Properties of H_2O confined in Silica Mirco-spheres

From Los Alamos to Lund

Günter Muhrer

WG-42 kick-off meeting

LANSCE – Los Alamos Neutron Science Center

Linearbeschleuniger(1km):
1MW,800 MeV H+
(=0.85 c)

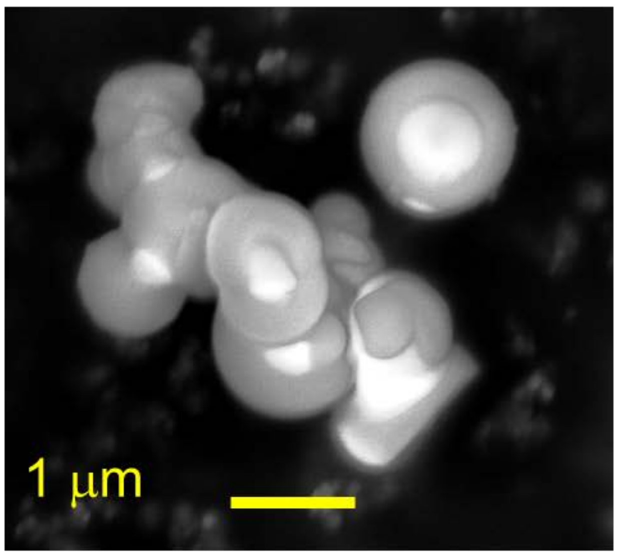
Moderator Materials

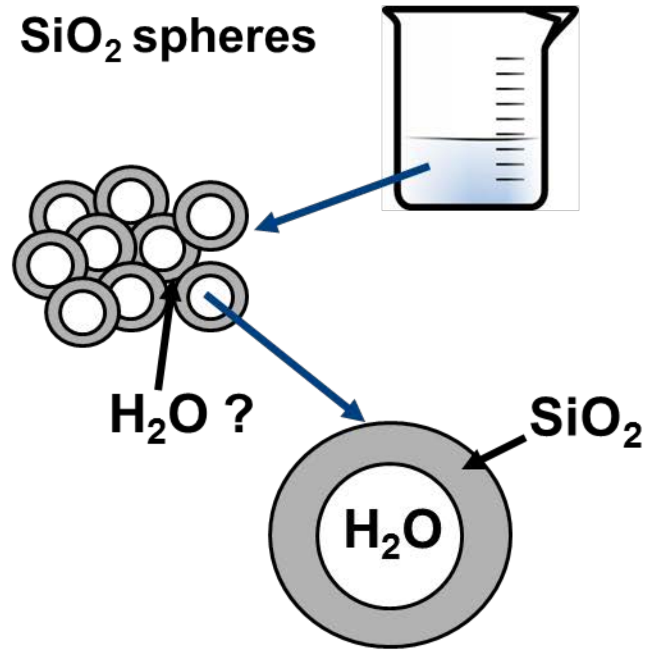
- **Water as a neutron moderator – why not stick with it?**
  - Relatively high hydrogen concentration
  - Operational advantages (easy cooling, cheap & abundant)
  - **Limited operation temperature range !**
- **Next generation neutron source**
  - More neutrons AND broader wavelength range (very-cold neutron regime)
  - **More flexible operating range (100-300K)**
- **Solutions**
  - Use materials that are liquid or solid at r.t. (no phase transition(s) or predictable phase transitions while cooling)
  - **Adsorb materials on a surface** to prevent phase transition while cooling.

Next generation: Choosing the right moderator temperature for each experiment ?

Water in Silica Microspheres

- **Silica is inert/ lightweight**
- **TEOS + NaOH + H_2O/EtOH** $\xrightarrow[\text{45 min}]{\text{Ultra sound}}$ **SiO_2 spheres**

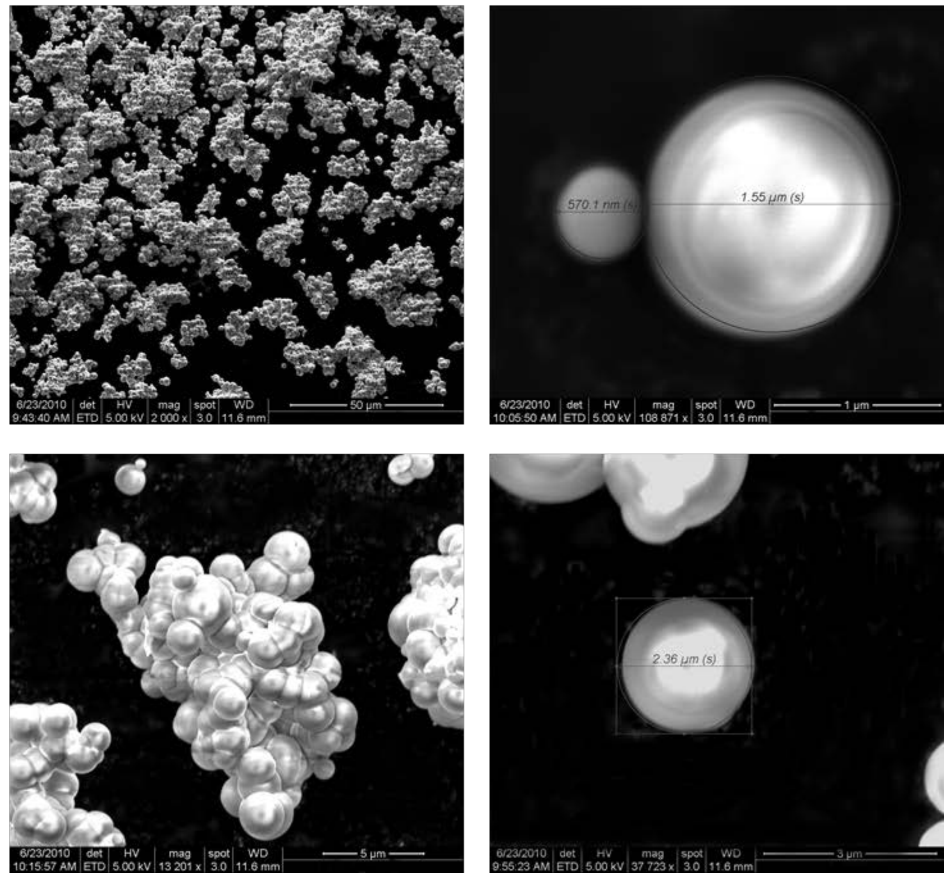




- **40 weight-% water in silica**

SEM of the silica spheres

- **Spheres are agglomerated**
  - Room for water in the spaces between the spheres?
- **Three different sizes of spheres are present:**
  - d = 2.4 μm
  - d = 1.5 μm
  - d = 600 nm



Water in Confined Geometry

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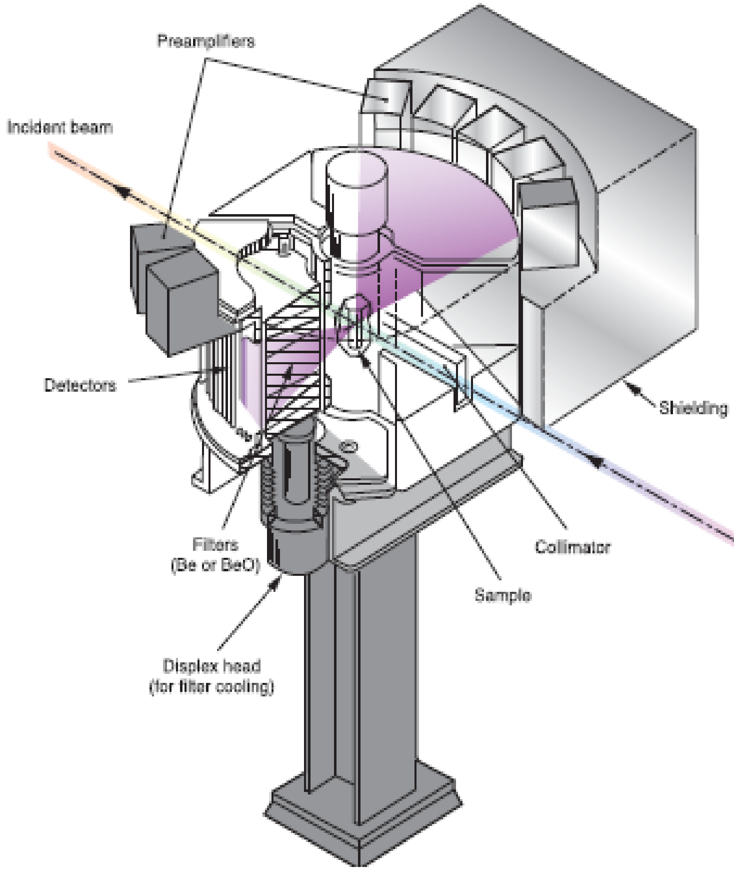
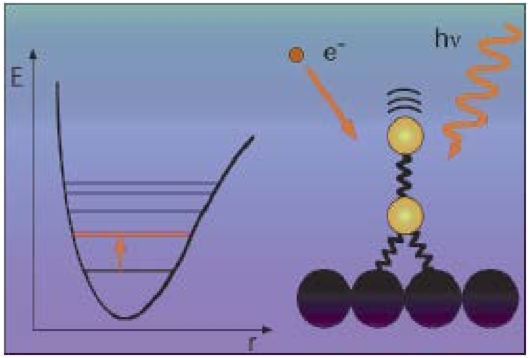
- Confined Geometry
  - has a strong effect on hydrogen bonded networks
  - causes water to be supercooled (e.g. water in mesoporous silica with pores of 35 Å to about -40 °C)
  - can lead water to forms certain forms of ice (e.g. mesoporous silica with pores of 35 Å forms cubic ice in the pores) *Dore et al. J. Phys. Condens. Mater 16(2004)5449*

- IINS – Excitation spectra, vibrations
- SANS – Where is the water?
- Transmission measurements – Total scattering cross section

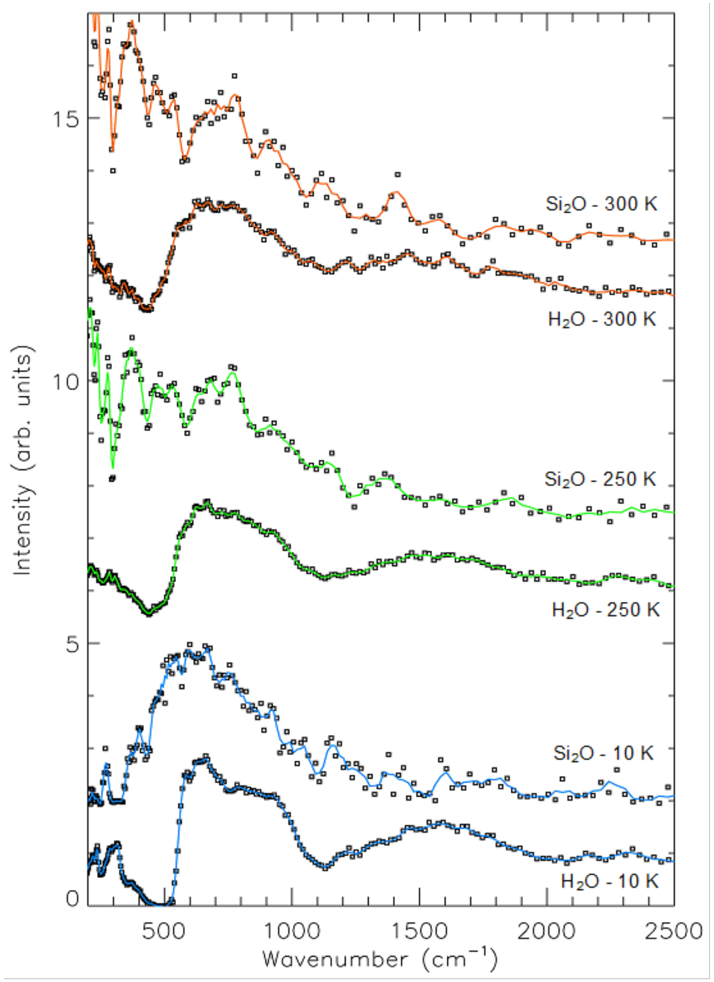
Filter Difference Spectrometer (FDS)



Energy transfer:	6-620 meV (50-5000 cm^{-1})
	2-5 % resolution
Beam size at sample	2.5 cm x 10 cm (W x H)
Sample size	0.5 – 100 g
Detector	^3He tubes (60)
Filter analyzers	Be (refrigerated)



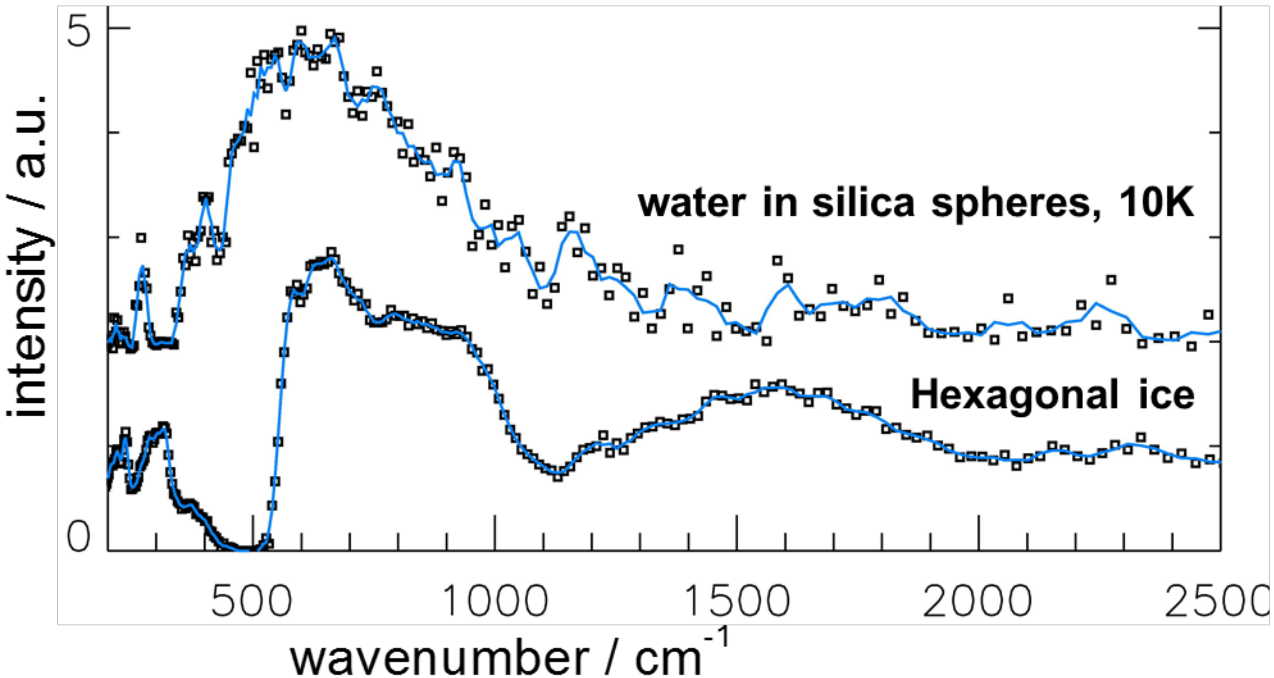
IINS Data of H_2O in Silica Spheres



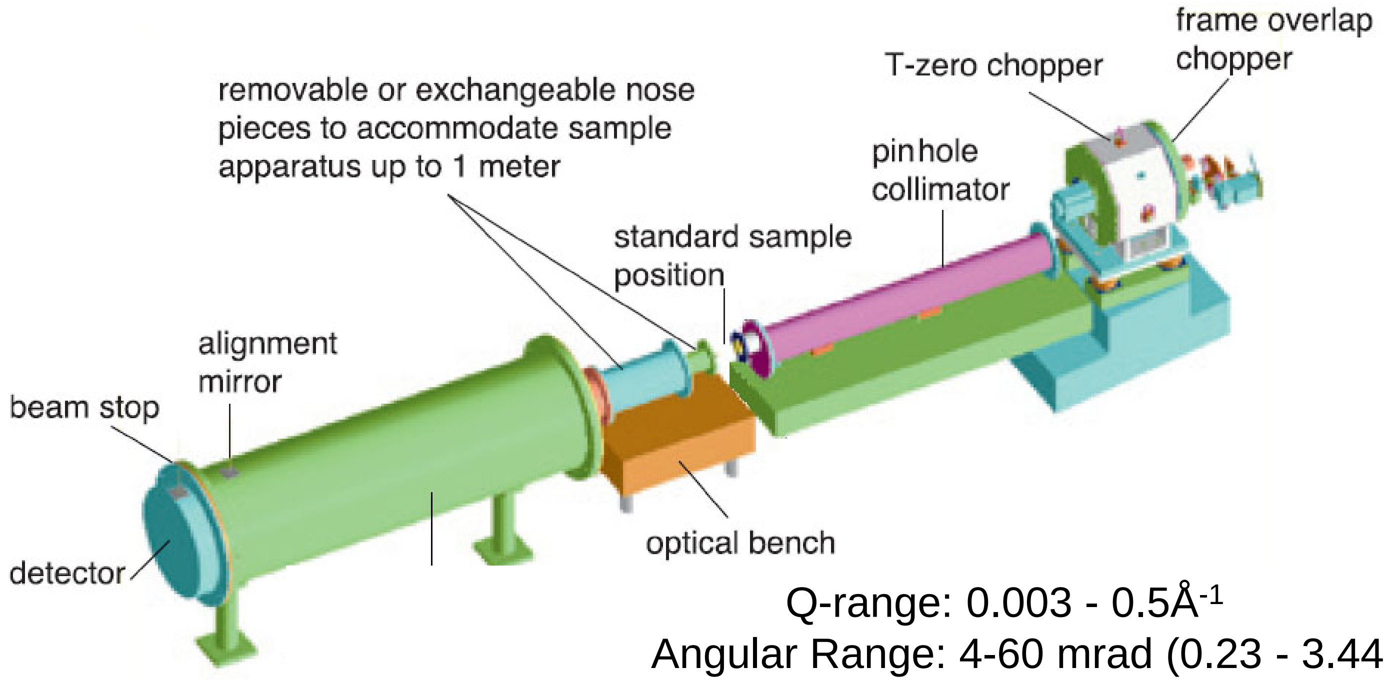
- **IINS: Incoherent Inelastic Neutron Spectroscopy**
- **Water at 250 K is still liquid**
- **Modes for liquid H_2O:**
  - **Librational bands of "free" water: 550-1000 cm^{-1}**
  - OH-bending: 1645 cm^{-1}
  - OH-stretch: 3280-3920 cm^{-1}

IINS Data of H_2O in Silica Spheres

- **Modes for frozen water in silica spheres**
  - Shift of librations to fairly low wavenumbers (300 cm^{-1})
  - surface interaction



Low-Q Diffractometer (LQD)



Q-range: 0.003 - 0.5Å^{-1}

Angular Range: 4-60 mrad (0.23 - 3.44 °)

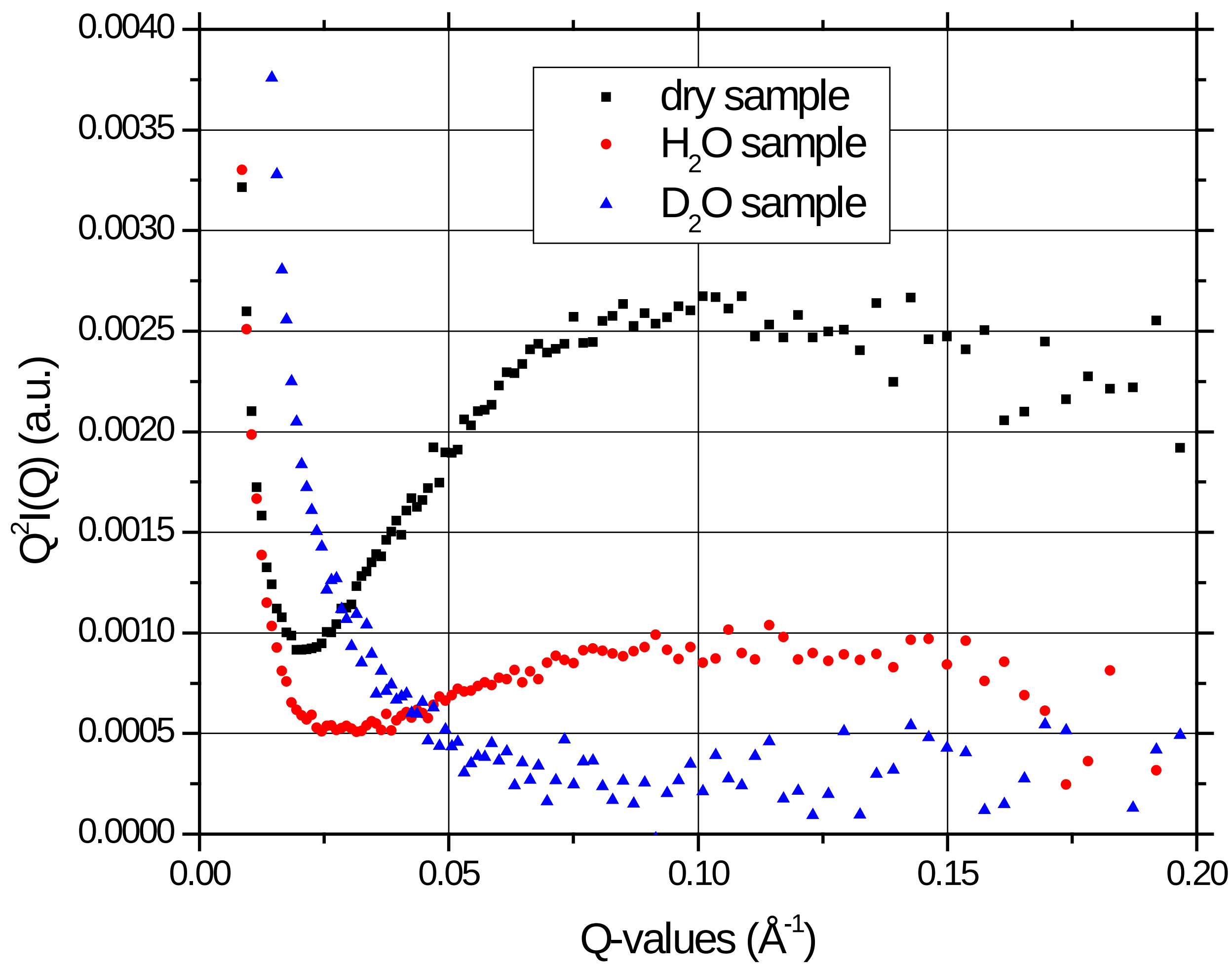
Moderator: liquid H_2 at 20K (partially decoupled)

Detector: 2D area detector

Source/sample aperture: 2 - 8mm

Wavelength Range (incoming): 1 - 16Å

SANS: Kratky plot



SANS: Fitting models

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Broad Peak model:

$$I(Q) = \frac{A}{Q^n} + \frac{C}{1 + \left(\left|Q - Q_0\right|\xi\right)^m} + B$$

Guinier-Porod model:

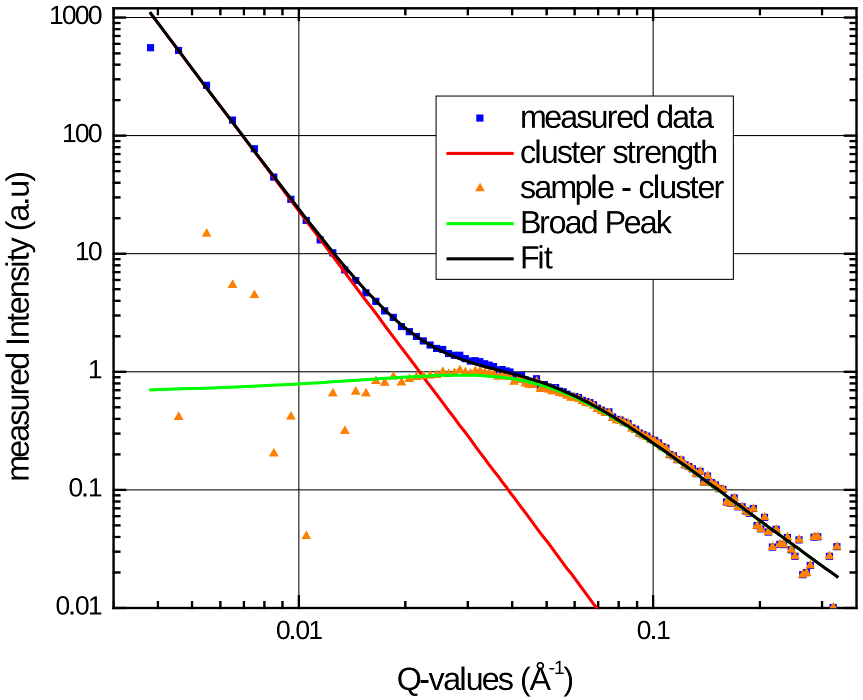
$$I(Q) = \frac{G}{Q^s} e^{-\frac{Q^2 R_g^2}{3-s}} : \forall\, Q \le Q_1$$

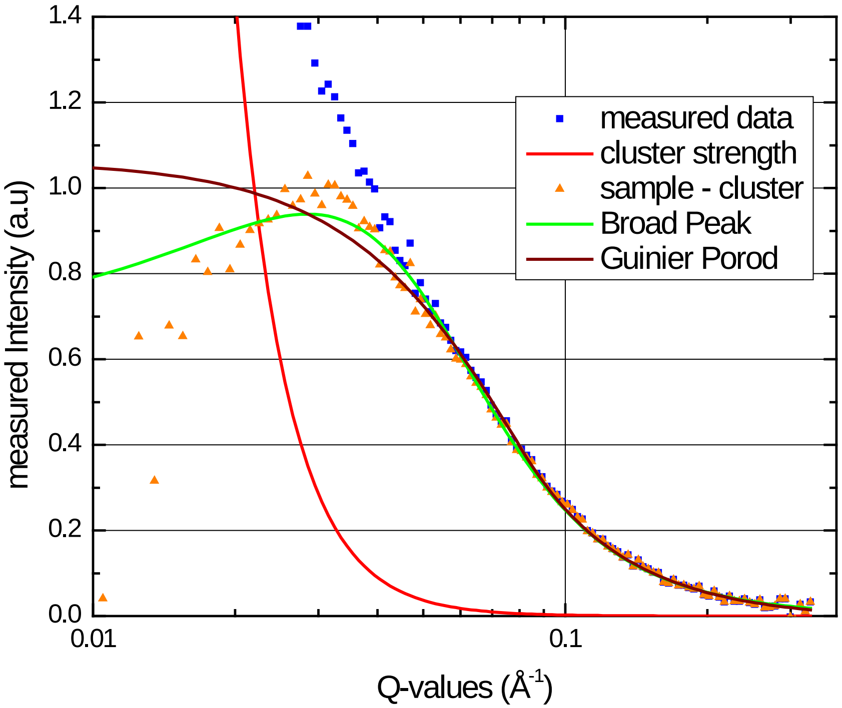
$$I(Q) = \frac{D}{Q^m} : \forall Q \ge Q_1$$

$$Q_1 = \frac{1}{R_g}\sqrt{\frac{(m-s)(3-s)}{2}}$$

$$D = Ge^{-\frac{Q_1^2 R_g^2}{3-s}} Q_1^{m-s}$$

SANS Data of dry Silica Spheres

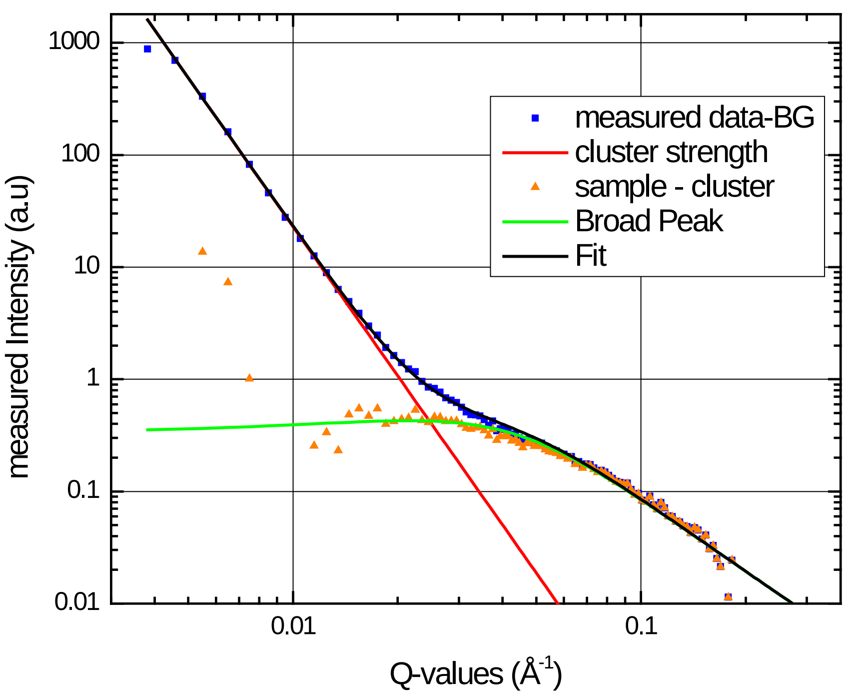




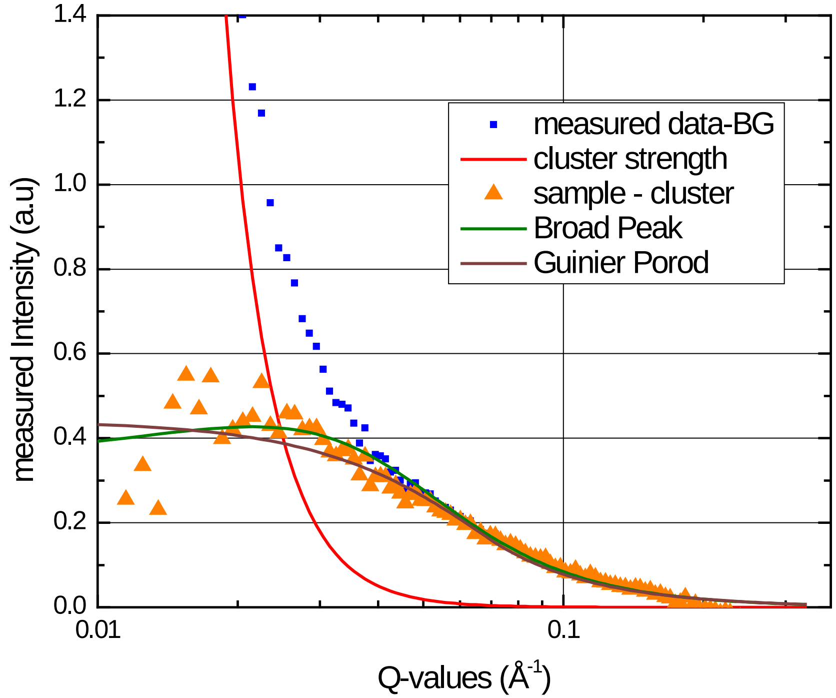
BP: ξ=23.4Ǻ
m=2.0 (Gaussian chains)
Q_0=0.0285Ǻ$^{-1}$ (d=220Ǻ)

GP: R_g=21.3Ǻ (R=27.6Ǻ)
m=2.0 (Gaussian chains)
s=0 (spheres)

SANS Data of Silica Spheres with H_2O

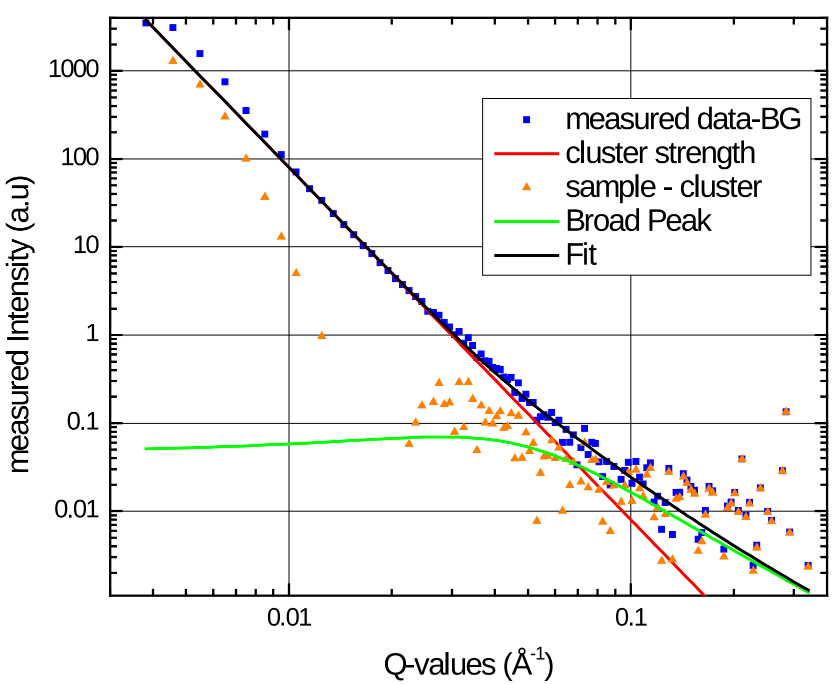


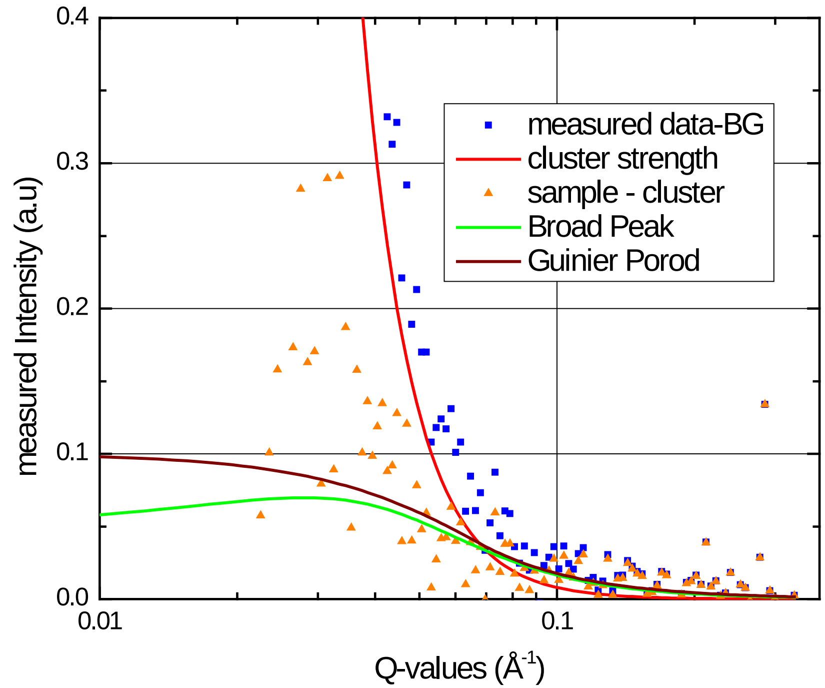
BP: ξ=25.7Å
m=2.0
Q_0=0.0215Å^{-1} (d=292Å)



GP: R_g=25.0Å (R=32.3Å)
m=2.0
s=0

SANS Data of Silica Spheres with D_2O



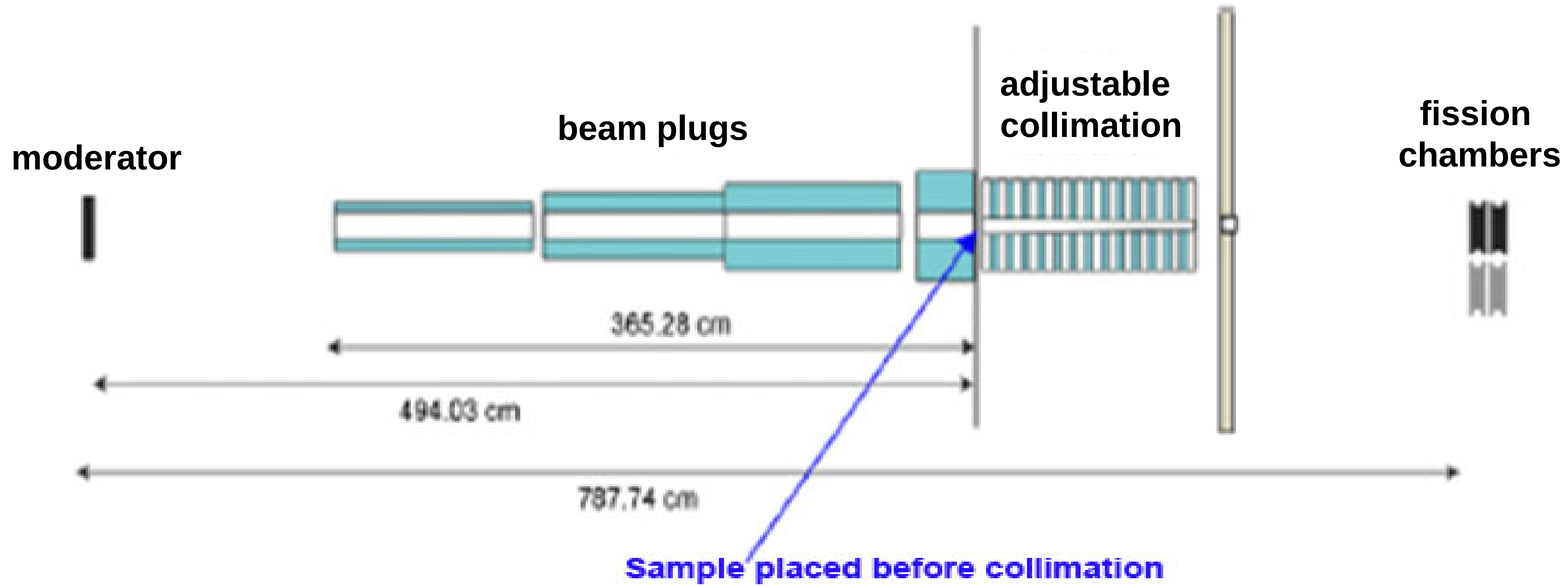


BP: ξ=25.0Å
m=2.0
Q_0=0.028Å^{-1} (d=225Å)

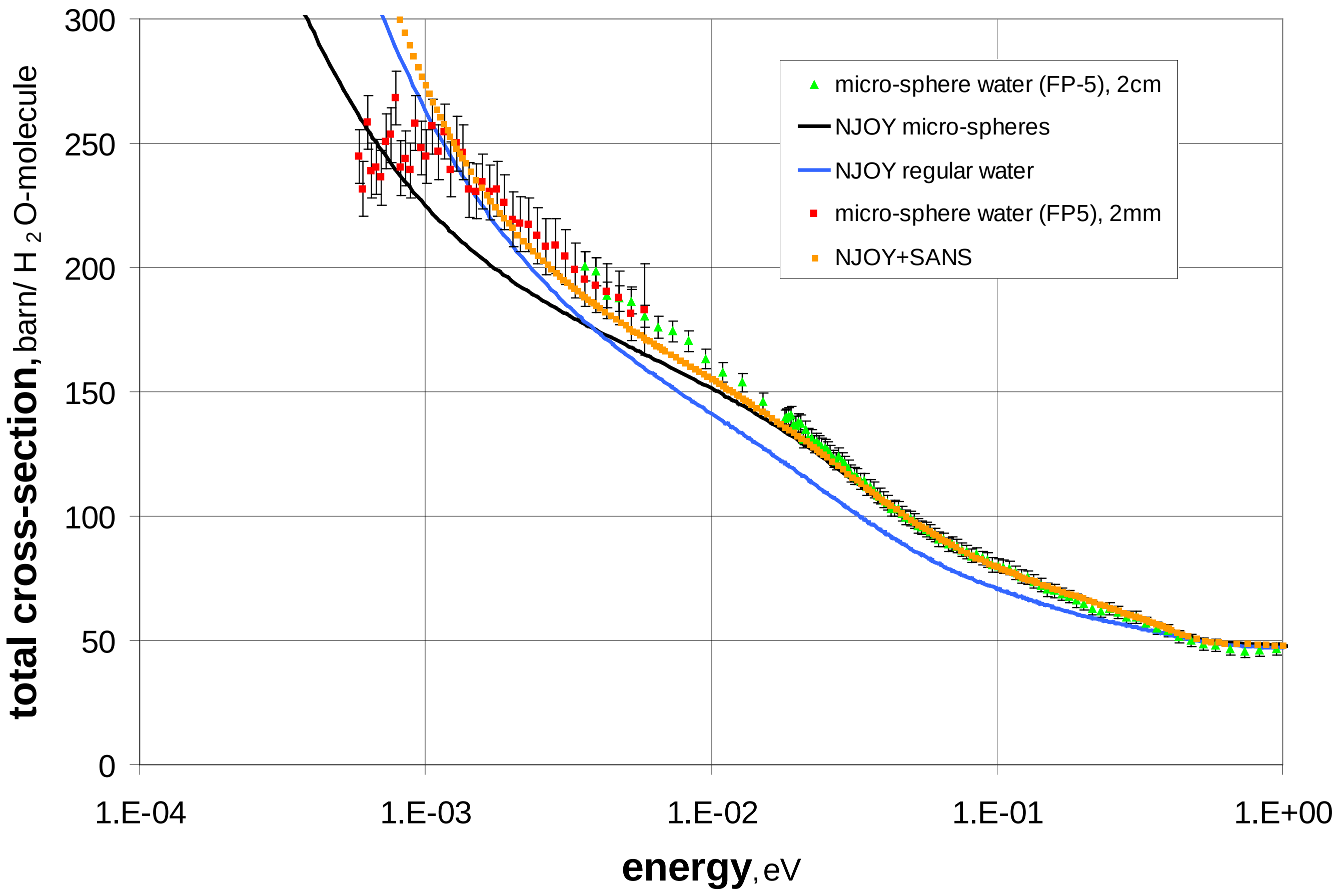
GP: R_g=25.0Å (R=32.3Å)
m=2.0
s=0

FP5: Total Cross Section

- The fission chamber detector measures the time-dependent neutron beam flux after passing through the sample by using the 235U(n,f) standard reaction.



Total Cross Section of H_2O in Silica Spheres

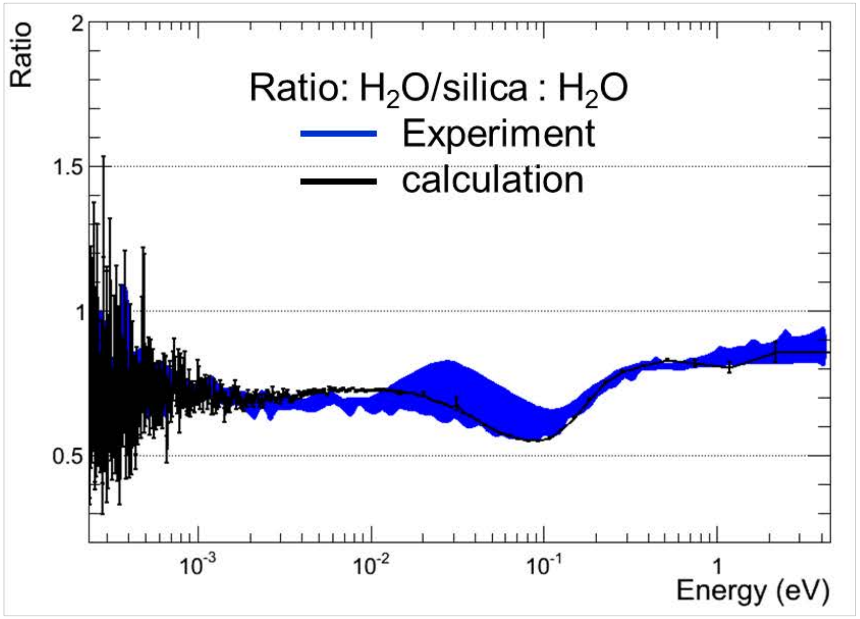


Properties of H_2O in SiO_2

- no OH-bending mode (E=208mV)
- more phonon modes at low energies
- solidification below 250K
- water confined in spheres (R~30Ǻ)
- spheres build Gaussian chains
- correlation length of the chains is about 250Ǻ

Blue Room Experiment H_2O / Silica-spheres

"Real-size" moderator testing



Spectrum ("Maxwellian") is shifted to lower energy -"colder" spectrum

Proof of principle that shape of spectrum can be manipulated through confinement (usually spectrum defined by material)

Lujan Neutron Scattering Center

Road to realizing the world's leading facility for research using neutrons

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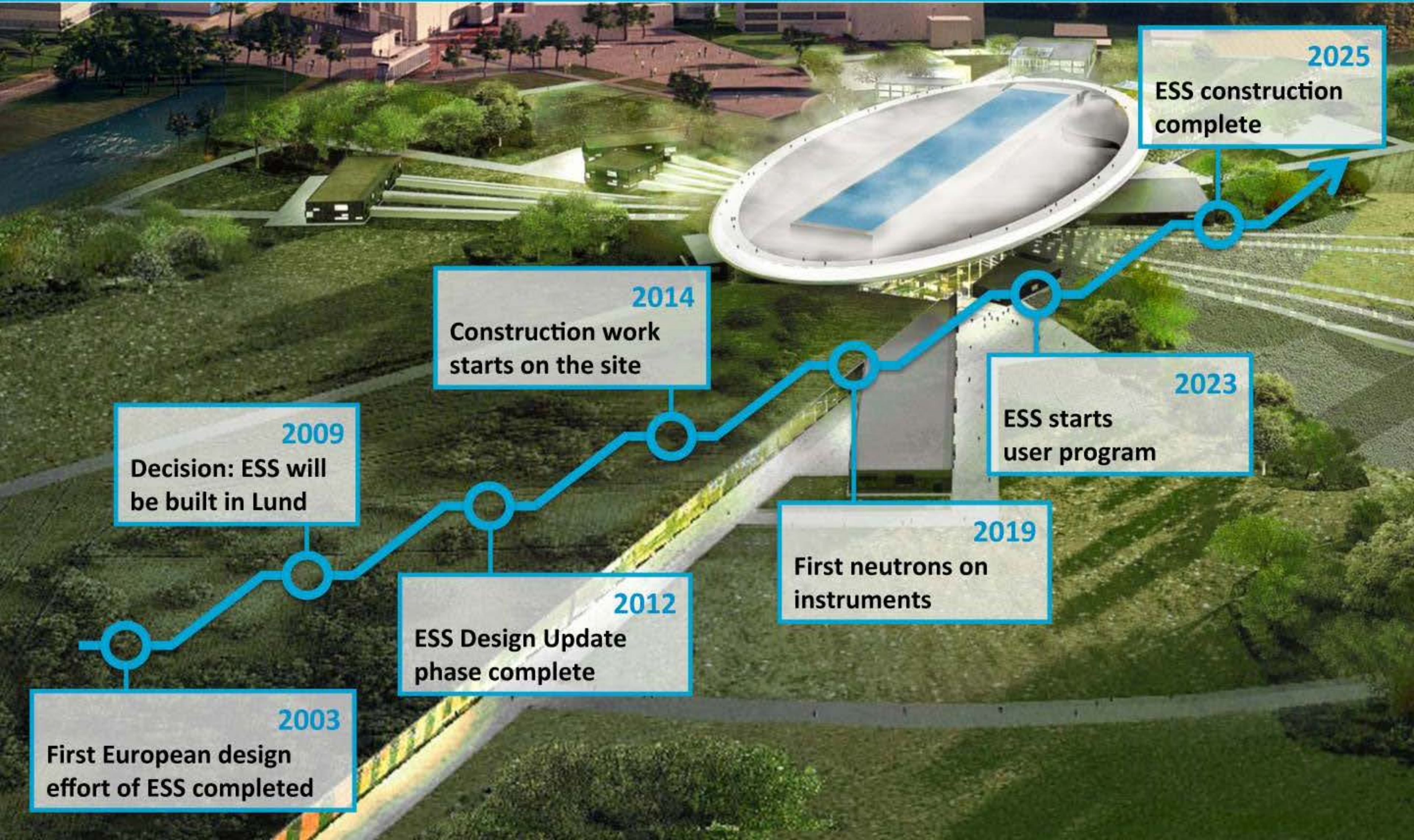


December 9

Goals for ESS

- Build up scattering kernel competence
- Build up experimental program to develop scattering laws for materials of interest for target physics
- Add small angle scattering to NJOY

Acknowledgement

EUROPEAN SPALLATION SOURCE

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