# Rozpraszanie neutronów dla nauk o materiałach

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# Neutrony i promienie X – komplementarność

## Neutrony

- mają masę
- mają spin i moment magnetyczny
- są stosunkowo powolne
- oddziałują z jądrami
  *(rozpraszanie magnetyczne wymaga magnetycznych formfaktorów)*

## Fotony (promienie X)

- bezmasowe
- nie mają momentu magnetycznego
- bardzo szybkie
- oddziałują z gęstościami elektronowymi
  *(wymaga atomowych formfaktorów)*

## Cechy wspólne

$$k = \frac{2\pi}{\lambda} \qquad \left(\text{dla } \lambda = 1.5604\text{Å} \qquad k = 4.02665\text{Å}^{-1}\right)$$

## Neutrony

$$E(meV) = 2.07k^2\left(\text{Å}^{-2}\right)$$

$$E_{1.5604\text{Å}} = 33.6\ \text{meV}$$

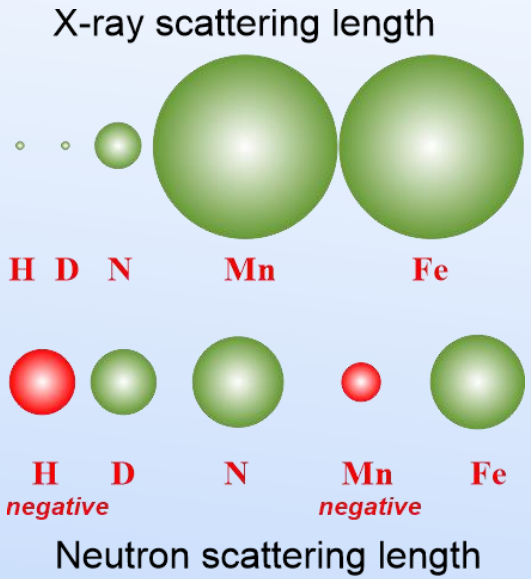
## Fotony (promienie X)

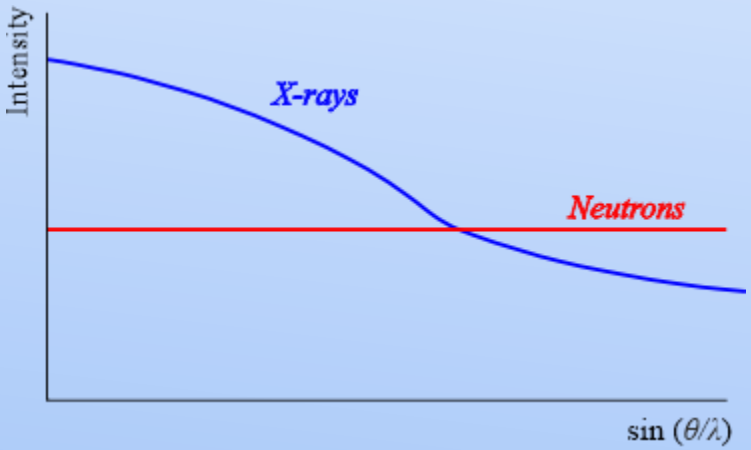
$$E_{CuK\alpha} = 1.97k\left(\text{Å}\right)$$

$$E_{\text{Cu}_{\text{K}_\alpha}} = 8.04\ \text{keV}$$

# Neutrony i promienie X – komplementarność

## Długości rozpraszania



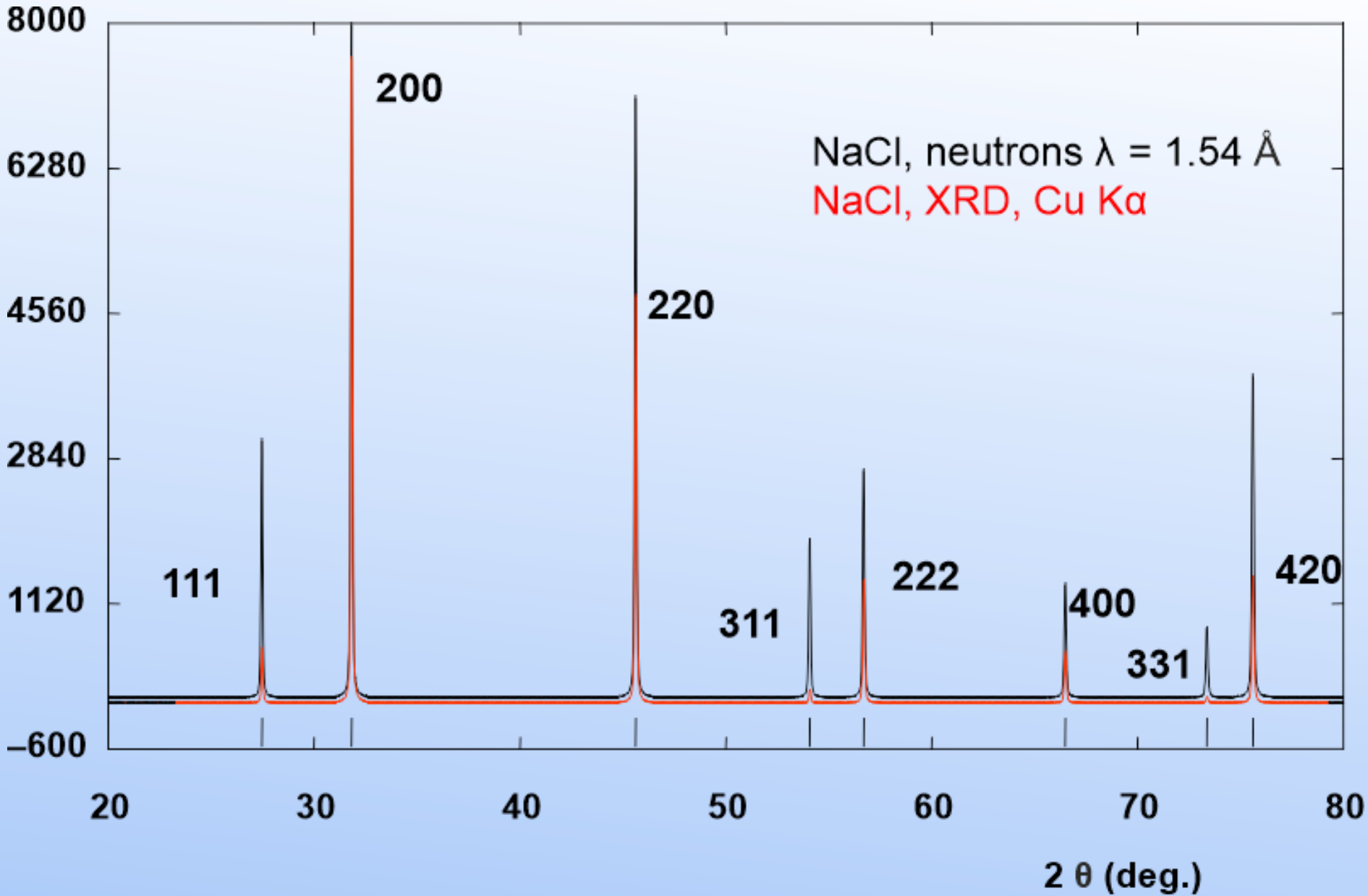

## Fotony

- wysoka wydajność
- rozdzielczość czasowa (ms)
- sterowanie energią (ASAXS)
- mikro- i nanowiązki skanujące (dyfrakcja, obrazowanie)
- badanie ultra-cienkich warstw (GISAXS)

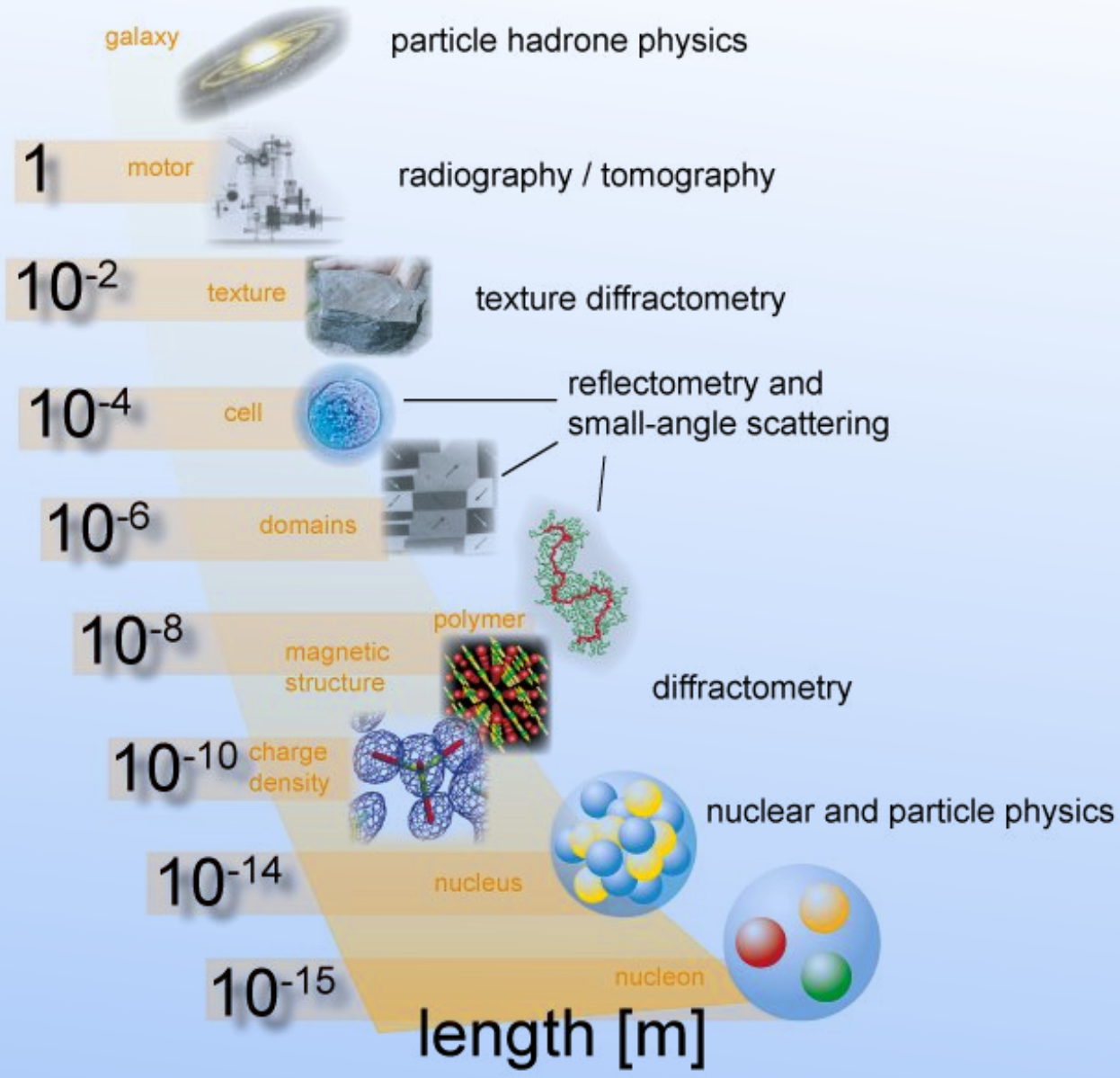
## Neutrony

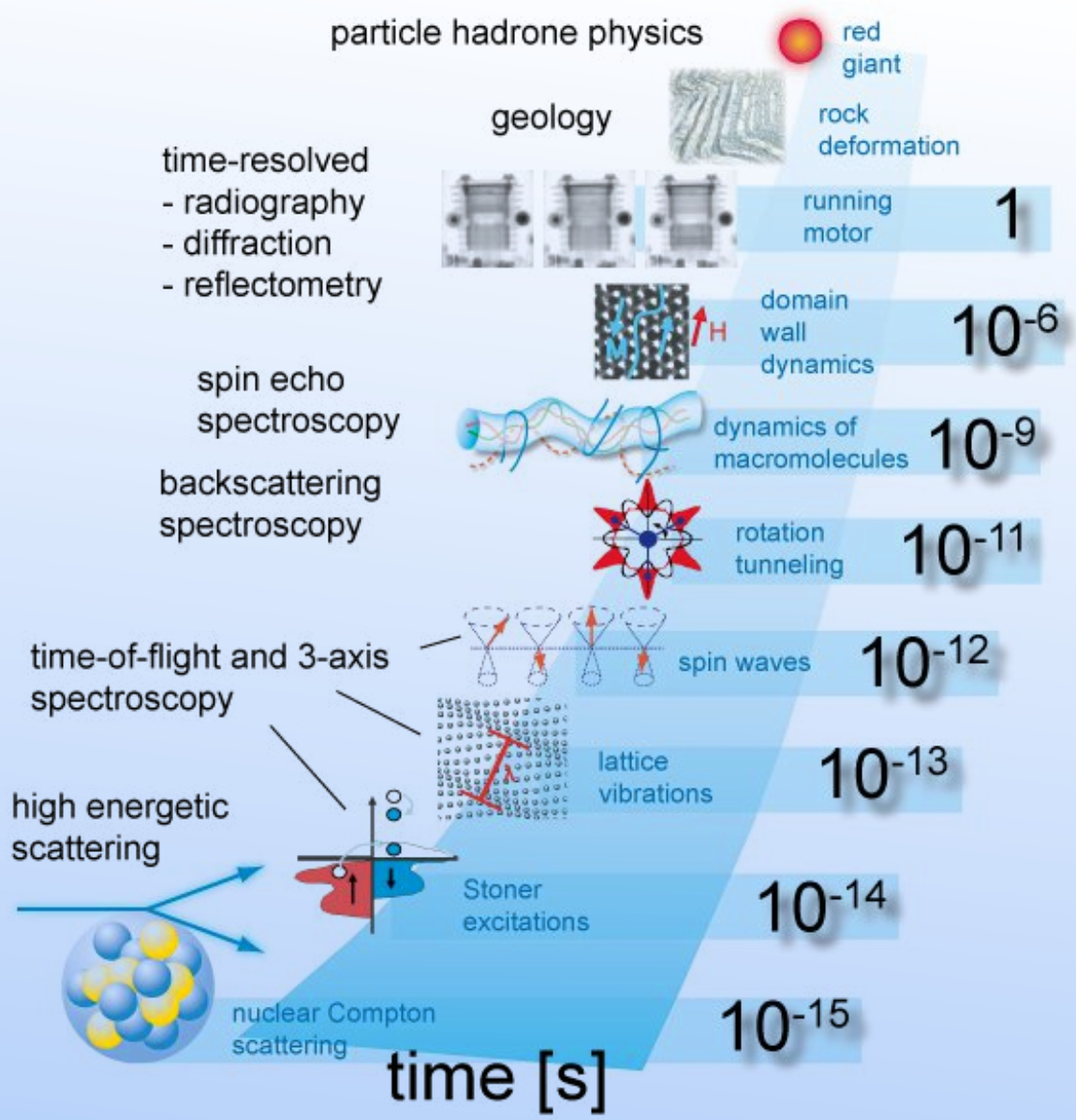
- czułe na lekkie atomy (polimery, biologia, materia miękka, wodór w metalach)
- rozróżniają izotopy (układy wieloskładnikowe)
- brak uszkodzeń radiacyjnych
- głęboka penetracja
  - próbki dużych rozmiarów (inżynieria)
  - trudne środowiska (p,T)
- kontrast magnetyczny

# Neutrony i promienie X – komplementarność

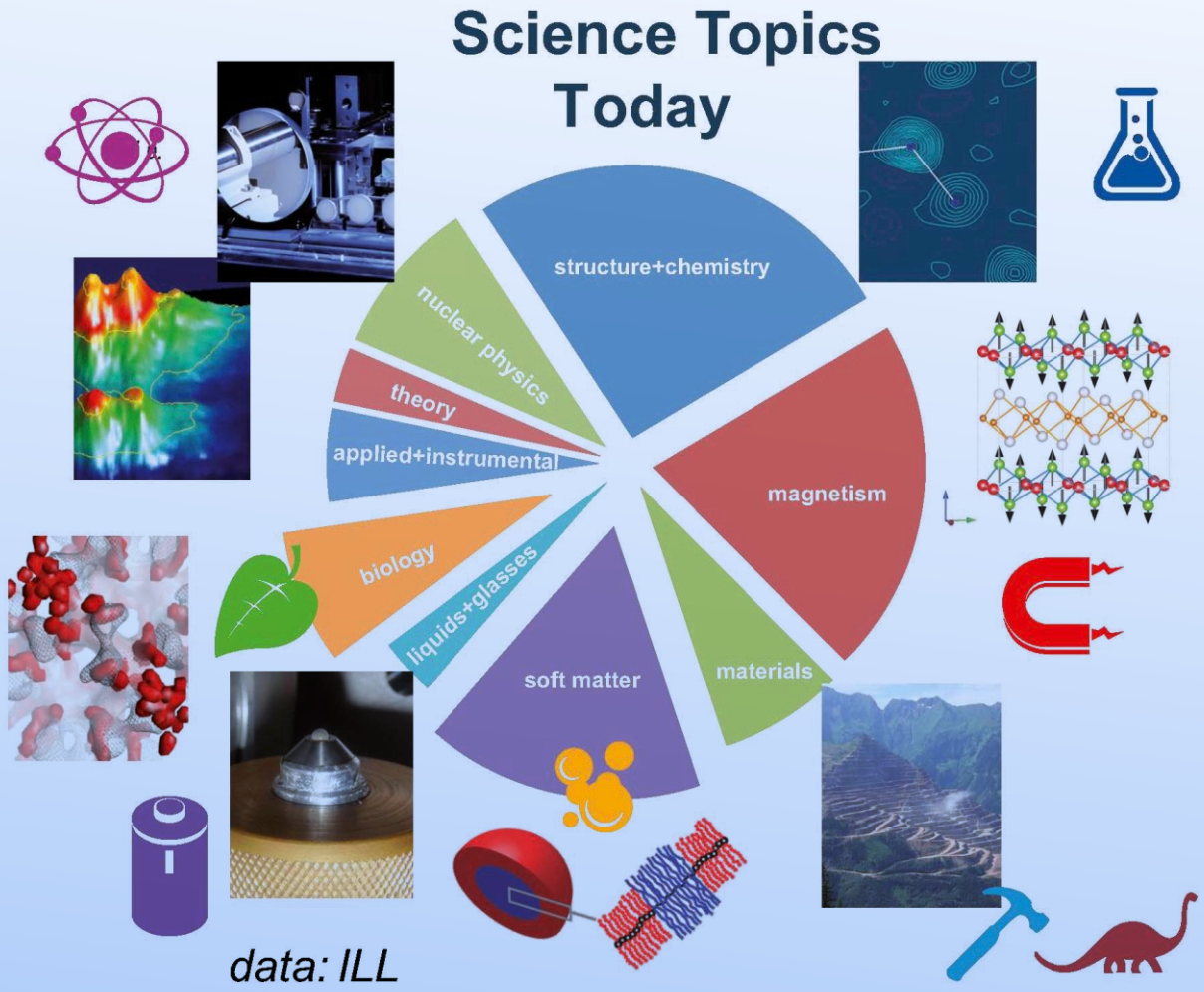


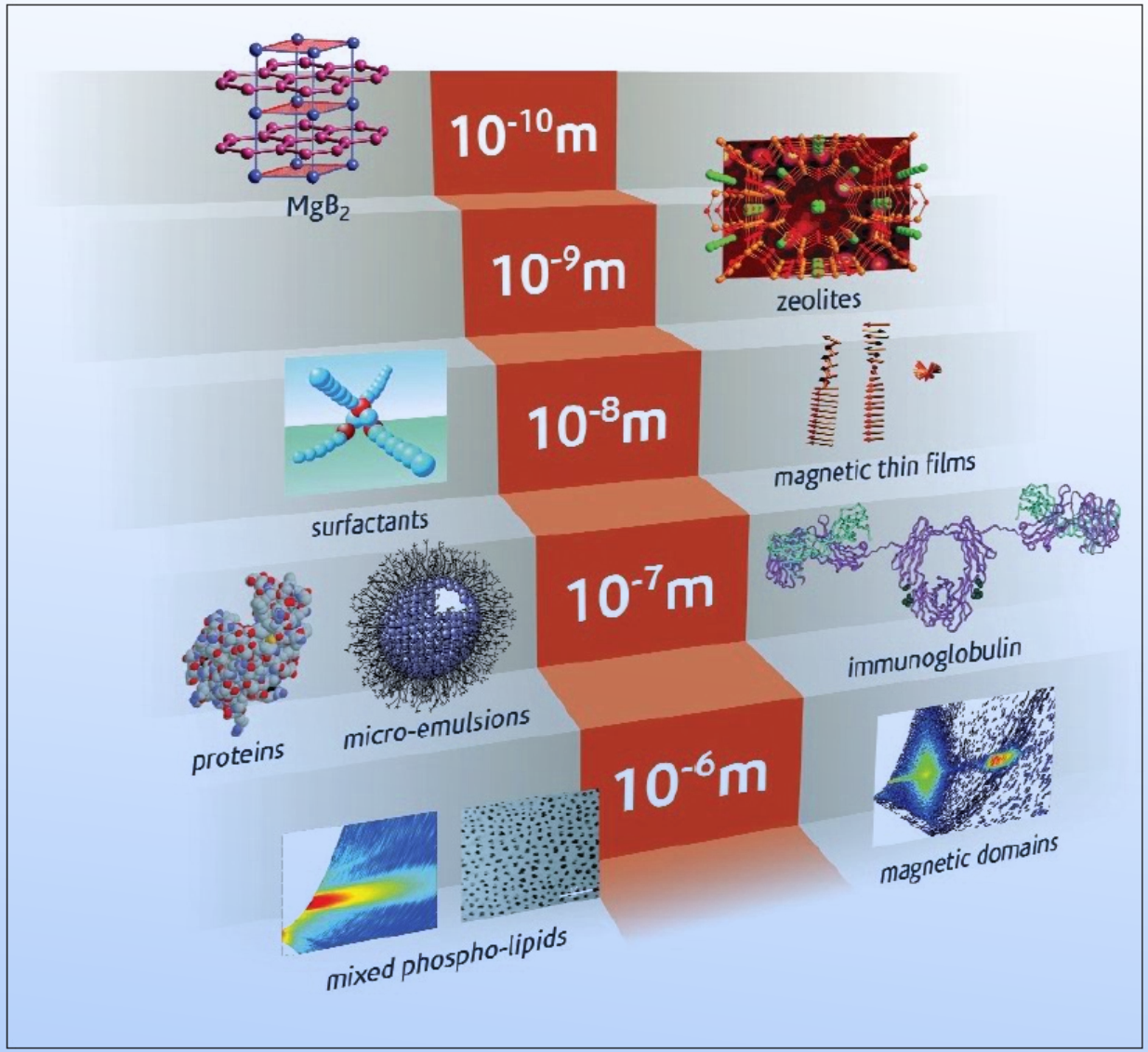
# Dostępne zakresy czasowe i przestrzenne



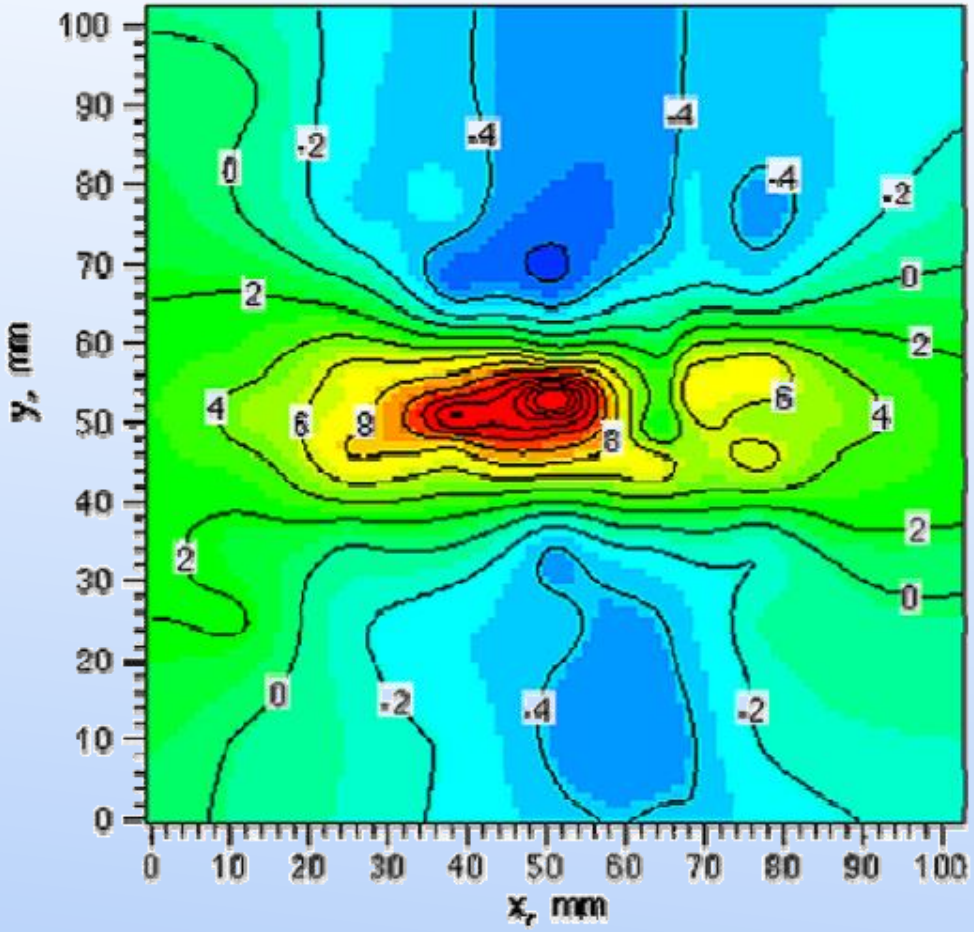



# Co badamy i w jakich skalach



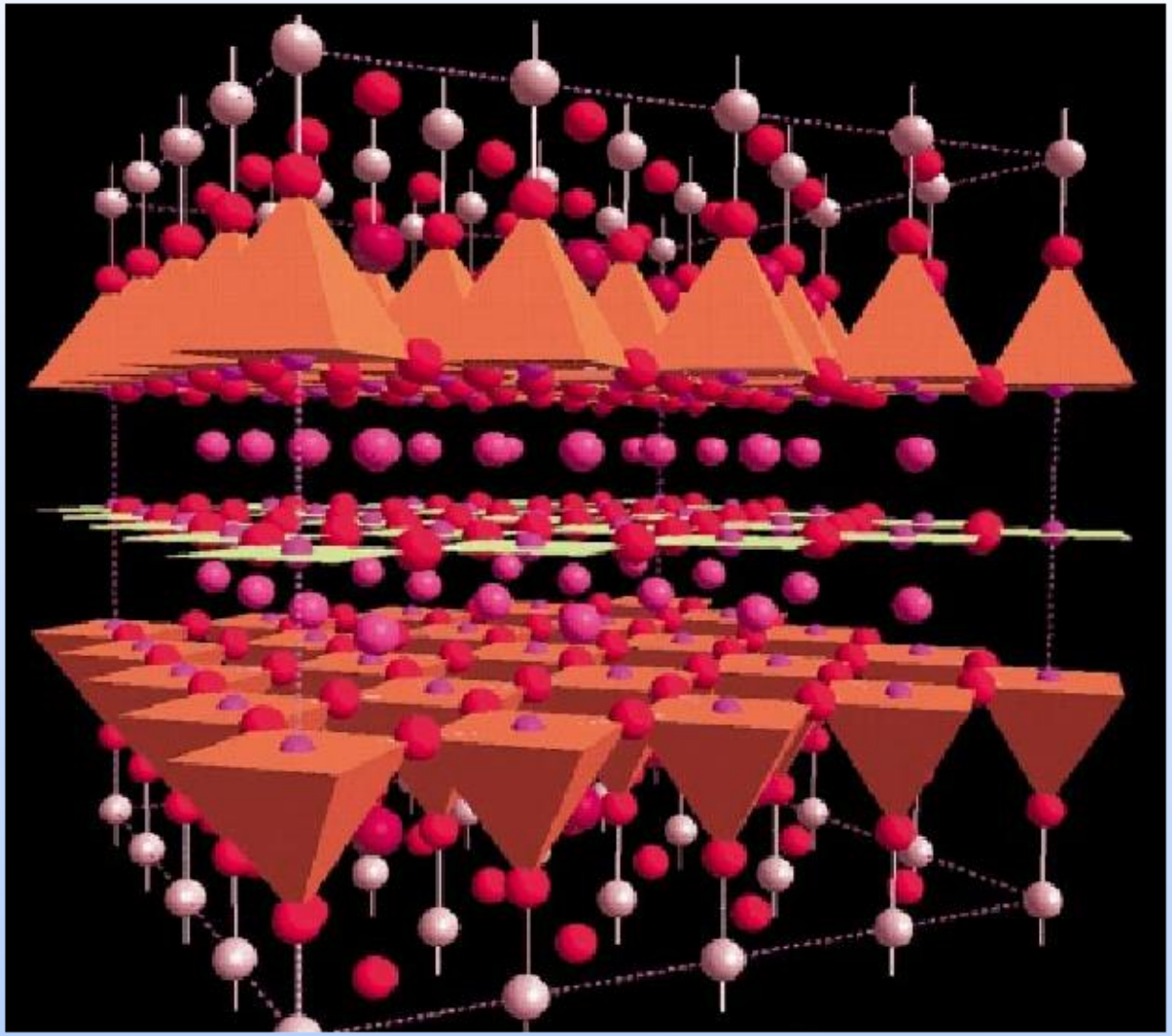



# Naprężenia resztkowe w połączeniach spawanych



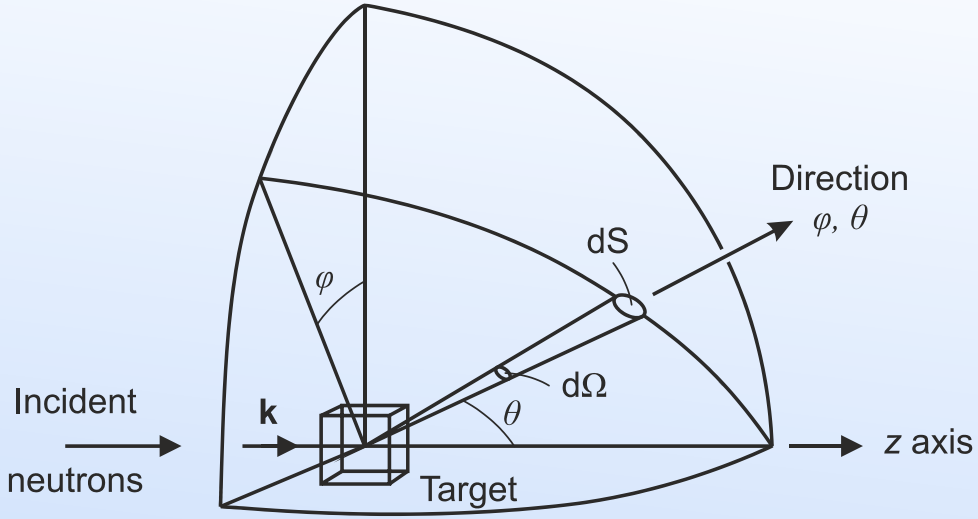

Nowoczesny przemysł lotniczy – połączenia spawane zamiast nitowanych

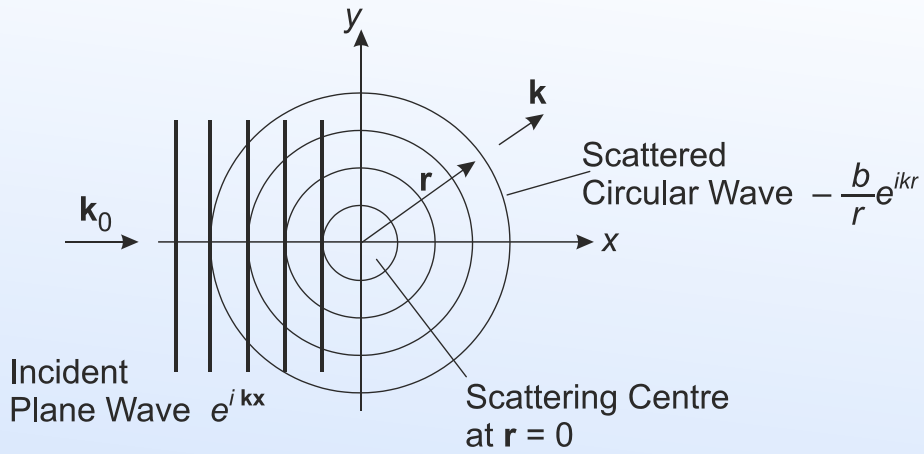
# Wysokotemperaturowe nadprzewodniki

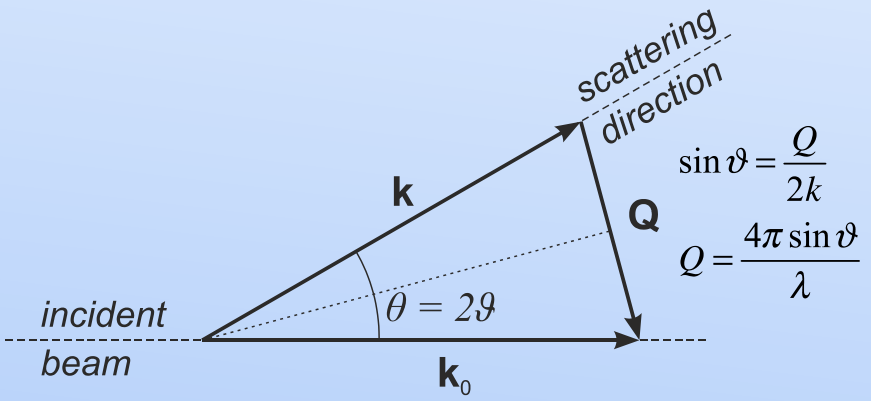


Bardzo istotna znajomość
Położeń atomów tlenu.
Pozwala je określić
**dyfrakcja neutronów**

# Rozpraszanie neutronów –geometria eksperymentu



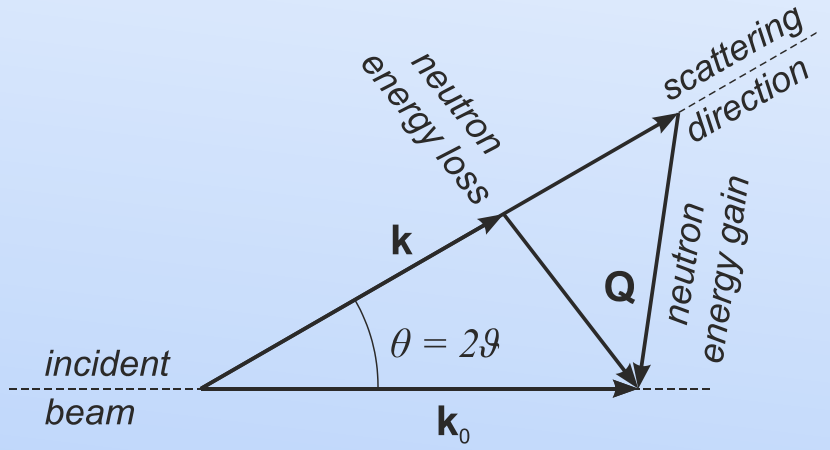




$$\sin\vartheta = \frac{Q}{2k}$$

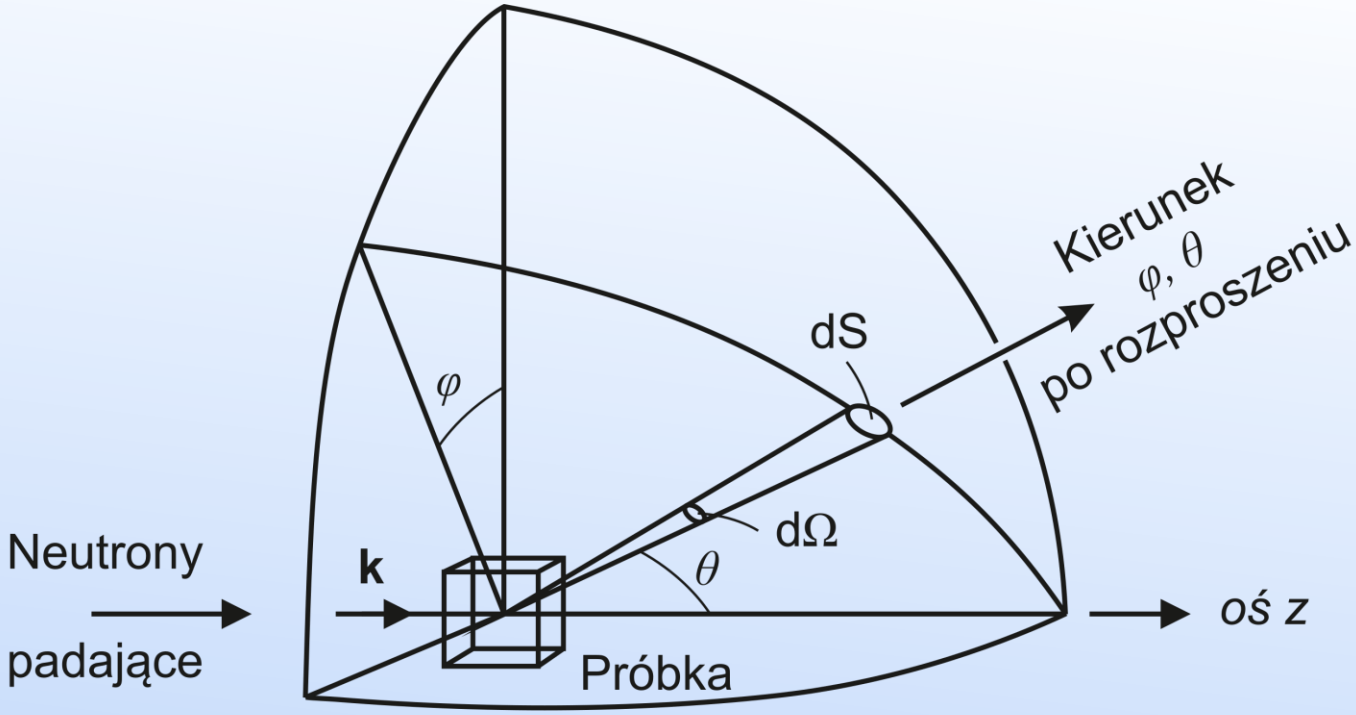
$$Q = \frac{4\pi \sin\vartheta}{\lambda}$$

**Elastic scattering**



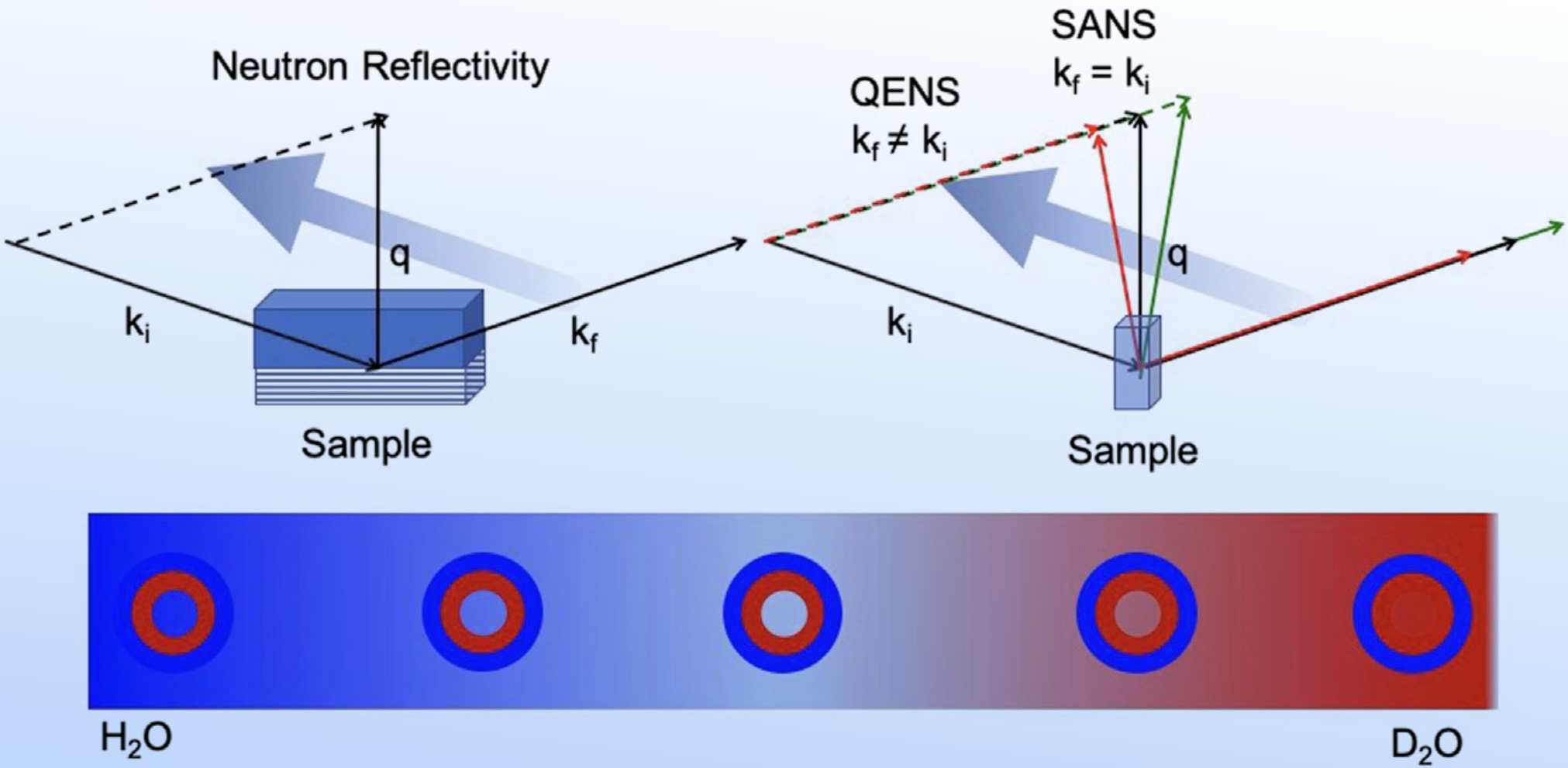

**Inelastic scattering**

# Rozpraszanie neutronów –geometria eksperymentu



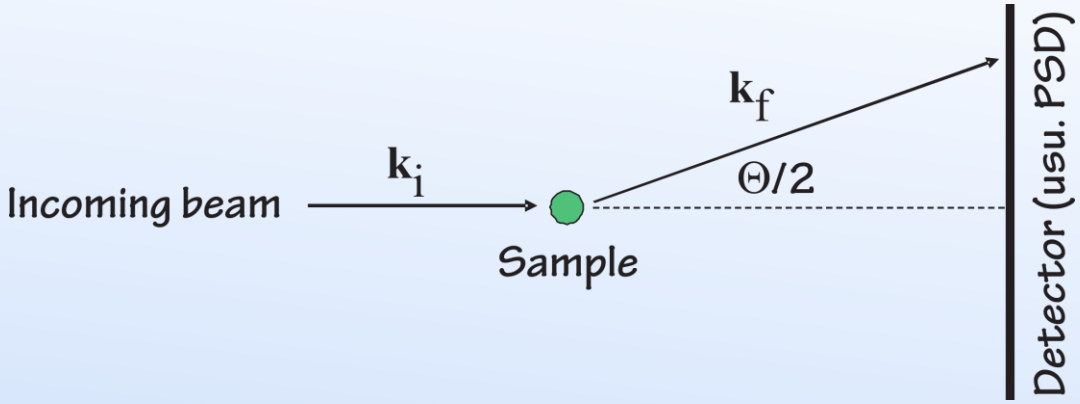

$$\frac{d\sigma}{d\Omega} = \sum_{i,j} \langle b_i^\star b_j \rangle \exp\left(i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right) = \underbrace{N\left(\bar{b^2} - (\bar{b})^2\right)}_{\text{spin incoherent}} + \underbrace{\bar{b}\sum_{i,j} \exp\left(i\mathbf{Q}\cdot(\mathbf{r}_i - \mathbf{r}_j)\right)}_{\text{spin coherent}}$$

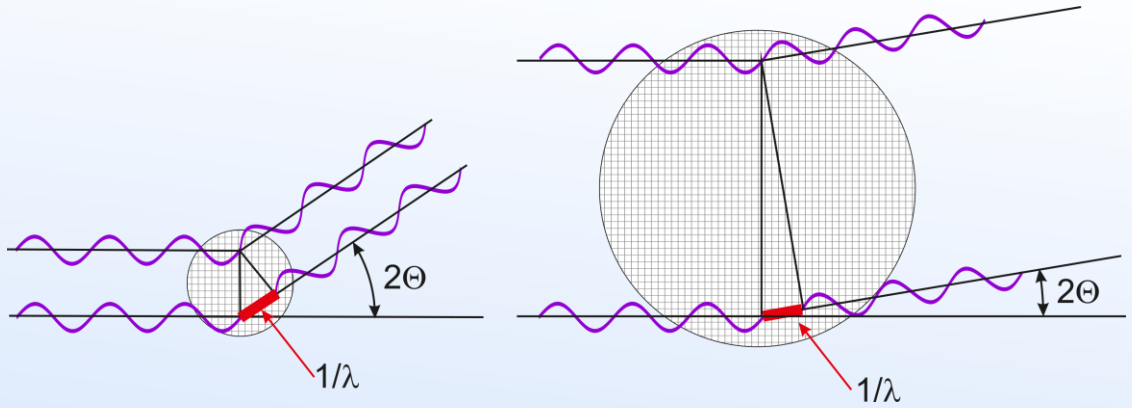
# Struktura i dynamika membran

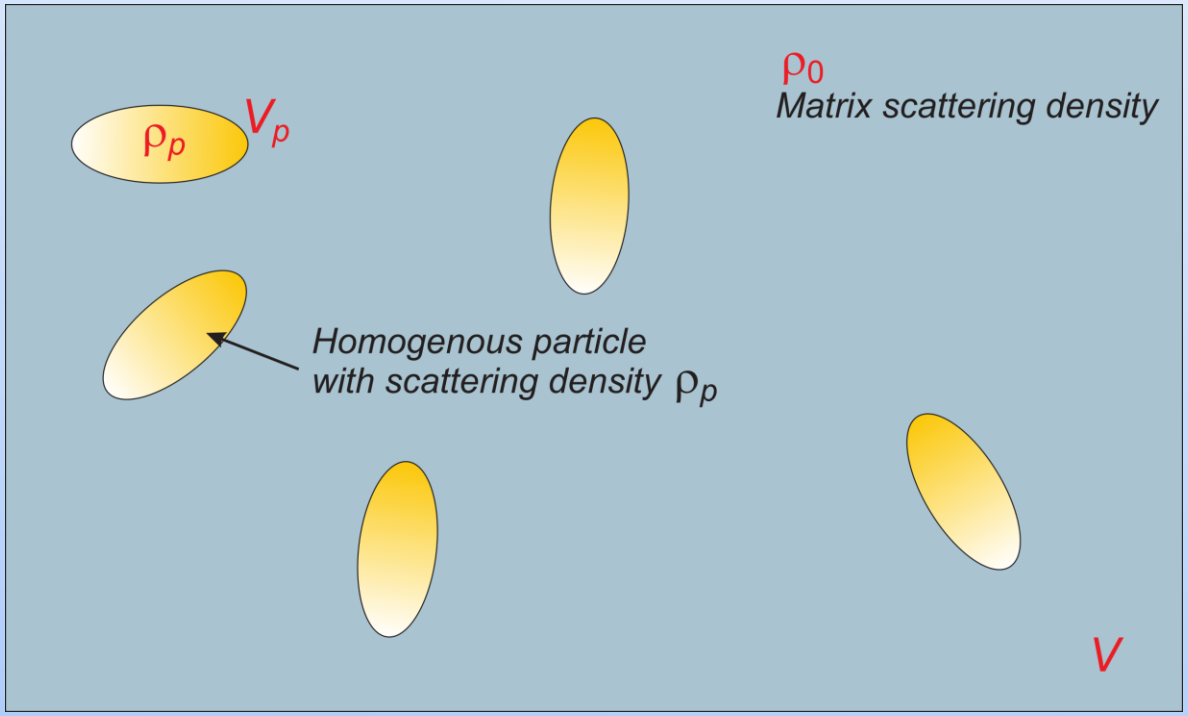


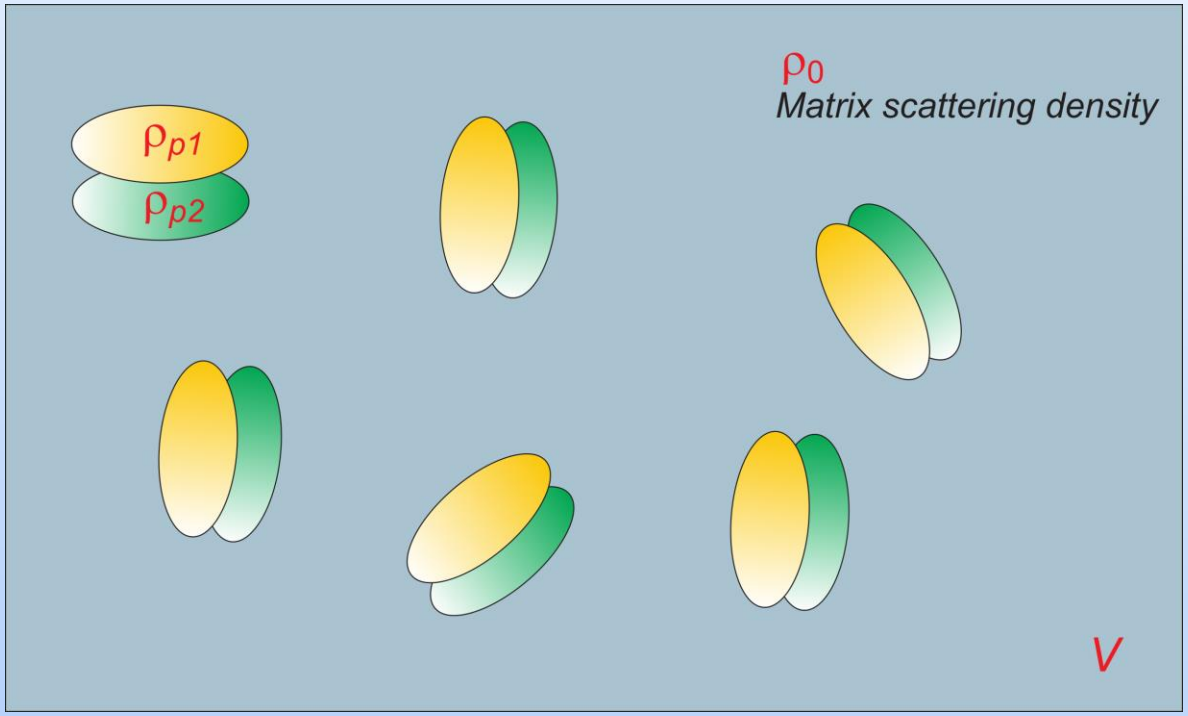

Samo-złożone *(sef-assembled)* membrany są wszechobecne (surfaktanty, fosfolipidy, systemy biologiczne). **Reflektometria** sonduje warstwową strukturę wgłębną, szorstkość, itp., **SANS** — strukturę objętościową, zaś **QENS** — dynamikę.
Nieocenione jest przy tym podstawienie izotopowe, tak w badaniach strukturalnych, jak w dynamicznych.

# SANS – badanie struktur „wielkoskalowych”

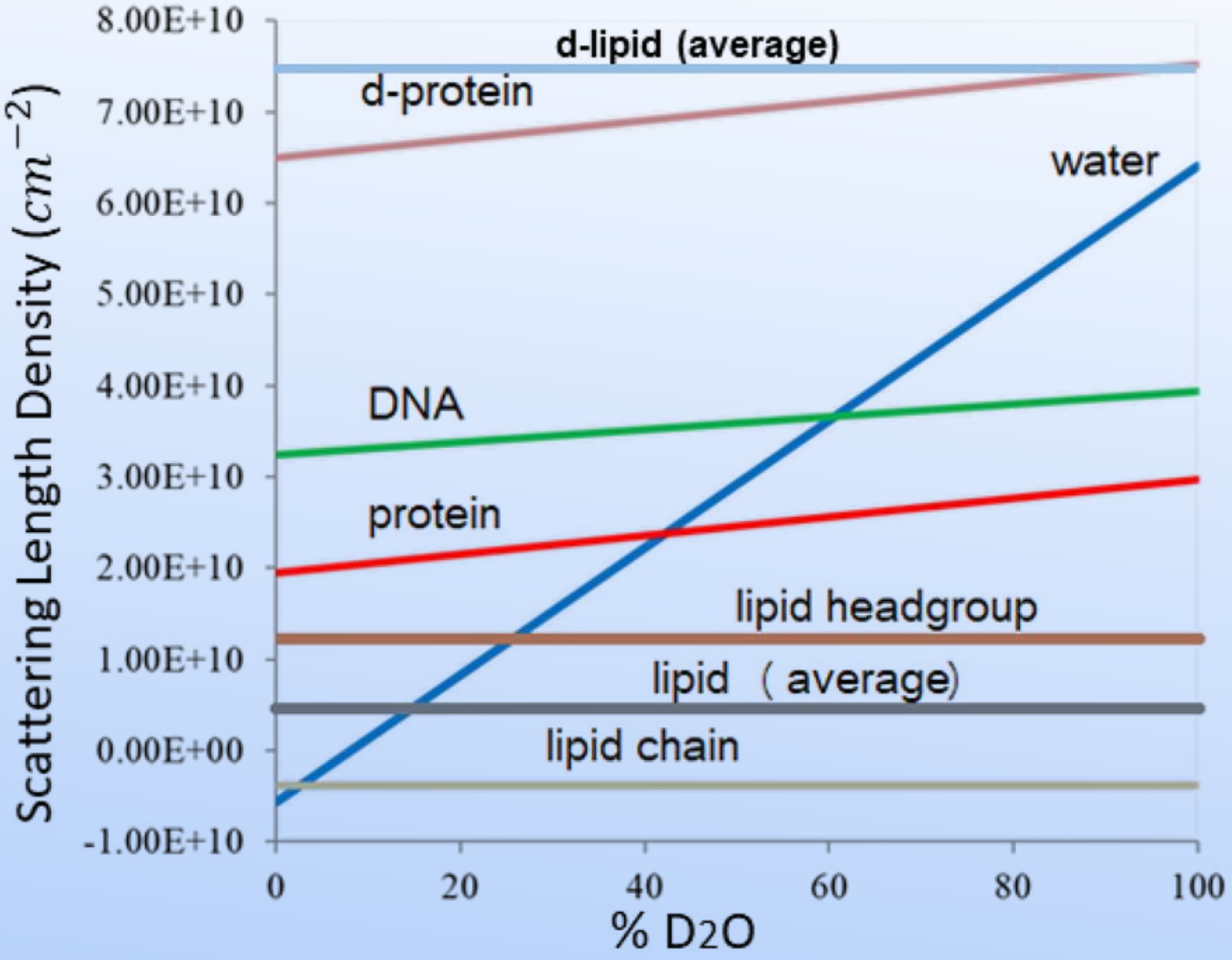


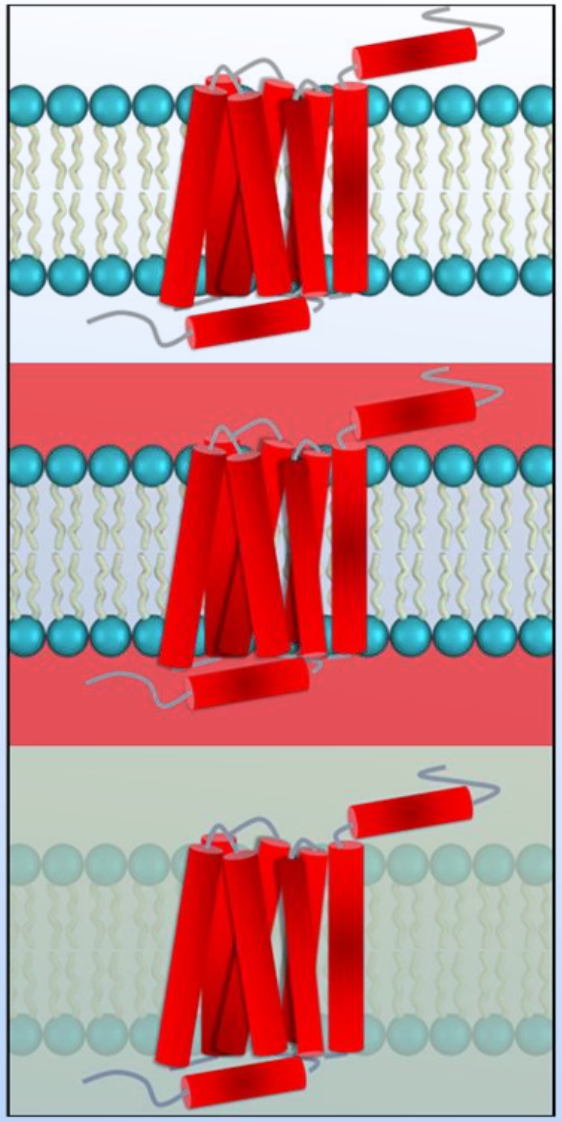



# Jeszcze o podstawieniu izotopowy w badaniu membran

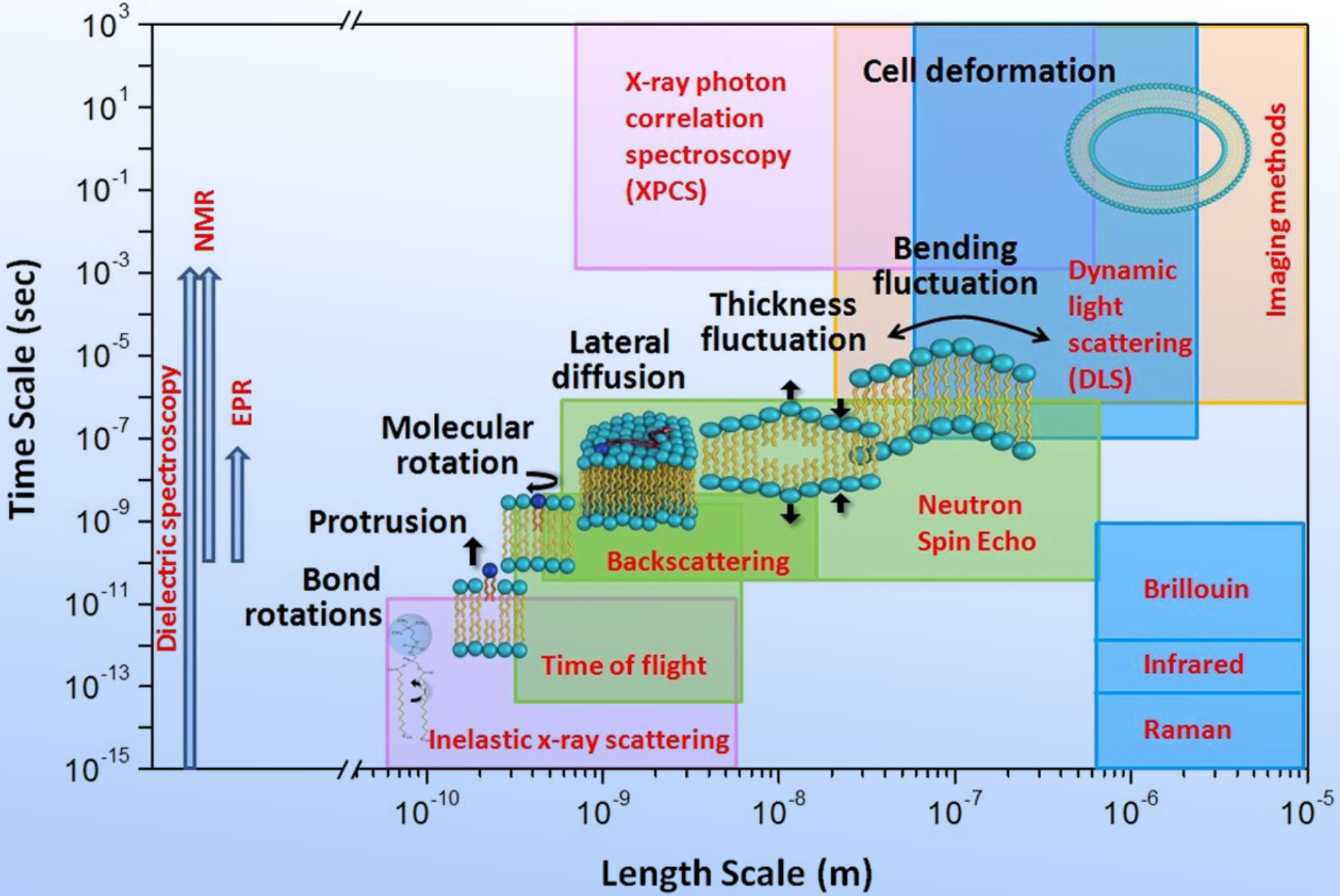



A

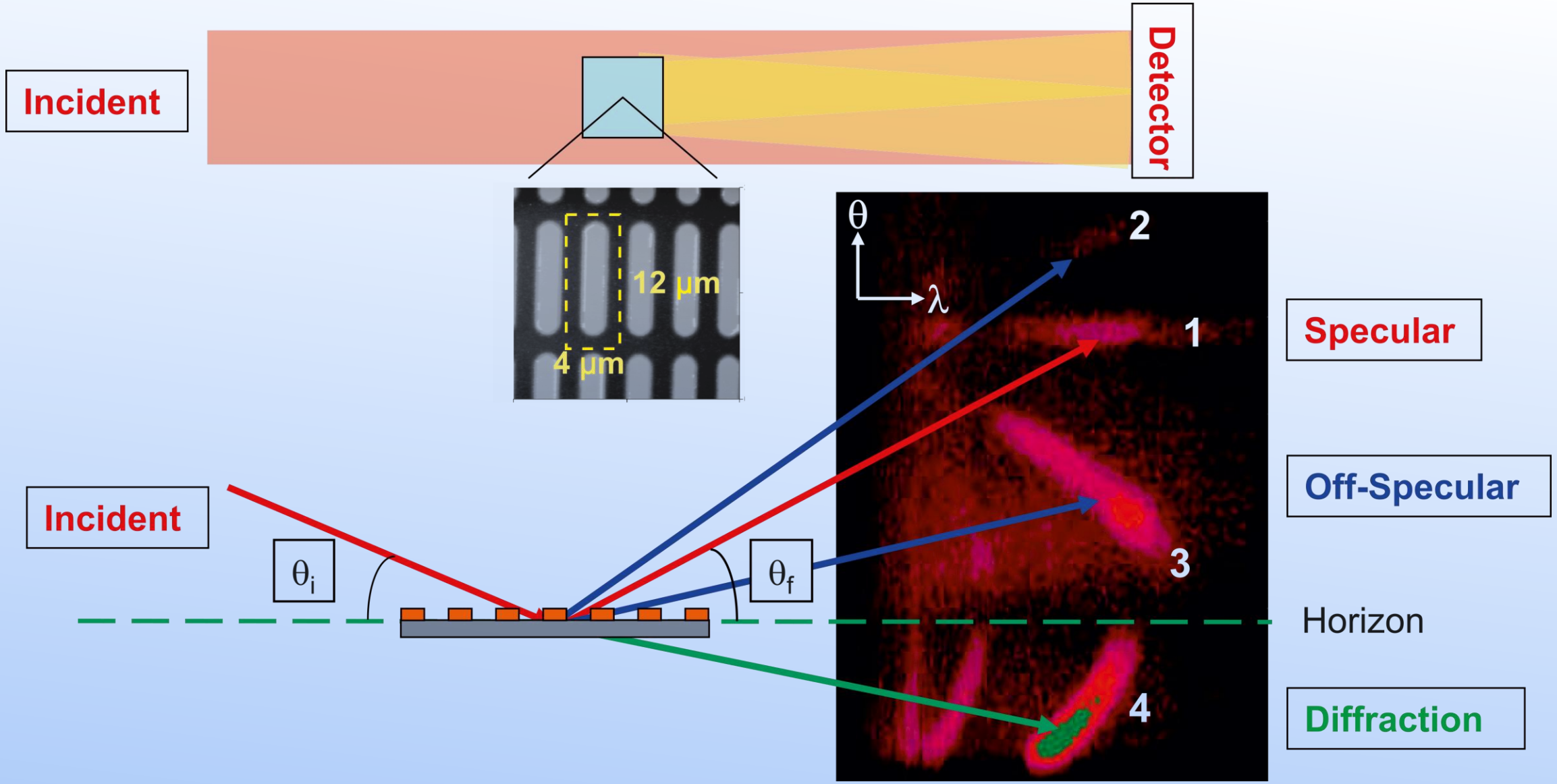


B

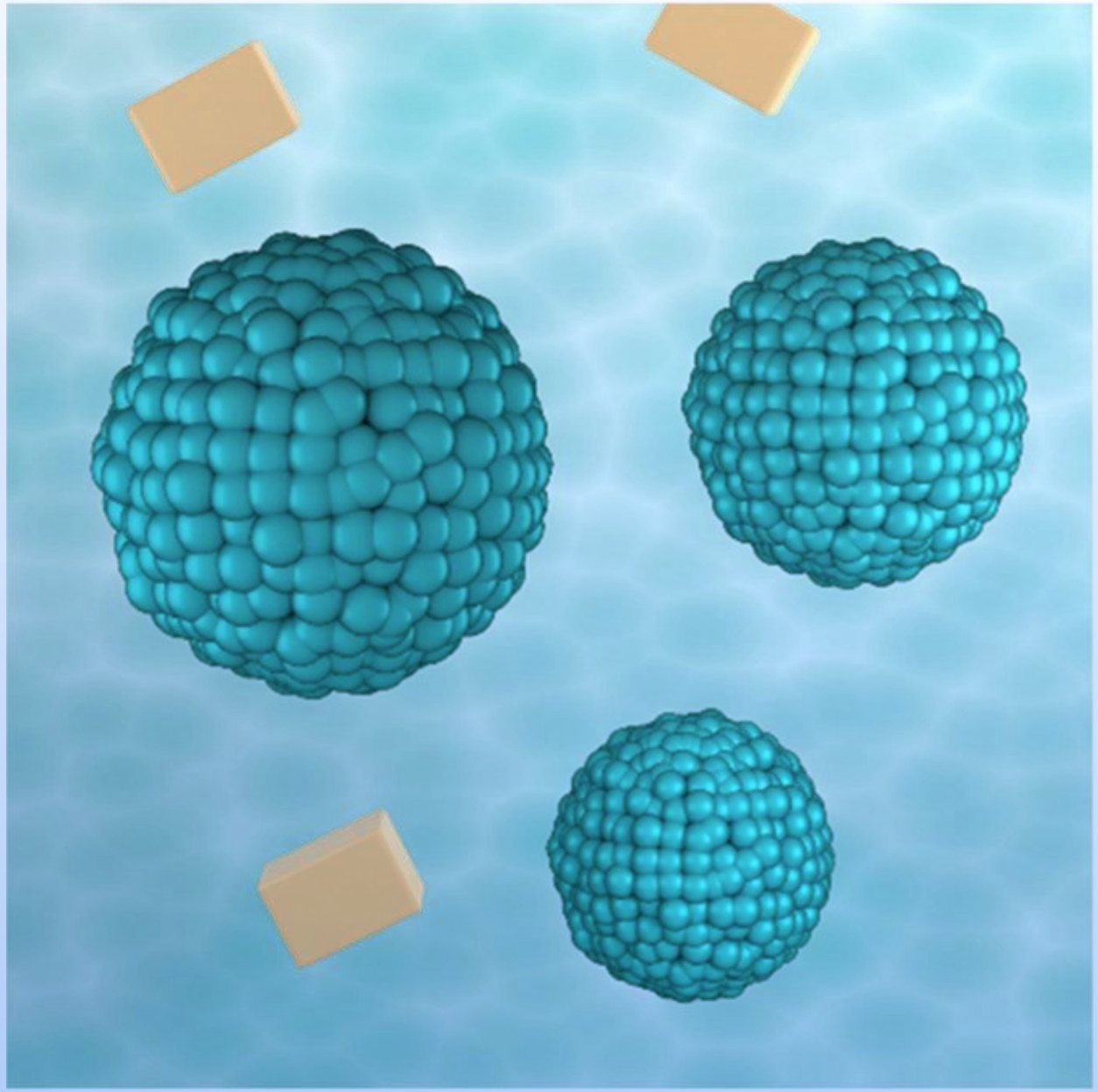
# Dynamika membran

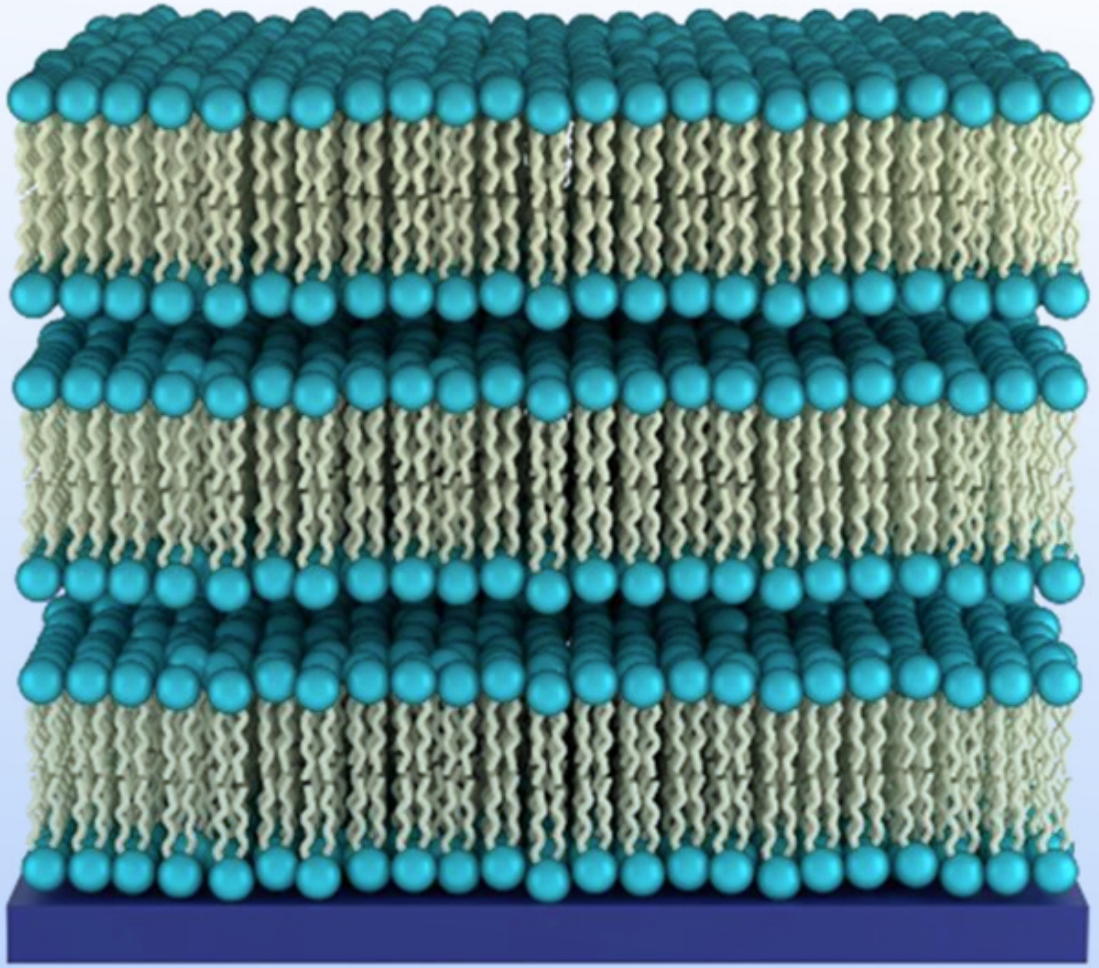


# Spin Echo Small Angle Measurement (SESAME)



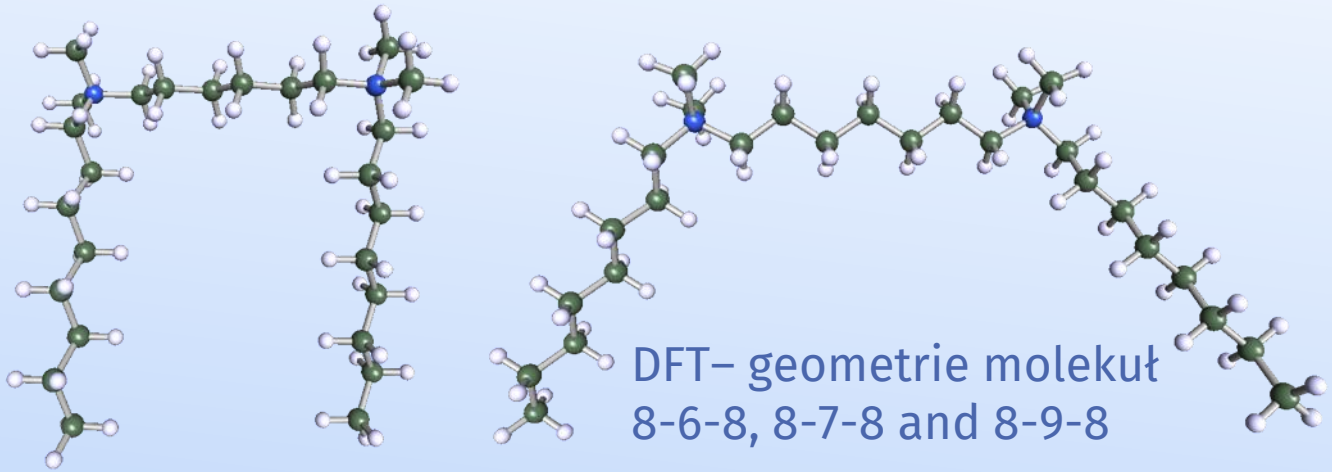
# SANS – badanie struktur „wielkoskalowych”



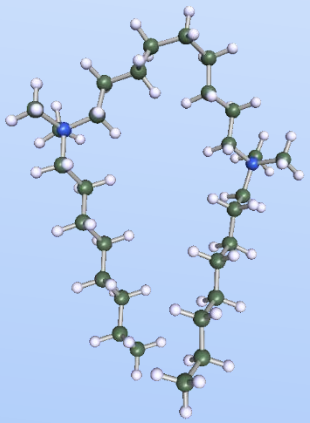


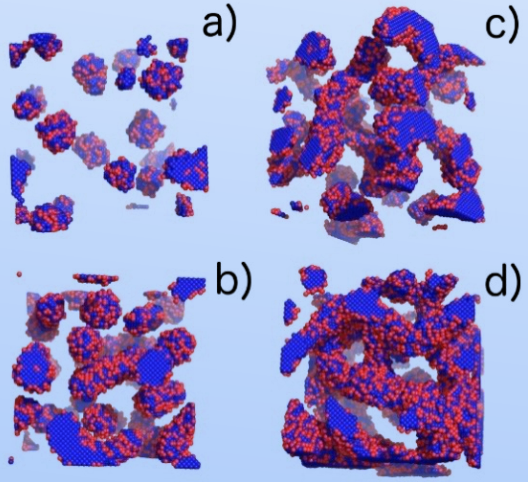
# Micelizacja „bliźniaczych” surfaktantów *(gemini surfactants)*

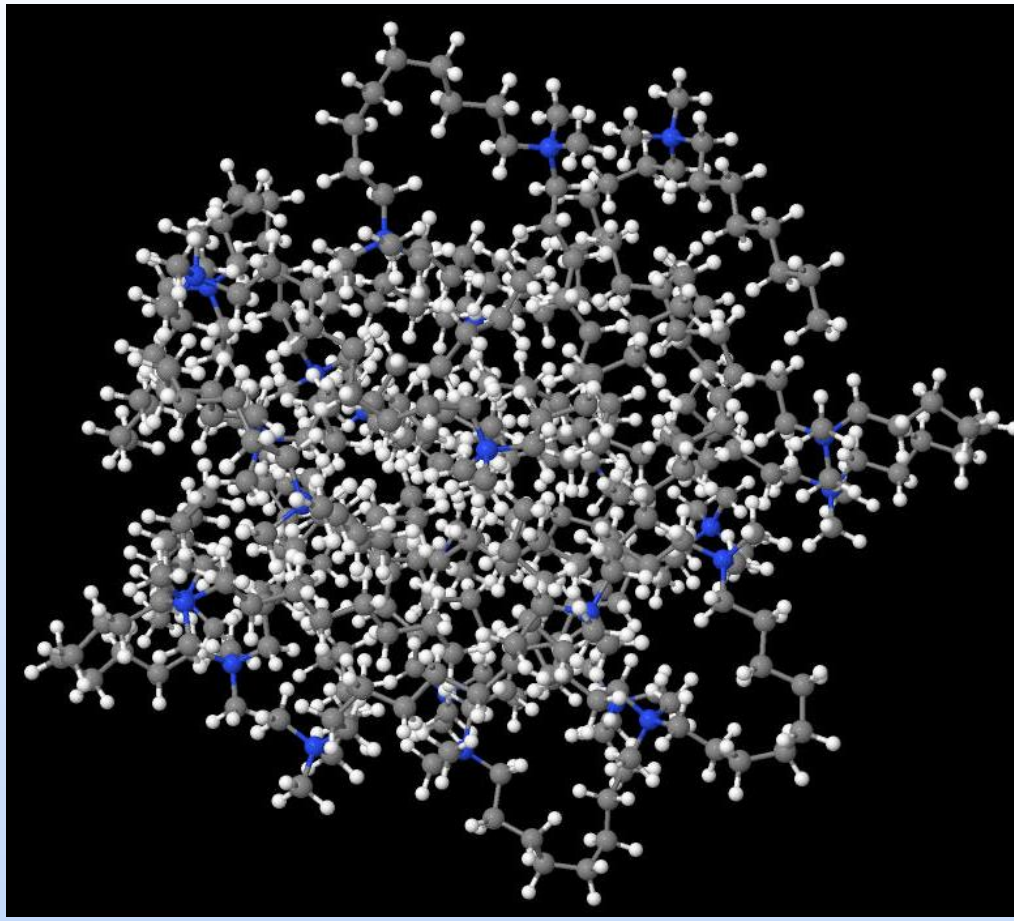
K. Łudzik, S. Wołoszczuk, W. Zając, M. Jażdżewska, A. Rogachev, A.I. Kuklin, et al. Can the Isothermal Calorimetric Curve Shapes Suggest the Structural Changes in Micellar Aggregates? Int. J. Mol. Sci. 2020, 21, 5828; doi:10.3390/ijms21165828



DFT– geometrie molekuł
8-6-8, 8-7-8 and 8-9-8

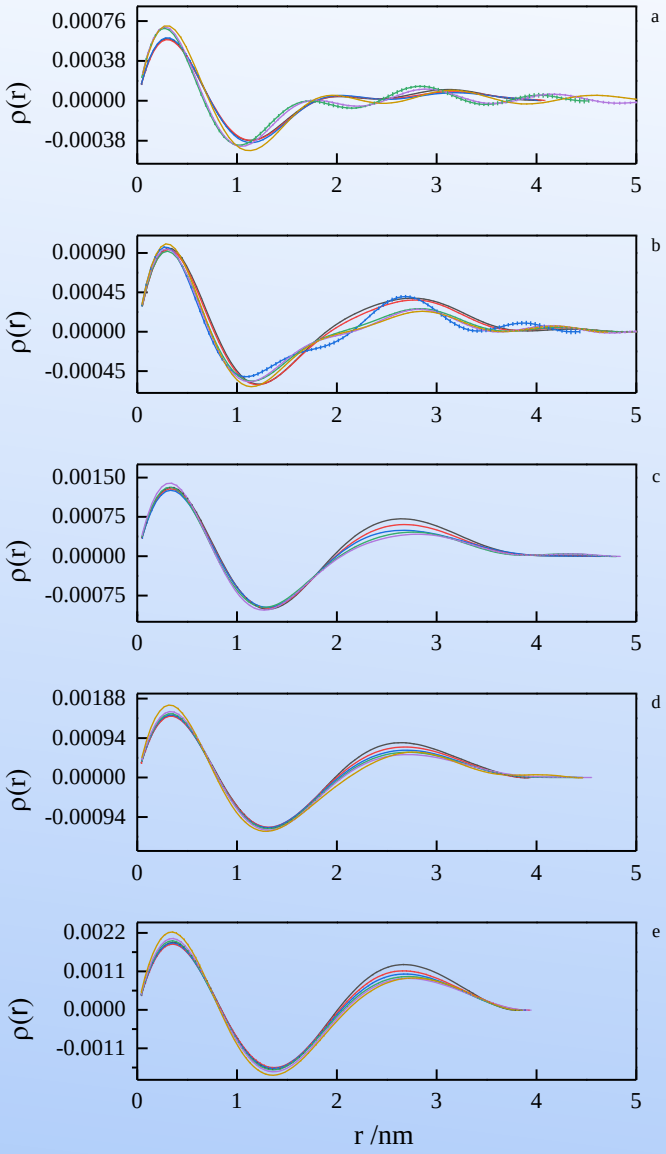


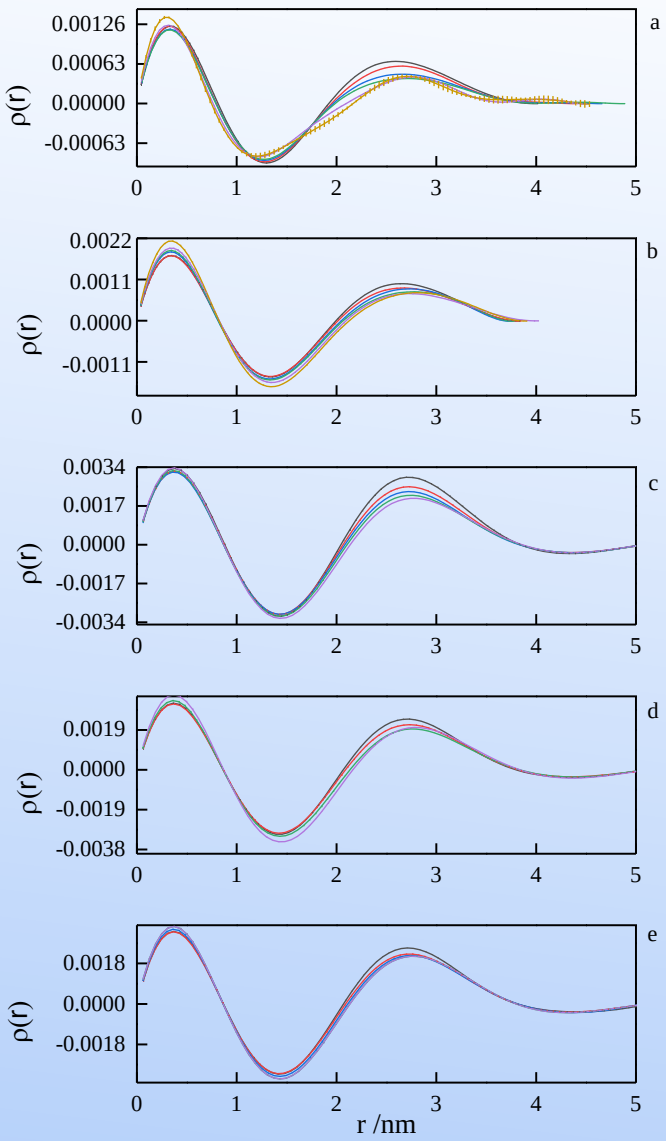


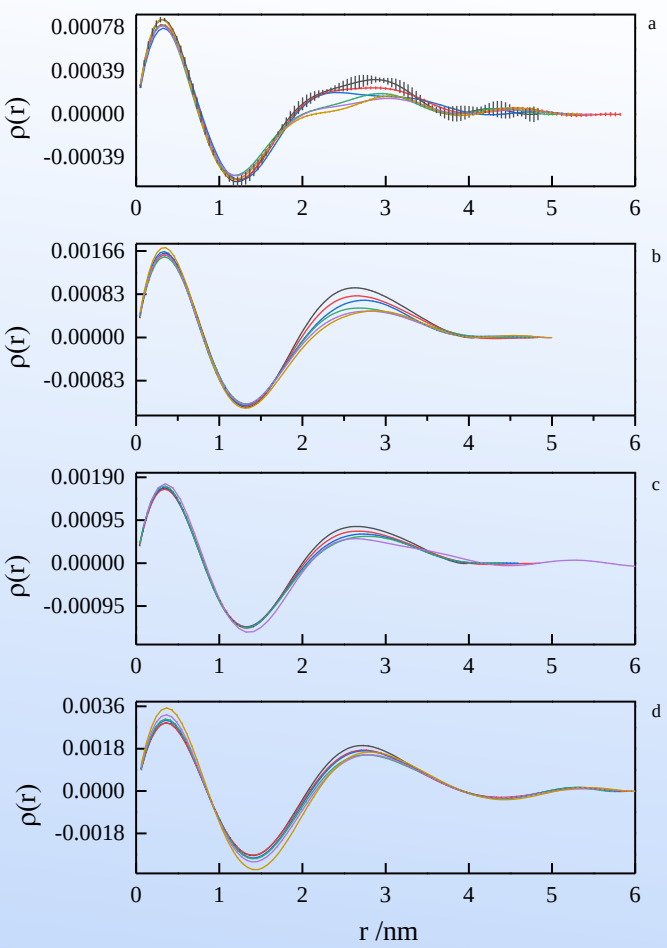



Symulacja komputerowa miceli of 8-9-8
*Conductor-like Screening Model (COSMO)*

# Micelizacja „bliźniaczych” surfaktantów *(gemini surfactants)*



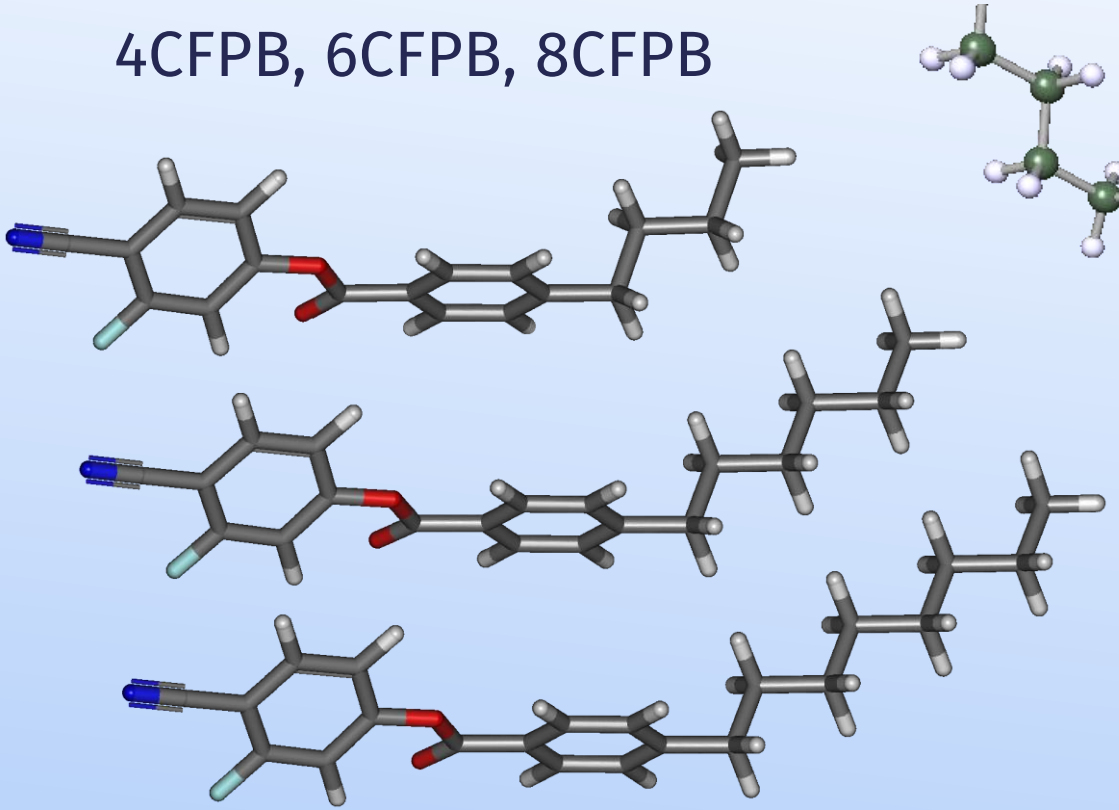

*Pair distance distribution functions (PDDF)* otrzymane z SAS przez pośrednią transformację Fouriera (IFT)

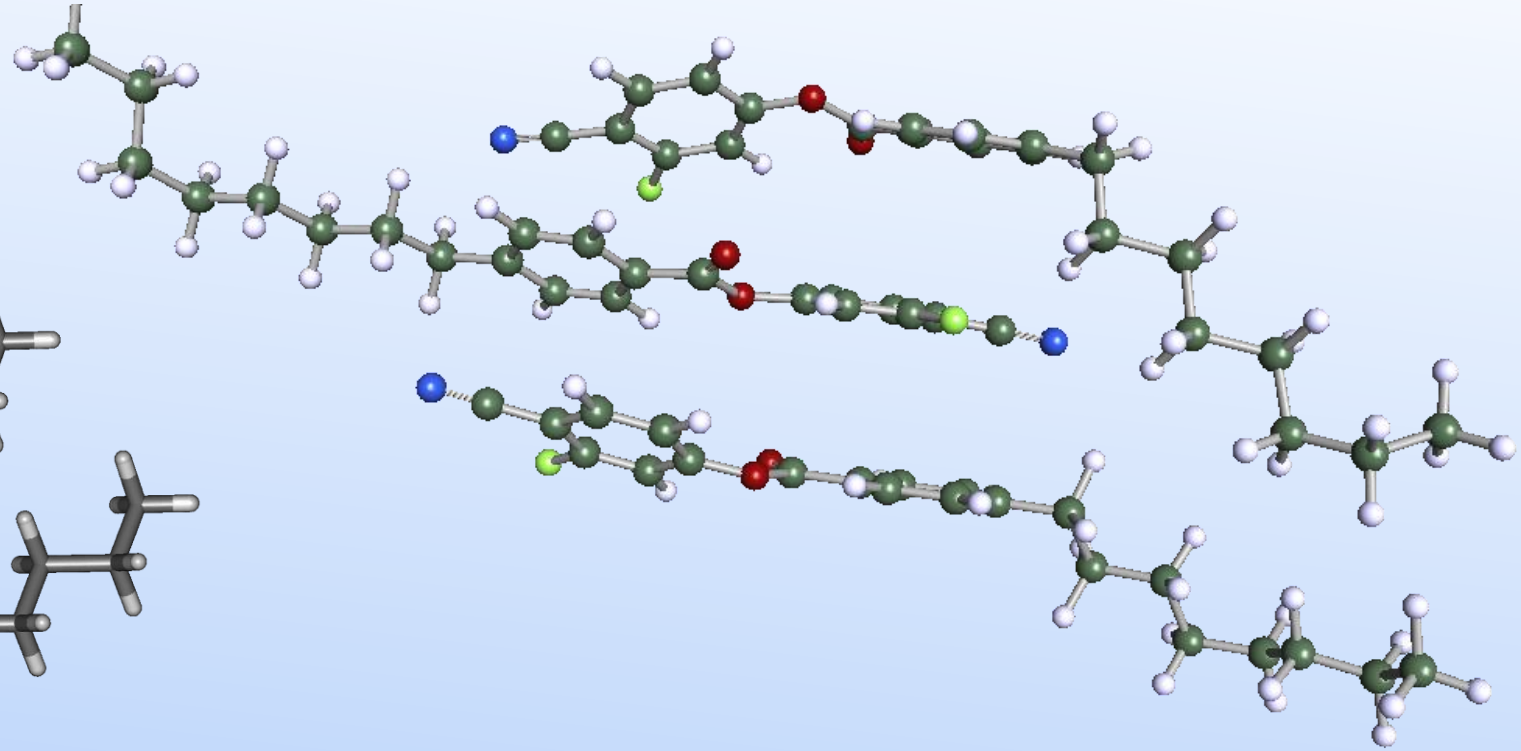
# Ciekły kryształ w nanoporach (membrany AAO)

E. Juszyńska-Gałązka, W. Zając, D. Soloviov

*To be published soon, further work in progress.*

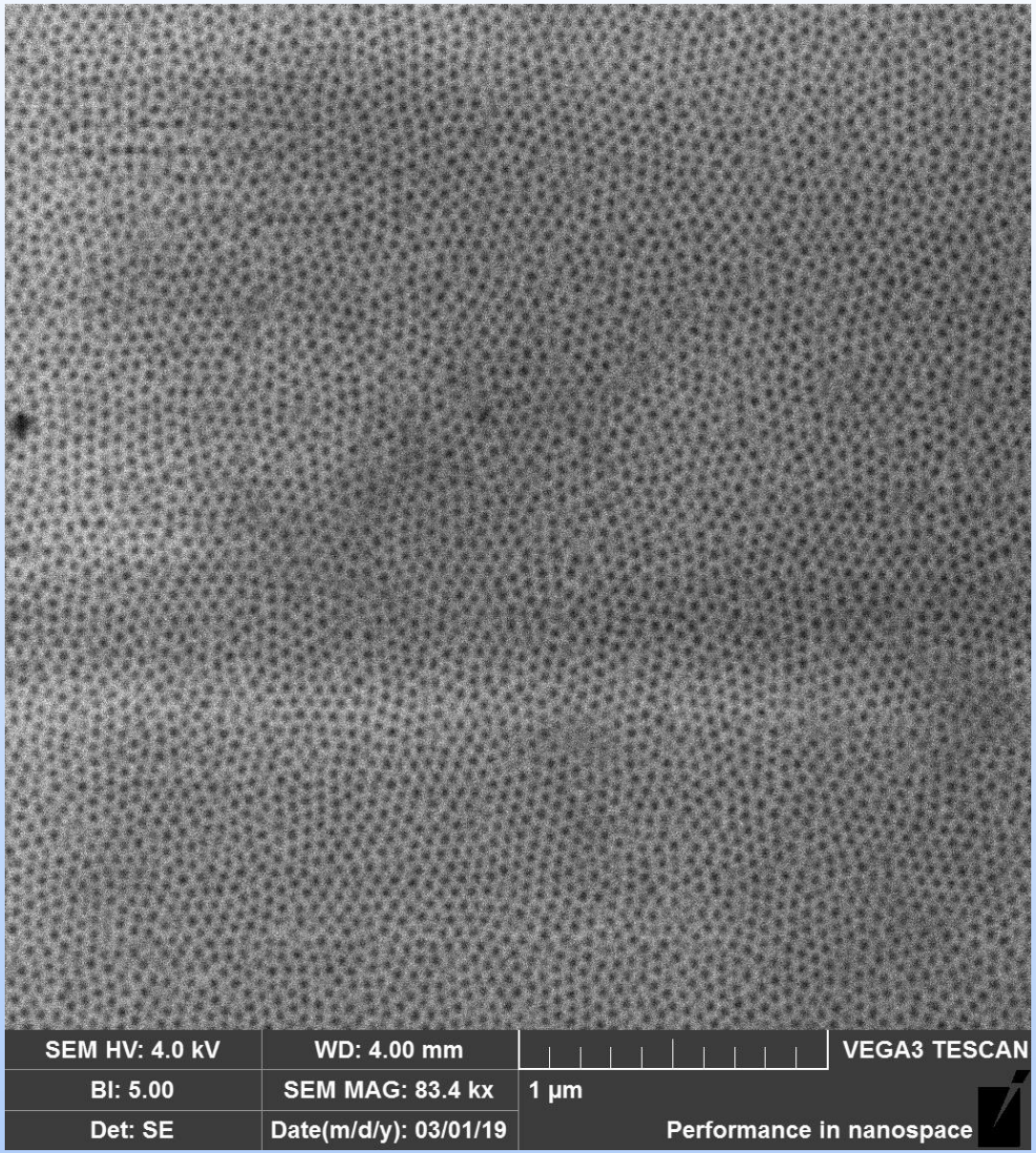
4CFPB, 6CFPB, 8CFPB

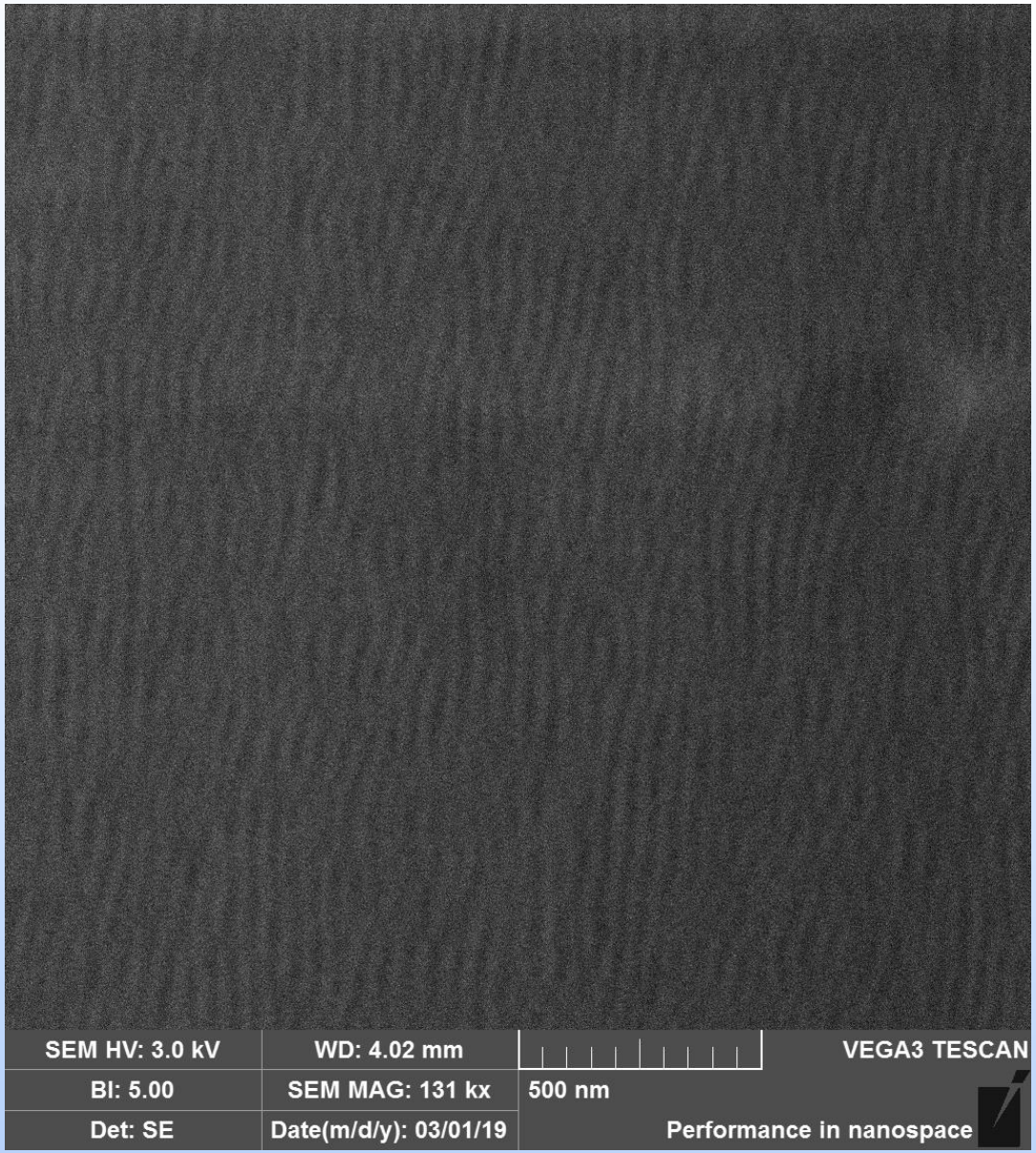




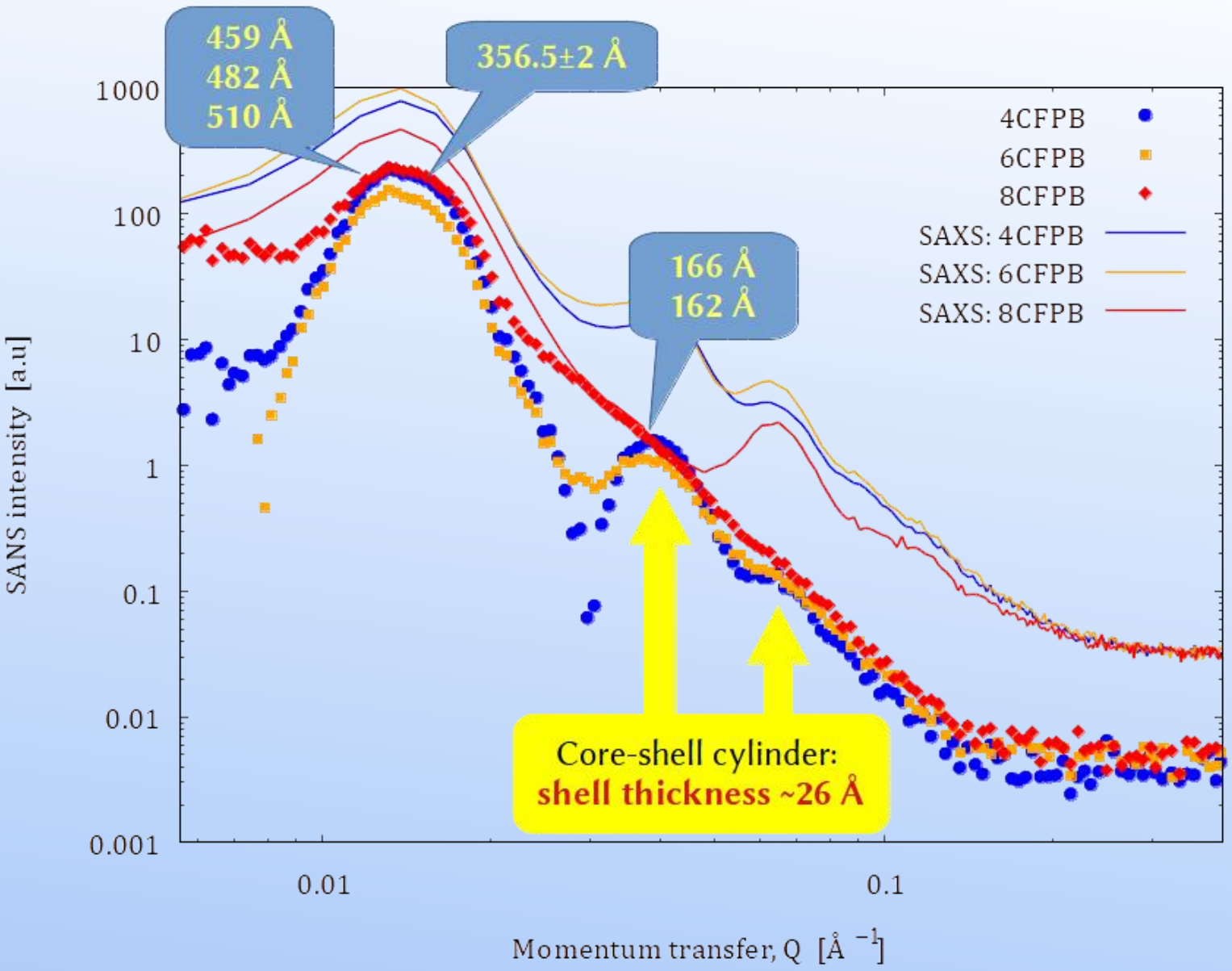
Tak porządkują się cząsteczki

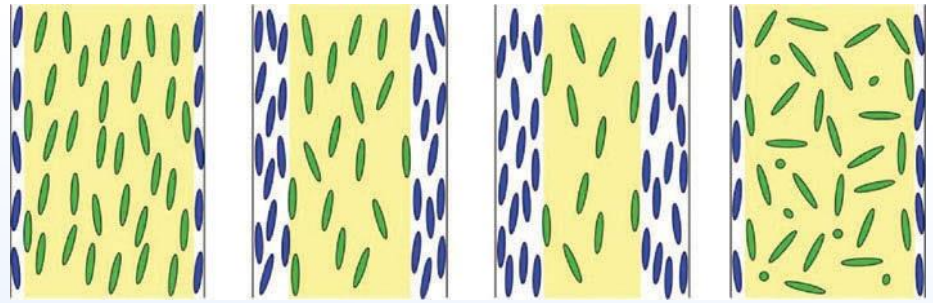
# Membrany AAO



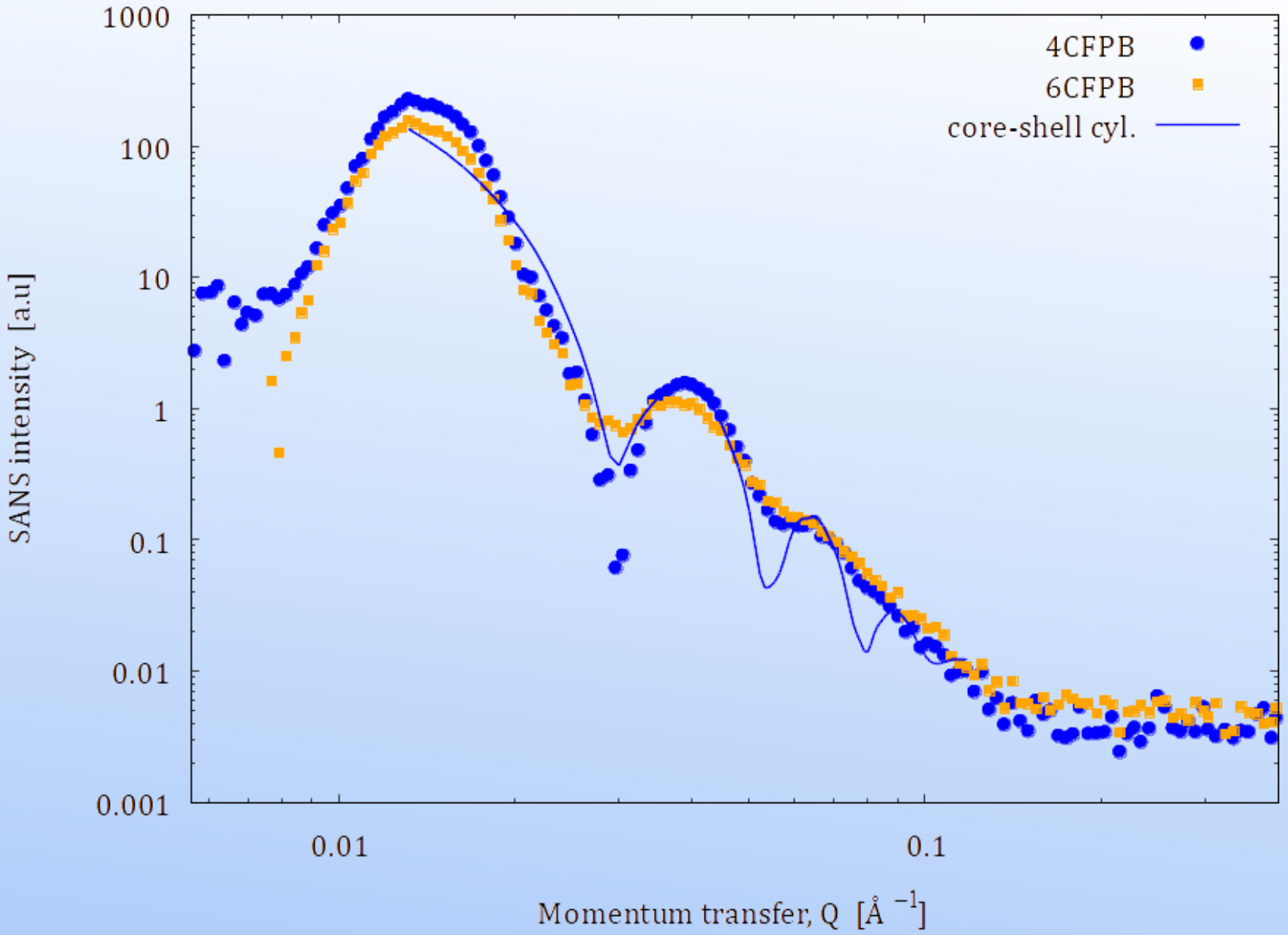
# Ciekły kryształ w nanoporach



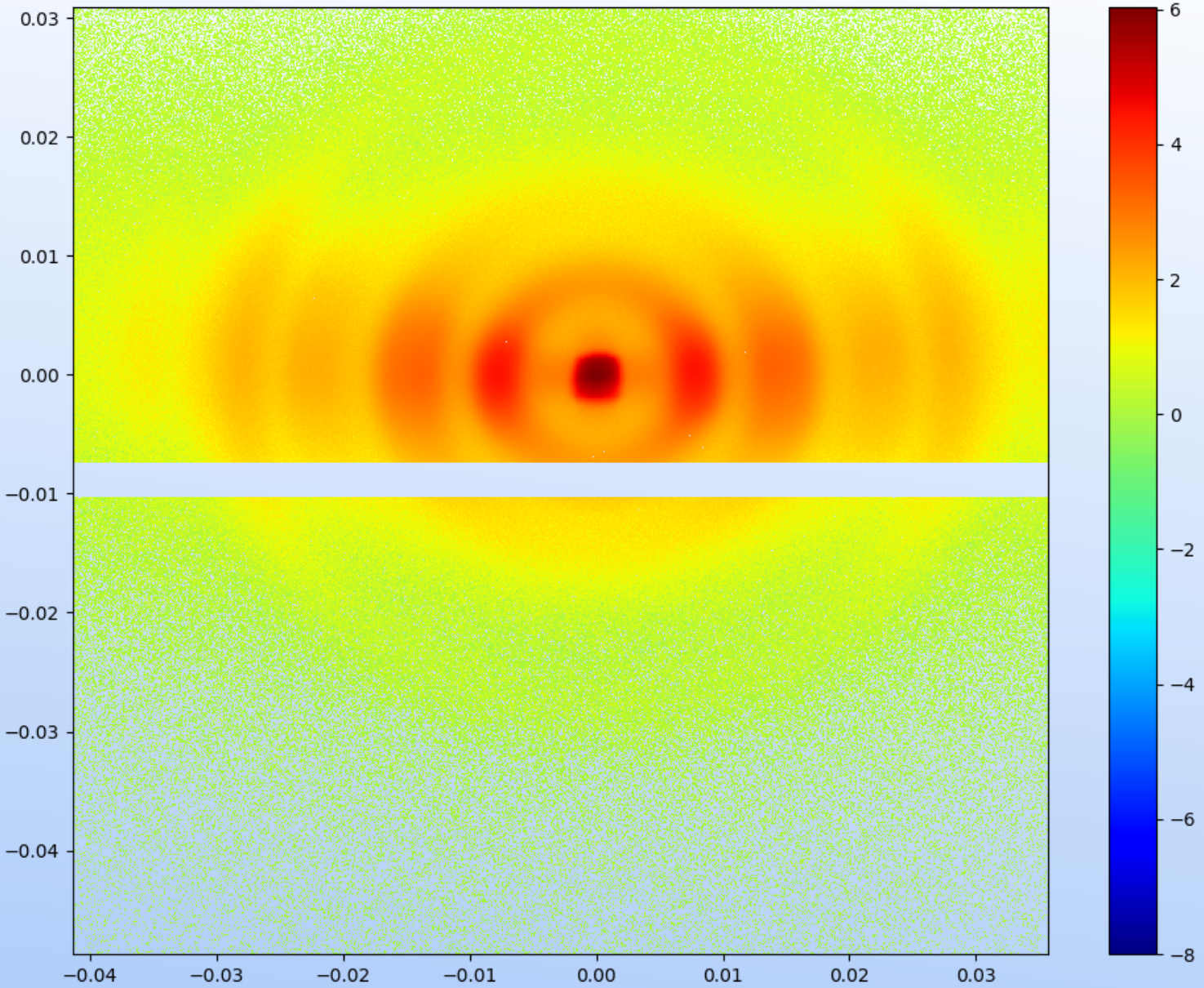
Przyścienna warstwa paranematyczna

# Ciekły kryształ w nanoporach – analiza danych SANS




Po odjęciu czynnika strukturalnego (brak efektów koherencji „międzycząsteczkowej”)

# Efekty absorpcji w pomiarach SAXS




BBOA
membrana 20nm, S-D: 4400mm

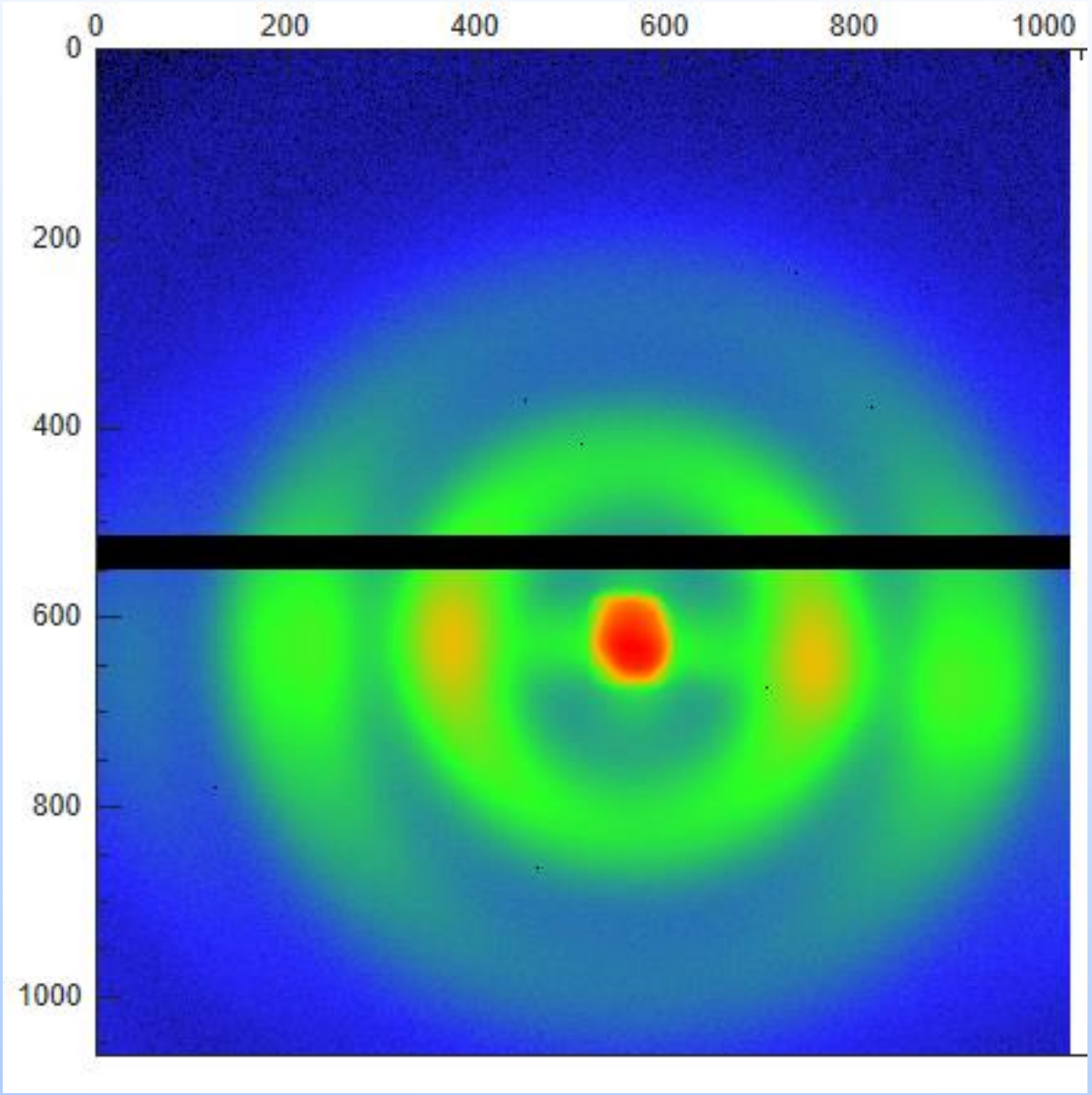
efekt pochylenia próbki
o kąt rzędu 0.5°

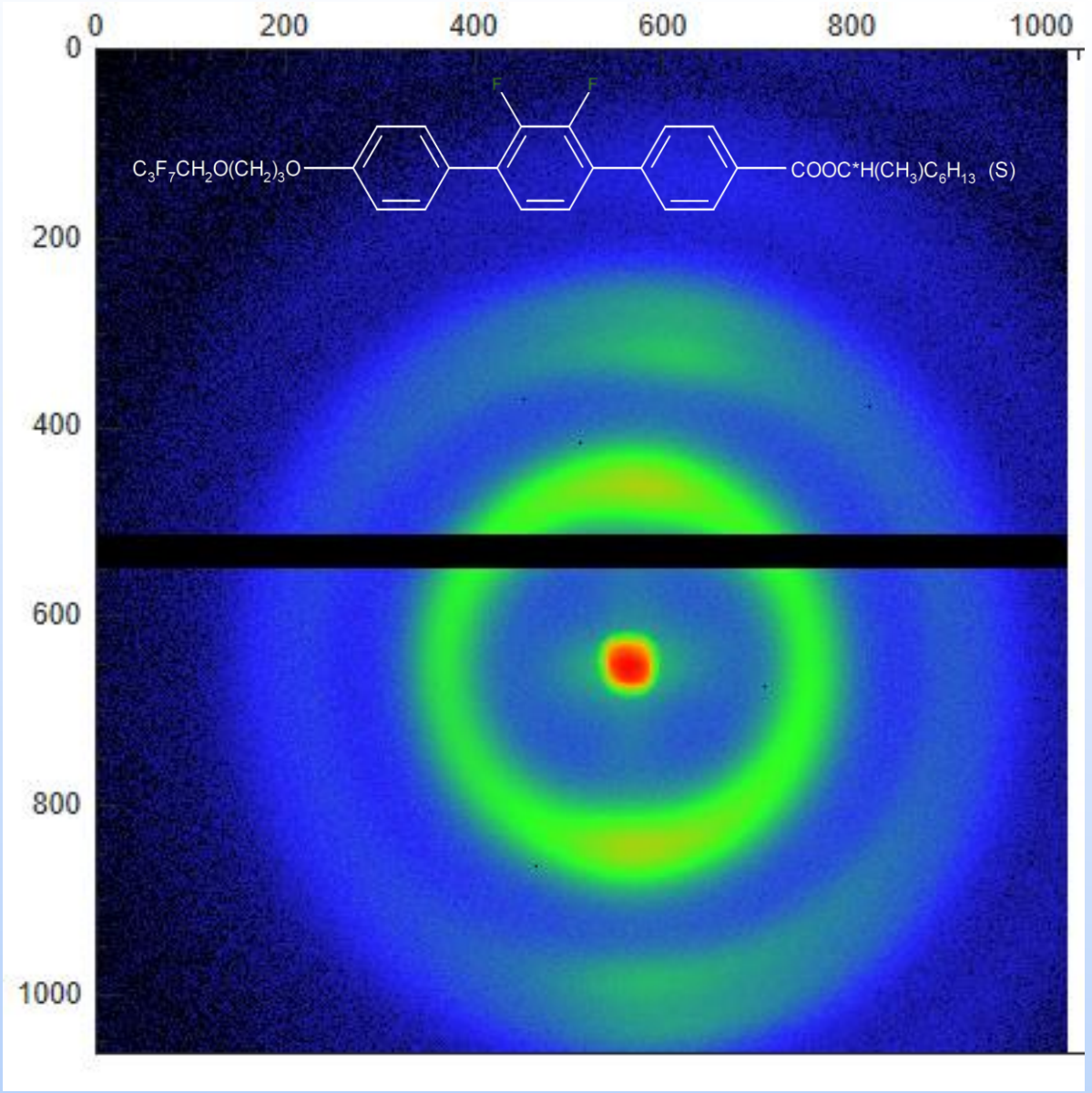
Problemy:

- orientacja próbki
- kontrast

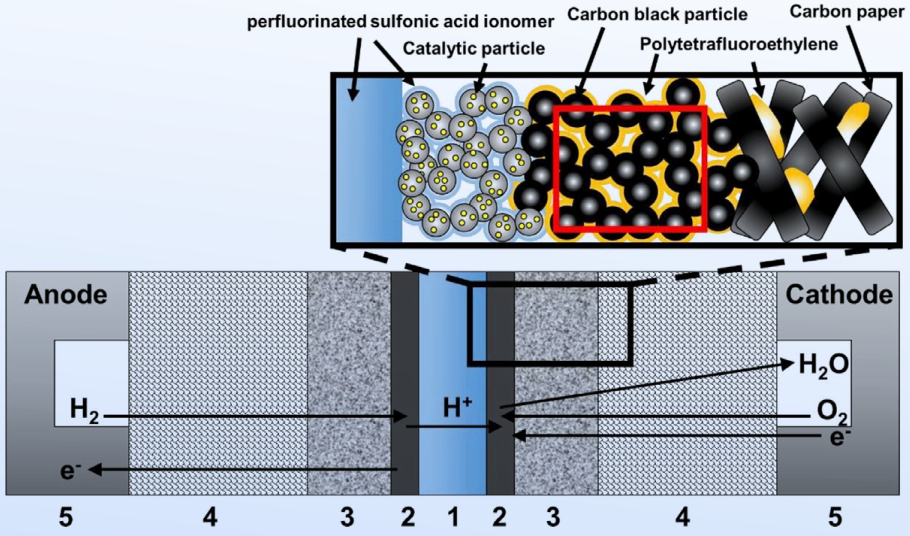
# Efekty absorpcji w pomiarach SAXS

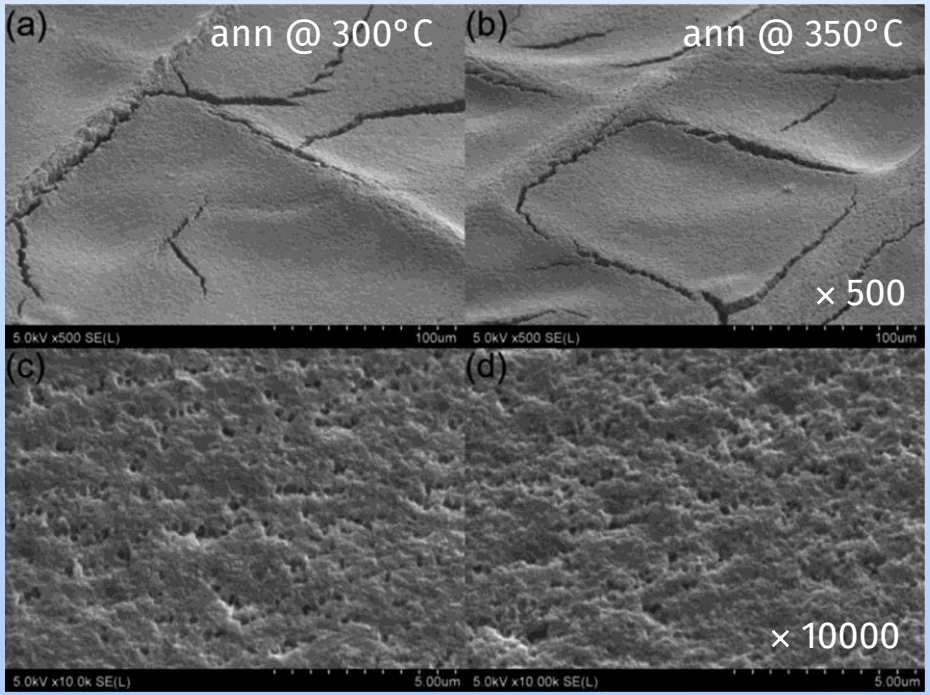
membrana 20nm, S-D: 4400mm



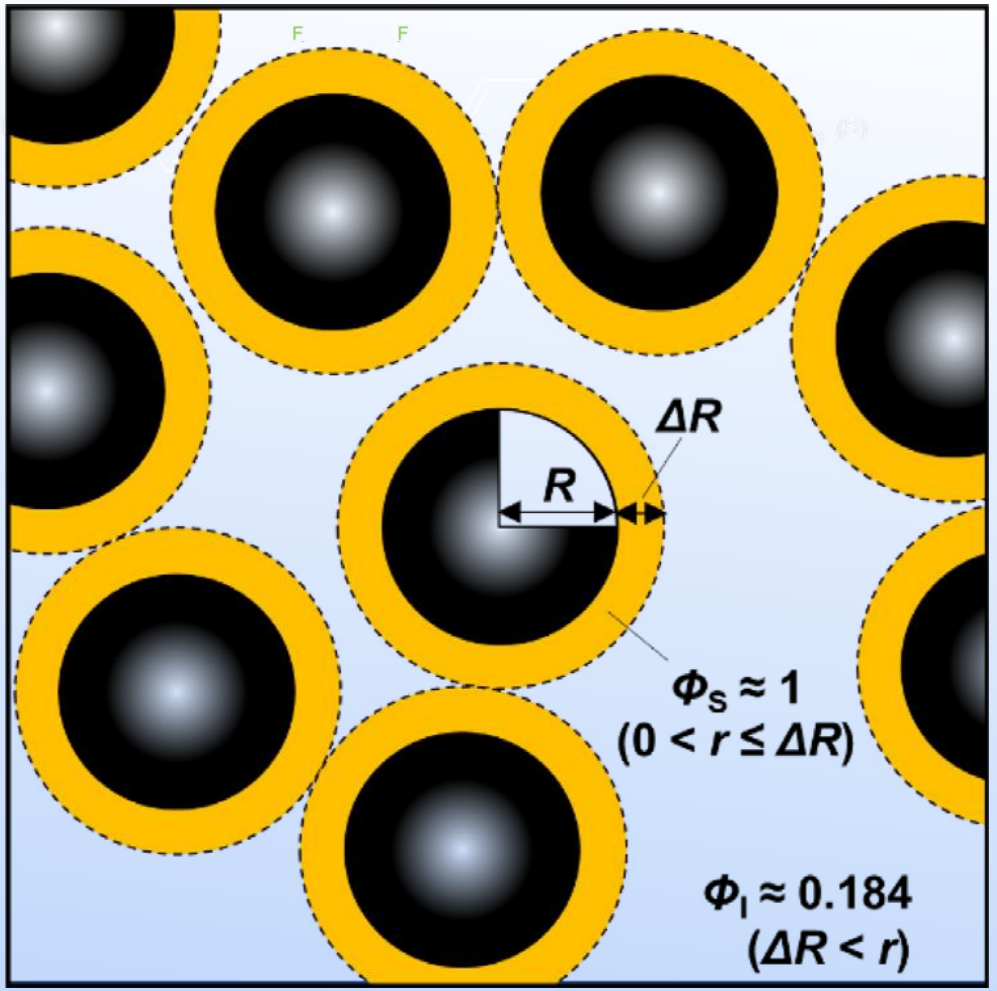
# Ogniwa paliwowe z elektrolitem polimerowym



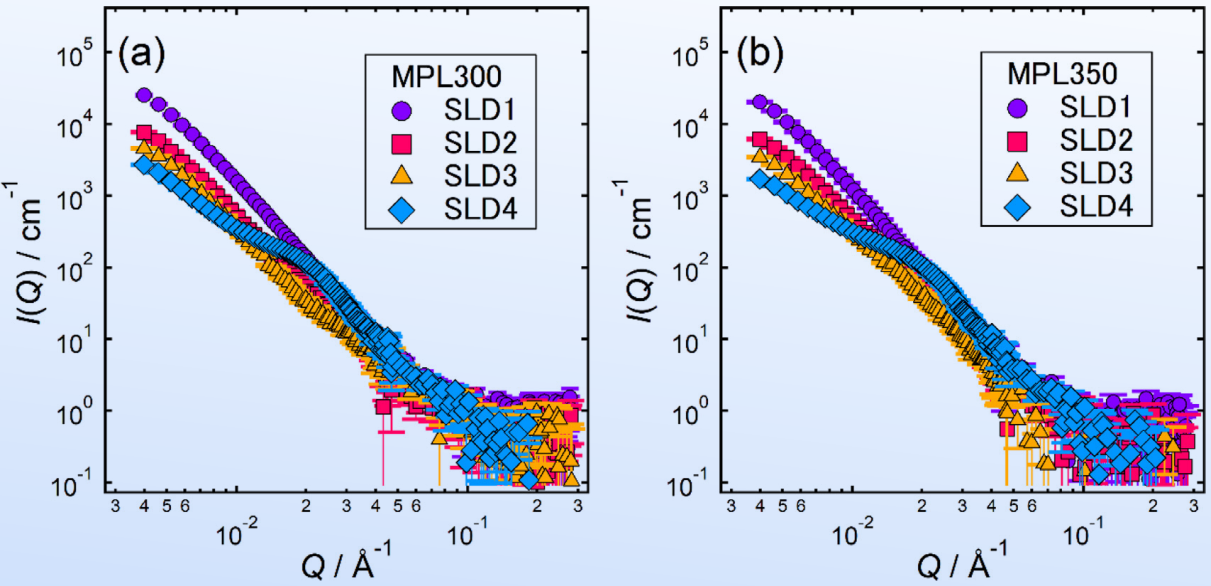

1. membrana pe
2. katalizator
3. warstwy mikroporowate
4. papier węglowy
5. kanały przepływu

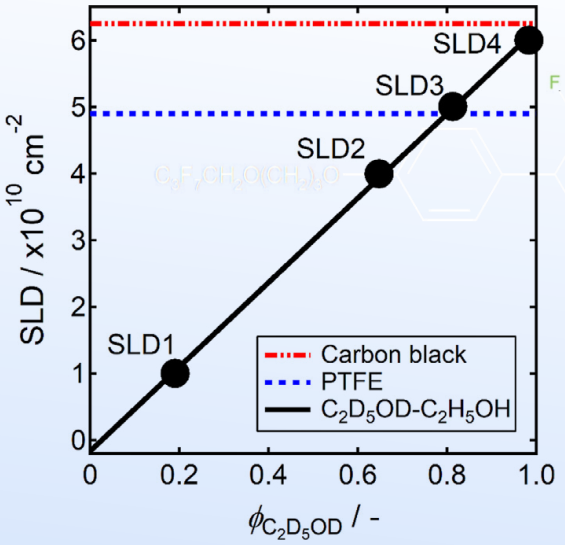
obszar badany SANS



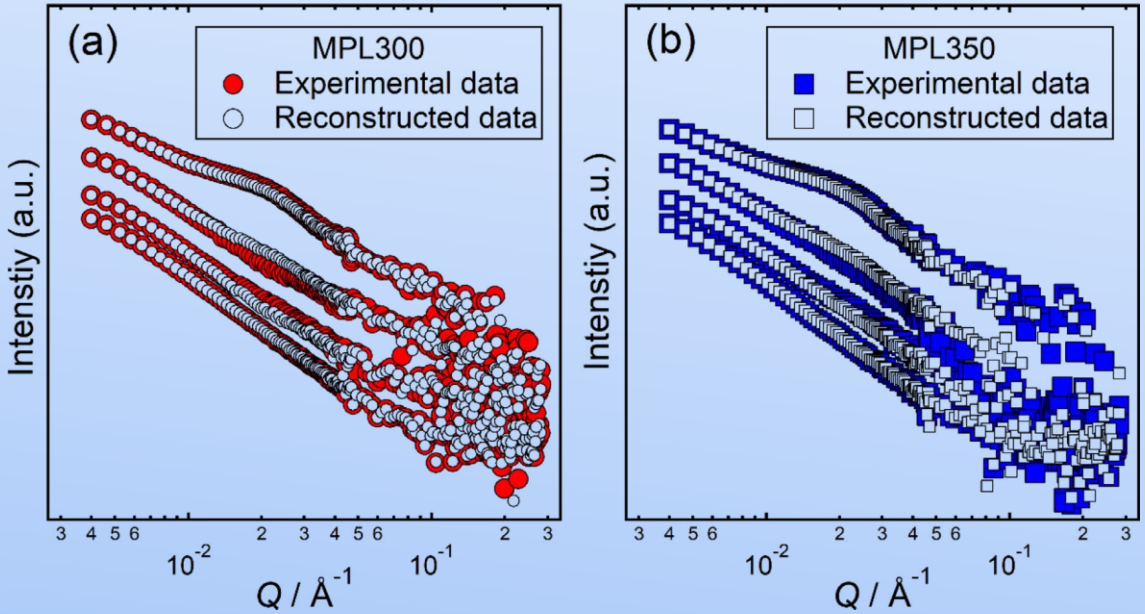

warstwa mikroporowata: węgiel/PTFE – model «core-shell»

# Ogniwa paliwowe z elektrolitem polimerowym




SANS — *contrast variation / contrast matching*

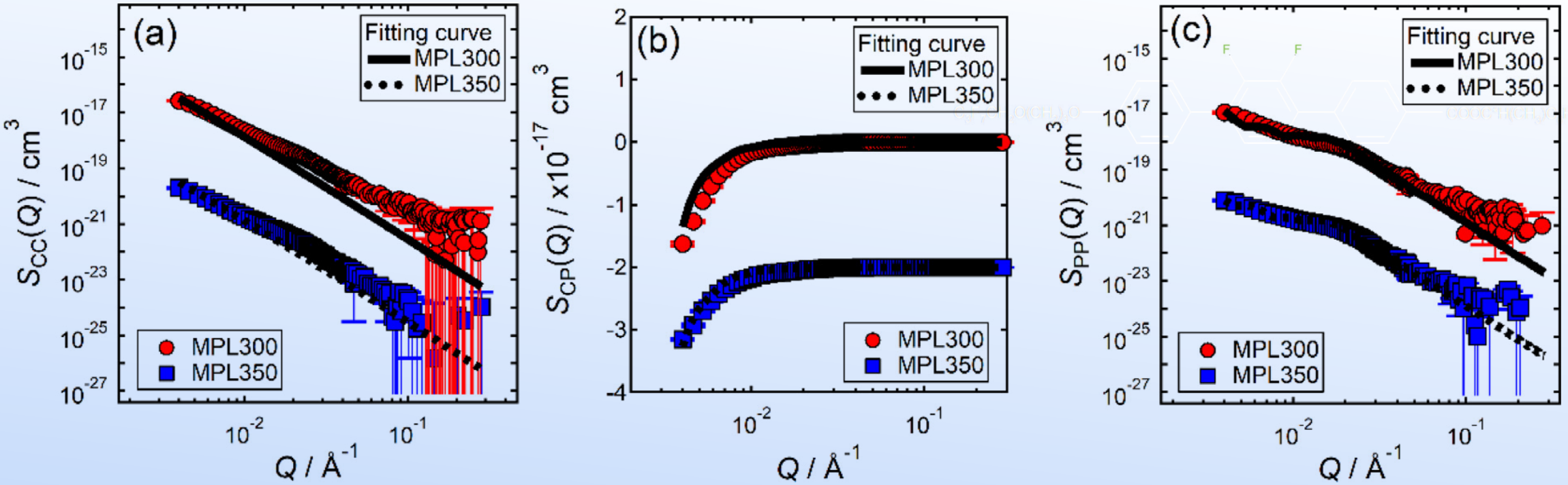



The best-fit parameters for MPL300 and MPL350.

| Samples | $\bar{R}$ (nm) | $\sigma$ (nm) | $\Delta R$ (nm) |
|---|---|---|---|
| MPL300 | 71.6 ± 6.2 | 71.3 ± 0.5 | 76.6 ± 2.0 |
| MPL350 | 73.6 ± 6.2 | 73.1 ± 0.4 | 90.1 ± 0.2 |

W. Yoshimune, M. Harada , Y. Akimoto, Composites C: **2** (2020) 100015

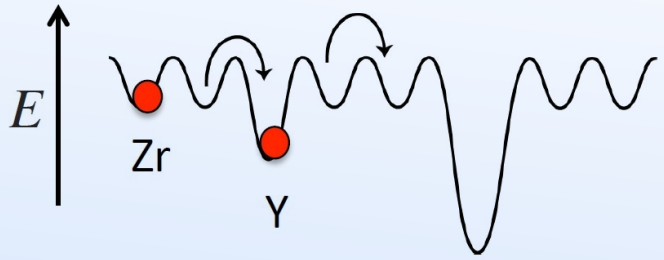
# Ogniwa paliwowe z elektrolitem polimerowym



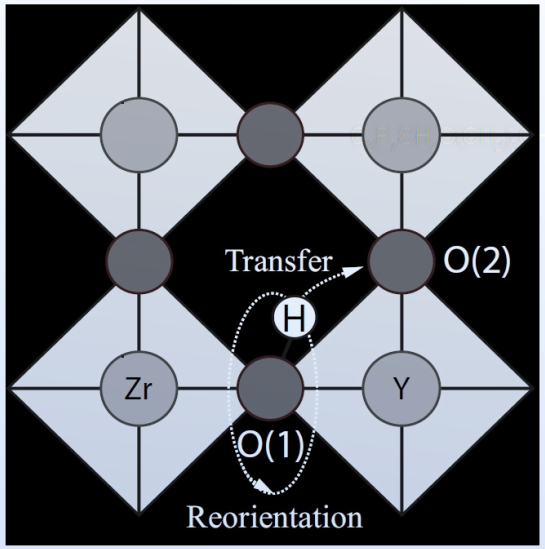

Cząstkowe funkcje rozpraszania: (a) $S_{CC}(Q)$, (b) $S_{CP}(Q)$, (c) $S_{PP}(Q)$

*A post-annealing process, using tem- peratures above the PTFE melting point, reduced the quantum of PTFE self-aggregates. Based on fuel cell testing, we established that lowering PTFE self-aggregates within the MPLs reduced mass-transport losses under high-humidity cell conditions, and that the origin of PTFE adhesion to carbon black could be explained by the low surface energy of PTFE.*

# Ogniwa paliwowe – dynamika w układach złożonych




*M. Karlsson et al. Chem. Mater. (2010)*




Trapping- detrapping processes,
e.g. in Y-doped $BaZrO_3$ ($BaZr_{1-x}Y_xO_3H_x$)

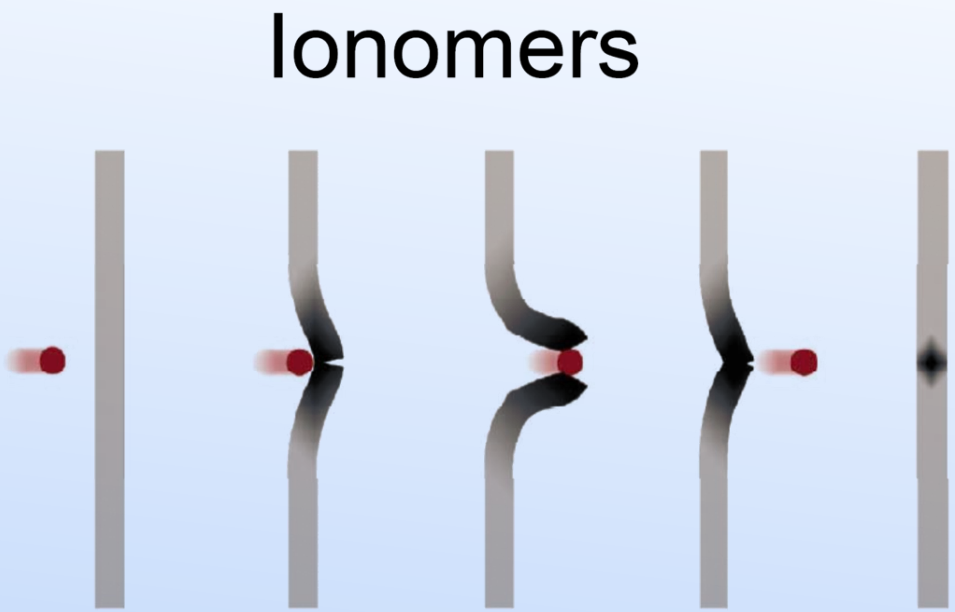
Karlsson: “Killer experiments: proton diffusion over large (Q,t) range
t = 1 ps - 100 ns, Q = 0.2 – 4 $Å^{-1}$ “

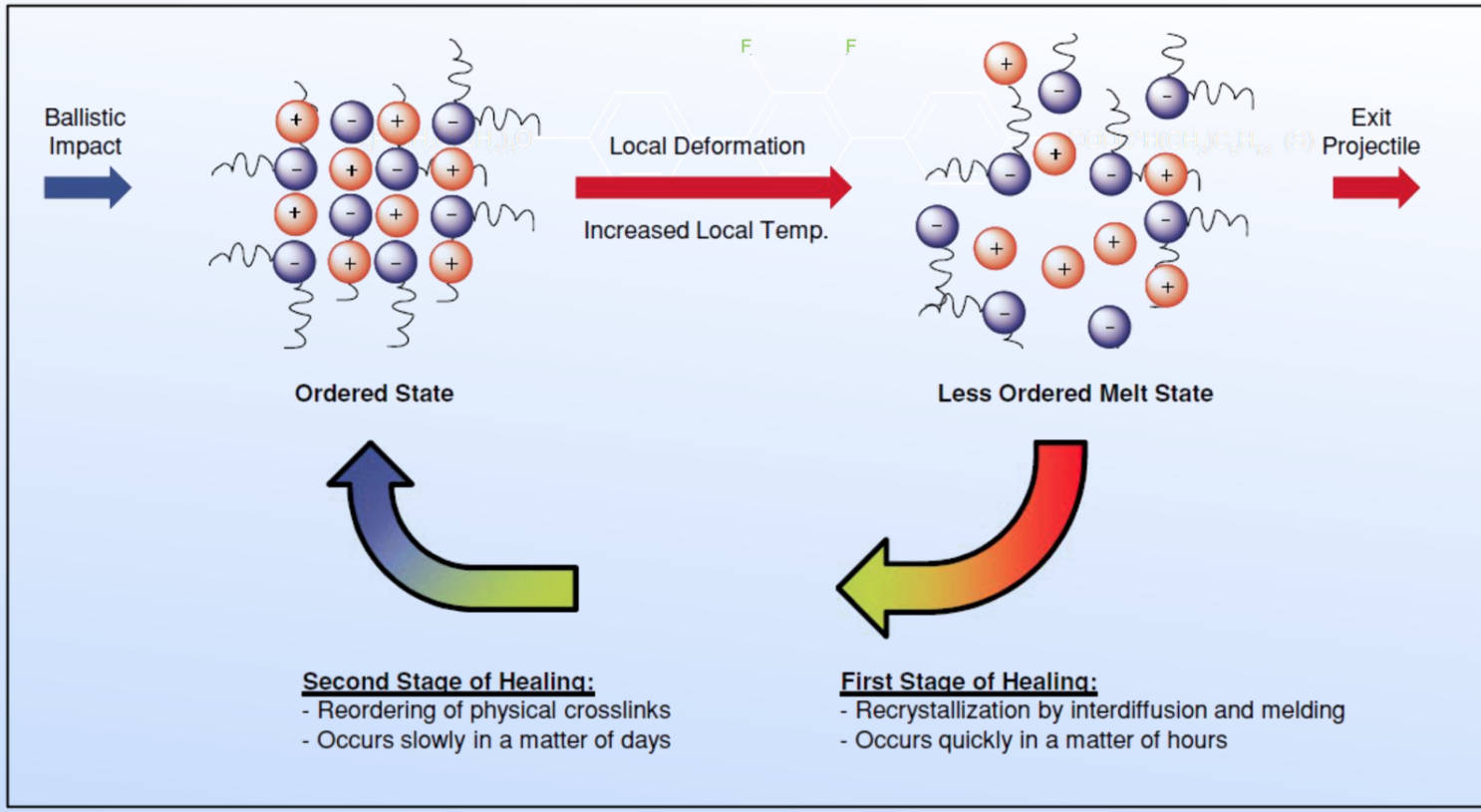
**To oznacza NSE wysokiej rozdzielczości!**

e.g. : Q ~ 3 $Å^{-1}$ @ λ = 3 Å ⇨ Energy of 0.07 μeV

Ogniwa paliwowe, daleko poza spektroskopią w rozpraszaniu wstecznym *(backscattering)*

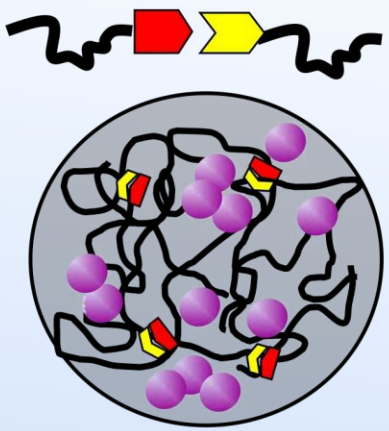
# Ogniwa paliwowe – dynamika w układach złożonych



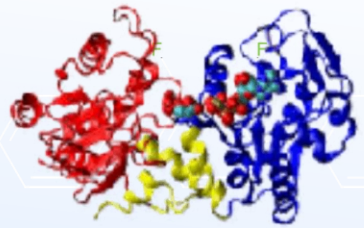




- Materiały „samoleczące się” (self-healing materials)
- Makromolekularne struktury hierarchiczne w skali nano-
  **Rozmiar rzędu nanometrów** $\rightarrow$ wkład do $S(Q)$ przy małych $Q$.
  **Skala czasowa rzędu mikrosekund** $\rightarrow$ niezbędna wysoka rozdzielczość

# Ogólnie: dynamika układów złożonych

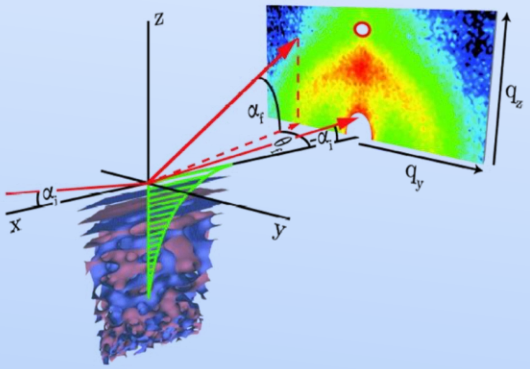


**Materiały funkcjonalne**
dynamika grup molekularnych

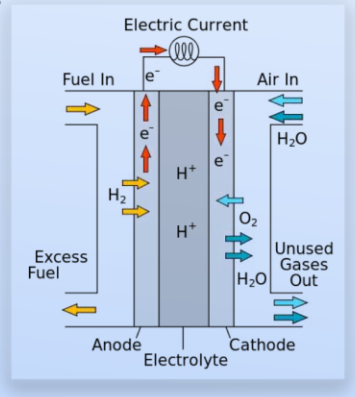


**Biodynamika**
leki:
**działanie i projektowanie**

**NSE**
**Science drivers**



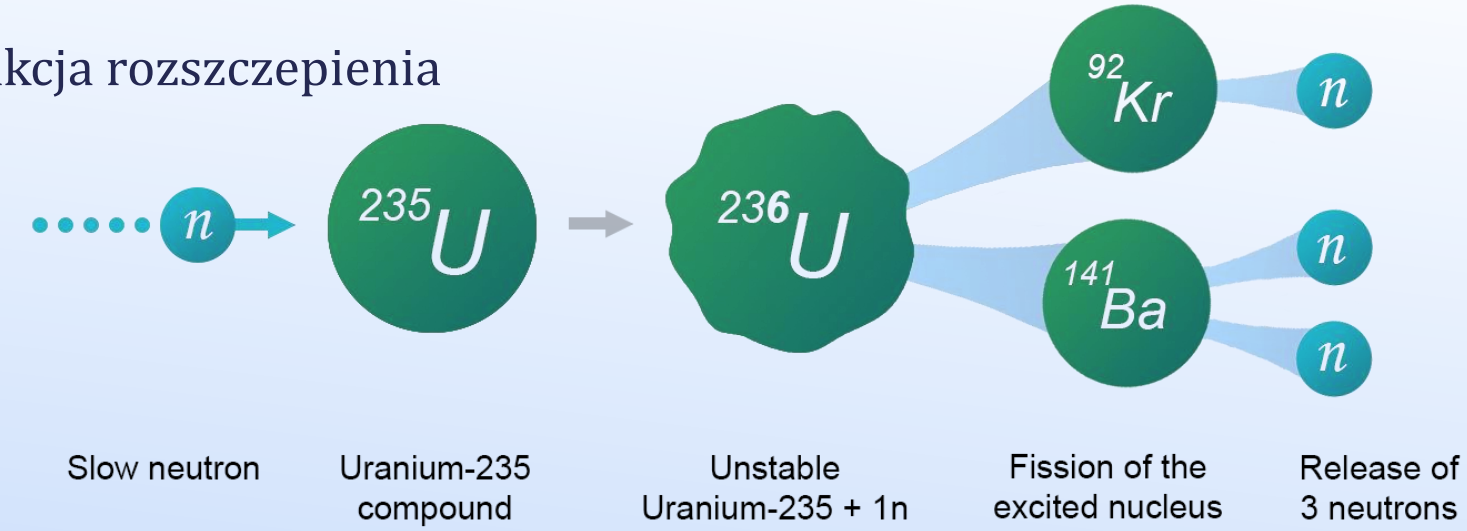

**Dynamika powierzchni**
**i warstw (interfaces)**
(trybologia i warstwy biol.:
GINSES)




**Ogniwa paliwowe**
(wysoka rozdzielczść
przy dużych Q)

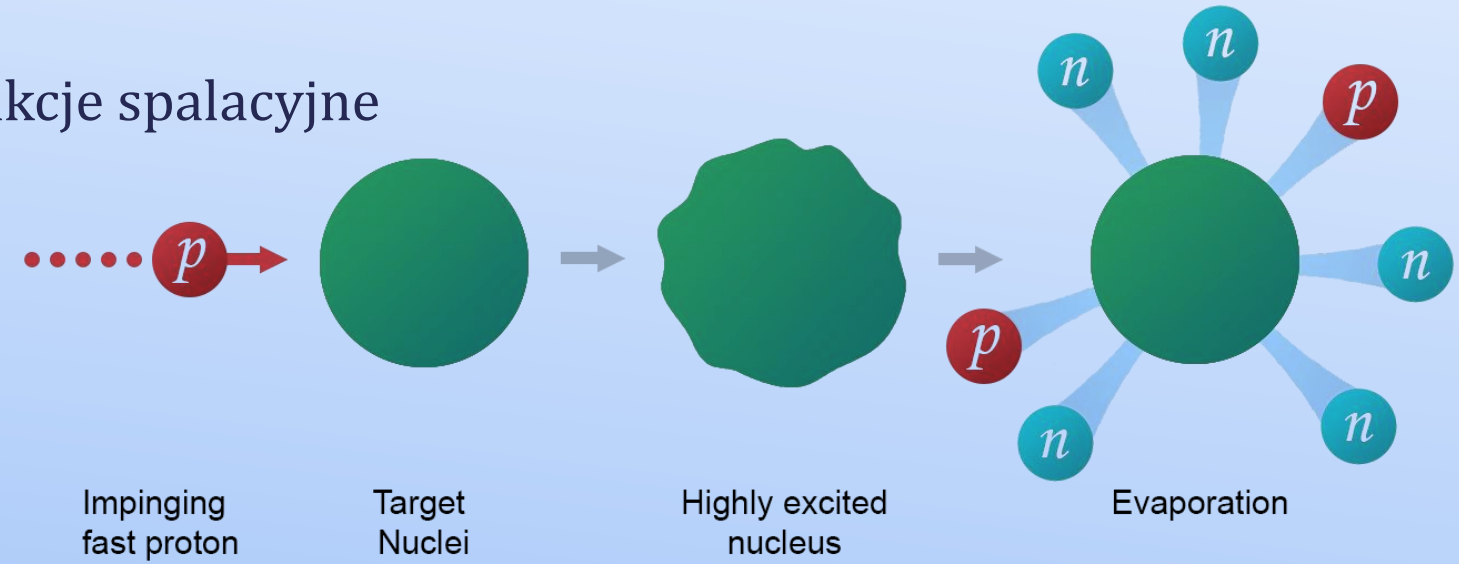
# Jak produkujemy neutrony do badań materii

## Reakcja rozszczepienia




- Reakcja łańcuchowa
- Praca źródła ciągła
- 1 neutron/reakcję

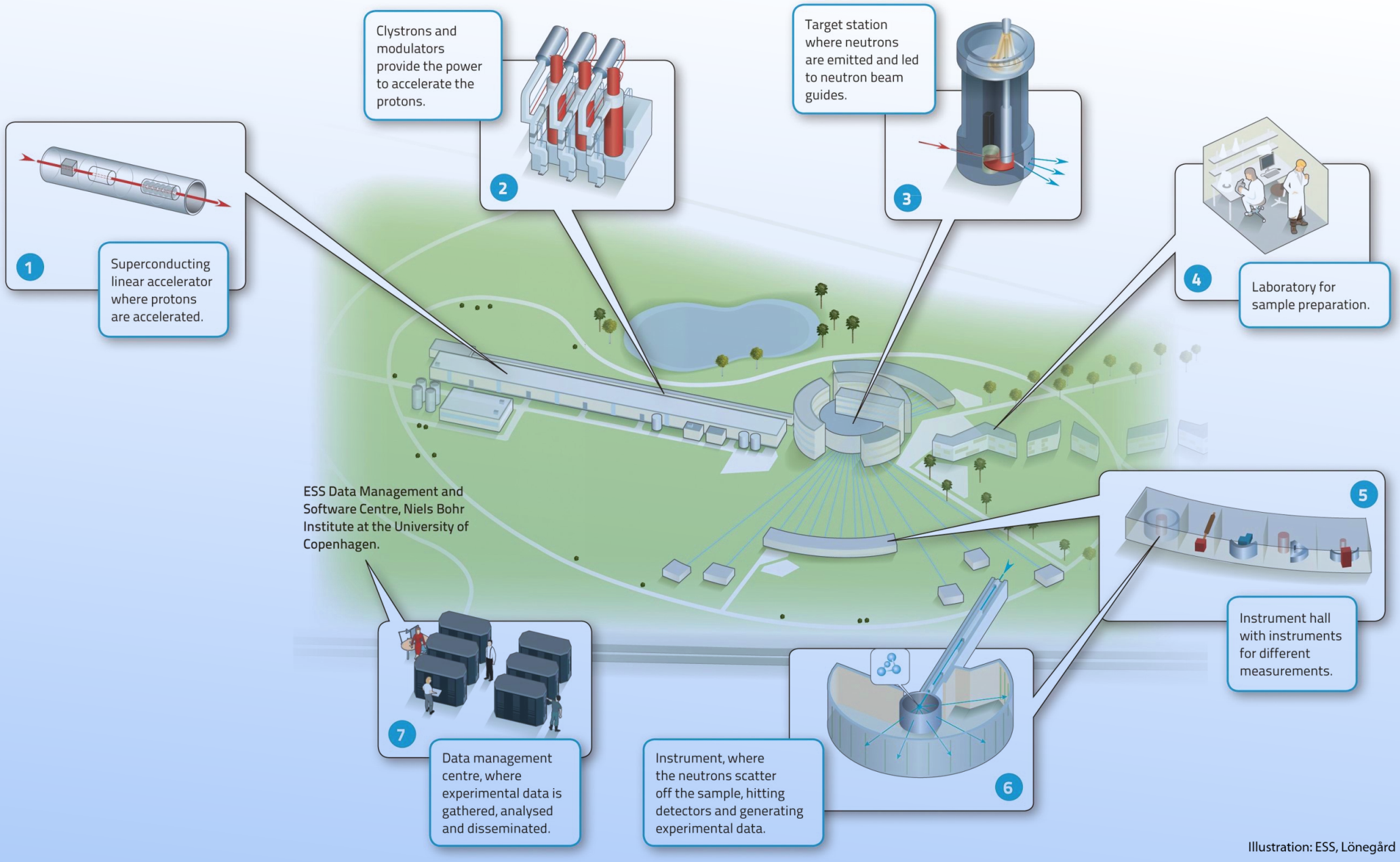
## Reakcje spalacyjne



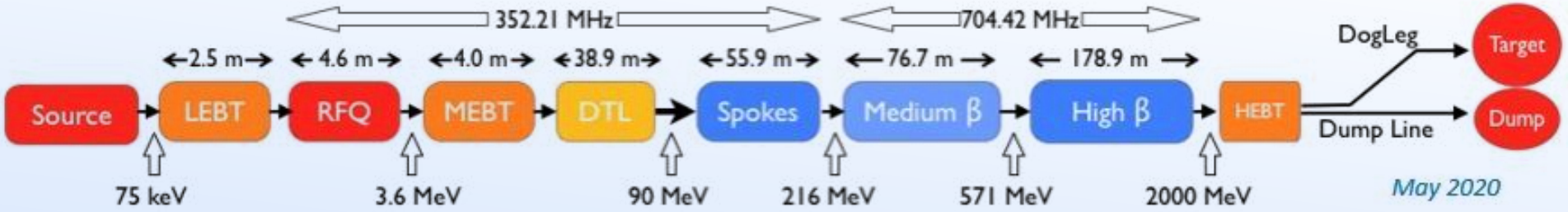

- Spalacja jądrowa (brak reakcji łańcuchowej)
- Praca źródła impulsowa
- ~30 neutronów/proton

# Europejskie Źródło Spalacyjne ESS

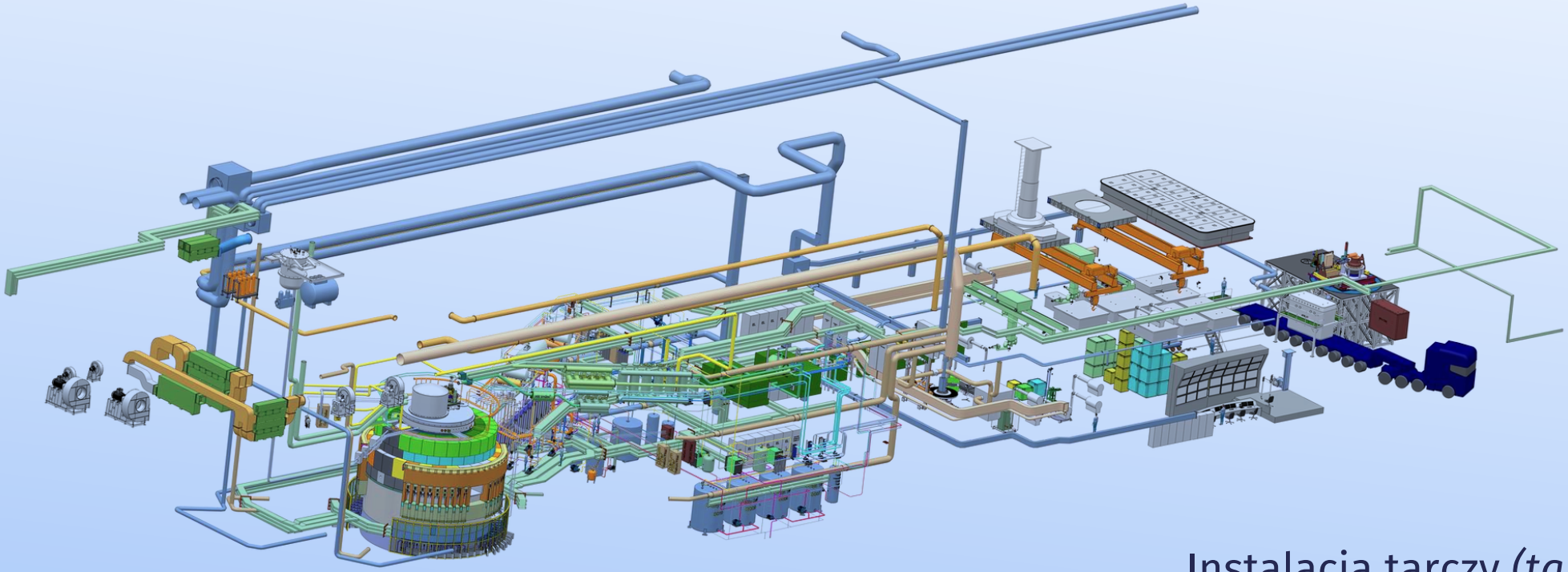
# Europejskie Źródło Spalacyjne ESS



# Europejskie Źródło Spalacyjne ESS

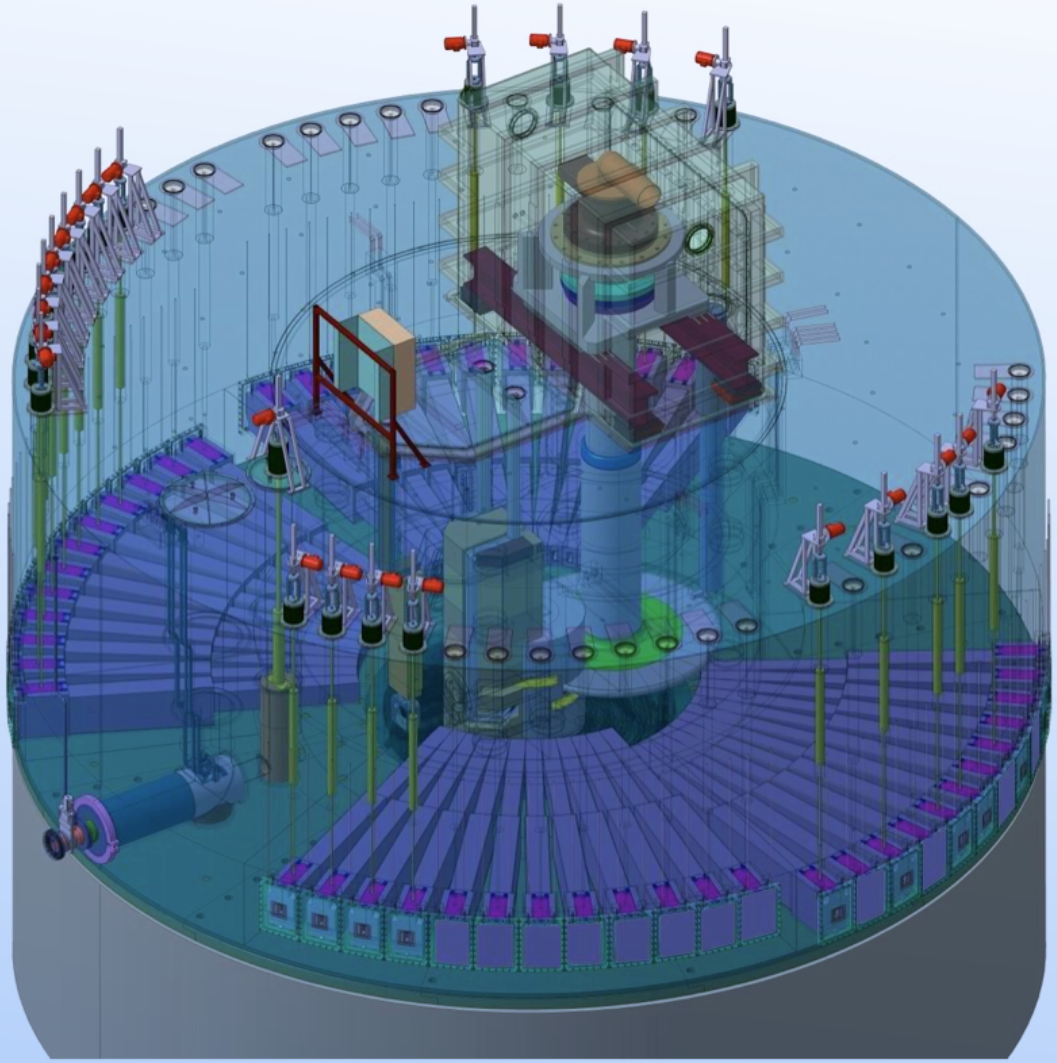


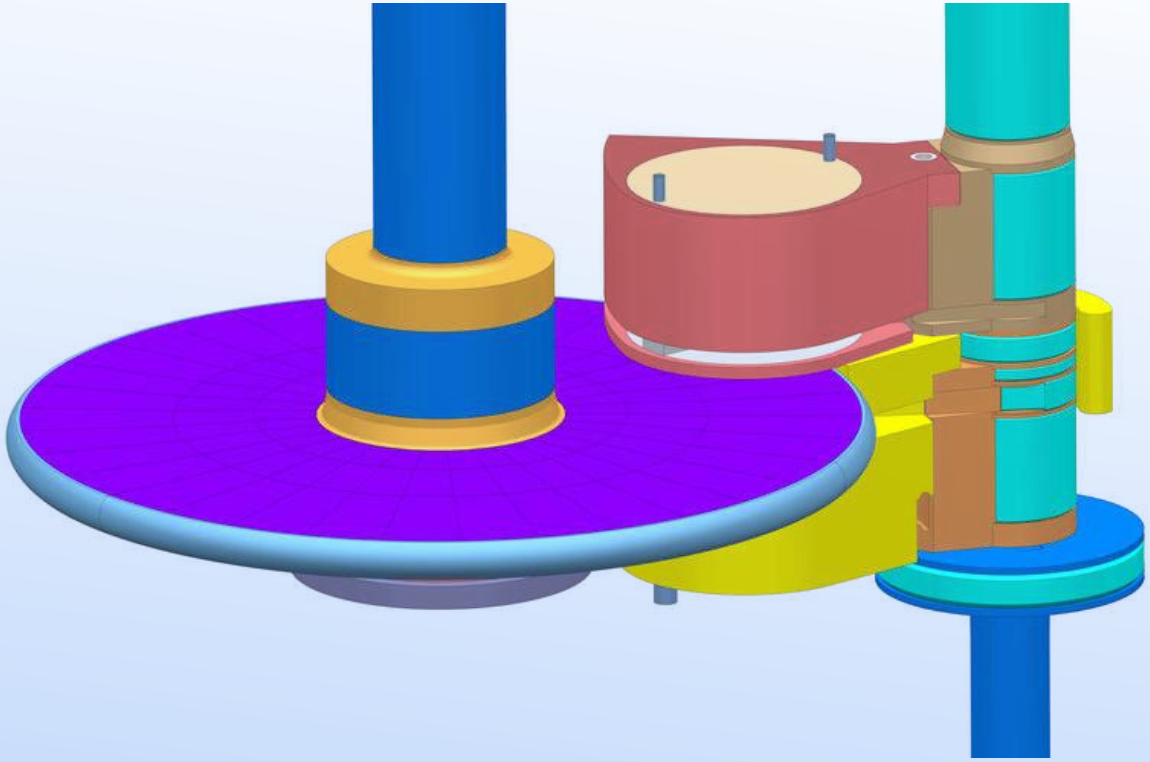

Akcelerator liniowy dostarcza na tarczę protony 2—2.5 GeV



Instalacja tarczy *(target station)*

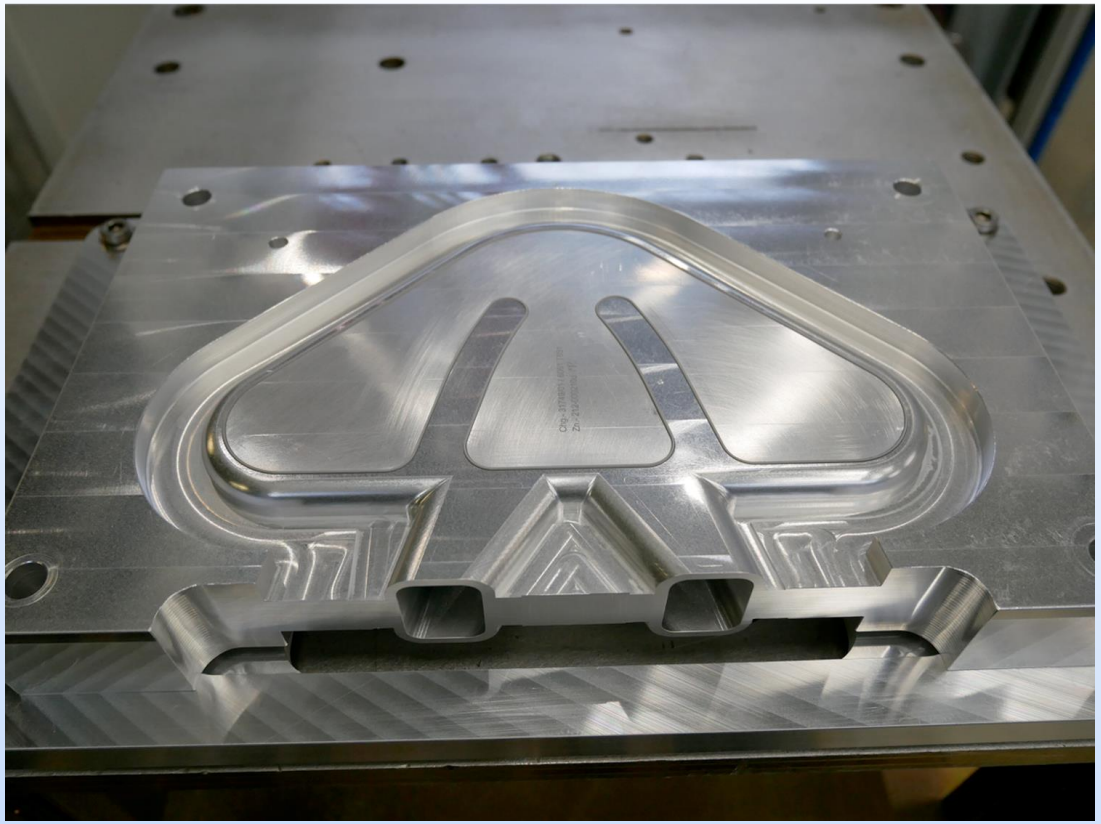
# Europejskie Źródło Spalacyjne ESS





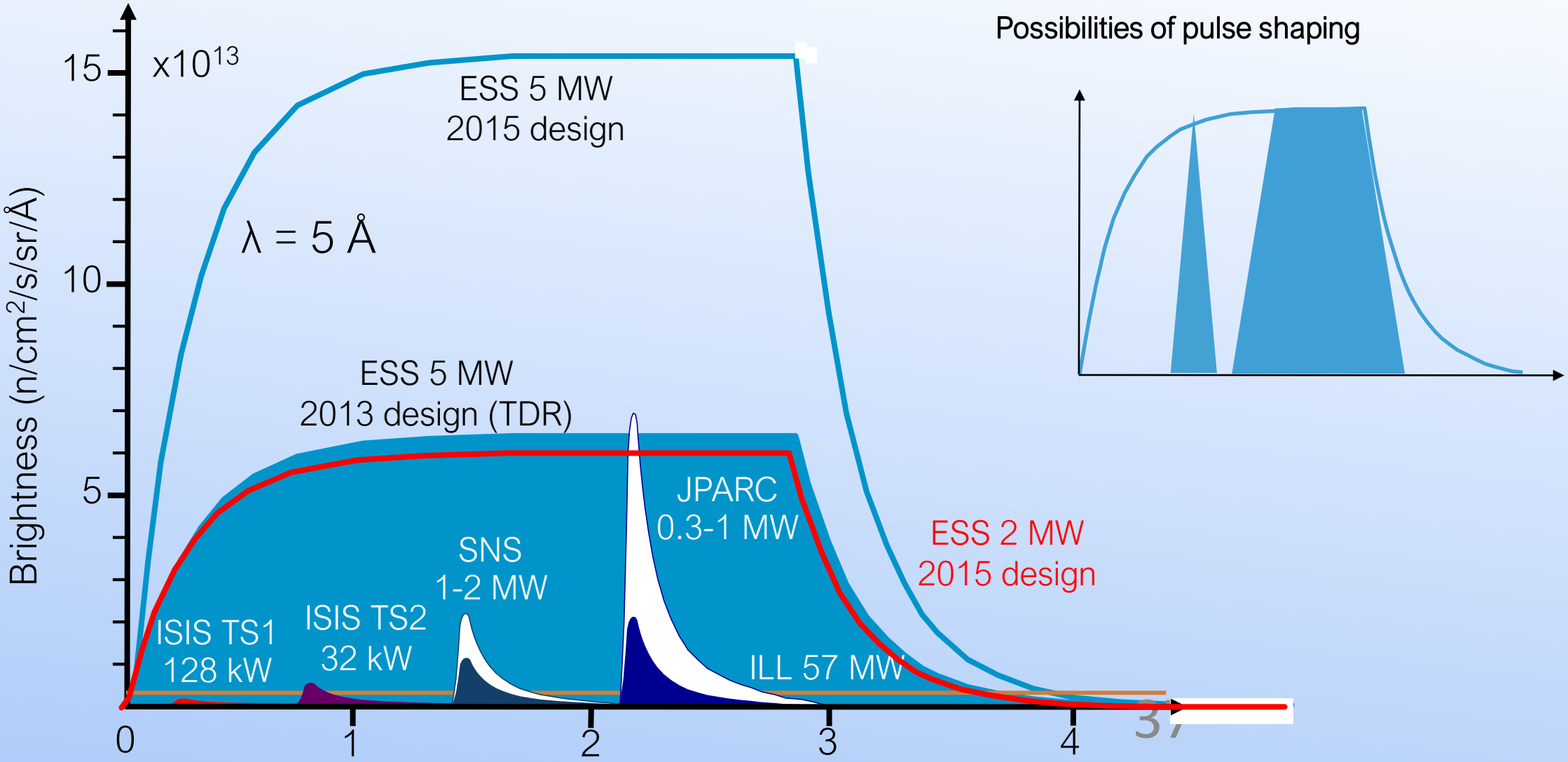
Tarcza i moderatory

# Europejskie Źródło Spalacyjne ESS

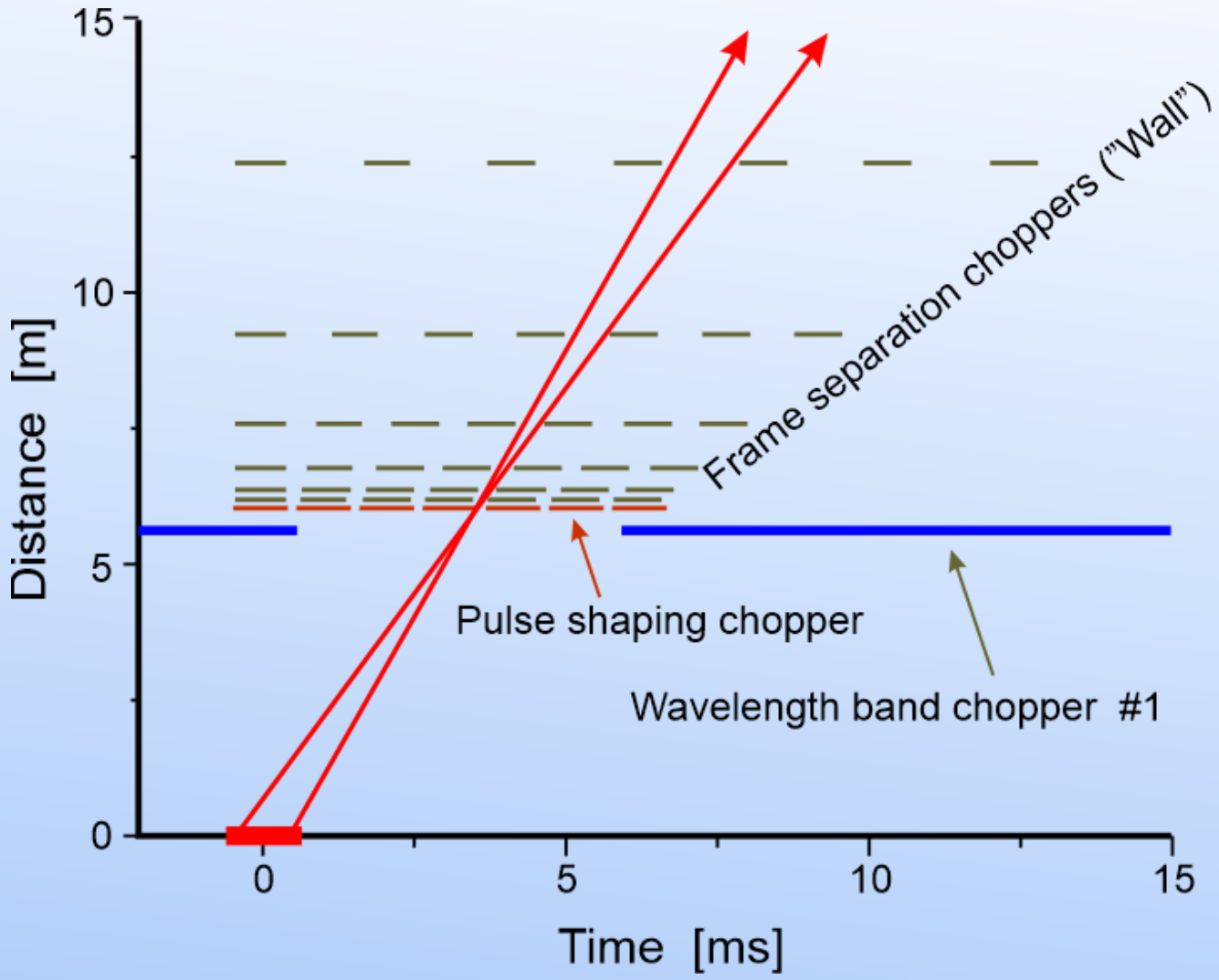


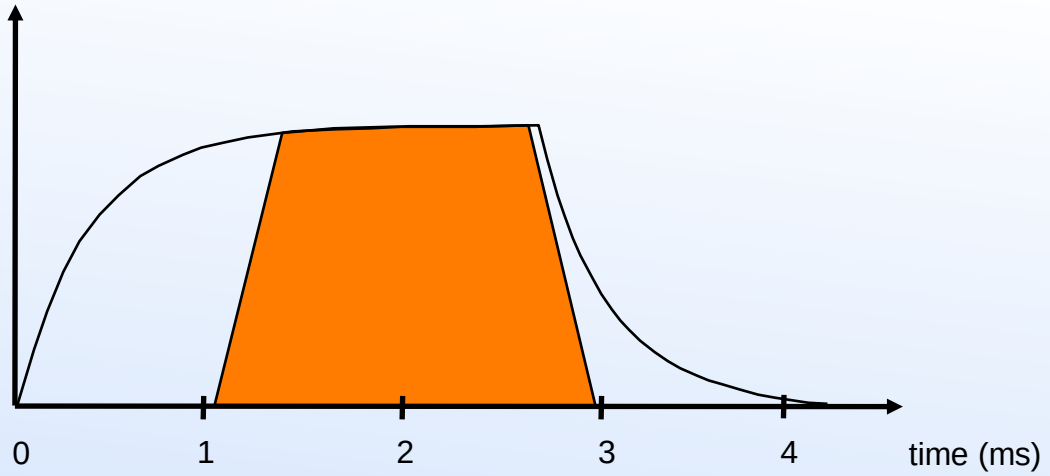
Tarcza i moderatory

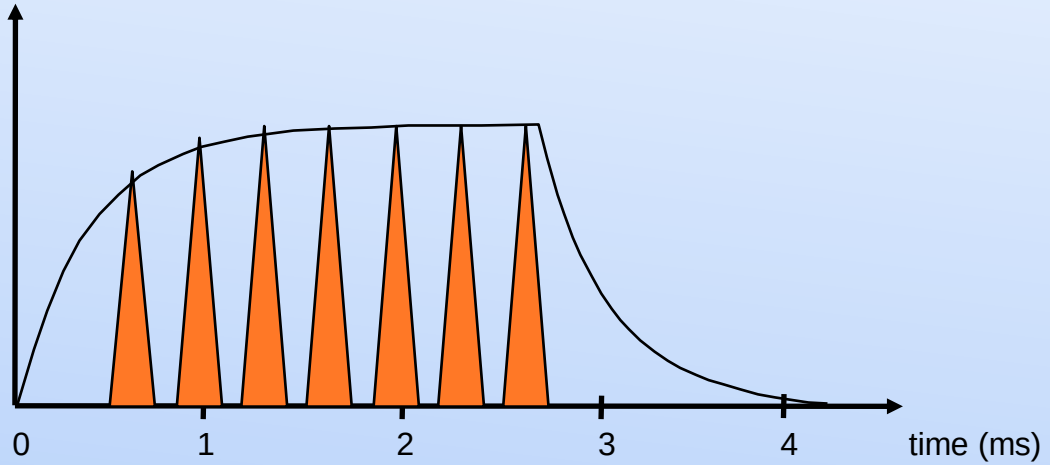
# ESS – źródło o długim impulsie



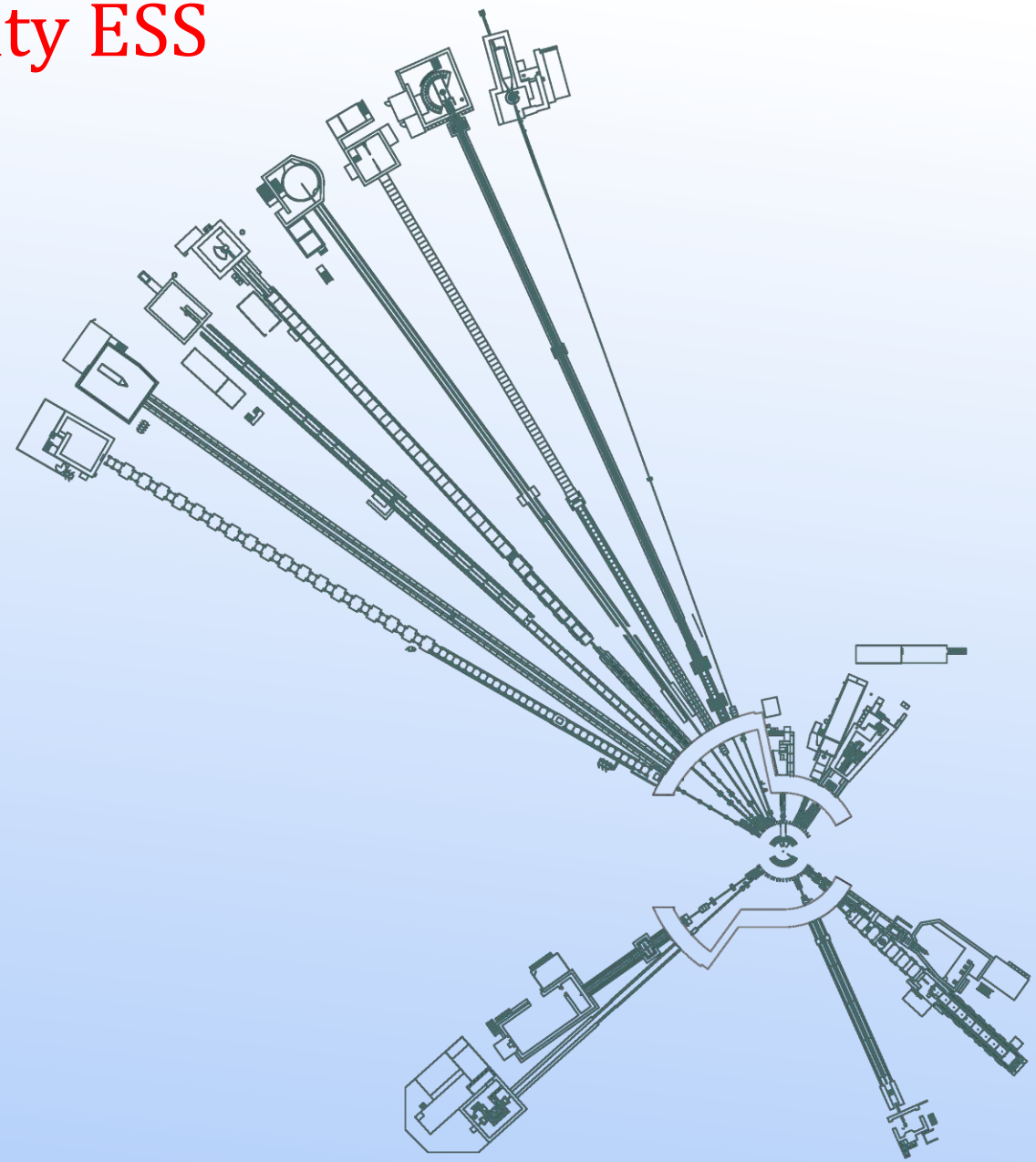
# ESS – formowanie impulsów wtórnych



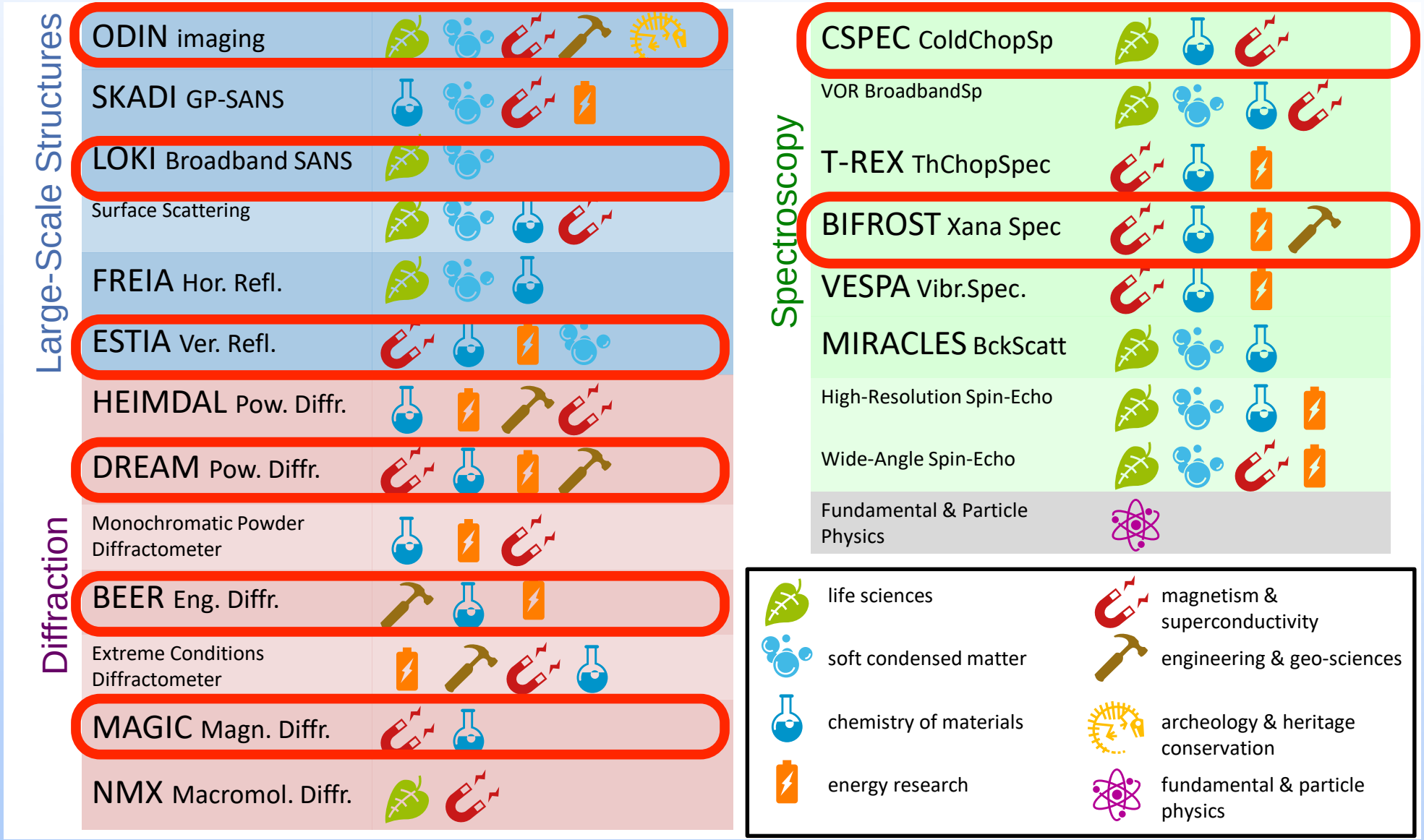



# Instrumenty ESS



- 15 zatwierdzonych
- 8 w roku 2023

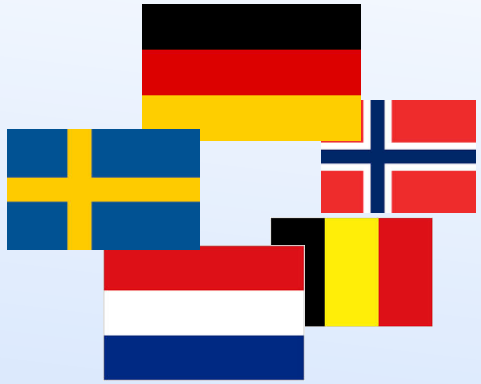
# Instrumenty ESS

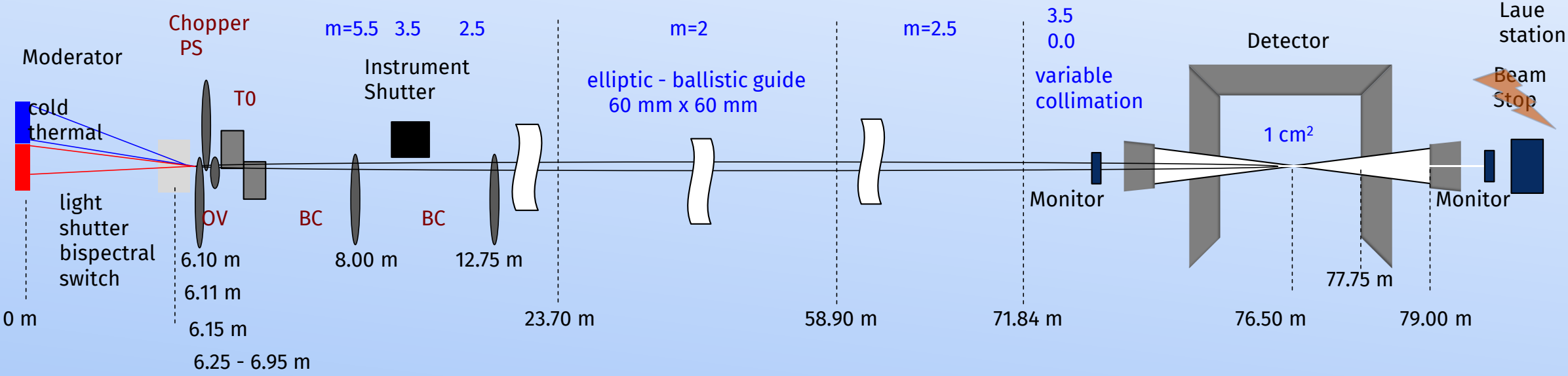



15 zatwierdzonych
8 w roku 2023

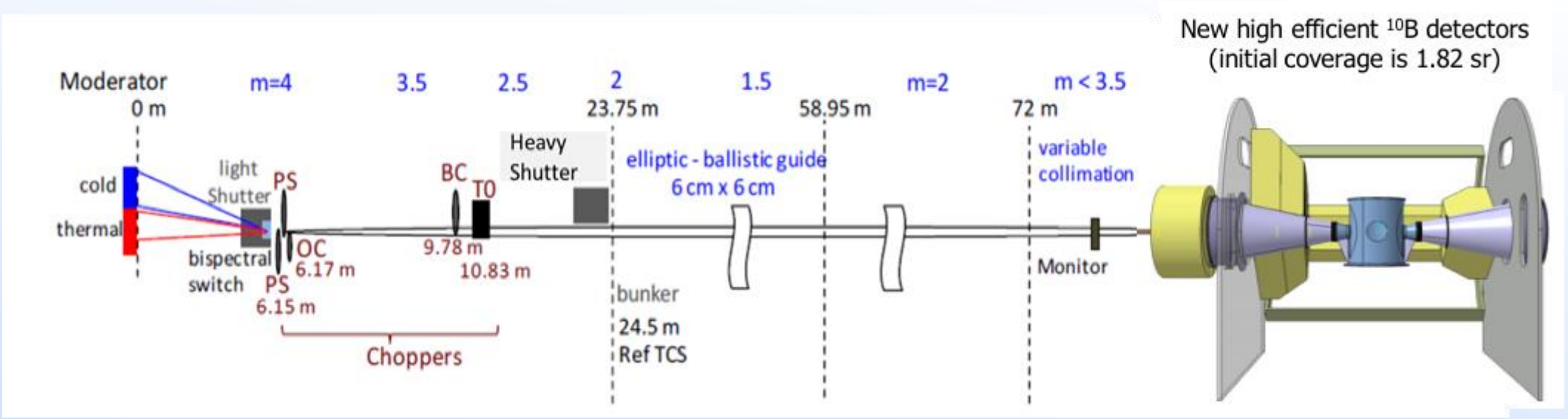
# DREAM – bispectral powder diffractometer

## Diffraction Resolved by Energy and Angle Measuements

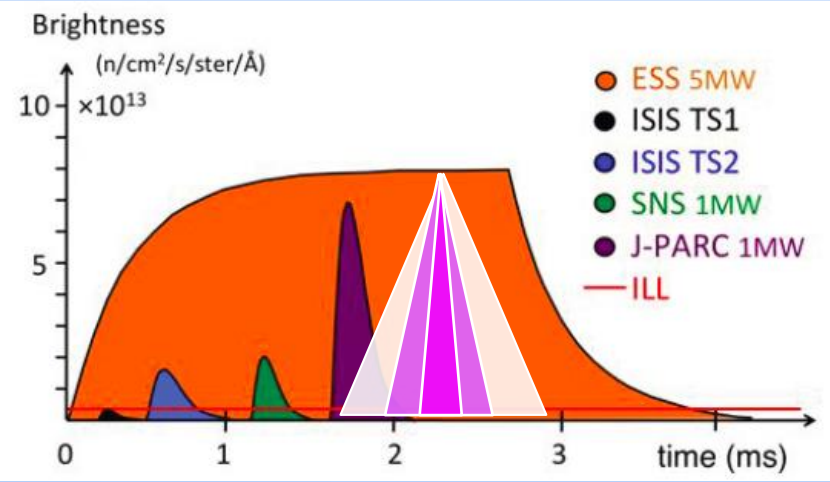




# DREAM – bispectral powder diffractometer




Brightness




*pulse shaping*

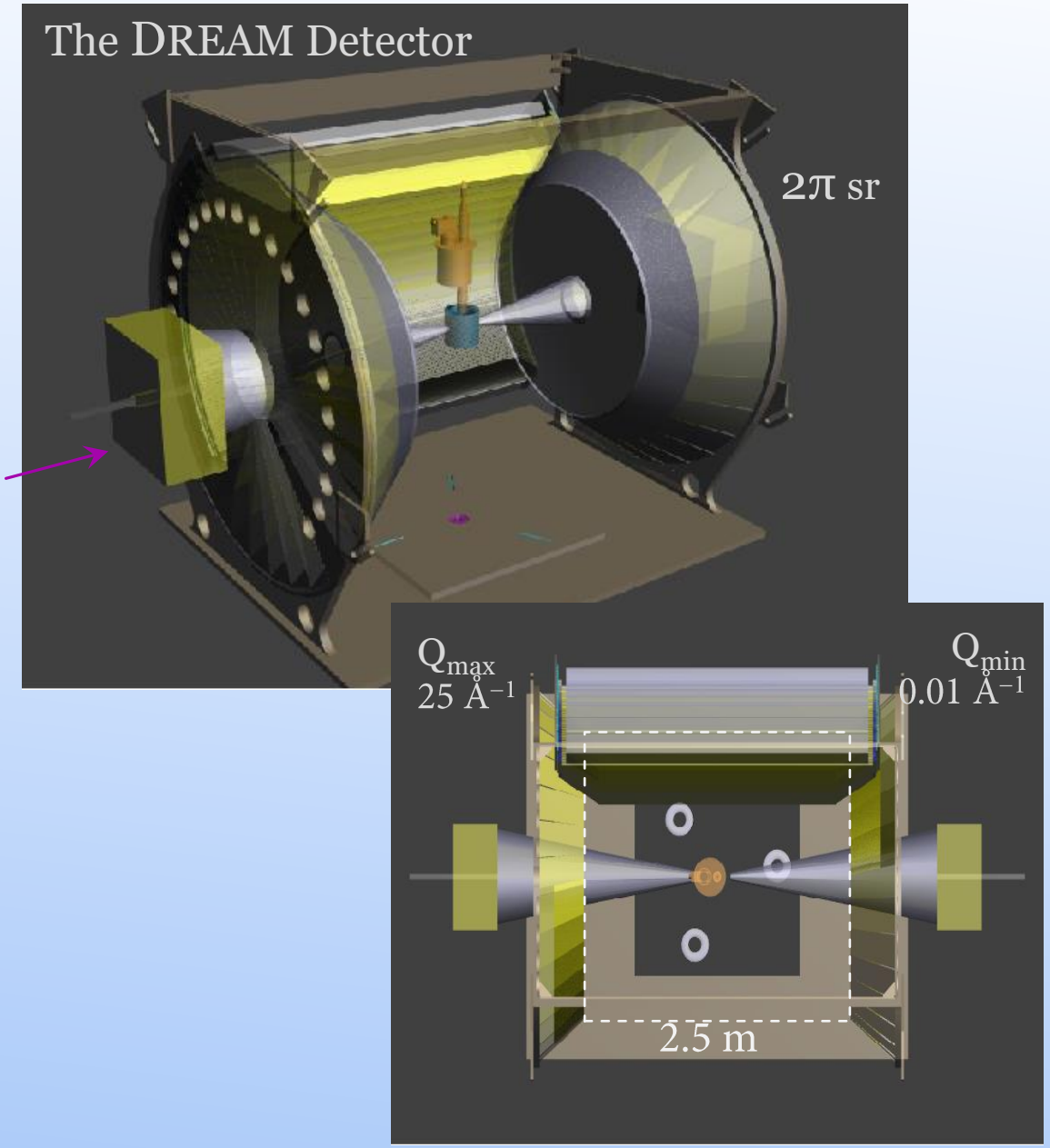
75 m length
bandwidth includes thermal and cold peak

thermal spectrum gives $Q_{max} < 25$ Å$^{-1}$

high flexibility in trading resolution *vs* intensity
ideal peak shape

using the intense cold spectrum with best ever resolution

# DREAM – bispectral powder diffractometer



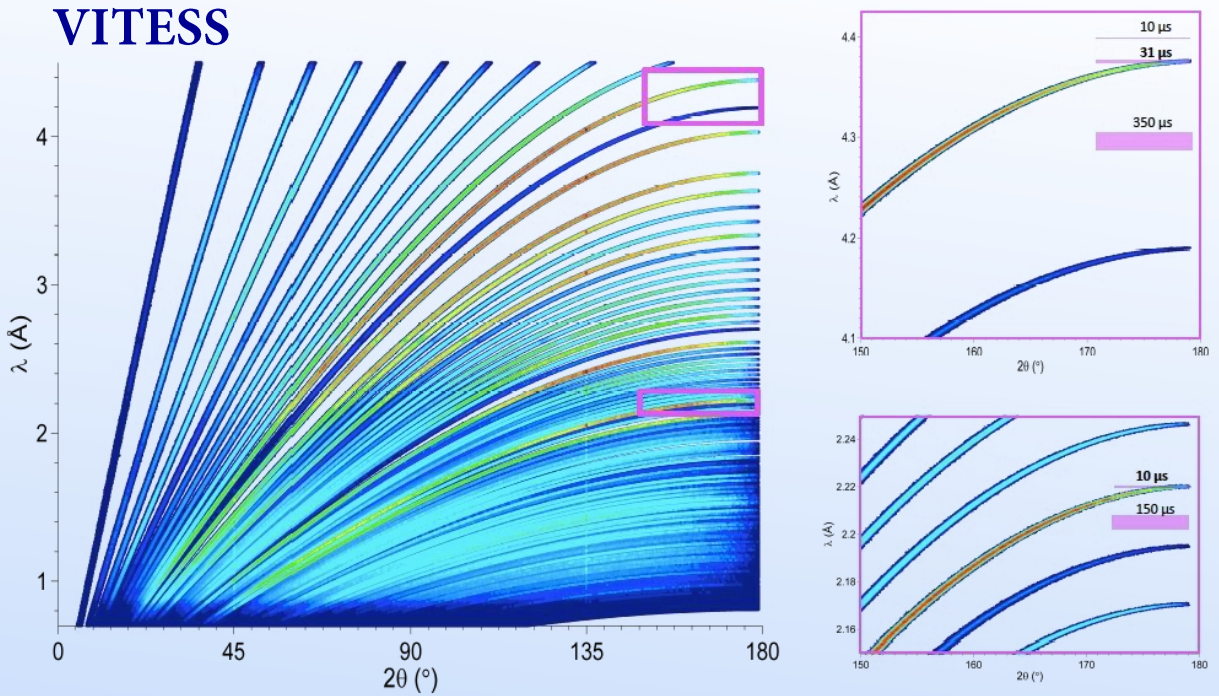
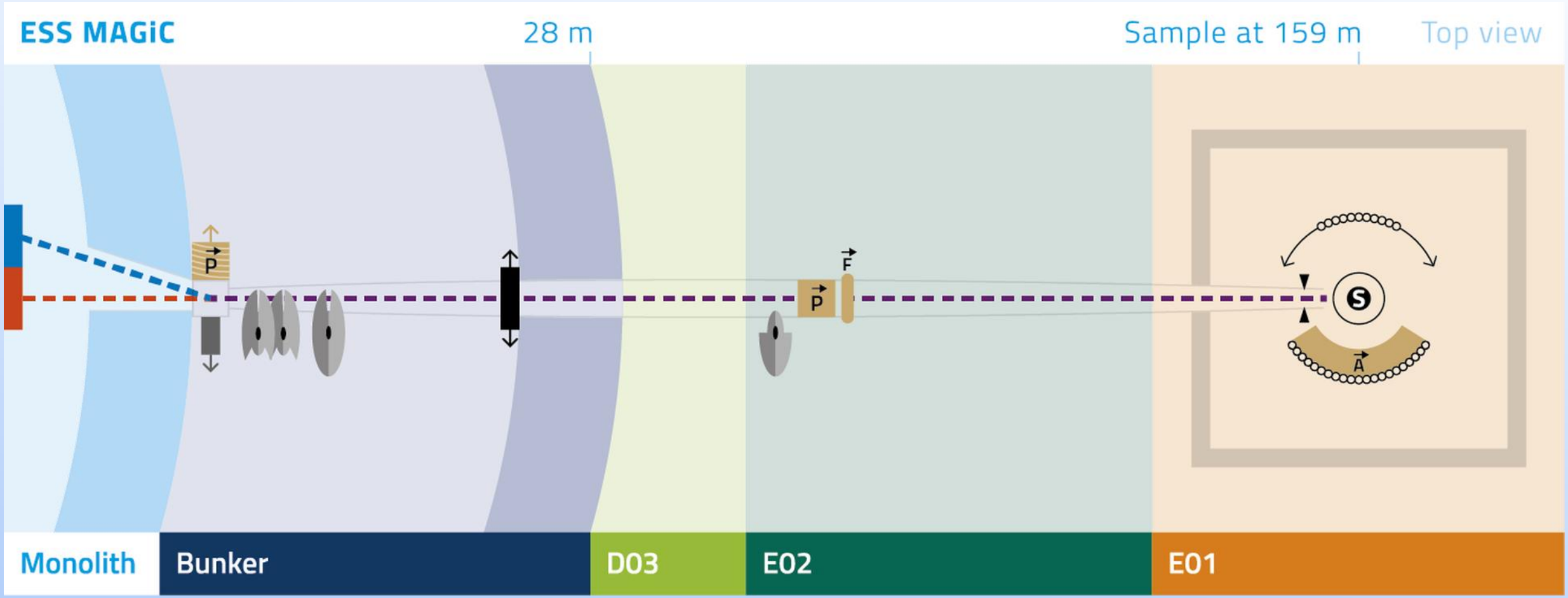




*Fig. 5 Diffraction diagram of a reference sample (0.4 cm³ $Na_2Ca_3Al_2F_{14}$ ) in high resolution mode (left). In backscattering, the asymptotic limit is essentially determined by the time resolution, see enlarged regions (right)*

# MAGIC – Magnetism single crystal diffractometer

## Polarized time-of-flight single-crystal diffractometer

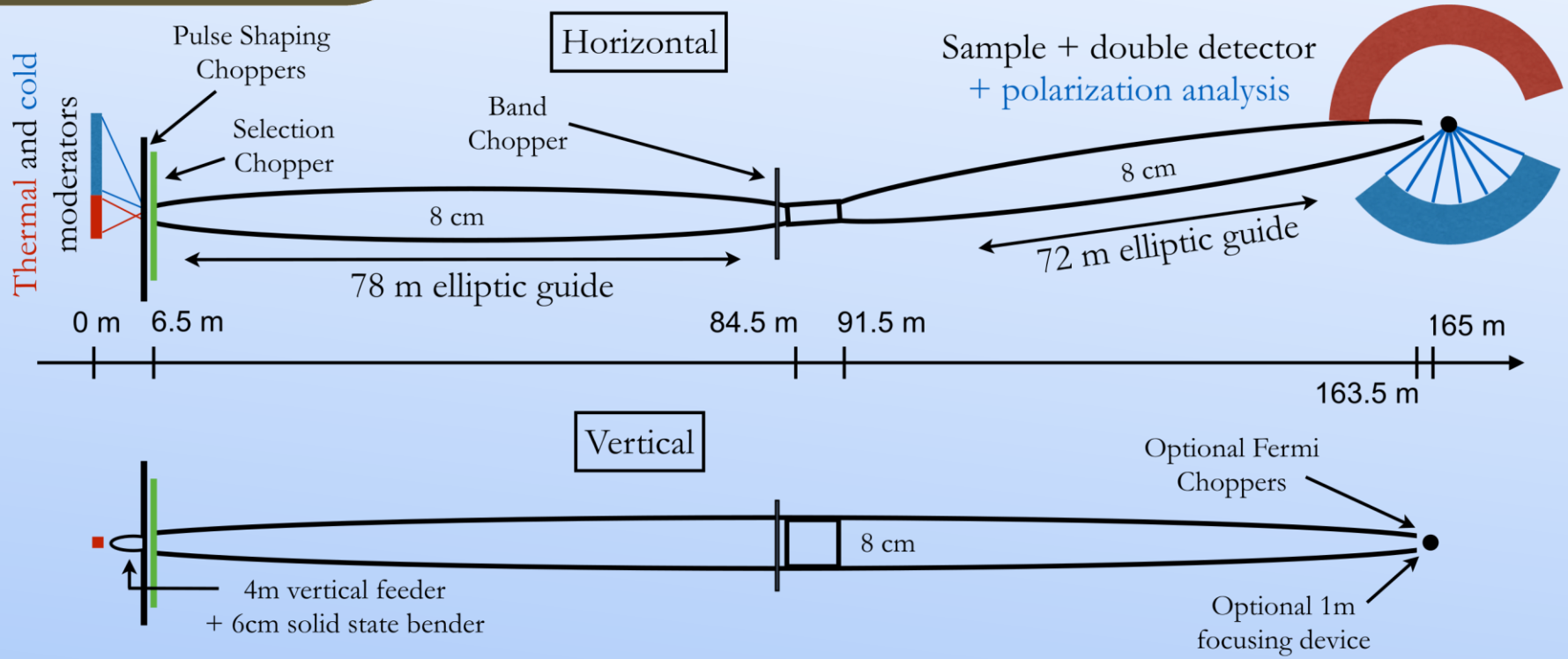


# MAGIC – Magnetism single crystal diffractometer

The magnetic moment is a vector 

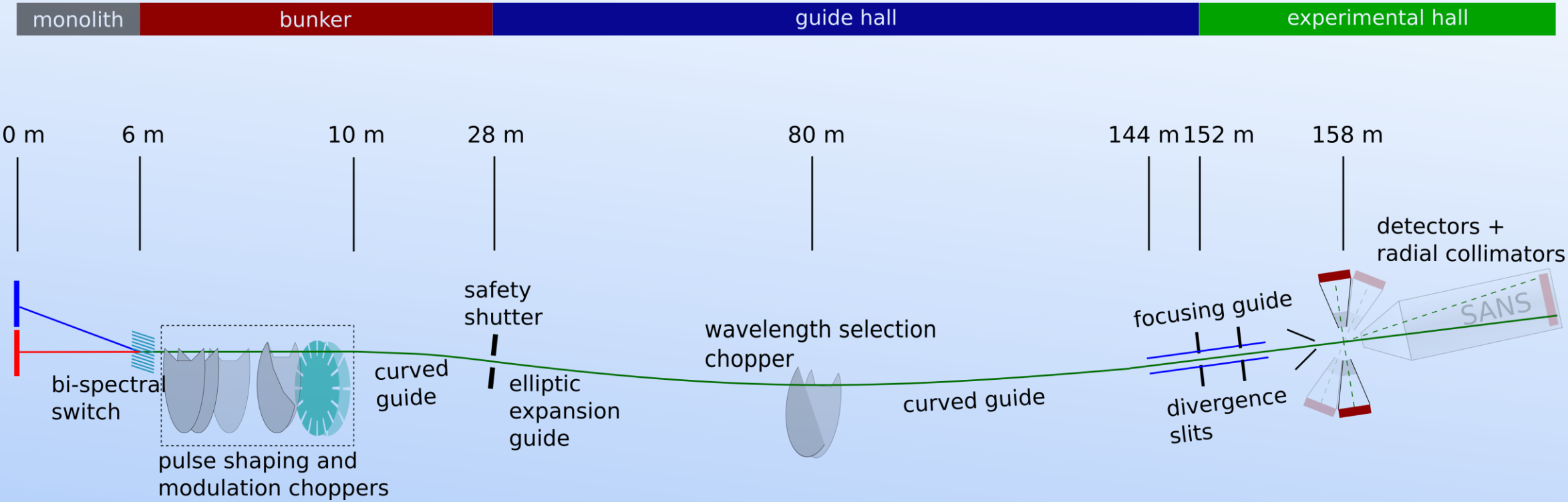
Usually intensities are only measures of scalar products.
The neutron dipolar interaction probes magnetic moments perpendicular to the scattering vector $\vec{S}_{\perp\vec{Q}} \cdot \vec{S}'_{\perp\vec{Q}}$

**Polarized neutrons** measure vector properties, vector products and vector directions $\vec{S}_{\perp\vec{Q}} \times \vec{S}'_{\perp\vec{Q}}$



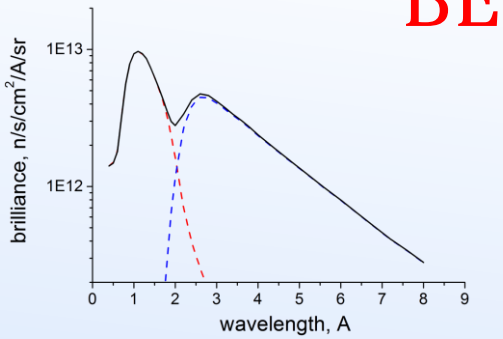
# BEER – engineering diffractometer

## **B**eamline for **E**uropean **E**ngineering Materials Research

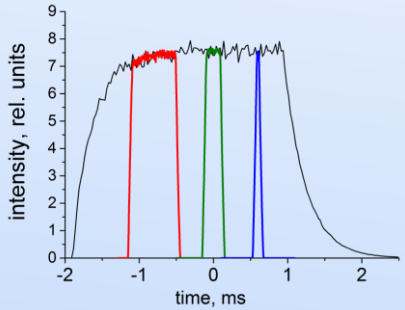


# BEER – engineering diffractometer

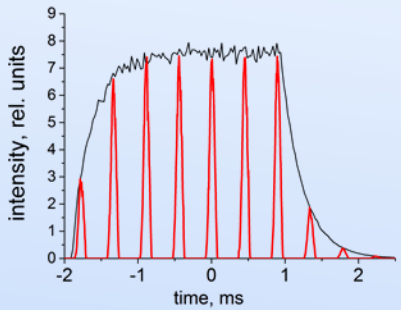
bi-spectral source




chopper system for wide range of resolutions

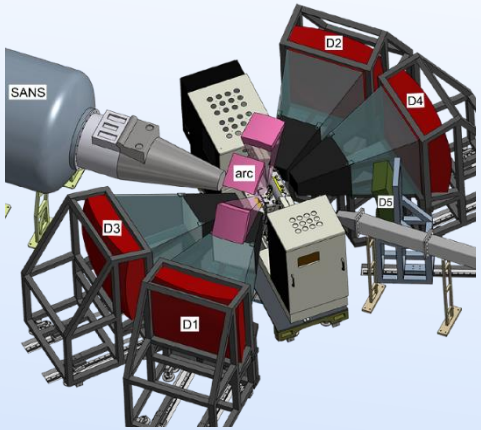


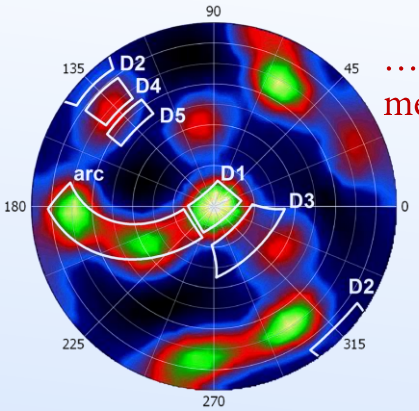

pulse shaping




pulse modulation

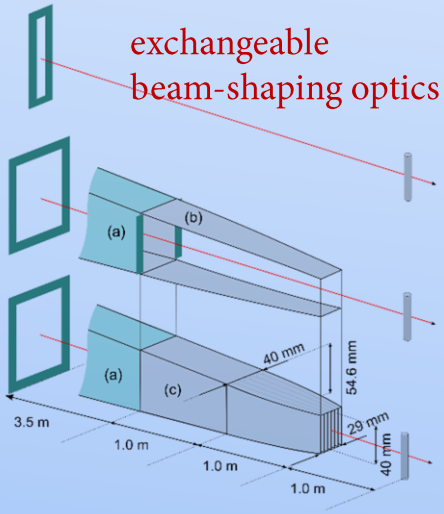
retractable detector banks allowing for large sample environment …

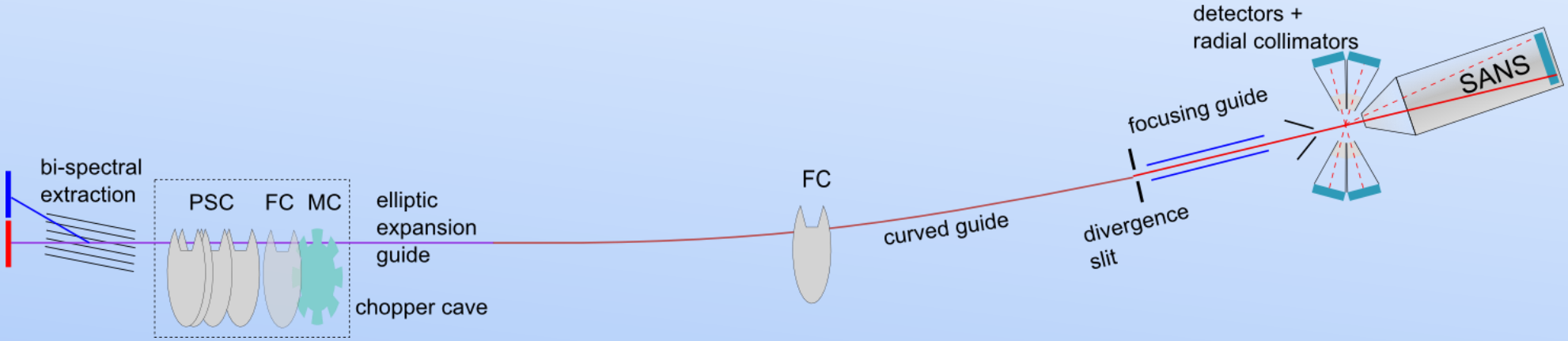


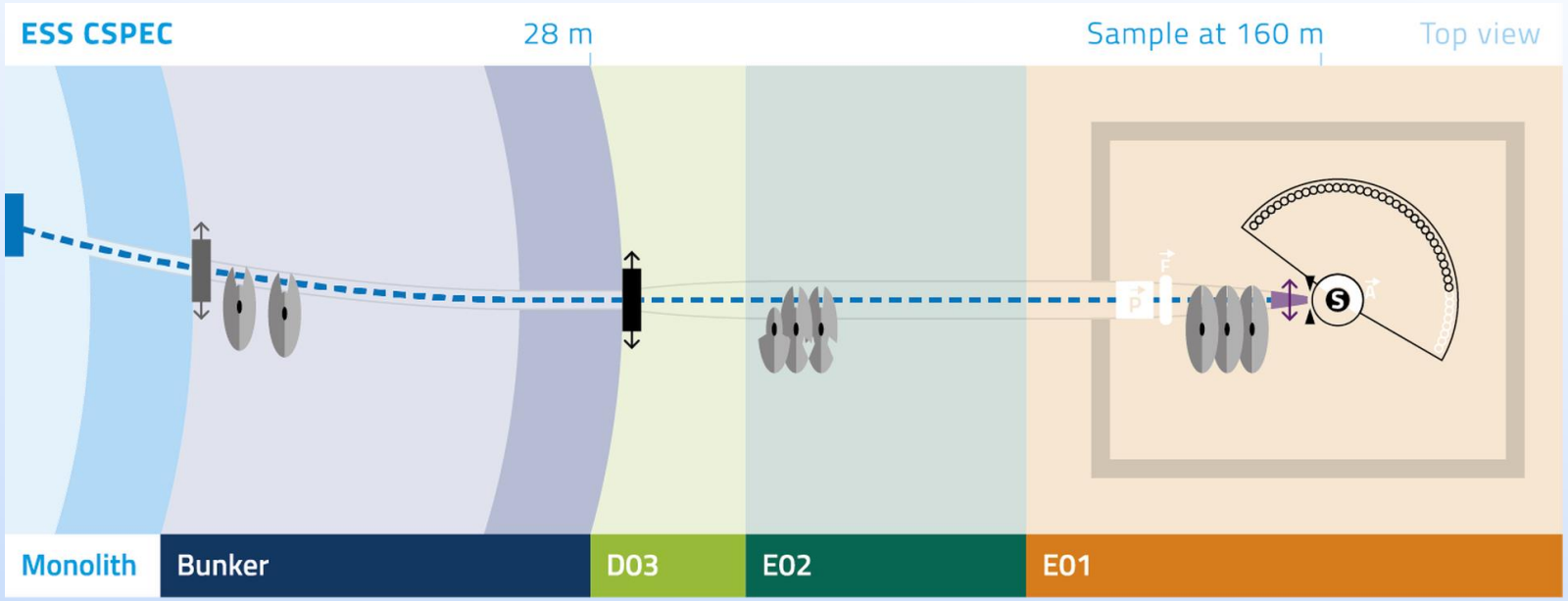

… and texture measurements

exchangeable beam-shaping optics



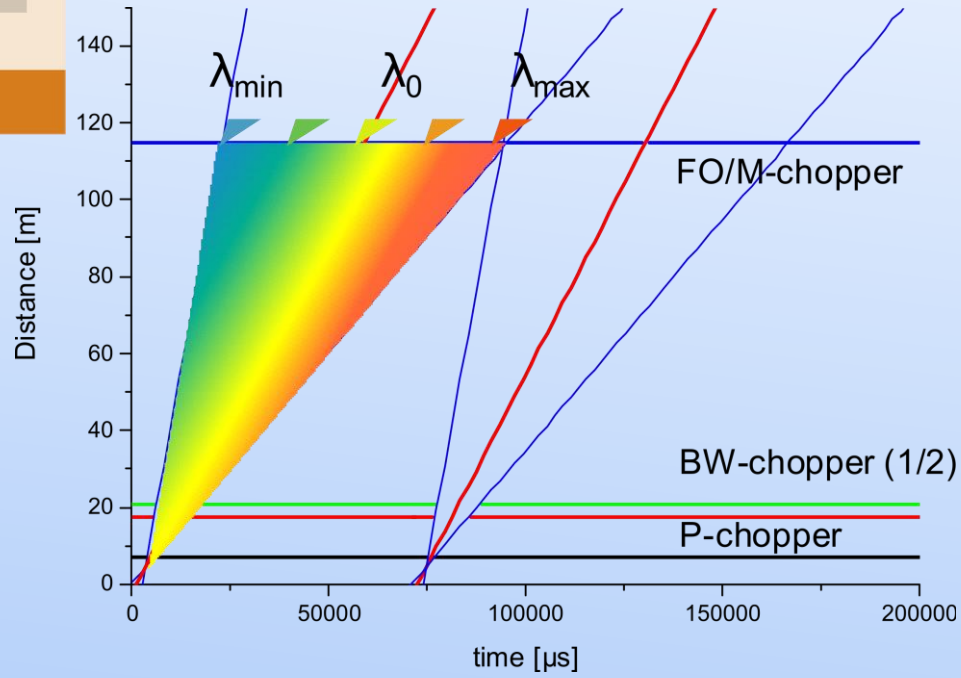



# CSPEC – cold **c**hopper **spec**trometer



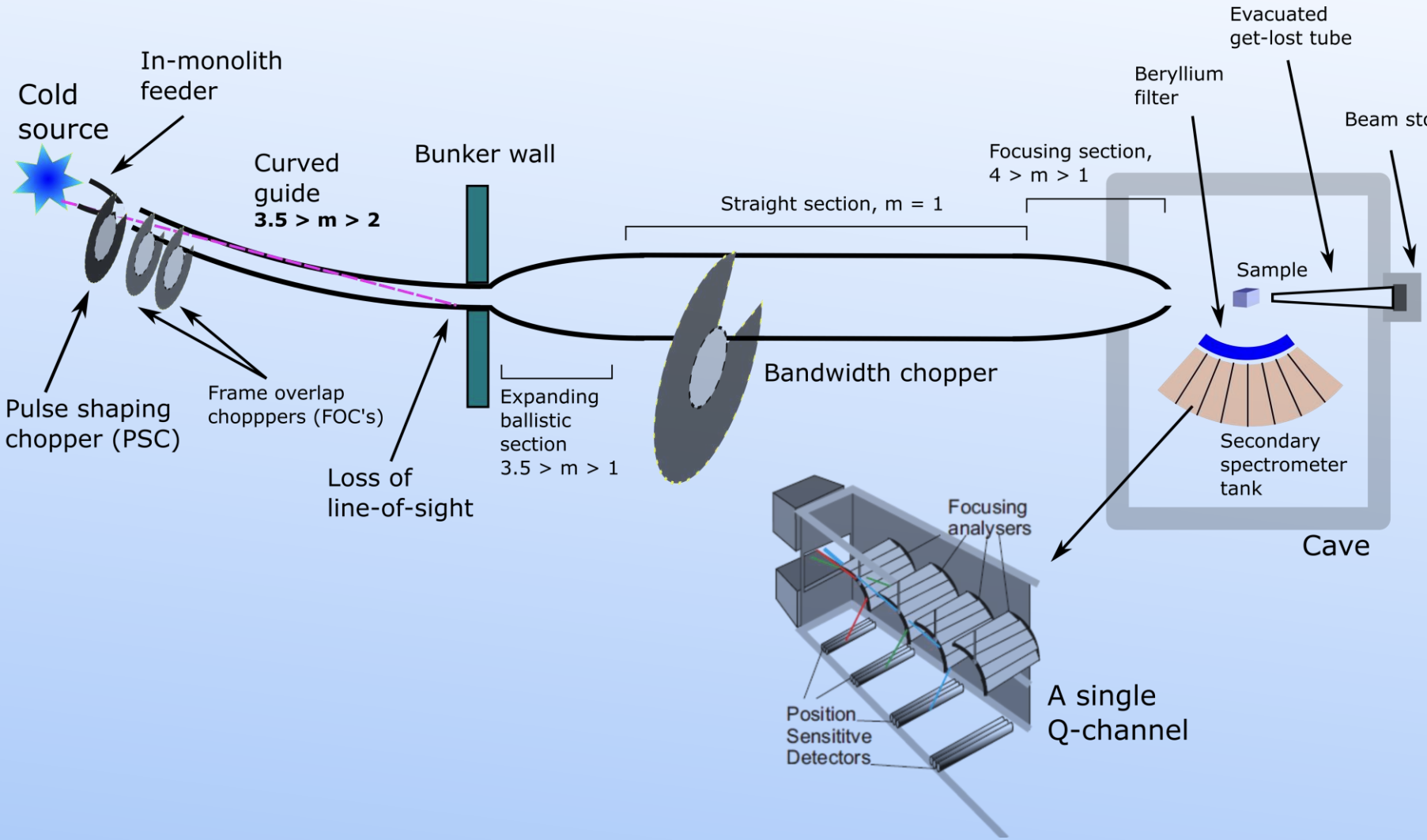

**CSPEC** will used in a wide variety of scientific applications, spanning the life sciences, functional materials and chemistry. *Its key capability is to follow kinetic events in situ or in operando, enabled by very high flux.*

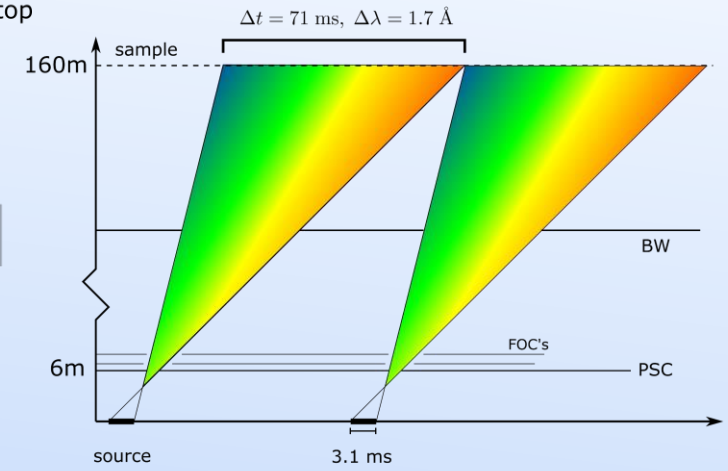
**CSPEC** is a direct geometry time of flight spectrometer developed as a German/French collaboration between FRM II and LLB.

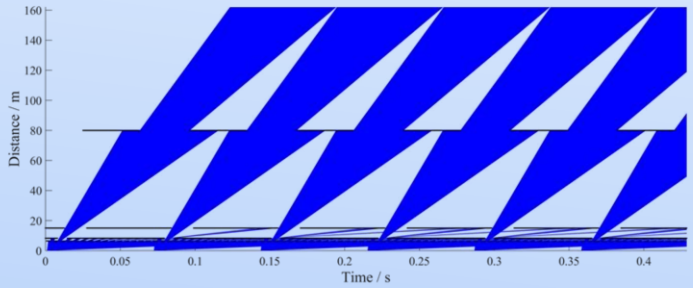


# BIFROST – extreme environment spectrometer

**BIFROST** — inverted geometry spectrometer (evolved from **CAMEA**)

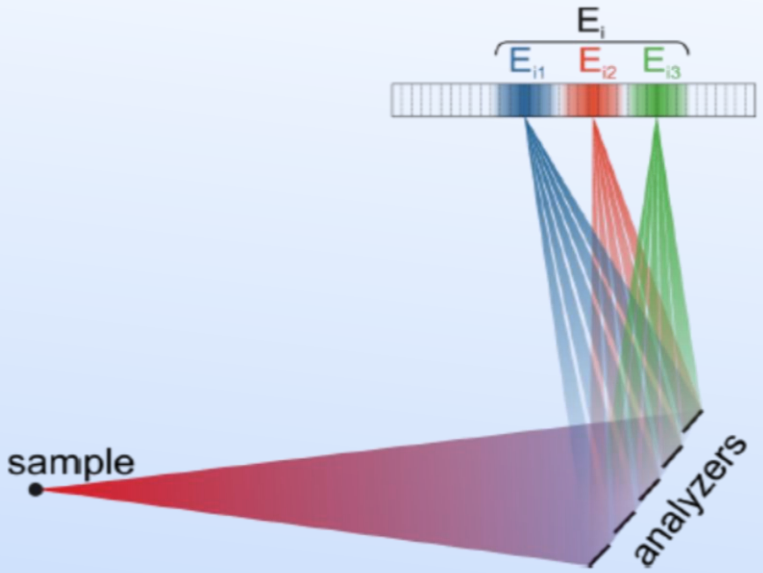


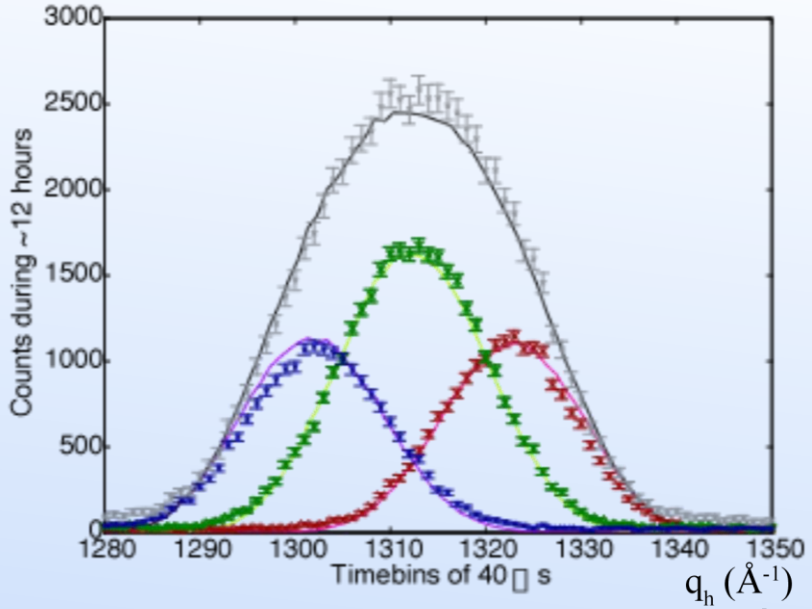



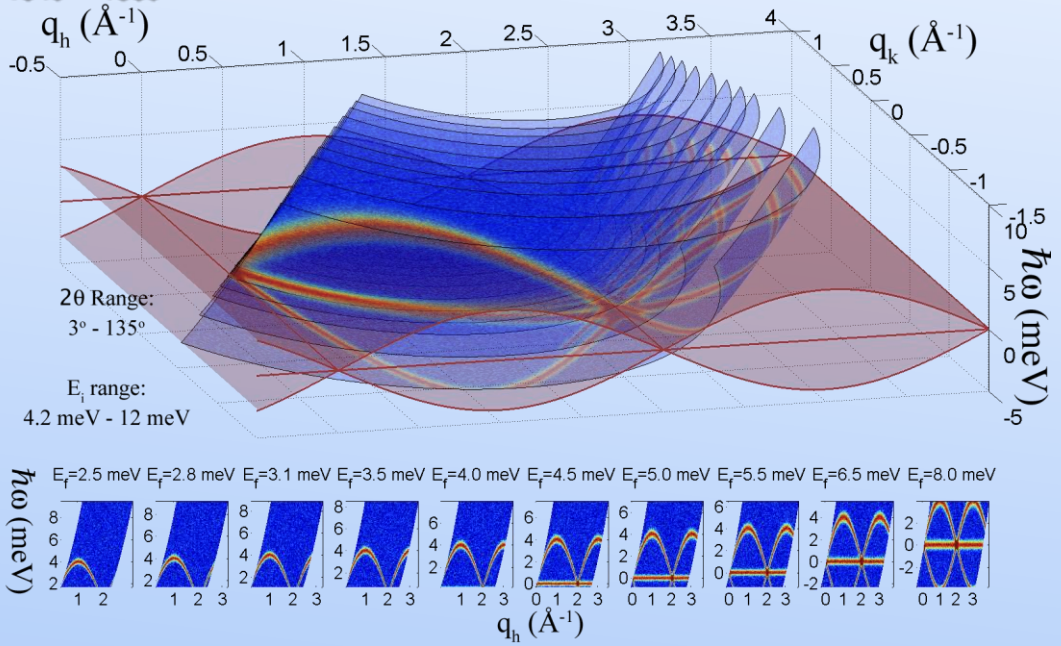




**BIFROST** primary spectrometer

# BIFROST – extreme environment spectrometer

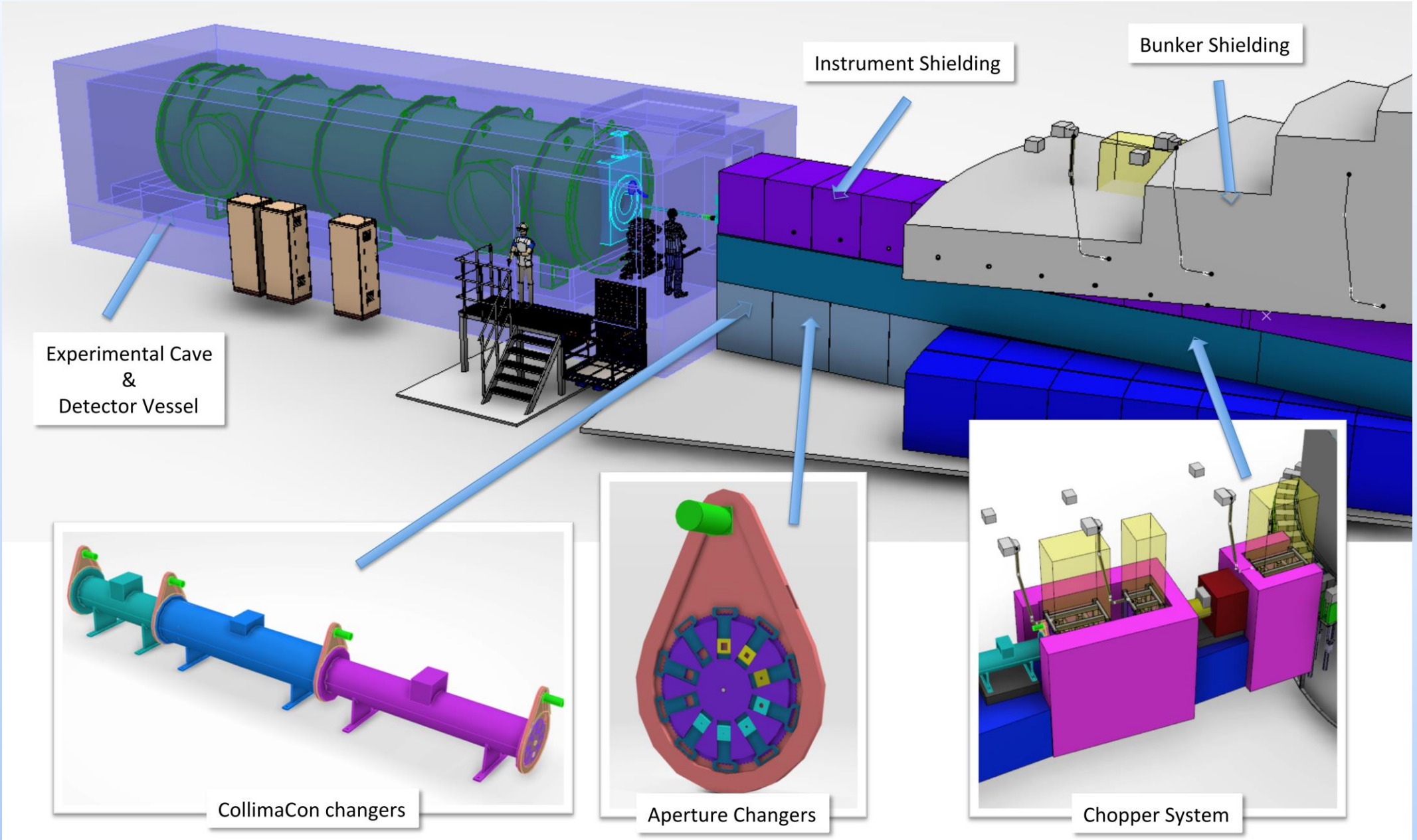


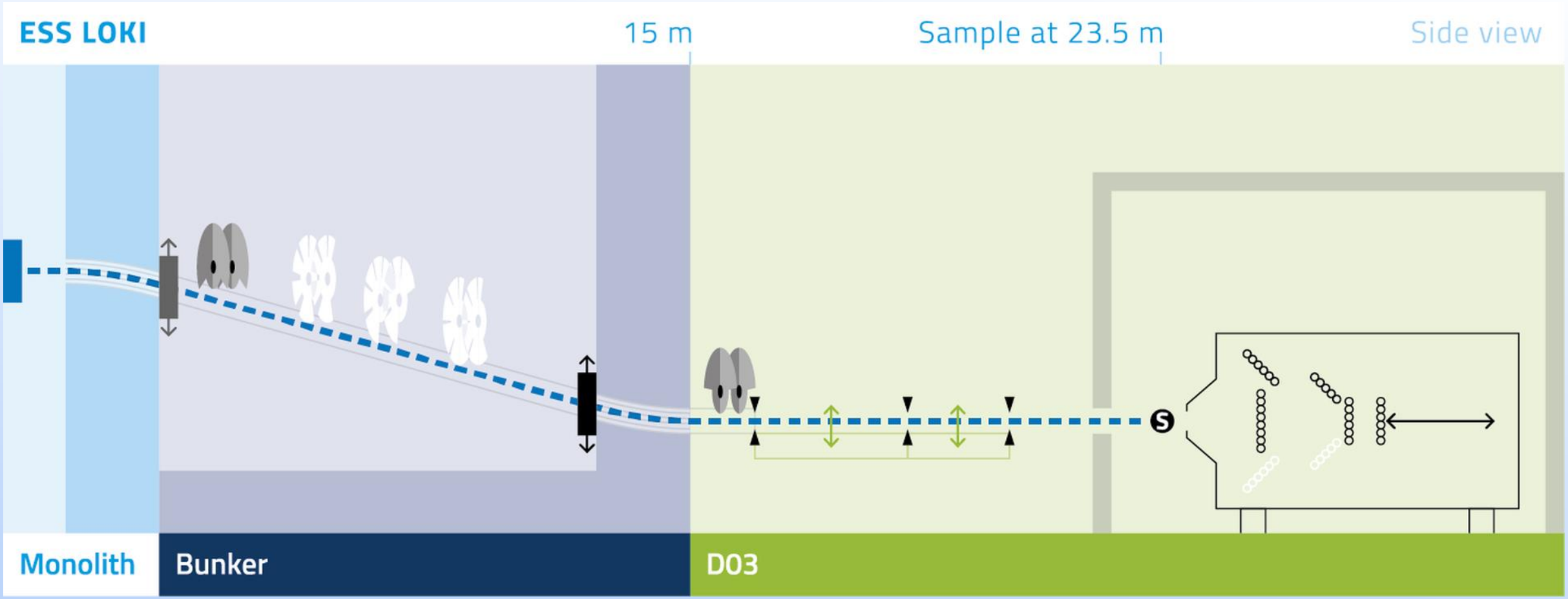

**BIFROST** — the concept of prismatic spectroscopy

# LOKI – broadband SANS



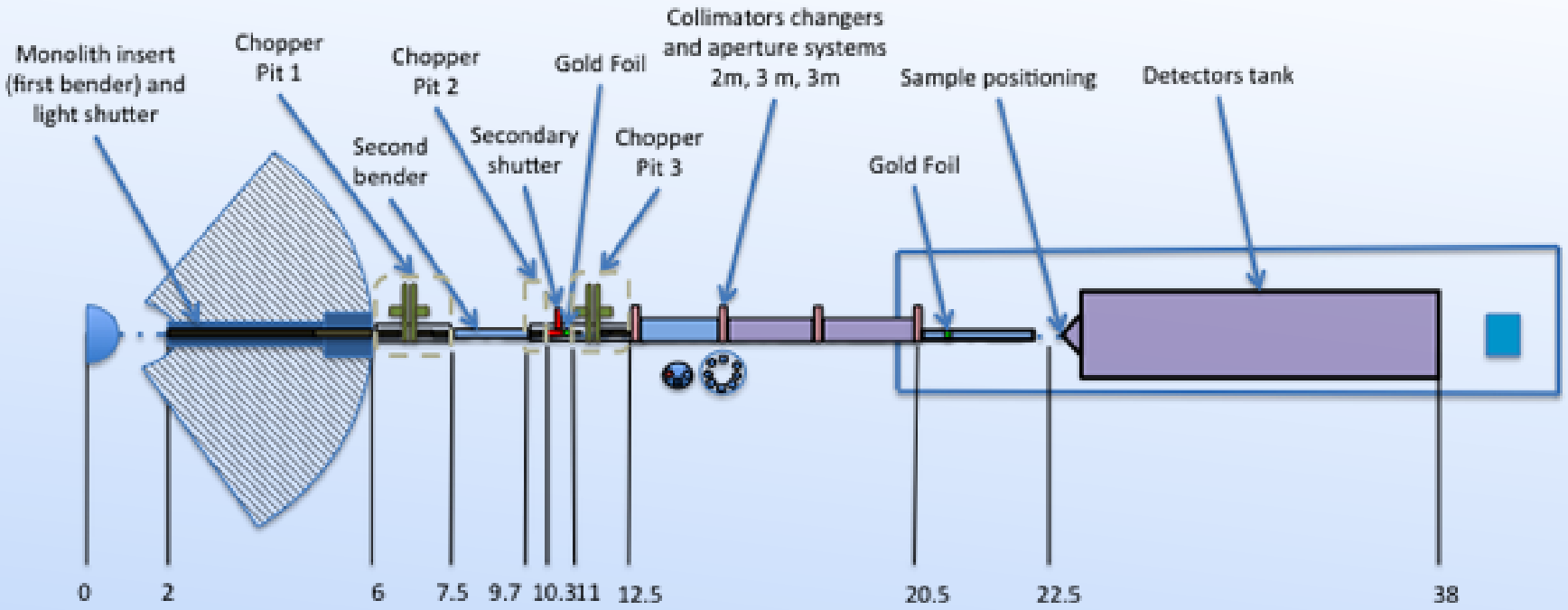
# LOKI – broadband SANS

A broad Q range, high flux SANS instrument for soft matter, bio–science and materials science




**LoKI** is the shorter of the two SANS instruments being built at ESS. The sample position is located at 23.5 m from the source and the maximum sample-to-detector distance is 10 m.

# LOKI – broadband SANS




**Loki**, the Norse god of mischief

(appears in Richard Wagner's opera cycle Ring of the Nibelung)

$L1_{max}$ = 10m
$L2_{max}$ = 10m
Repetition rate = 14Hz or 7Hz
$\delta\lambda_{max}$ = 10Å at 14Hz

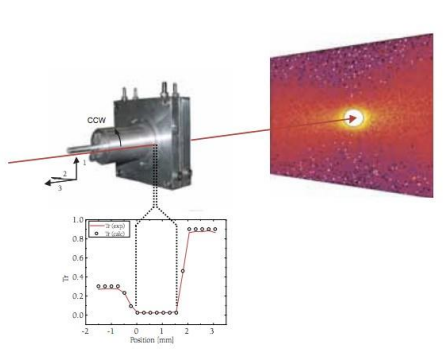
Max flux on sample ~$1x10^9$ n/$cm^2$/s

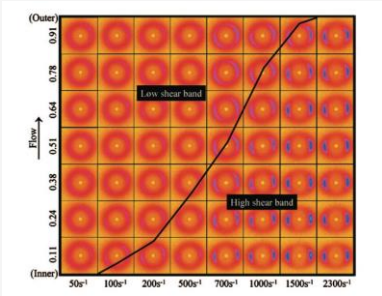
2x line-of-sight closure

# LOKI – broadband SANS

Shear Banding in CTAB wormlike micelles providing confirmaCon of rheological model. (Helgeson et al. (2009) J. Rheol 53, 727)

## FLOW

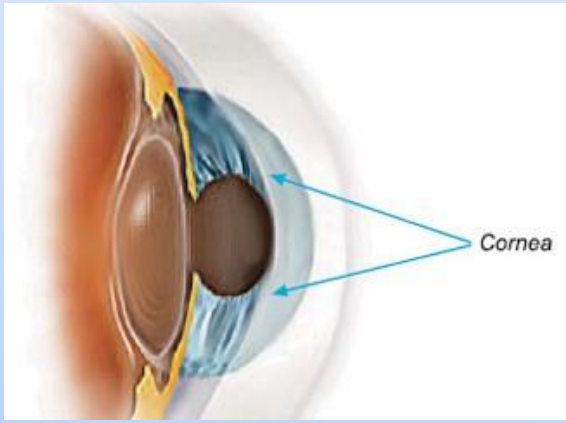


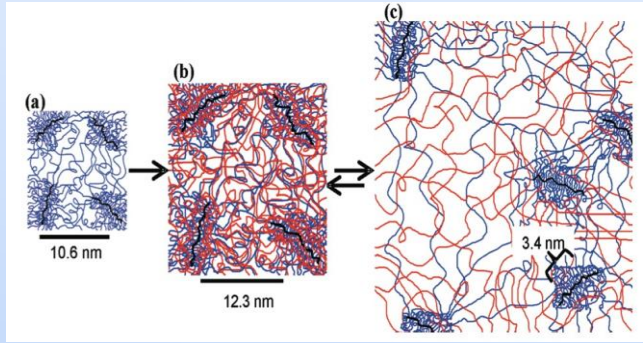




The flow of **complex fluids** through **complex geometries** is relevant to many industrical processes. There is a need to understand **structur effects of flow** both for pracCcal purposes and to compare with fluid flow models.

## KINETICS

Gel structure forms over **mulDple length scales. KineDcs** of gelaCon can be rapid needing **sub–second** time resolution. Neutrons provide the structure of each component in the presence of the other.

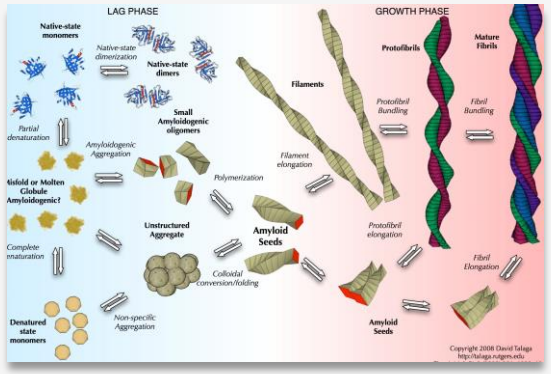



Swelling of a double network hydrogel designed for use as a cornea replacement. (Frank Group, Stanford)

# LOKI – broadband SANS

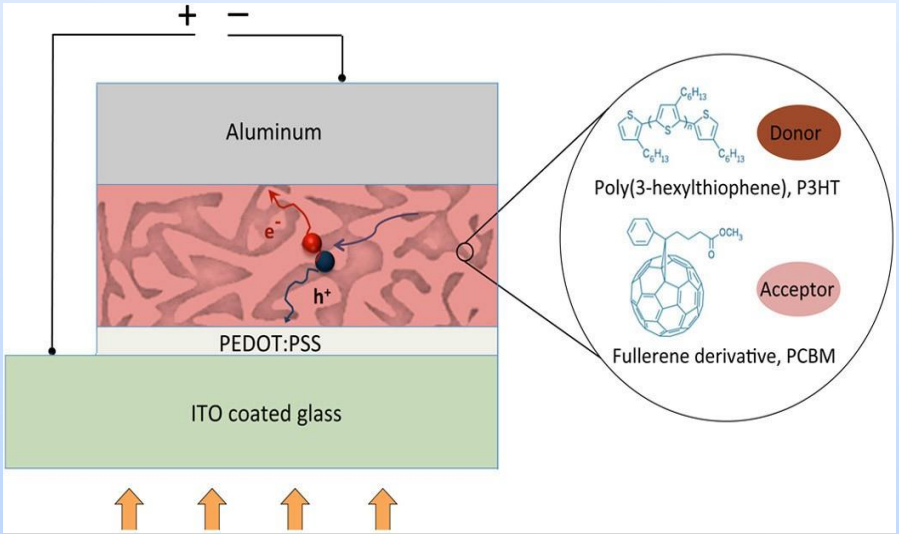
**MULTI SCALE**



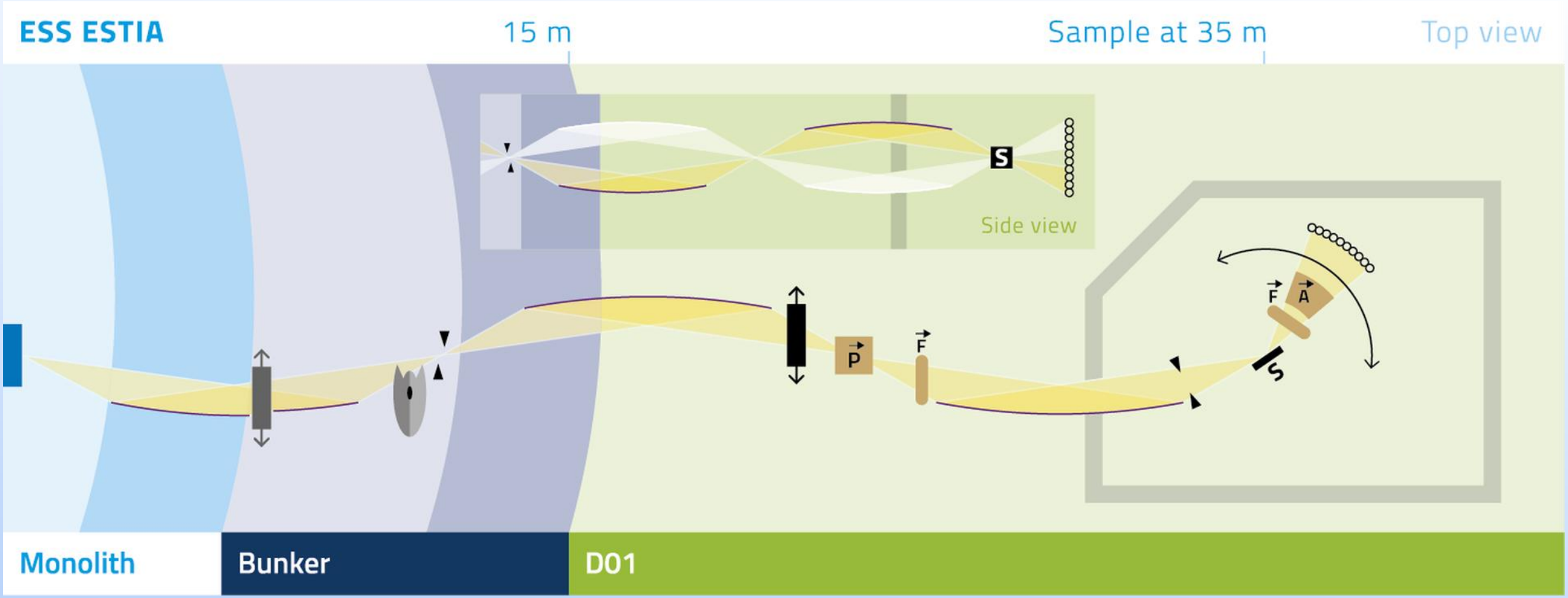

**Amyloid fibril** formation and growth is a **multi-length scale problem** and to understand methods of formation and inhibition the structural evolution must be observed.

**DEVICES**

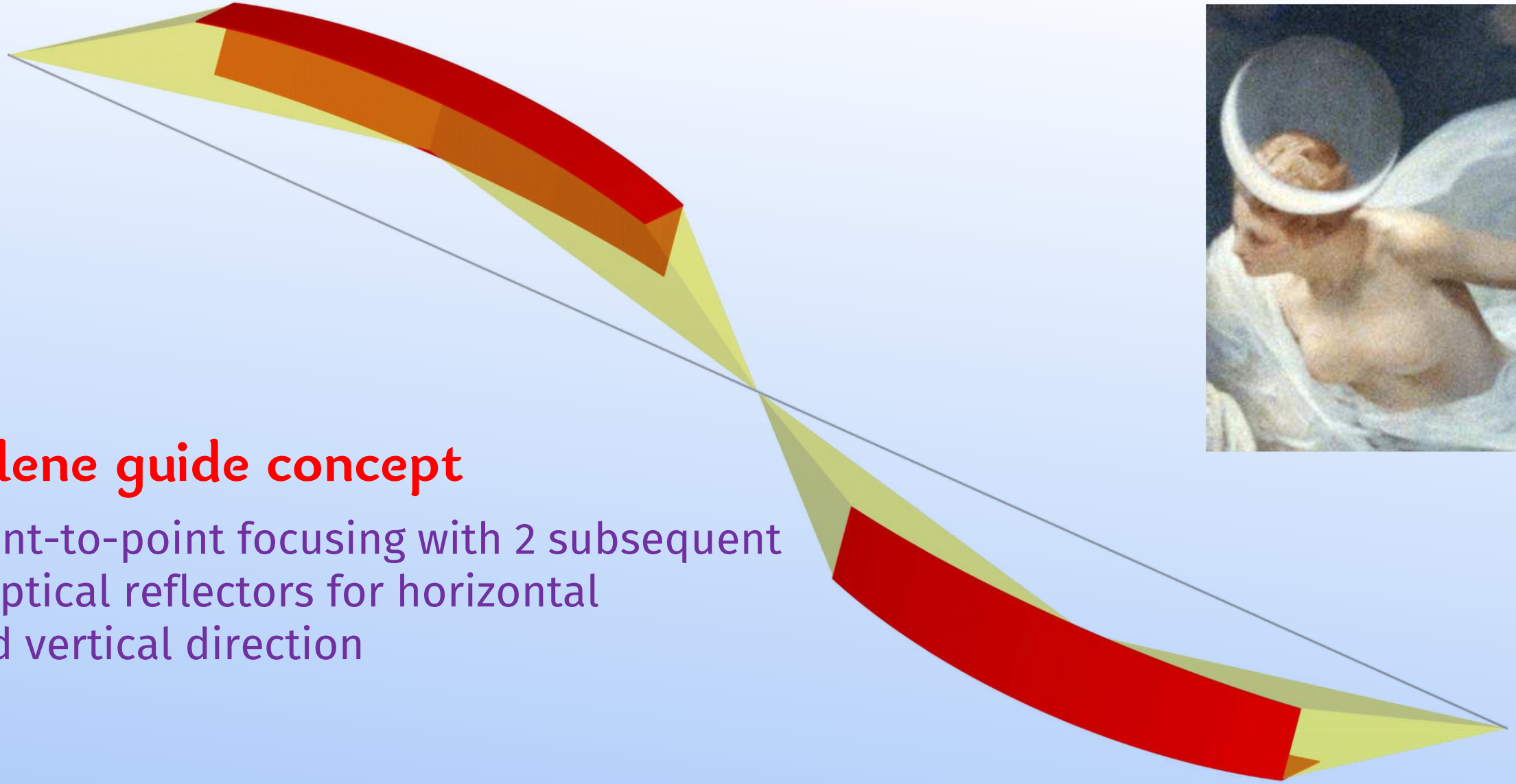
**Organic Solar Cells** promise to provide cheap and accessible solar energy. The **lifespan** and **efficiency** of the devices depends on the **nano–structure** polymer mixture. Understanding the **structural evolution** under operation guides development of new devices.



# ESTIA – focusing reflectometer



# ESTIA – the concept of Selene guide

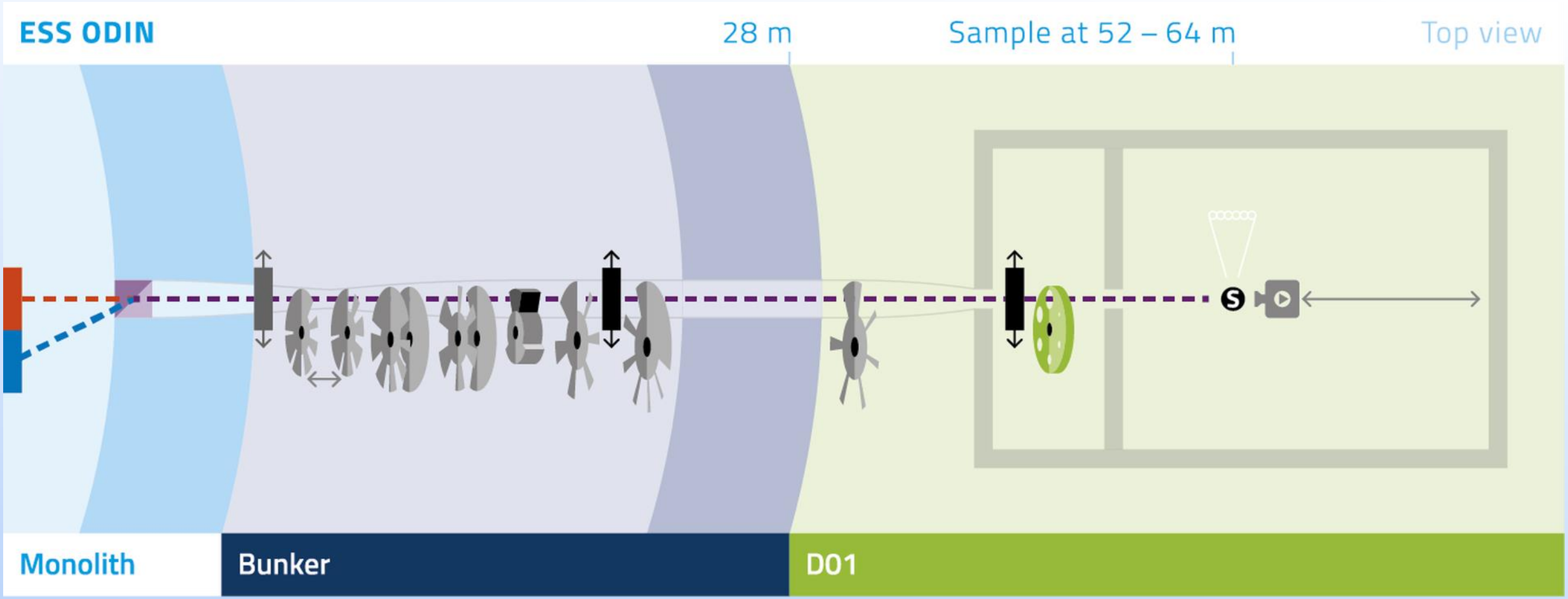




## Selene guide concept

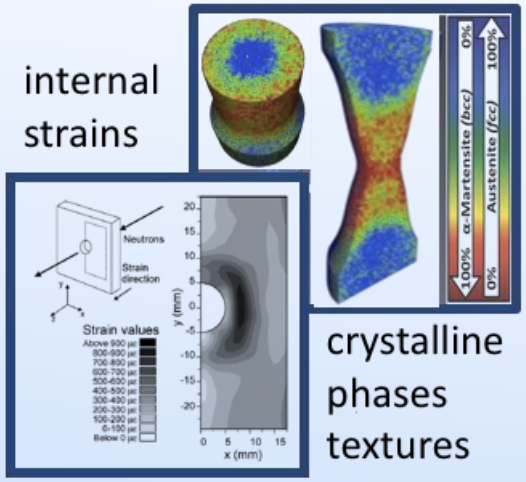
point-to-point focusing with 2 subsequent elliptical reflectors for horizontal and vertical direction

# ESTIA – multipurpose imaging




**Neutron imaging** is a real-space technique examining the inner structure of potentially highly complex components and samples by detecting the transmitted beam.

# ESTIA – multipurpose imaging





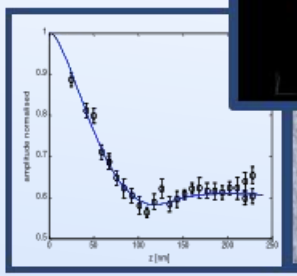


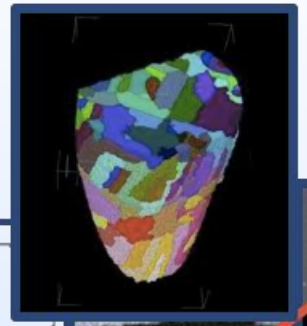
internal strains

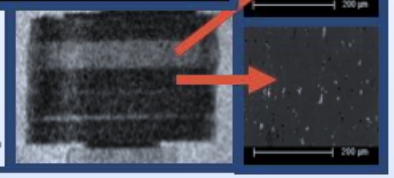
crystalline phases textures

Diffraction regime

polymers, microstructure, magnetic domain structures







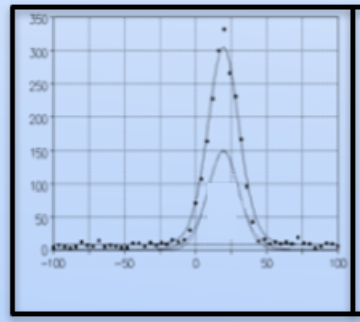
cracks pores precipitates

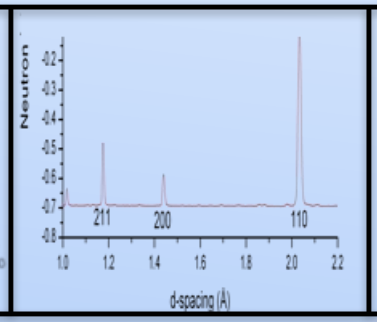
SANS and Dark-field imaging regime

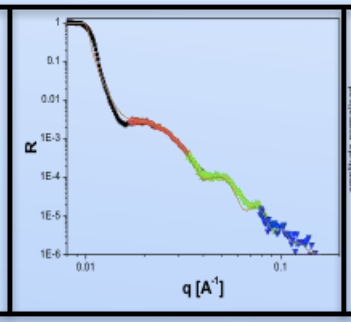
Length scale in nm

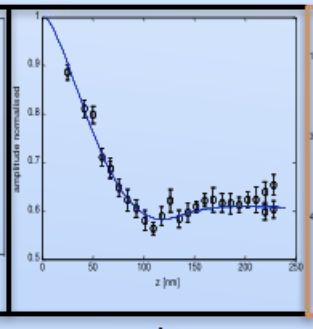
0.01 0.1 0.3 1.0 3.0 10 100 1000 10000 100000

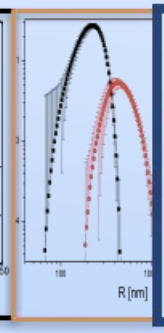
Conventional imaging regime

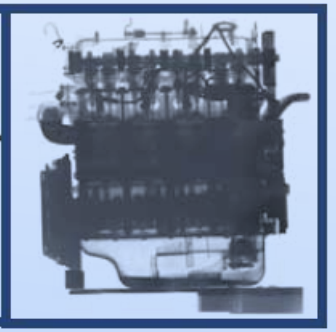




*atomic and magnetic structures*

*organic molecules*

*surfaces and multilayers*

*inhomogeneities*

*viruses*

*cracks and voids*

*magnetic defects*

*micelles*

*critical phenomena*

*pharmaceuticals*

*proteins*

*internal strain*

*supermolecules*

*polymers*

Systems and components