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WALLENBERG WOOD SCIENCE CENTER

KTH VETENSKAP OCH KONST

CHALMERS

Online orientation measurements of elongated particles by X-ray scattering

Karl Håkansson

June 3rd 2014

WWSC is a joint research center at KTH and Chalmers

Bulletproof Vest from Trees?

Courtesy of E. Arkema

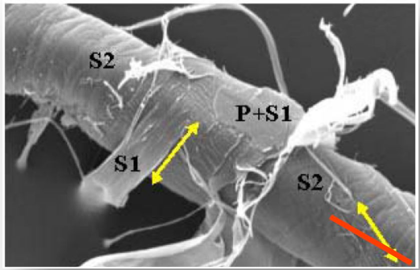
Courtesy of E. Arkema

?

Wood Structure and Properties

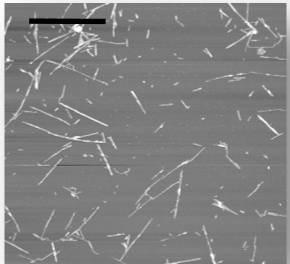
m

mm

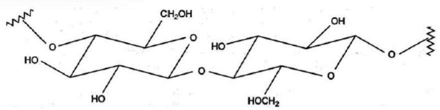


Courtesy of L. Salmén

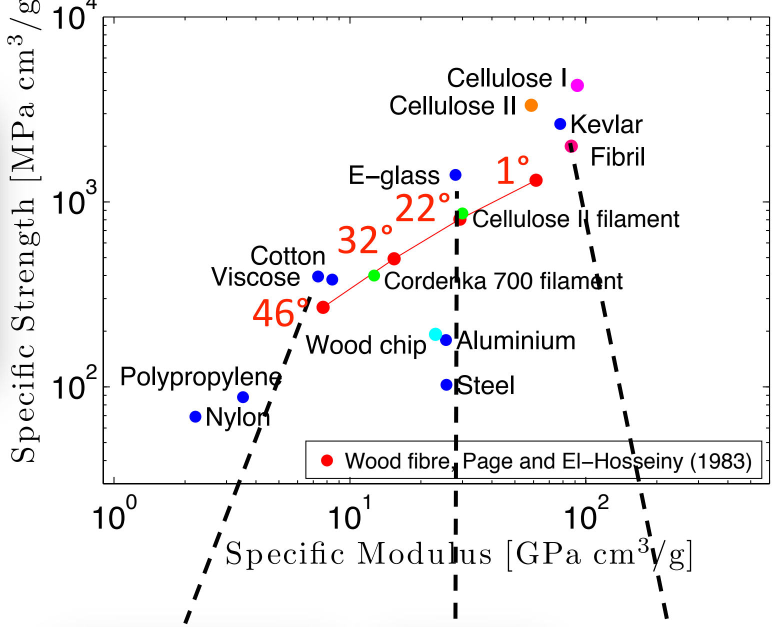
µm

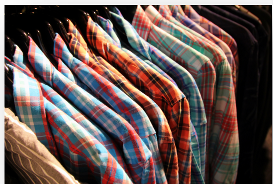


nm



Material properties





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Siró & Plackett, Cellulose (2010)
Eichhorn *et al.*, J Mater Sci (2001)
Eichhorn *et al.*, J Mater Sci (2009)
Page & El-Hosseiny, J. Pulp and Paper (2083)

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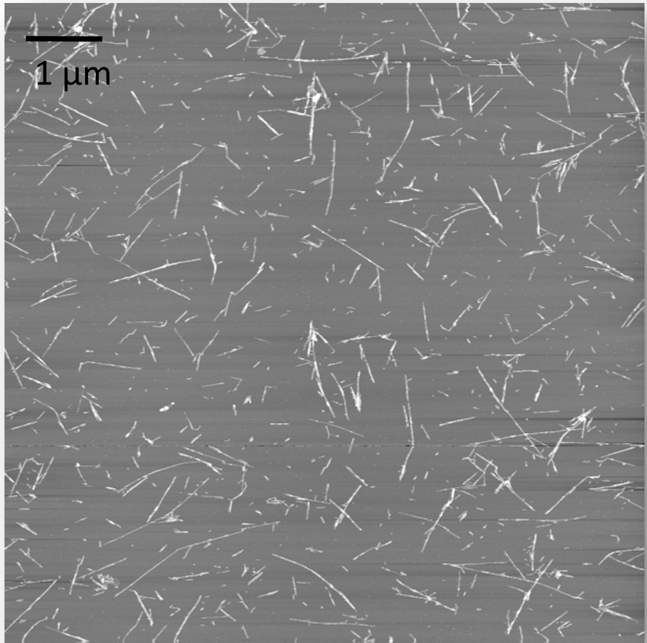
Cellulose nanofibrils, CNF

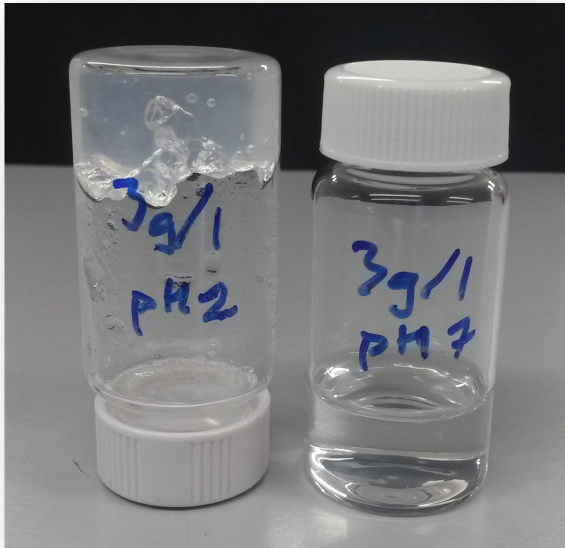
AFM image of CNF



Courtesy of A. Fall and G. Nyström

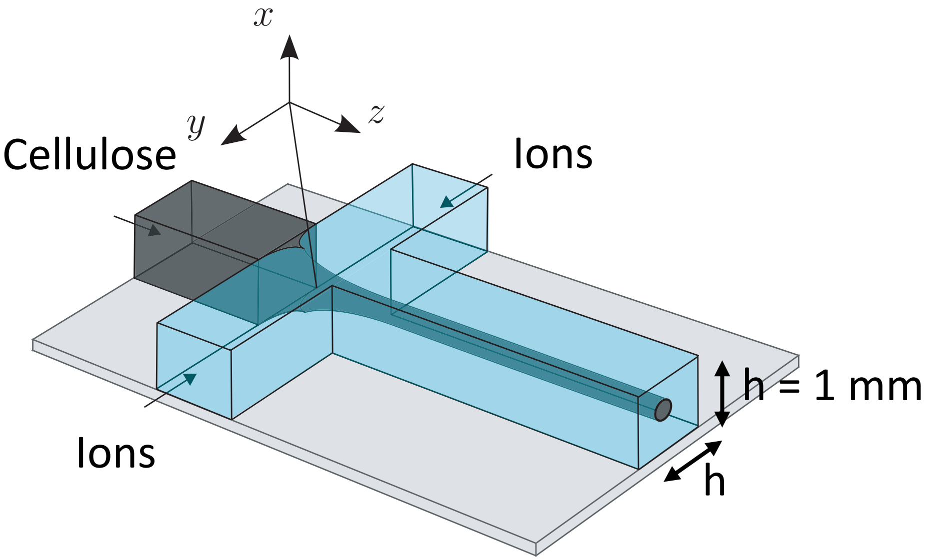
Gel
Locked

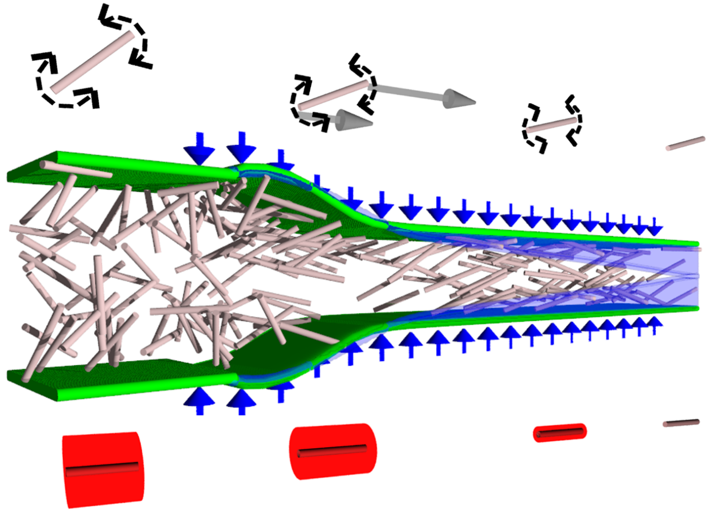
Dispersion
Freely moving

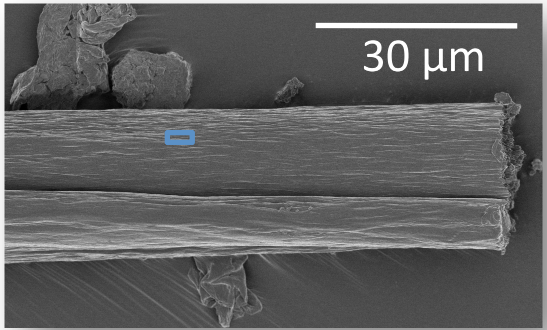


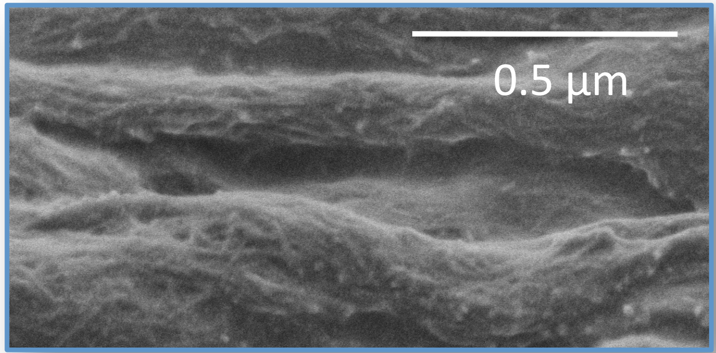
3 g/l ≈ 0.3 % by weight

Fibre process and dry fibre



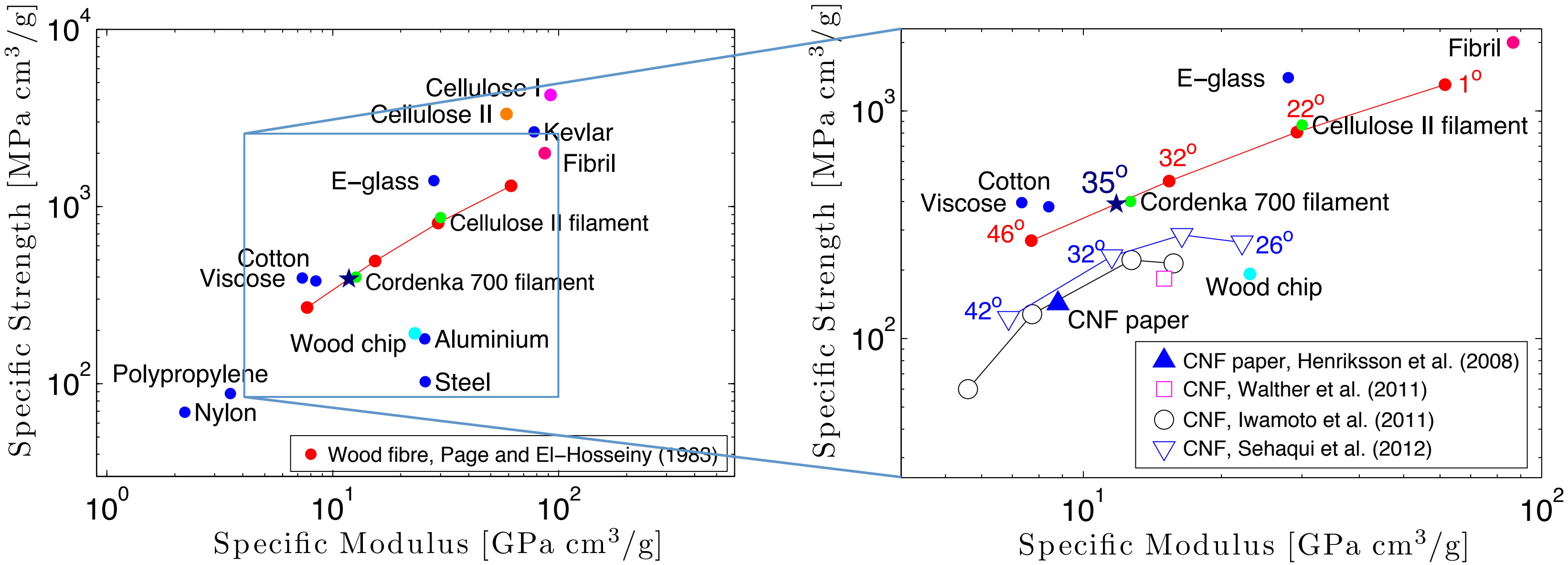






Material Properties, updated!

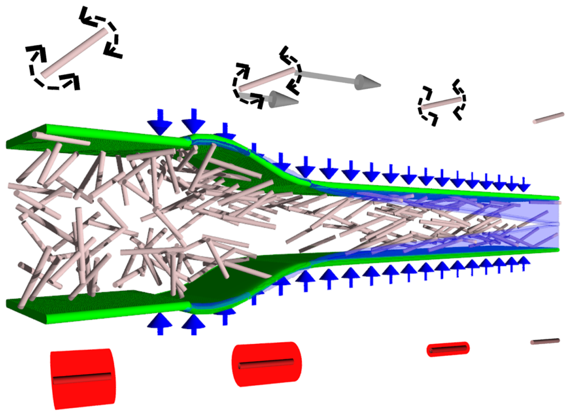
★ Our first filament



Aims

Align the nano scale fibrils with a macro scale fluid flow.

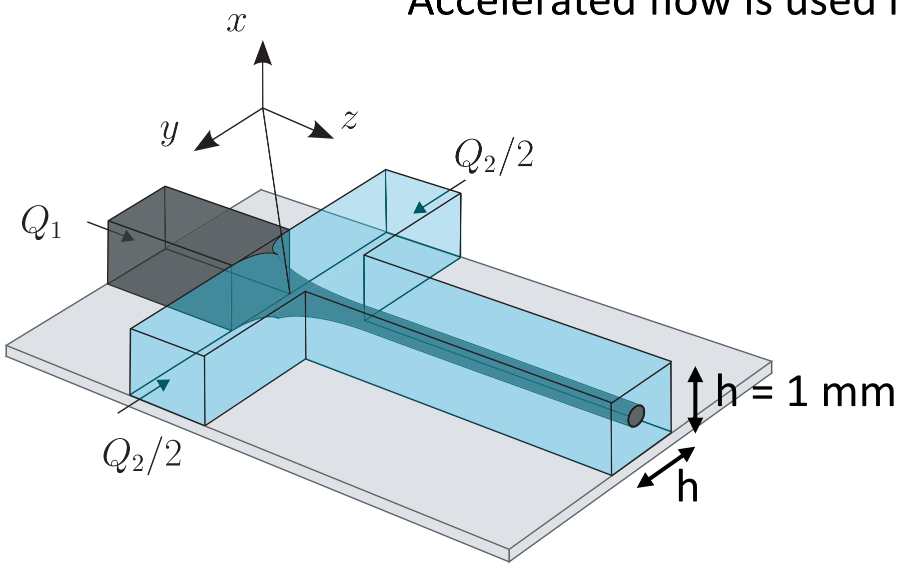
Quantify the alignment by performing:

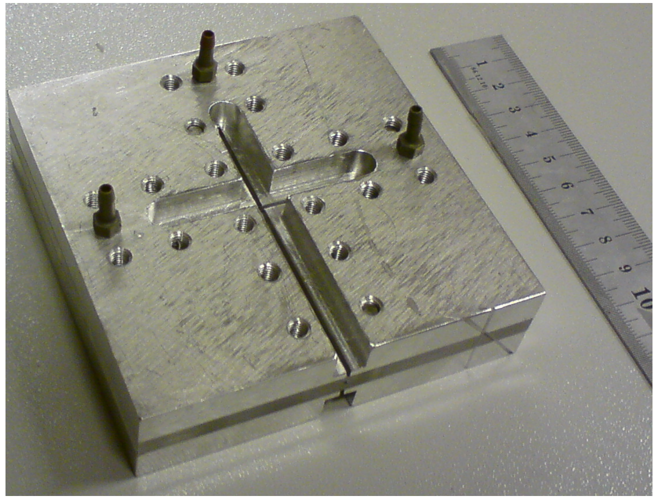


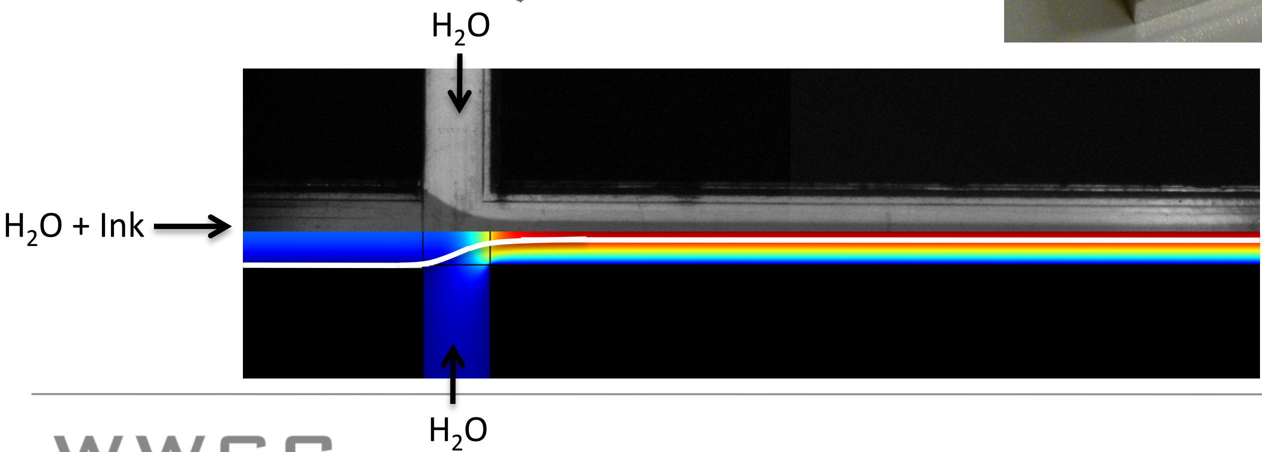
- X-ray scattering experiments
- Modelling the alignment

Experimental Setup

Accelerated flow is used in order to align nano-cellulose







Parameters

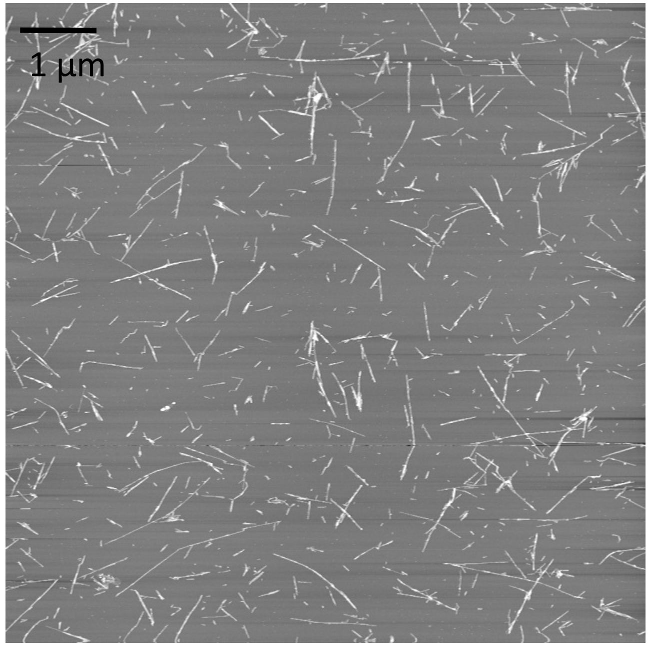
NFC, Innventia gen 2
c_v = 0.3 %
nl^3 = 10-20 => semi-dilute

Q_1 = 6.5 mm^3/s
h = 1 mm

$$1 \le \mathrm{Re}_i = \frac{\rho_i Q_i}{\eta_i h} \le 50$$

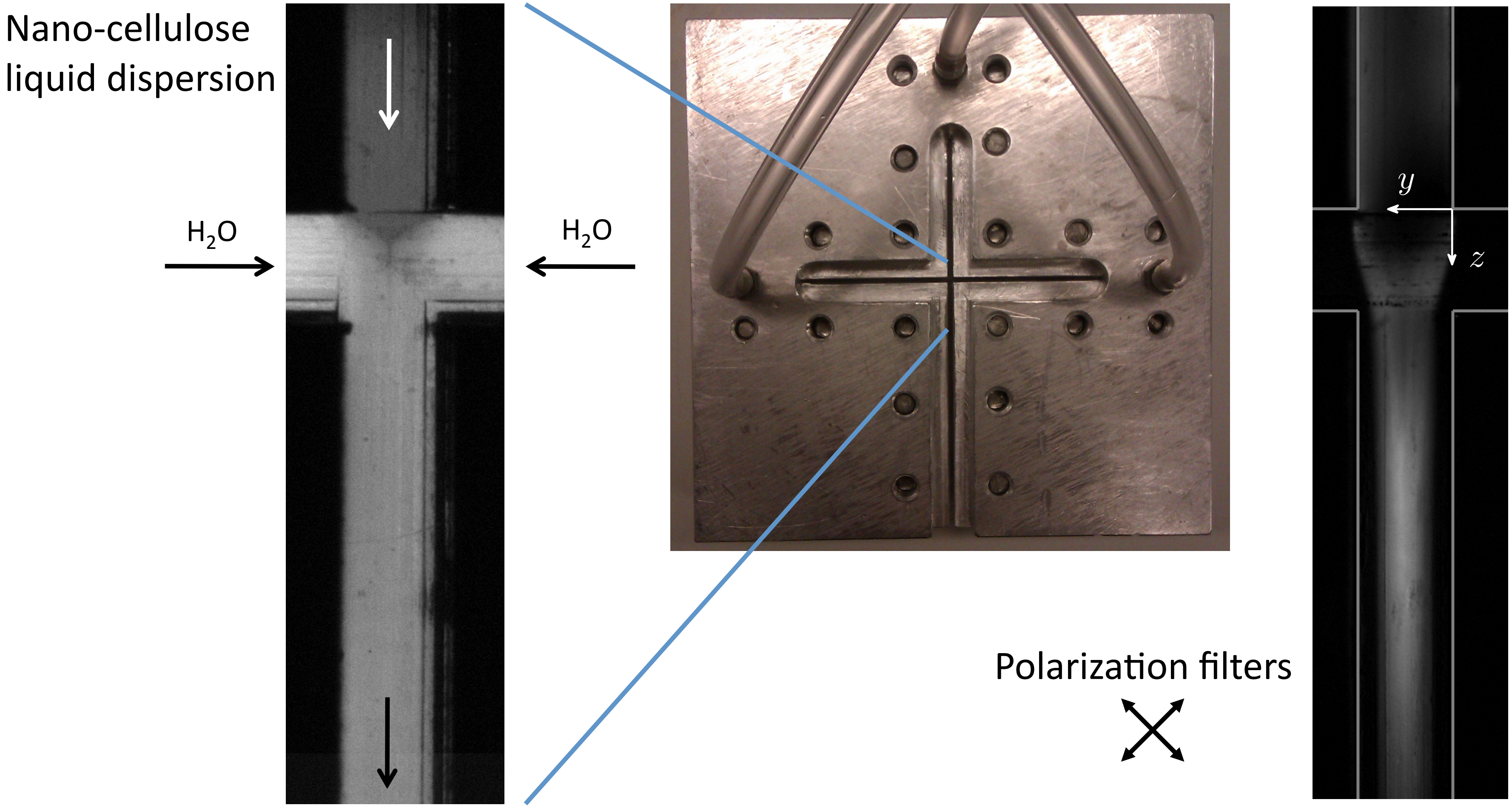
η, Dynamic viscosity
Q_i, Volume flow rate
ρ, Density
h, Channel height

Atomic force microscopic image of nanofibrils

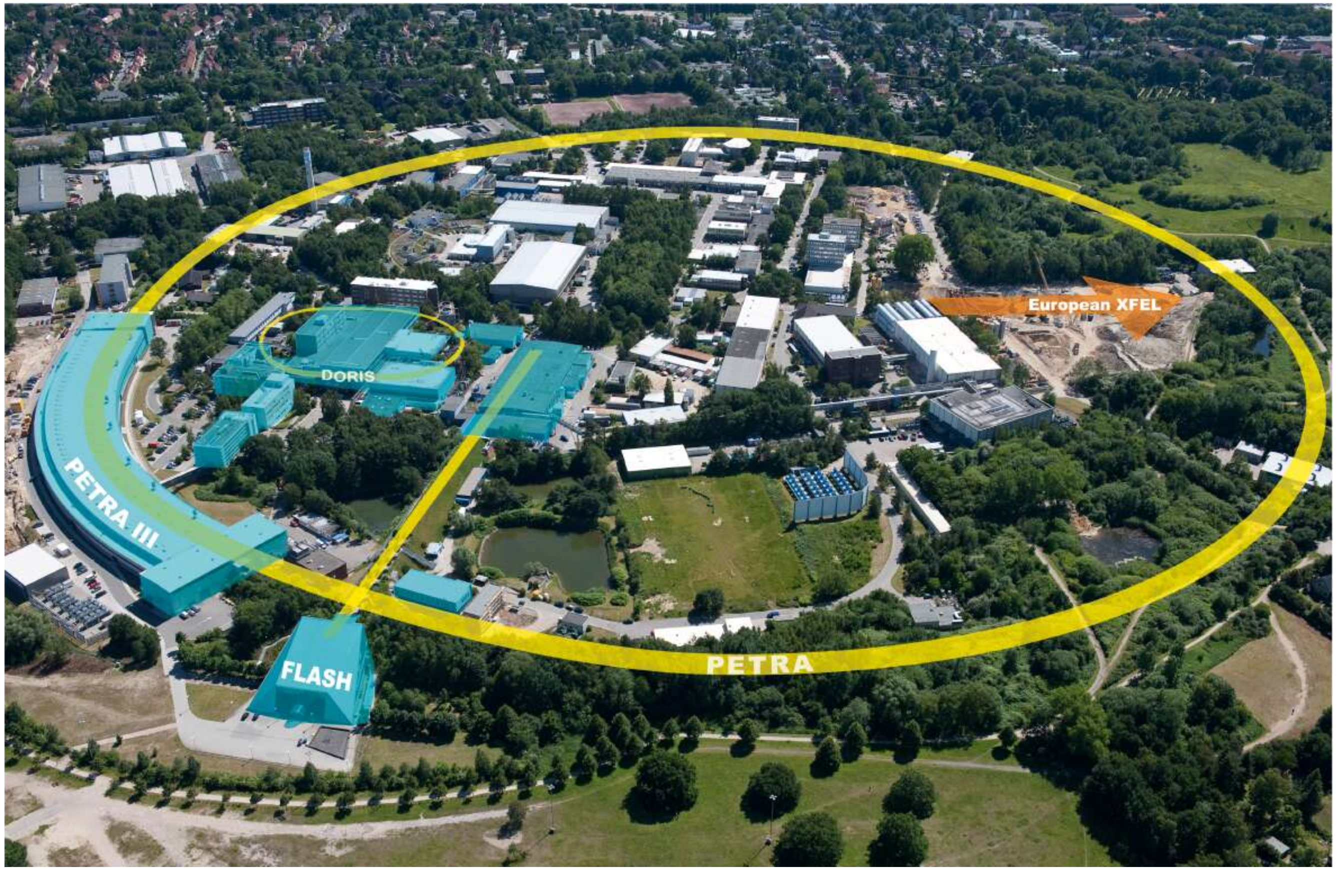


Courtesy of A. Fall and G. Nyström

Hydrodynamic Alignment



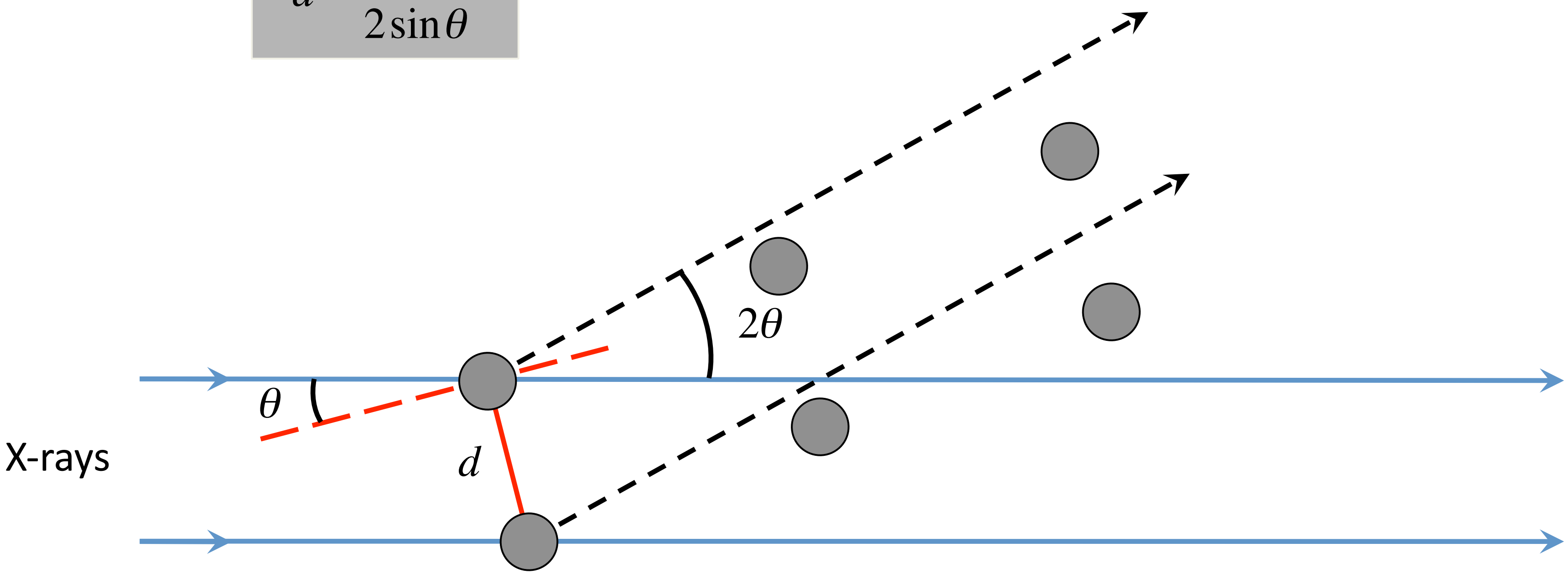
PETRA III, Synchrotron in Hamburg



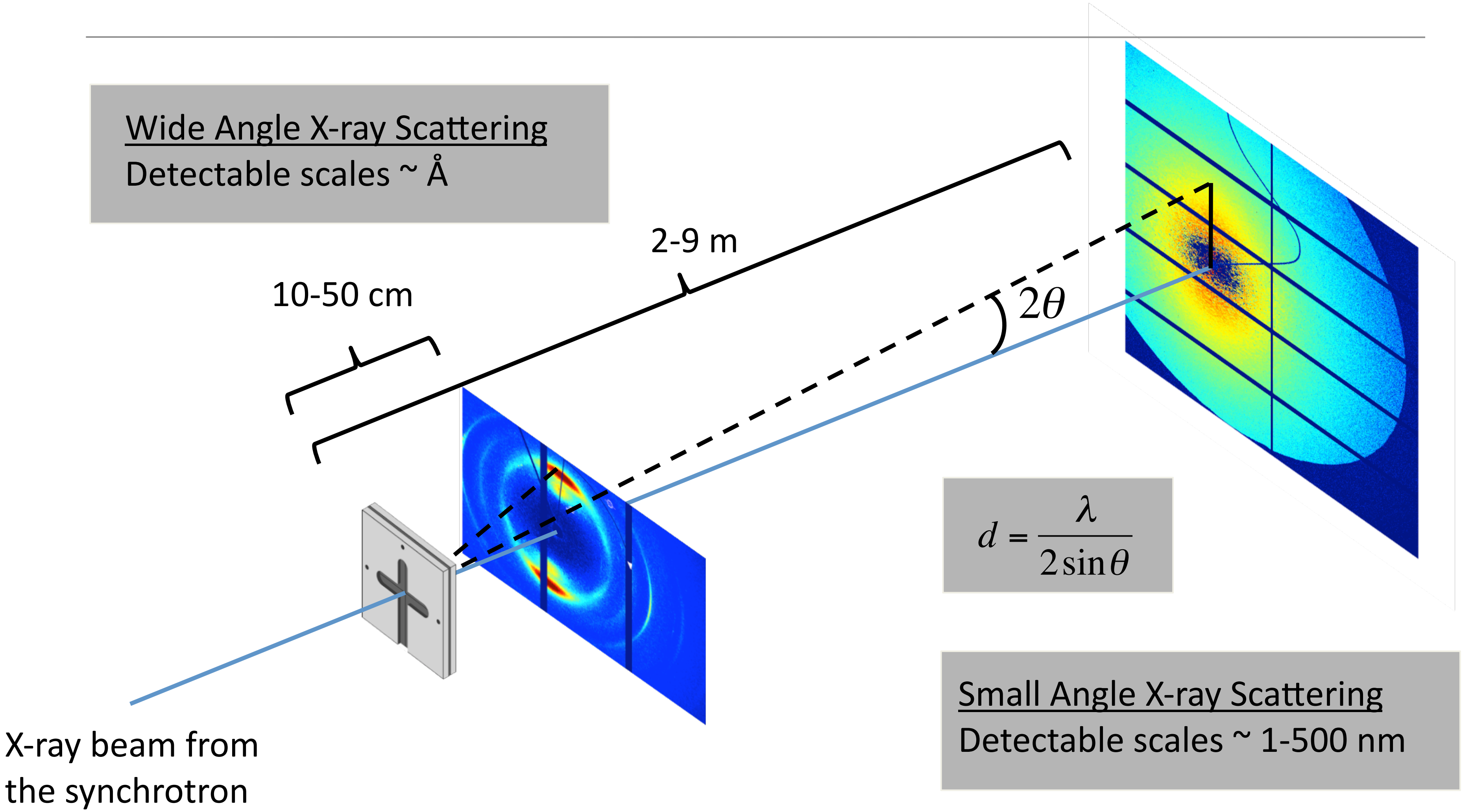
X-ray Scattering

Constructive interference when:

$$d = \frac{\lambda}{2\sin\theta}$$

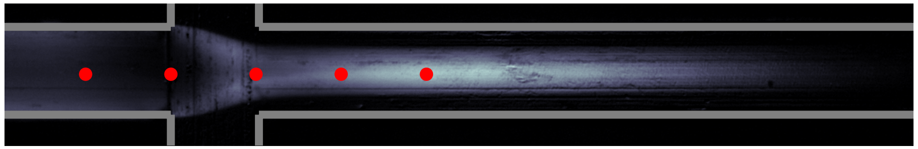


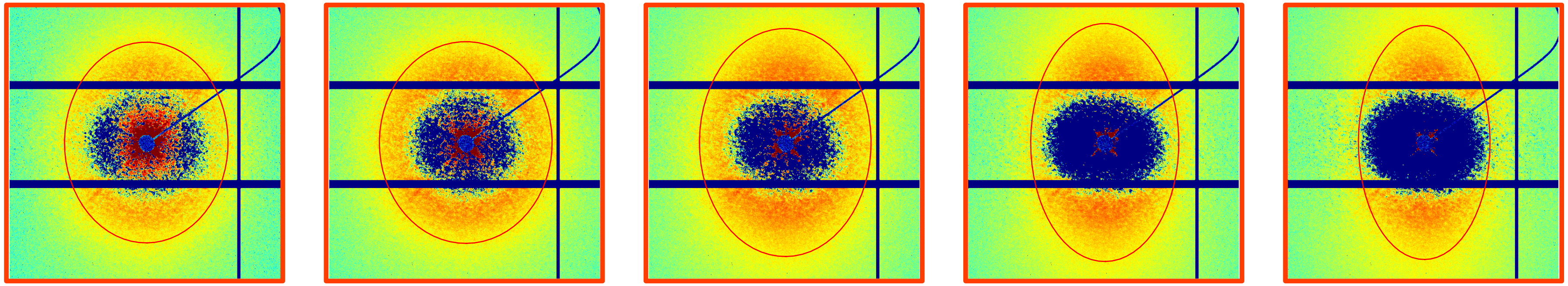
X-ray Scattering



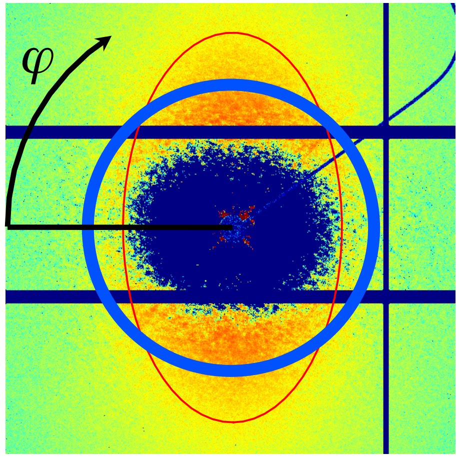
Small Angle X-ray Scattering

Wavelength:	0.957 Å
Beam size:	25 x 10 μm^2
Sample detector dist:	8422 mm
Scales:	5-20 nm





Orientation from X-ray data

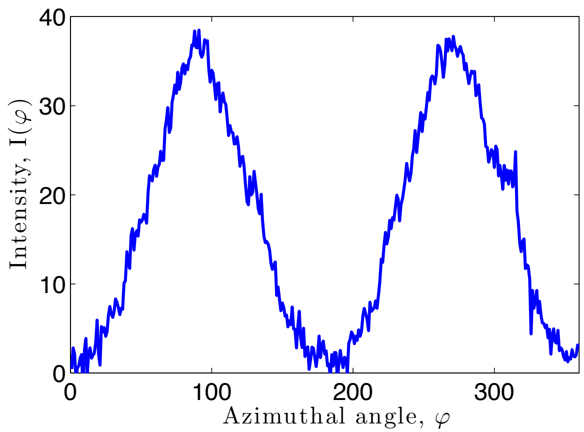


The order parameter, S:

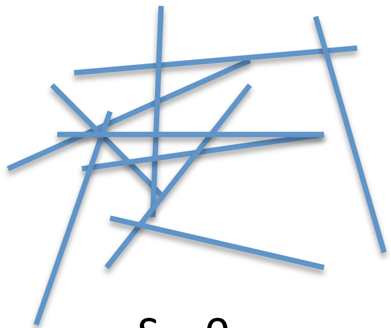
$$S = \langle P_2(\cos\varphi) \rangle = \left\langle \frac{3}{2}\cos^2\varphi - \frac{1}{2} \right\rangle$$

In this case:

$$S = \int_0^{\pi} I(\varphi)\left(\frac{3}{2}\cos^2\varphi - \frac{1}{2}\right)\sin\varphi \, d\varphi$$

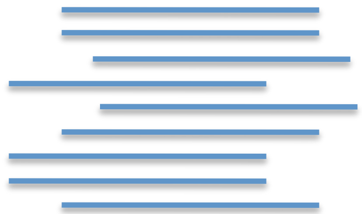


Random orientation



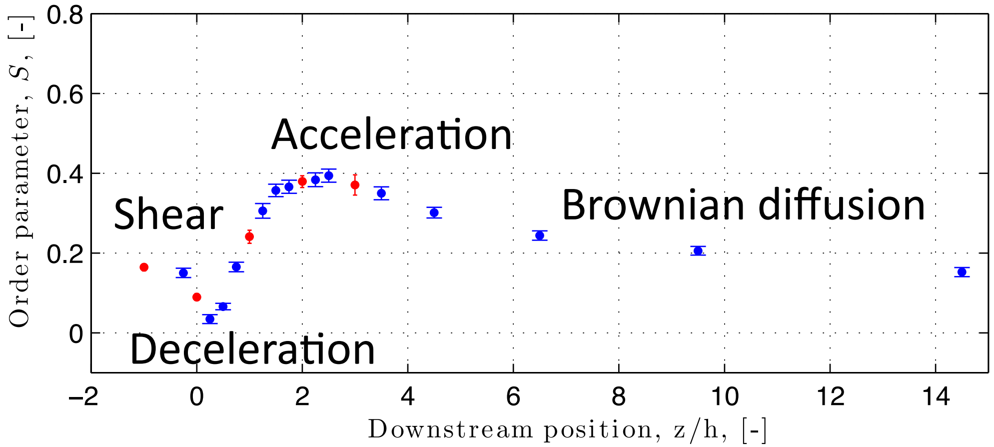
S = 0

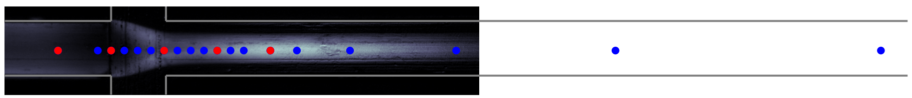
Aligned

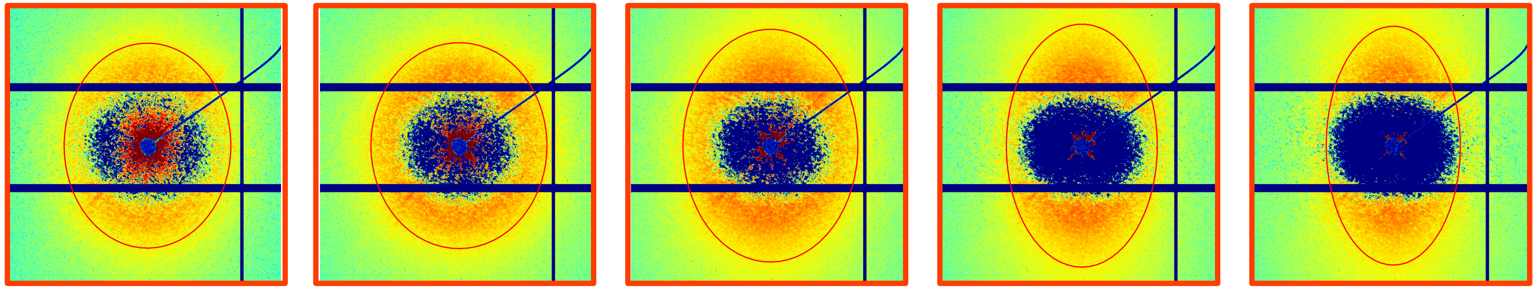


S = 1

Extensional Flow and Fibril Orientation

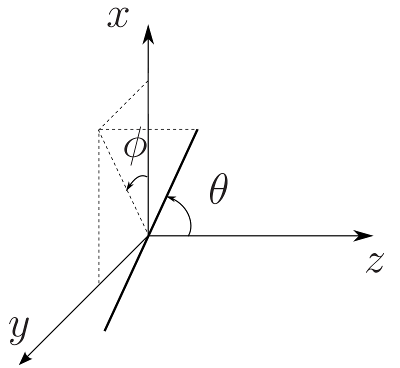






Computation, Smoluchowski eq.

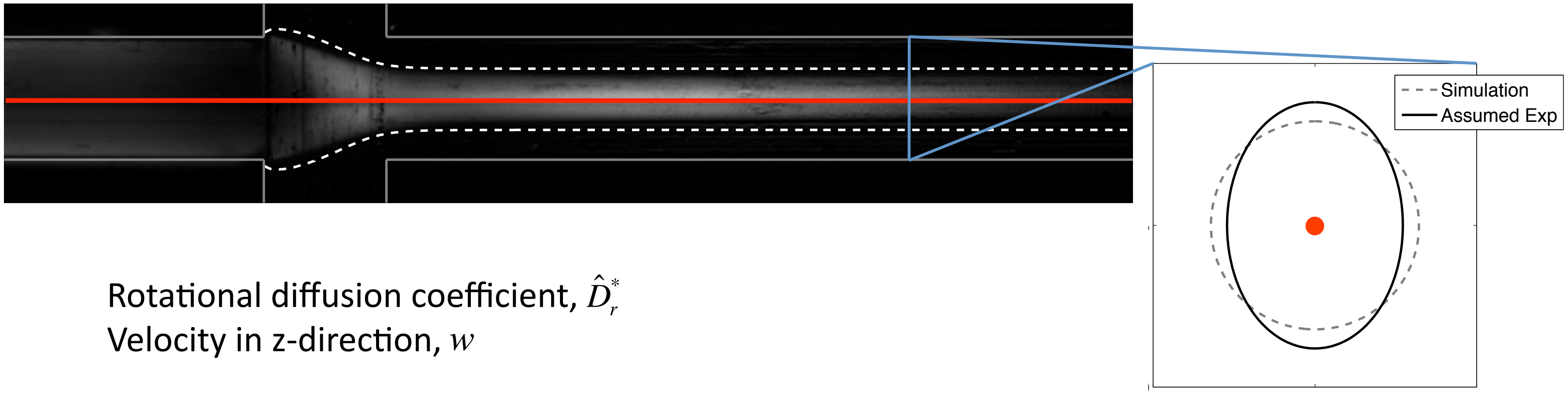
The development of the orientation distribution, $\Psi(z,\theta)$, along the centre line is studied.



1D and biaxial symmetry:

$$w^* \frac{\partial \Psi}{\partial z^*} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\hat{D}_r^* \sin\theta \frac{\partial\Psi}{\partial\theta} - \sin\theta\dot{\theta}\Psi\right)$$

Convection | Diffusion | Force from flow



Rotational diffusion coefficient, $\hat{D}_r^*$

Velocity in z-direction, w

Computation, Smoluchowski eq.

1D Smoluchowski equation:

$$w^* \frac{\partial \Psi}{\partial z^*} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\hat{D}_r^* \sin\theta \frac{\partial\Psi}{\partial\theta} - \sin\theta\dot{\theta}\Psi\right)$$

Rotational diffusion coefficient, $\hat{D}_r^*$
Aspect ratio, r_p
Velocity in z-direction, w
Orientation distribution, Ψ

Rotational diffusion coefficient, Doi & Edwards (2086):

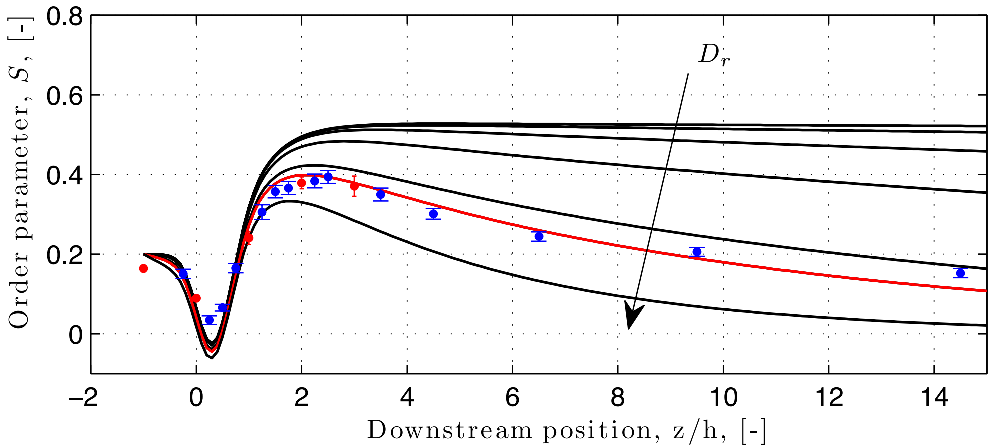
$$\hat{D}_r = \boxed{\frac{3k_B T(2\ln(2r_p)-1)}{16\pi\eta_s a^3}}\boxed{\beta(nl^3)^{-2}}\boxed{\left[\frac{4}{\pi}\int d\mathbf{p}'|\mathbf{p}\times\mathbf{p}'|\Psi_s(\mathbf{p}')\right]^{-2}}$$

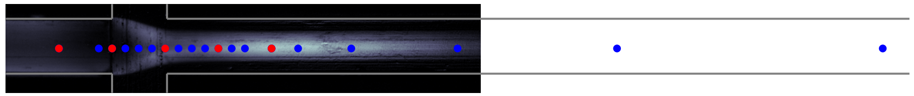
Brownian diffusion   Conc   Orientation

Angular velocity from Jeffery (2022) for a biaxial flow:

$$\dot{\theta} = \frac{\partial\theta}{\partial t^*} = -\frac{\partial w^*}{\partial z^*}\left(\frac{r_p - 1}{r_p + 1}\right)\frac{3}{2}\cos\theta\sin\theta$$

Fibril Alignment Calculation



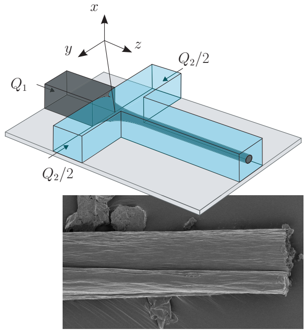


1D Smoluchowski equation with velocity, *w*:

$$w^* \frac{\partial \Psi}{\partial z^*} = \frac{1}{\sin\theta} \frac{\partial}{\partial \theta}\left(\hat{D}_r^* \sin\theta \frac{\partial \Psi}{\partial \theta} - \sin\theta \dot{\theta} \Psi \right)$$

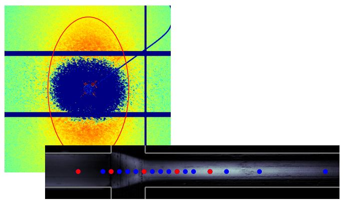
Rotational diffusion coefficient, $\hat{D}_r^*$
Velocity in z-direction, w
Orientation distribution, Ψ

Conclusions

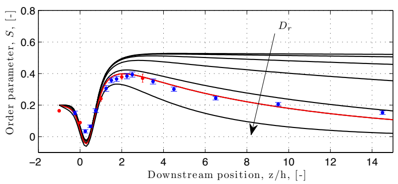


A filament manufacturing process was designed and tested.

The first filament showed unique properties.



The orientation of fibrils in a laminar semi-dilute dispersion was studied with SAXS.



The Smoluchowski equation could be used to describe the orientation evolution.

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Kungliga Tekniska Högskolan (KTH)
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Lic. M. Kvick

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PhD. S. V. Roth
PhD. C. Krywka

Innventia AB:
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PhD. C. Aulin

INNVENTIA

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