Micromechanical characterization of wood pulp fibers

Caterina Czibula[1,2], Ulrich Hirn[1,2]

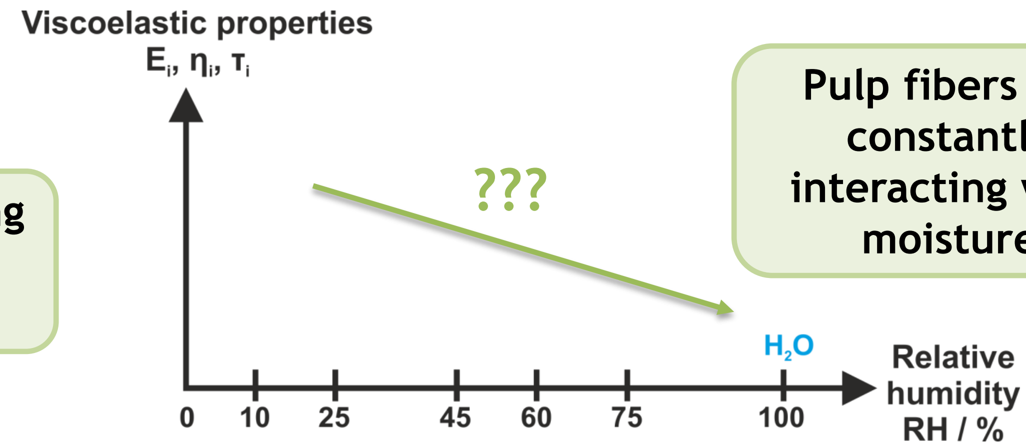
[1] Institute of Bioproducts and Paper Technology, TU Graz, Austria
[2] CD Laboratory for Fiber Swelling & Paper Performance, TU Graz, Austria

6th INTERNATIONAL CONFERENCE IN MEMORY OF PROF. V. KOMAROV,
Arkhangelsk – 10.09.2021

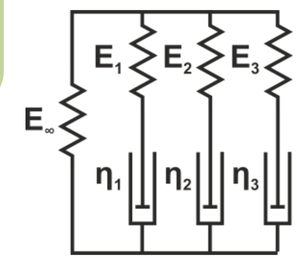
www.tugraz.at

Motivation

Varying processing speeds in paper industry

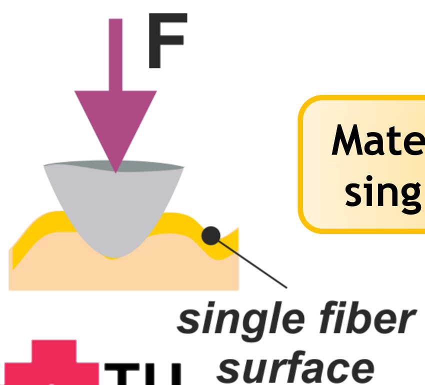


Pulp fibers are constantly interacting with moisture



Christian Doppler Forschungsgesellschaft

Atomic force microscopy (AFM)



Experimental results as input into material models for single pulp fibers and paper.

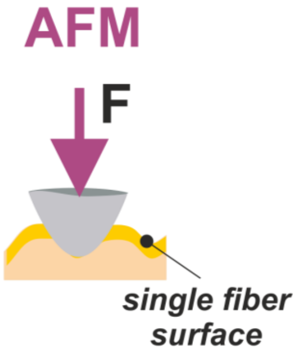
Material models of single pulp fibers

Ultimate goal: understanding paper performance

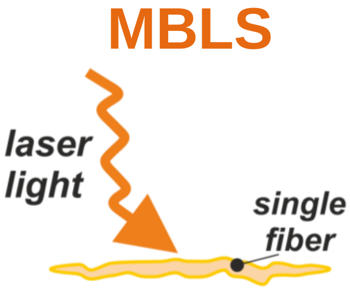
Mandelstam-Brillouin light scattering (MBLS)

Outline

- **Atomic force microscopy (AFM)-based method to investigate the viscoelastic behavior of wood pulp fibers at different relative humidity levels**
  - Background
  - Experimental
  - Contact mechanics & viscoelastic models
  - Results

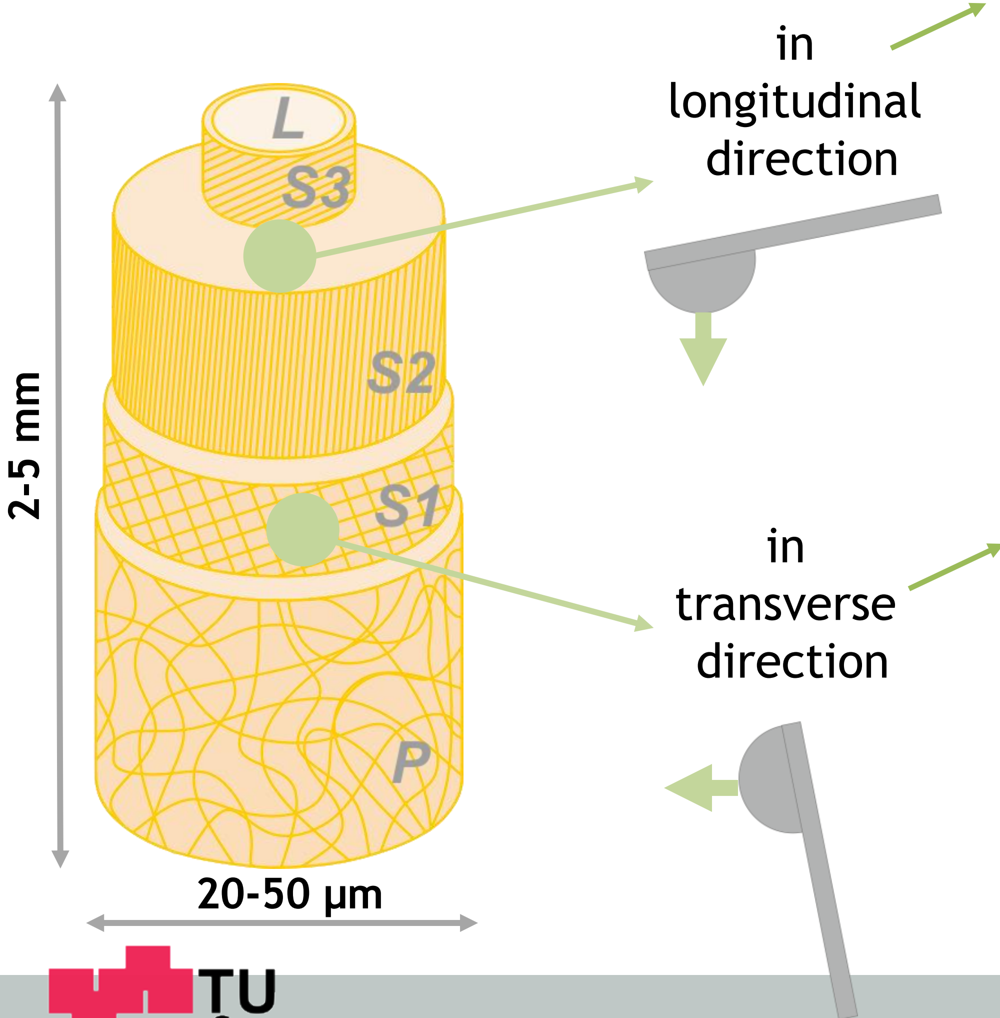


- **Transverse modulus of cellulosic fibers obtained with Mandelstam-Brillouin light scattering microspectroscopy (MBLS)**
  - First results

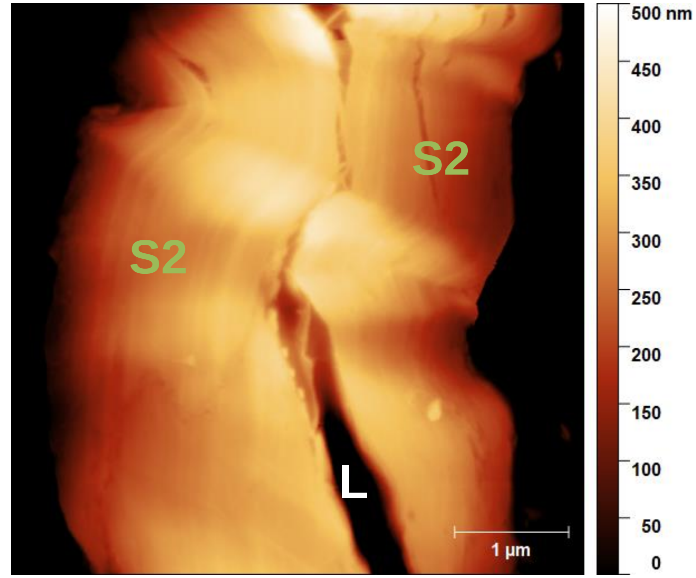


AFM based viscoelastic characterization of wood pulp fibers

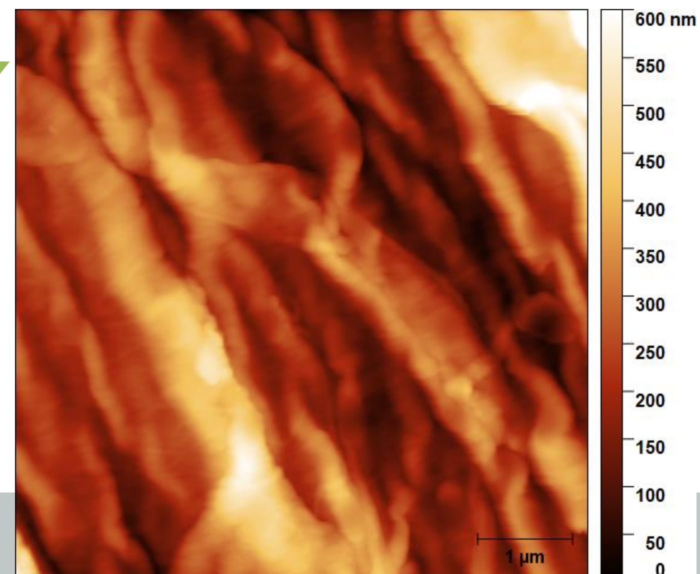
wood fiber cell wall layers



AFM topography of a fiber cross-section

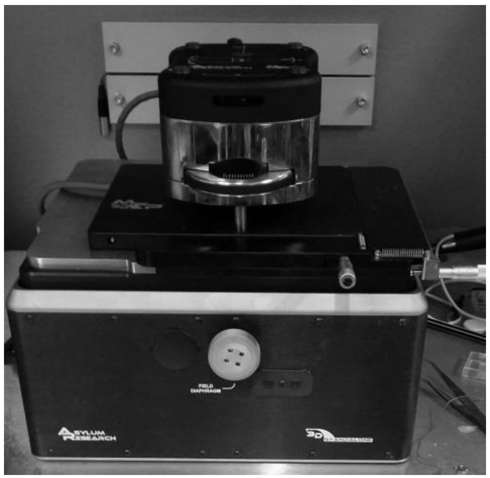


AFM topography of a fiber surface



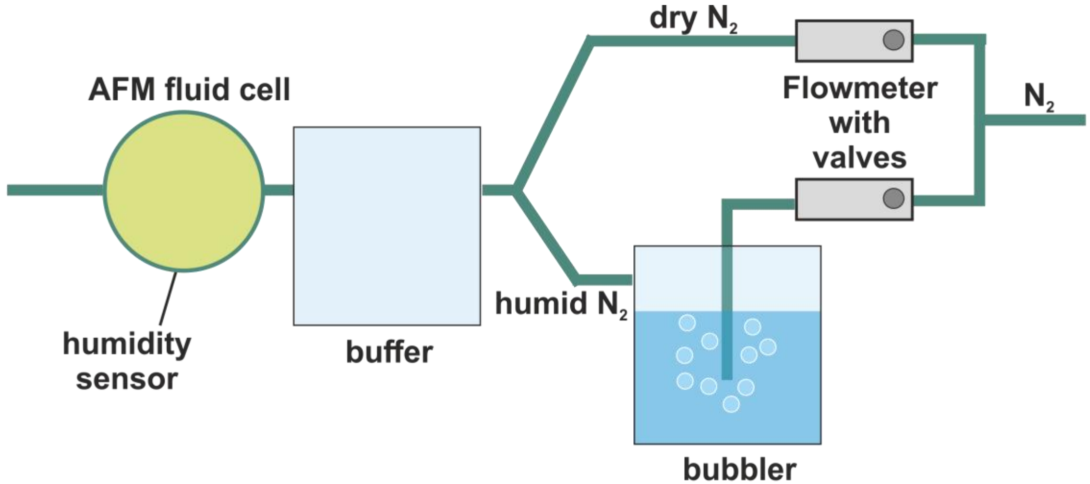
Experimental AFM setup

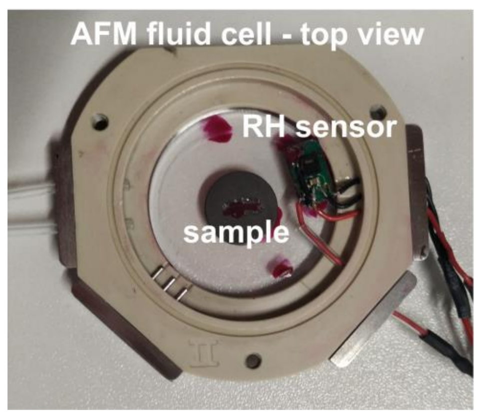
Christian Doppler Forschungsgesellschaft

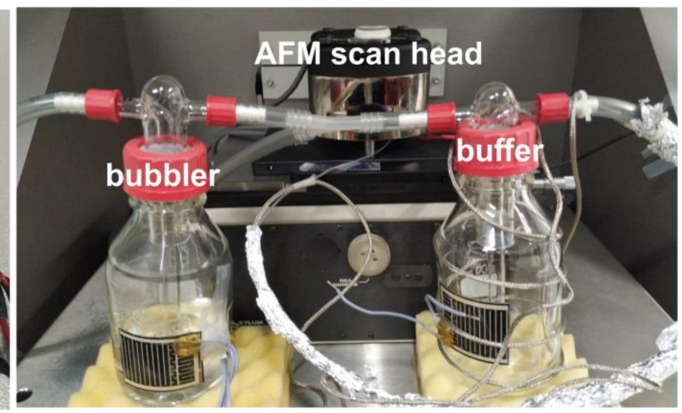


AFM: Asylum Research MFP 3D (Santa Barbara, CA)

Relative humidity (RH) setup







With the setup it is possible to control reliably between ~10 and ~80 % RH for the viscoelastic experiments.

C. Ganser et al., Holzforschung 70:1115-23, 2016
C. Ganser, C. Teichert, in "Applied Nanoindentation of Advanced Materials", Ed. A. Tiwari, pp 247-267, Wiley, 2017

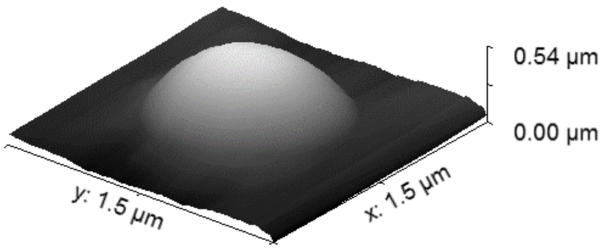
Load schedule designed for viscoelastic probing

Viscoelastic deformation with a hemispherical probe

Christian Doppler Forschungsgesellschaft

AFM probe

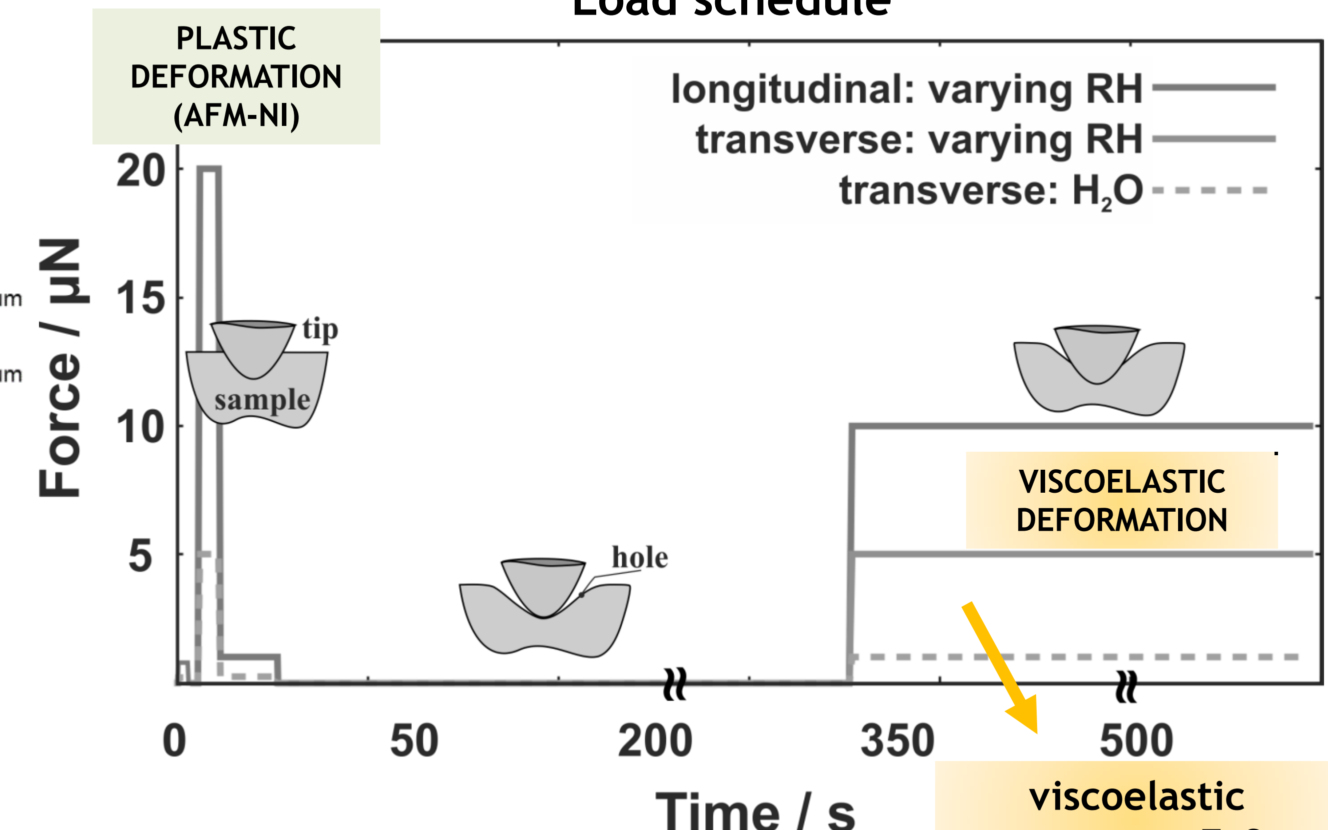
Large radius hemispherical probe
tip radius ~ 300 nm
spring constant of the cantilever ~ 250 N/m
(Team Nanotec)



- **Tip geometry** is well known
- **Larger radius → lower strain → higher applied forces** possible & larger area over which is averaged

Drawback: reduced lateral resolution

Load schedule

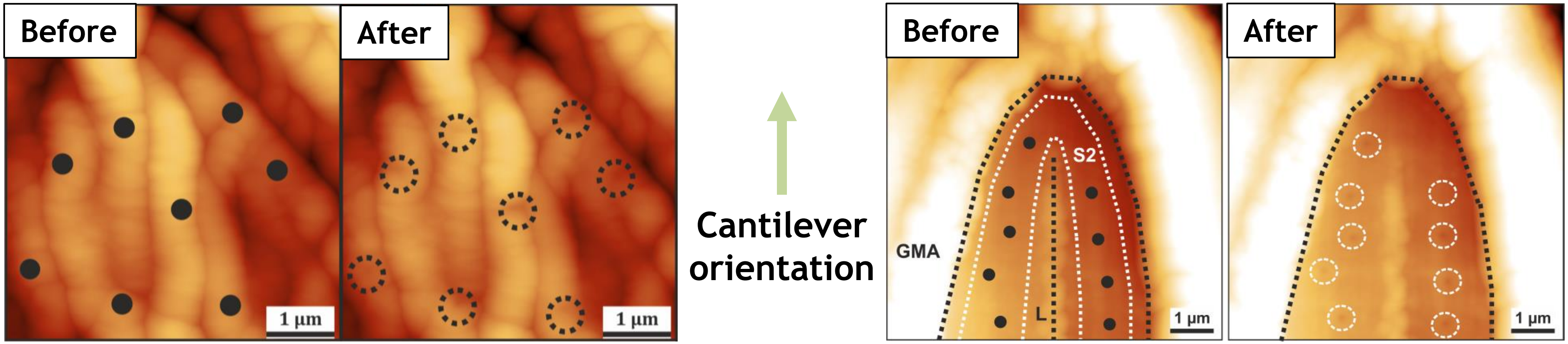


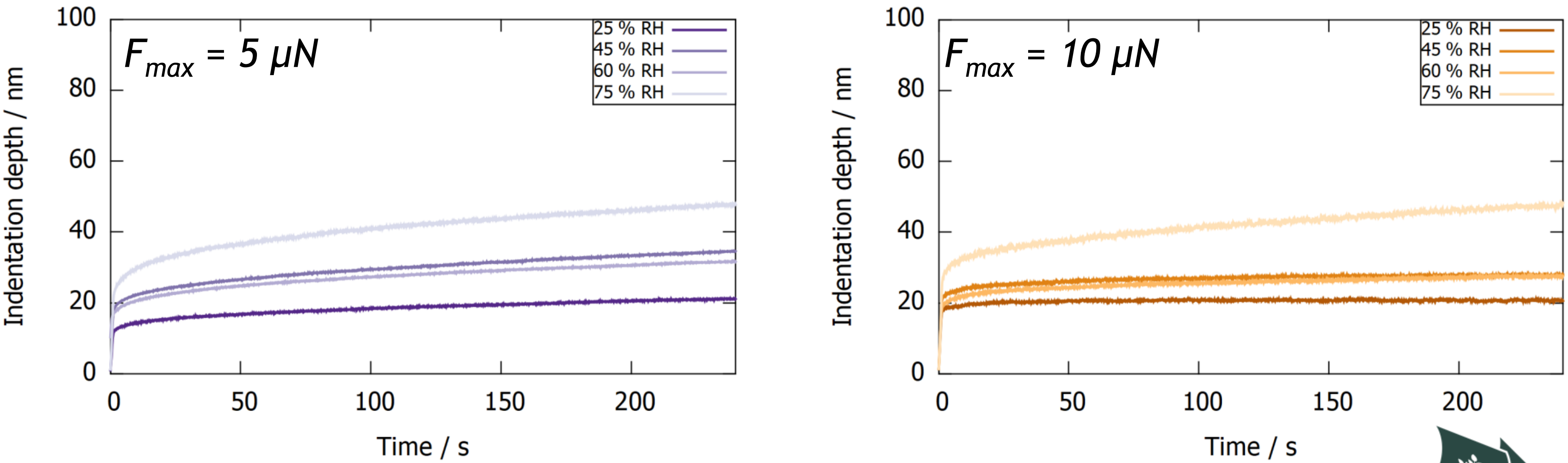
viscoelastic parameters: E_i & η_i

Experimental creep curves

Transverse direction

Longitudinal direction



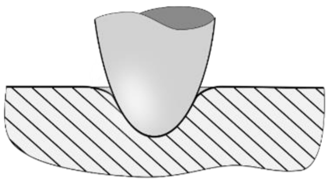


With increasing RH, the indentation depth is increasing.

Theory behind data analysis

Christian Doppler Forschungsgesellschaft

Contact mechanics model



Johnson-Kendall-Roberts (JKR) model

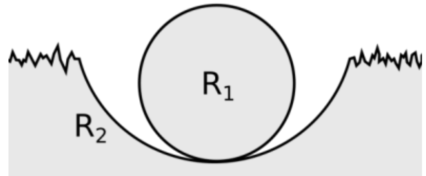
Assumptions:

- Tip is a sphere
- Sample: plane, sphere, or **hole**
- Topography: smooth
- Regime: elastic
- Adhesion: **YES**

In our studies, adhesion cannot be neglected (~300 – 800 nN)

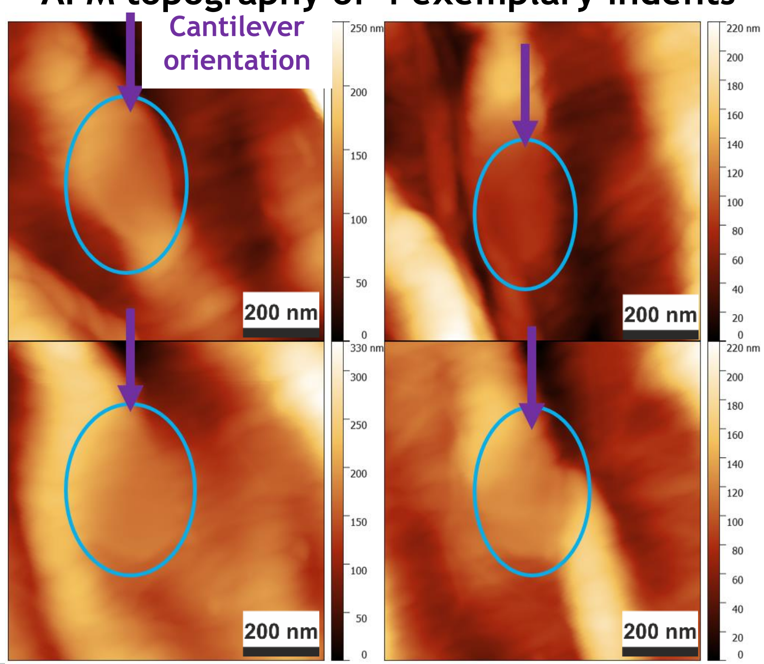
\+

How to define the tip-surface contact ?

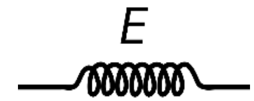


Contact in a hole

AFM topography of 4 exemplary indents

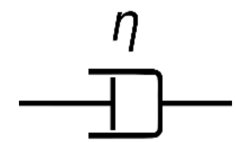


\+



springs → elastic behavior

Viscoelastic model



dashpots → viscous behavior

Johnson et al., Proc. R. Soc. Lond. A 324:301-313, 1971

D. Roylance. *Engineering Viscoelasticity*. Massachusetts Institute of Technology. Cambridge, 2001

Generalized Maxwell (GM3) model of order 3

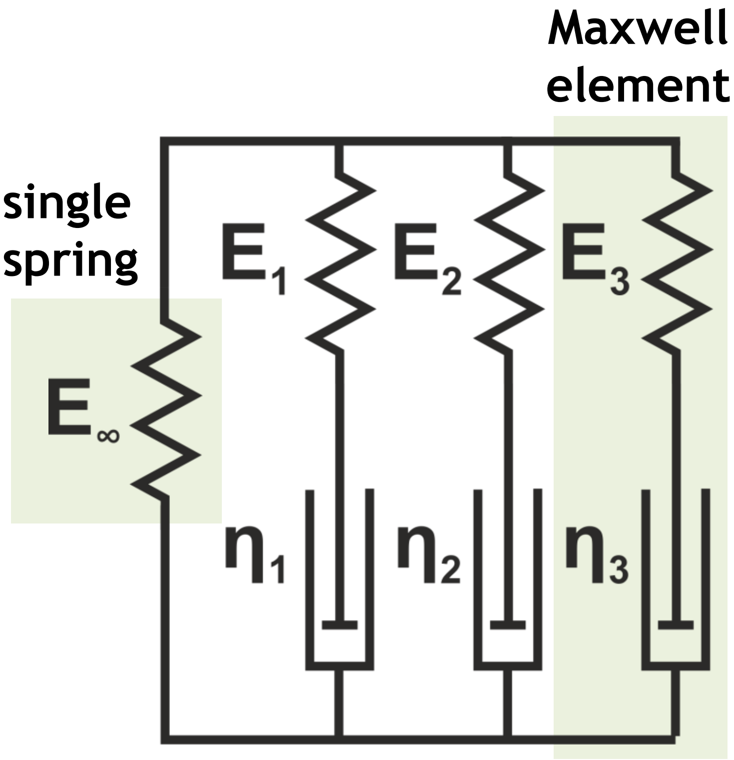
Christian Doppler Forschungsgesellschaft

infinitely slow loading:

$$E_\infty$$

infinitely fast loading:

$$E_0 = E_\infty + \sum E_i$$



Relaxation time

$$\tau_i = \frac{\eta_i}{E_i}$$

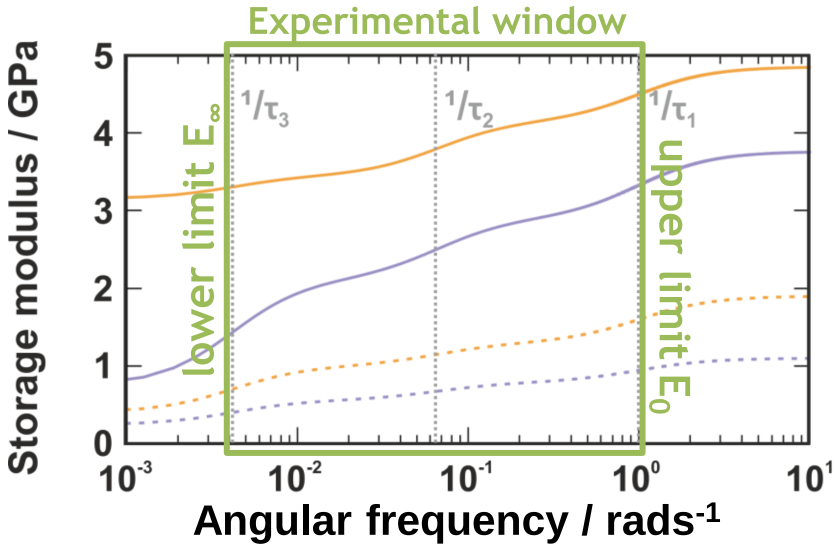
ratio between viscosity and stiffness

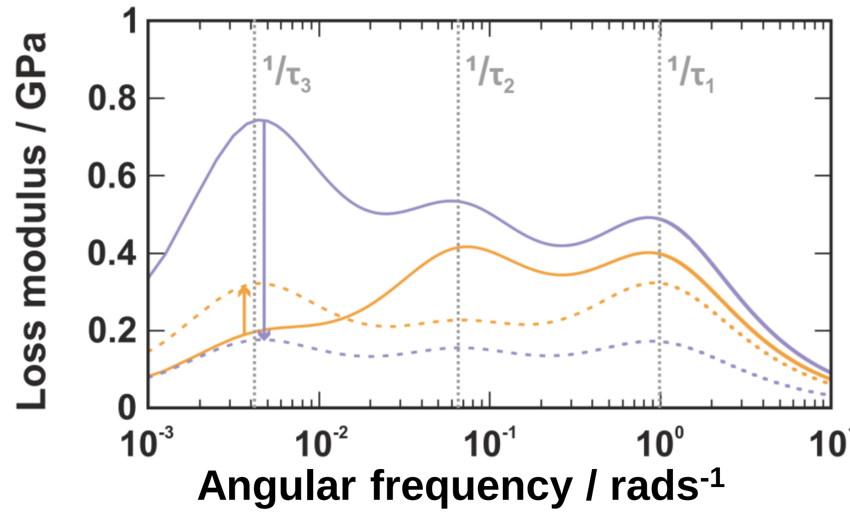
Viscoelastic characterization:

- ***Elastic parameters:*** E_∞, E_0
- ***Fixed relaxation times:*** *to avoid too many fitting parameters*
  $\tau_1 = 1$ s, $\tau_2 = 15$ s, $\tau_3 = 240$ s

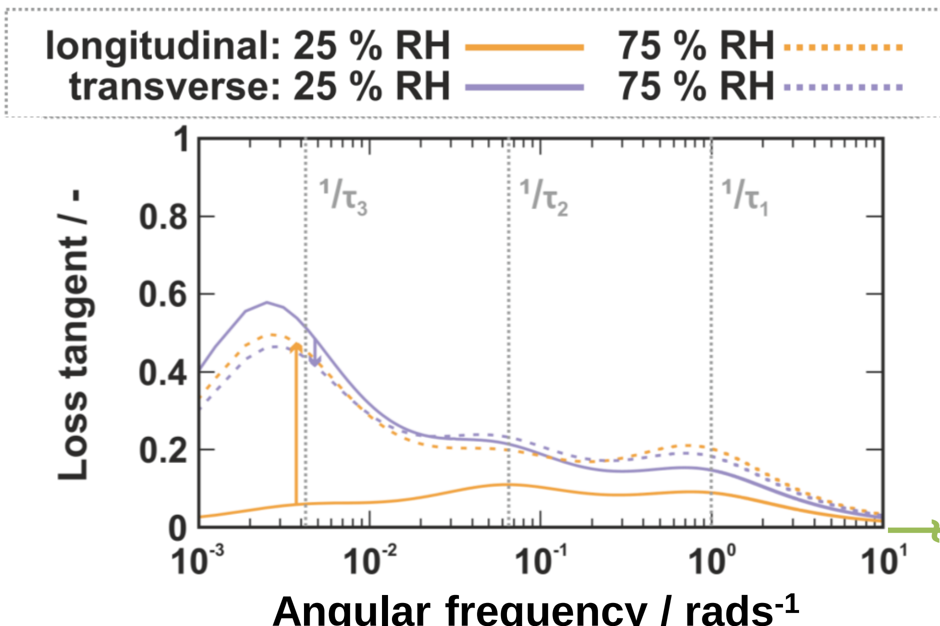
D. Roylance. *Engineering Viscoelasticity*. Massachusetts Institute of Technology. Cambridge, 2001

Spectral representation of the results





In **longitudinal direction**, the fibers have a **higher storage** and **lower loss modulus**.

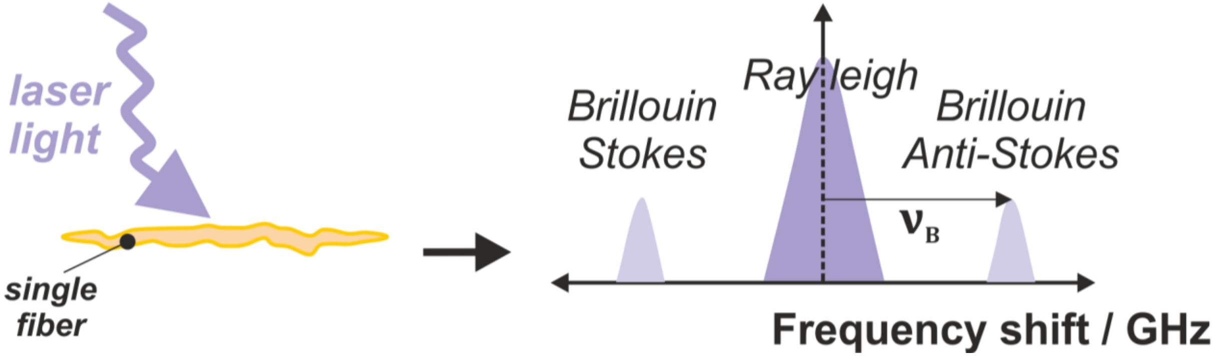


The **damping behavior** of the **longitudinal** results is **more affected by the change in RH** – especially at low f.

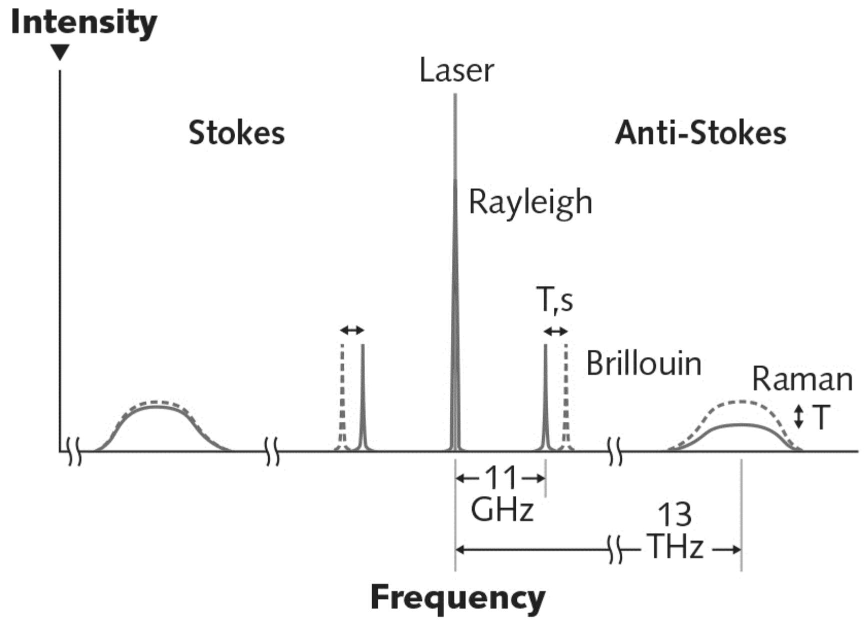
$\tan(\delta)$ ~ 0.04 @ GHz (MBLS)

C. Czibula, T. Seidlhofer et al., Materialia, 16:101094, 2021
for details on the spectral representation: T. Seidlhofer et al., Mech. Mat. 135:149-161, 2019

Mandelstam-Brillouin light scattering (MBLS)



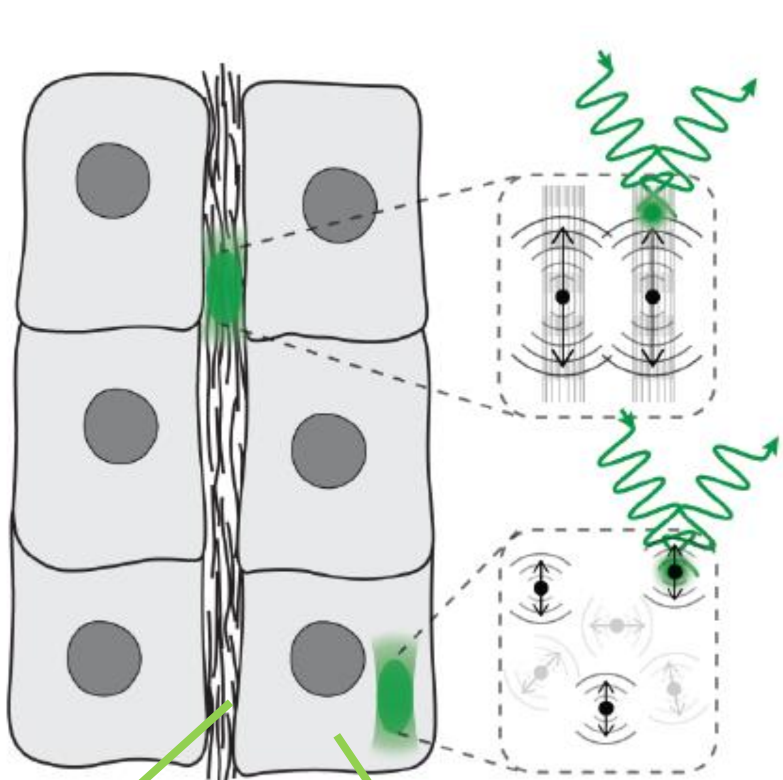
Ultra-low frequency regime
< 1 cm^{-1}
-1 to 1 cm^{-1}
-30 to 30 GHz



L. Mandelstam, Zh. Russ. Fiz. Khim. Ova. 58:381, 1926
L. Brillouin, Annales de Physique, 9(17):88-122, 1922
https://www.laserfocusworld.com

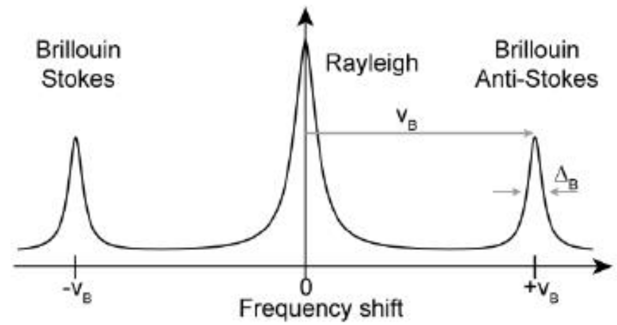
MBLS principle

Frequency shift v_B, line width Γ_B

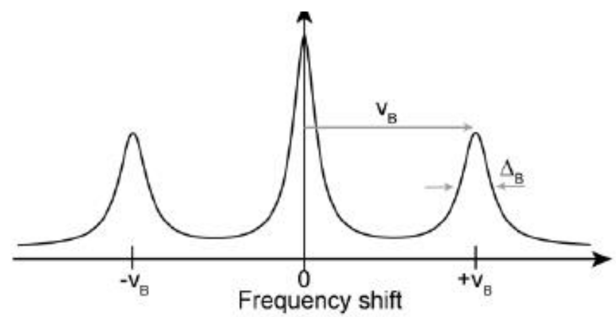


collagen fibers
solid

cytosol
liquid-like



collagen fibers:
larger frequency shift v_B, smaller line width Γ_B → stiffer material

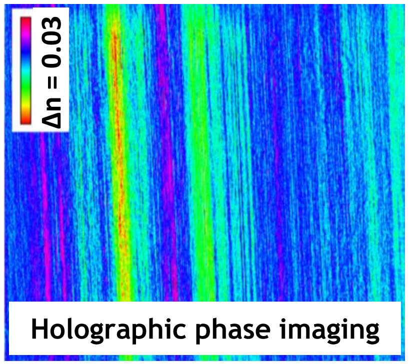


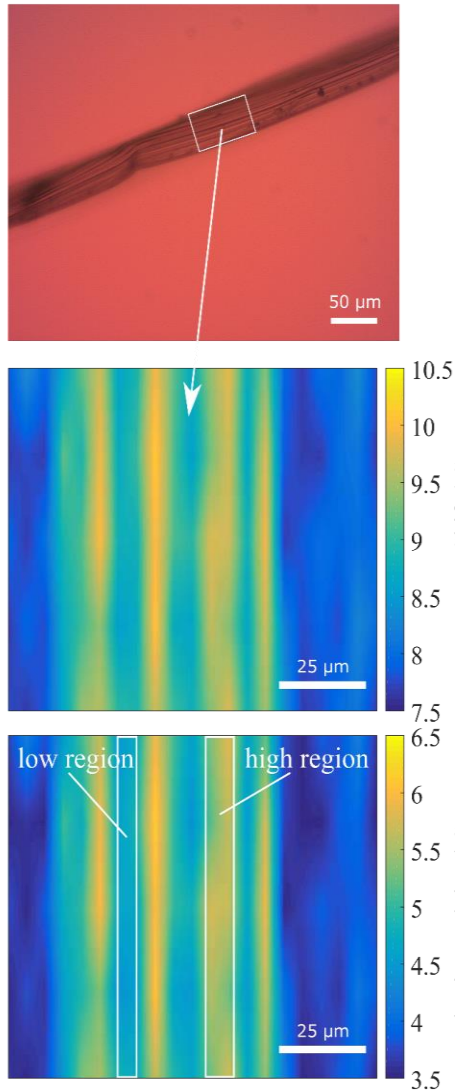
cytosol:
smaller frequency shift v_B, larger line width Γ_B → softer, more viscous material

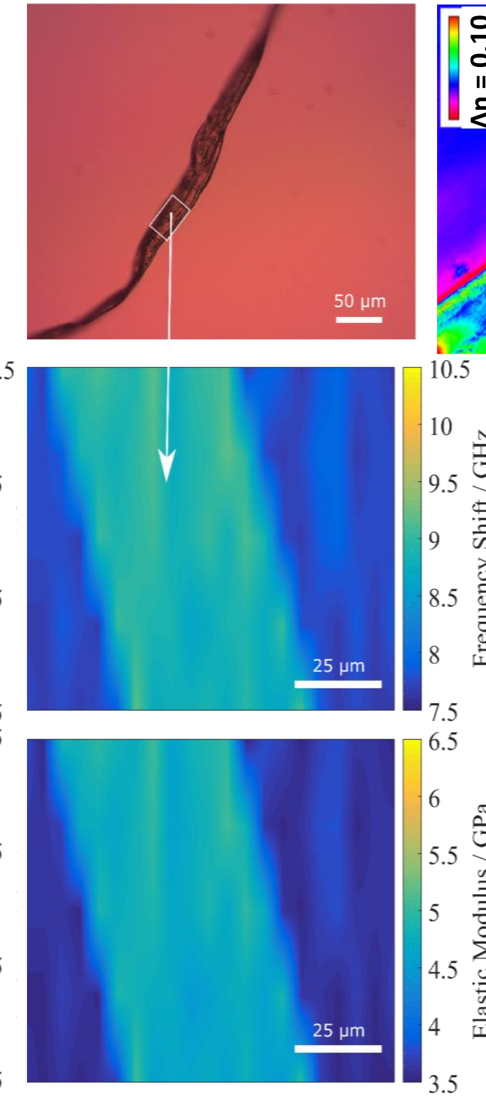
R. Prevedel et al., Nature Methods 16:969-977, 2019

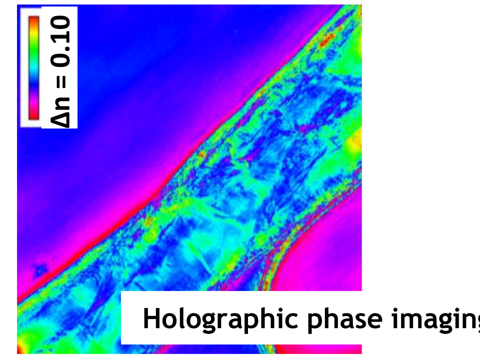
First results: transverse modulus of cellulosic fibers

Viscose fiber | **Bleached softwood fiber**









100 x 100 µm² images
(21 x 5 positions)

The elastic modulus of the viscose fiber shows a striped pattern.
high region: 5.4 ± 0.1 GPa
low region: 4.2 ± 0.1 GPa

AFM-based nanoindentation (AFM-NI):
E_r ~ 5 GPa

The elastic modulus of the pulp fiber is uniform.
4.5 ± 0.1 GPa

AFM-NI:
E_r = 1.3 ± 0.7 GPa

K. Elsayad et al., Cellulose 27:4209-20, 2020

Conclusions

Christian Doppler Forschungsgesellschaft

- An AFM-based method combining adhesive contact mechanics and spring-dashpot models to investigate the viscoelastic properties of single pulp fibers at different RH and in water has been developed.
- The longitudinal and transverse direction of pulp fibers have been investigated at different RH. Unexpectedly, comparison of the longitudinal and transverse direction showed little differences.
- First MBLS results show that the method can be adapted to cellulosic fibers and yields results which are comparable to AFM-NI measurements.

Outlook

- We want to establish MBLS as a technique to investigate single fiber properties of lignocellulosic materials
  - Characterization of different lignocellulosic fibers and materials
  - Investigation of the influence of moisture changes
  - Measurements of the full elastic stiffness tensor of single pulp fibers

FWF *Hertha Firnberg fellowship "Micromechanics of lignocellulosic fibers"*

Christian Doppler Forschungsgesellschaft

THANKS FOR YOUR ATTENTION !!

MONTAN UNIVERSITÄT

SPM Scanning Probe Microscopy Group Leoben

mondi

Canon CANON PRODUCTION PRINTING

Kelheim Fibres

SIG

TU Graz