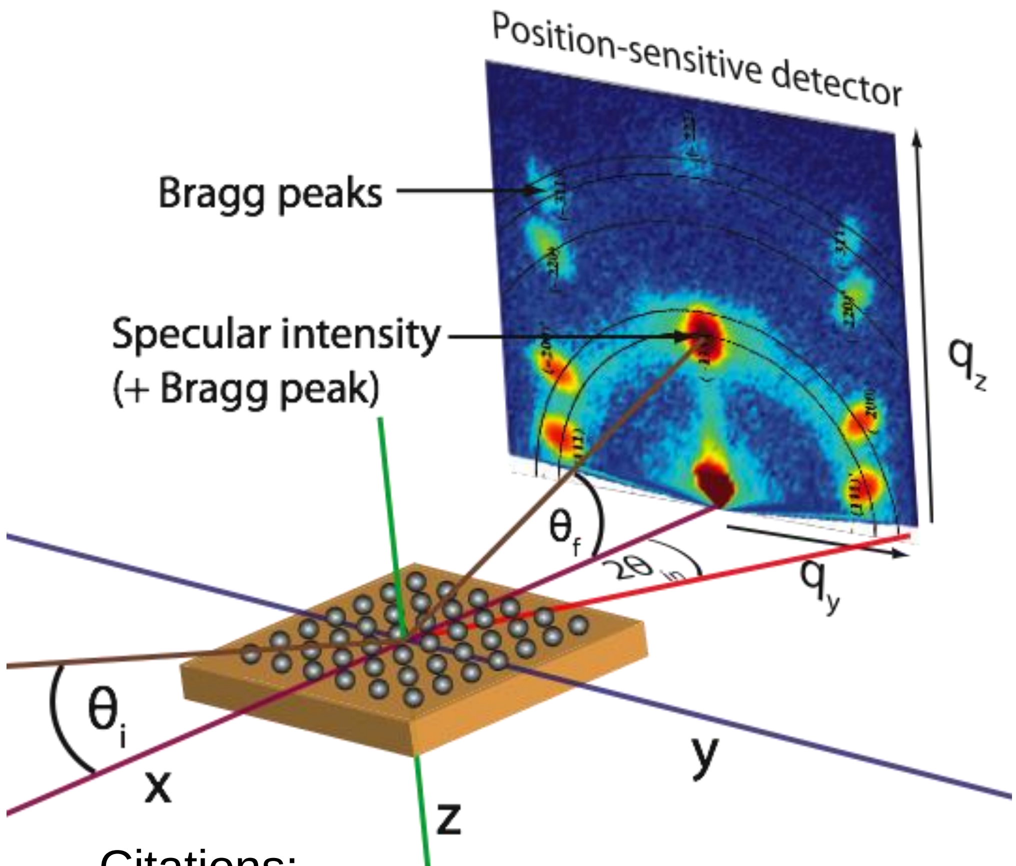
The GISANS option on FIGARO: Some science examples

Philipp Gutfreund

Institut Laue-Langevin, Grenoble, France

MUROMETS 2015
September 25, 2015

Off-specular scattering (OSS) and GISANS



$$q_x = \frac{2\pi}{\lambda}(\cos\theta_f \cos 2\theta_{in} - \cos\theta_i)$$

$$q_y = \frac{2\pi}{\lambda}(\cos\theta_f \sin 2\theta_{in})$$

$$q_z = \frac{2\pi}{\lambda}(\sin\theta_i + \sin\theta_f)$$

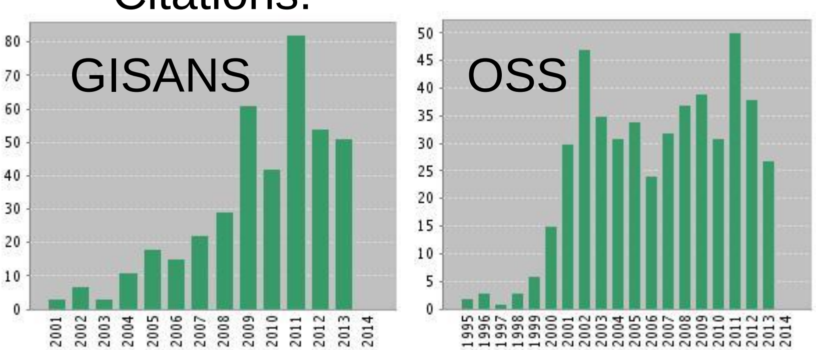
Accessible q-range:

$$10^{-5}\,\text{Å}^{-1} \leq q_x \leq 10^{-3}\,\text{Å}^{-1} \equiv 1 - 100\,\mu m$$

$$10^{-3}\,\text{Å}^{-1} \leq q_y \leq 10\,\text{Å}^{-1} \equiv 1 - 10000\,\text{Å}$$

$$10^{-3}\,\text{Å}^{-1} \leq q_z \leq 1\,\text{Å}^{-1} \equiv 10 - 10000\,\text{Å}$$

Citations:



Outline

I. GISANS on FIGARO

II. Polyelectrolyte multilayers

III. Surfactants at the solid/liquid interface under shear

IV. Structure of highly entangled polymer solutions under shear

GISANS on FIGARO

Richard Campbell, Erik
Watkins

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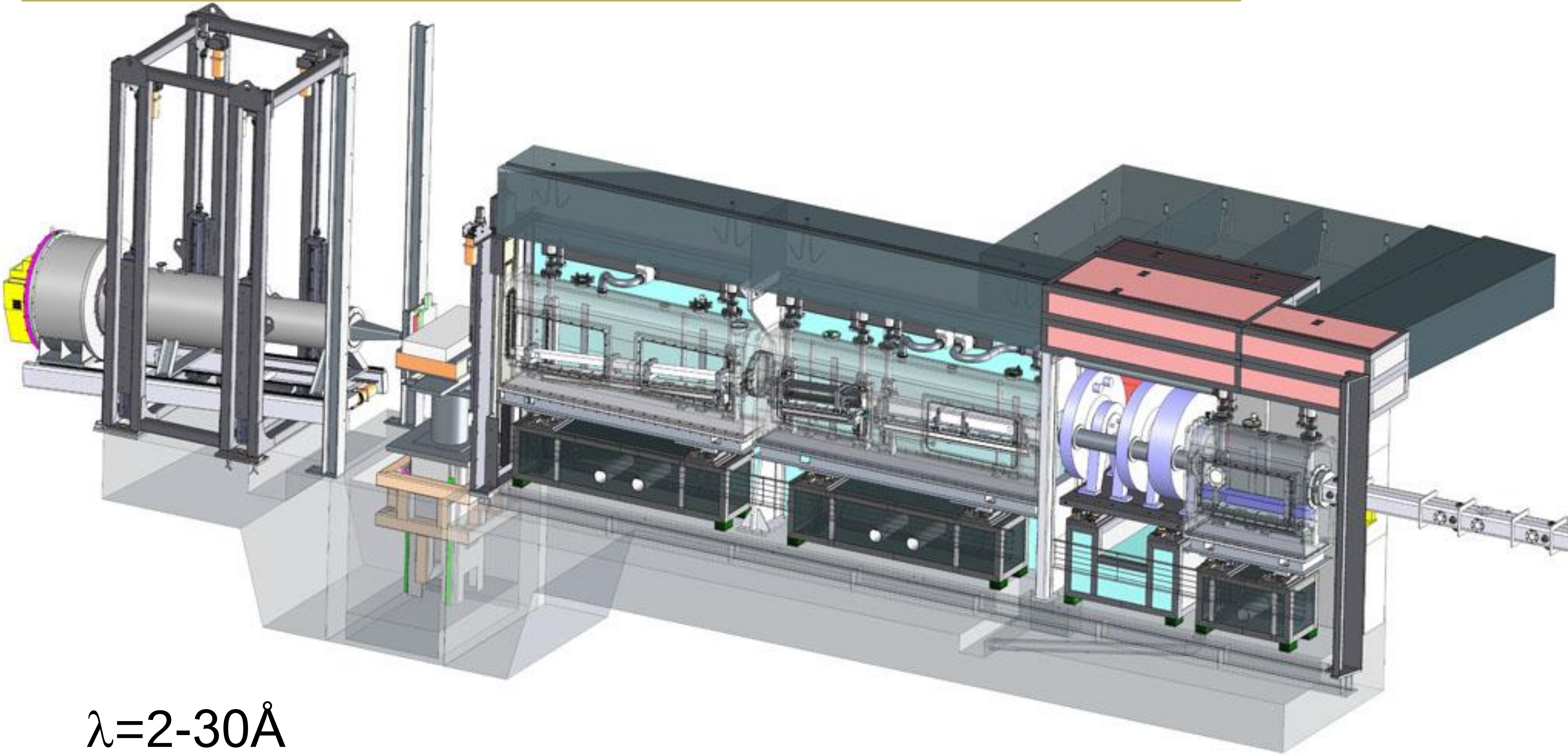
Fluid Interfaces Grazing Angles ReflectOmeter

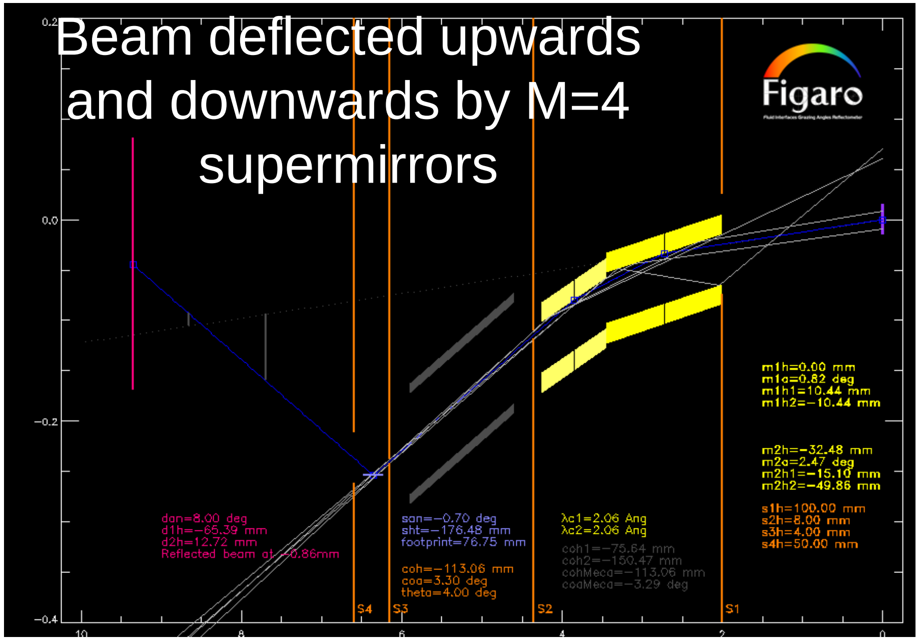


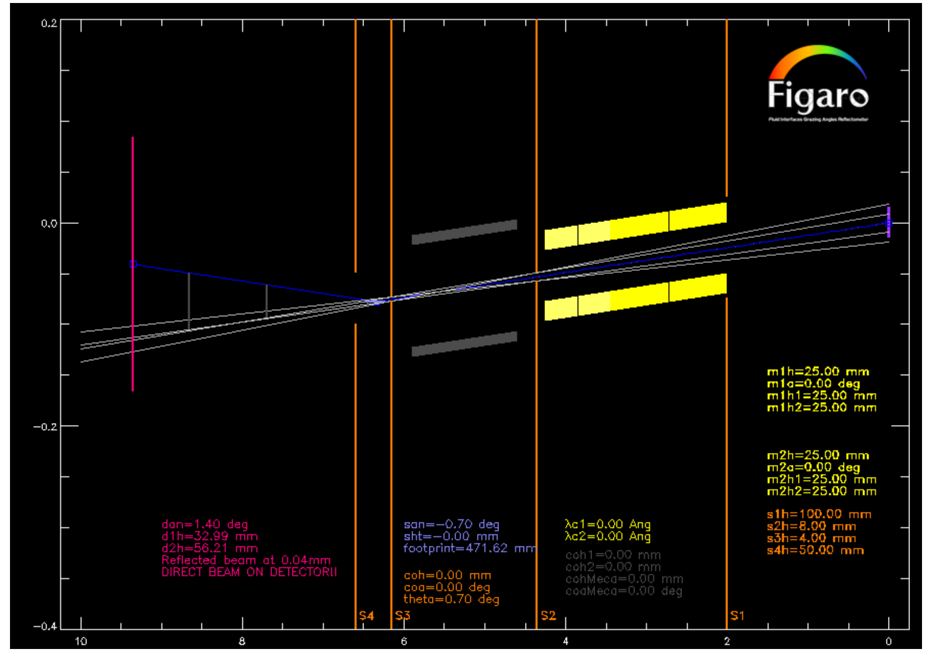
λ=2-30Å

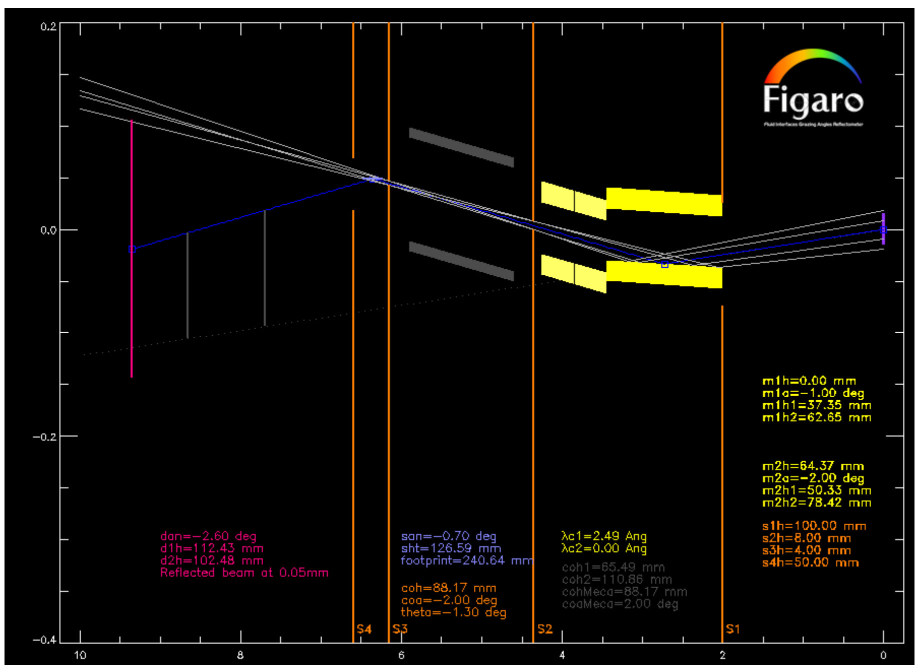
$\Delta\lambda/\lambda$ 0.8-10%

Beam strikes both sides of interfaces

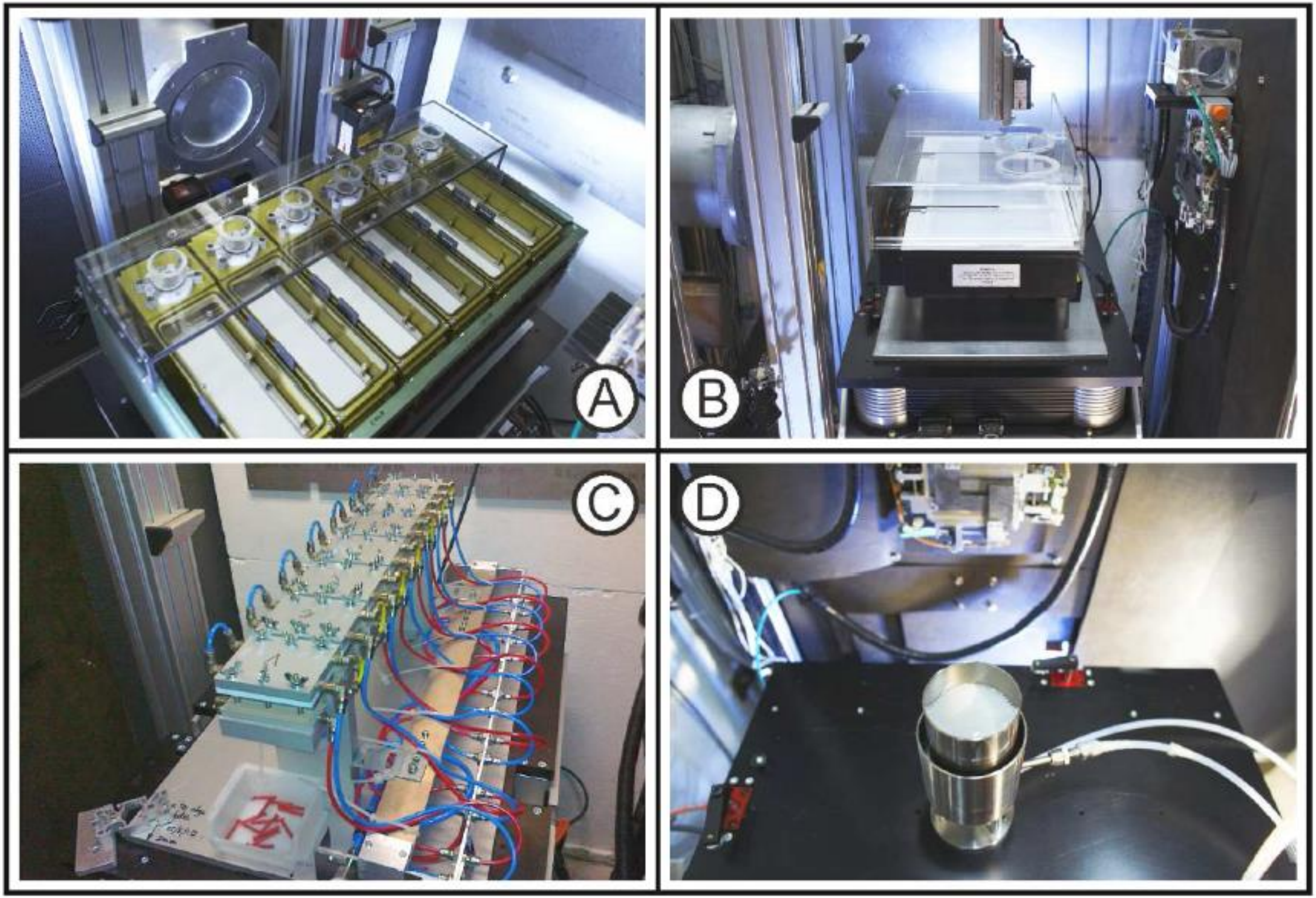
Beam deflected upwards and downwards by M=4 supermirrors





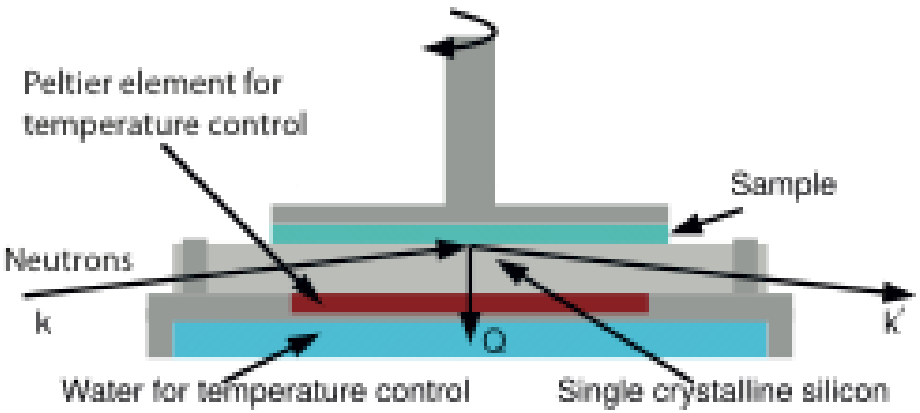


some sample environment....



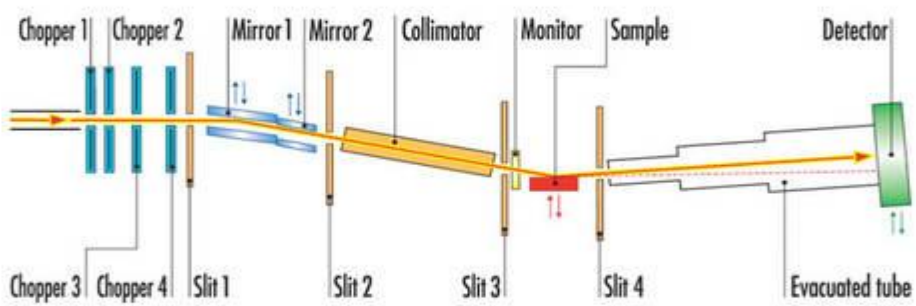
In situ Rheo-Reflectometry on FIGARO

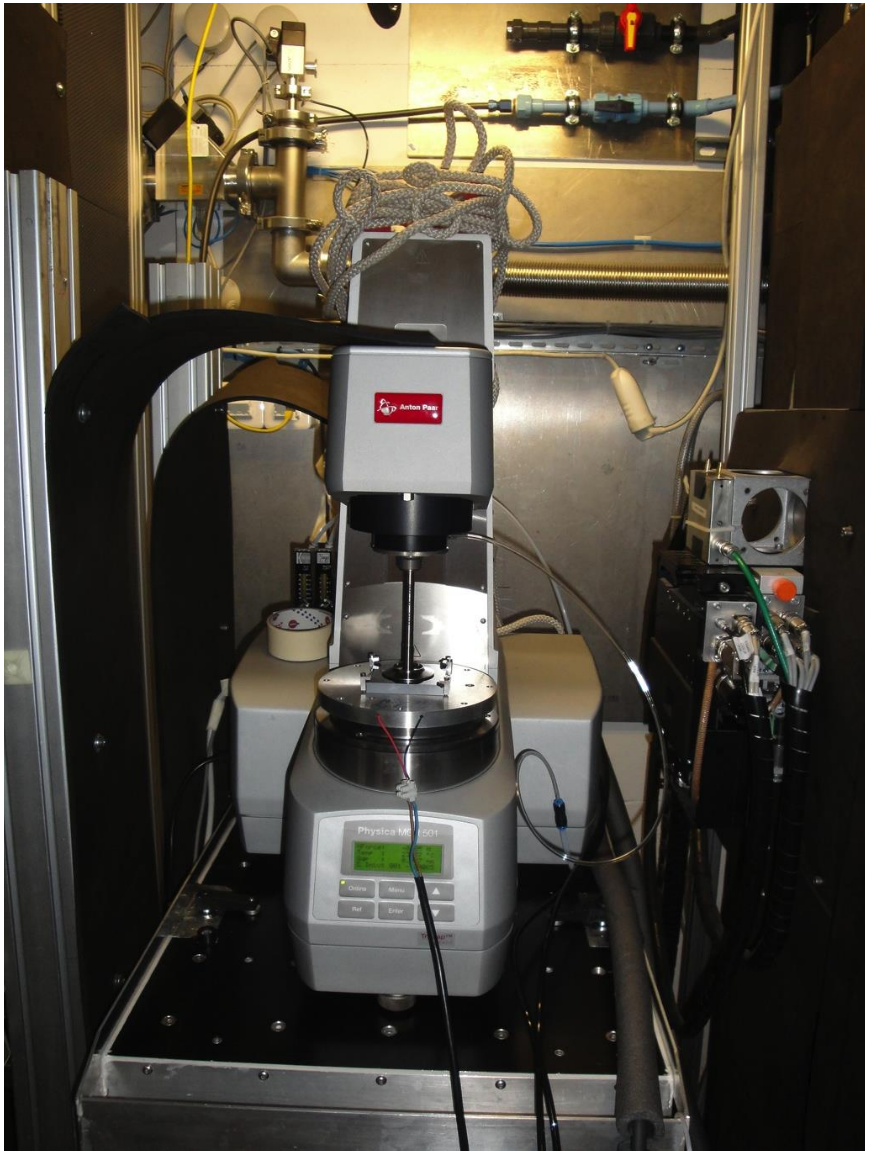
In situ-shear neutron reflectometry:



Temperature range: 15 - 160 °C
Shear rates up to 10^5 s^{-1}

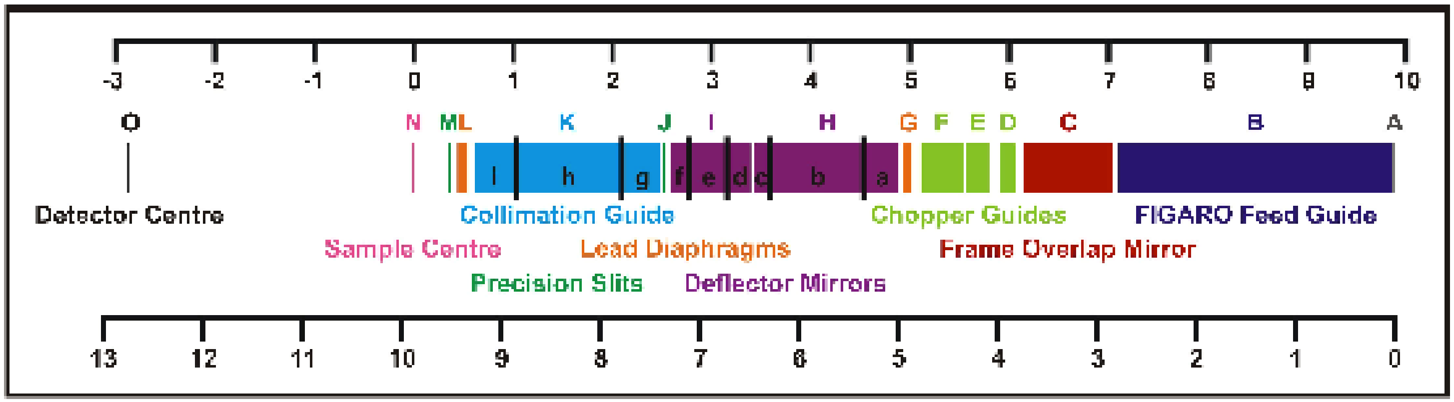
Reflectometer FIGARO (ILL,Grenoble):

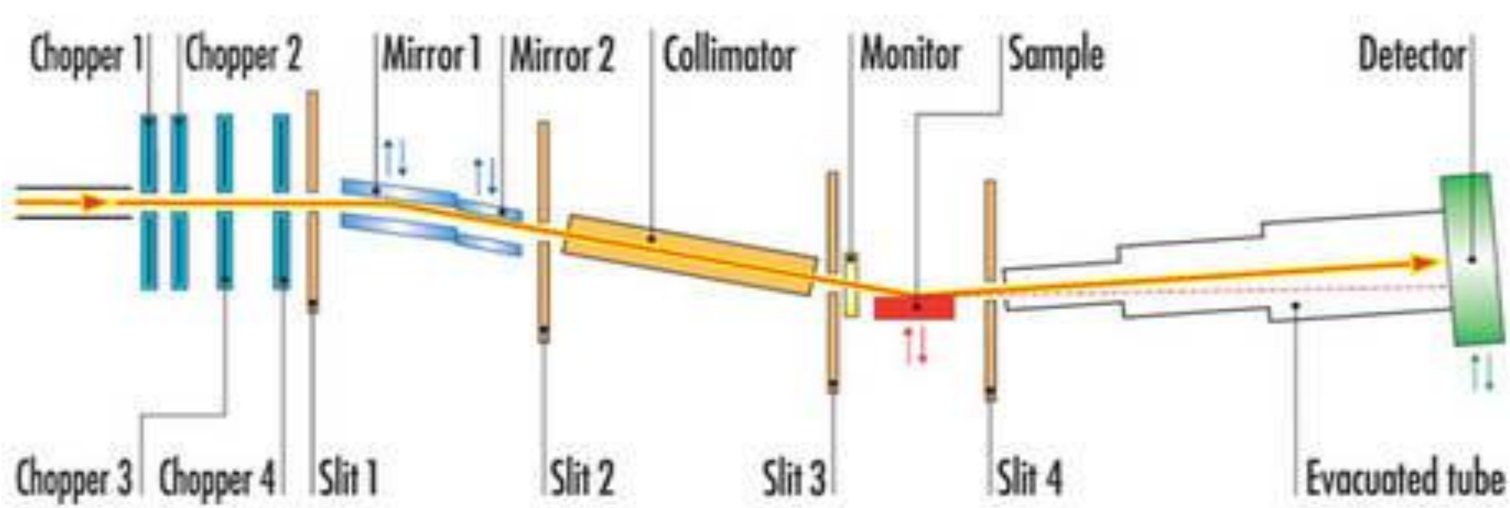




FIGARO

Typical incoming beam divergence (5 m collimation) (v x h) FWHM: 0.005°- 0.1° x 0.05 -
Detector resolution at 2.8 m (v x h) FWHM: 0.045° x 0.09°





Example I: Polyelectrolyte multilayers

Christophe Higy, Gero Decher

UNIVERSITÉ DE STRASBOURG

cnrs

Giovanna Fragneto

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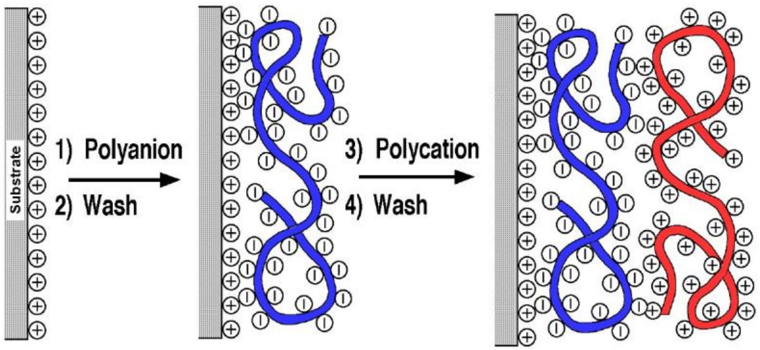
Institut Laue-Langevin

Polyelectrolyte multilayers (LbL)

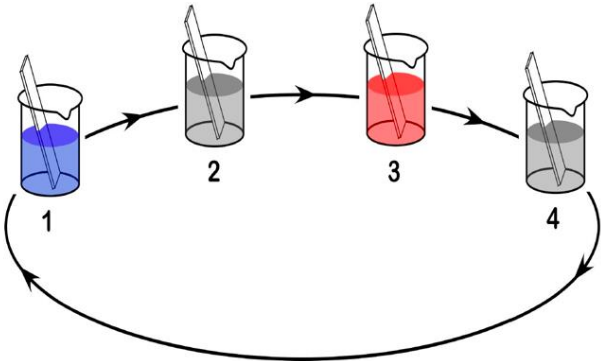
Layer-by-Layer method (LbL):



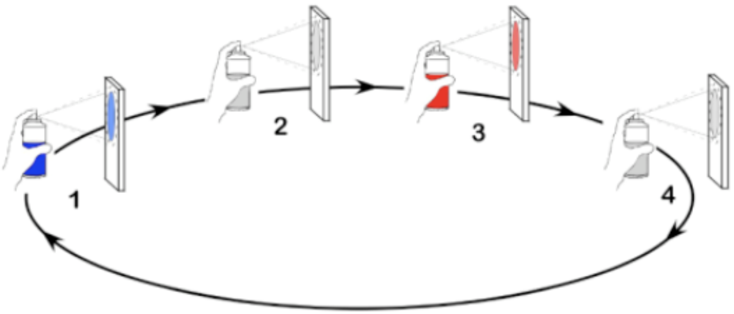
Decher, G., Science (1997) 277, 1232-1237.

- Easy and environment friendly production.
- General applicability to organic, polymeric inorganic and biological materials.
- Applications: tissue engineering, biocatalysis, electroluminescent devices, antireflective coatings, corrosion protection, ...

Dipping:



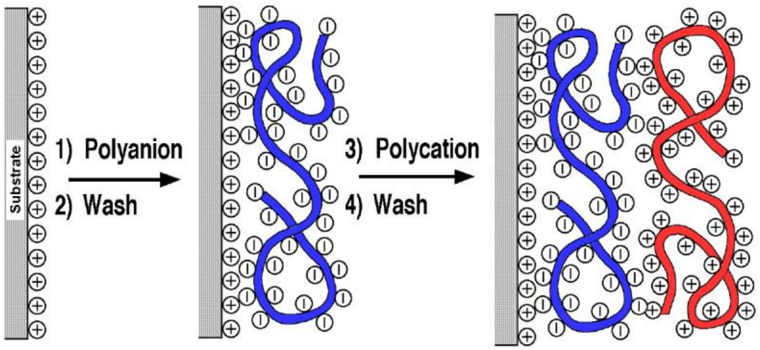
Spraying:



Polyelectrolyte multilayer (LbL)

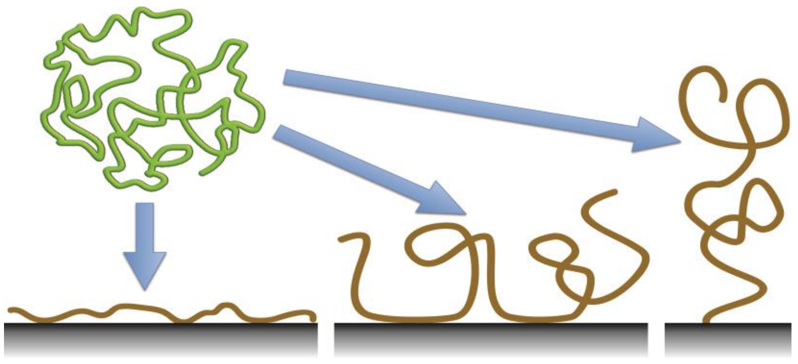
Poly(styrenesulfonate) (PSS)/ poly(allyl amine hydrochloride) (PAH)

Layer-by-Layer method (LbL):

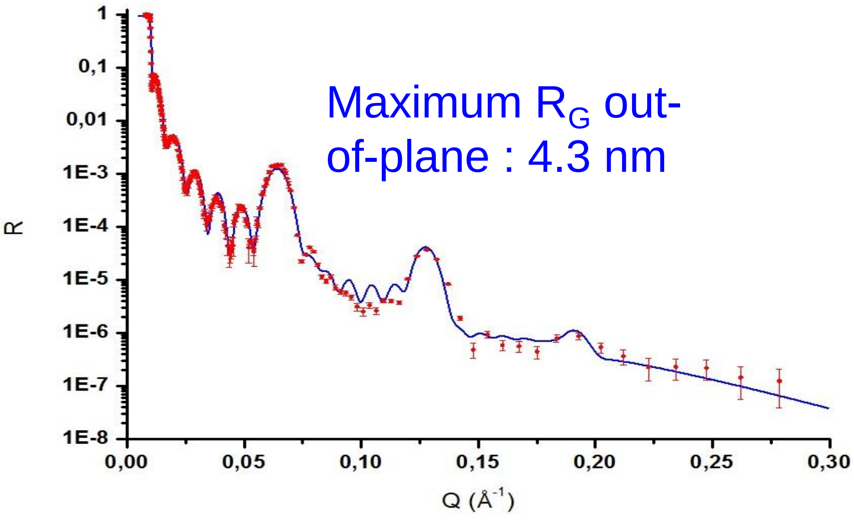


Decher, G., Science (1997) 277, 1232-1237.
Zhang, H. N., and Rühe, J., Macromolecules (2005) 38, 10743-10749.

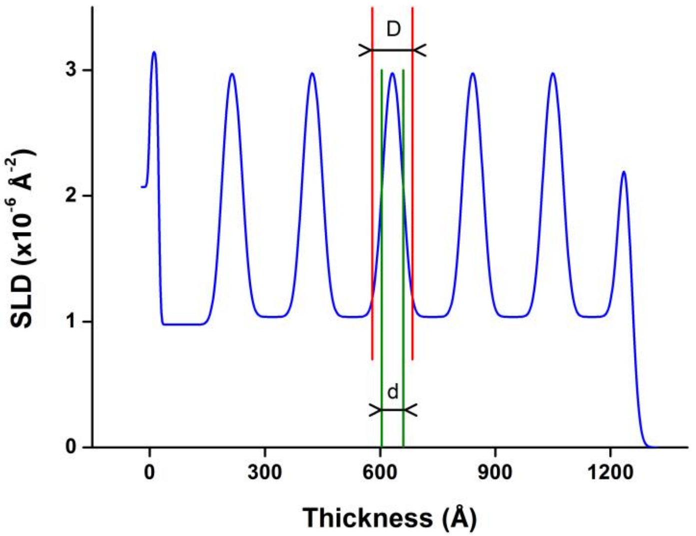
Polymer Conformation:



Specular Neutron Reflectivity (D17):

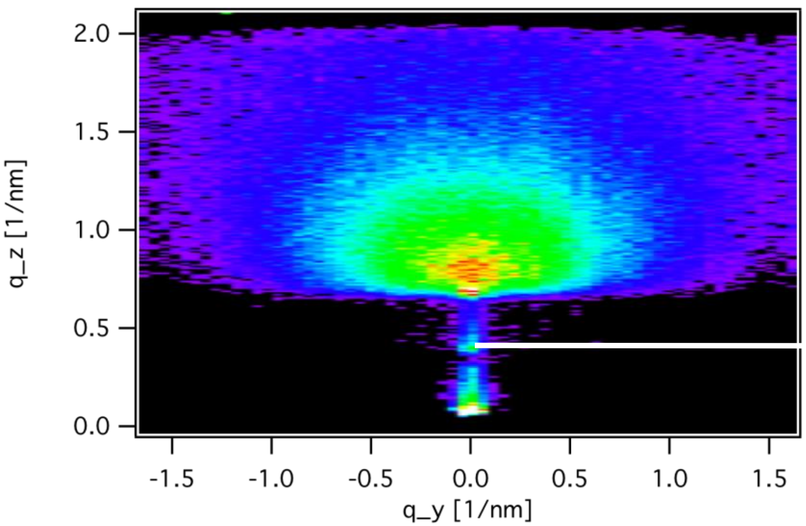


Scattering length density profile:

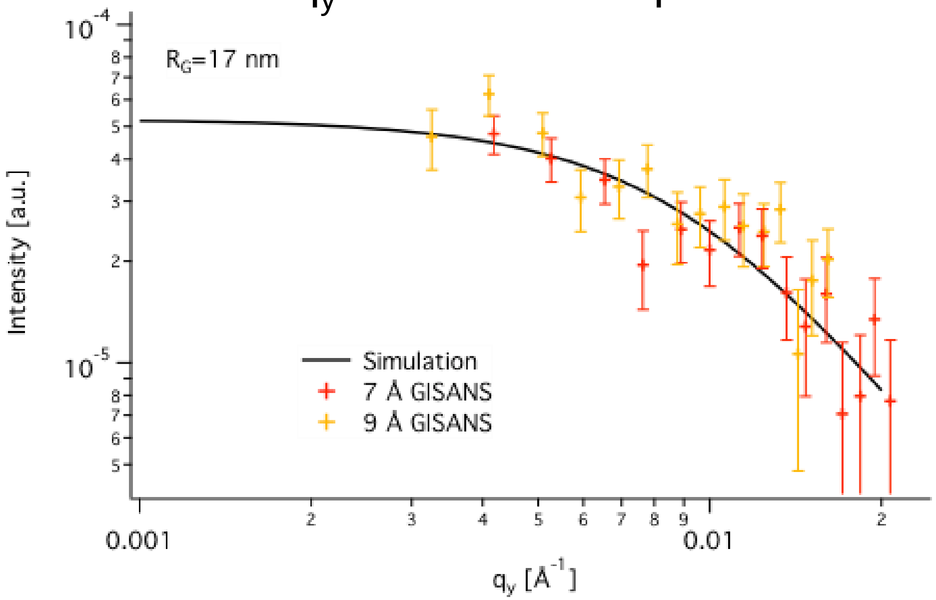


GISANS on thin polymer films

GISANS:



q_y cut at Yoneda peak:

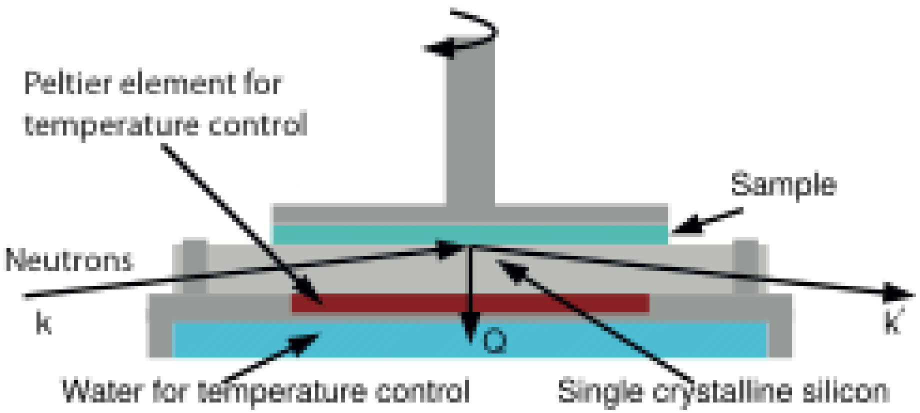


- GISANS reveals that the in-plane radius of gyration is 17 nm.

→ The combination of NR and GISANS on polyelectrolyte multilayer films reveals the pancake like conformation of the polymer chains.

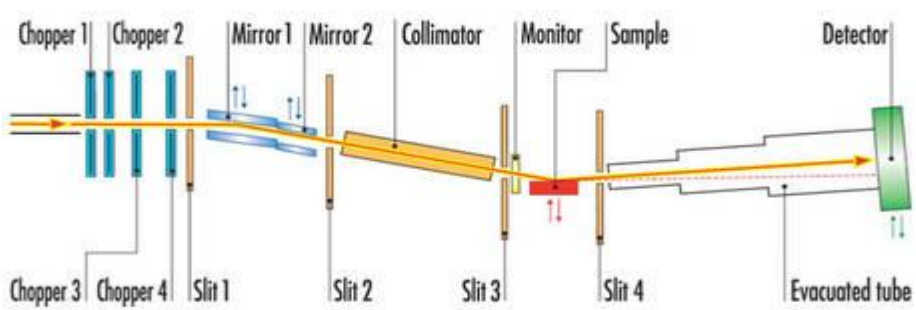
In situ Rheo-Reflectometry on FIGARO

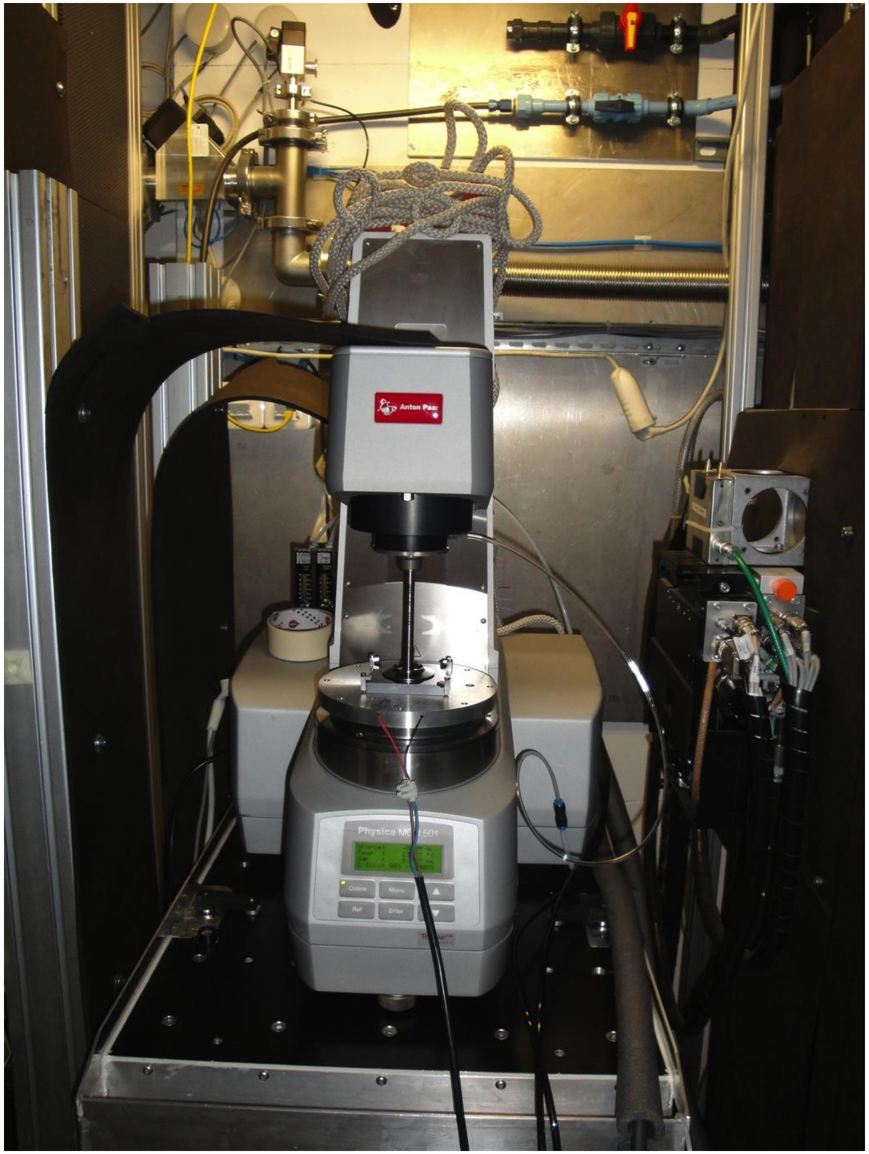
In situ-shear neutron reflectometry:



Temperature range: 15 - 160 °C
Shear rates up to 10^5 s^{-1}

Reflectometer FIGARO (ILL,Grenoble):





Example II: AOT in D_2O in contact with sapphire under shear

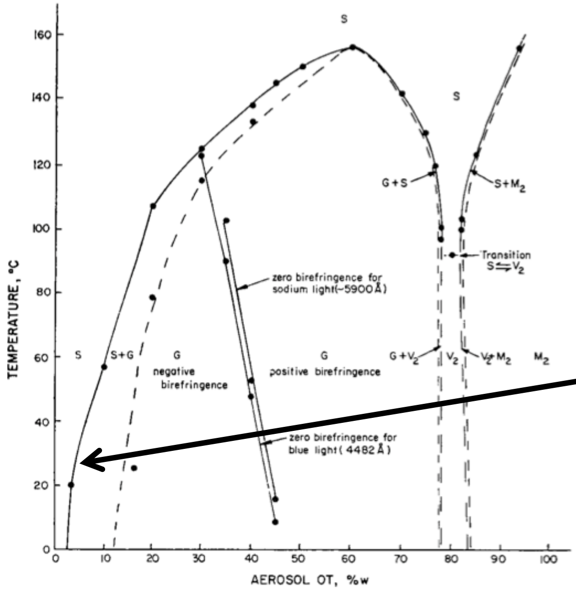
Rebecca Welbourn, Felicity Bartholomew, Stuart Clarke

BP INSTITUTE FOR MULTIPHASE FLOW

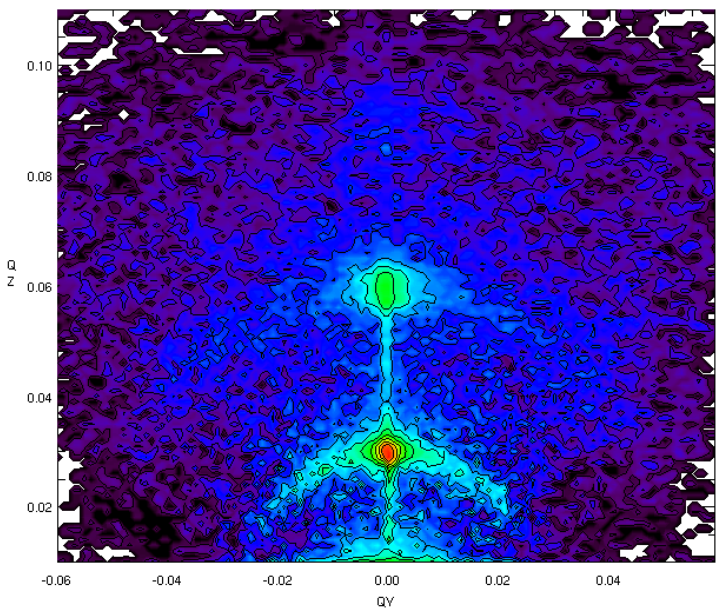
UNIVERSITY OF CAMBRIDGE

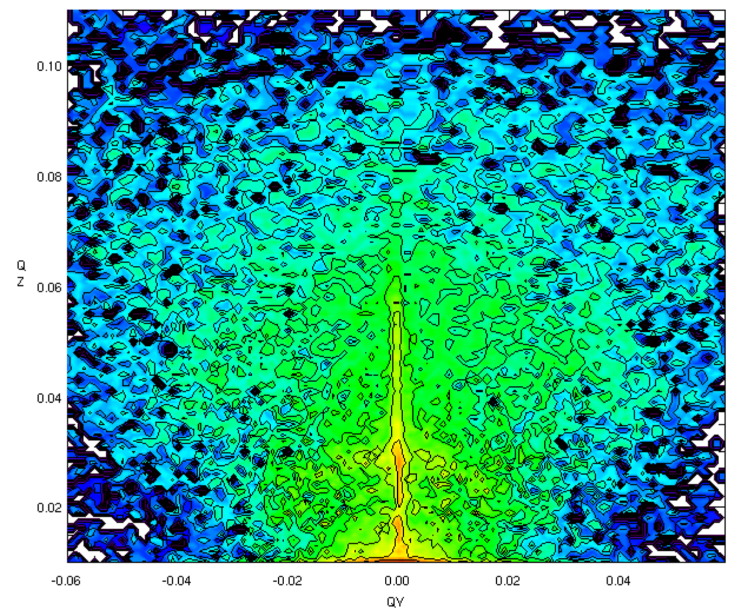
Rogers & Winsor, J. Colloid Interface Sci. 30 (246) 1969.

2% AOT solution



Aerosol (sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (2% aq.) in D_2O in contact with sapphire -> randomly oriented lamellae with preferred orientation at the interface



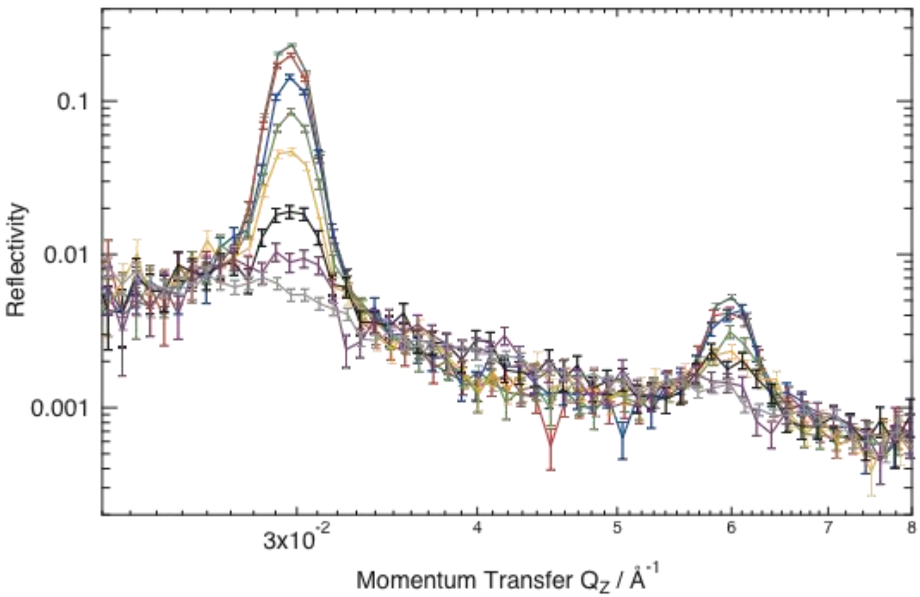


GISANS static θ_i = 1.4° λ = 2-20 Å < λ_C

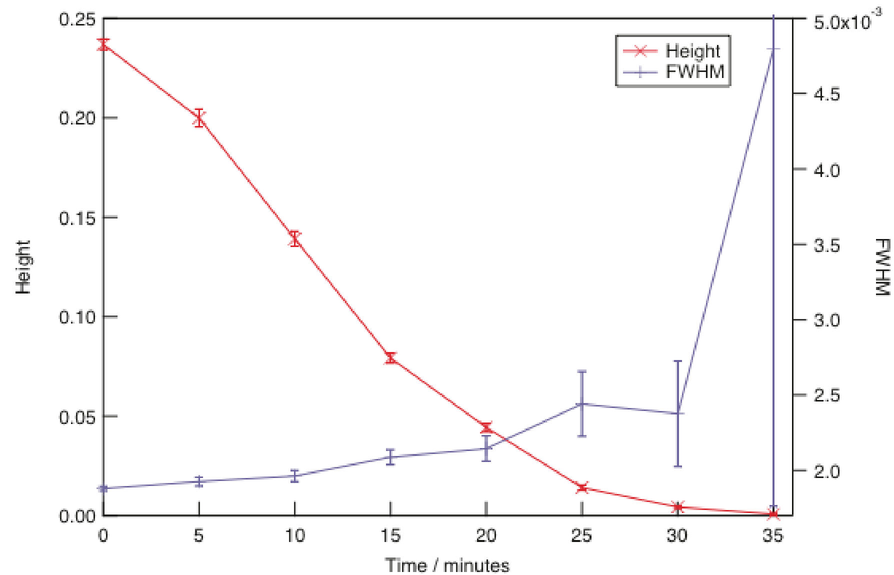
GISANS shear 2 s^{-1}

2% AOT solution

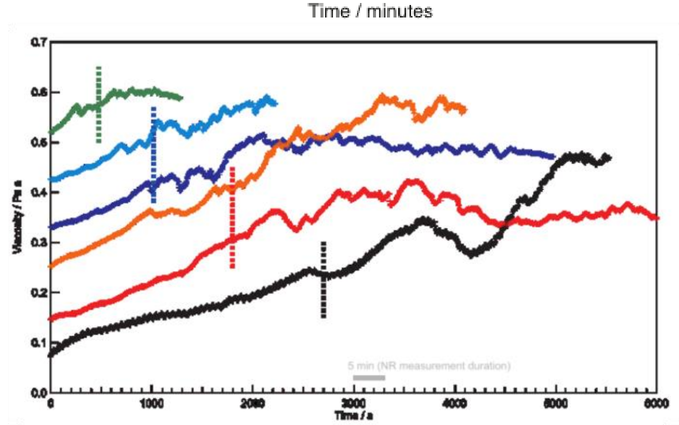
Specular NR evaluation under steady shear at 1 s^{-1}:



First Bragg-peak height and width:



Viscosity evaluation with time for different shear rates:



Combination of NR and GISANS shows that bulk lamellae are destroyed with shear but surface bilayer stays!

Example III: Highly entangled polymer solution under shear

Shear cell: Max Wolff, Maciej Kawecki

UPPSALA UNIVERSITET

Computer simulations and theory: Jean-Louis Barrat

UNIVERSITE JOSEPH FOURIER
SCIENCES, TECHNOLOGIE, MEDECINE

Students: Airidas Korolkovas
Georg Liesche

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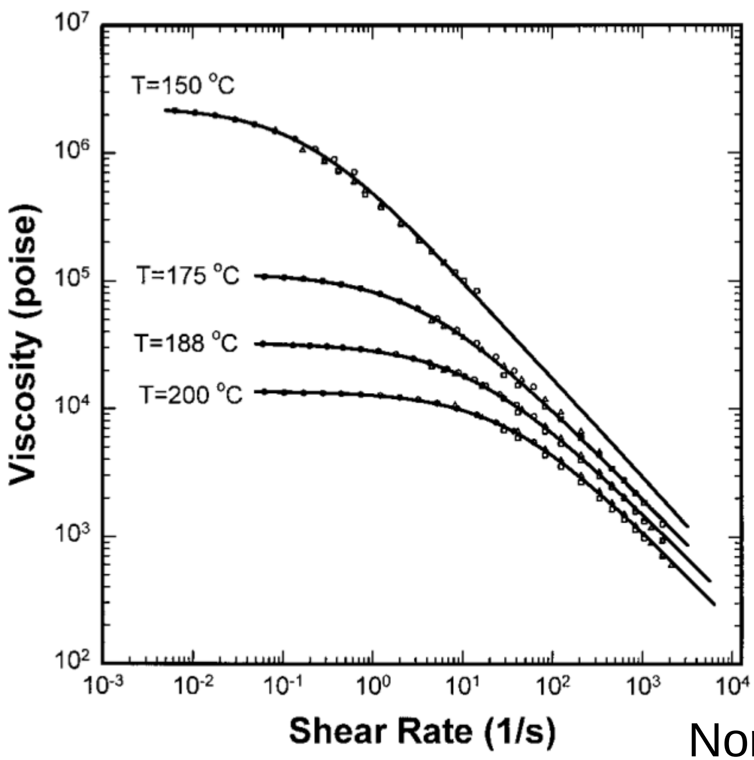
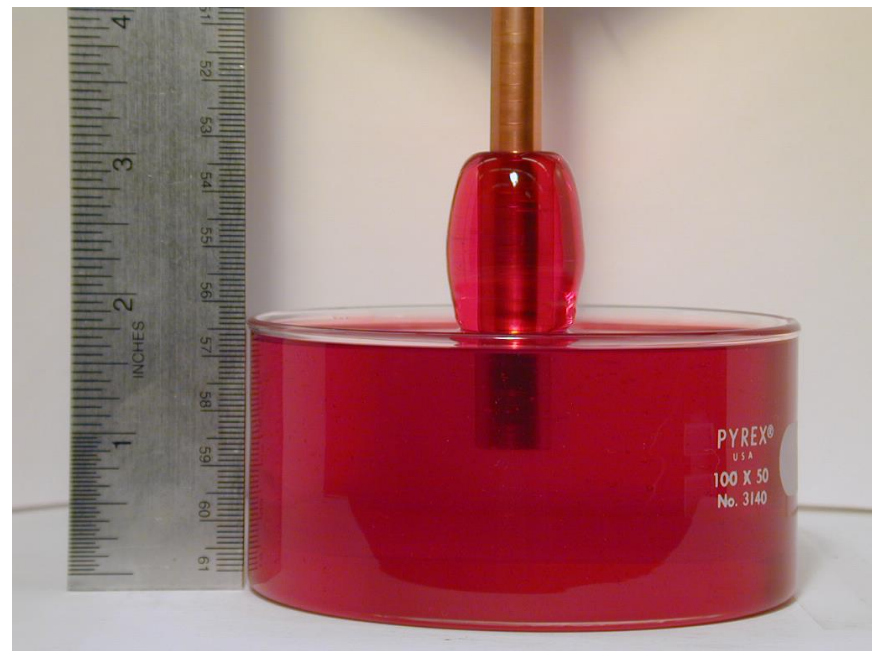
Visco-elastic liquids

Shear thinning:



Kwag et al., J. Pol. Sci. B 2771 (37) 1999.

Rod-climbing (Weissenberg effect):



Normal stress difference

$$Wi = \frac{|\tau_{xx} - \tau_{yy}|}{|\tau_{xy}|} = \lambda_t \dot{\gamma}$$

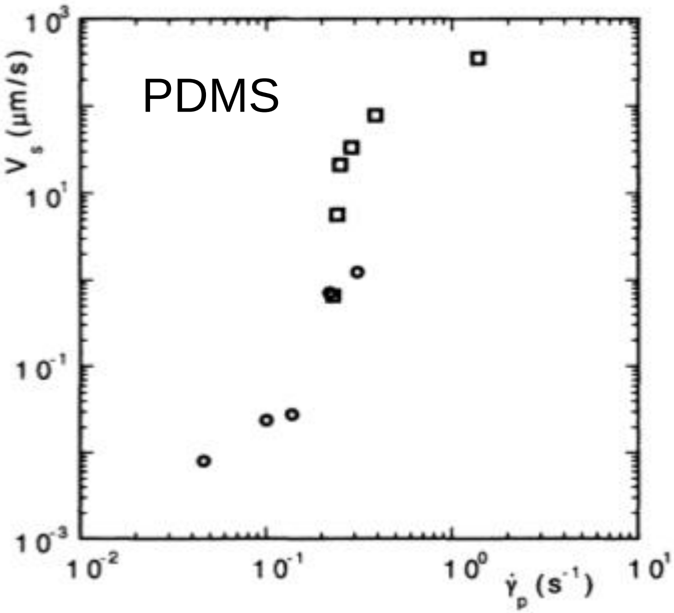
Shear stress

Shear rate: $\dot{\gamma}$

Longest relaxation time: λ_t

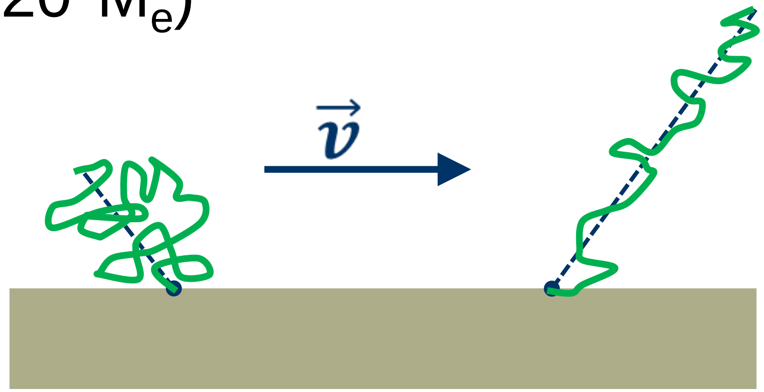
→ *Visco-elastic fluids can be scaled by using the Weissenberg number Wi*

Stick-Slip-Transition (SST)



Migler et al., Phys. Rev. Lett. 287 (70) 1993.

- Arises for highly entangled polymers (M_n > 20*M_e)



Brochard and de Gennes, Langmuir 8 (3033) 1992.

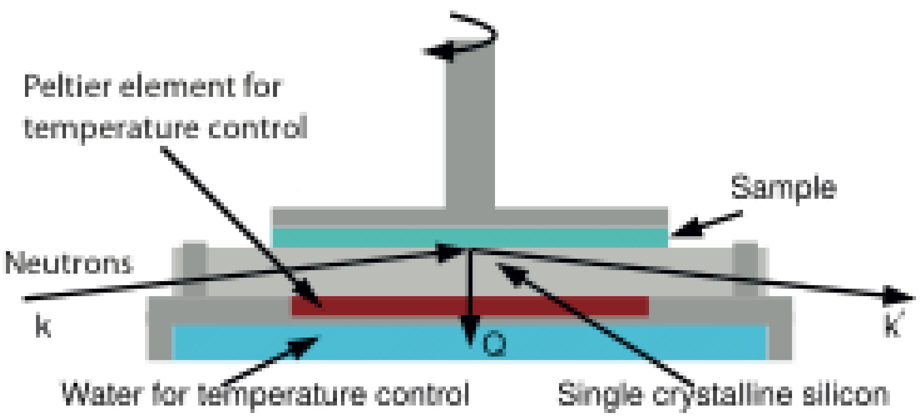
Allal and Vergnes, J. Non-Newtonian Fluid Mech. 61 (1) 2009.

Polystyrene in DEP (good solvent for all T)

Molecular weight: M_n = 575 kg/mol (for d 500 kg/mol for h)
Polymerization: P = 5135
Free chain density in DEP: c=0.3
Overlapping: c/c*=10
Dense limit: c**=0.5
Polydispersity: PDI=1.09
Temperature: T =45 °C
Longest relaxation time: τ_t = 0.14 s
Sear rates: 0.4 s^{-1} - 730 s^{-1} (0.05<Wi<104)

→ Moderately dense polymer solution.

Plate-plate rheometry:



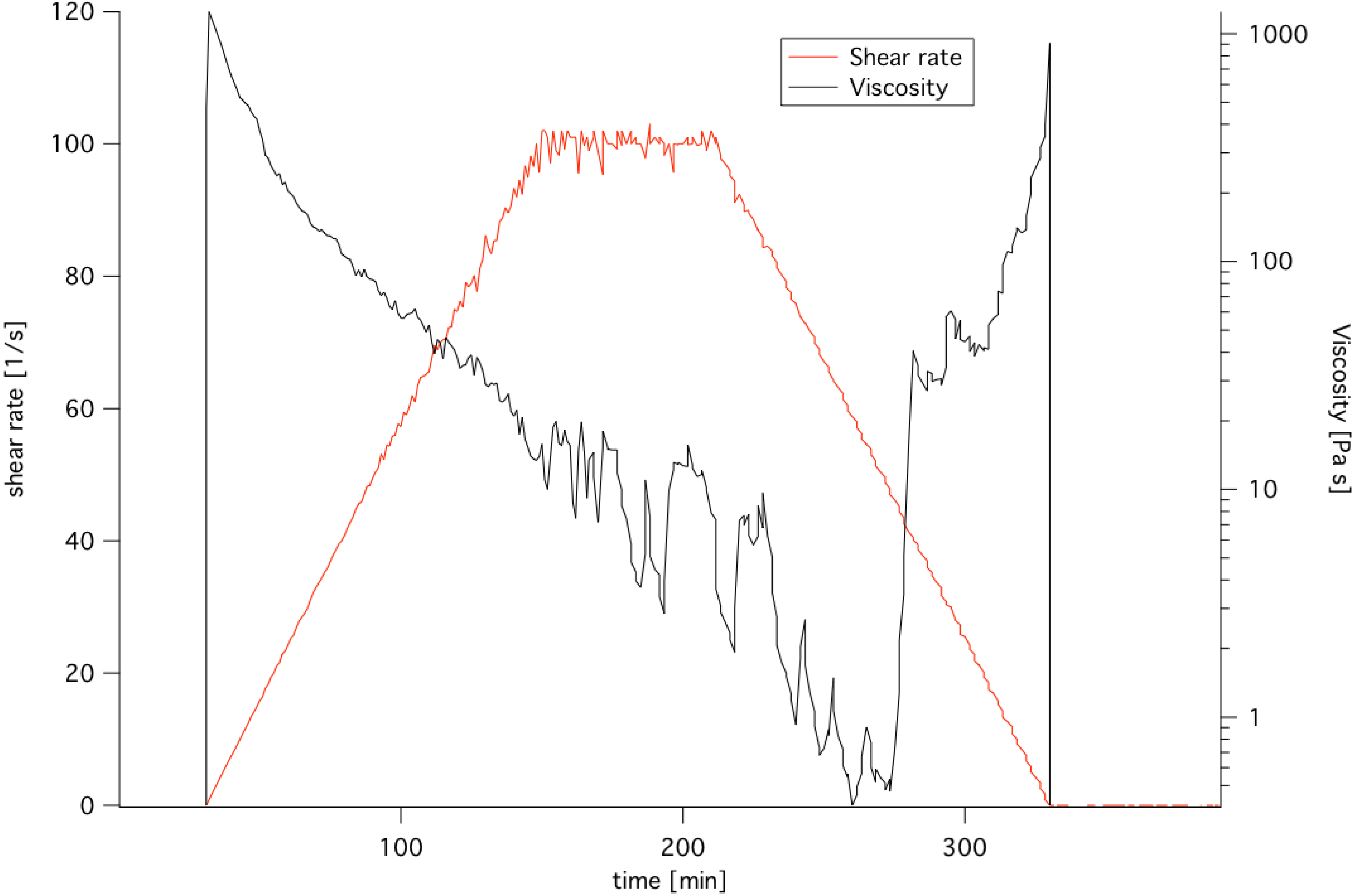
$Wi_{ws\text{-}sb}$= 30

H < 100 µm

→ We are crossing the shear band

(bulk stick-slip) condition

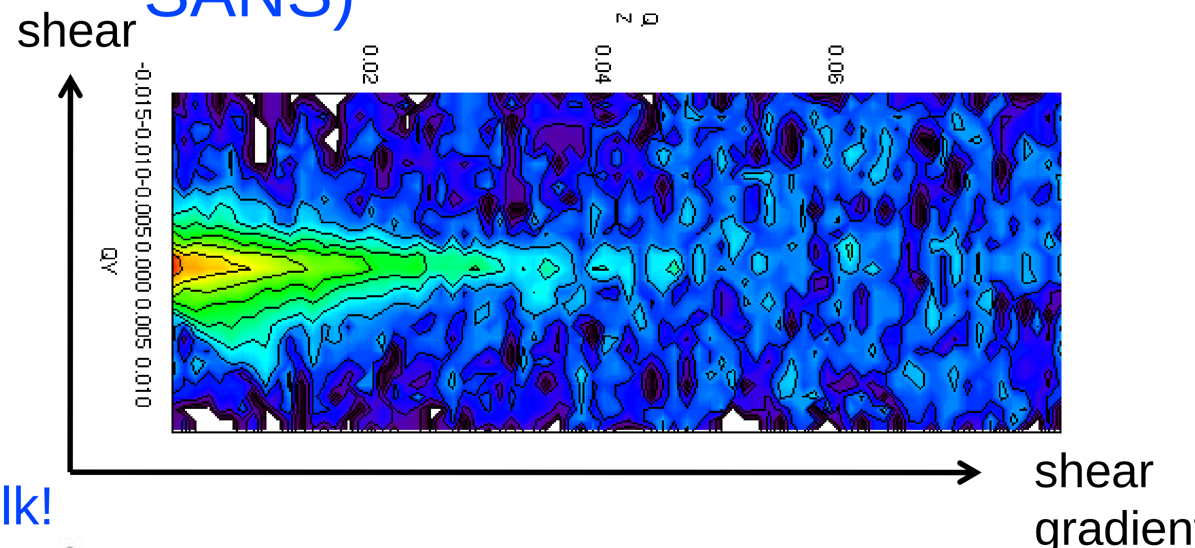
Polystyrene in DEP (good solvent for all T)



Grazing Incidence Transmission Small Angle Scattering (GT-SANS)

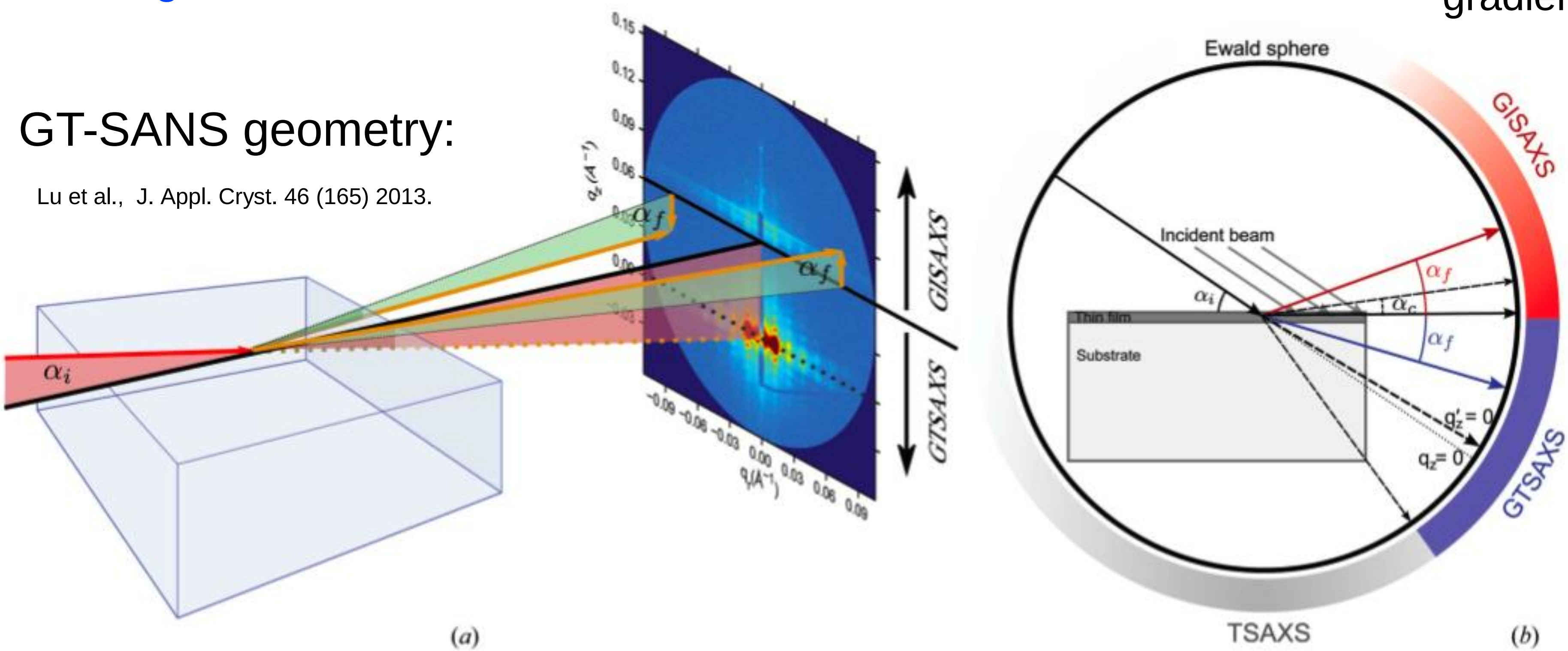
30% dPS in DEP:
Only interchaincorrelations (structure factor) visible (screening length/entanglement distance)

→ Signal comes from bulk!



GT-SANS geometry:

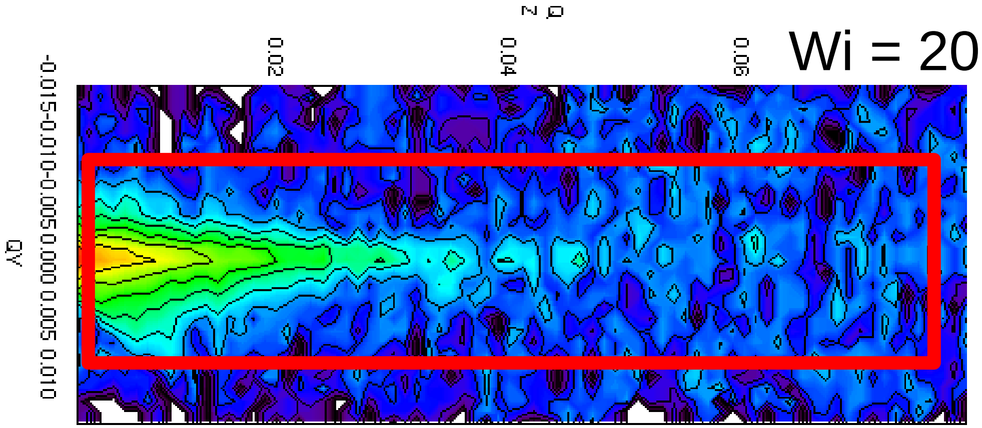
Lu et al., J. Appl. Cryst. 46 (165) 2013.



(a) (b)

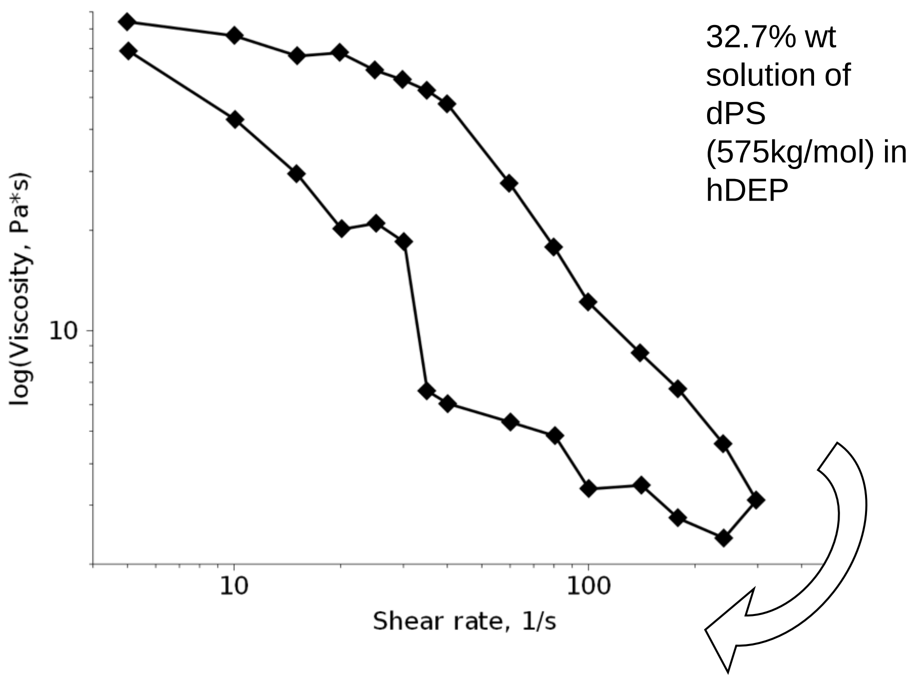
Grazing Incidence Transmission Small Angle Scattering

Apparent viscosity is correlated
with SANS signal!

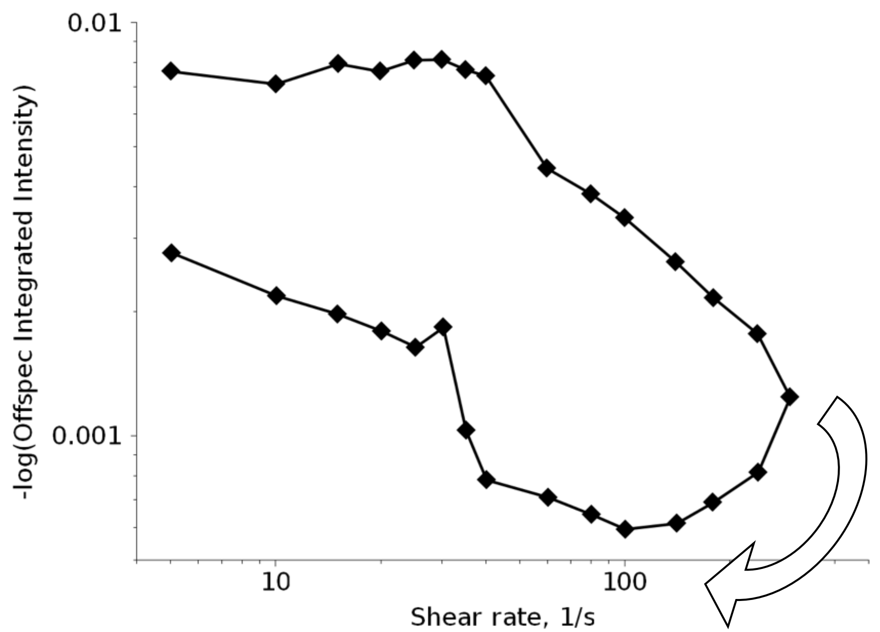


Wi = 20

Apparent viscosity:



GT-SANS box integrated intensity:



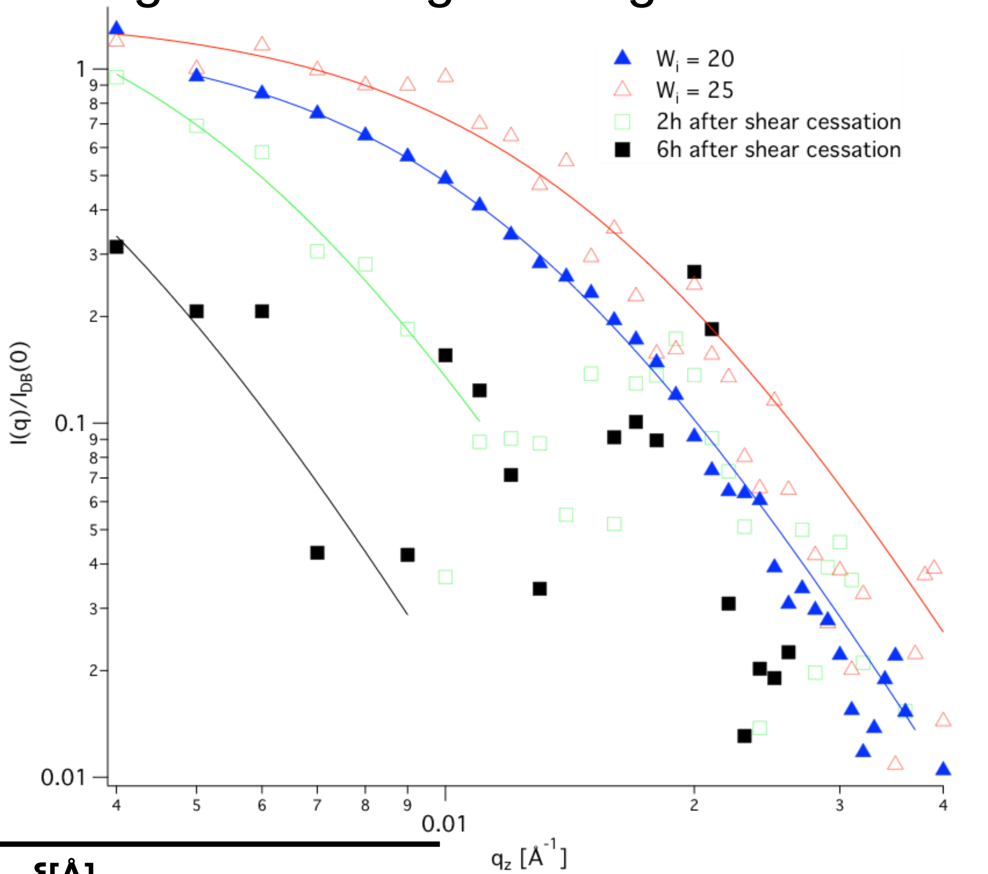
Grazing Incidence Transmission Small Angle Scattering

30% dPS in DEP:
Only interchaincorrelations (structure factor) visible (screening length/entanglement distance)

Fits are Squared Lorentzian Function:
$I(q)=A/(1-q^2\ \xi^2)^2$

→ Correlation length diminishes with shear!

Integration along shear gradient:



Shear	A	ξ[Å]
Wi = 25	1.42±0.06	63±3
Wi = 20	1.29±0.01	80±4
2h after shear cessation	2.08±0.03	171±16
6h after shear cessation	2.08 (fixed)	305±25

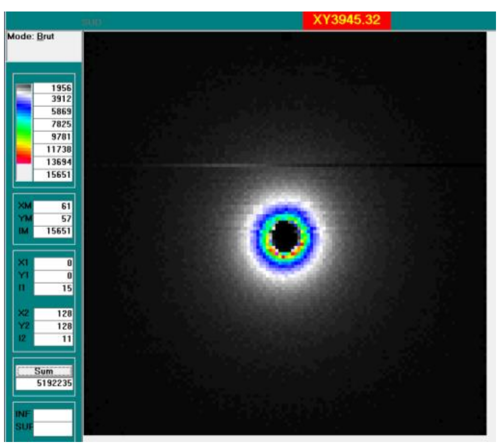
Molecular shape

Molecular weight d-PS: M_n = 575 kg/mol
Polymerization: N_d = 5135 PDI=1.09
Volume fraction: Φ_d=0.2
Molecular weight h-PS: $M_{n=}$ 520 kg/mol
Polymerization: N_d = 5000 PDI=1.1
Volume fraction: Φ_h=0.1
in d-toluene

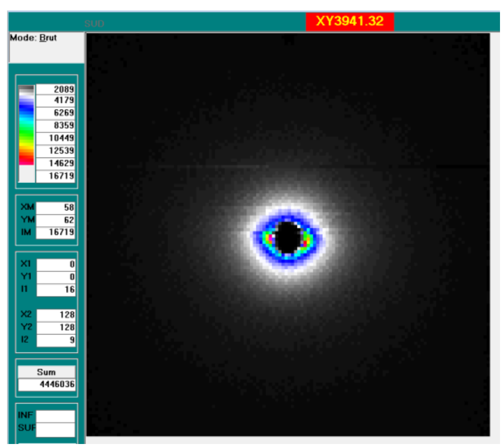
→ Mainly polymer form factor visible.

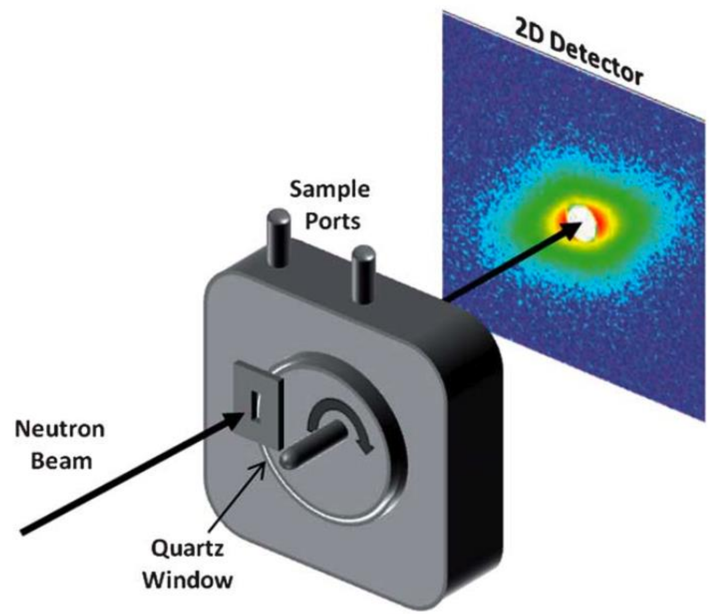
flow direction

static:



shear:



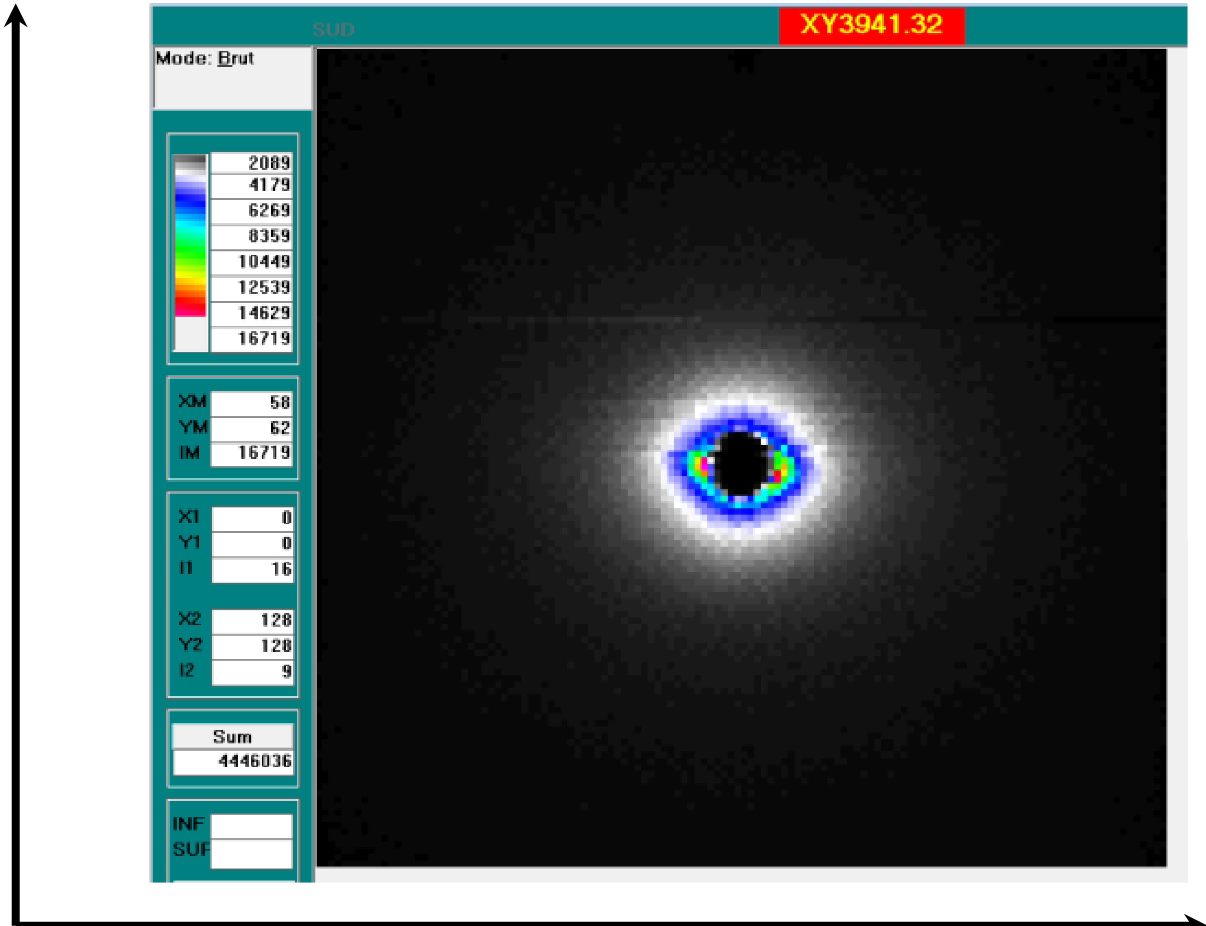


Anisotropy with shear!

Figure from Weigandt *et al.*, Soft Matter 7 (9997) 2011.

Molecular shape

flow direction x Wi=30



neutral direction y

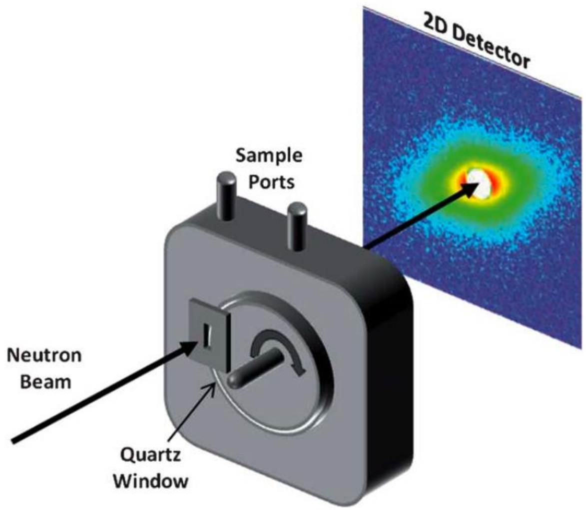
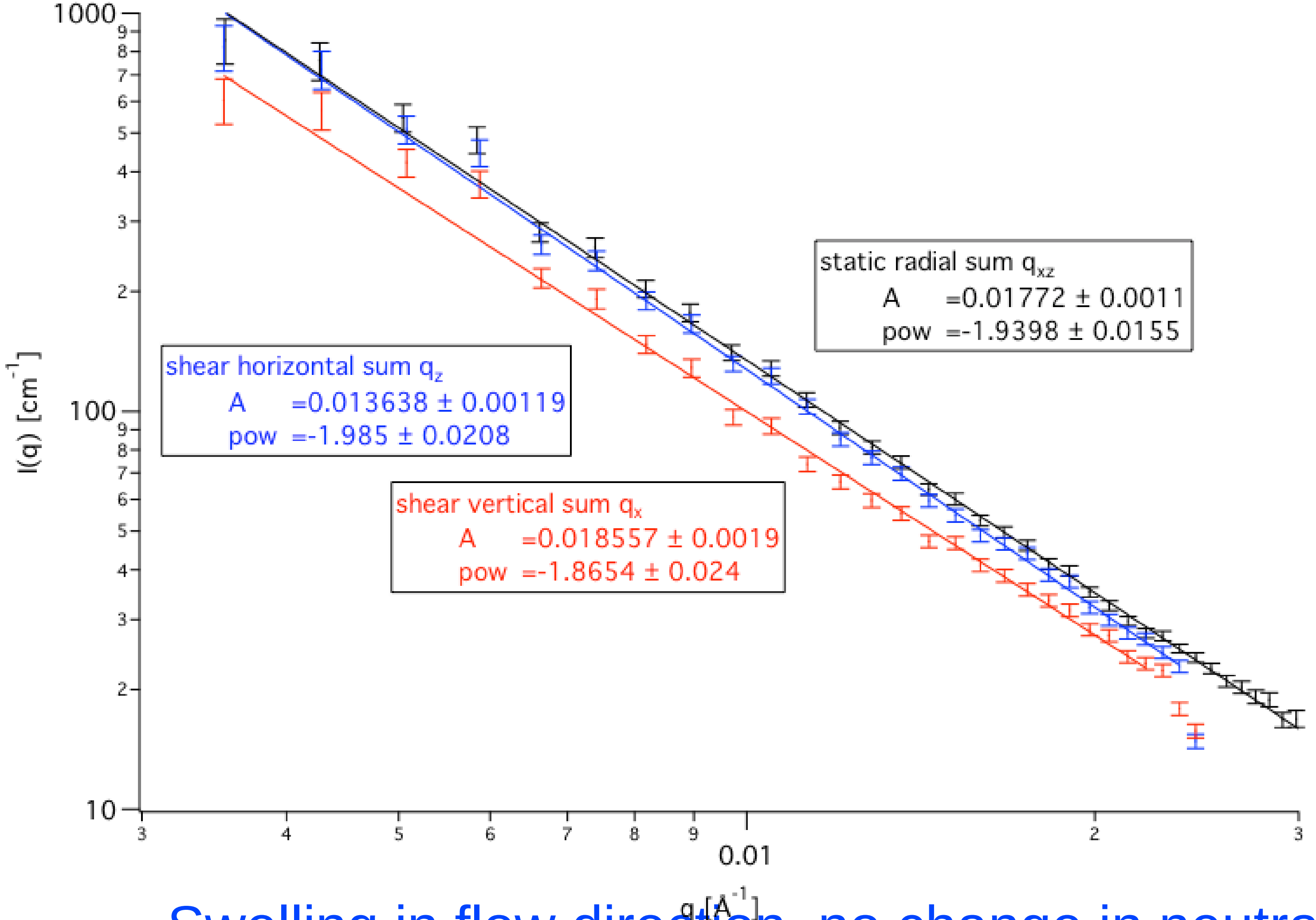


Figure from Weigandt *et al.*, Soft Matter 7 (9997) 2011.

Molecular shape

flow direction: x Wi=30



Swelling in flow direction, no change in neutral direction.

Conclusion

- SANS shows that form factor of sheared polystyrene chains in moderately dense solution (good solvent) shows a swelling of chains in flow direction at high Weissenberg numbers (~30).

- GT-SANS shows that structure factor gets highly anisotropic at Weissenberg numbers > 5 and a significant increase in SANS intensity in the shear gradient direction is obsereved featuring a decrease in correlation length for increasing shear rates.

→ Tube alignment?!

Thank you for your attention!

CALL FOR PAPERS

Both oral and poster contributions related to different topics of the conference are solicited. Template for the abstract will be soon available at the conference website. All submitted abstracts will be reviewed by the Programme Committee.

Start of the conference

Monday 12 September 2016
9:00 – Start of Registration 12:00 - Welcome Buffet
14:00 – Start of Scientific Program

End of the conference

Friday 16 September 2016
15:00 – End of Scientific Program

Important dates

Deadline abstract submission :
1st March 2016

Authors notification :
30th April 2016

End of early bird registration :
1st June 2016

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Institut Laue-Langevin
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BP 156 F-38000 Grenoble
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E-mail : info@ismc2016.org

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