The University Of Sheffield.

S M A L L
Soft Matter AnalyticaL Laboratory

Laboratory Small-Angle X-ray scattering Instrument: State-of-the-Art and Applications

Oleksandr Mykhaylyk

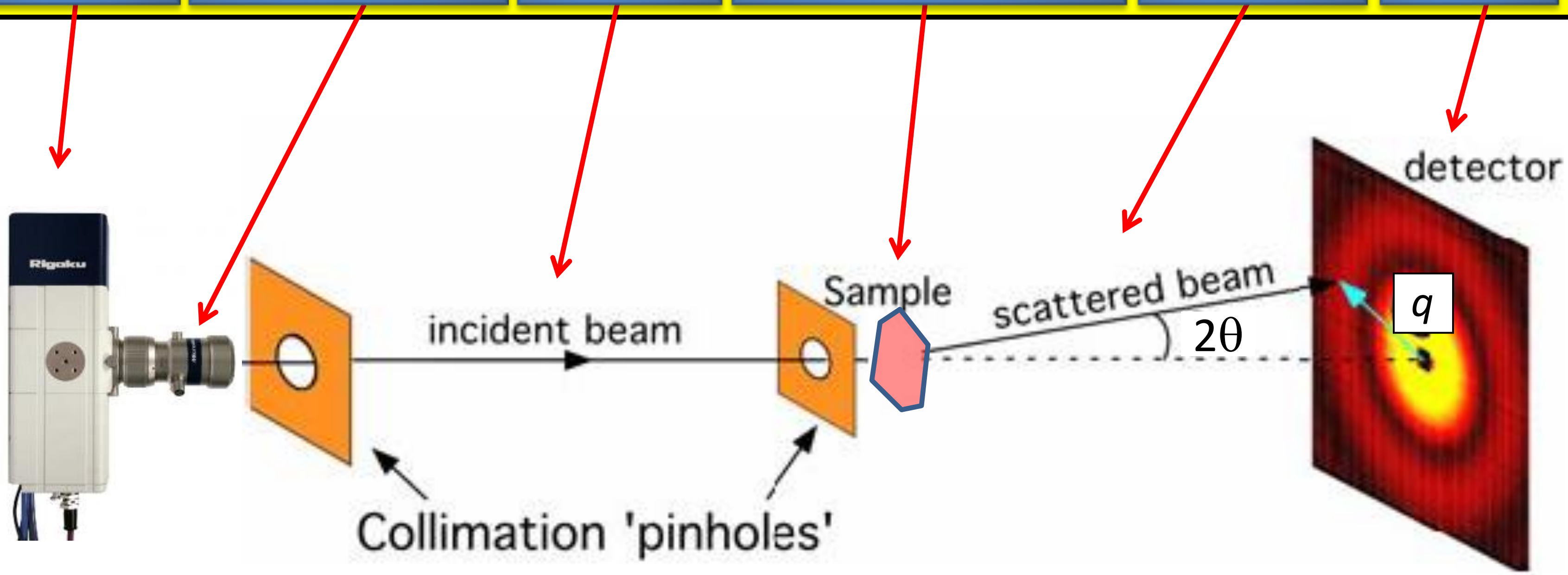
Soft Matter AnalyticaL Laboratory
Department of Chemistry, The University of Sheffield, UK

SAS school @ Diamond 2019, UK

General layout of SAS instrument

By no means a complete outline!

Radiation source	Optics, Monochromators	Collimator	Sample holder and/or sample environment	Scattering camera	Detector



$$q = 4\pi \sin\theta / \lambda$$

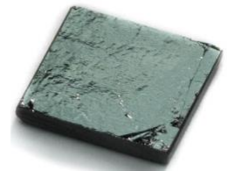
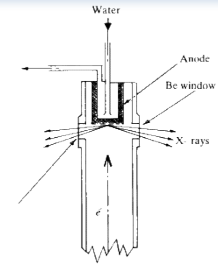
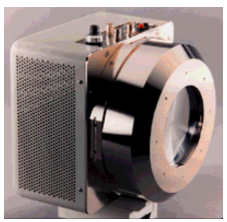
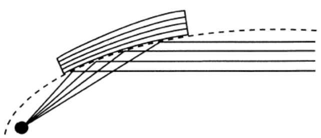
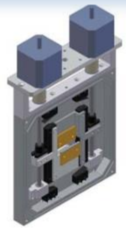
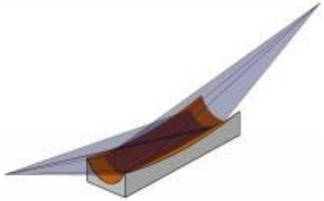
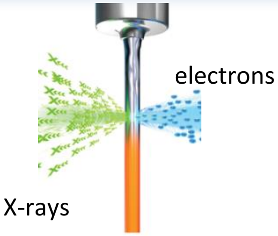
Experimental facilities for data collection

Diamond Light Source (X-rays)

ISIS Spallation Source (neutrons)

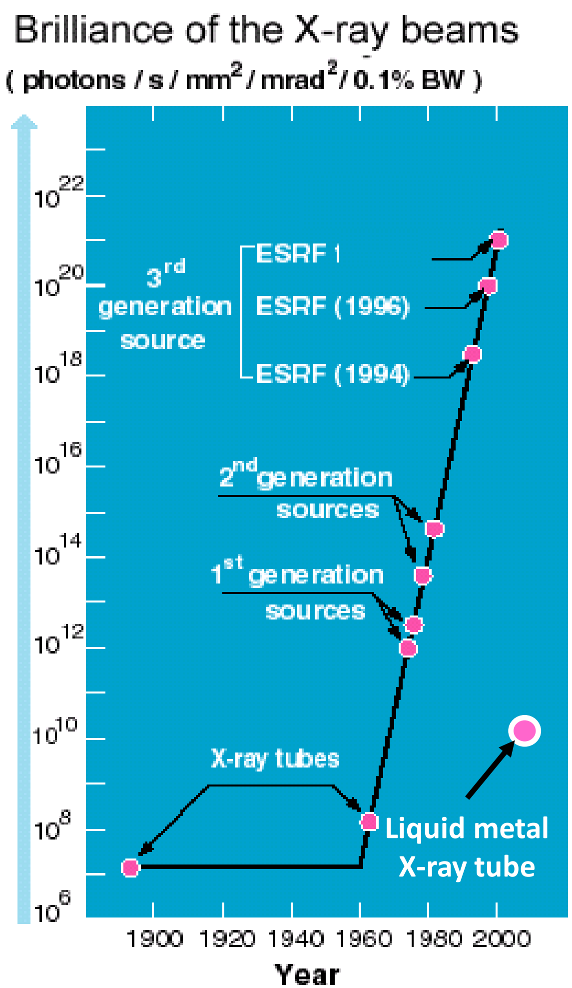
Laboratory SAXS
Xenocs Xeuss + Excillum MetalJet
Bruker Nanostar

Evolution of SAXS instrument components

Detector	Collimating slits	Monochromator	X-ray source	
 X-ray films	 Lead pinholes	 Graphite crystal	 Solid anode	1990s
 Multi-wire gas detector	 Lead pinholes	 Gobel mirror	 Solid (rotating) anode	2000s
 Pixel detector	 Scatterless slits comprised of motorized single crystal blades	 Montel optics or 3D multi-layered mirror	 Liquid metal anode	Current state of play

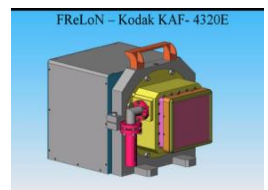
Performance of some components

X-ray source



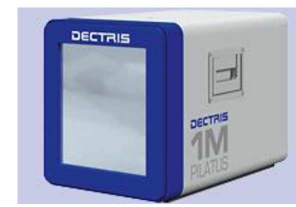
Detector

CCD



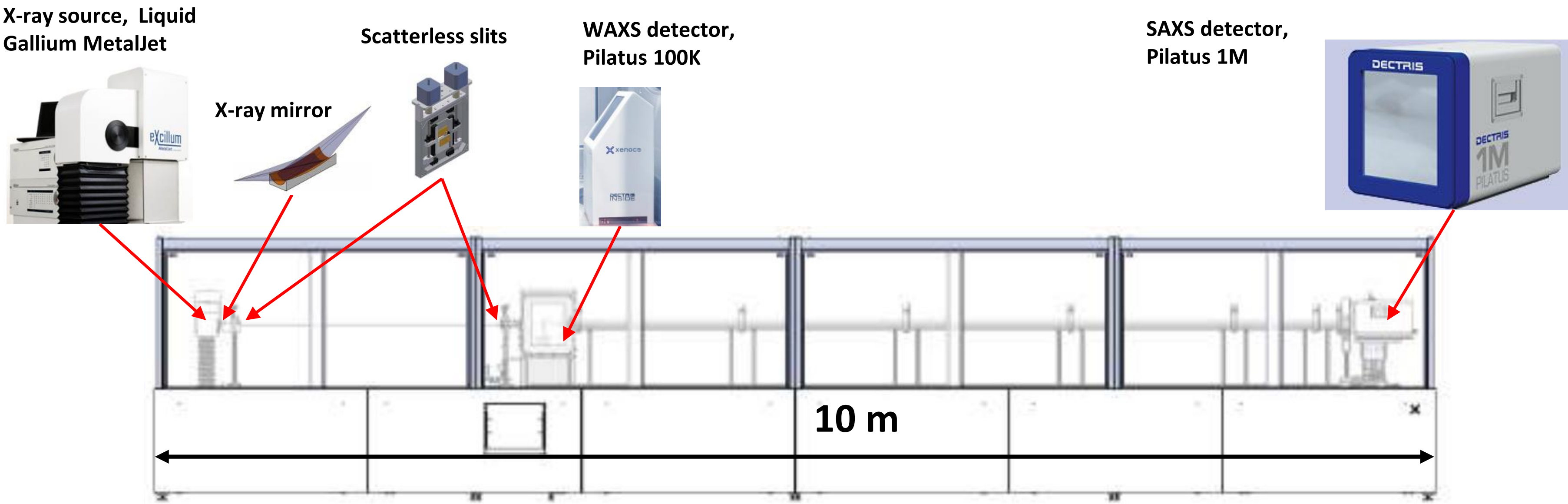
Multi-wire detector

Pixel detector



Characteristics	FReLon	RAPID 2	Pilatus
Dynamic range, bits	16	16	20
Counting rate limit, photons/mm²/s	low	~ 10^6	~ 10^7
Pixel size	>6x6 μm	~100x100 μm	>75x75 μm
Framing rate, Hz	< 15	10^6	100

Outline of our laboratory SAXS instrument



MetalJet Liquid Gallium X-ray source

3D multilayered X-ray mirror

Two sets of motorized scatterless slits

Two Dectris detectors: Pilatus1M (SAXS) and Pilatus 100K (WAXS)

Sample-to-detector distance 6.4 m

Resolution: 0.001 Å^{-1} (~ 6000 Å)

Simultaneous SAXS/WAXS

GiSAXS/GiWAXS

X-ray reflectometry

Xenocs/Excillum SAXS instrument @ Sheffield

Outline of modern laboratory SAXS instrument

MetalJet Liquid Gallium X-ray source

3D multilayered X-ray mirror

Two sets of motorized scatterless slits

Two Dectris detectors: Pilatus1M (SAXS) and Pilatus 100K (WAXS)

Sample-to-detector distance 6.4 m

Resolution: 0.001 $Å^{-1}$ (~ 6000 Å)

Simultaneous SAXS/WAXS

GiSAXS/GiWAXS

X-ray reflectometry

Thus, modern laboratory X-ray scattering instrument can be used pretty much for all standard X-ray scattering techniques

SAXS

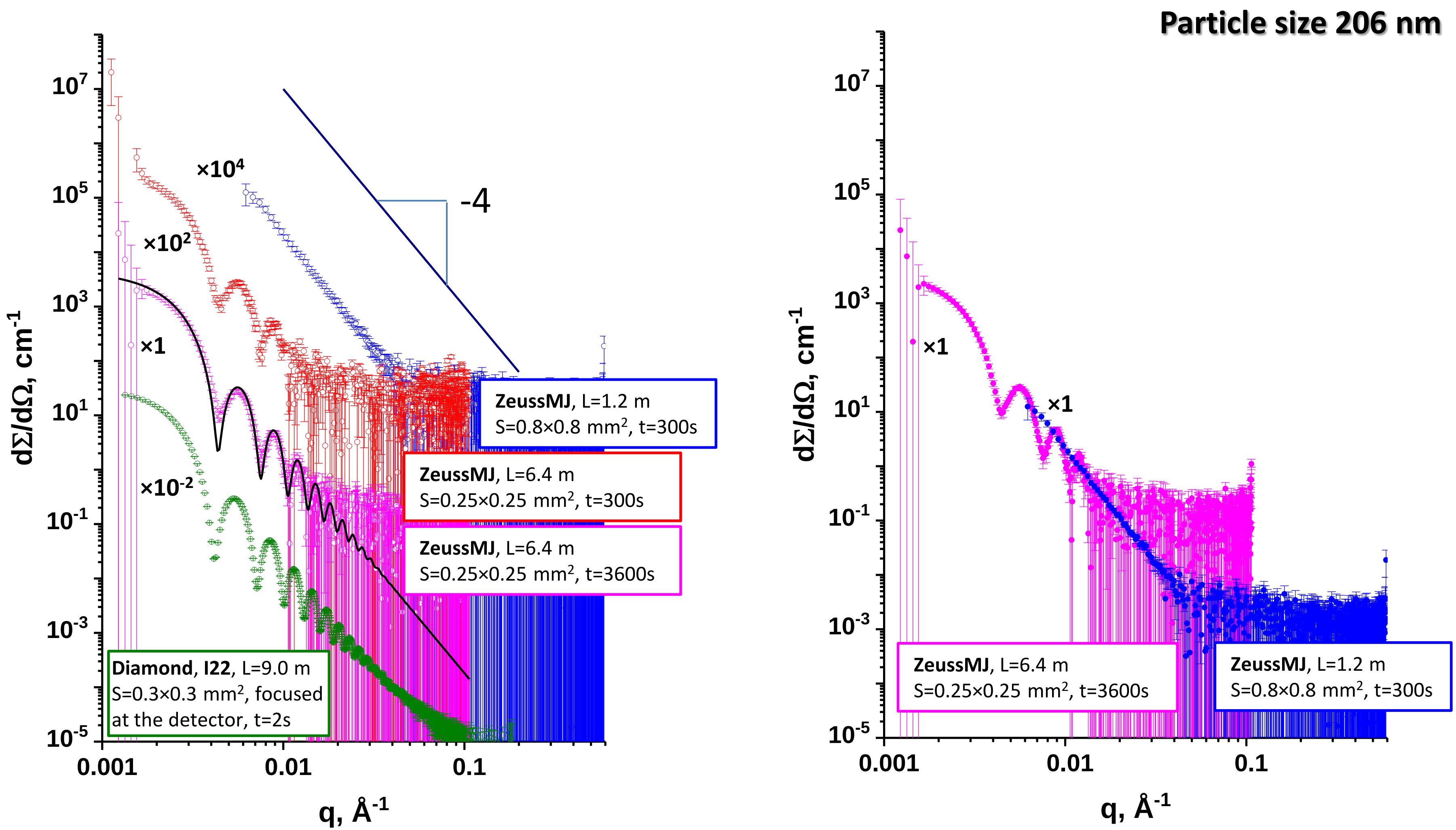
WAXS

GiSAXS

GiWAXS

X-ray reflectometry

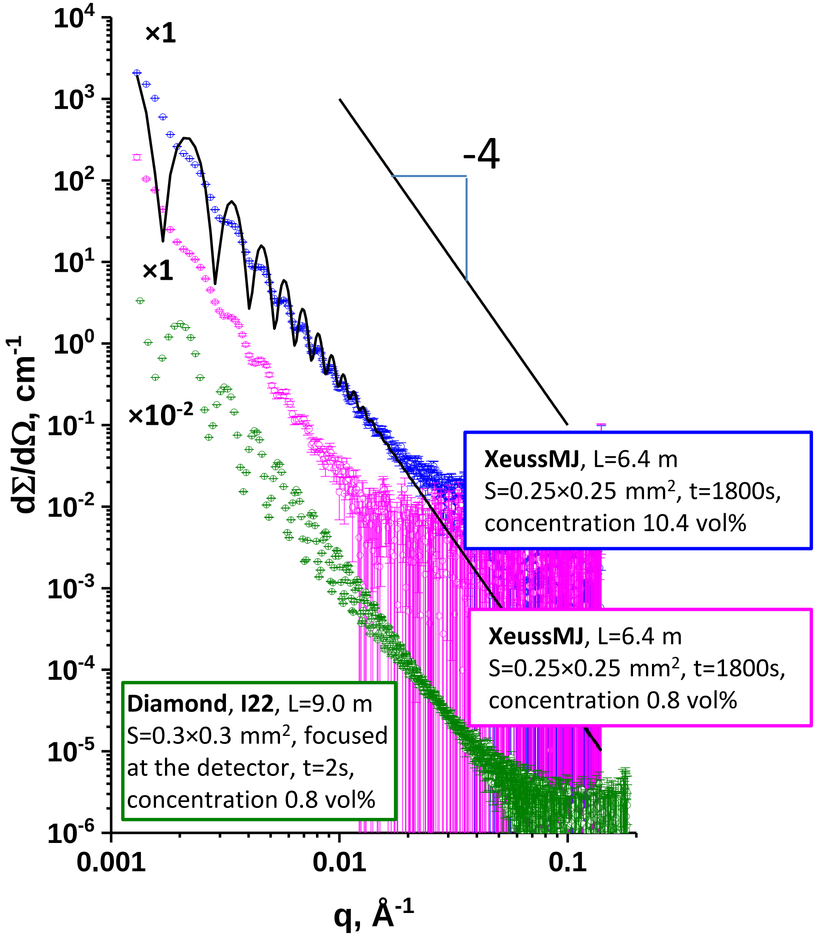
Spatial Resolution of the Instrument

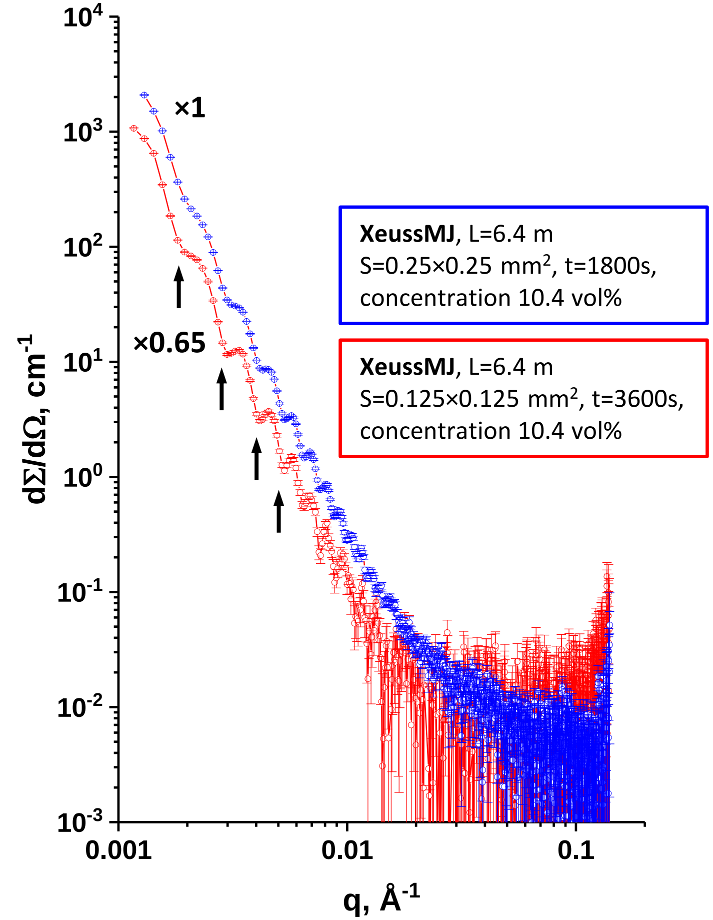


1wt% (0.8 vol%) P2VP $(C_7H_7N)_n$ spherical particles in water, R = 1030 Å, σ_R = 35 Å, $\Delta\rho^2 = 1.335\times10^{20}$ cm^{-4}

Spatial Resolution of the Instrument

Particle size 540 nm

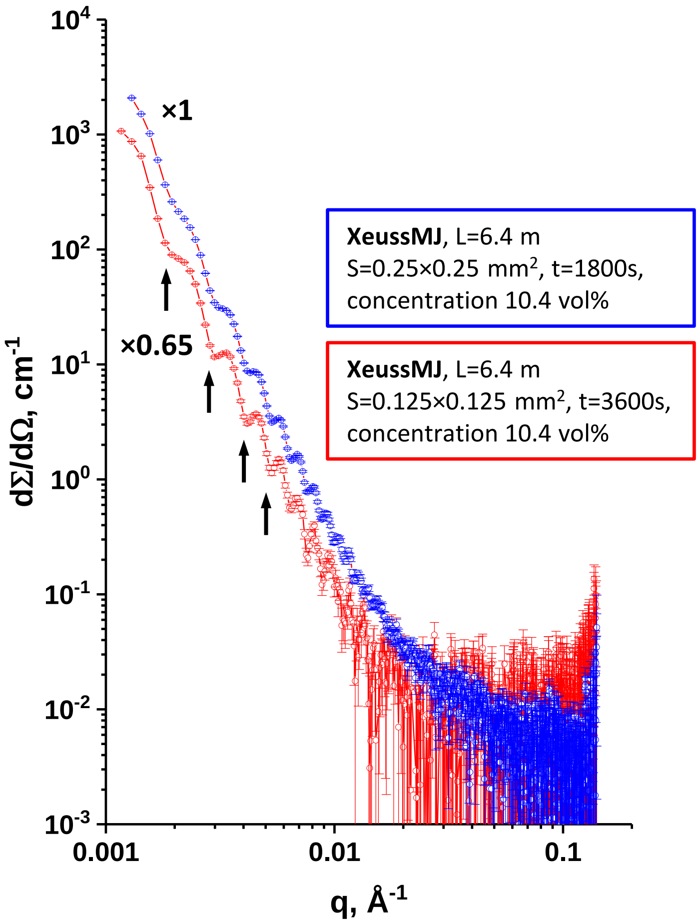




P2VP $(C_7H_7N)_n$ spherical particles in water, R = 2700 Å, σ_R = 35 Å, $\Delta\rho^2 = 1.335\times10^{20}$ cm^{-4}

Spatial Resolution of the Instrument

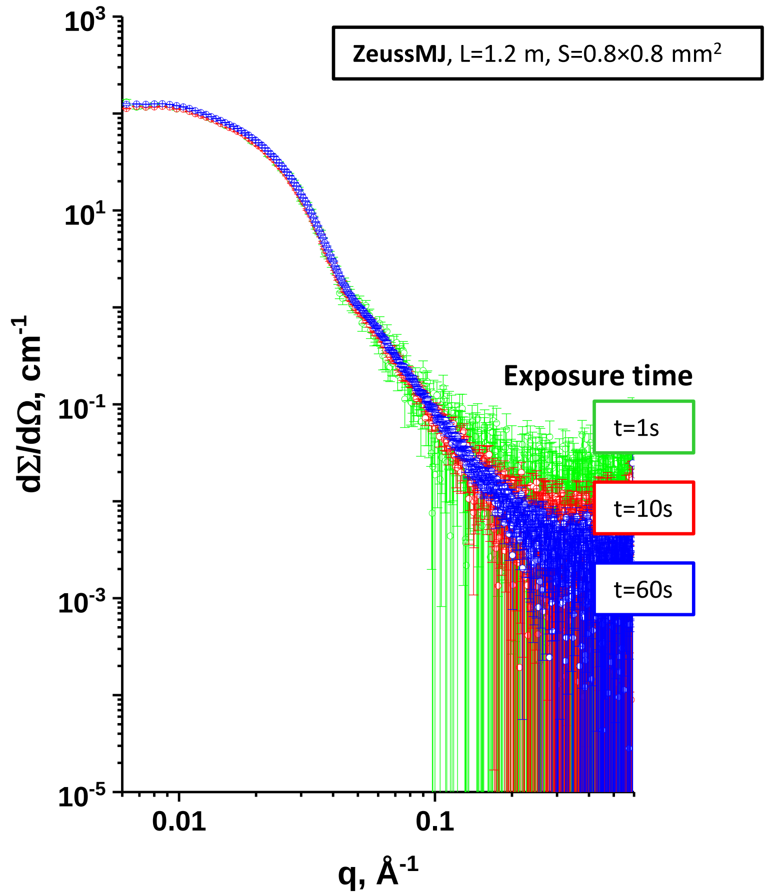
Particle size 540 nm

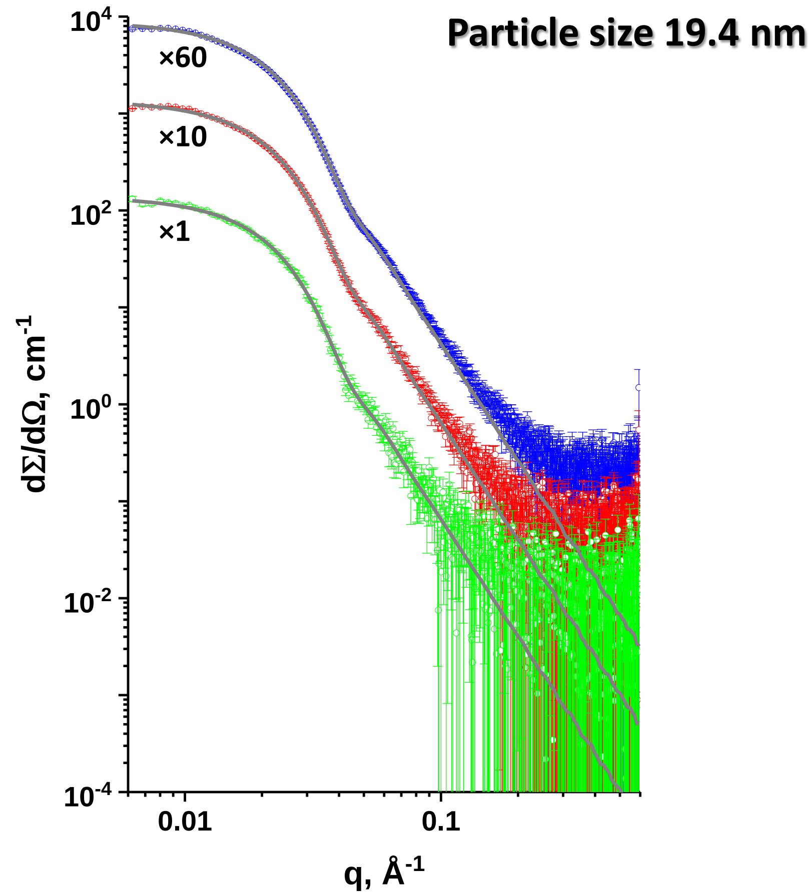


Thus, in terms of spatial resolution a modern laboratory X-ray scattering instrument can be used for analysing structural formations/morphologies/objects as large as 0.5 micron reaching the lower limit of resolution of standard optical microscopes.

P2VP $(C_7H_7N)_n$ spherical particles in water, R = 2700 Å, σ_R = 35 Å, $\Delta\rho^2 = 1.335\times10^{20}$ cm^{-4}

Time Resolution of the Instrument





1wt% (0.49 vol%) Silica spherical particles in water,

R = 97 Å, σ_R = 22 Å, $\Delta\rho^2 = 65.9\times10^{20}$ cm^{-4}

Exp. conditions	Vol%	R, Å	σ_R, Å
As prepared	0.49	-	-
SAXS, 1s exposure	0.47	97.6	21.2
SAXS, 10 exposure	0.47	97.2	21.6
SAXS, 60s exposure	0.50	97.2	21.9

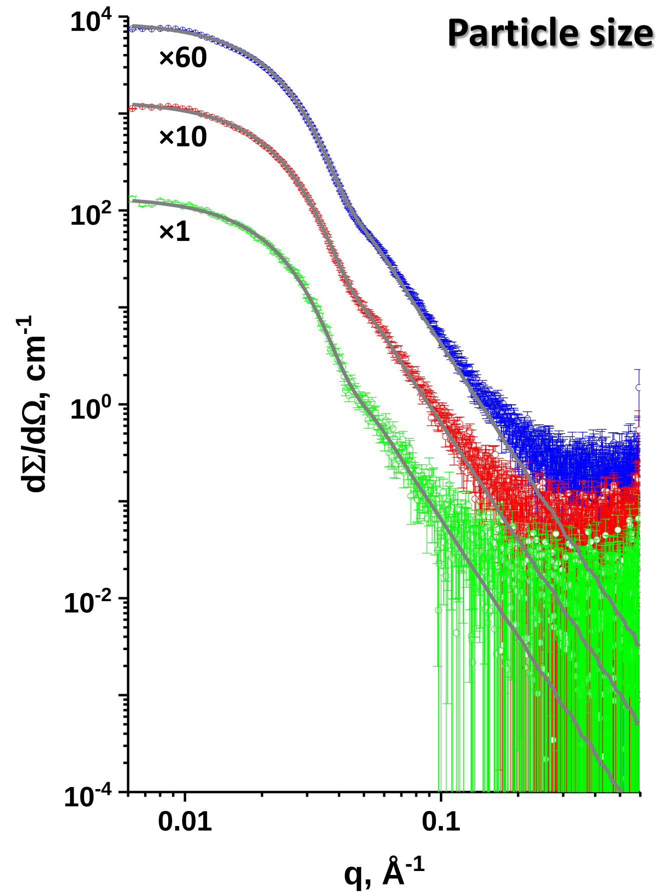
Time Resolution of the Instrument

Thus, in terms of time resolution a modern laboratory X-ray scattering instrument can be used for analysing structural formations/morphologies/objects at a time resolution as low as one second enabling to perform standard (not highly demanding) time-resolved measurements of structural formations/transformations.

1wt% (0.49 vol%) Silica spherical particles in water,

R = 97 Å, σ_R = 22 Å, $\Delta\rho^2 = 65.9\times10^{20}$ cm^{-4}

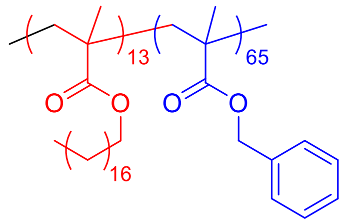
Particle size 19.4 nm

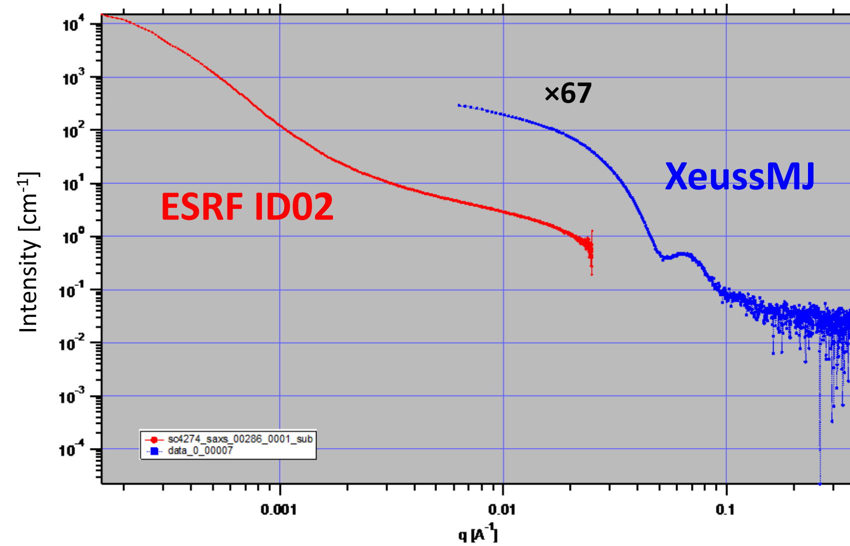


Exp. conditions	Vol%	R, Å	σ_R, Å
As prepared	0.49	-	-
SAXS, 1s exposure	0.47	97.6	21.2
SAXS, 10 exposure	0.47	97.2	21.6
SAXS, 60s exposure	0.50	97.2	21.9

Combined synchrotron and laboratory SAXS measurements

SAXS of 1.0% w/w $PSMA_{13}$-$PBzMA_{65}$ diblock copolymer worm-like micelles in mineral oil



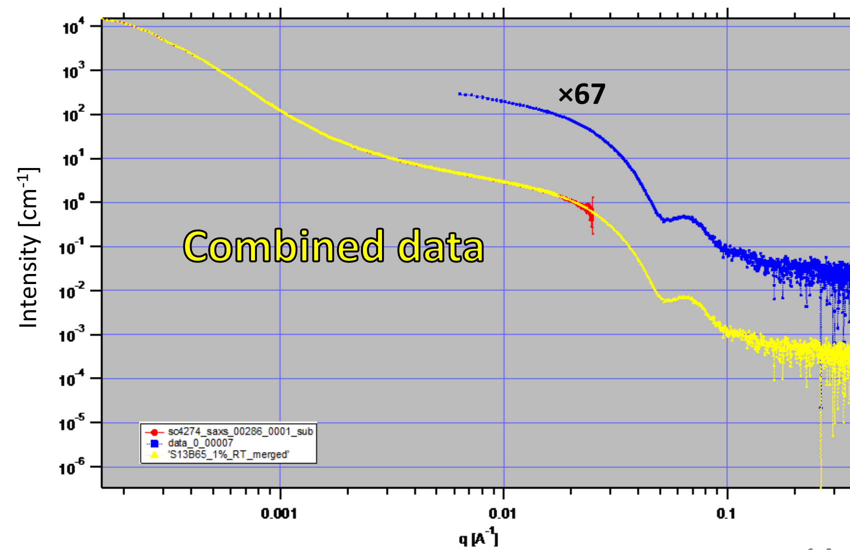


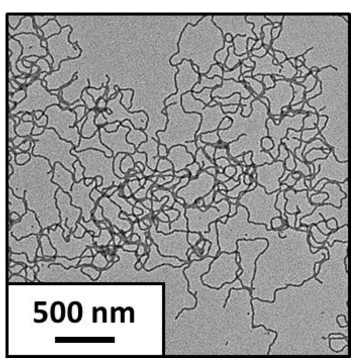
Synchrotron source

ESRF ID02, L=31 m, 300 ms acquisition

Laboratory SAXS instrument

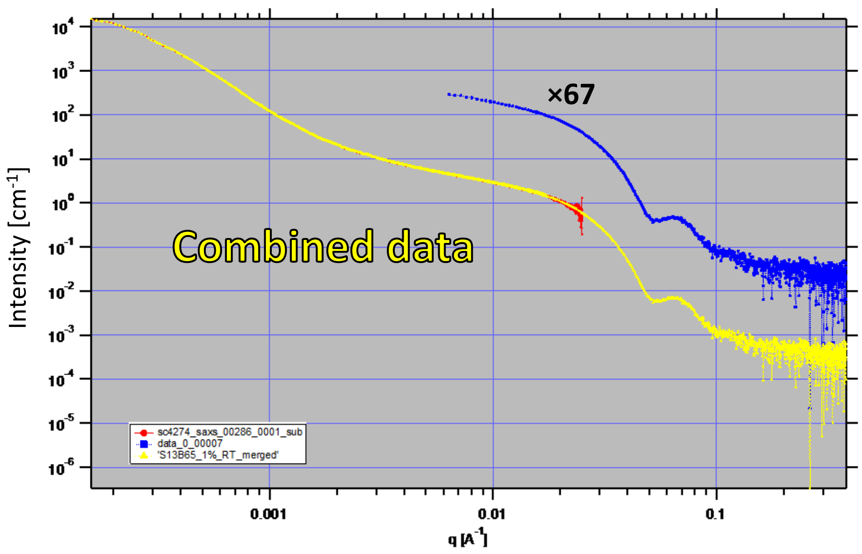
XeussMJ, L=1.9 m, 600 s acquisition



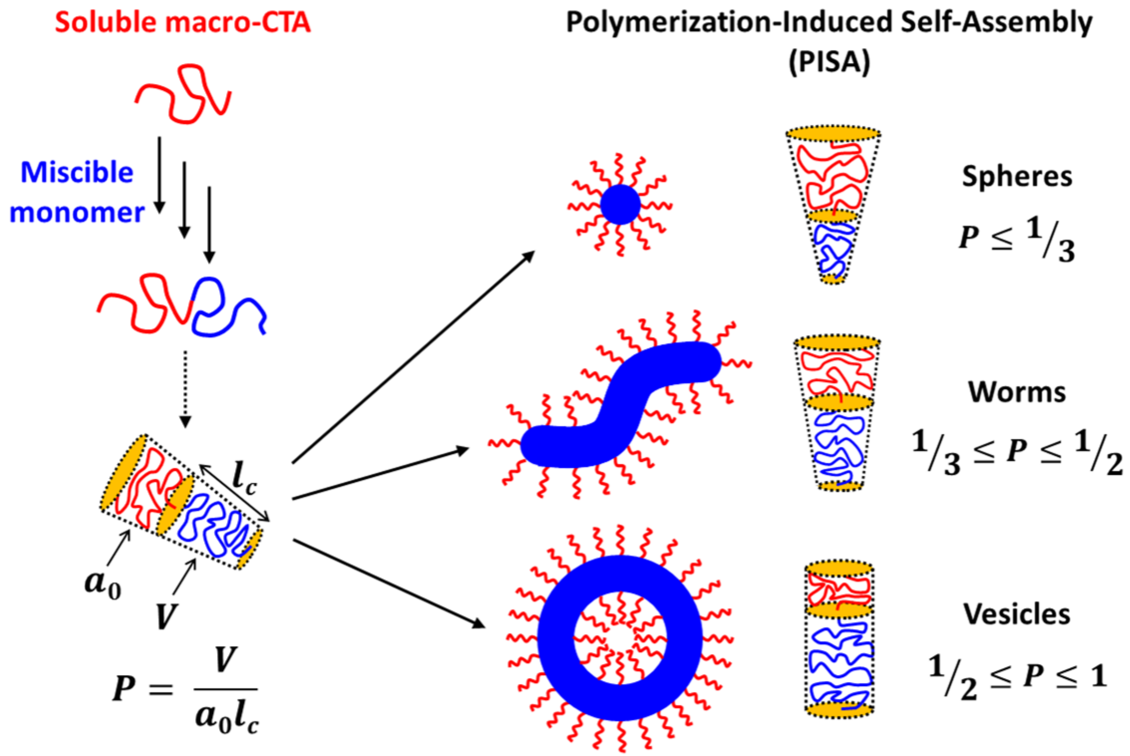


Branched worm-like micelles at RT

Thus, a modern laboratory X-ray scattering instrument can be successfully used for analysing structural formations/morphologies/objects in a combination with synchrotron measurements which can save expensive synchrotron time for advanced measurements and improve quality of collected data.



Block Copolymer Self-Assembly via Polymerization-Induced Self-Assembly (PISA)



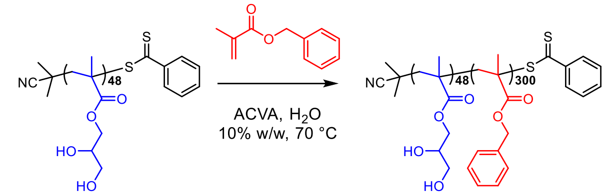
In practice, particle morphology also depends on copolymer concentration

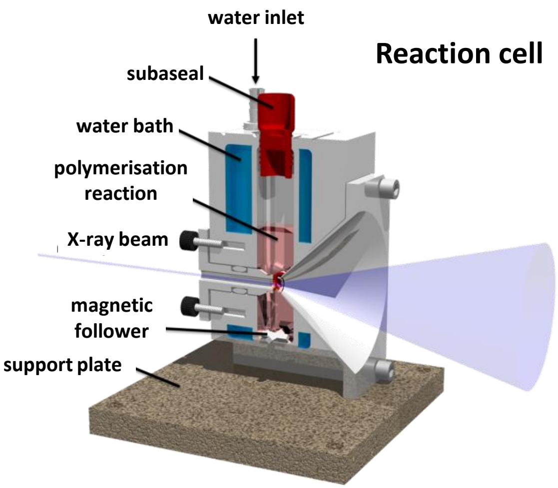
*N. J. Warren & S. P. Armes, J. Am. Chem. Soc., **2014**, 136, 10174*
*M. J. Derry, L. A. Fielding & S. P. Armes, Prog. Polym. Sci., **2016**, 12, 1*
*S. L. Canning, G. N. Smith & S. P. Armes, Macromolecules, **2016**, 49, 1985*

Time-resolved SAXS

RAFT polymerization and PISA of $PGMA_{48}$-$PBzMA_{300}$ in water

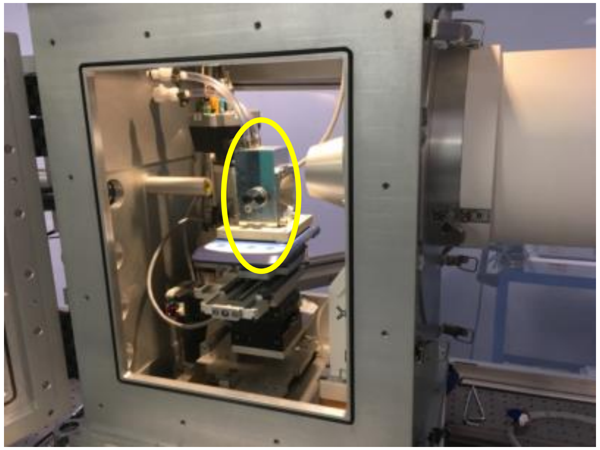
Reaction conditions: 10% w/w, reaction temperature 70 °C



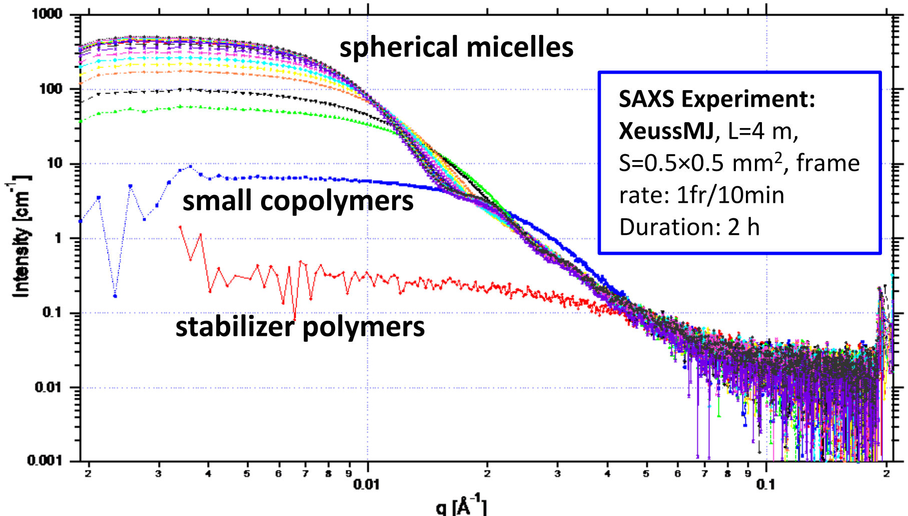


Details of the synthesis:
*V. J. Cunningham et al, Macromolecules, **2014**, 47, 5613–5623*

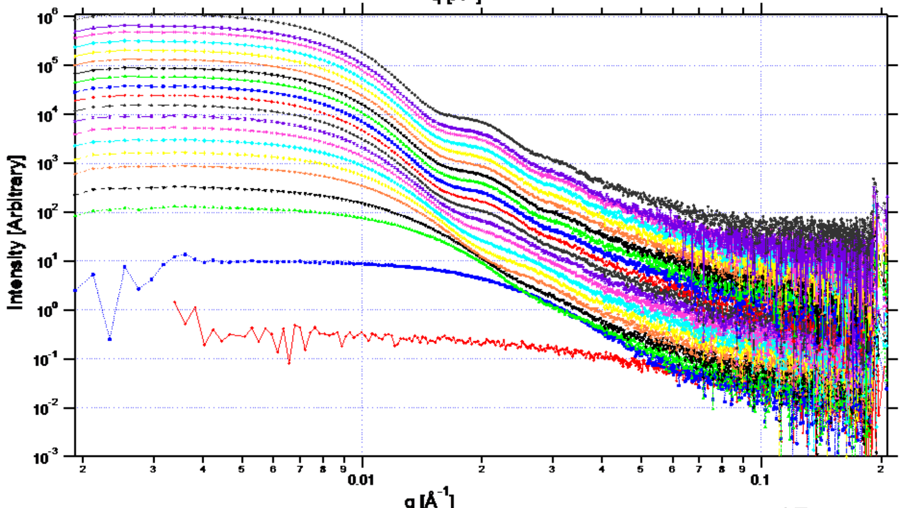
Details of SAXS analysis:
*M. J. Derry et al, Chemical Science, **2016**, 7, 5078*



Reaction cell mounted on Xeuss



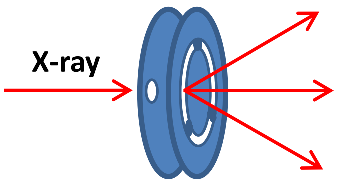
SAXS Experiment:
XeussMJ, L=4 m, S=0.5×0.5 mm², frame rate: 1fr/10min
Duration: 2 h



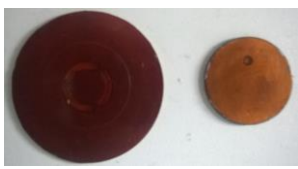
Rheo-SAXS/WAXS

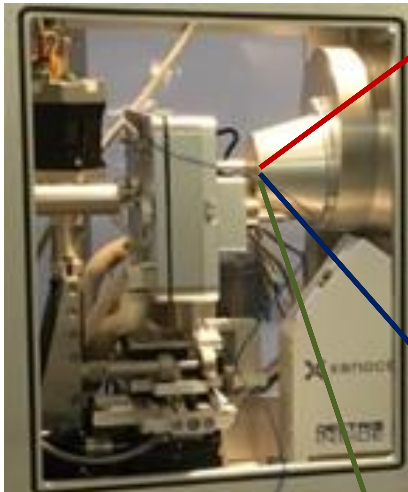
Linkam shear cell CSS-450 mounted on XeussMJ instrument

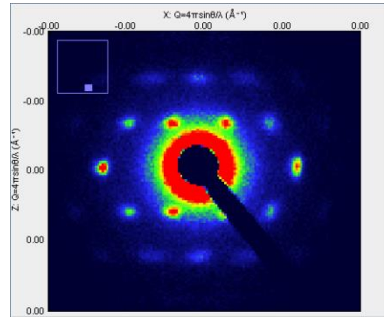
Parallel plate geometry



modified shearing disks
two kapton windows
transparent for X-rays
(70 microns each)

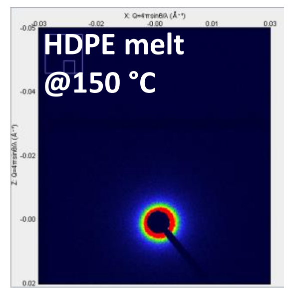


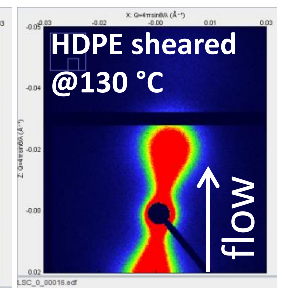




Shear-alignment of PS-PI block-copolymer spherical micelle dispersion

- 5 wt% dispersion of PS-PI copolymer micelles
- Sample-to-detector distance 2.5 m
- Exposure time 300 s
- Oscillatory shear

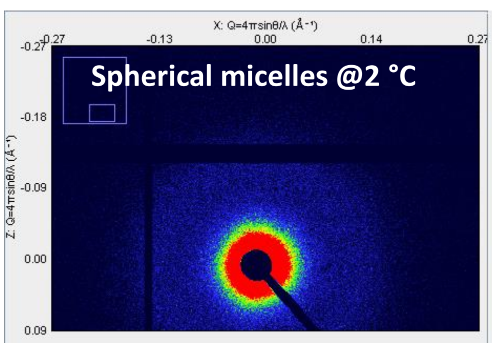


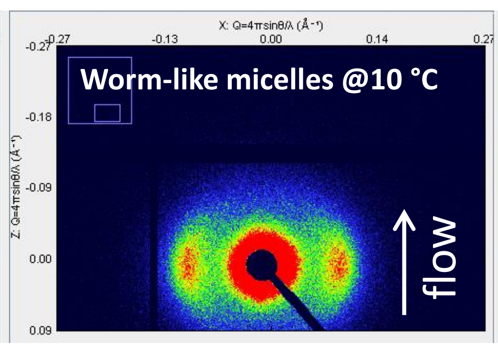


Flow-induced crystallization of semi-crystalline polymer (HDPE)

- HDPE melt
- Sample-to-detector distance 3.8 m
- Exposure time 60 s
- Shear pulse

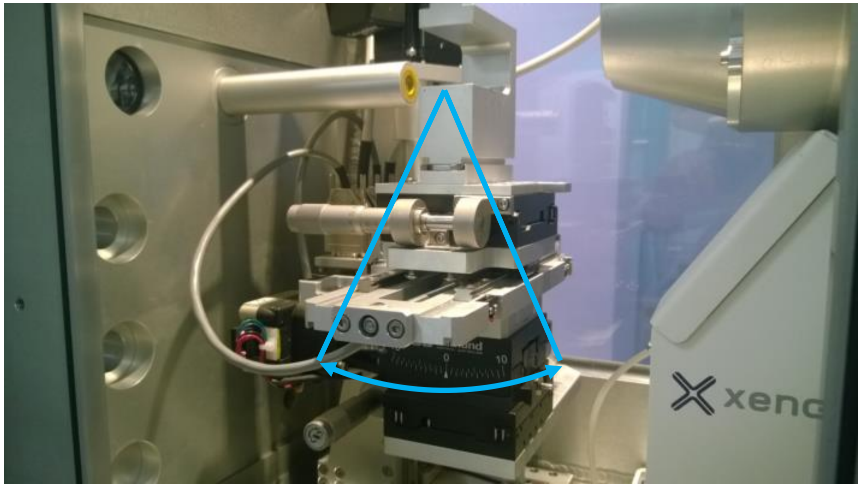
Transformation of block copolymer self-assembled morphologies under shear and temperature



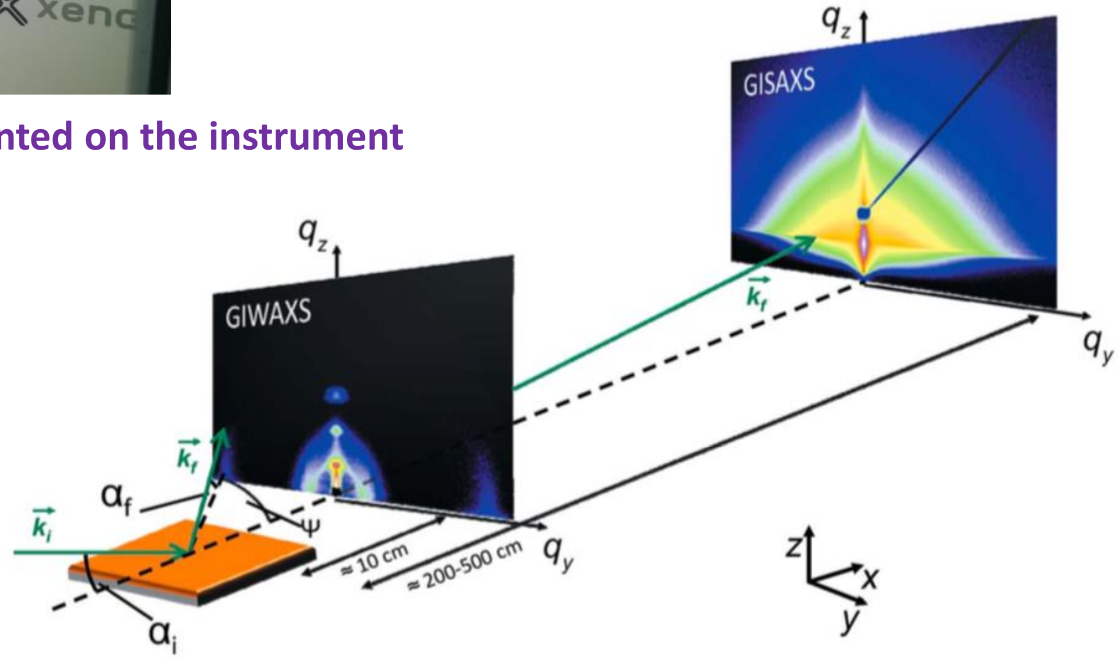


- 15 wt% aqueous dispersion of thermo-responsive block-copolymers
- Sample-to-detector distance 3.8 m
- Exposure time 60 s
- Continuous shear

GISAXS/GIWAXS



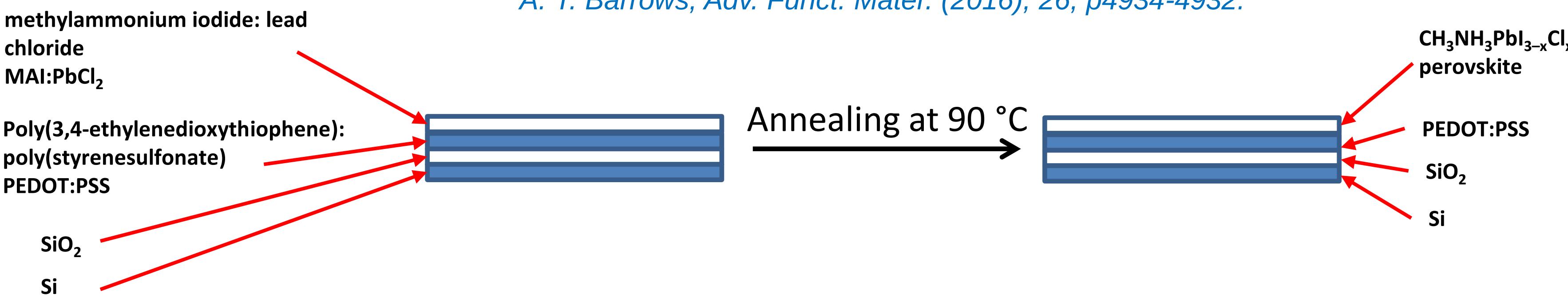
Standard GISAXS/GIWAXS stage mounted on the instrument



taken from A. Hexemer & P. Muller-Buschbaum, IUCrJ (2015), 2, p106–125

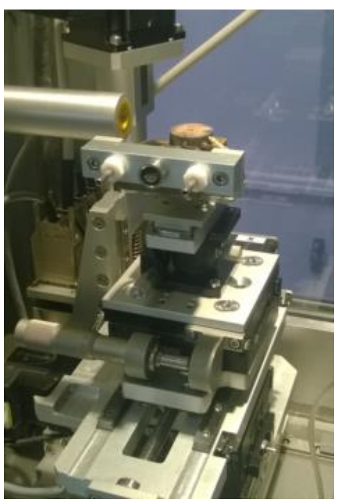
$CH_3NH_3PbI_{3-x}Cl_x$ Perovskite photovoltaic device manufacturing

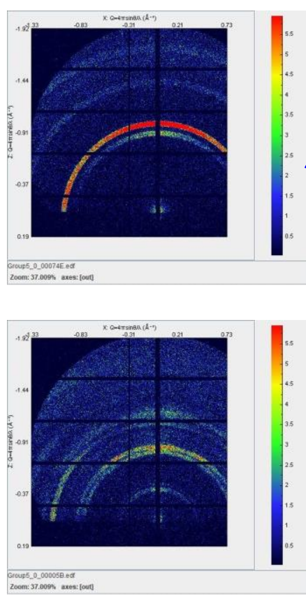
A. T. Barrows, Adv. Funct. Mater. (2016), 26, p4934-4932.

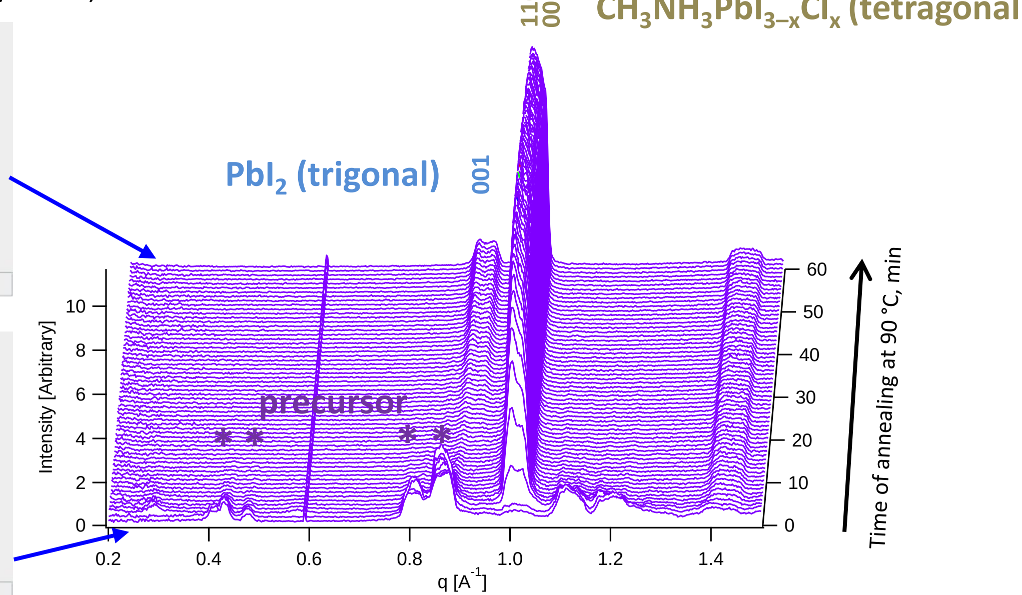


$$MAI{:}PbCl_2 \longrightarrow CH_3NH_3PbI_{3-x}Cl_x \longrightarrow CH_3NH_3PbI_{3-x}Cl_x + PbI_2$$

<u>Conditions for the data collection</u>: exposure time 1 min/frame, film thickness < 400 nm

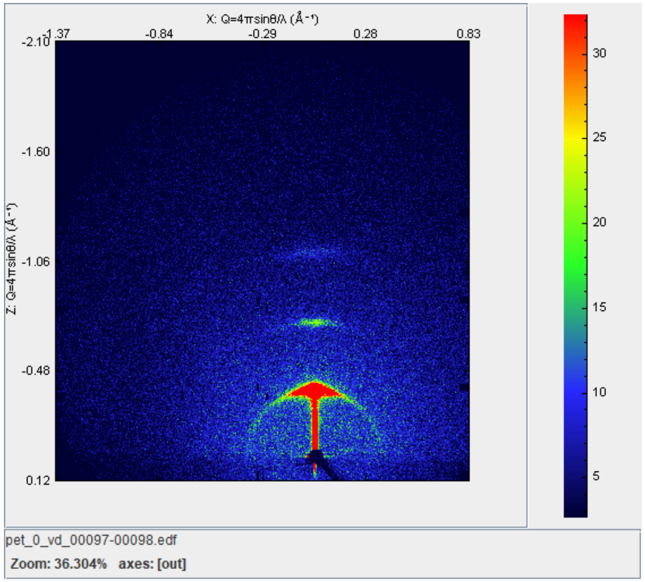


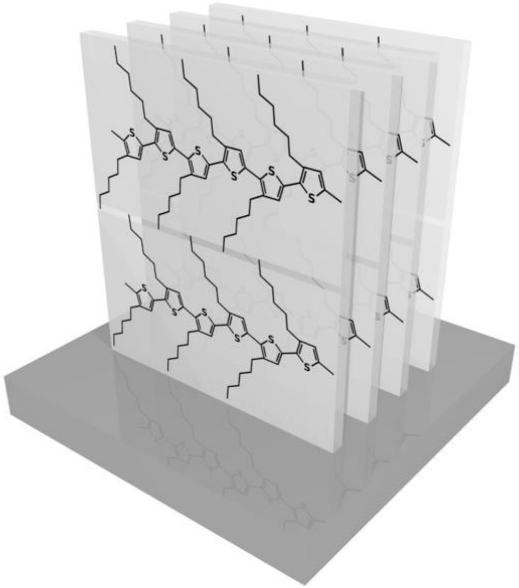




Organic solar cells

P3HT – conjugated polymer – edge on orientation





Conditions for the data collection: exposure time 10 min; film thickness < 200 nm
two positions of the detector were used in order to erase the detector dead stripes from 2D scattering patterns

To Take-Home Message

Laboratory X-ray scattering instruments and, in particular, **SAXS instruments** have undergone significant development for the last decade and become **powerful devices available for researchers with 24/7 access all year round**.

Due to high X-ray flux and improved collimation it is possible to reach both **size resolution** of the scattering objects **up to 0.5 microns** and **time resolution of a few seconds**.

The recent developments of X-ray sources, detectors and X-ray optics opened up **new opportunities for in-house experiments on structural characterisation of nano-scaled morphologies** formed by inorganic and organic materials especially biomaterials, gels, colloids, nanoparticles and polymers.

Design of the modern X-ray scattering instruments enables **simultaneous SAXS/WAXS measurements in-situ using different sample environments** such as heating stages, shear cells and reactor cells.

Acknowledgements

Sheffield University users of the SMALL

From Physics Department

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Fabio Pontecchiani

From Chemistry Department

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Cate O'Brien
Steve Armes
Sarah Bayard
Andrew Campbell
Thomas Franklin
Fiona Hutton
Anthony Ryan

EPSRC Engineering and Physical Sciences Research Council
erc European Research Council
FLIPT
xenocs Exploring the very small
excillum