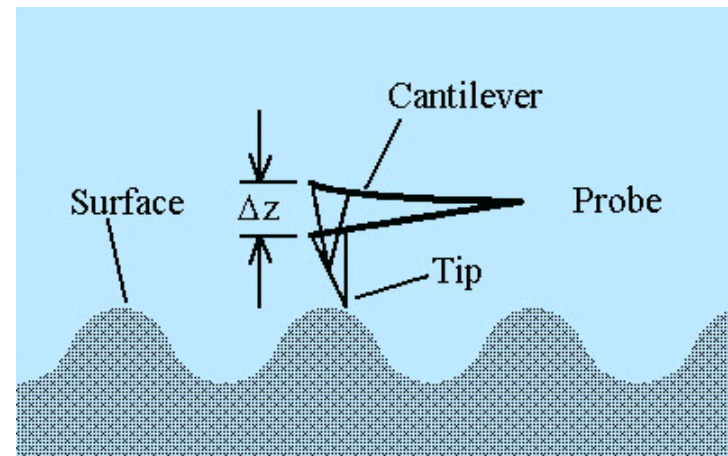
An image of topography occurs.

Scanning Tunnelling Microscopy (STM)

- Introduced in 1981-1982 by Gerd Binnig and Heinrich Rohrer
→ Nobel Prize in physics in 1986

- Based on the tunnelling current between two objects brought in very close contact

Distance between the sample and the probe increased 1 Å.

Tunnelling current decreases by a factor of ten.

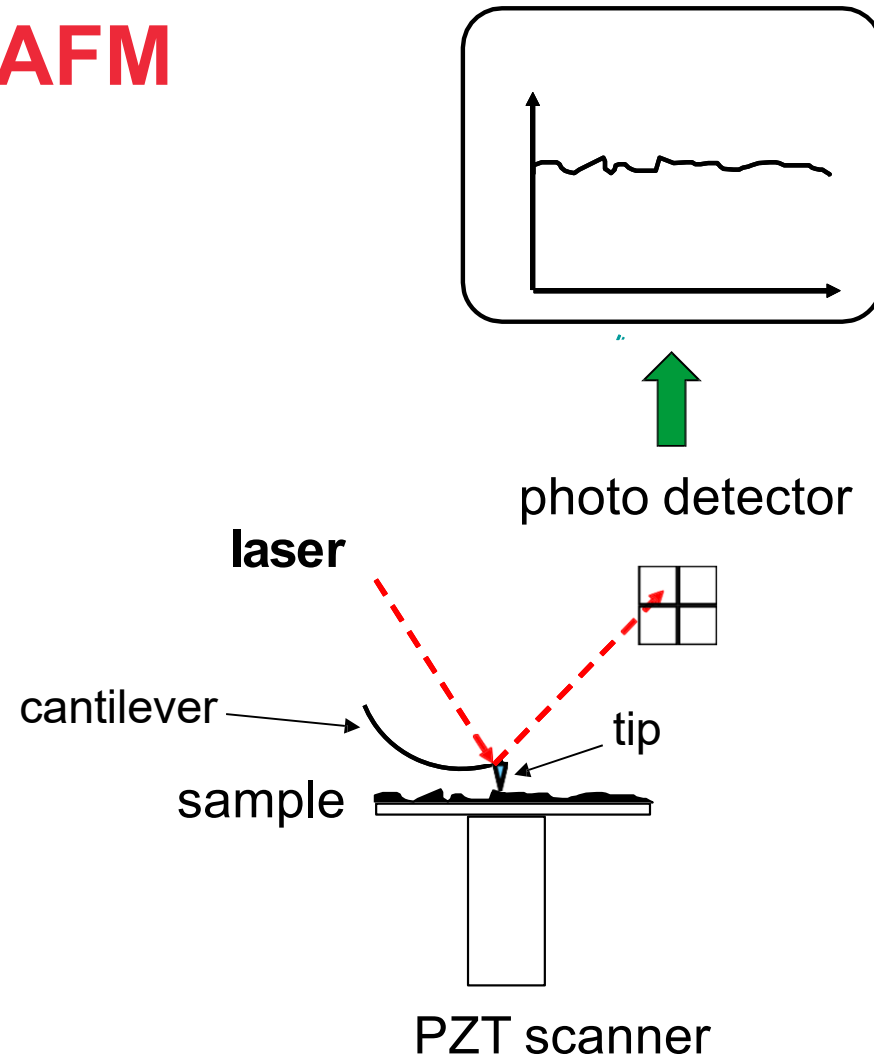- First images of atomic resolution were published in 1983

LIMITATION: STM requires that samples be conductive And (nearly) atomically smooth.

AFM – general remarks

- Introduced in 1986 by Binnig et al.

- Does not require conductive samples
  $\rightarrow$ introduced SPM to most organic materials

- Gained increased popularity in the 1990s

- Has become a routine technique during this decade

- Much of the "revolution" in nanotechnology owes to AFM: otherwise the visualization of nano-objects would not have been feasible (to an extent)
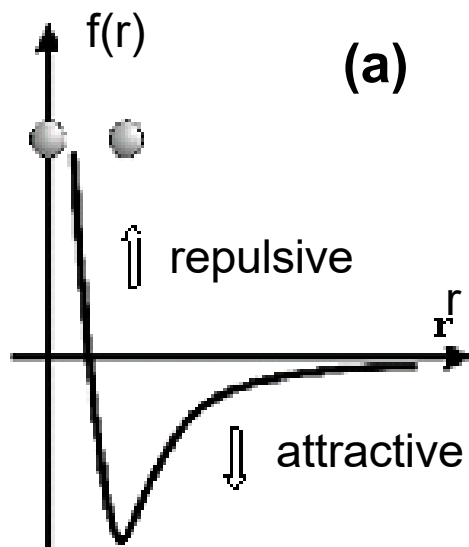
Basic principle of AFM

(1) Surface forces between the tip and the sample deflect cantilever.

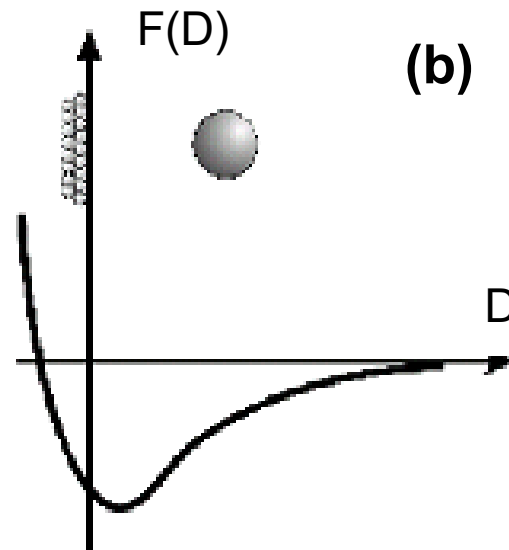(2) Deflections are recorded by reflecting a laser from the tip of cantilever

photo detector

laser

cantilever

tip

sample

PZT scanner

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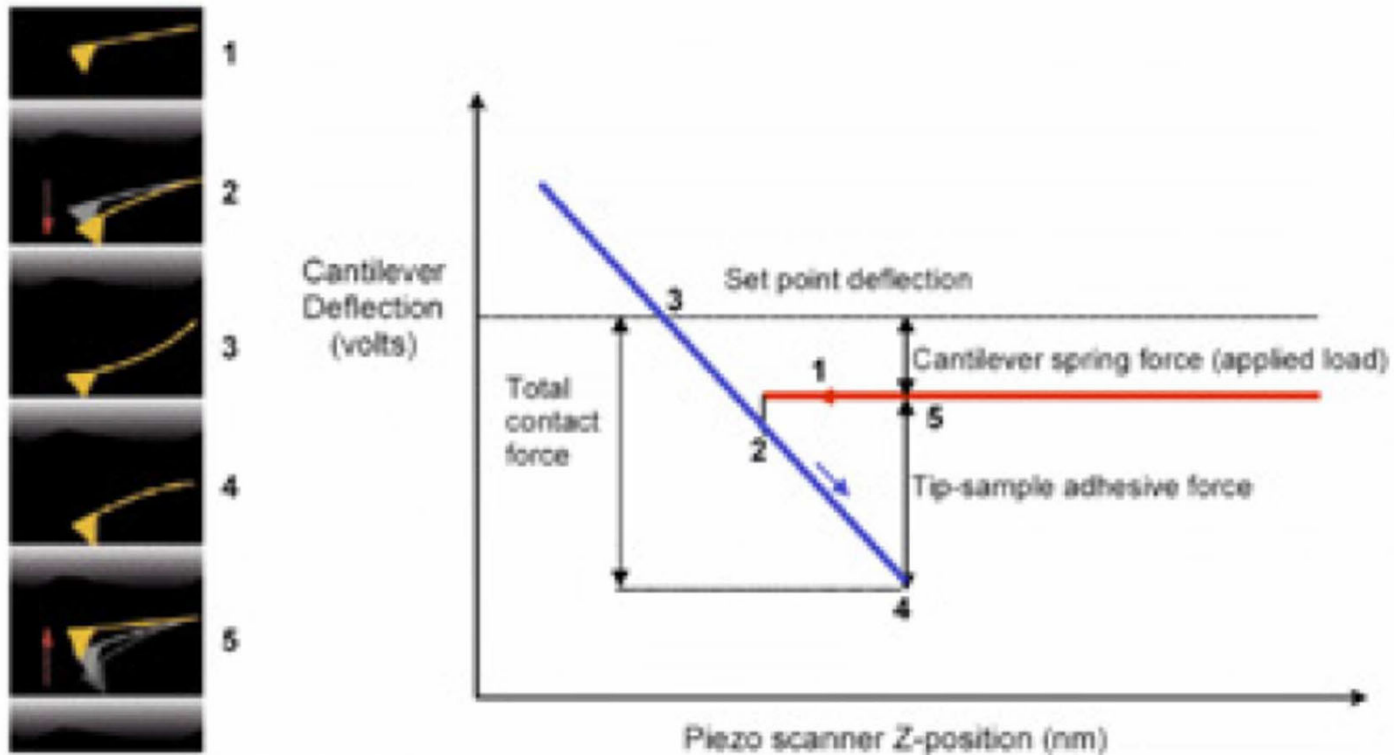# Basic principle of AFM

- high force sensitivity

IDEAL

REALITY

Interaction between
two atoms F~r $^{-7}$

Interaction between a sphere (tip)
and a surface (sample): F~D $^{-2}$

Basic force curve in contact mode AFM

Operating modes of AFM

Contact mode:
- Tip scans in the immediate vicinity (contact) of the sample

Tapping mode (or intermittent contact mode):
- Cantilever is vibrated near its resonance frequency
- Tip-sample interaction causes changes in the amplitude of the vibration
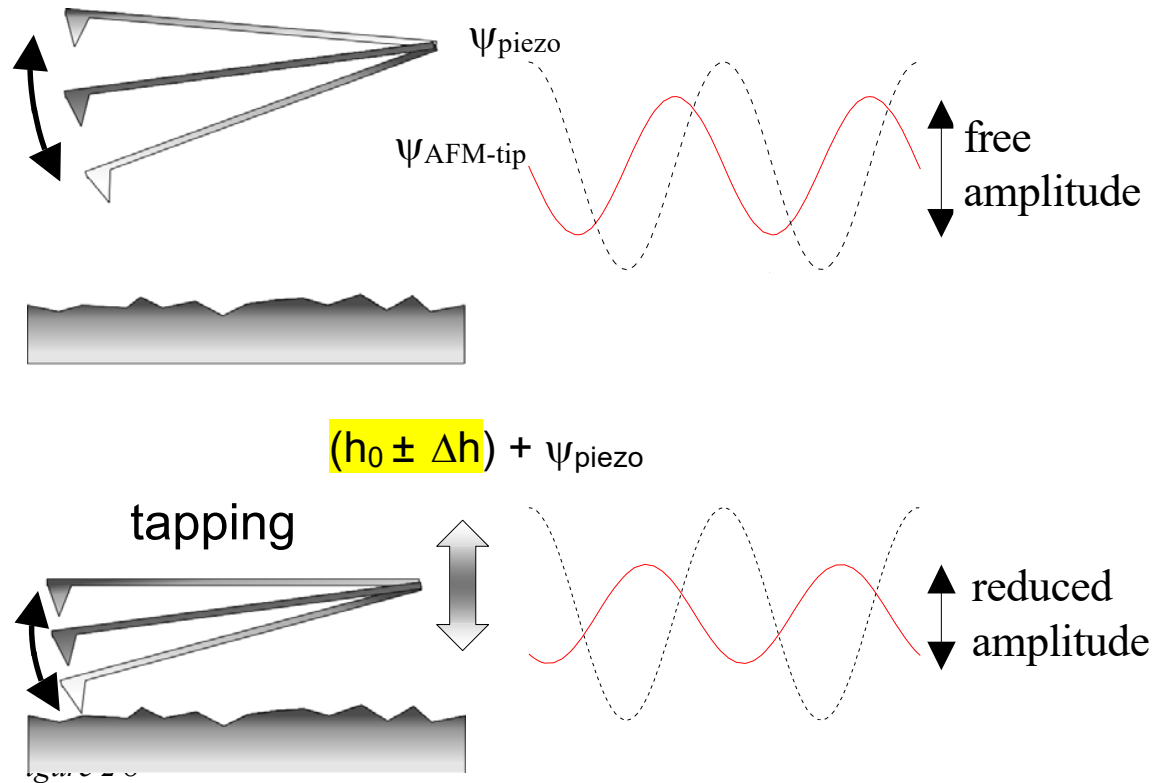- Changes in the amplitude are monitored

Non-contact mode:
- Same as tapping mode, but changes in the frequency are monitored

NOTE: Tapping mode is mandatory for compliant materials which would be destroyed (scratched) in contact mode imaging, resulting in artefacts in the image.
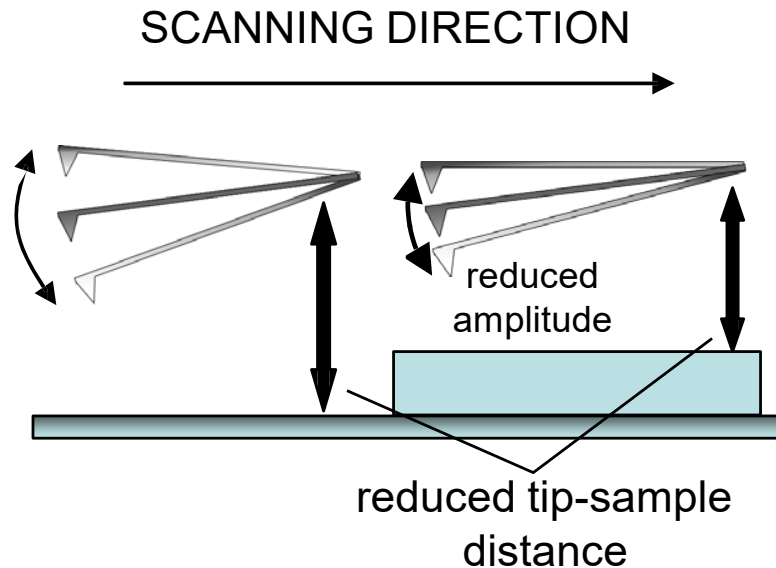**Practically all polymeric samples are imaged in tapping mode.**

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Tapping mode

- interaction with the sample surface causes amplitude displacement

ψ_{piezo}

$\psi_{AFM-tip}$

free amplitude

$(h_0 \pm \Delta h) + \psi_{piezo}$

tapping

reduced amplitude

Tapping mode

(a) No tip adjustment

(b) Tip-sample distance adjusted

SCANNING DIRECTION

corrected height

reduced amplitude

reduced amplitude

reduced tip-sample distance

same tip-sample distance

If the height of the vibrating tip is not adjusted, the amplitude reductions will not genuinely map the surface features.
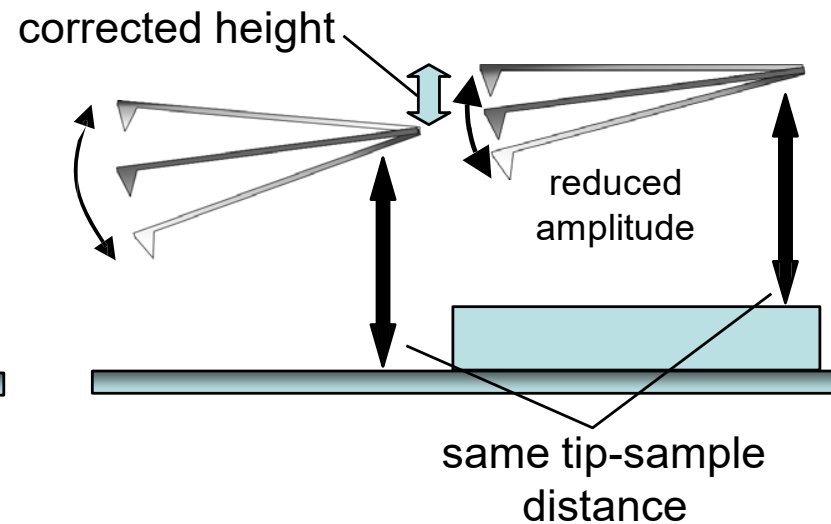
When the height of the vibrating tip is adjusted always to the same distance from the sample after each amplitude reduction, the imaging is correct.

Tapping mode: height image

Each height adjustment after each amplitude reduction is monitored.
→ Result: **HEIGHT IMAGE**

- height image yields information on the topography of the sample
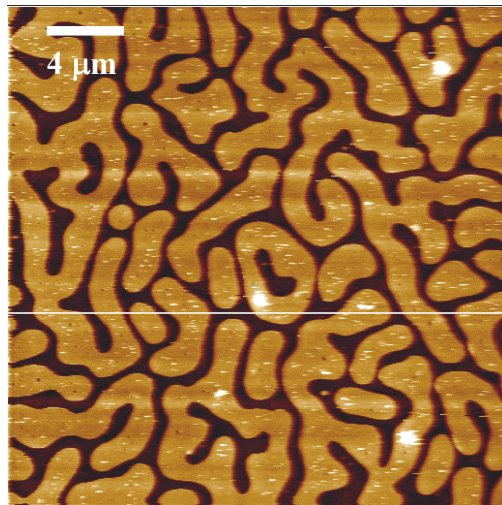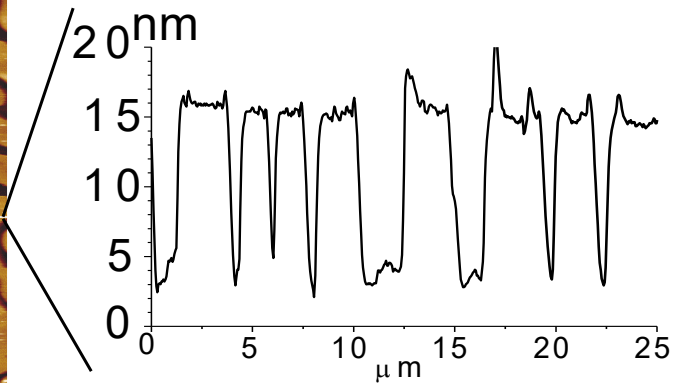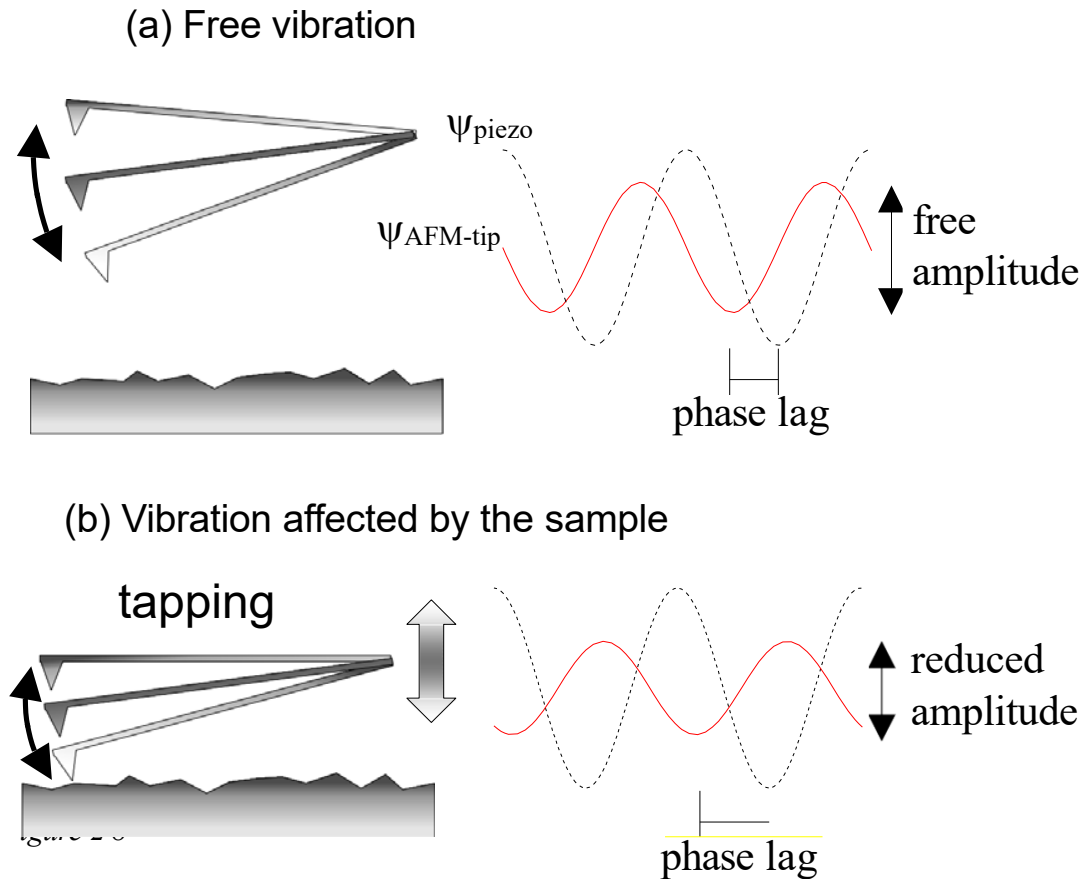
(a) Height image

(b) Individual height scan

4 µm

Image: cellulose islands

512 of individual scans make up the height image.

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Tapping mode: phase lag

(a) Free vibration

ψ_{piezo}

$\psi_{AFM-tip}$

free amplitude

phase lag

(b) Vibration affected by the sample
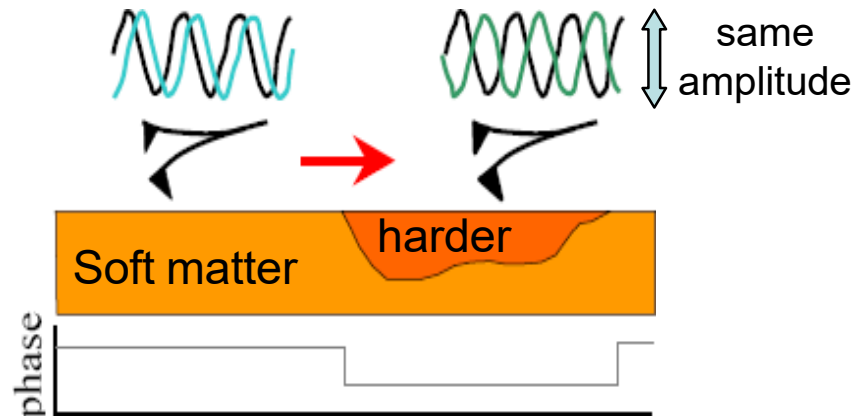

tapping

reduced amplitude

phase lag

- Tapping mode vibration is a standing wave with a sinusoidal shape

$$y = A\cos(\omega T + \phi)$$

phase of harmonic motion (unit: angle)

Tapping mode: phase image

same amplitude

harder

Soft matter

phase

- Phase lag yields important information on the elasticity of the sample

- If the two materials have the same height (amplitude unaffected), but they differ in elasticity, the phase lag reveals the difference
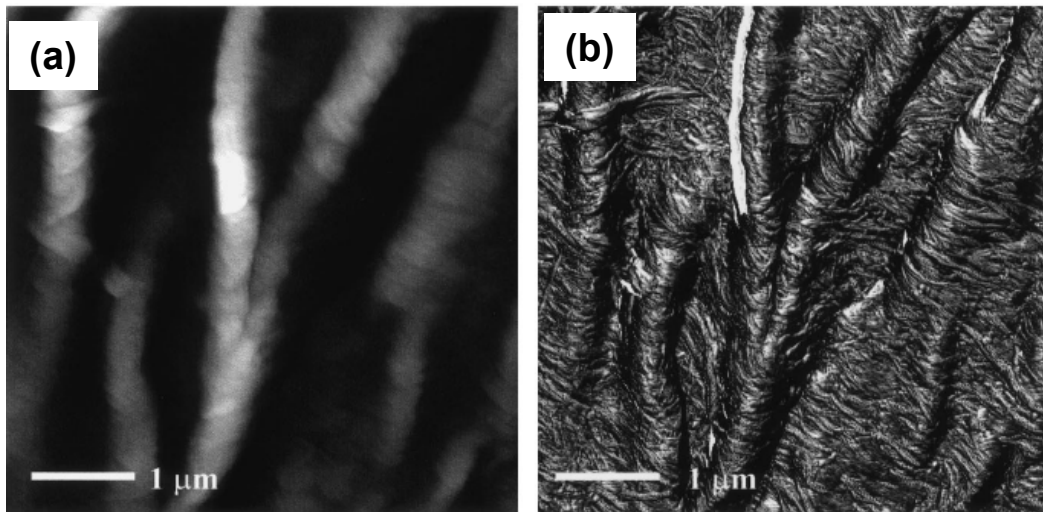
Phase image **(based on mapping the phase lag) distinguishes different materials in the sample.**

Height image vs. phase image

- Imaging the surface of a single fibre in kraft pulp

Height image   **Phase image**

Fibre contains: crystalline cellulose microfibrils (hard)
amorphous hemicellulose and lignin (soft)

Phase image is able to resolve the microfibrils.

Peak Force Tapping Technology

- Like tapping mode, based on oscillating the cantilever

- Unlike tapping mode, PeakForce Tapping operates in *non-resonant* mode

- Tapping oscillation is perfomed at frequencies well below the cantilever resonance

$\rightarrow$ Dynamics of a resonating system are avoided

$\rightarrow$ Direct force control is enabled

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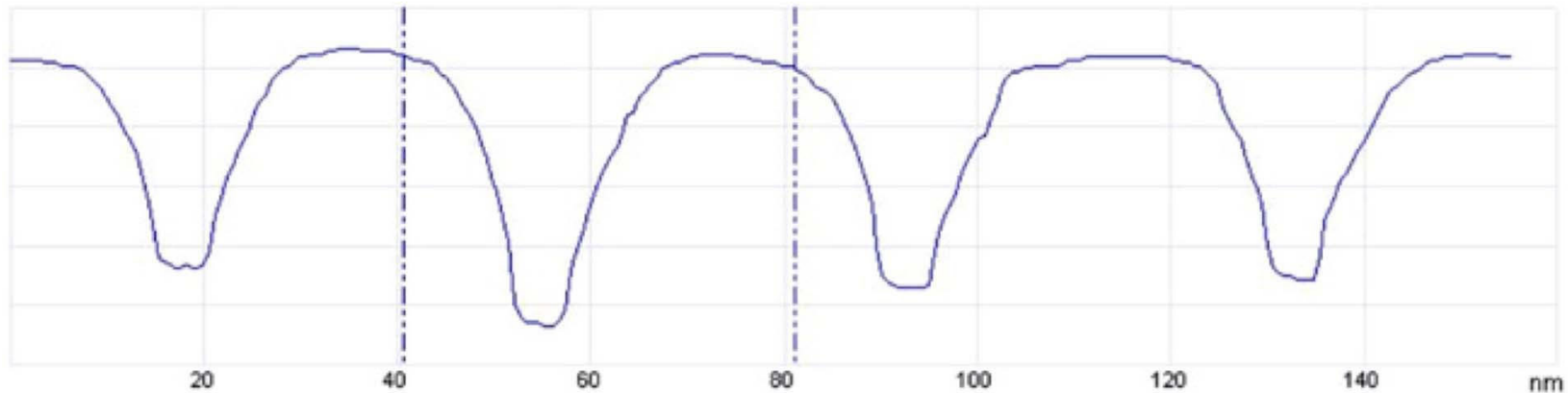**School of Chemical**
Technology

Peak Force Tapping Technology

- Position of the tip is modulated by a sine wave
→ Unwanted resonances at turn points are avoided
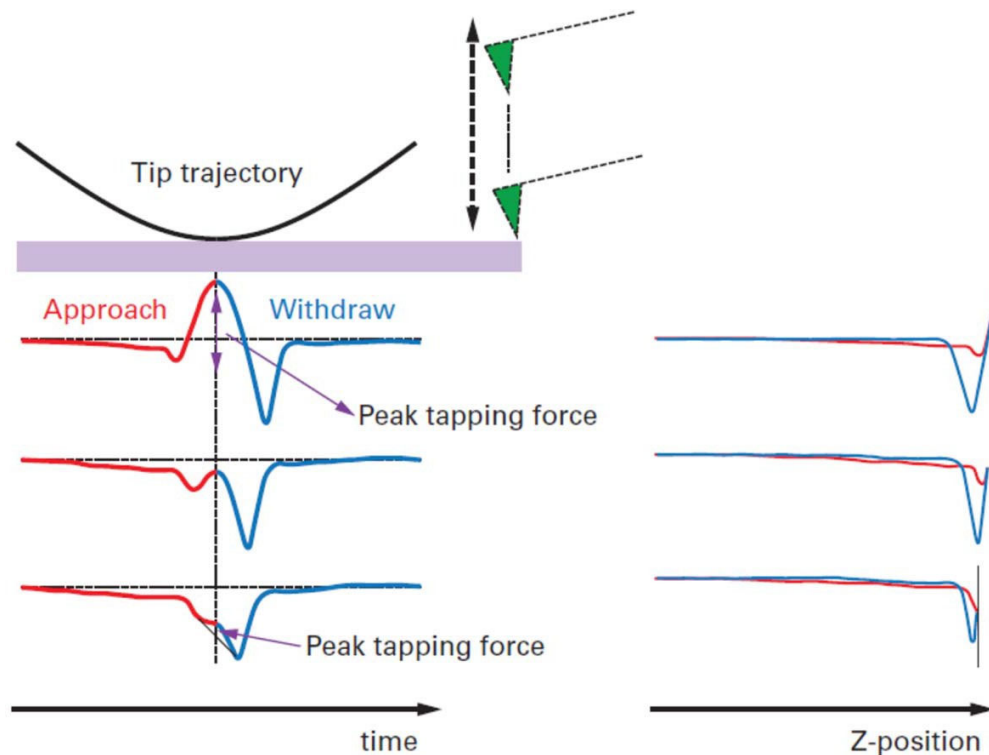
Peak Force Tapping Technology

Example: Peak Force Tapping line scan of narrow and steep, frequently recurring trenches in nanoscale


- In tapping mode the high frequency oscillation would cause the tip to "stick" to the sidewalls; flat bottoms would not be visible
- In Peak Force Tapping, there are fewer artefacts due to tip-surface interactions and cantilever dynamics
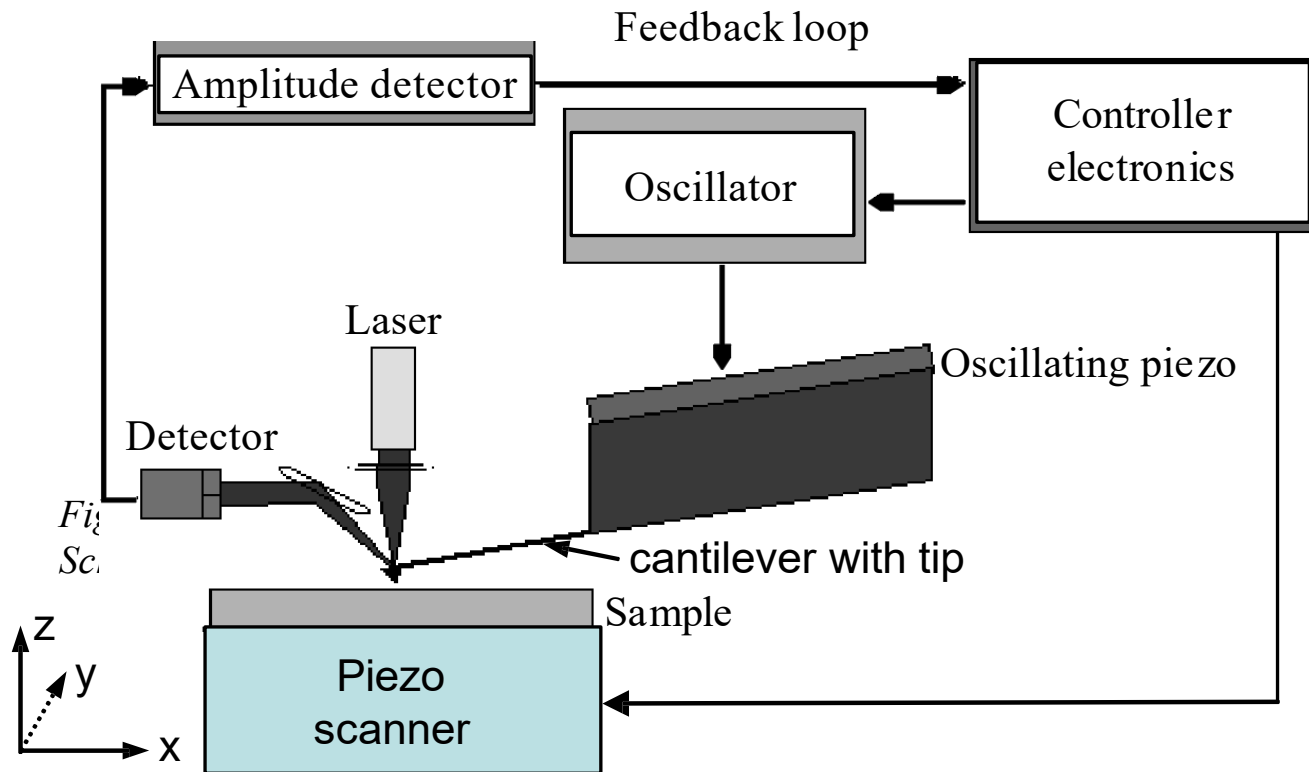
EXPERIMENTAL ASPECTS

Limitation by the tip size

- Vertical resolution of AFM is outstanding: < 0.1 nm
- Lateral resolution is limited by the size of the tip

(a) "Hill"

(b) "Slope"

real   image   real   image
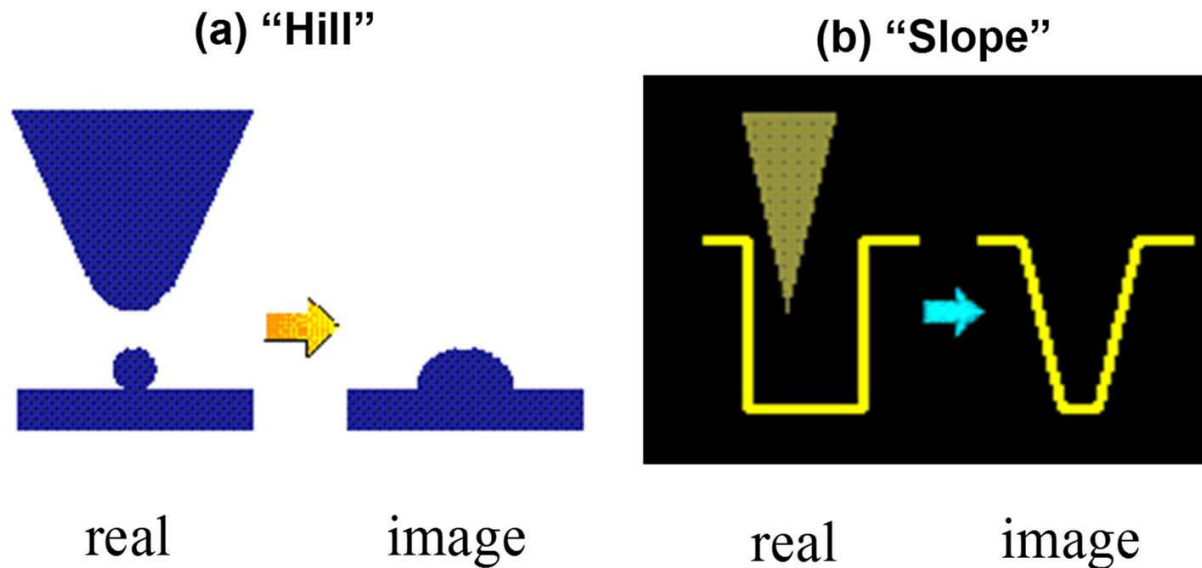
- The lateral exaggeration only concerns features whose size is close to the size of the tip

- Radius of an ordinary AFM tip: 5-10 nm

AFM instrumentation

Sample preparation and limitations

- AFM requires no sample preparation

- Roughness of the sample sets limitation

- Rule of thumb: roughness >1µm cannot be imaged
  (piezo scanner is too sensitive for "high" roughness)

Imaging of lignocellulosic fibres

- **Width of individual fibres is > 10 μm**
→ **Fibre joints and "holes" between fibres are too rough for AFM**

Paper or pulp
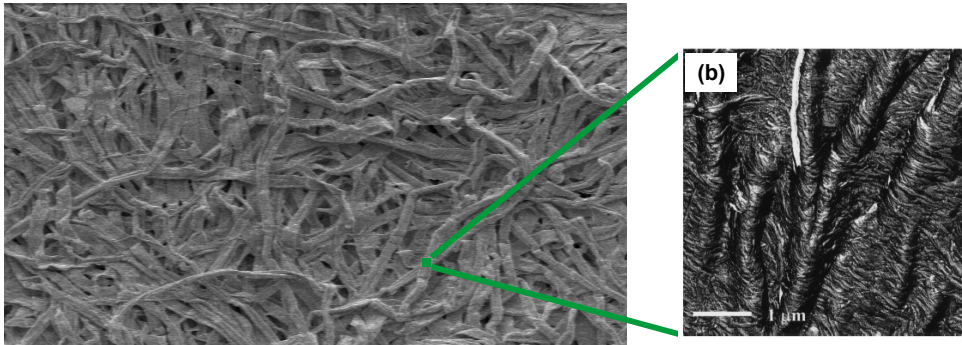
(1) AFM is usually combined with optical microscope
(2) Individual fibre is chosen
(3) Surface of individual fibre is imaged with AFM

AFM in practice

- Scan size is usually between 1×1 µm^2 and 5×5 µm^2

- If roughness of the sample allows, 50×50 µm^2 images are feasible (some instruments allow even 100×100 µm^2 scans)

- Acquiring (scanning) one image takes about 15 minutes

- Modern equipment can scan multiple (adjacent) images at one go

- Acquiring a decent image can take several hours or days, depending on how challenging the material is

AFM in practice

Difficulties on AFM imaging often depend on the material:

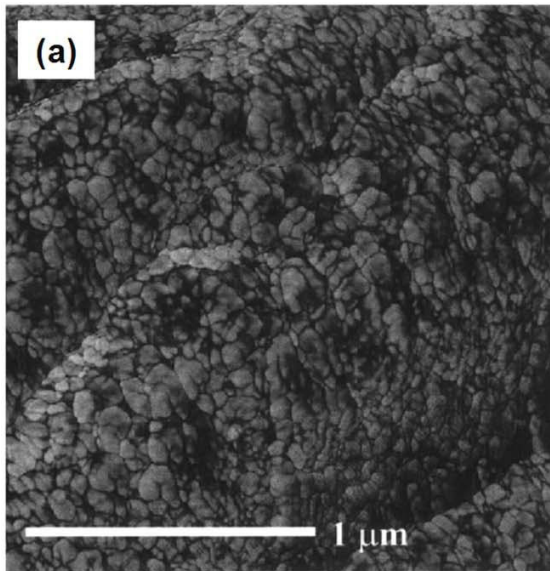- **hard material: easy to image**
- **soft material: difficult to image**

Soft materials may deform during tapping.
Soft materials may also get stuck on the tip.
→ Image is distorted.
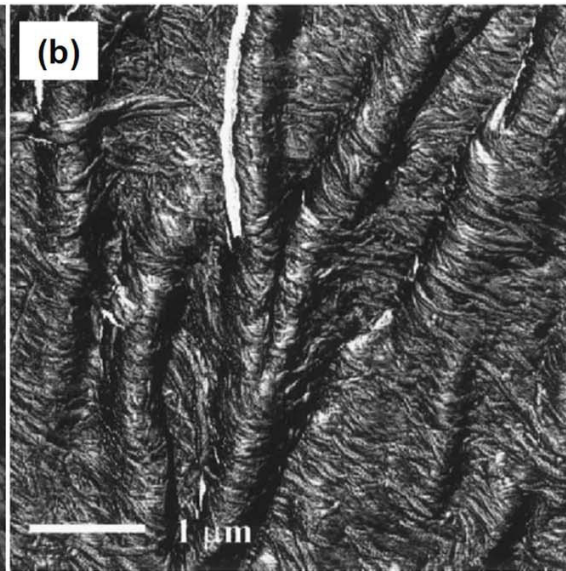

Cantilever w/ tip
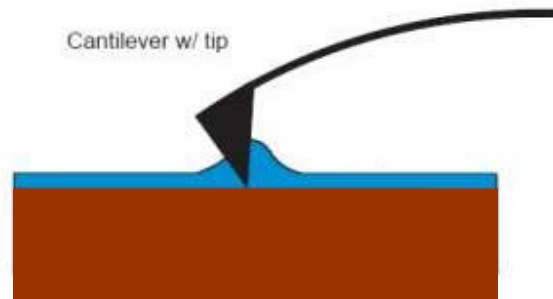
APPLICATIONS WITH NATIVE MATERIALS

Visual changes during chemical pulping

**Kraft pulp
cooked for 10 min**

**Kraft pulp
cooked for 220 min
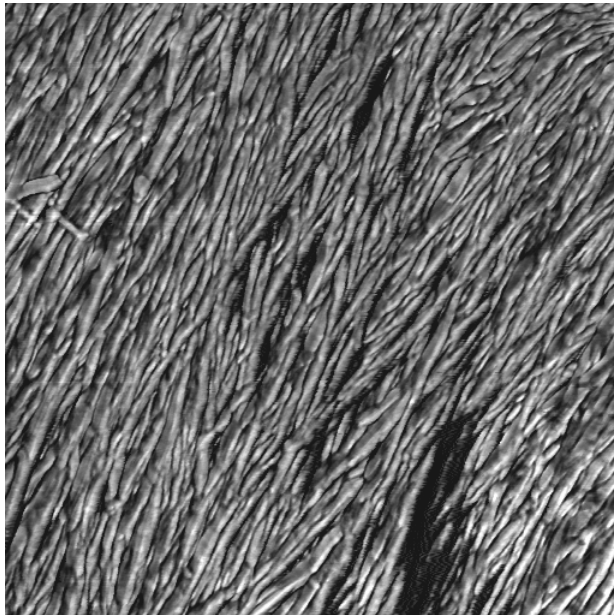and oxygen delignified**

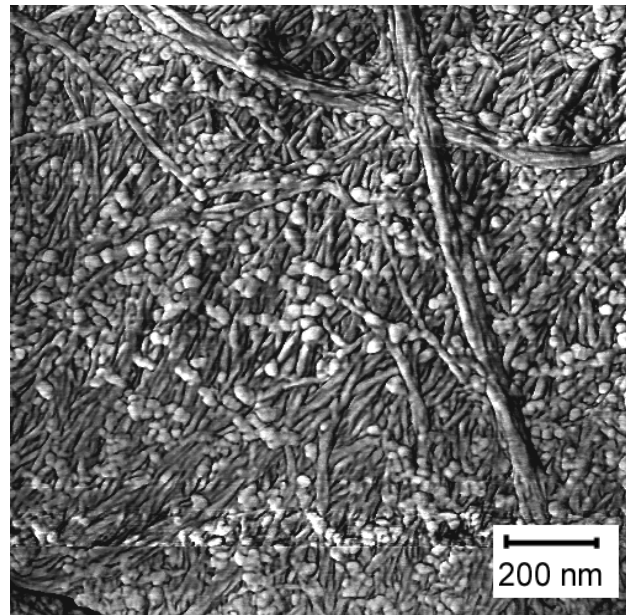
Low delignification

High delignification

➡️ **Lignin enriched on surface as granular structures (~10-100 nm width)**

# Deliberate adsorption of lignin

**Bleached pulp,
no lignin added**

**Bleached pulp,
lignin adsorbed artificially**

200 nm

➡ **Hard evidence for the appearance of lignin.
(AFM is only an imaging technique; it yields no chemical information.)**

Adsorption of lignin and polyelectrolyte

**Bleached pulp,
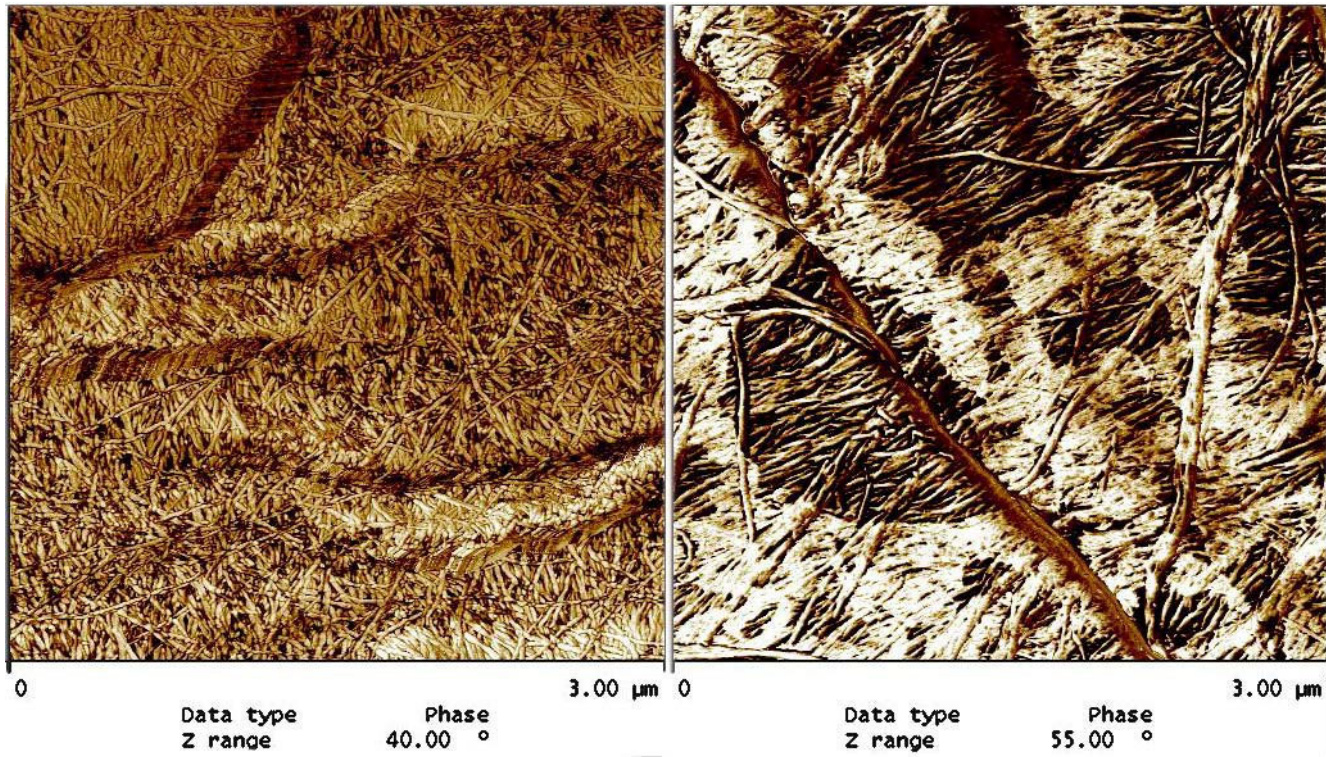no lignin added**

**Bleached pulp,
lignin+PDADMAC
adsorbed artificially**

retention aid
in
papermaking

(a)

200 nm

(b)
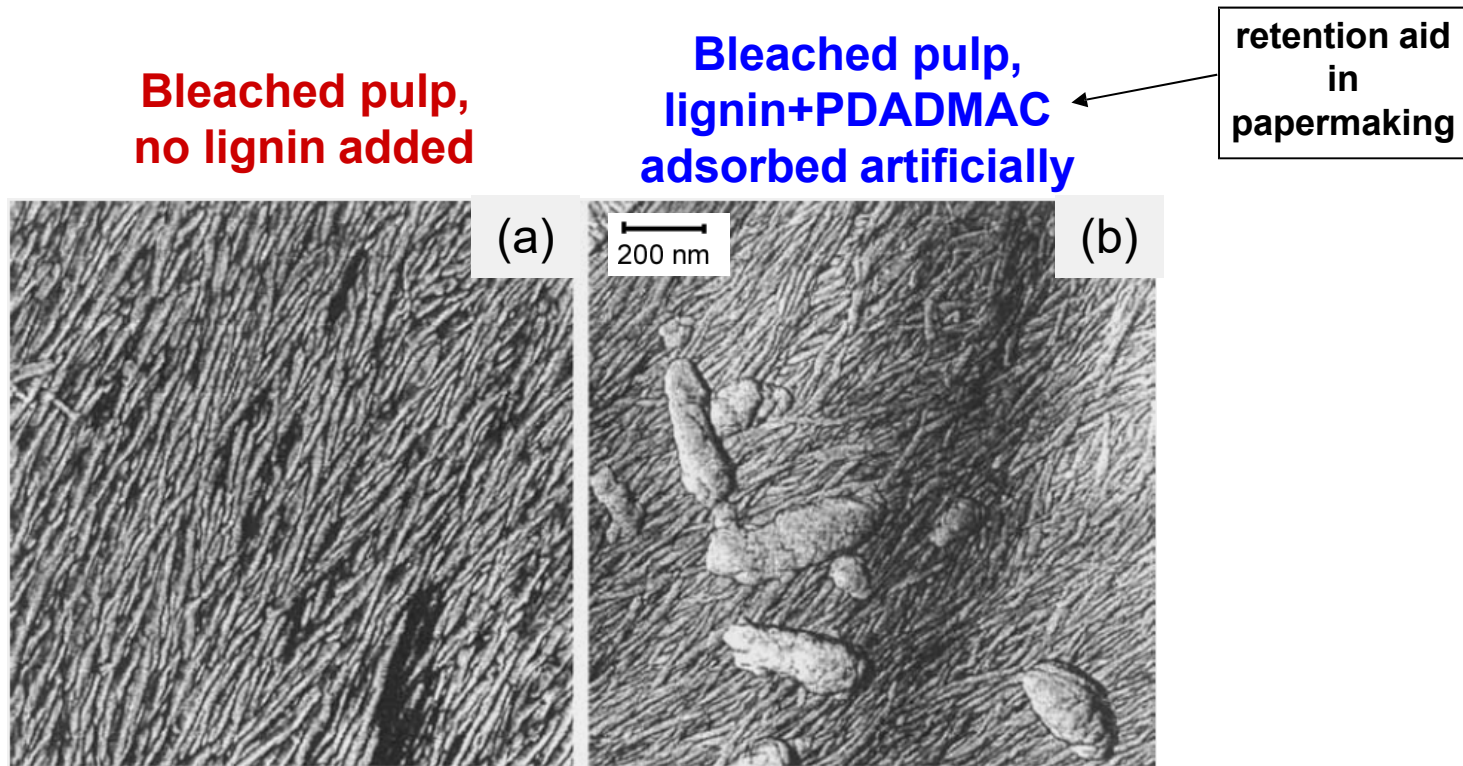
➡ **Lignin and adsorbed cationic polyelectrolyte form a gel-like complex.**

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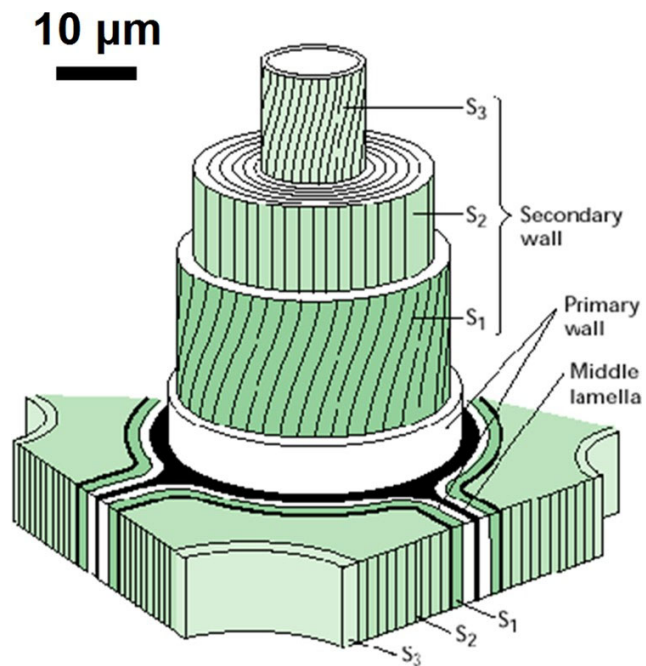
Adsorption of extractives

Bleached pulp, no extractives added

Bleached pulp, extractives adsorbed artificially

Imaging a wood cell
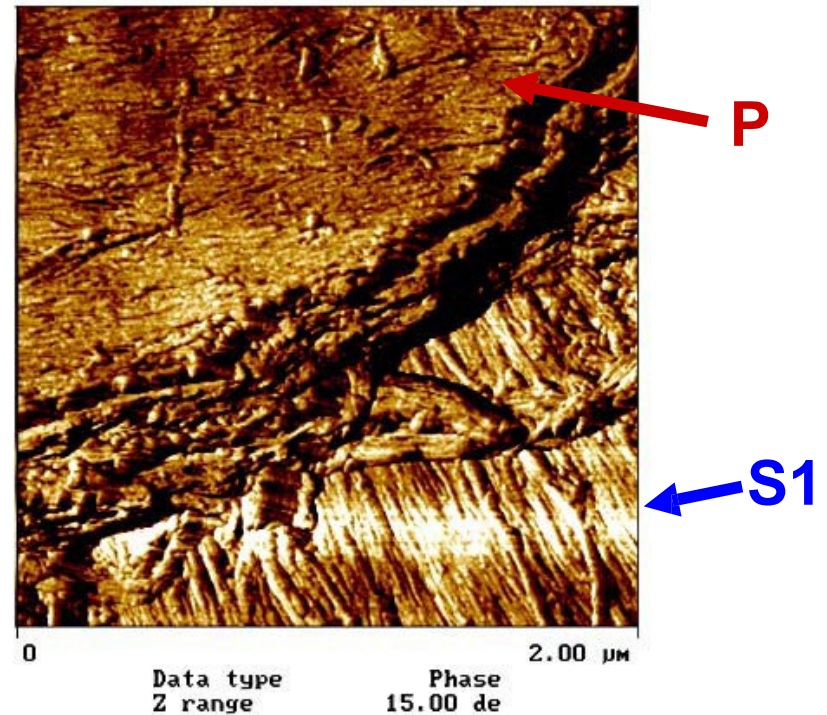
Cell wall layers – schematic view

10 µm

S3

S2 — Secondary wall

S1 — Primary wall

Middle lamella

S1

S2

S3

Surface of a TMP fibre* (unbleached) by AFM

P

S1

0   2.00 µm

Data type   Phase
Z range   15.00 de

Easy to detect the cell wall layers by microfibril orientation.

*) Isolated wood cell

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Microfibril aggregates

- Individual microfibril* width in wood: 3-4 nm
- Microfibrils tend to form aggregates of ca. 10-20 nm

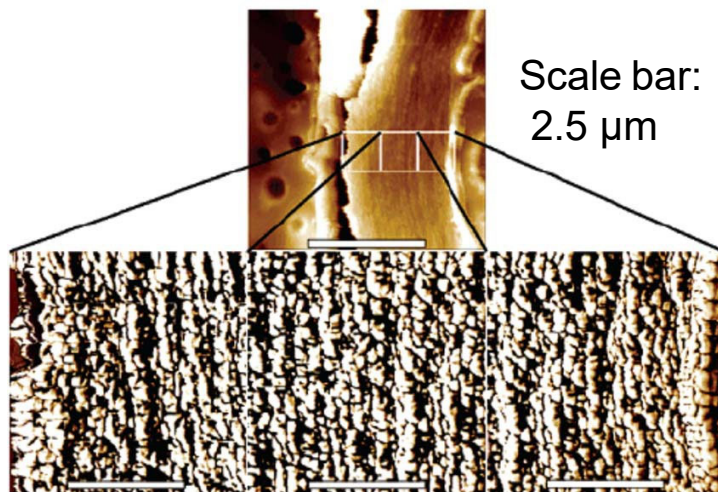**Cross-sections of different cell wall layers**

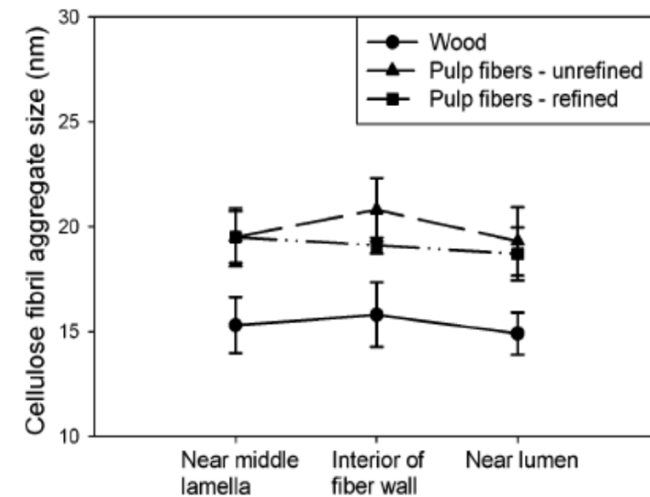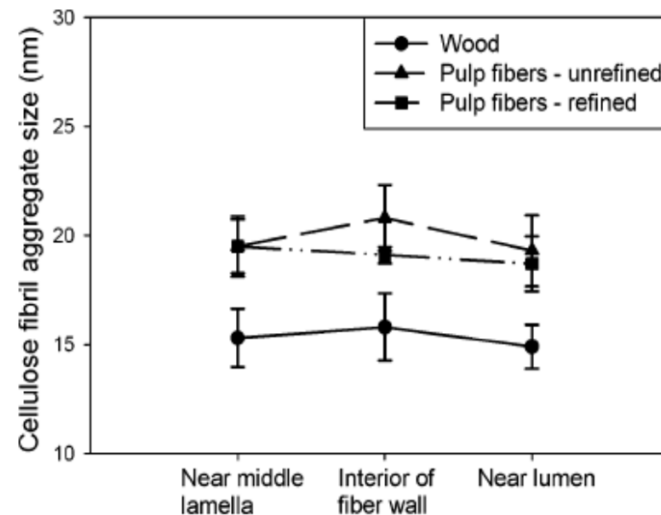**Image analysis**

Scale bar: 2.5 μm

Scale bar: 500 nm (=0.5 μm)

→ **Width of microfibril aggregates change during pulping, not during beating**

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*) Basic supramolecular unit of cellulose in plants

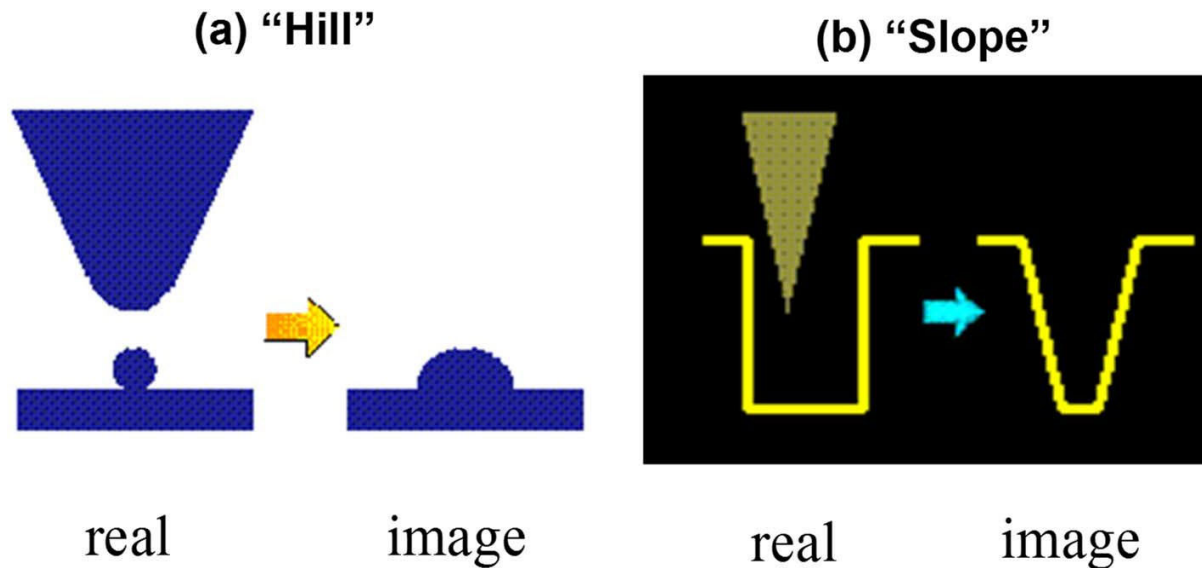# Microfibril aggregates

**CAREFUL OF THE
TIP ERROR!**

**Tip error can be neglected in several
cases but it always has to be considered.**

In this case, the microfibril cross-sections are close to each other
(no significant height differences) that the error can be neglected.

Reminder: limitation by the tip size

- Vertical resolution of AFM is outstanding: < 0.1 nm
- Lateral resolution is limited by the size of the tip

(a) "Hill"   (b) "Slope"

real   image   real   image

- The lateral exaggeration only concerns features whose size is close to the size of the tip

- Radius of an ordinary AFM tip: 5-10 nm

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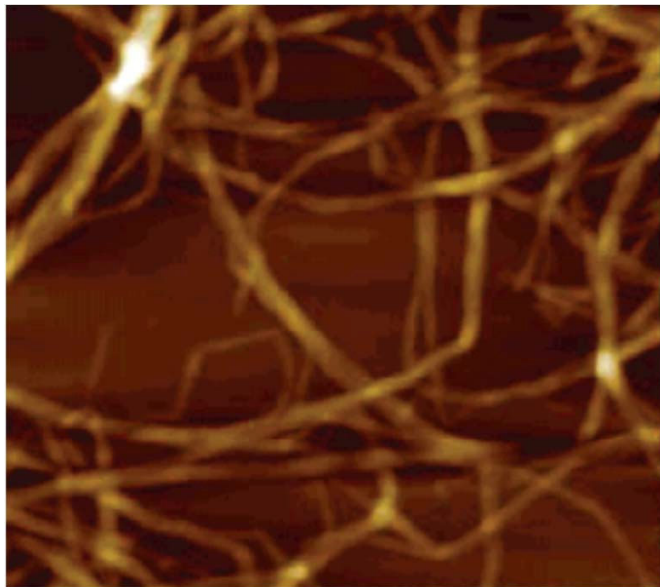# Dimensional analysis of nanosized cellulose

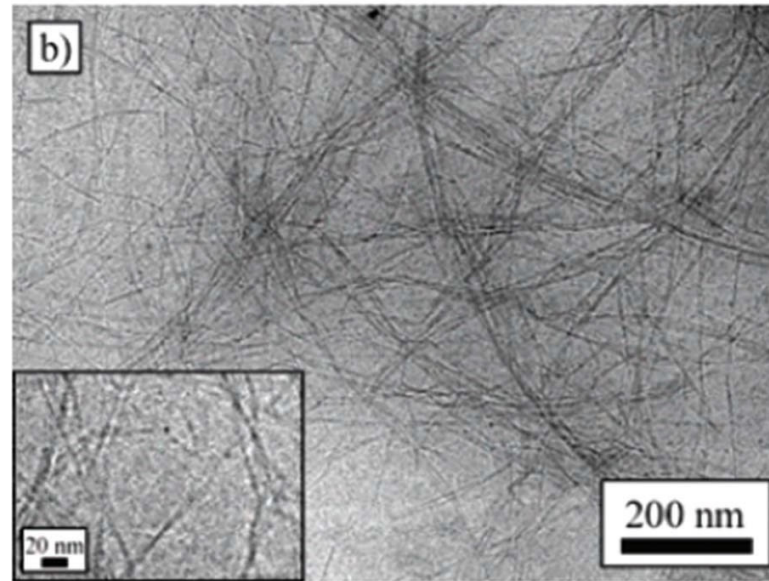Spread individual crystals on a flat substrate
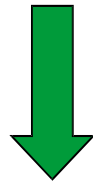
Atomic Force Microscopy (AFM)

Nanofibrillar cellulose: AFM vs. TEM

AFM image of
nanofibrillar cellulose (NFC)

Cryo-TEM image of
nanofibrillar cellulose (NFC)

Fibril size: 10-30 nm

Fibril size: 5-10 nm

TIP EXAGGERATION YIELDS UNRELIABLE WIDTHS FOR NFC

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Cellulose nanocrystals

concentration of casting solution

125 mg dm^{-3} | 250 mg dm^{-3} | 500 mg dm^{-3} | 1000 mg dm^{-3} | 1650 mg dm^{-3}

SiO$_2$ | TiO$_2$ | cellulose

Substrate

~100 mg dm^{-3} on TiO$_2$ substrate enables statistical image analysis.

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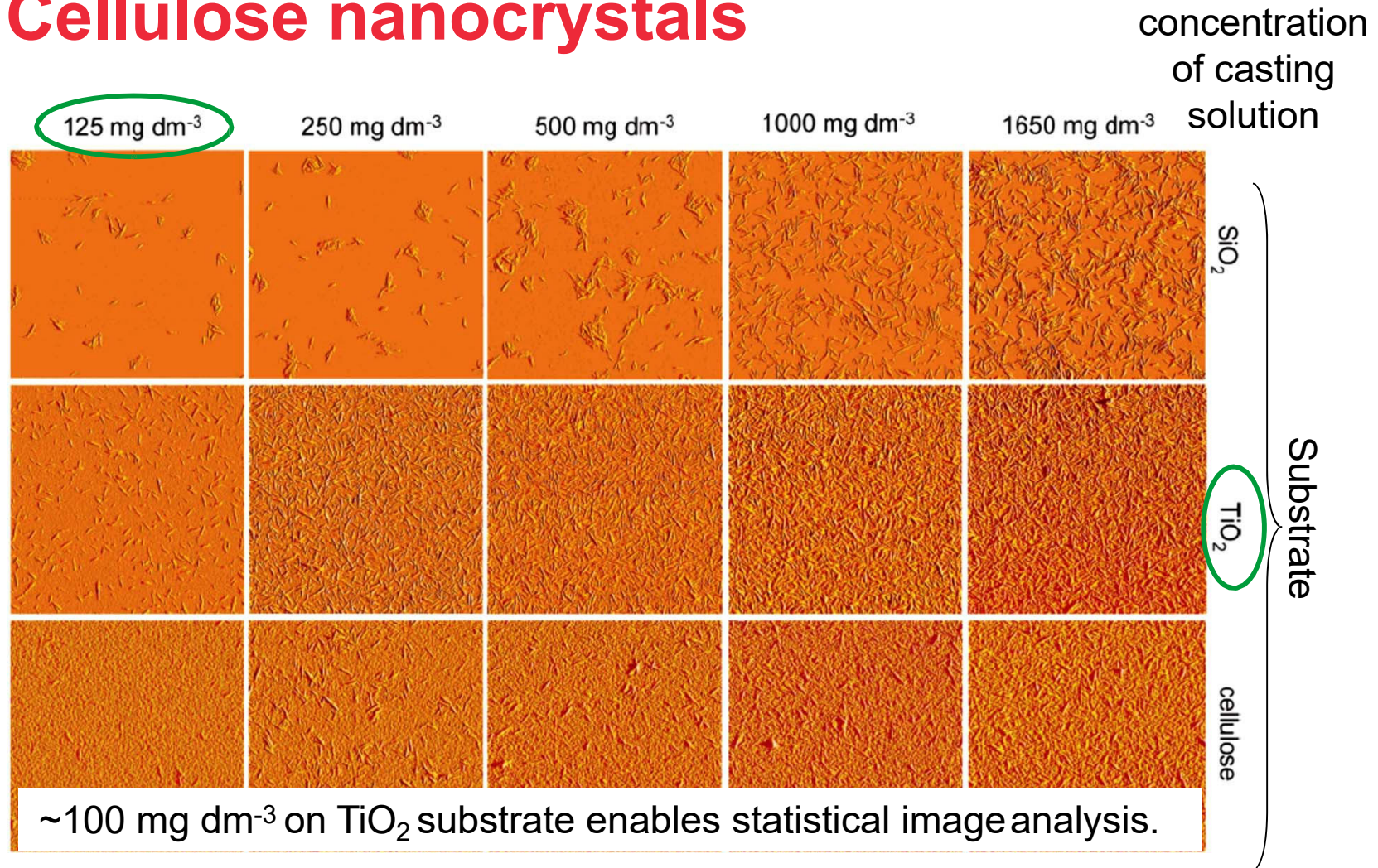
Cellulose nanocrystals

Nanocrystals from bleached softwood kraft pulp with different pretreatments

(a) Never-dried   (b) Oven dried   (c) Dried in 50% RH   (d) Beaten (4000 PFI)
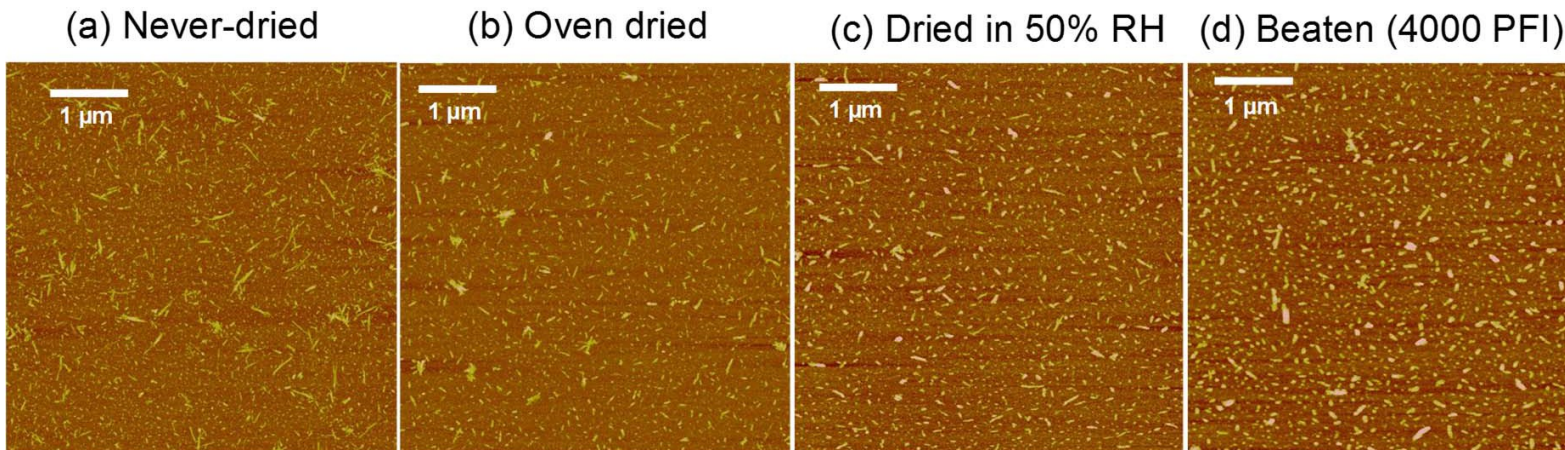
- Most of the nanocrystals in all samples are very small (<100 nm)
- Nanocrystals from never-dried pulp contains visibly nanocrystals that are visibly larger than in the other pulps
- Width (height) of the nanocrystals is constant in all samples (~ 4 nm)

Cellulose nanocrystals – width

Remember that AFM yields 3D information.

Heigth distribution histogram of cellulose nanocrystals (CNC) on TiO_2 substrate
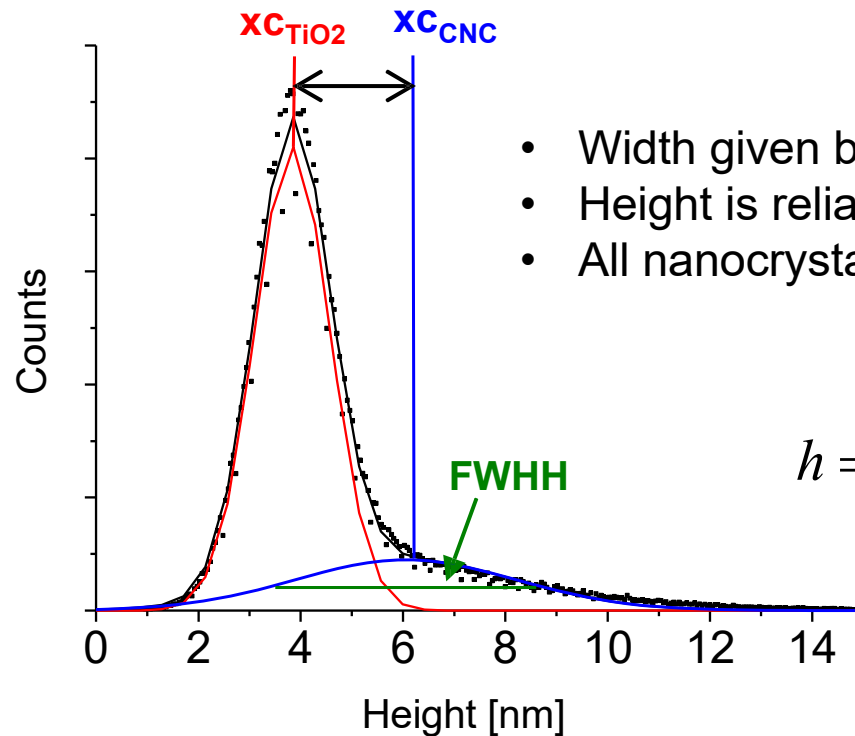
- Width given by AFM is not reliable (tip exaggeration)
- Height is reliable
- All nanocrystals in the sample had a height of ~4 nm

$$h = (xc_{CNC} - xc_{TiO2}) + \frac{FWHH}{2}$$

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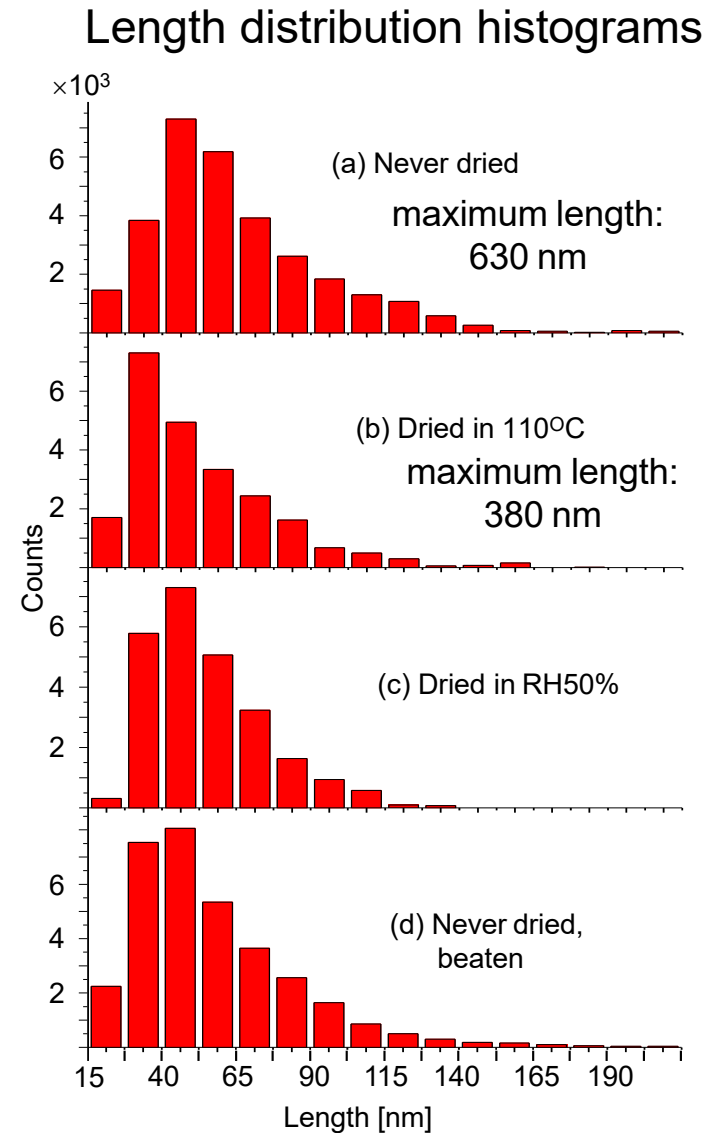Technology

Cellulose nanocrystals – length

Average length is roughly
similar in all samples (~60 nm)

- higher number of longer
nanocrystals in never dried samples

- higher amount of shorter
nanocrystals in dried samples

**ACID HYDROLYSIS IS MORE
EFFECTIVE ON DRIED FIBRES**

Length distribution histograms

(a) Never dried
maximum length: 630 nm

(b) Dried in 110°C
maximum length: 380 nm

(c) Dried in RH50%

(d) Never dried, beaten

Counts

Length [nm]

Summary

- AFM is based on a tip that scans across the sample surface
- Surface forces interact between the tip and the sample → image
- Extremely high resolution (down to < 1 nm, **limited by tip error**)

- Height image shows topographical contrasts
- Phase image can distinguish different materials

- AFM can resolve individual cellulose microfibrils (or microfibril aggregates)
- AFM can detect different cell wall layers (fibril angle)
- Morphological appearance of e.g. residual lignin on surface can be visualized by AFM
- AFM enables characterising the distribution and size of pigment in paper coatings
- AFM enables the (statistical) dimensional analysis of cellulose nanocrystals

NOTE: AFM yields morphological information, not chemical
→ combination with other techniques like XPS yields added value

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