The future of GISAS: Challenges and opportunities in GISANS

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Outline

Introduction

Lubrication and surface anomalies at solid-liquid boundaries

Depth resolved experiments

using a polychromatic beam

Time resolved experiments

collecting data in absolute time

Conclusion

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Lubrication

5-6 % of gross national product is lost! (5 % of 75 T$)

Extremely thin liquid films ==> Boundary effects

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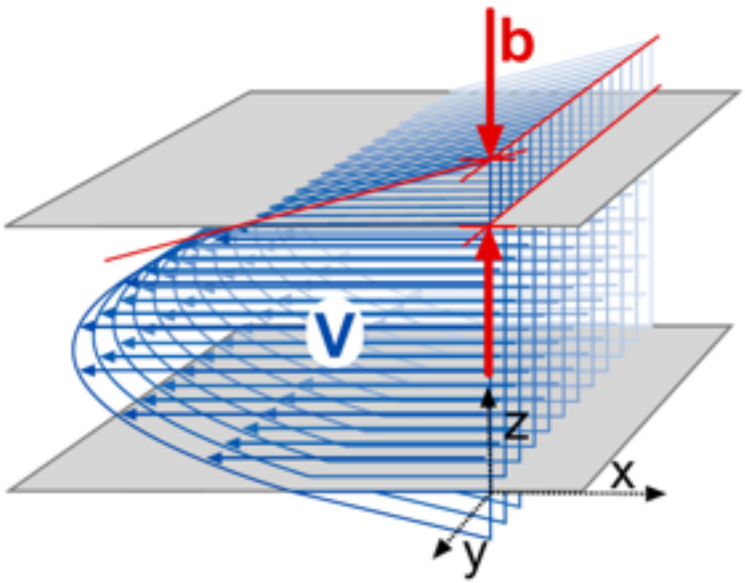
Surface Slip



Slip length:

$$b = v(0)\,\frac{\partial v(z)}{\partial z}^{-1}$$

True slip:

- Very high shear rates (> 10^9 s^{-1} for water)
- Roughness of the solid boundary differs vastly from the liquid molecules' size (molecules get trapped in pits of the surface)

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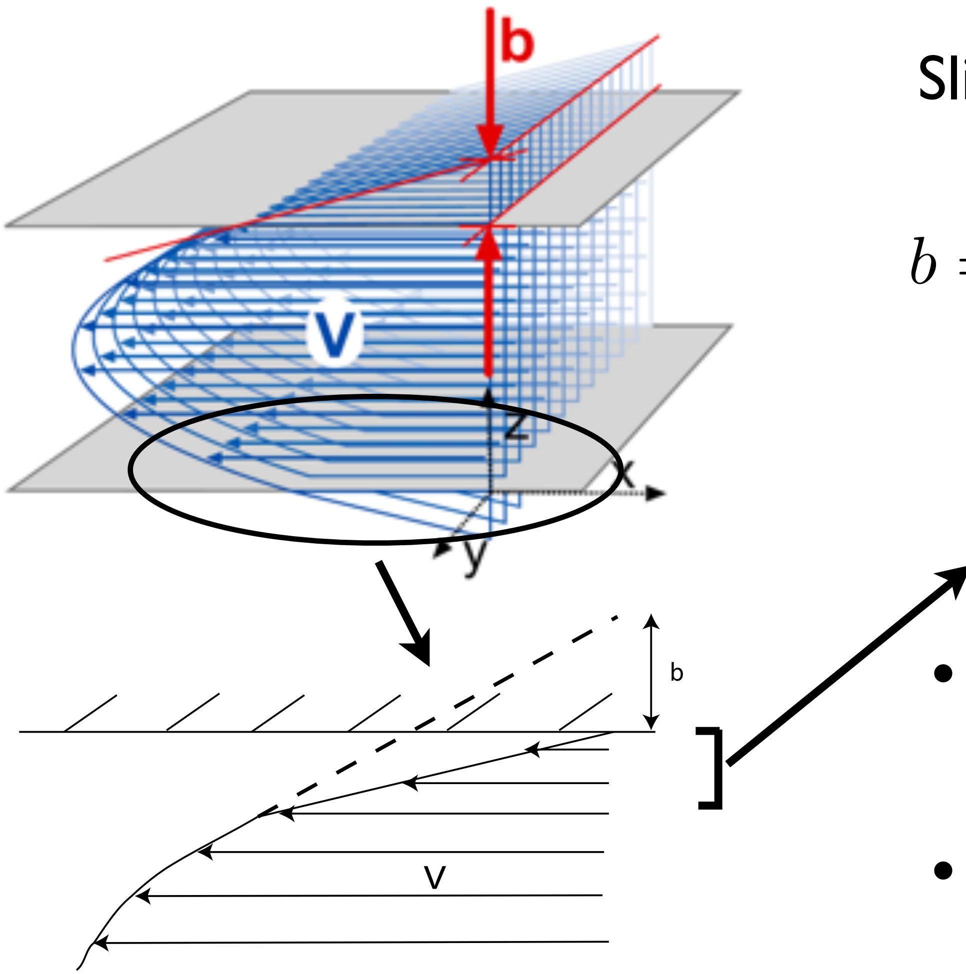
Surface Slip



Slip length:

$$b = v(0)\frac{\partial v(z)}{\partial z}^{-1}$$

Apparent Slip:

- Structural changes of the liquid near the surface (molecular ordering)
- Formation of a depletion layer
- Dynamical change near the surface (Shark skin effect)

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Experimental Methodes

Capillary techniques

(P. Debey et al., J. Appl. Phys., **30** 843 (1959))

Fluorescent recovery after photobleaching (FRAP)

(R. Pit et al., Phys. Rev. Lett., **85** 980 (2000))

Surface force aparatus (SFA)

(Y. Zhu et al., Phys. Rev. Lett., **87** 96105 (2001))

Atomic force microscopy (AFM)

(V. Craig et al., Phys. Rev. Lett., **87** 054504 (2001)

Quartz crystal resonators

(F. Ferrante et al., J. Appl. Phys., **76** 3448 (1994))

Other techniques:

Spinning disks, rotating cylinders, droplets moving down an inclined surface, particle sedimentation, excitation of surface waves

more engineering type of measurements:

Tribometer…

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The challenge

All indirect techniques!

Direct probe for the solid-liquid boundary with atomic resolution!

Neutrons with high penetration power and sensitivity to light elements are such a probe.

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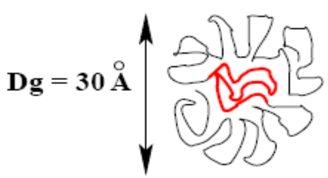
Model system - Pluronics

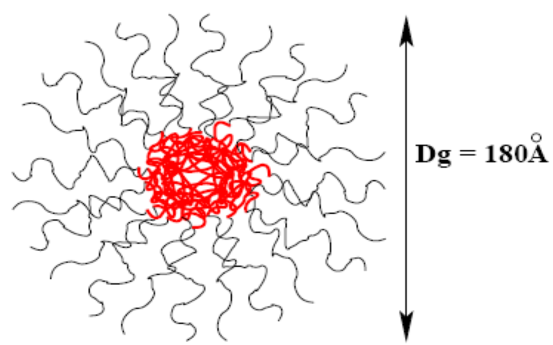
$$HO-[CH_2-CH_2-O]_X-[CH_2-CH(CH_3)-O]_Y-[CH_2-CH_2-O]_X-H$$

PEO hydrophilic | **PPO hydrophobic** | **PEO hydrophilic**

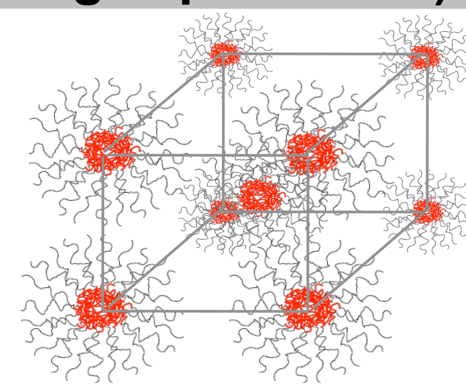
Solved in water (deuterated for the scattering experiments)



Unimer



Micelle



Crystal

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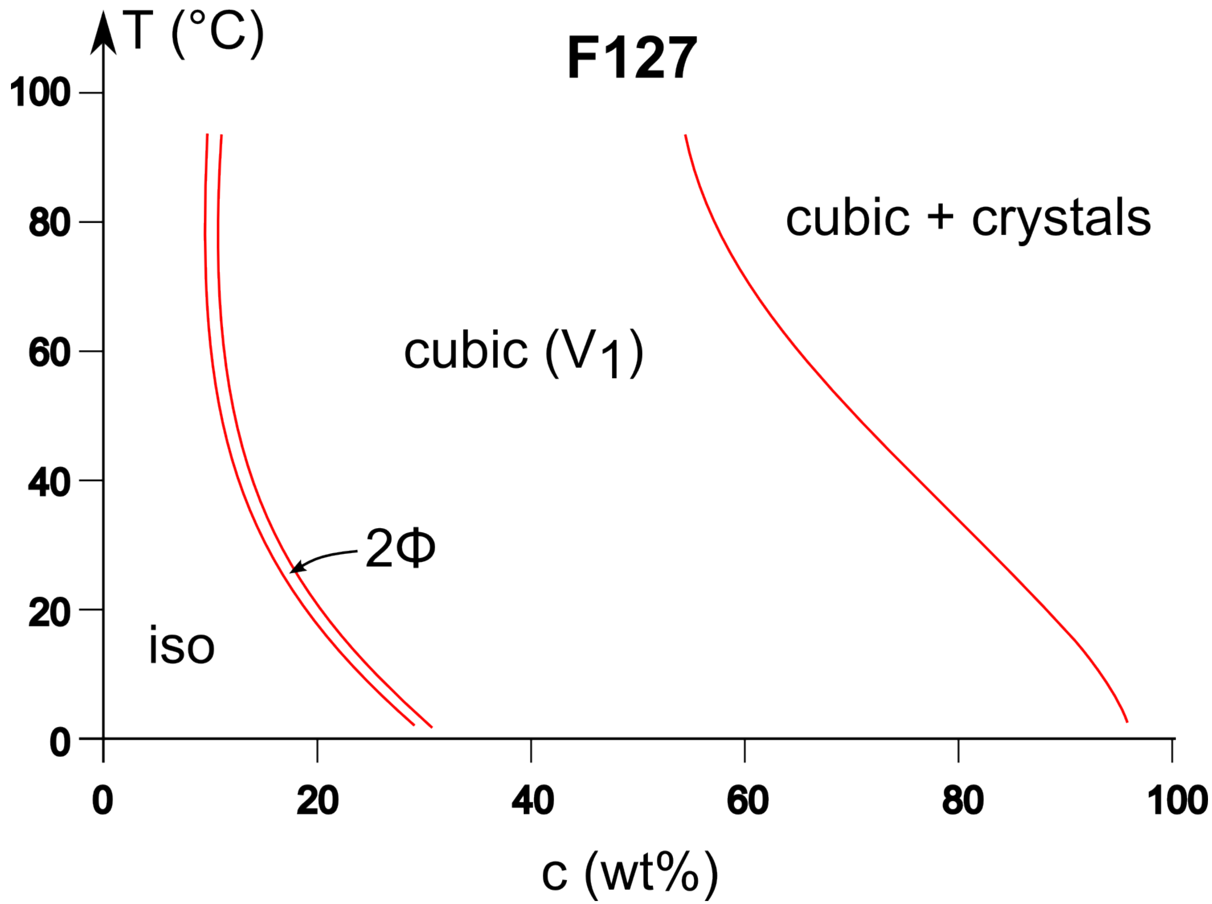
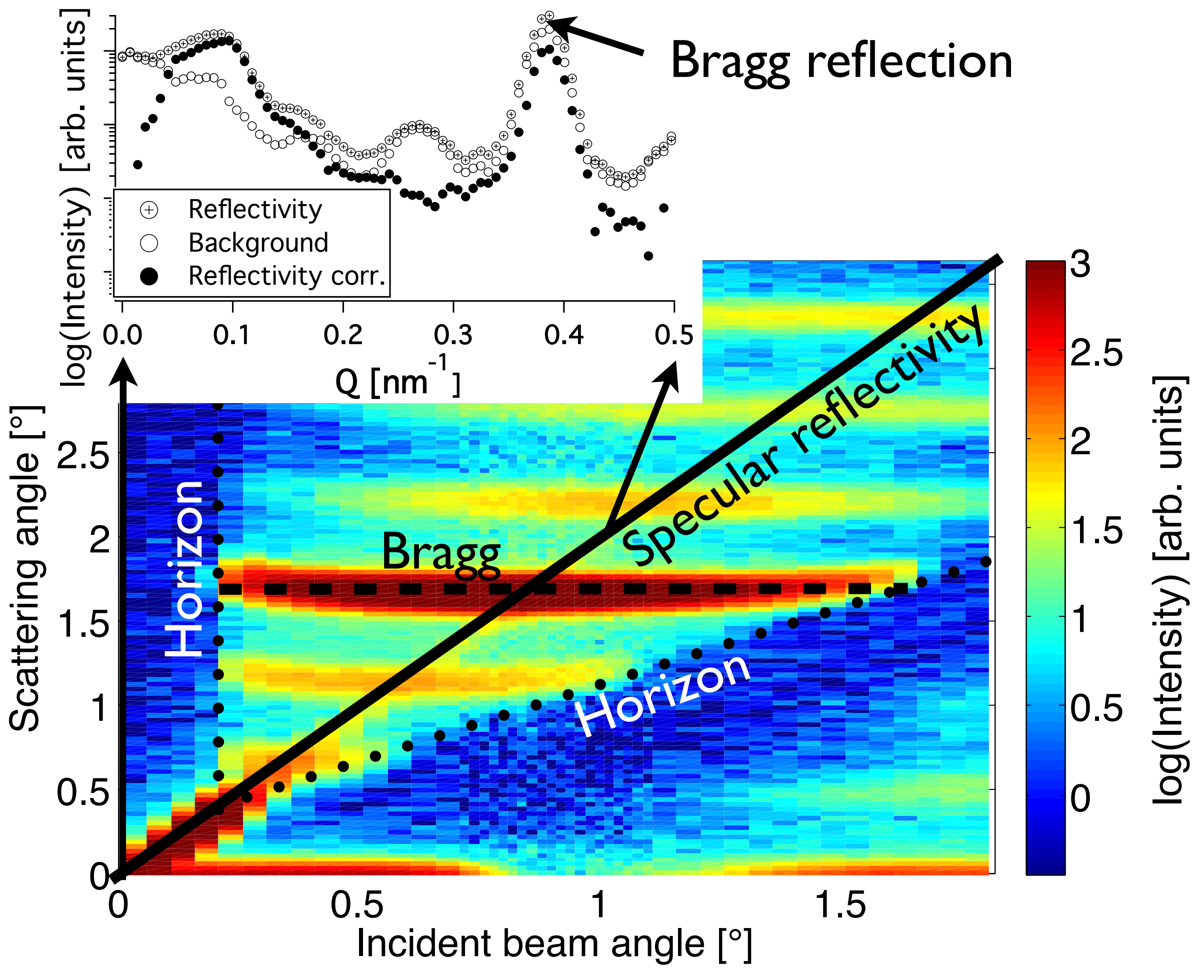
Phase diagram



G. Wanka et al., Macromolecules **27**, 4145 (1994).

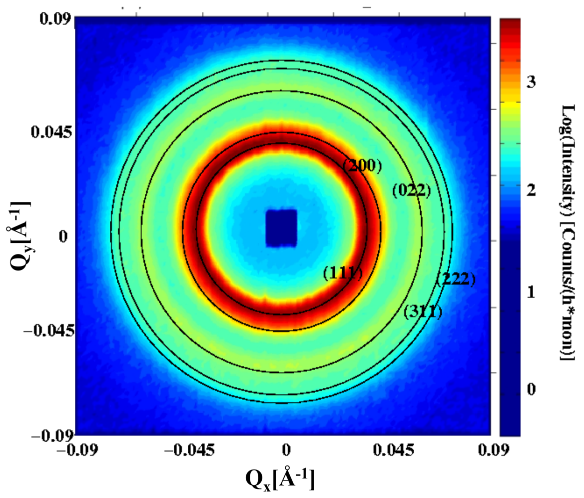
Reflectivity measurement



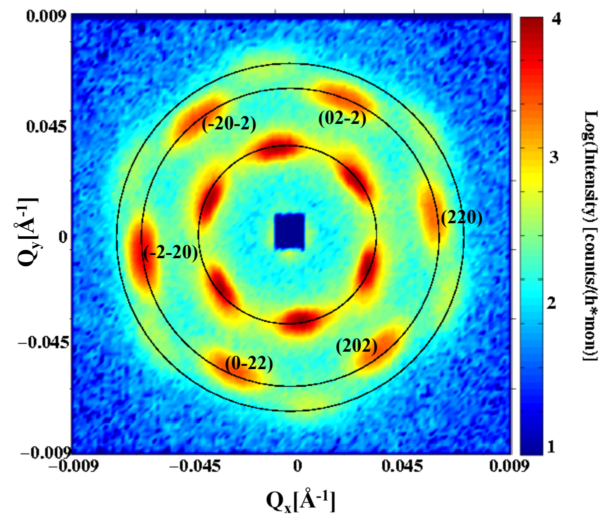
N. Wolff et al., Soft Matter, **10**, 8420 (2014)

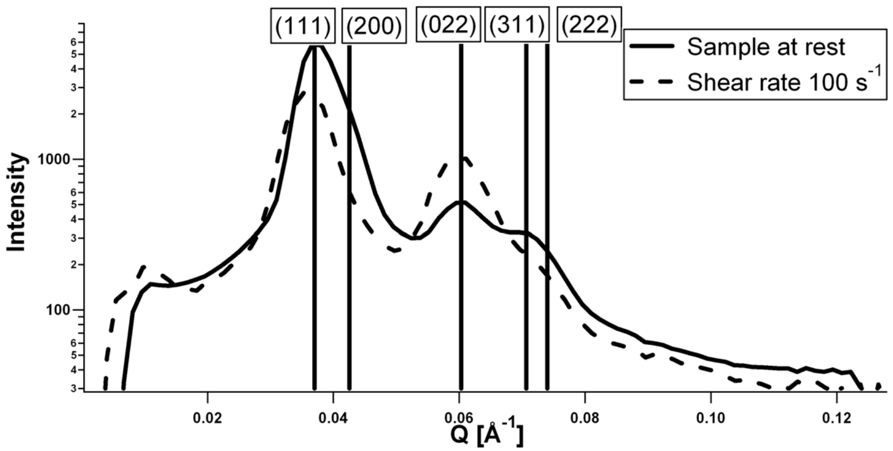
Transmission SANS

at rest

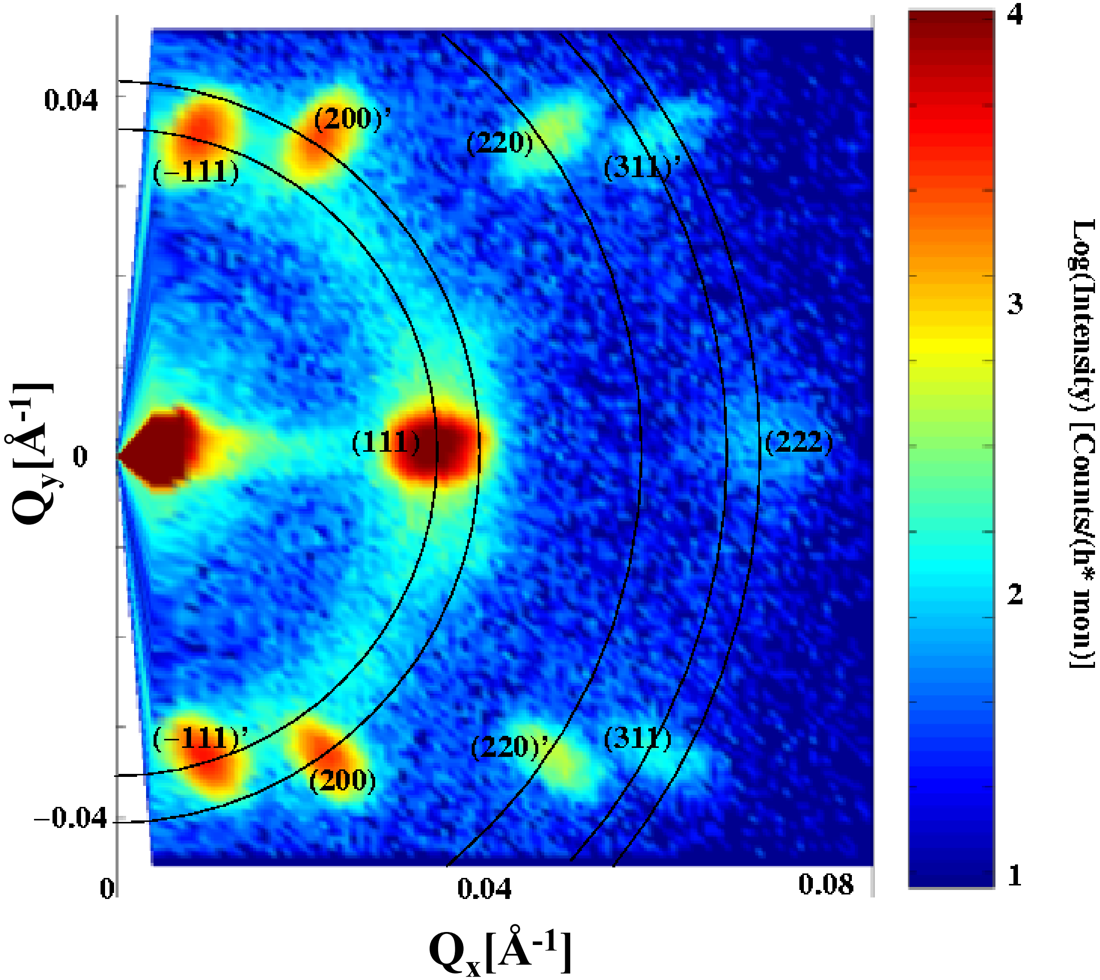


with shear





Gracing incidence geometry



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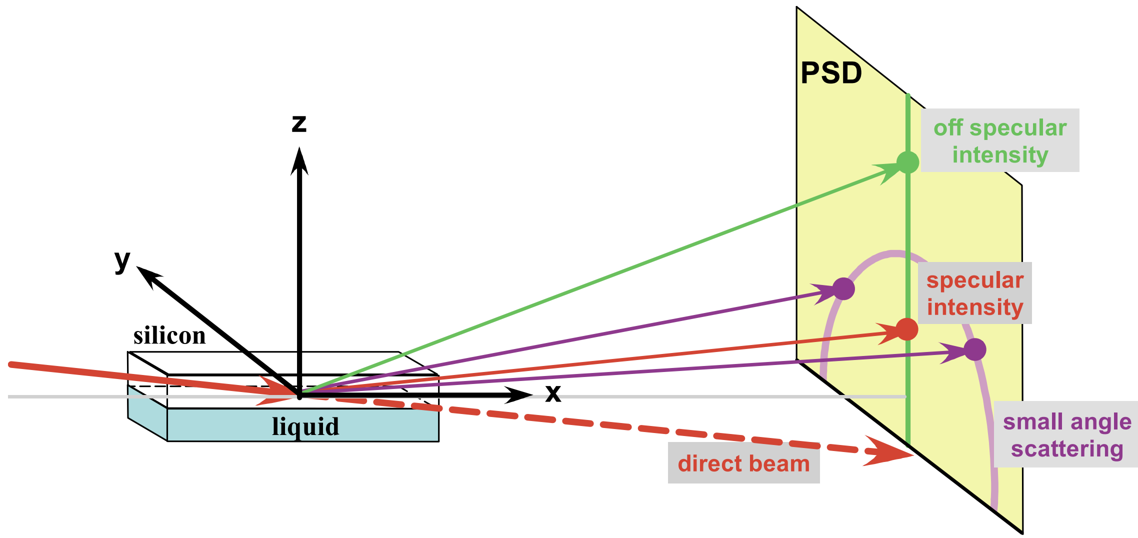
Grazing incidence scattering



$\Delta Q_x \sim 10^{-5}$ Å^{-1}

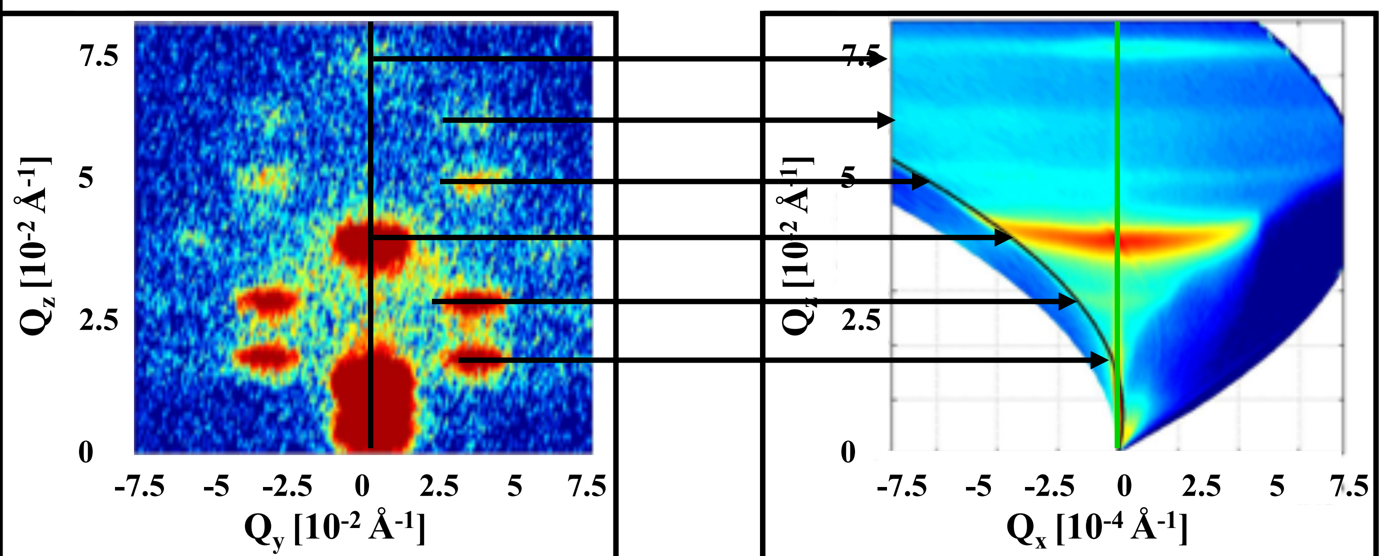
⇔ ~ 65 µm

$\Delta Q_y \sim 4*10^{-3}$ Å^{-1}

⇔ ~ 150 nm

$\Delta Q_z \sim 7*10^{-4}$ Å^{-1}

⇔ ~ 850 nm



M. Wolff et al., Euro. Phys. J. E **16**, 141 (2005).

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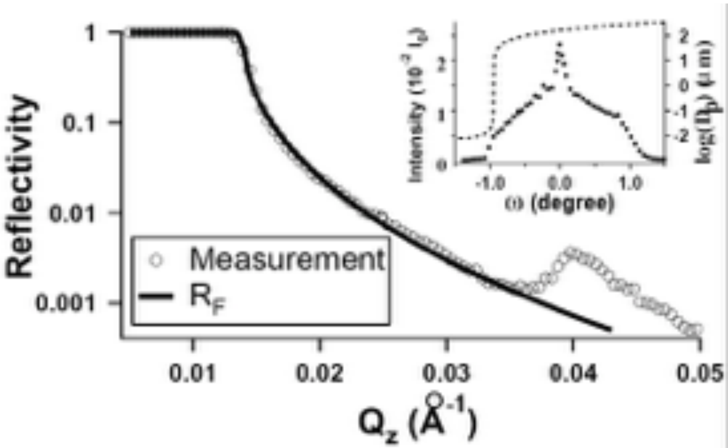
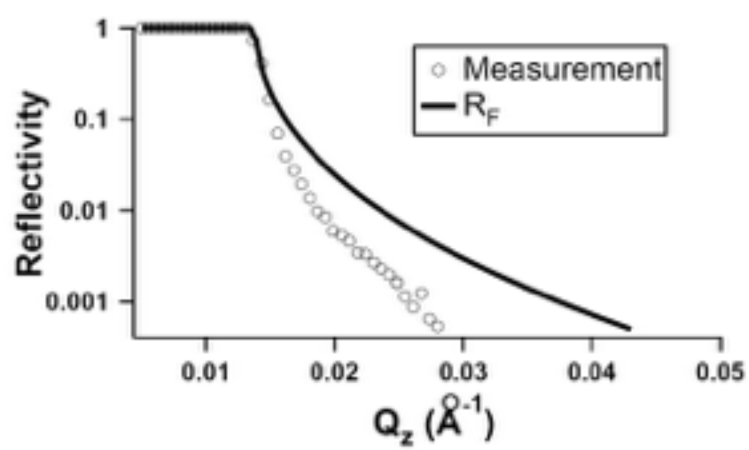
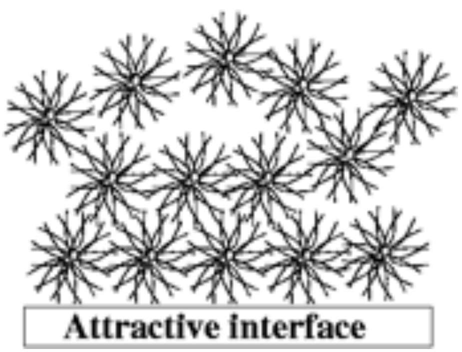
Micellar phase

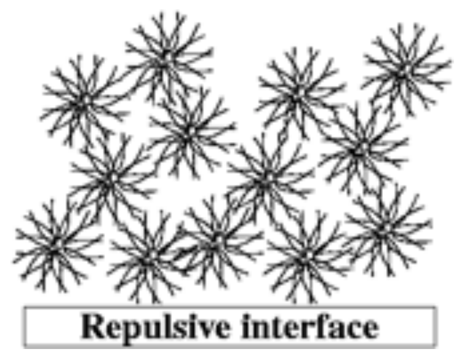
Attractive interface



Repulsive interface







⇒ **In-plane liquid like, out-of-plane tendency of layering**

M. Wolff et al., Phys.Rev. Lett. **92**, 255501 (2004).

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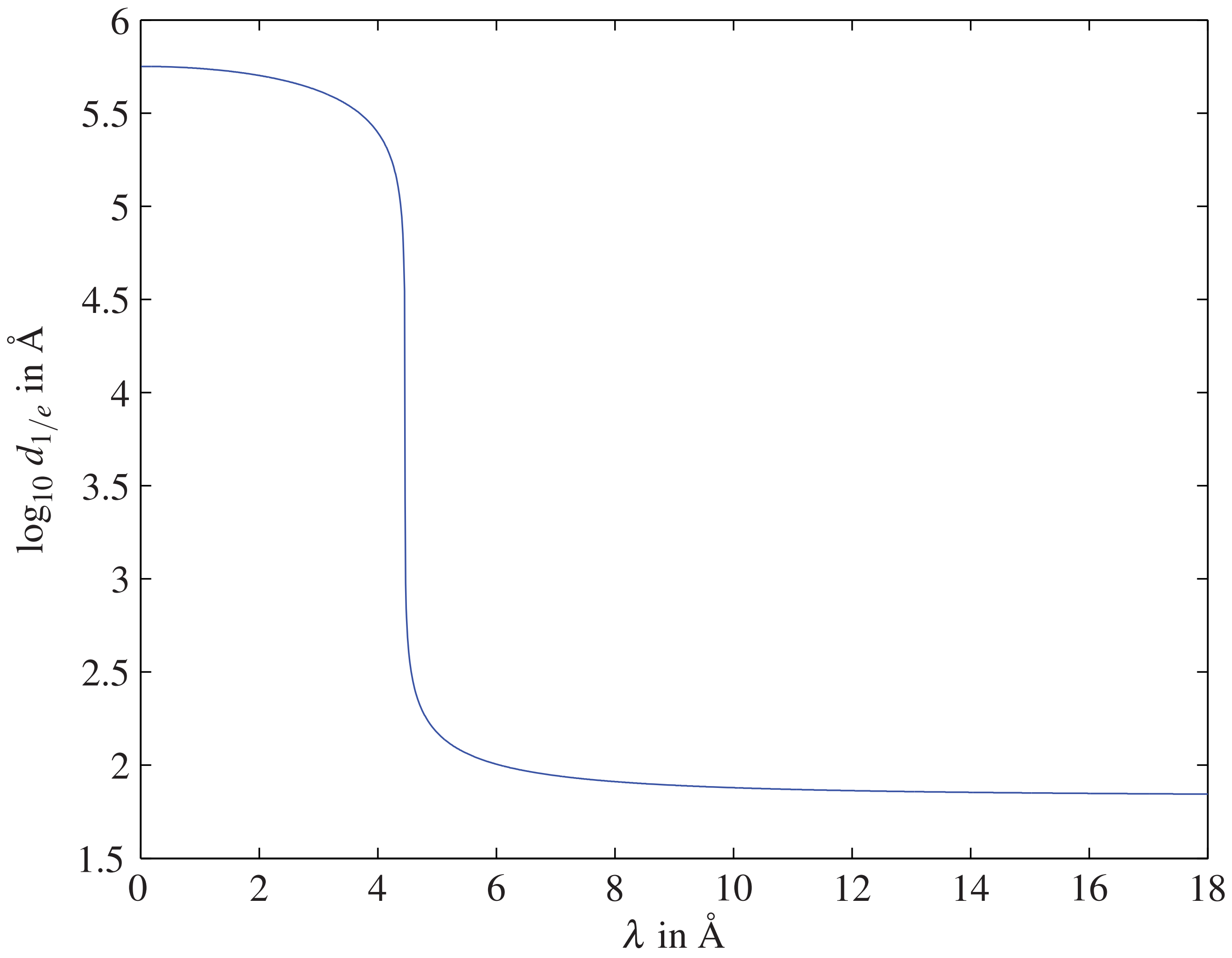
Penetration depth



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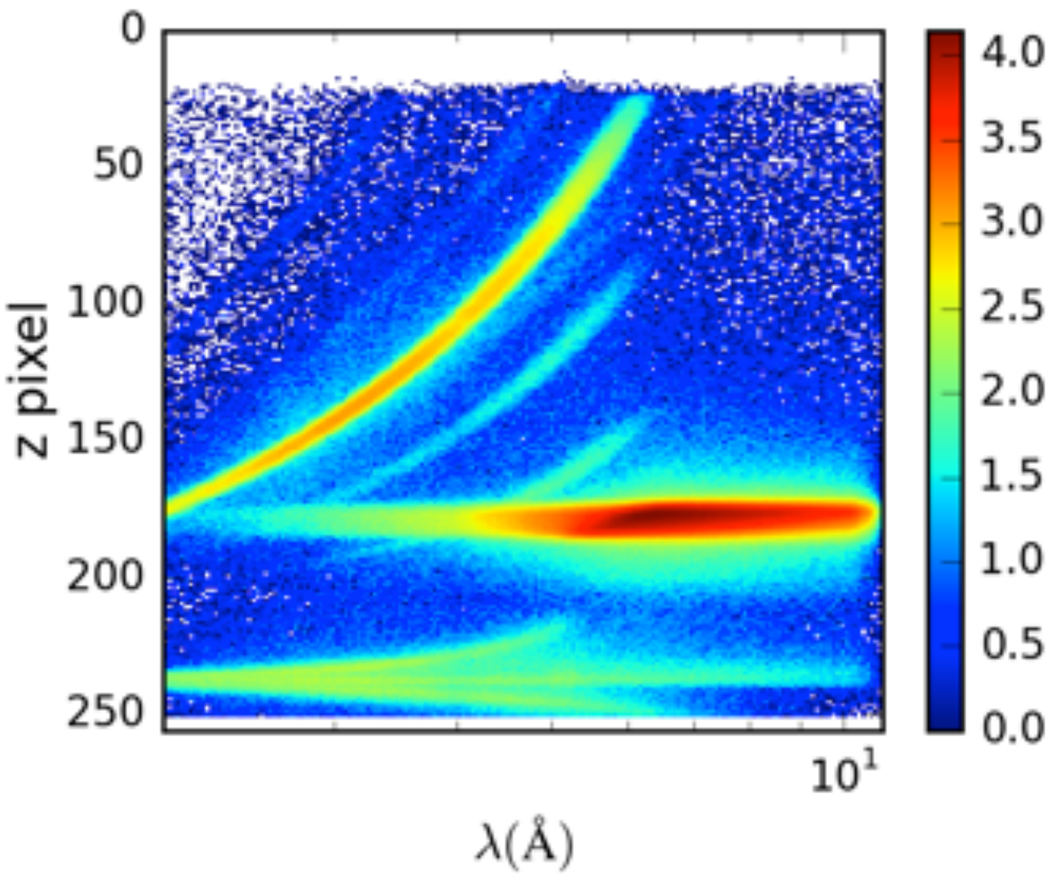
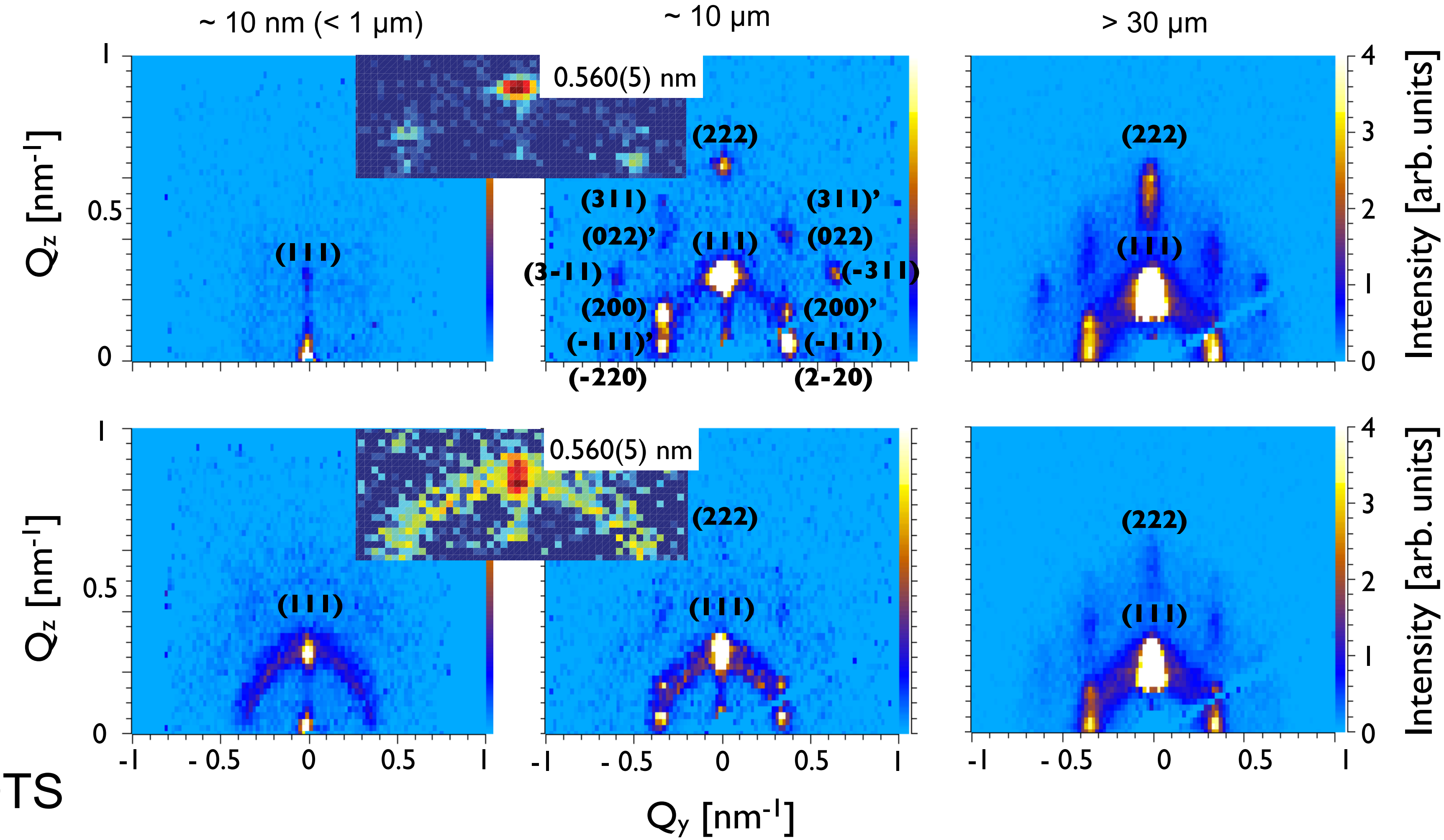
Time of flight - GISANS



Data from RefSANS (FRM-II)

Depth sensitivity (SANS-2D)

Piranha



OTS

M. Wolff et al., J. Appl. Cryst., **47**, 130 (2014).

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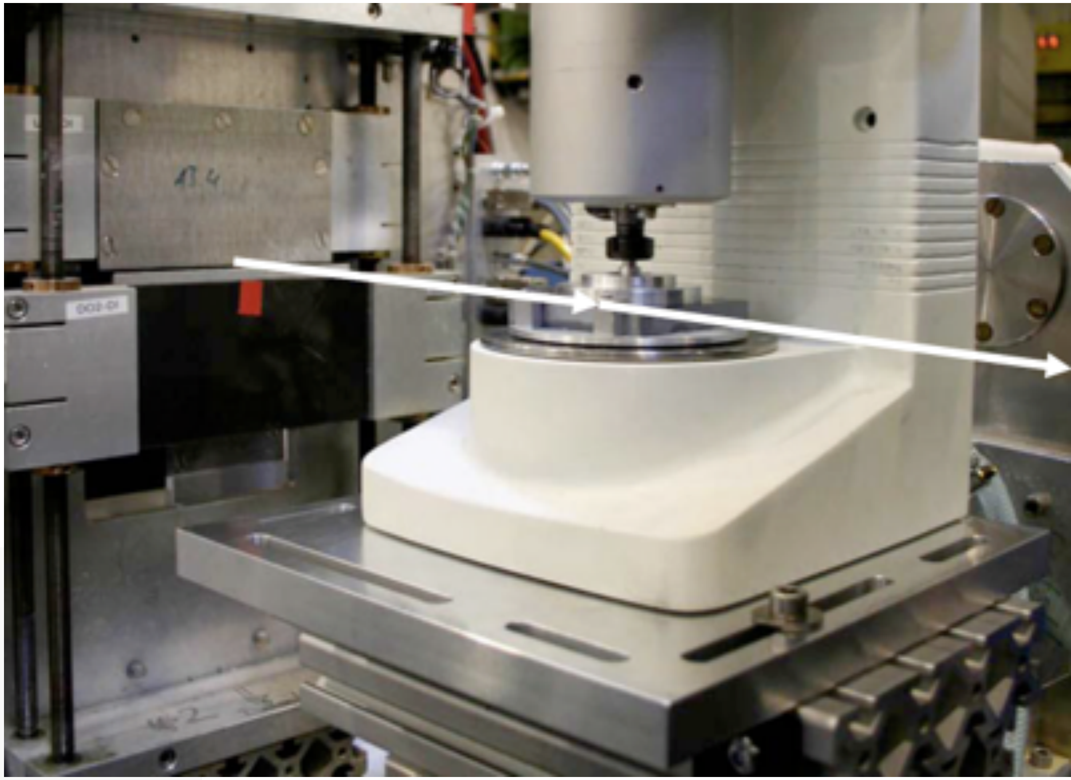
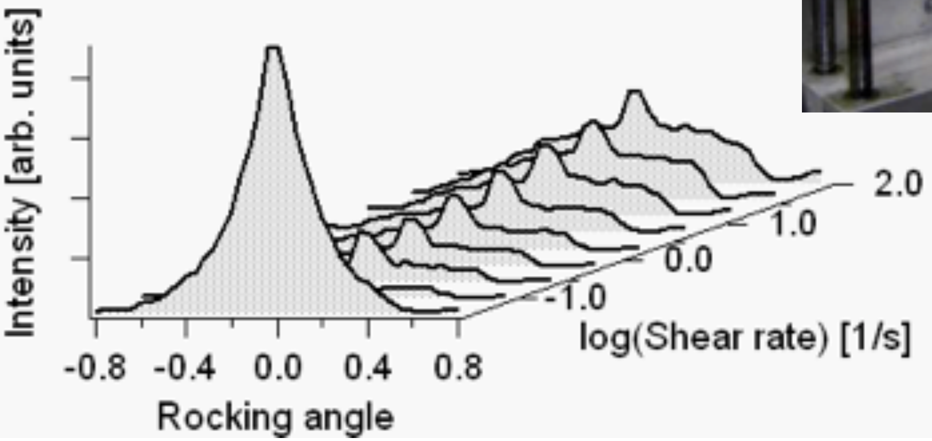
In-situ rheology - constant shear rate

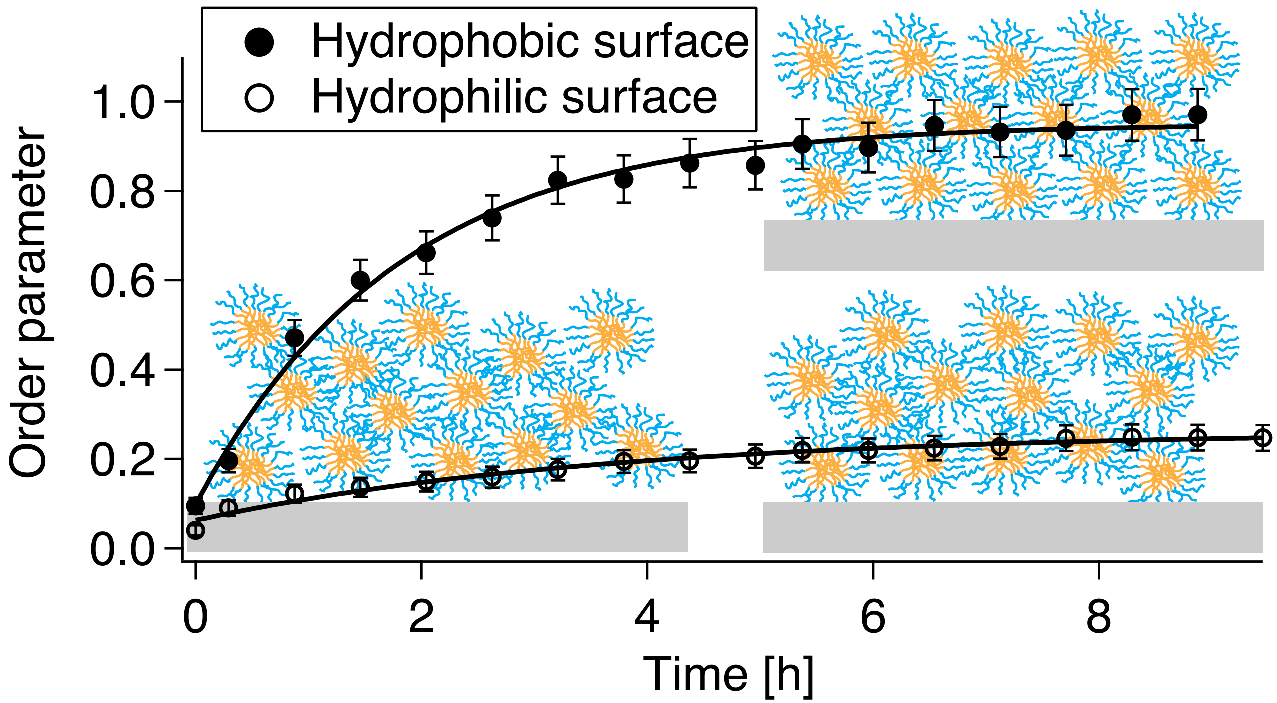


Rocking curve for different shear rates:



Commercial rheometer mounted on the sample stage of V6 (HMI).

Reconstruction

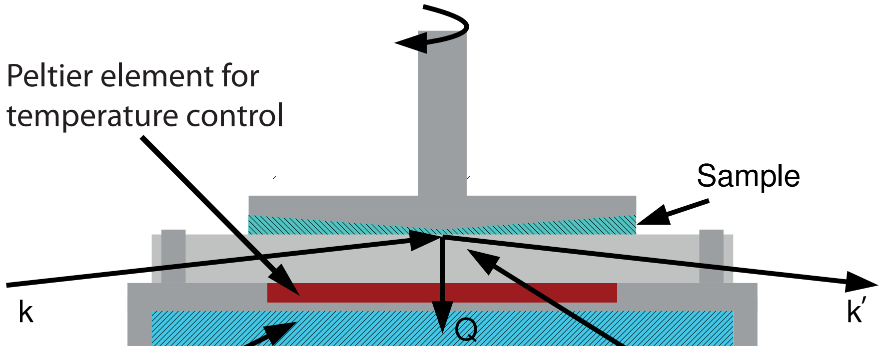


Reconstruction time: Hydrophilic: 5 h Hydrophobic: 2 h

M. Wolff et al., Langmuir **24(20)**, 11331 (2008).

In situ-rheology - oscillatory shear

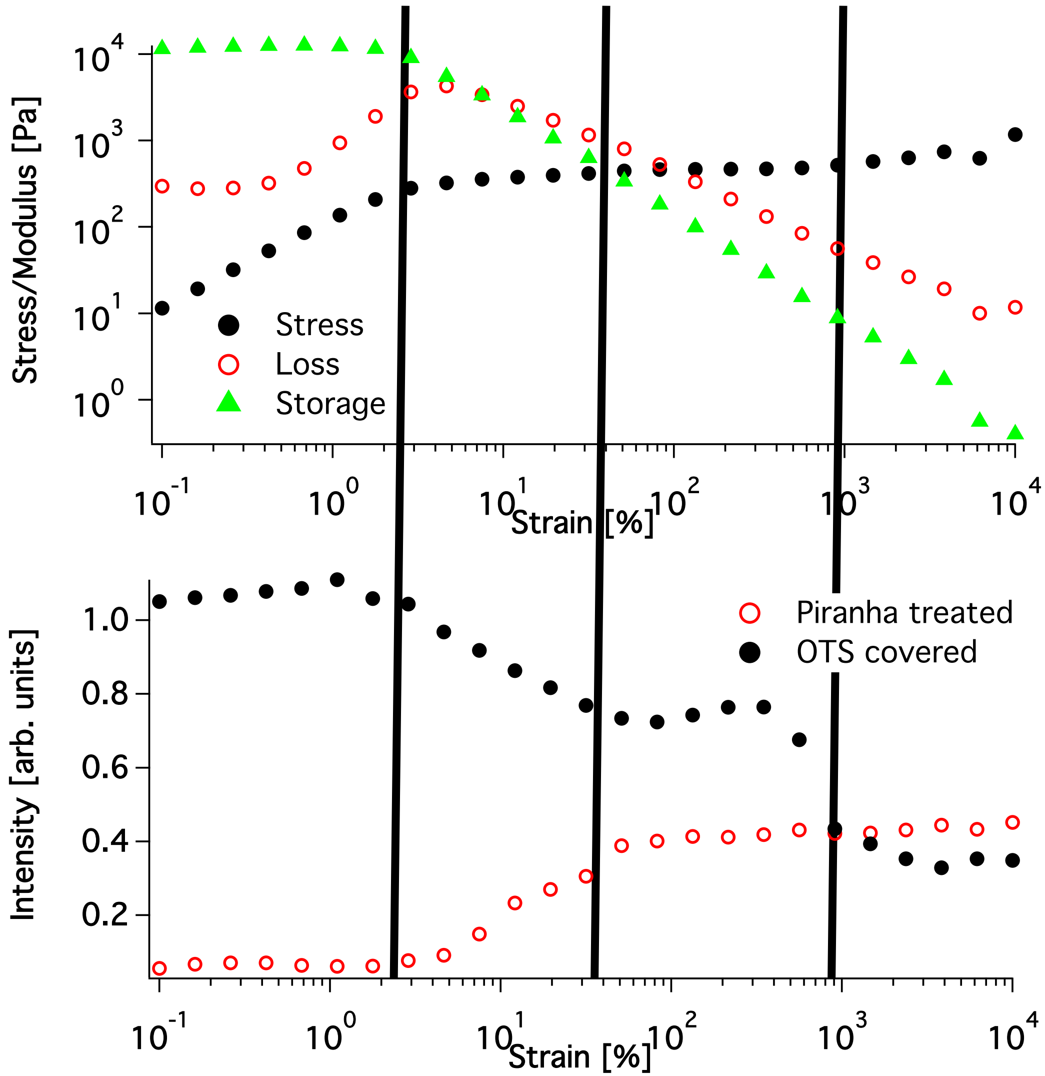
<u>*In situ*-shear neutron reflectometry:</u>



Temperature range: 15 - 160 °C

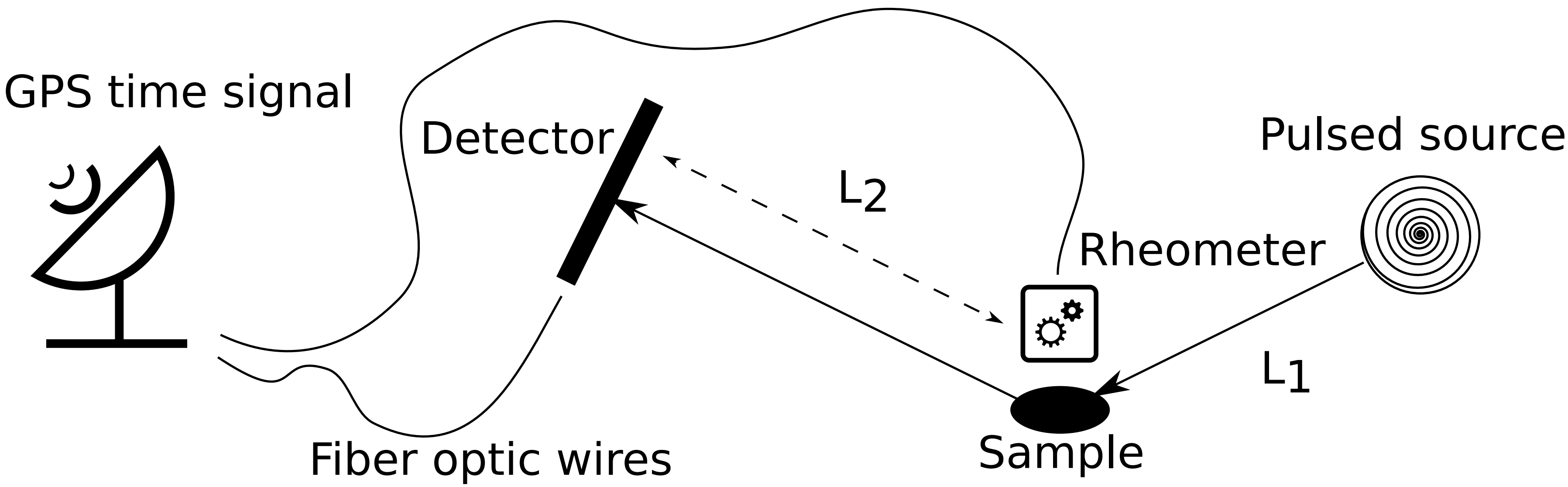
M. Wolff et al., J. Appl. Cryst., **46**, 1729 (2013).

Oscillatory shear

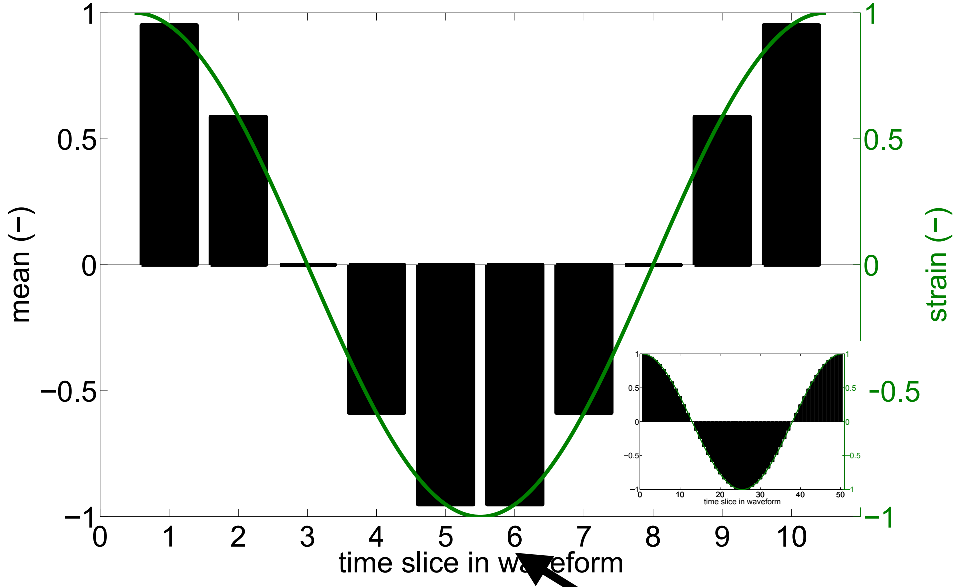


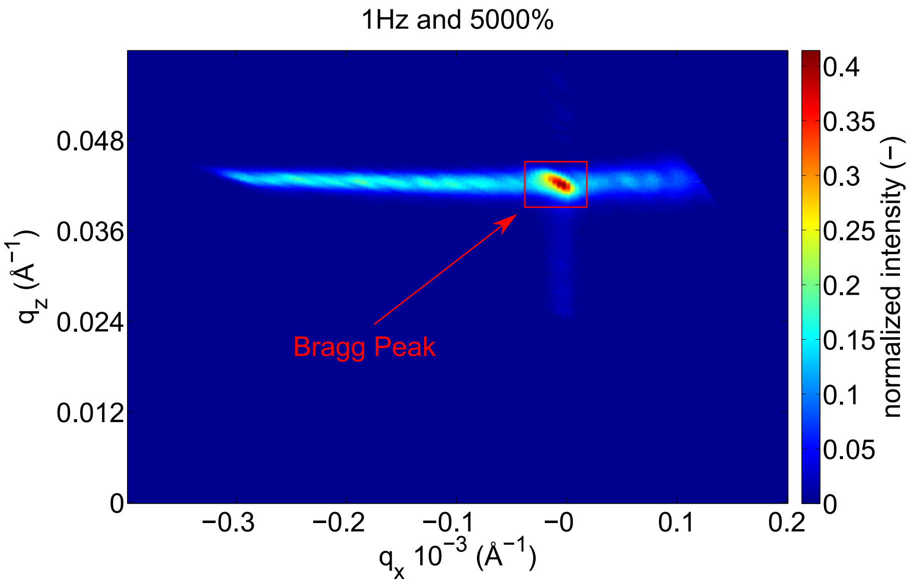
How is it done?

Save data in absolute time



Time slicing





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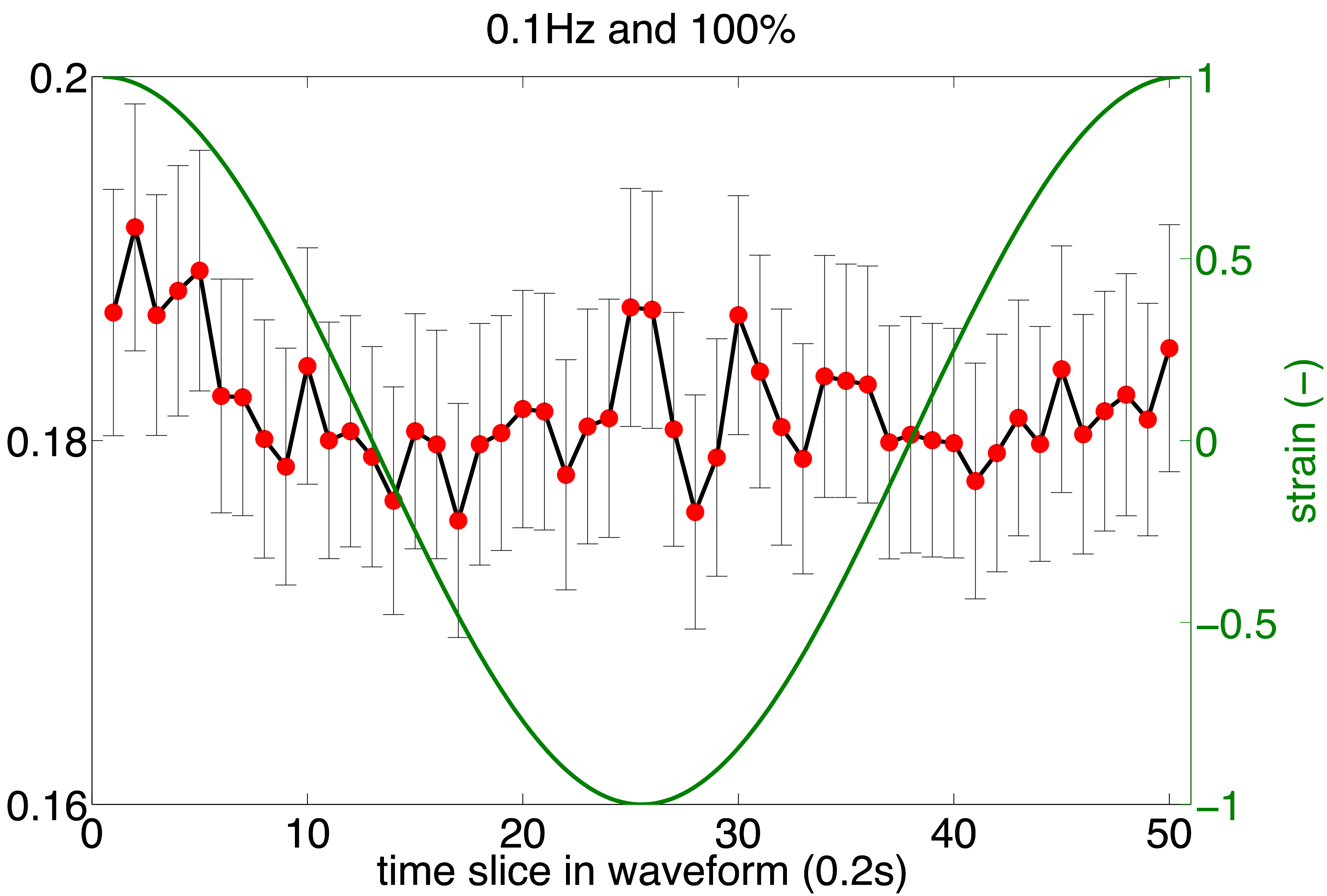
Result



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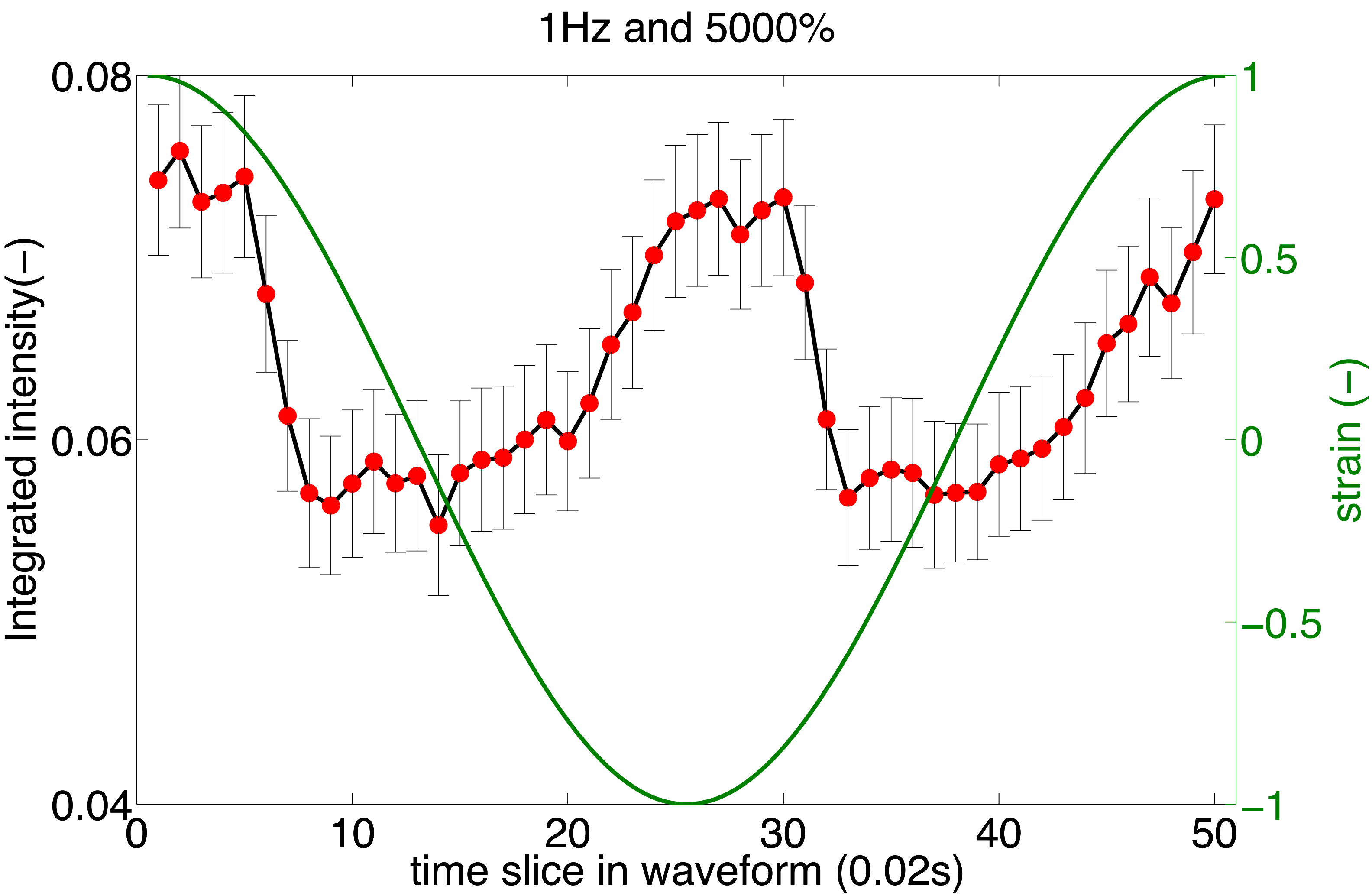
Result



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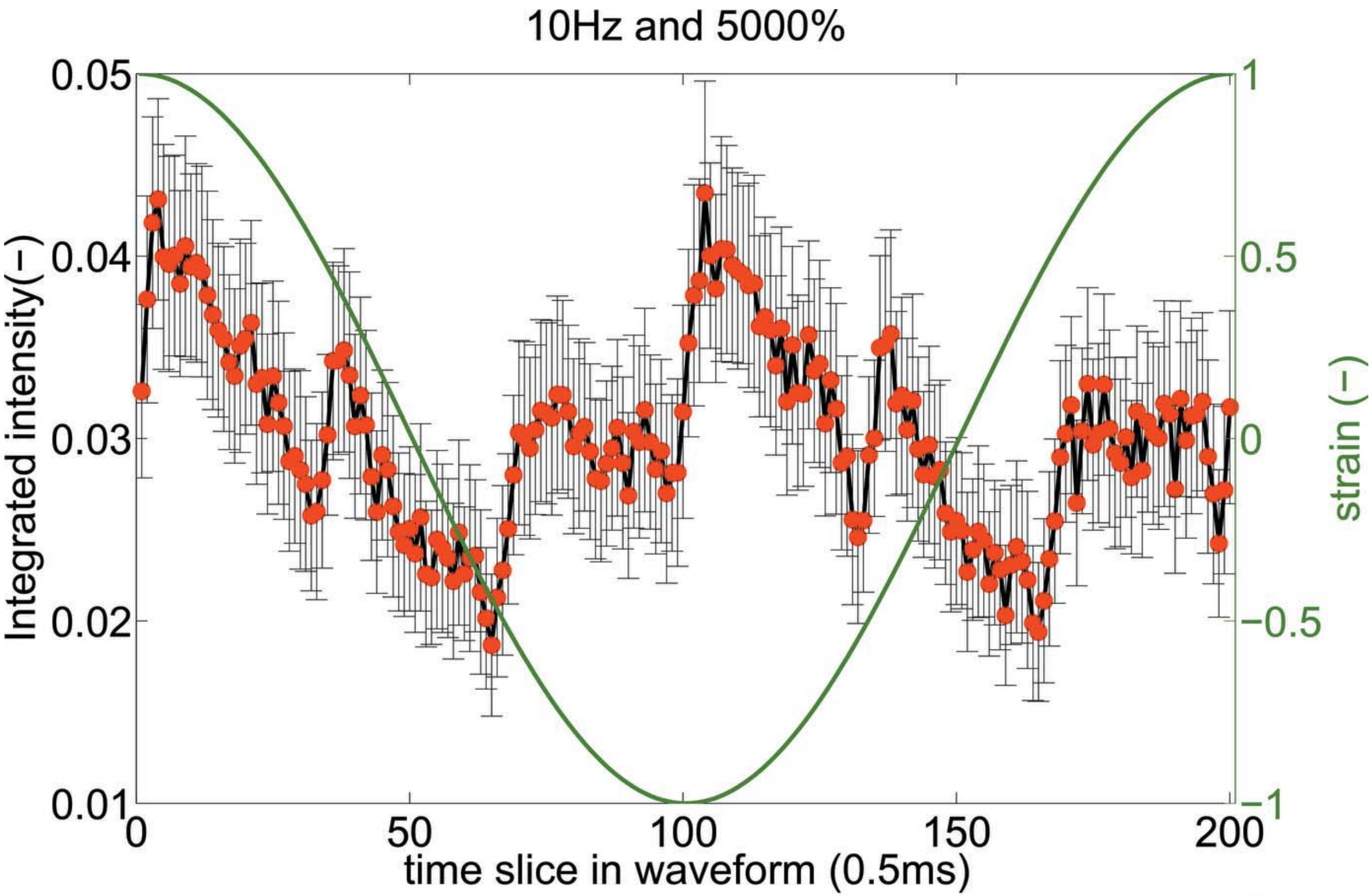
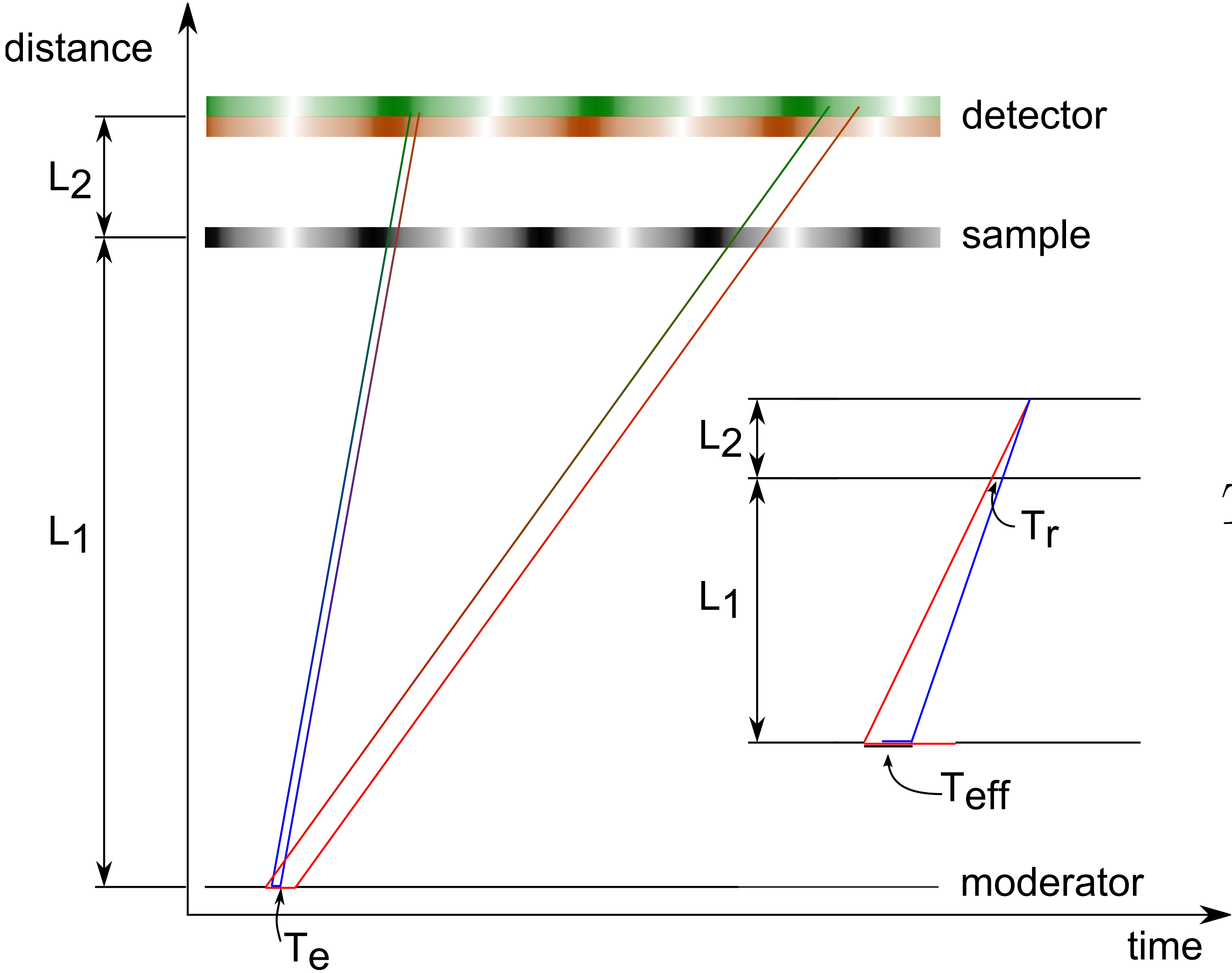
Result



F. Adlmann et al., J. Appl. Cryst., **48**, 220 (2015).

Limit - time resolution



Time resolution:

$$T_r = T_e \frac{L_2}{L_1 + L_2}$$

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Summary

Depth profile is straight forward to measure and analyse

Depth sensitive experiments:

Challenging data analysis

Often flux limited - Divergenz should meet wavelength spread

Time resolution experiments:

Resolution better than microseconds is possible

Pump probe time measurement of repeatable excitations

To get a full picture out of plane information is needed together with in-plane as well as the dynamics.

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Outlook

Time resolved measurements are not limited to any technique

Imaging, Diffraction, Inelastic, Quasielastic

nor scientific question

Soft materials, Biology, Magnetism, Electronics

How far could we get with inelastic measurements at low Q?

Storing of “real” raw data (event mode) allows:

Binnig during post processing

Including meta data

Data mining

Only price to pay CPU and data storage capacity (10^7 events/s).

Neutrons are too valuable, let us use them as efficient as possible!

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