# Introduction to Small Angle X-ray Scattering for Nanomaterials

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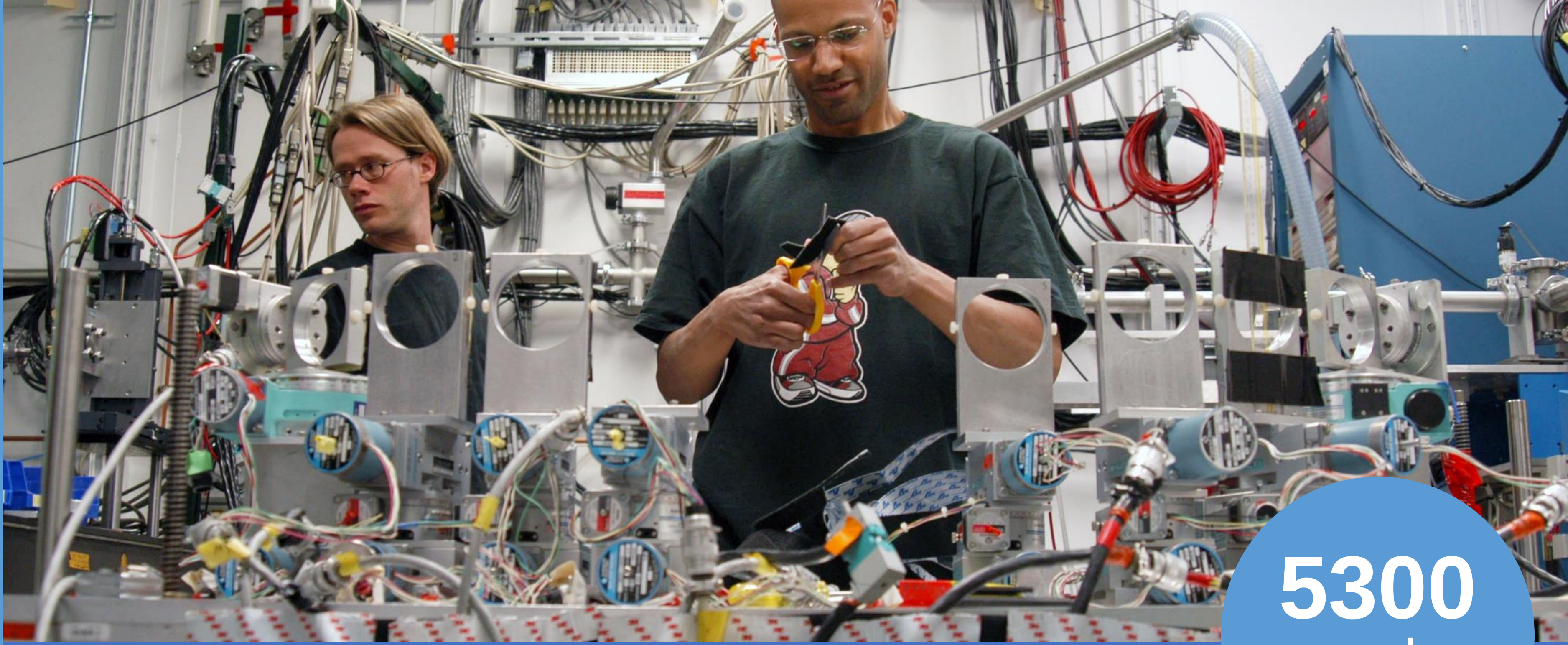
Thanks to Xiaobing Zuo, Byongdu Lee, Dale Schaefer, Pete Jemian, Jan Ilavsky, Randall Winans for some slides.

# Outline

- Introduction
- Experimental Setups
- Fundamentals of X-ray Scattering
- Theory and Applications of Small Angle X-ray Scattering
- Applications



5300
researchers
each year

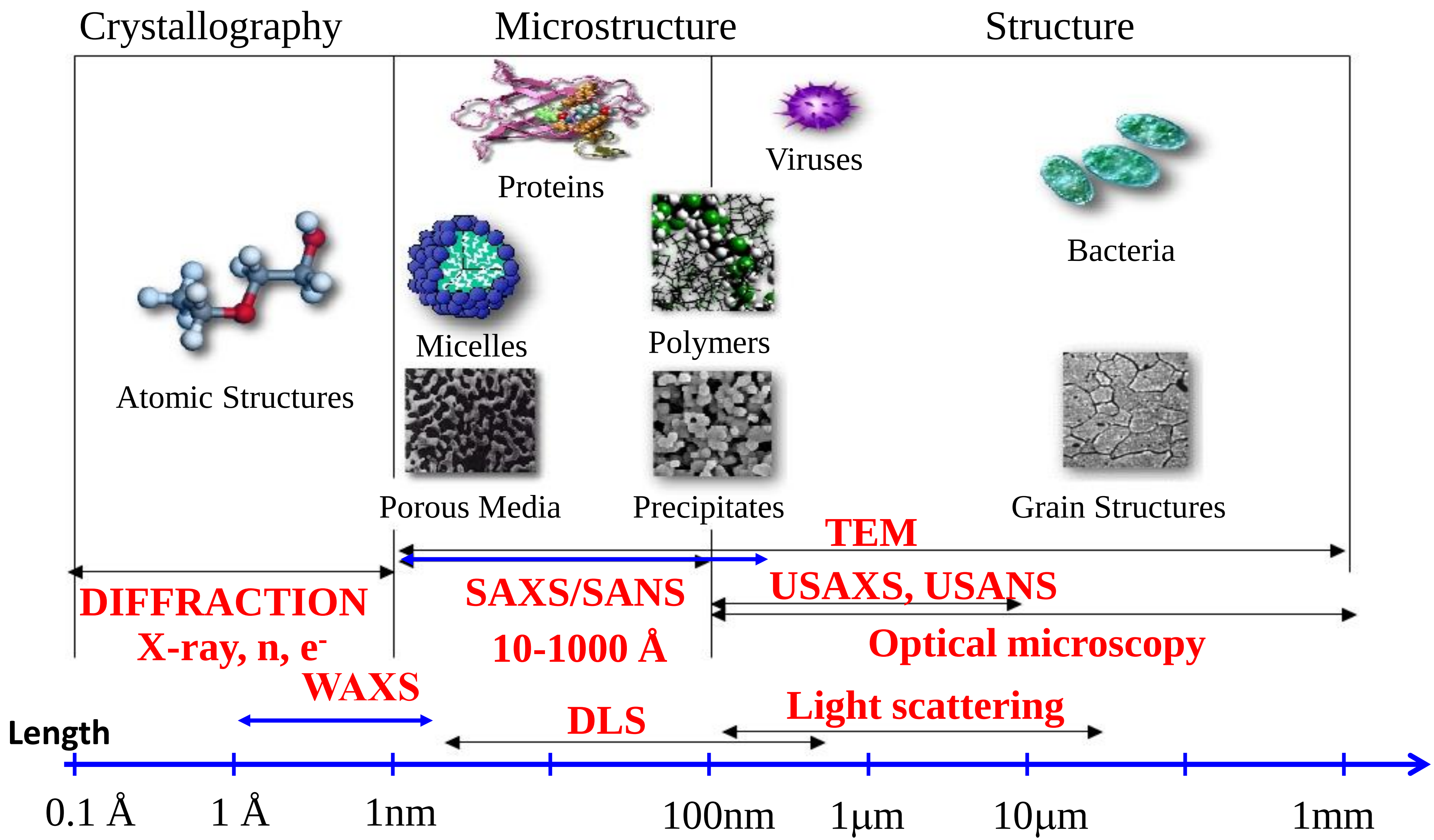
# ADVANCED PHOTON SOURCE

- Researchers come to the APS from:
- 50 states plus Puerto Rico and the District of Columbia
- 33 countries
- 150 companies
- 250 universities

# U.S. DEPARTMENT OF ENERGY OFFICE OF SCIENCE X-RAY LIGHT SOURCES


- Sources of scientific discovery and technological innovation
- A critical component of maintaining U.S. leadership in the physical sciences

# Length Scales Probed by SAS and Other Characterization Techniques



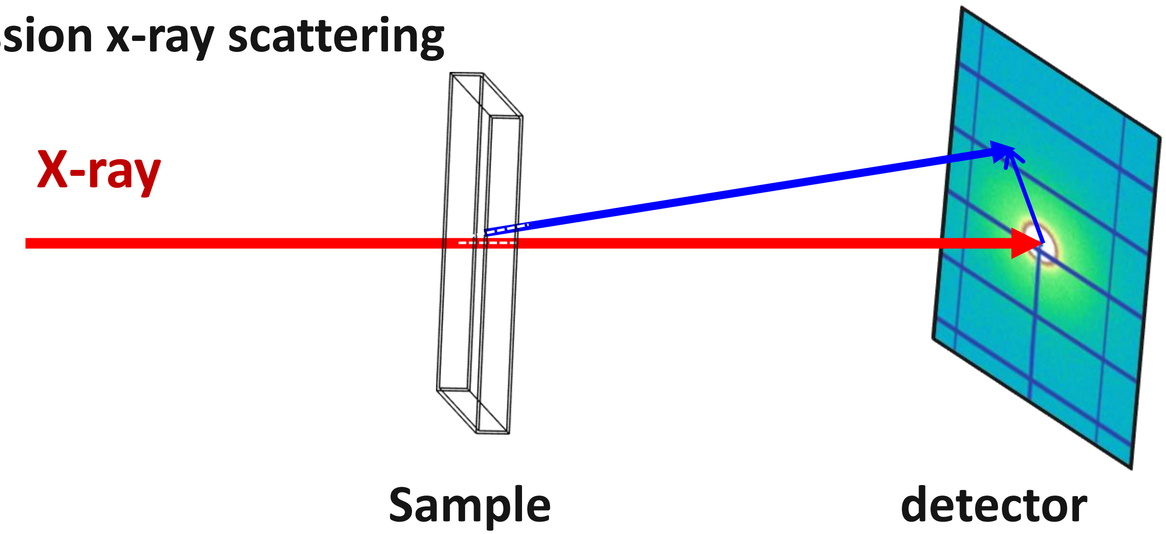
## 1. X-ray Scattering Setup

- Storage-Ring synchrotron
- X-ray scattering setup

# X-ray Scattering Setup Configuration

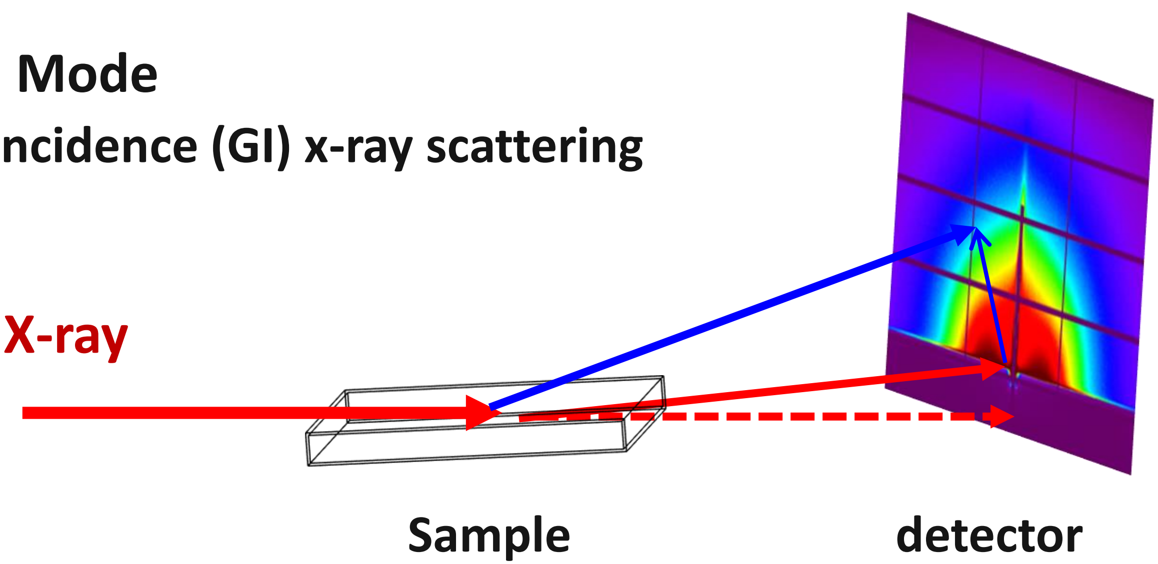
## Transmission Mode

Transmission x-ray scattering



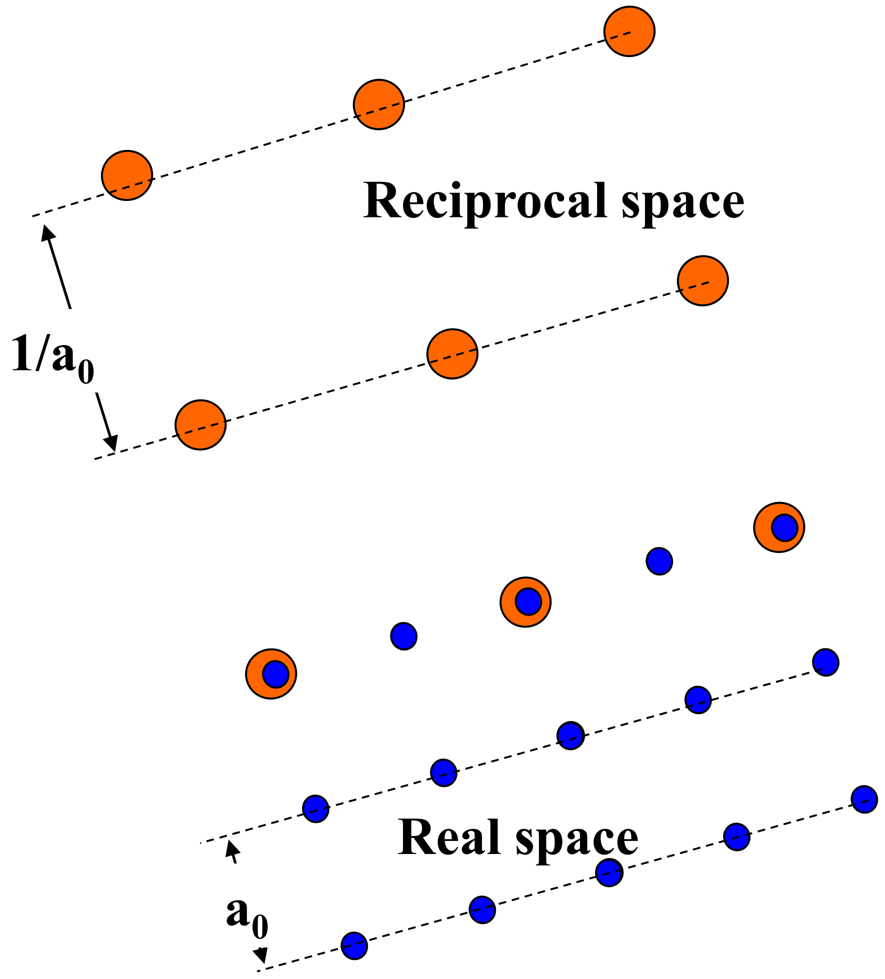

## Reflection Mode

Grazing incidence (GI) x-ray scattering

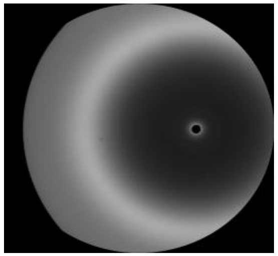


# Real space vs Reciprocal space

- Properties
- Unit in length $^{-1}$
- Length in reciprocal space is 1/length in real space
- Volume of reciprocal space is 1/volume in real space

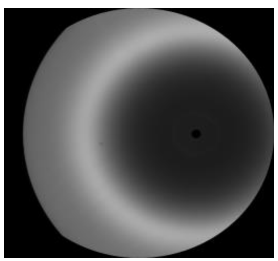


# (Solution) X-ray Scattering Data



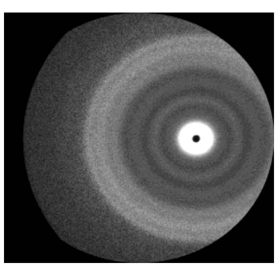
Solution (Solute + Solvent)

–



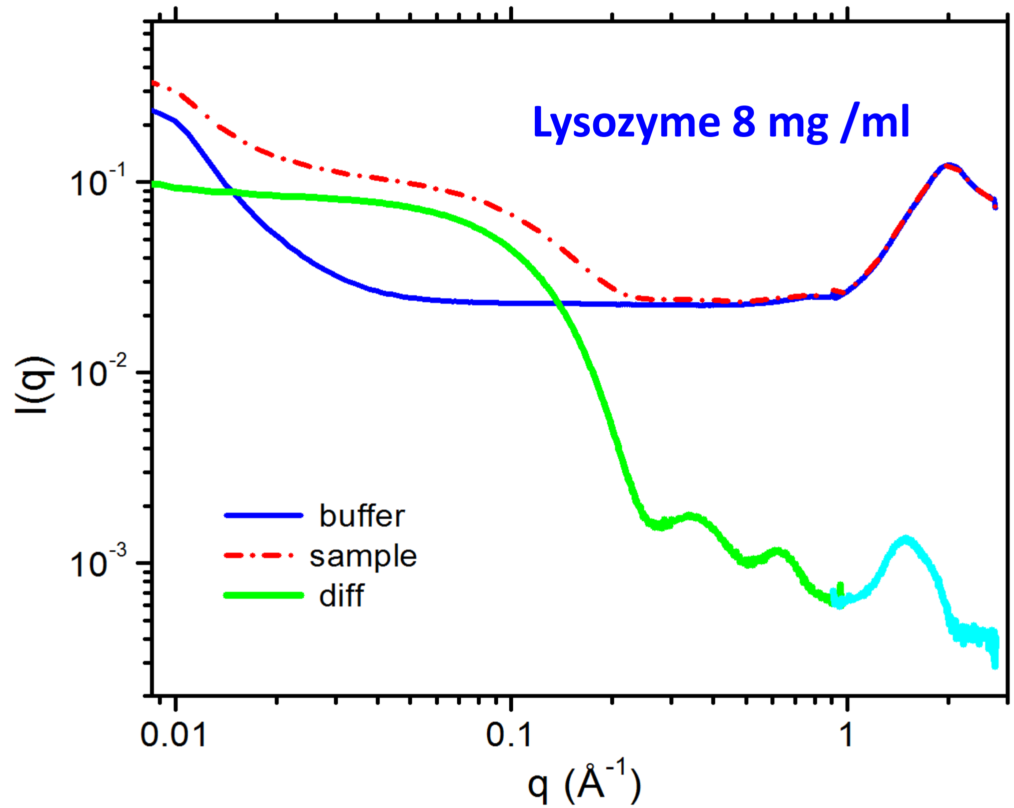
Solvent / Buffer

=



Solute (SAXS / WAXS)

1D SAXS profiles




When do you need synchrotron x-ray source?

1. High flux: high background exp
2. Small beam size: small amount of sample, etc
3. Fast data collection: in-situ, fast kinetics

# Lab source vs SR

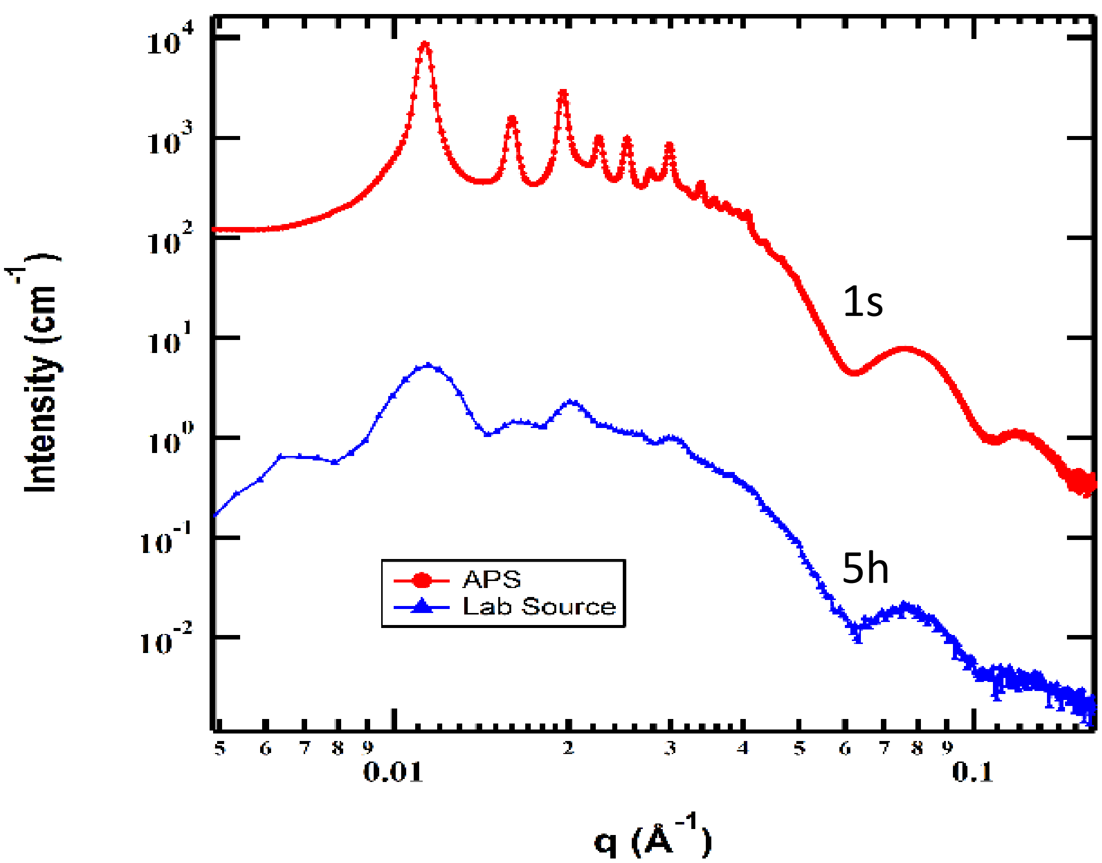
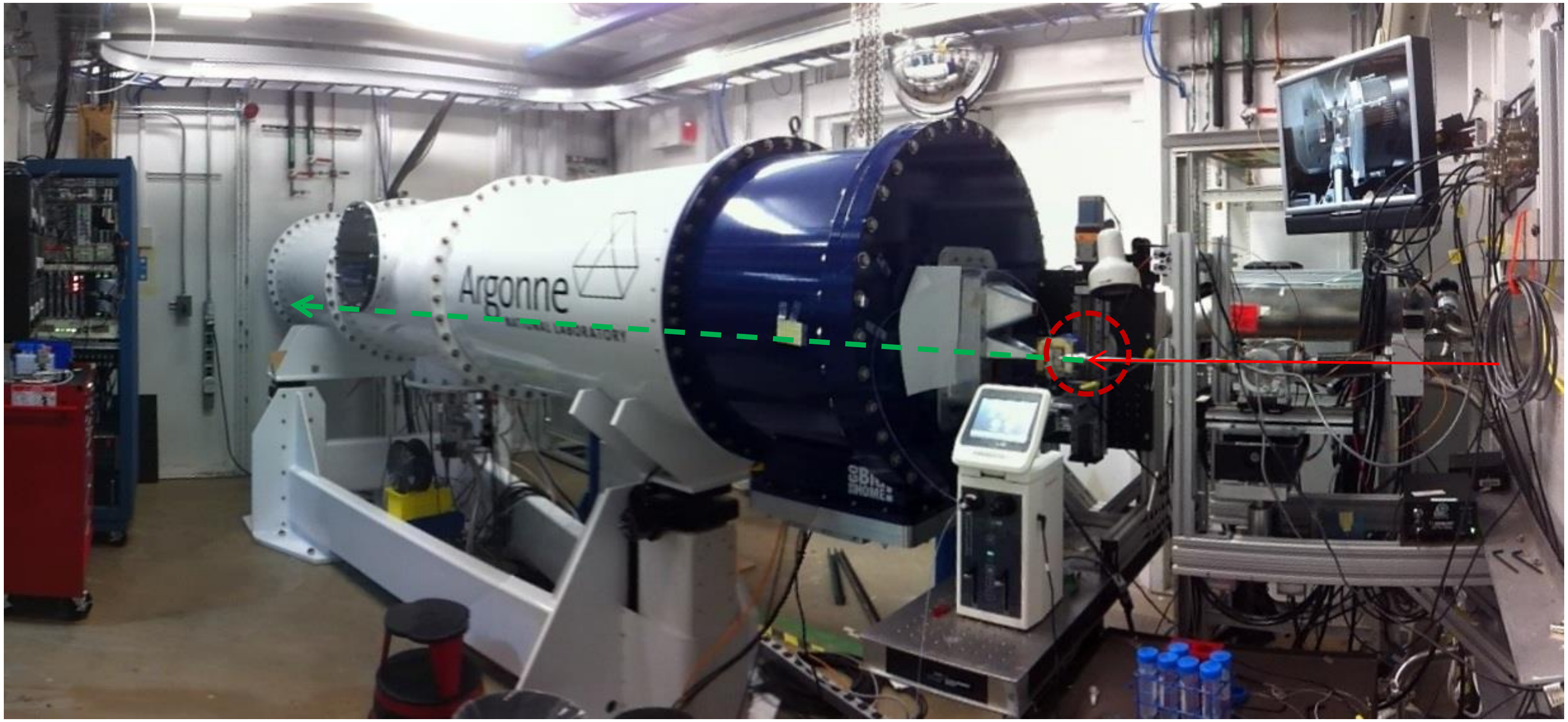



**Figure 3. SAXS data of BCC SL of 15nm gold spherical particles linked with DNA. The same sample were measured with APS and Lab sources.**

# New SAXS/WAXS Setup at Beamline 12ID-B of Argonne



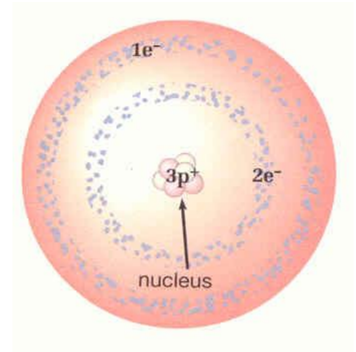

- From 1 to 150 nm
- High flux, one measurement less than 0.1 s
- In situ SAXS study : high temperature (up to 1500$^{o}$C) and high pressure (up to 20,000 psi)
- Element specific information from ASAXS
- Can be combined with many other techniques such as IR and other spectroscopy

# Fundamentals of X-ray Scattering

- **X-ray scattering and interference**
- **Form factor: size & shape**
- **Size polydispersity**
- **Structure factor**
- **X-ray contrast**

# Atomic Form Factor

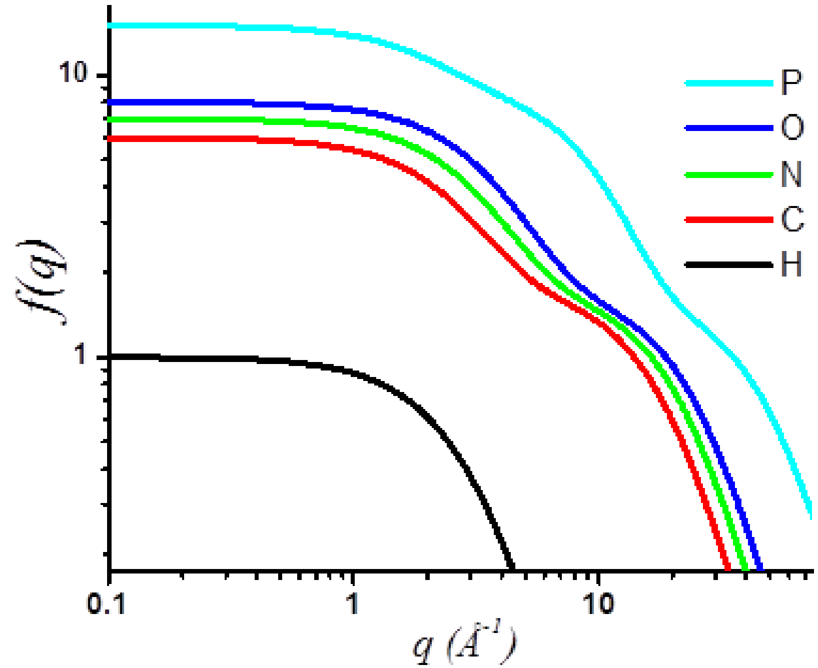
Electron cloud in atoms has radial density distribution $\rho(r)$




Atomic electron cloud

$$f(q) = 4\pi \int \rho(r) r^2 \frac{\sin(qr)}{qr} dr$$

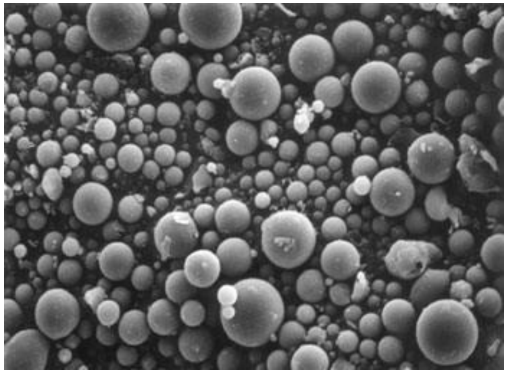
- Atomic form factors are fundamental parameters for X-ray techniques.
- ***f(0)=Z*** : the total electron of the atom, scattering length.
- Atoms with higher Z will scatter stronger.



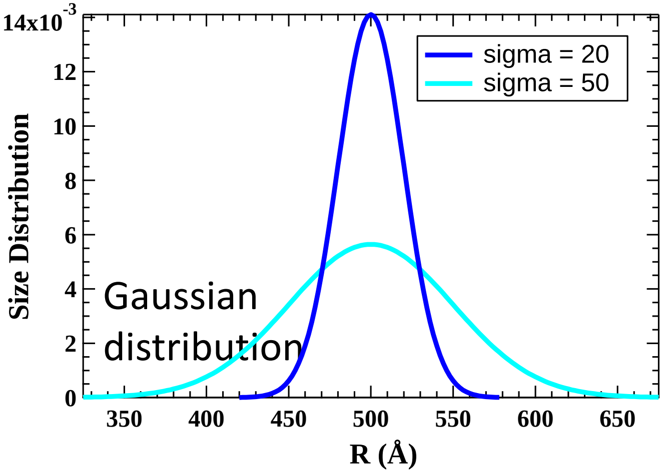

Data taken from **International Tables for Crystallography**, Vol. C, Table 6.1.1.1

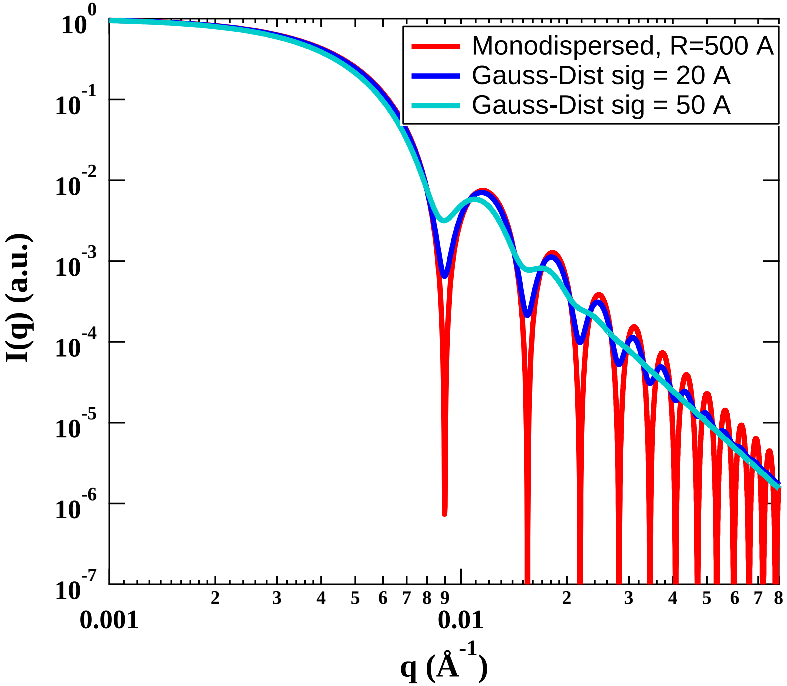
# Polydispersity: Size Distribution

Scattering for an ensemble with different sizes:



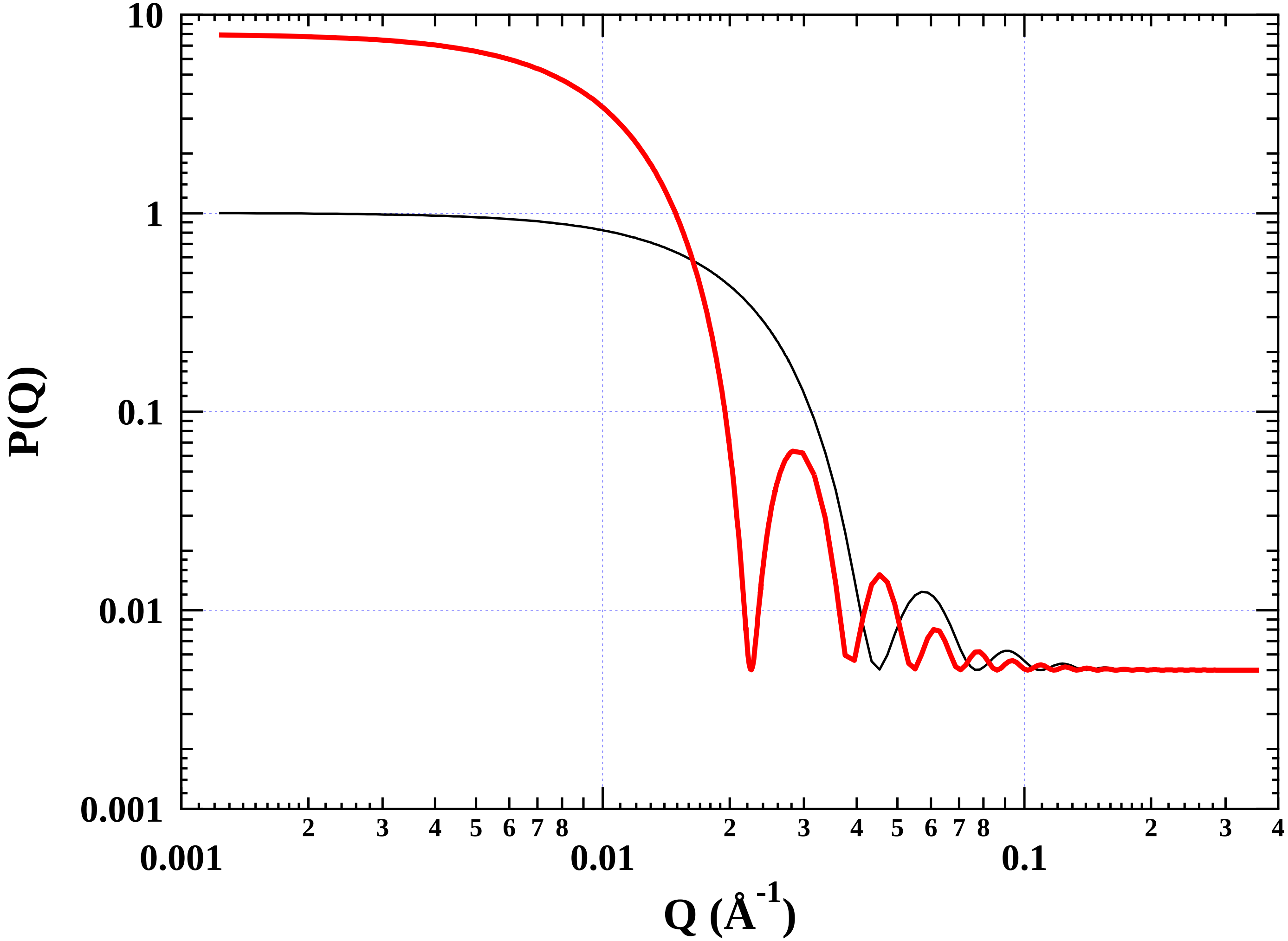
**Sphere radii with Gaussian distribution**

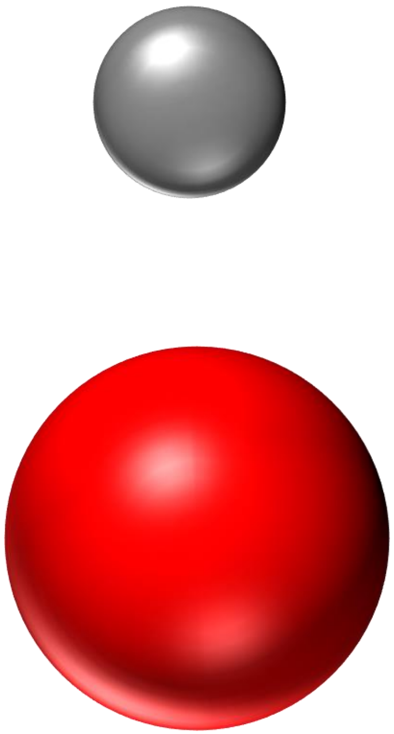


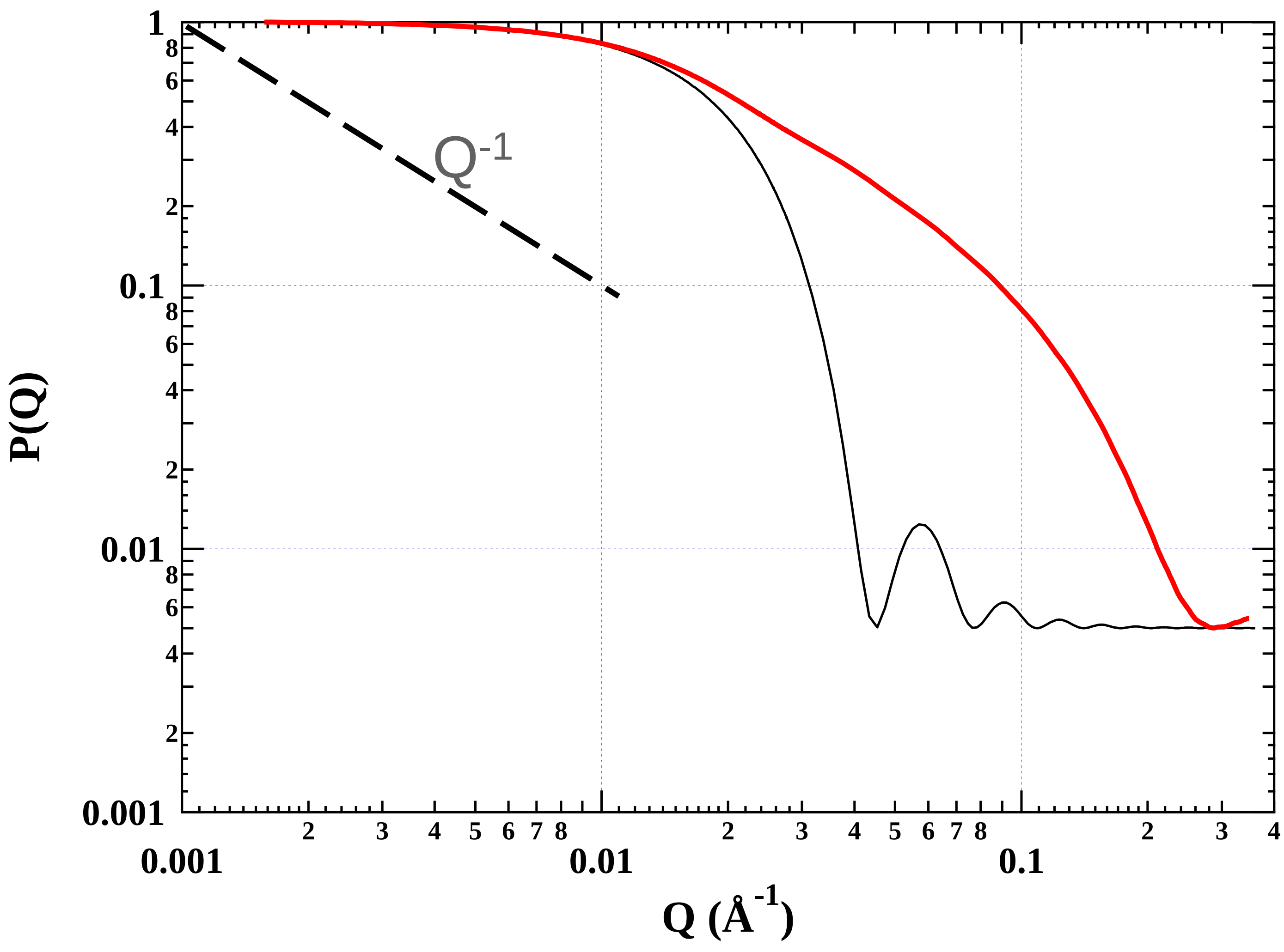

- Size polydispersity smears/dampens fine features in scattering profile.

# Spheres of different sizes



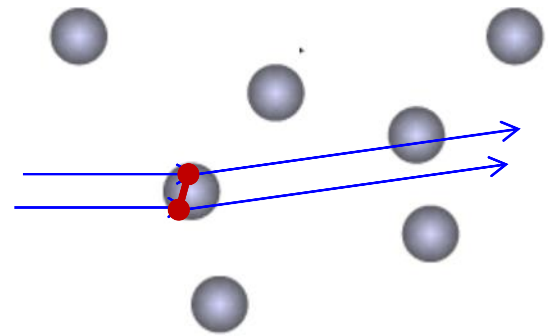
# “Long & thin” cylinder




# Particle Correlation: Structure Factor

Dilute, randomly distributed particles:

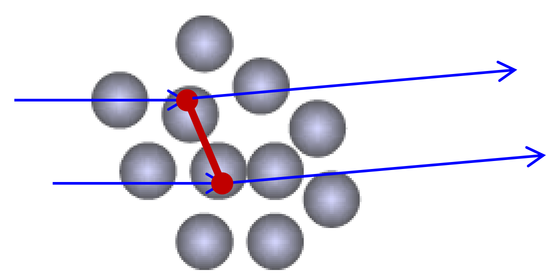
$$I(q) = NP(q)$$



Correlated particles:

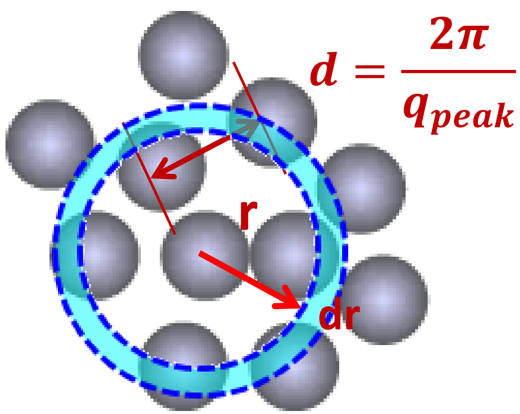
$$I(q) = NP(q)S(q)$$

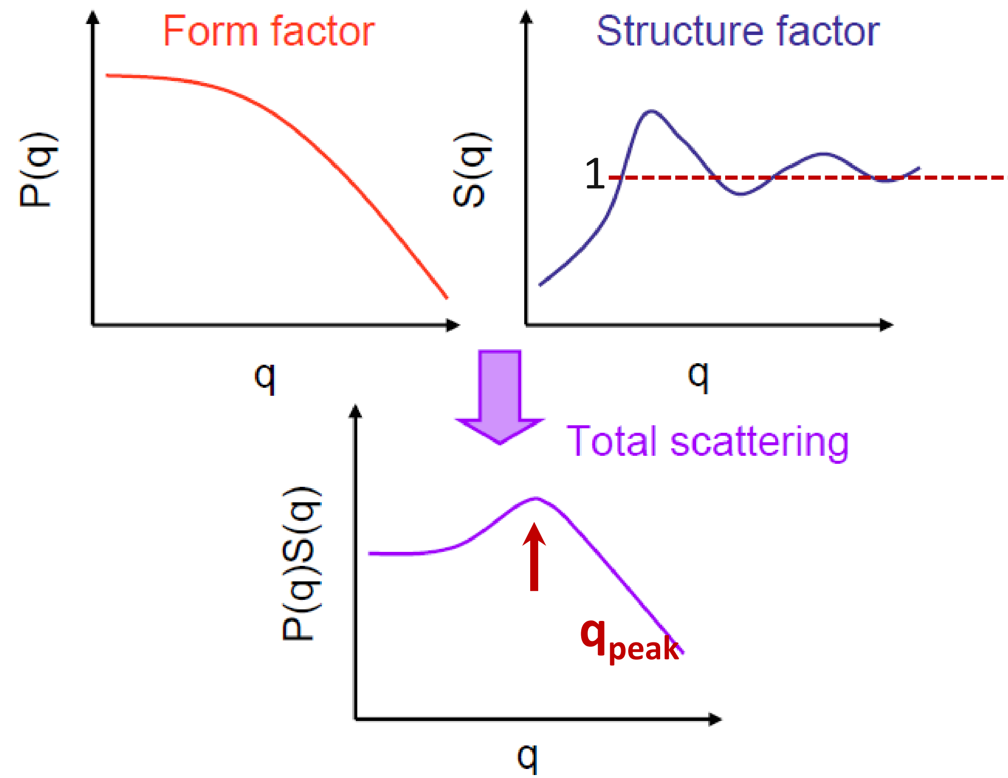
S(q) structure factor



# Structure Factor: Common Spacing(s) between Scatterers

$$S(q) = 1 + 4\pi \frac{N}{V} \int_0^{\infty} r^2 [g(r) - 1] \frac{\sin qr}{qr} dr$$




$$I(q) = NP(q)S(q)$$

- g(r): radial particle distribution function
- Low concentration, S(q)=1
- Higher concentration, S(q) oscillates about 1

# Theory and Applications of SAXS

- Guinier Approximation
- Porod Law
- Invariant
- Hierarchical structural Information

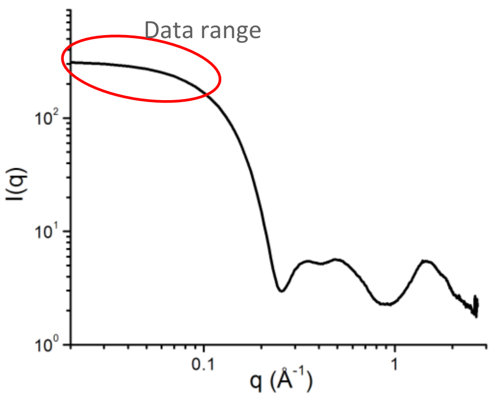
# Guinier Equation

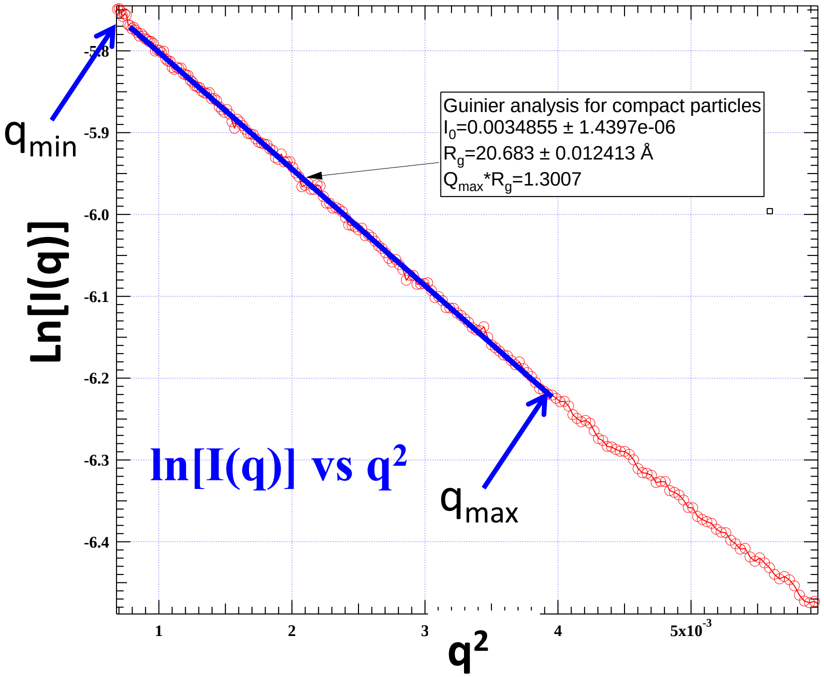
When q→0,

$$I(q) \cong I(0)\exp\left(\frac{-R_g^2 q^2}{3}\right)$$

$\boldsymbol{R_g}$: radius of gyration
$\boldsymbol{I(0)}$: forward scattering

André Guinier (1911-2000)



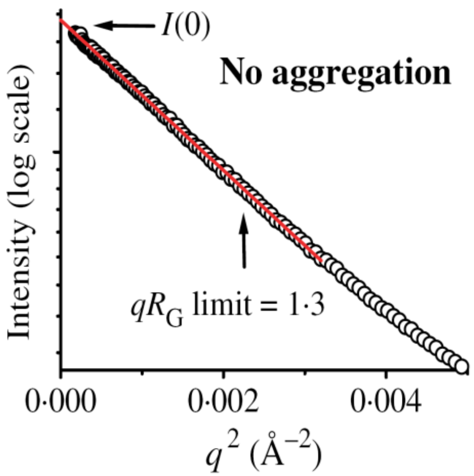

To get reliable Guinier plot / $R_g$ analysis:

- $q_{max}$*$R_g$<1.3 for globular; <0.8 for enlongate
- $q_{min} \leq \pi/D_{max}$
- Multiple (≥5???) data points in linear fashion

# Guinier Plot: Data Evaluation & Sample Condition

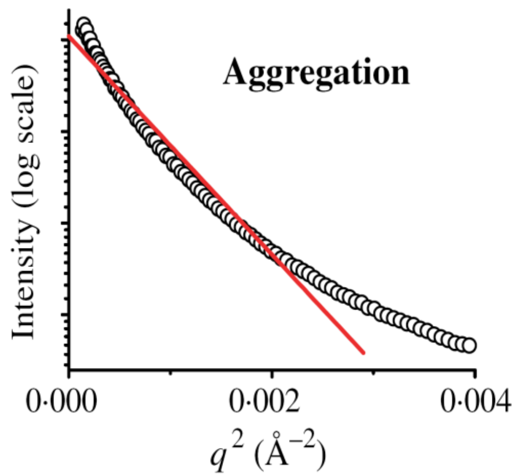
Mono-dispersed

**Normal / linear**



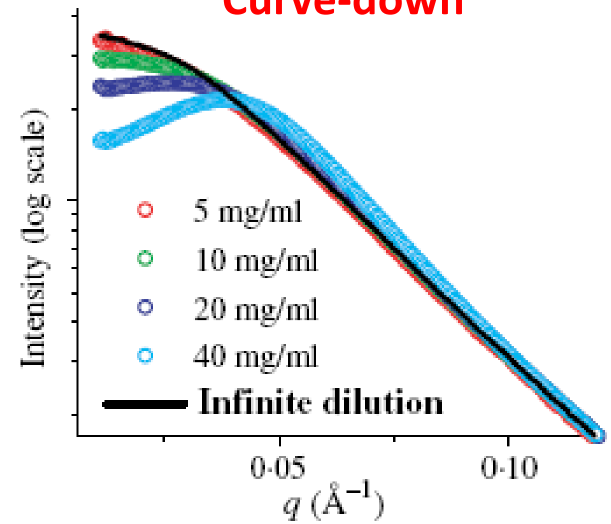

Poly-dispersed aggregates

**Curve-up**




Repulsion

**Curve-down**



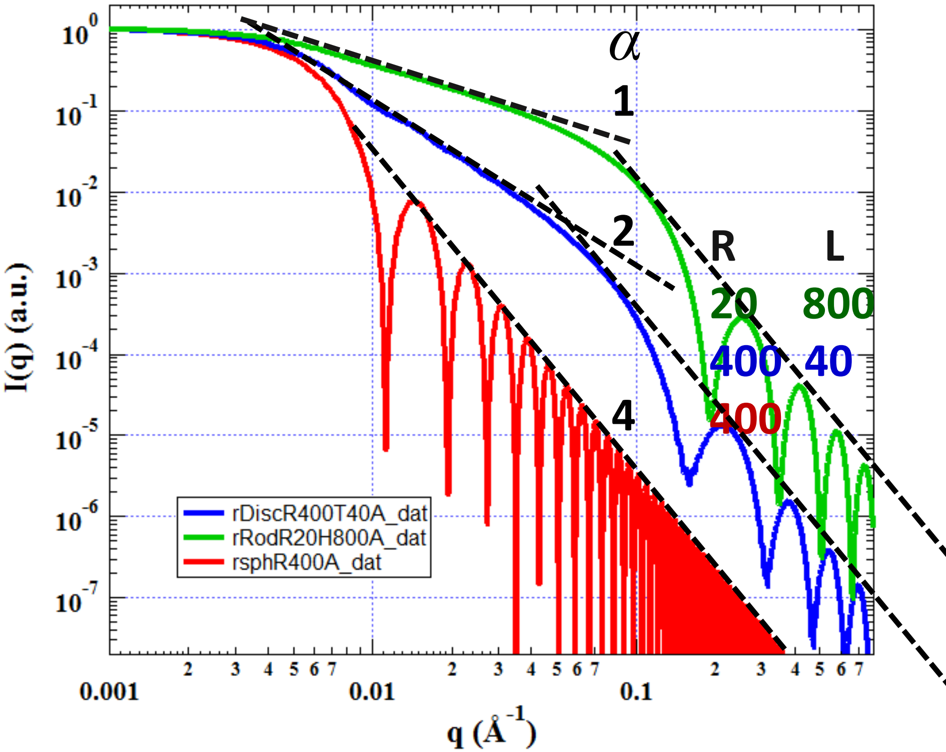

Putnam, D., et al. (2007) Quart. Rev. Biophys. 40, 191-285.

# Porod Law

Generalized form:

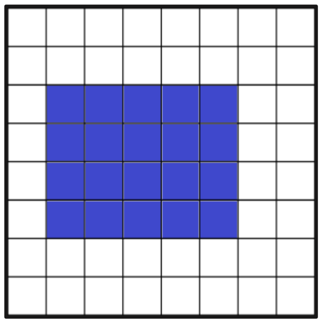
$$I(q) \propto q^{-\alpha}$$

| | | |
|---|---|---|
| $\alpha$ = | 1 | rod-like |
| | 2 | lamellar/disc |
| | 4 | sphere |
| | fraction: fractals | |



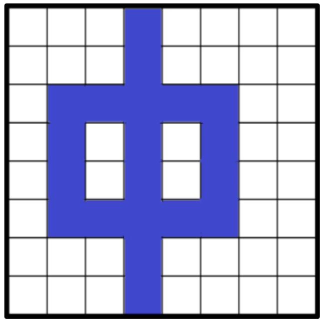

- Can provide morphology information
- May not be valid in atomic length region
- Could be misled by inaccurate background subtraction

# Porod Invariant and Porod Volume



Porod Invariant Q:

$$Q \equiv \int_0^\infty q^2 I(q)dq = 2\pi^2(\Delta\rho)^2 V$$



For uniform particles:

$$I(0) = (\Delta\rho V)^2$$

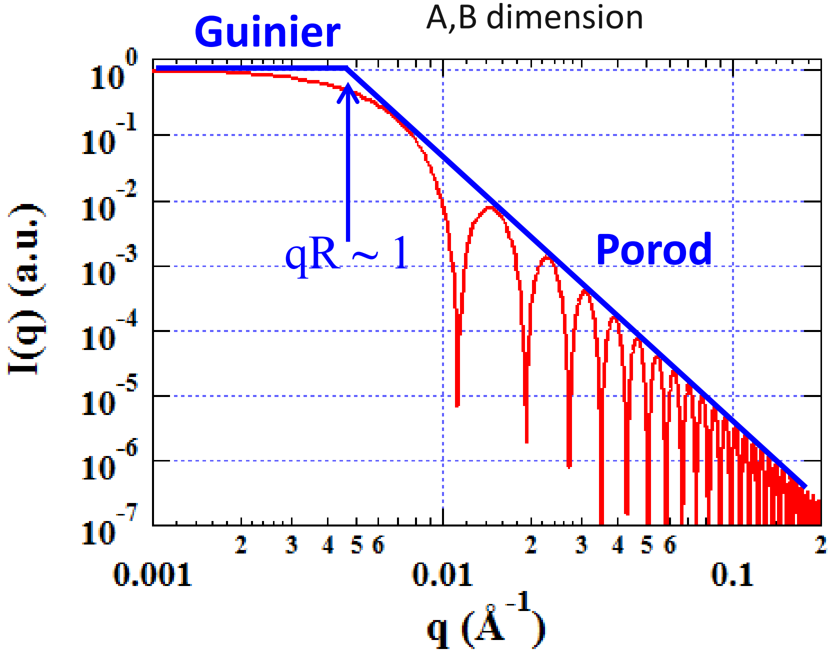
Porod volume:

$$V = \frac{2\pi^2 I(0)}{Q}$$

- The invariant measures the total electrons, does not depend on morphology.
- The volume of a molecule can be estimated solely from scattering data.
- Calculation of particle volume does not require absolute data scaling.

# Anatomy of SAXS Profile

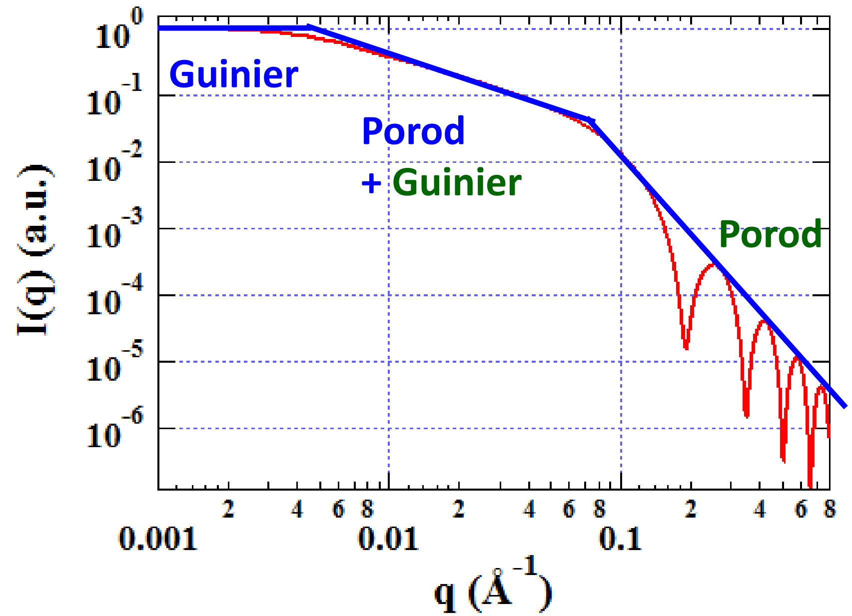
One characteristic length:
all dimensions similar
aspect ratio: $d_{max,A}/d_{max,B} \sim 1$
A,B dimension



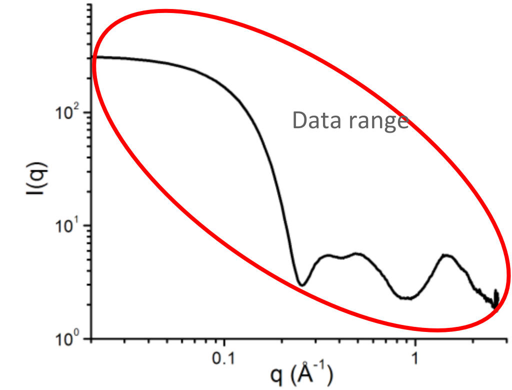


R=20 A, L = 800 A

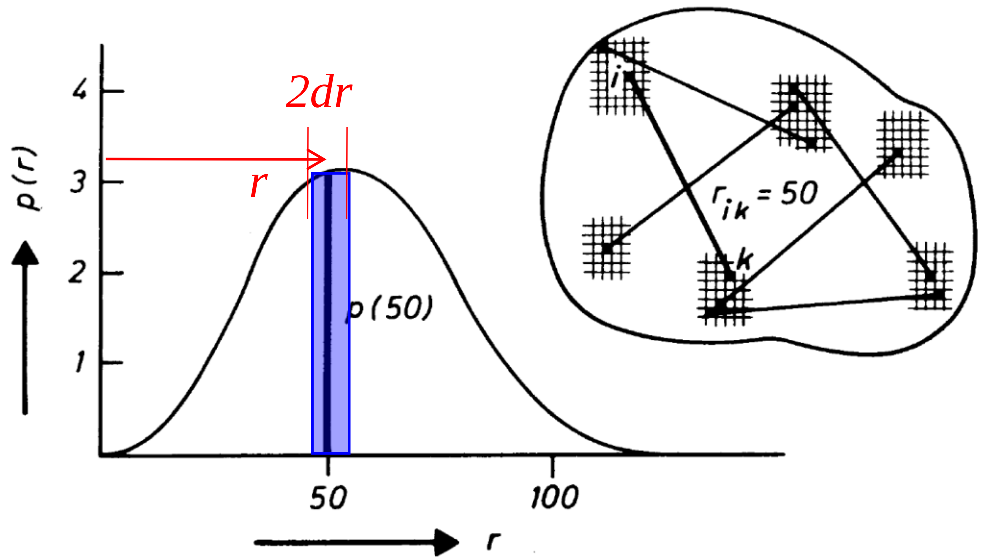
Two characteristic lengths:
L >> 2R



# Pair Distance Distribution Function (PDDF)




$$p(r) = \frac{r^2}{2\pi^2}\int_0^\infty q^2 I(q)\frac{\sin qr}{qr}\,dq$$ --- reverse FT of I(q)

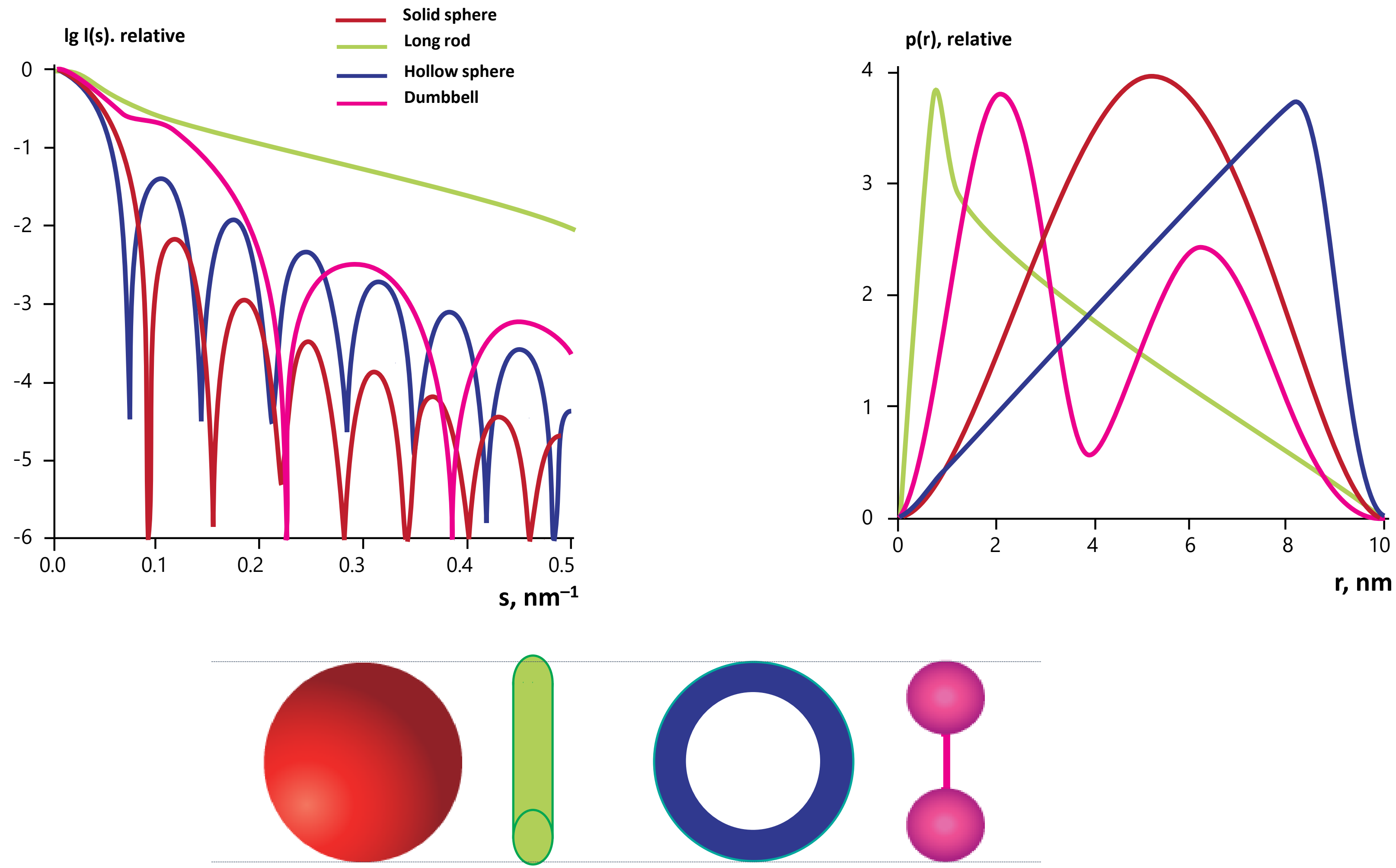



$$\boxed{p(r) \sim \sum_{|\vec{r}_j - \vec{r}_k| < r+dr} 1 \times \Delta n(\vec{r}_j) \times \Delta n(\vec{r}_k) \times r^2}$$

excess electrons of atom *j* over solvent

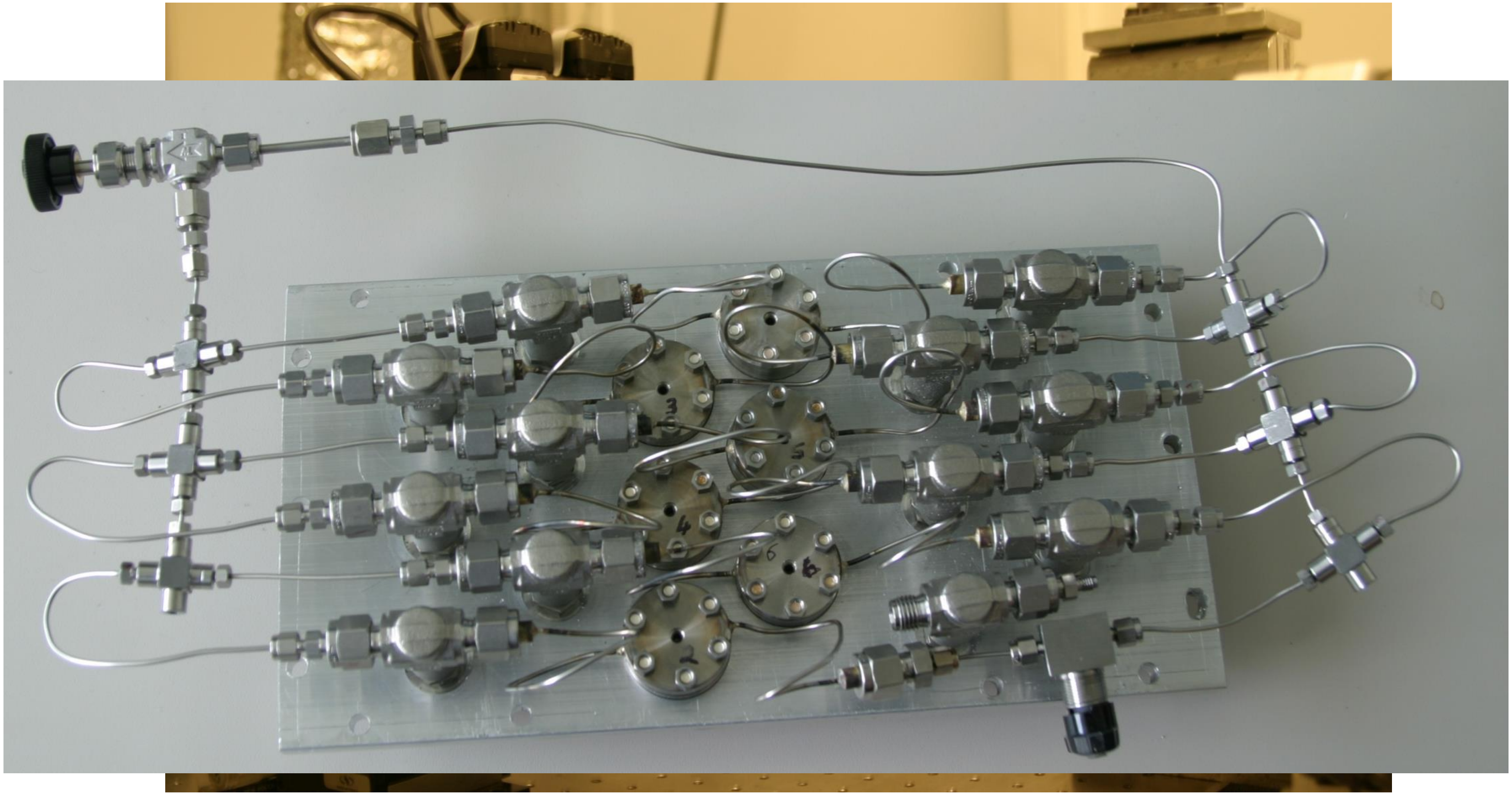
- The PDDF of a molecule is the (net-electrons and distance) weighted atom-pair distance histogram.

# Combination of SAXS & PDDF for Shape Determination

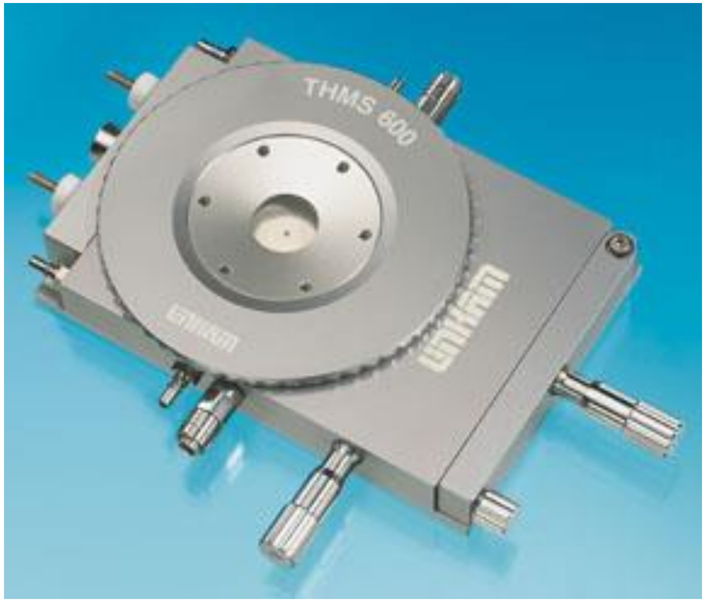



Adopted from: Svergun, D., Koch, M. (2003) Rep. Prog. Phys. 66, 1735-1782.

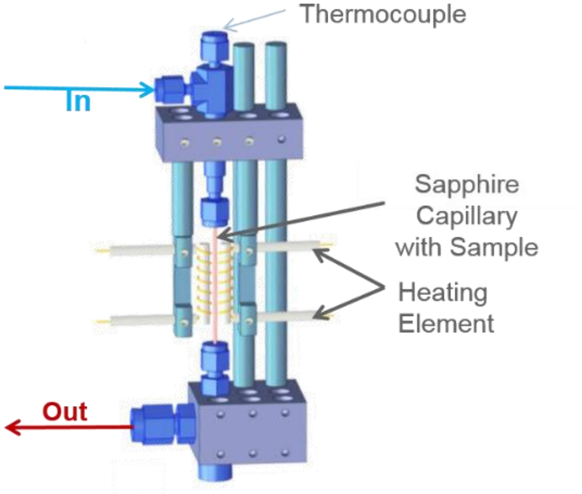
# SAXS Instruments at 12ID



# Setup



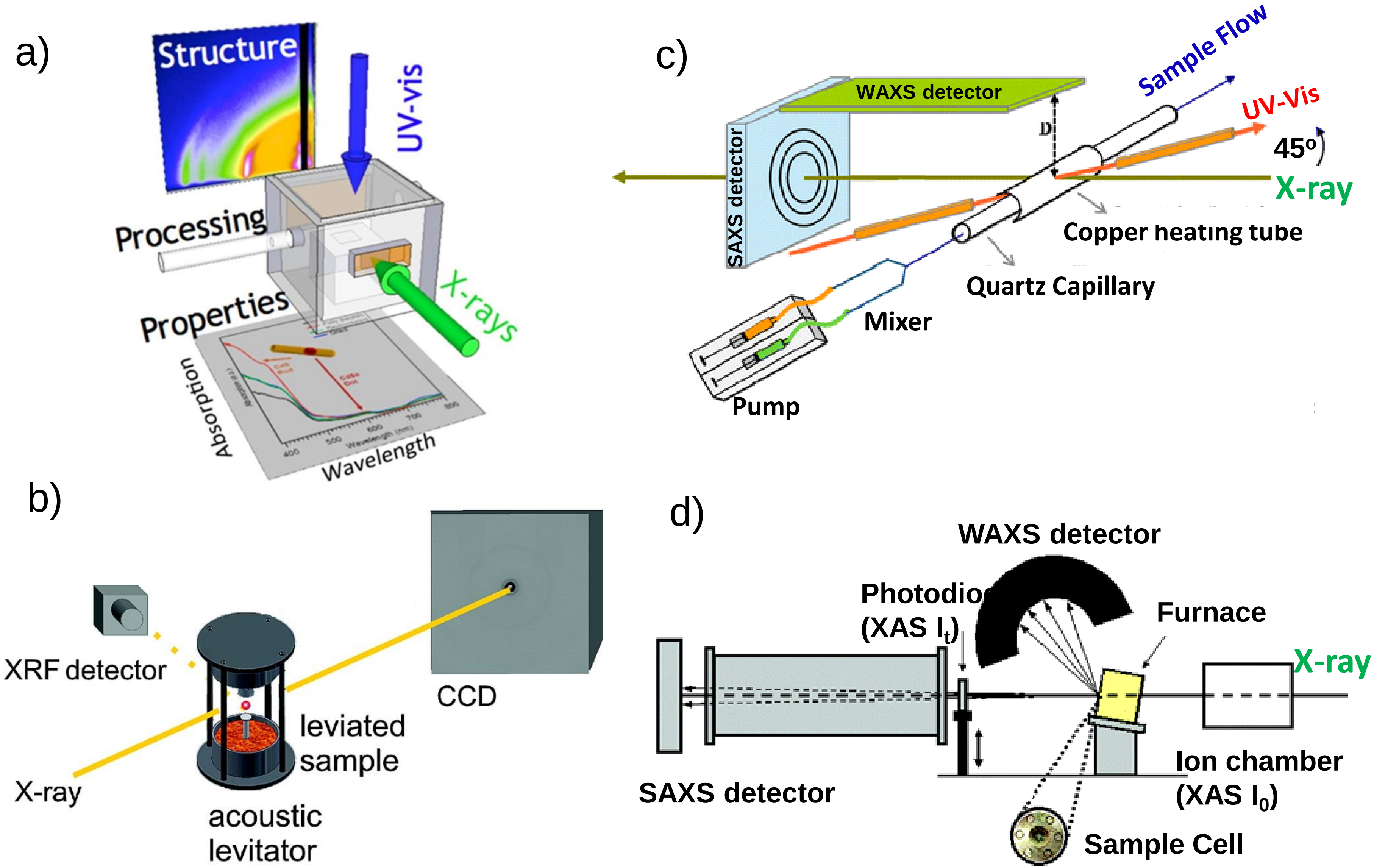

Heating up to 1500 °C



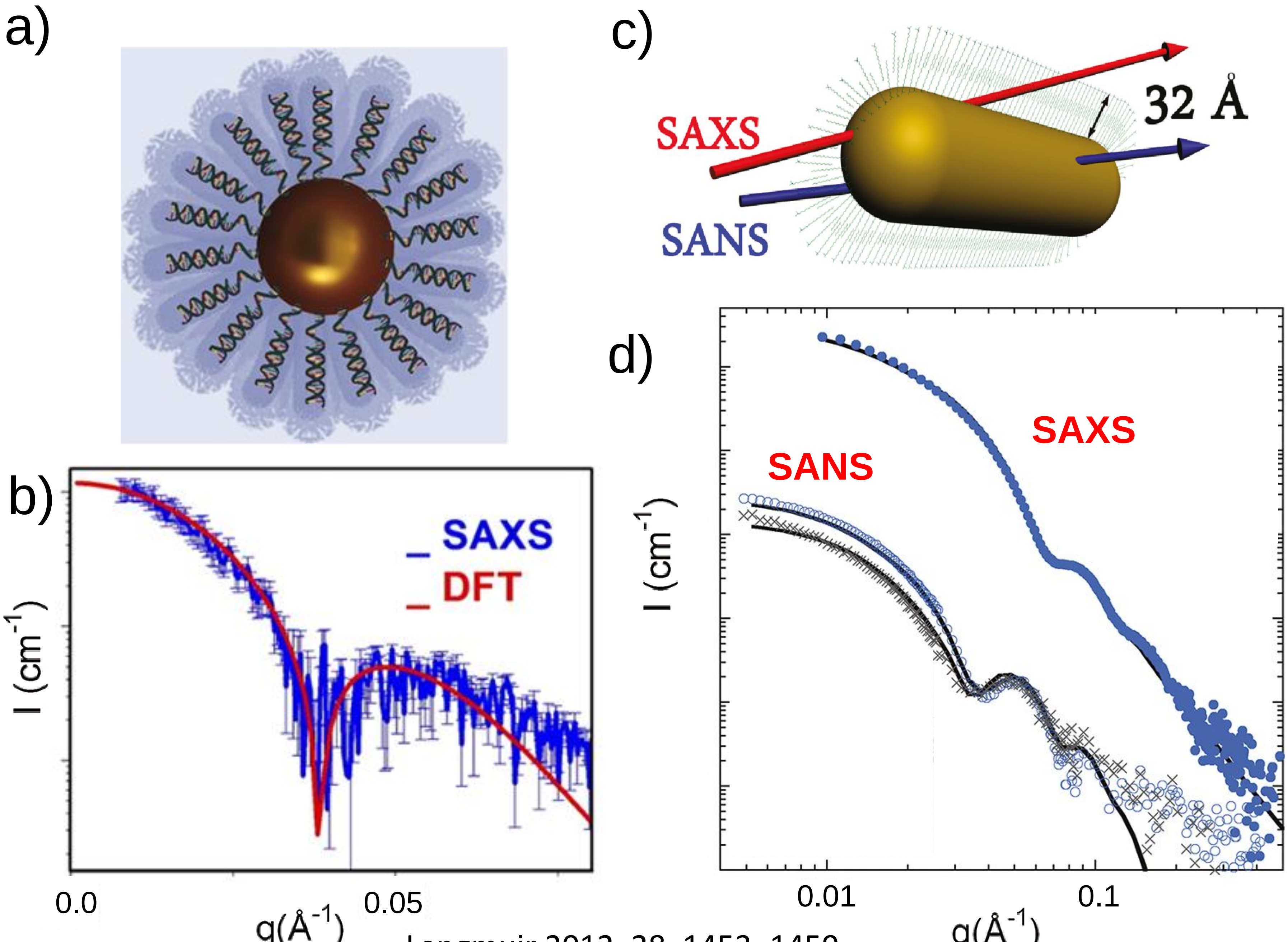

Heated capillary flow cell

GISAXS cell for high temperature and pressure reactions

# Combined SAXS with other technique

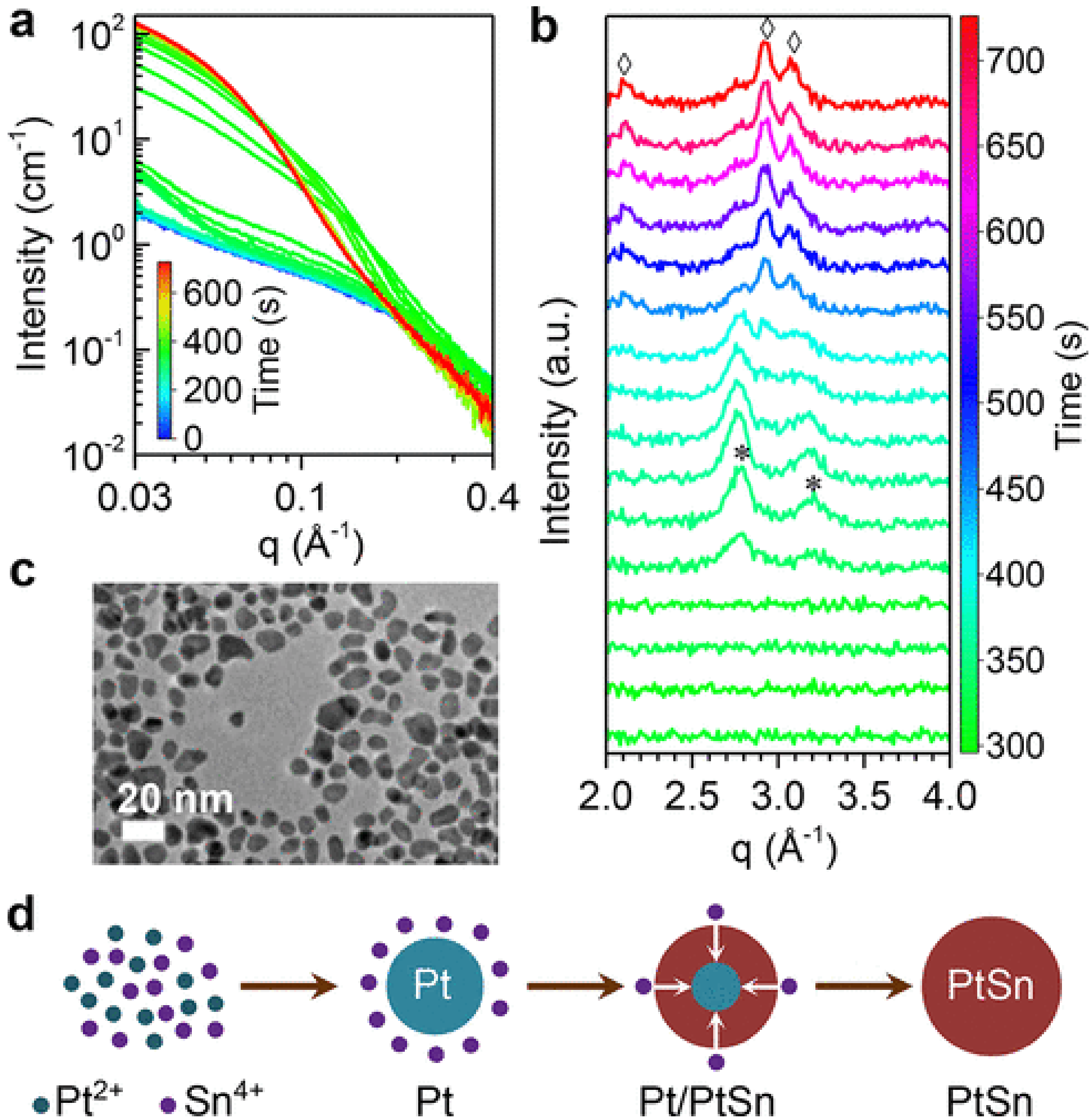


# SAXS and SANS



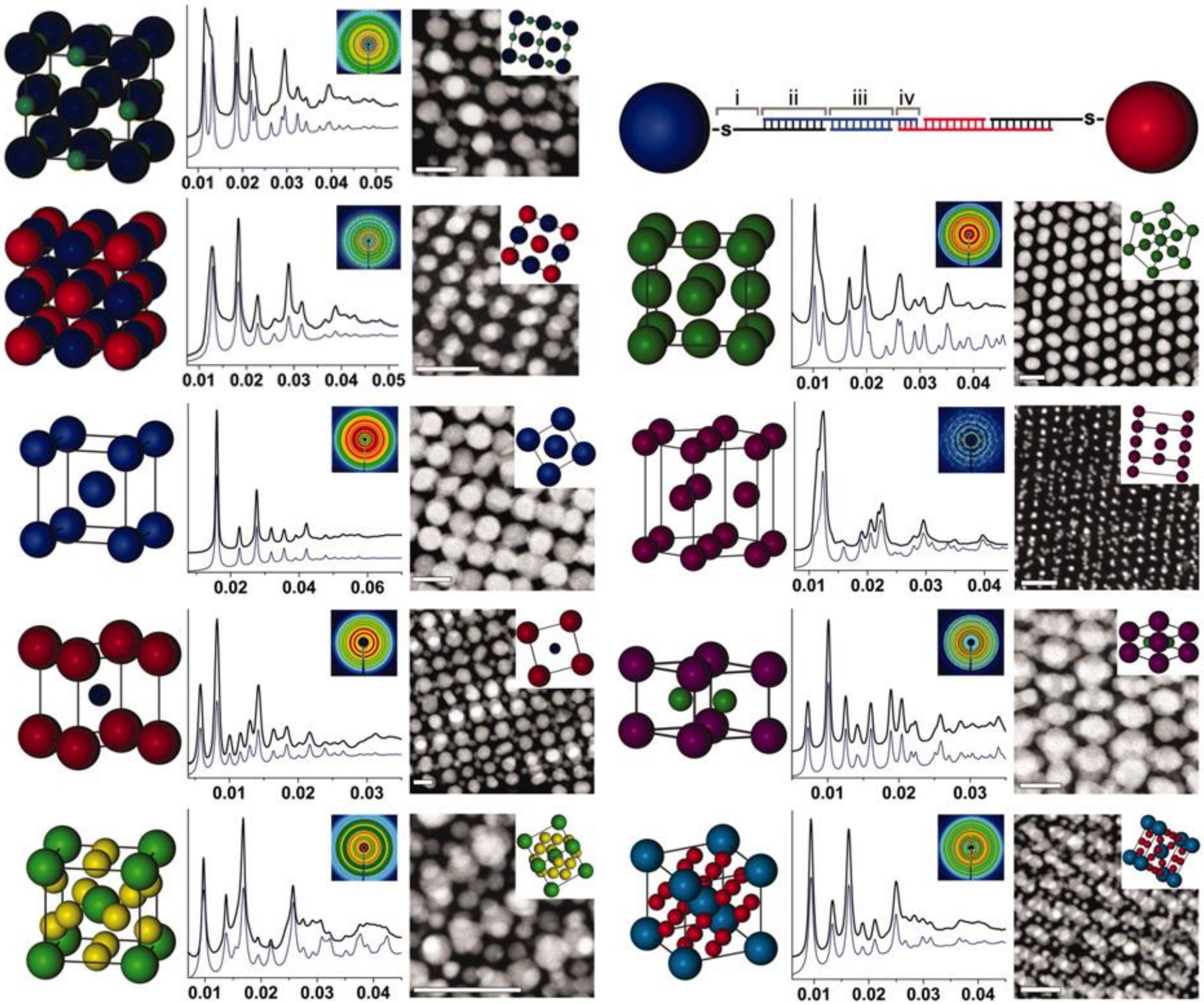

Langmuir 2012, 28, 1453−1459.

# In situ SAXS/WAXS



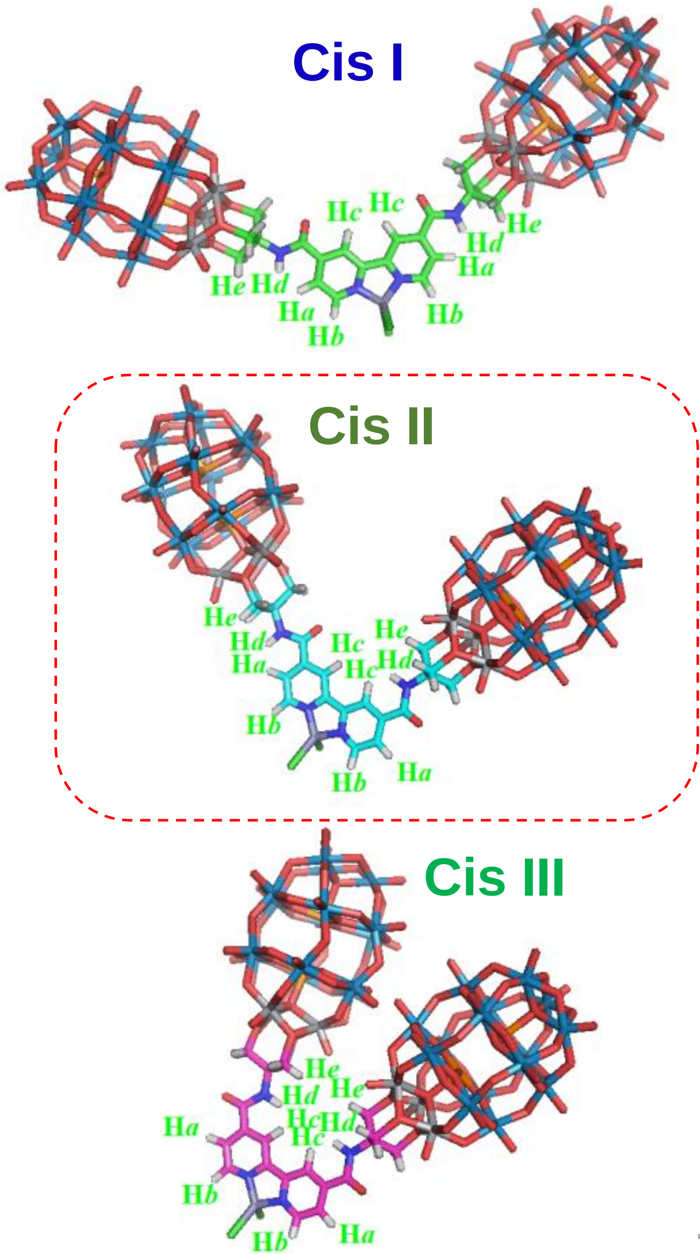

*Nano Lett.*, **2018**, *18* (6), pp 4053–4057

# SAXS of Au-DNA Superlattice

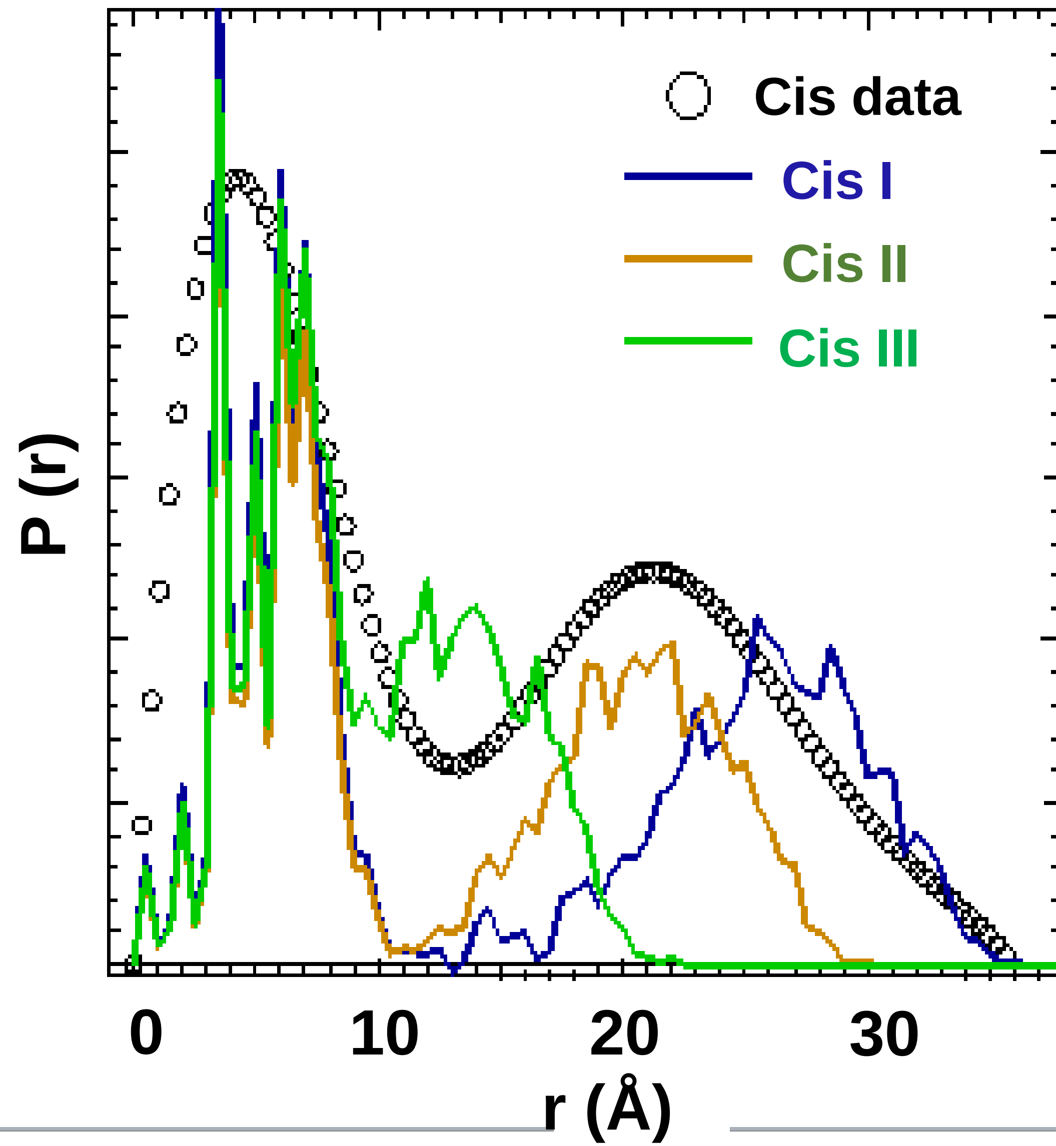



*Science* **2011**,334, 204– 208

# P(r) of dimmer structure



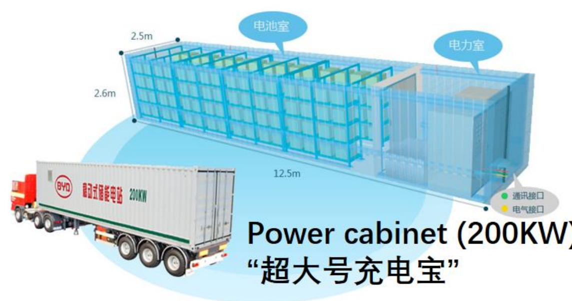

*J. Am. Chem. Soc.*, **2013**, *135* (36), 13425–13432



# Lithium Ion Battery

## Lithium ion batteries are powering the world.

**Consumer electronics** → **New applications**






# The Nobel Prize in Chemistry 2019

Ill. Niklas Elmedhed. © Nobel Media.

John B. Goodenough

Prize share: 1/3

Ill. Niklas Elmedhed. © Nobel Media.

M. Stanley Whittingham

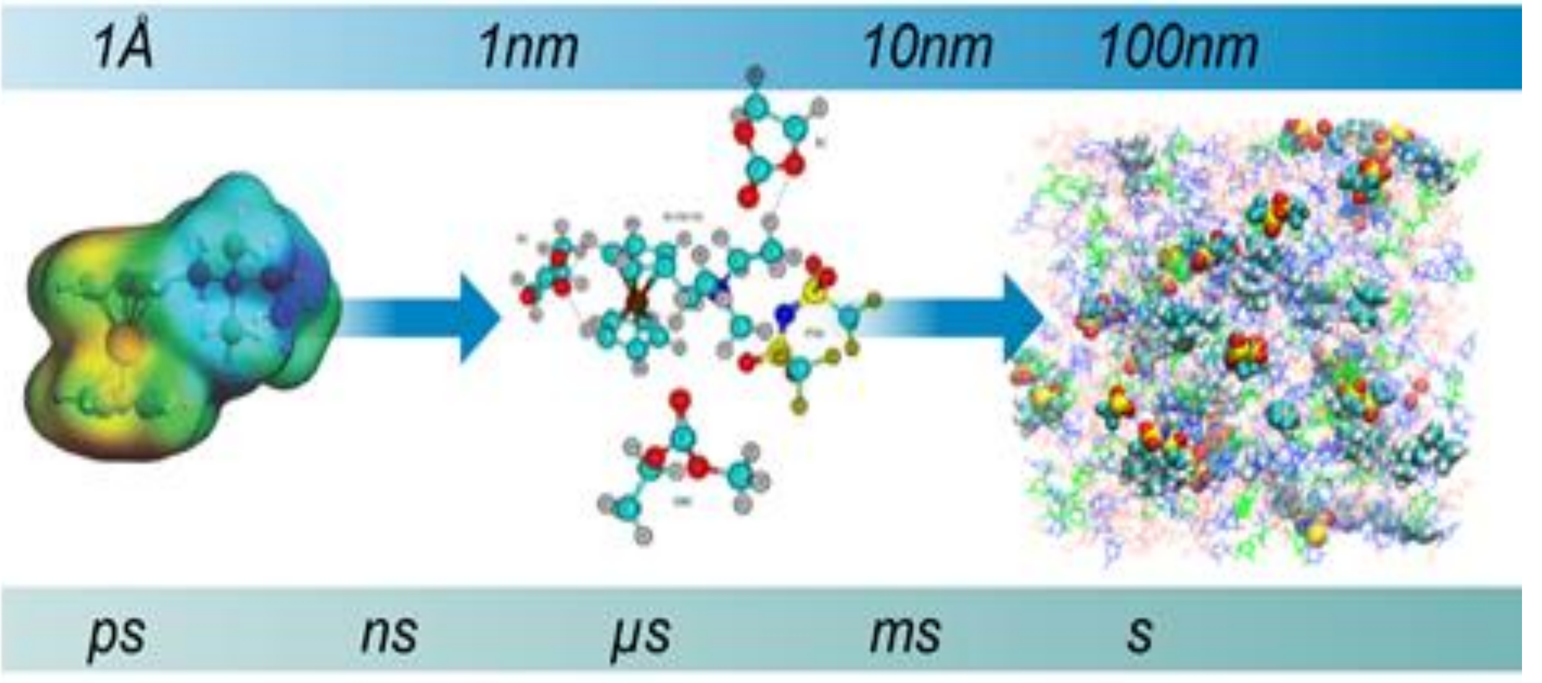
Prize share: 1/3

Ill. Niklas Elmedhed. © Nobel Media.

Akira Yoshino

Prize share: 1/3

# Electrolytes

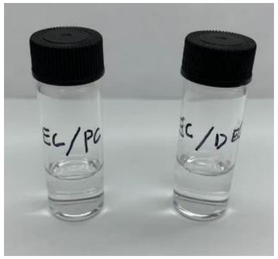



**How to characterize the electrolyte in the solution?**

K. Qian, R. Winans, **Tao Li*.** *Advanced Energy Materials,* **2021***,* 2002821.
K. Qian, Y. Liu, D. Gosztola, H. Nguyen, **Tao Li***. *Energy Storage Materials,* **2021***, 41,* 222-229.

Northern Illinois University

# Microscopic View of the Ethylene Carbonate Based Lithium-Ion Battery Electrolyte by SAXS

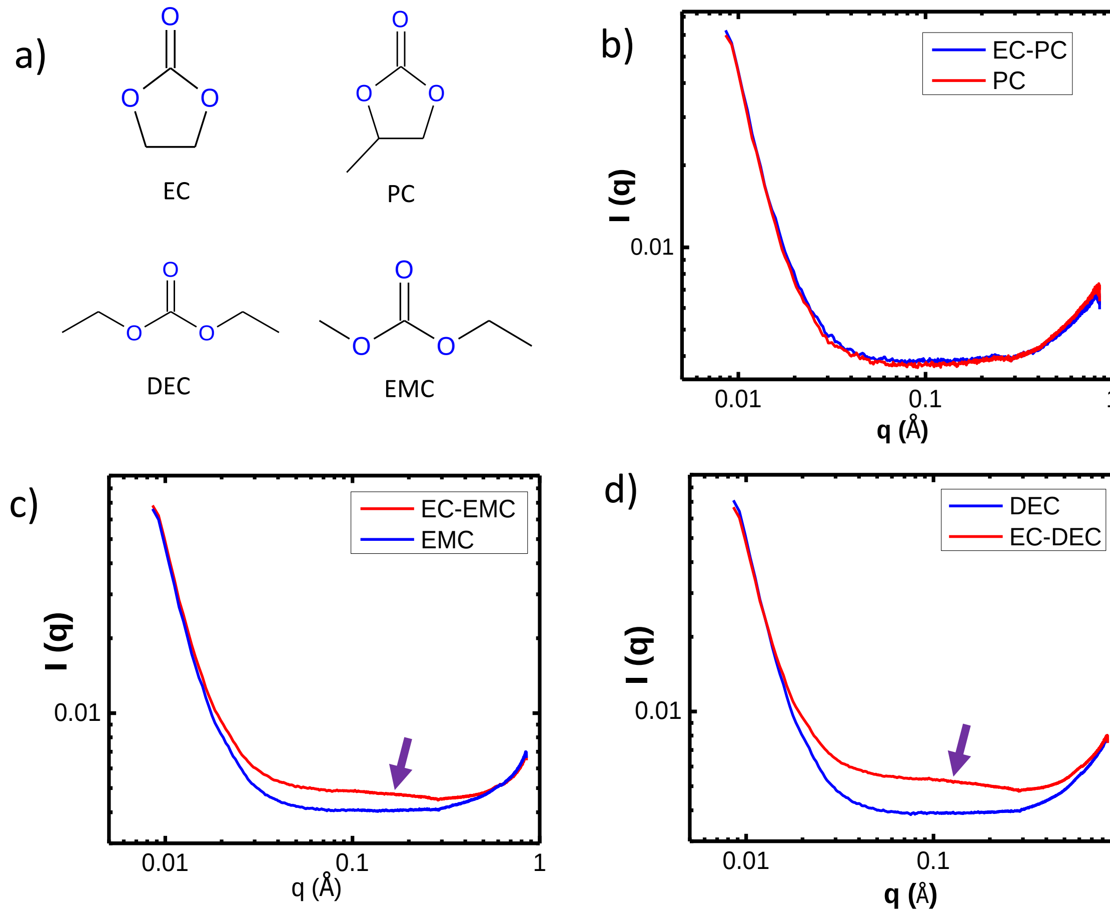





**Co-solvent: aggregates or single molecule?**



- **EC/PC form no aggregates**
- **EC/DEC, EC/MC, EC/DMC form ~ 2 nm aggregates**
- Cryo-EM, MD simulation: structures




Z. Feng, E. Sarnello, **Tao Li,** * L. Cheng.* *J. Electrochem. Soc.* **2019,** 166, 2, A47-A49.

# MD Study of LiTFSI Solvation Structure

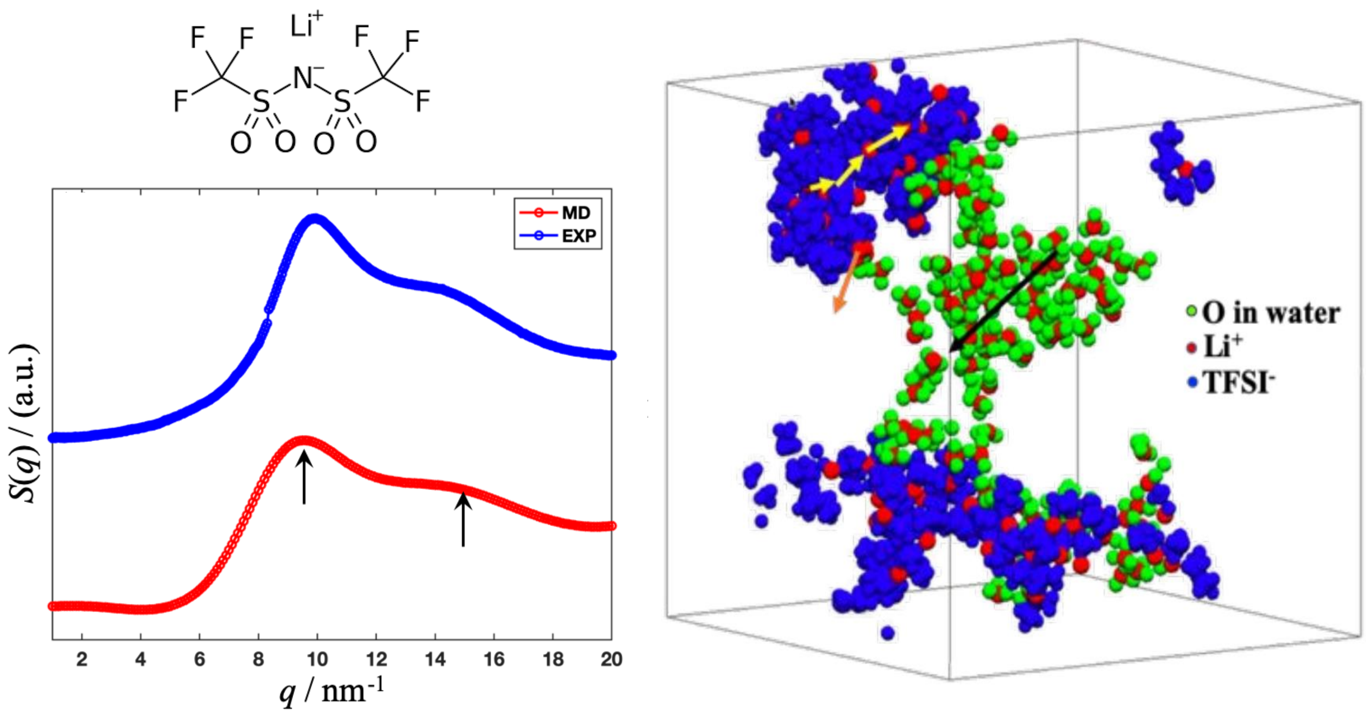
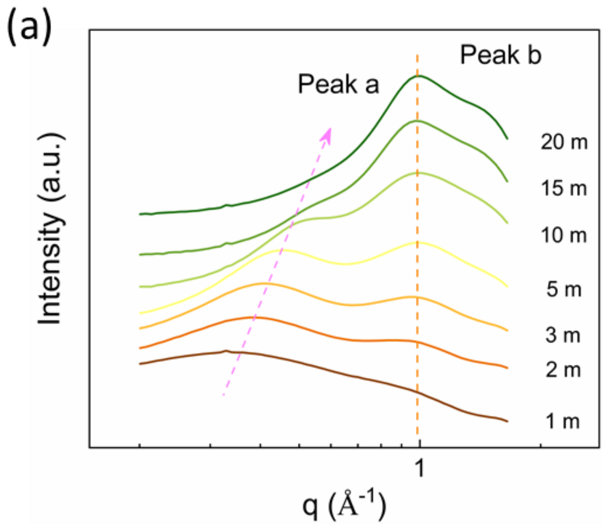


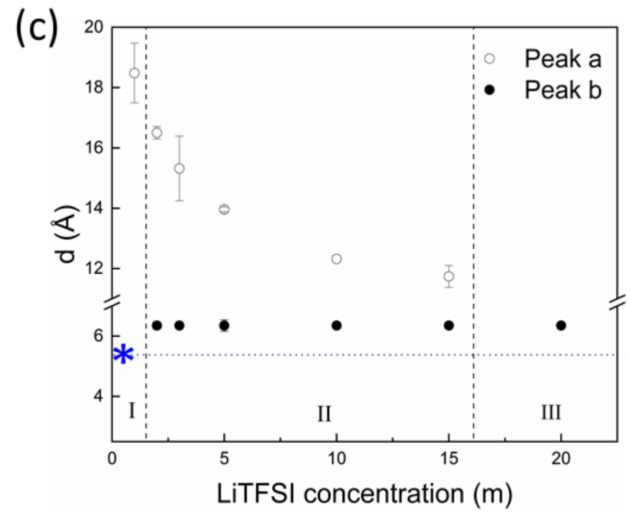

**Figure. Experimental and calculated SAXS data for 20 m LiTFSI in water.**

(Left) Peaks highlighted with black arrows indicates TFSI⁻ aggregates.
(Right) MD simulations show the heterogeneous structure of the electrolyte comprises percolating networks of ion and water domains consistent with experimental SAXS data.

Z. Yu, L. Curtiss, R. Winans, Y. Zhang, **Tao Li***. L. Cheng*. *Journal of Physical Chemistry Letter*, **2020**, *11*, 1276-1281.

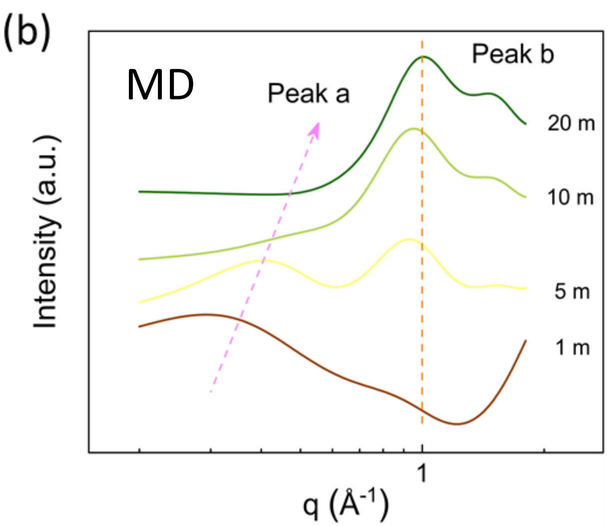
# SAXS/WAXS Study of LiTFSI Solvation Structure

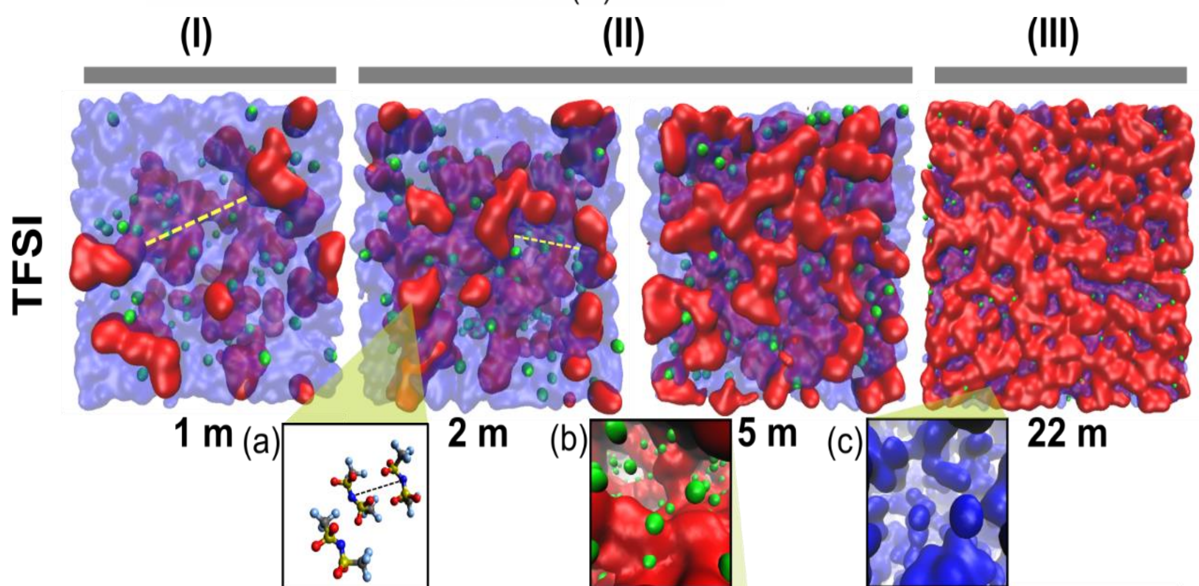



**Peak a**: TFSI $^{-}$ solvated structure

**Peak b**: TFSI$^{-}$ network (water molecules act as bridging bond)



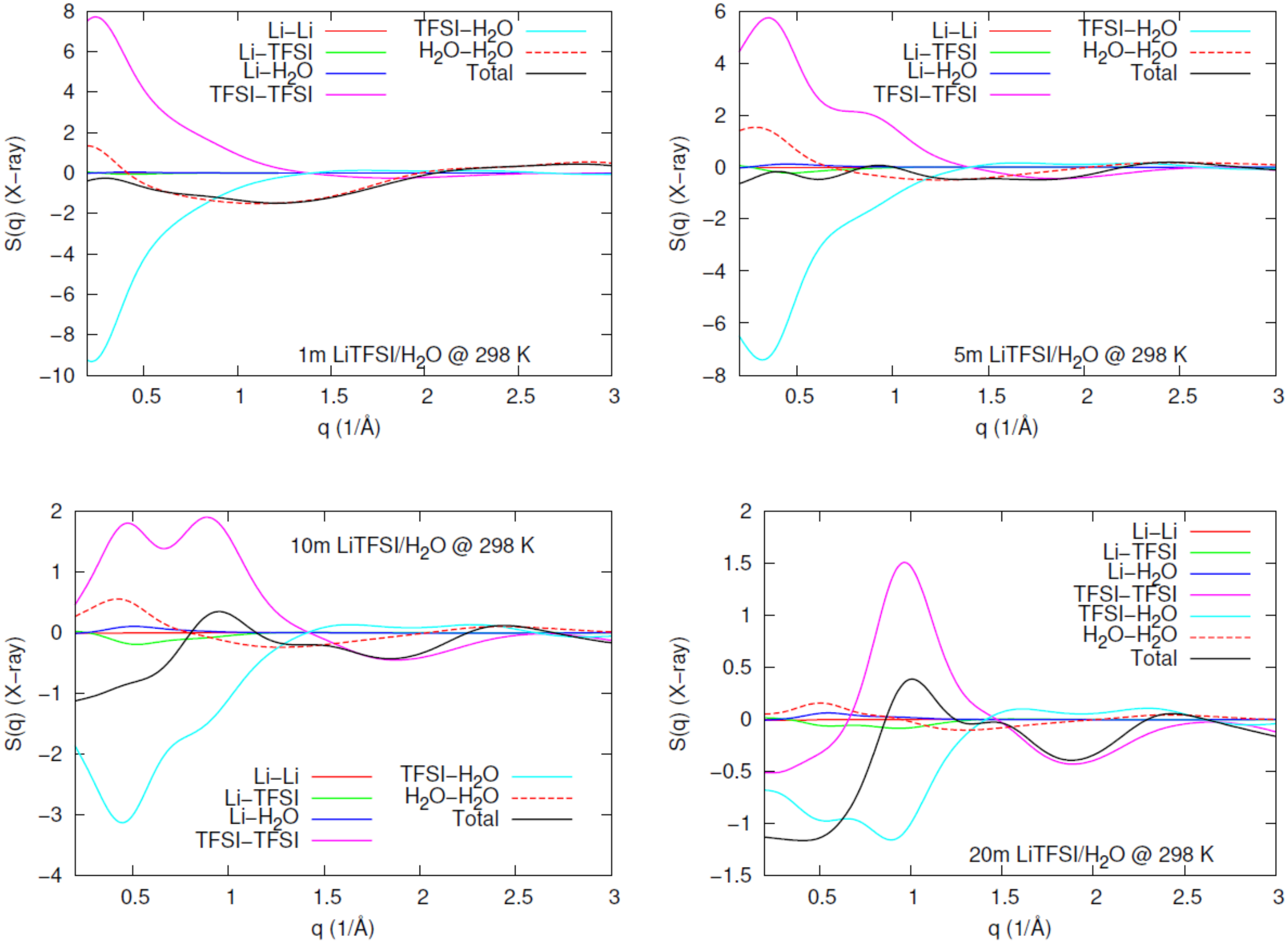

Y. Zhang, et al. *J. Phys. Chem. B* **2021**, 125, 4501−4513

X. Liu, Z. Yu, E. Sarnello, K. Qian, S. Seifert, R. E. Winans, L. Cheng*, **Tao Li**.* *Energy Materials Advances*, **2021**, 7368420.

Liu,# S.-C.Lee,# S. Seifer, R. E.Winans, L. Cheng, Y Z,* **Tao Li.*** *Energy Storage Materials* **2022**, 696-703.

# SAXS: Decomposition

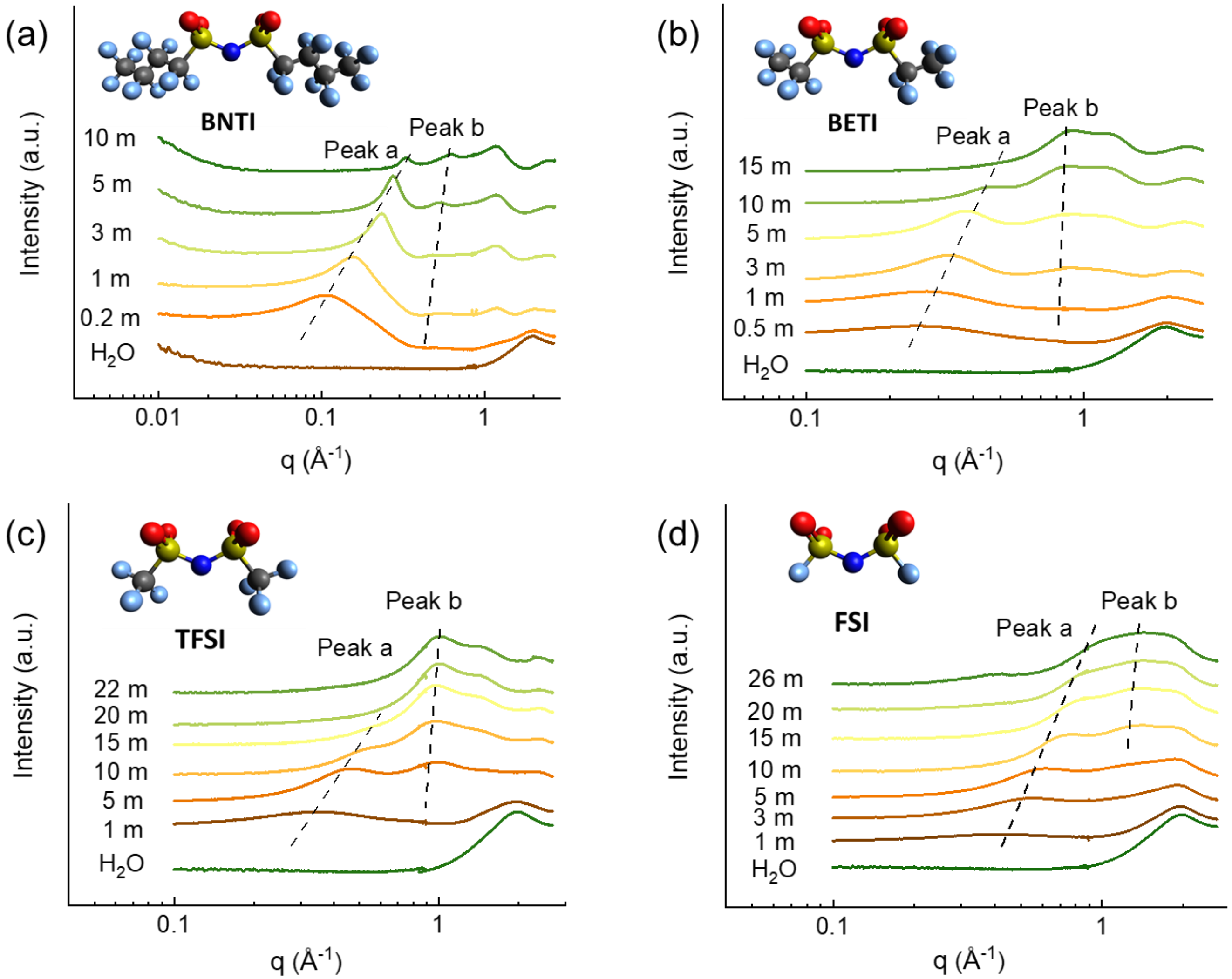
Northern Illinois University




- Feature in SAXS is due to TFSI-TFSI
- TFSI-$H_2O$ and $H_2O$-$H_2O$ also evolve with concentration change

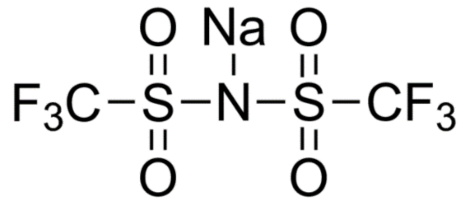
Y. Zhang, et al. *J. Phys. Chem. B* **2021**, 125, 4501–4513

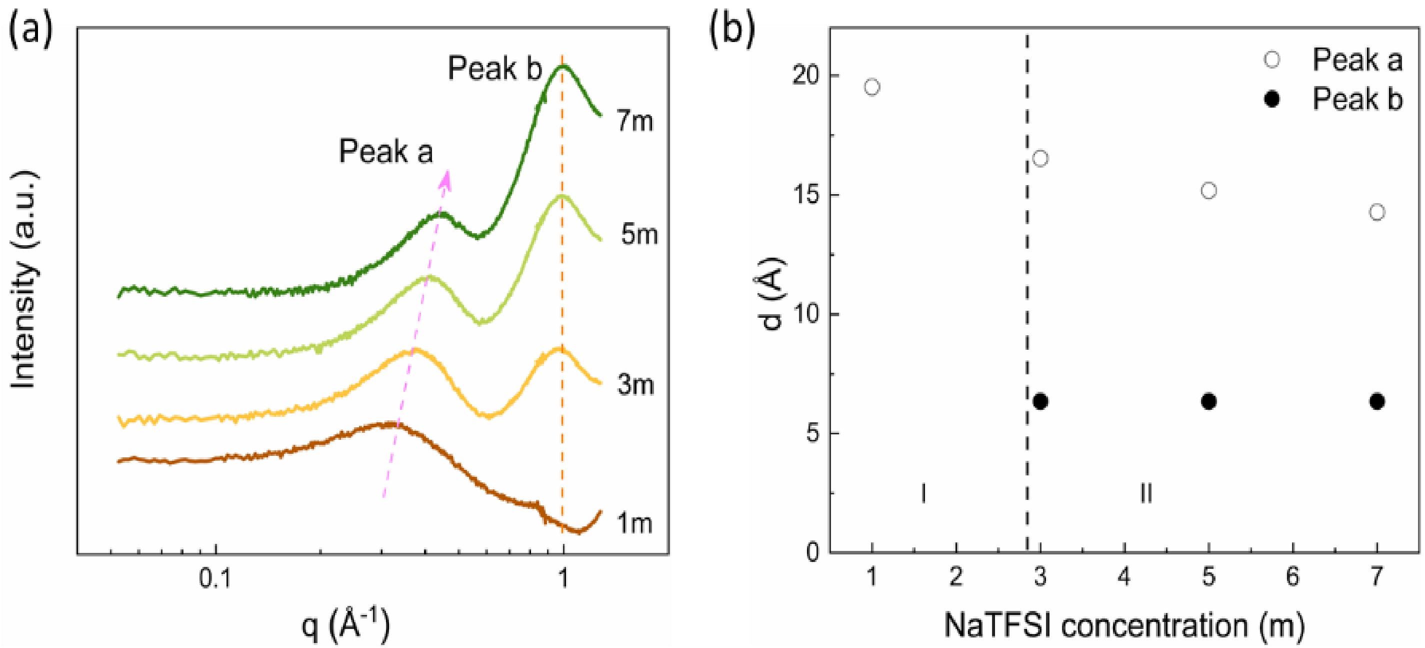
# SAXS/WAXS Study of Different Anions




Liu,# S.-C.Lee,# S. Seifer, R. E.Winans, L. Cheng, Y Z,* **Tao Li**.* *Energy Storage Materials* **2022**, 696-703.

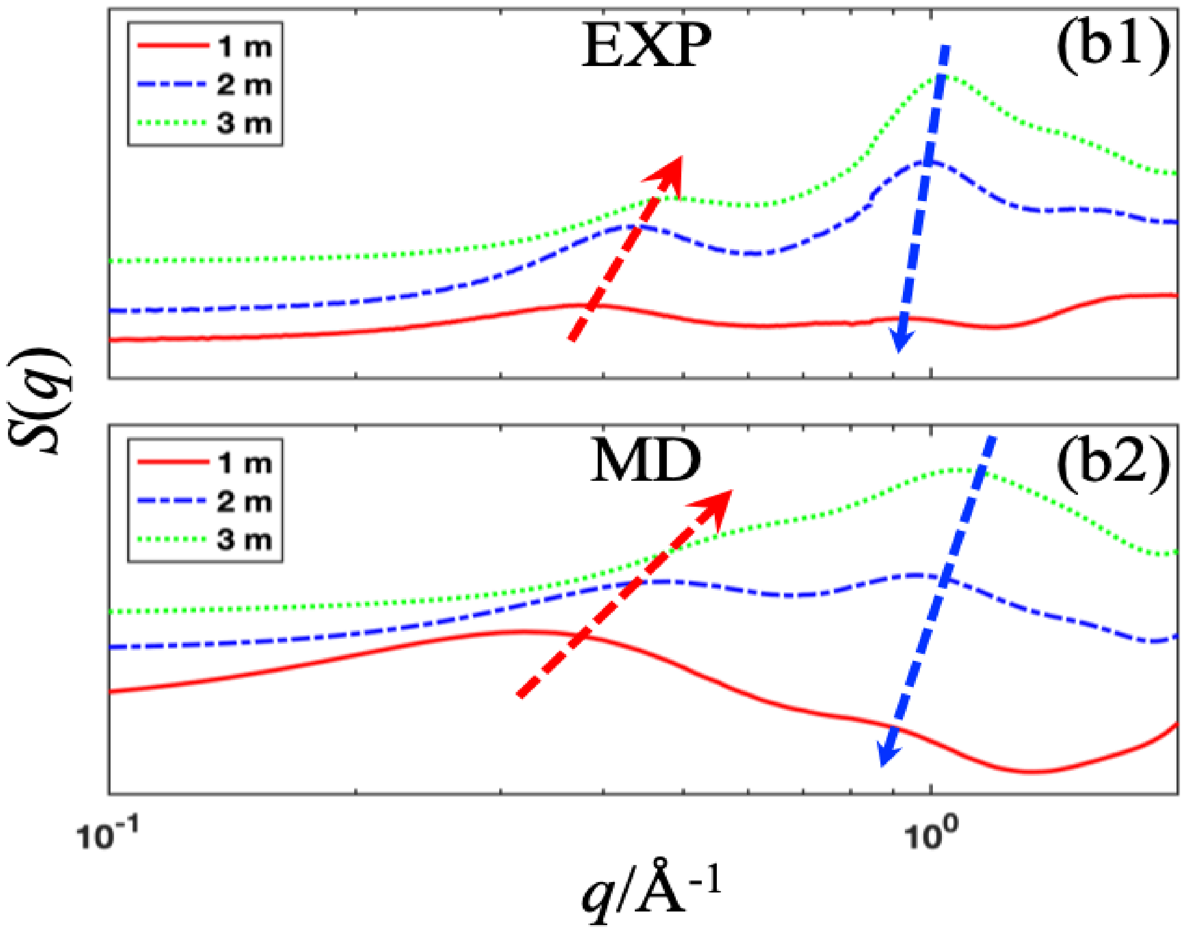
# SAXS/WAXS Study of NaTFSI in Water

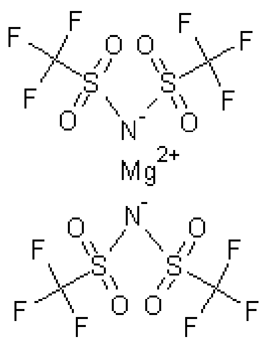





X. Liu, Z. Yu, E. Sarnello, K. Qian, S. Seifert, R. E. Winans, L. Cheng*, **Tao Li**.* *Energy Materials Advances*, **2021**, 7368420.

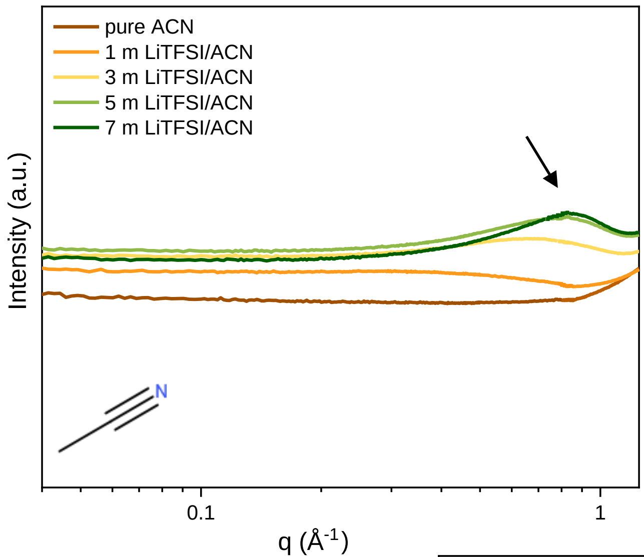
# SAXS/WAXS Study of $Mg(TFSI)_2$ in Water

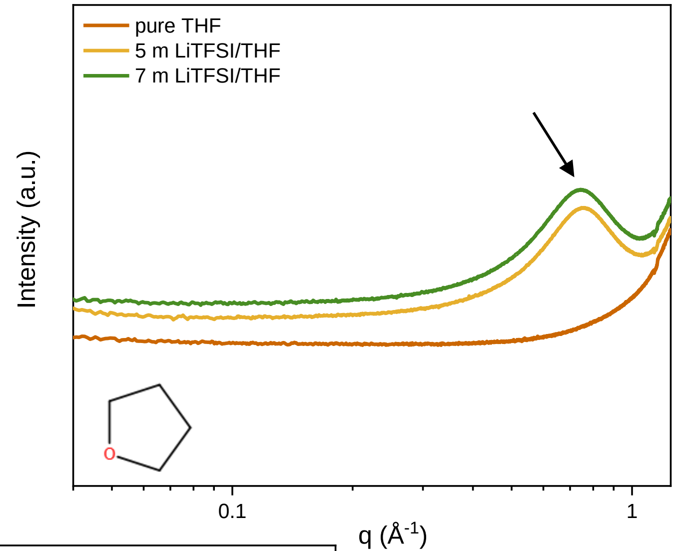


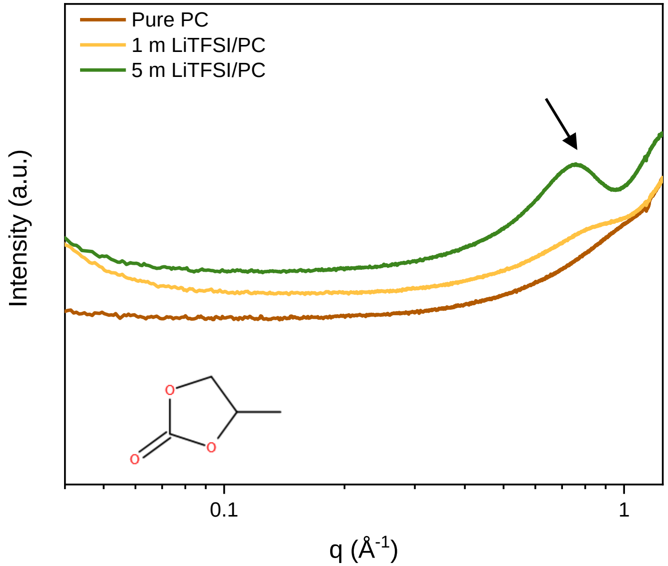




Y. Zhou, T. Juran, X. Liu, K. Han, H. Wang, K. Mueller, K. Xu, L. Curtiss, **Tao Li***, L. Cheng*. *Energy & Environmental Materials,* **2022**, *5,* 295-304.

# SAXS of LITFSI in Different Solvents



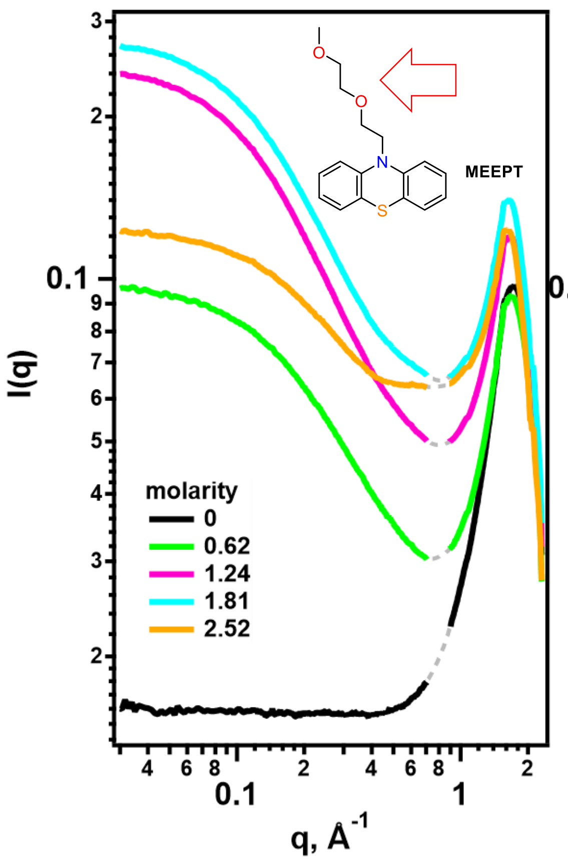



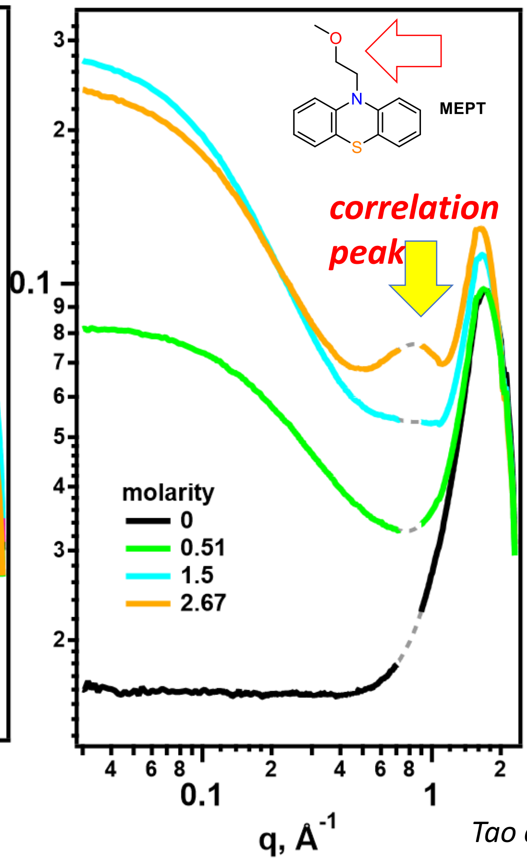




K. Qian, X. Liu, S. Seifert, R. Winans, **Tao Li***. *Energy and Fuel* , **2021,** *35, 23,* 19849–19855

# Molecular Aggregation in Catholyte Redoxmer Solutions

**Collaborator: Shkrob (ANL), Odom (Kentucky), Ewoldt (UIUC), Assary (ANL), L. Zhang (UIUC), Carino (ANL)**



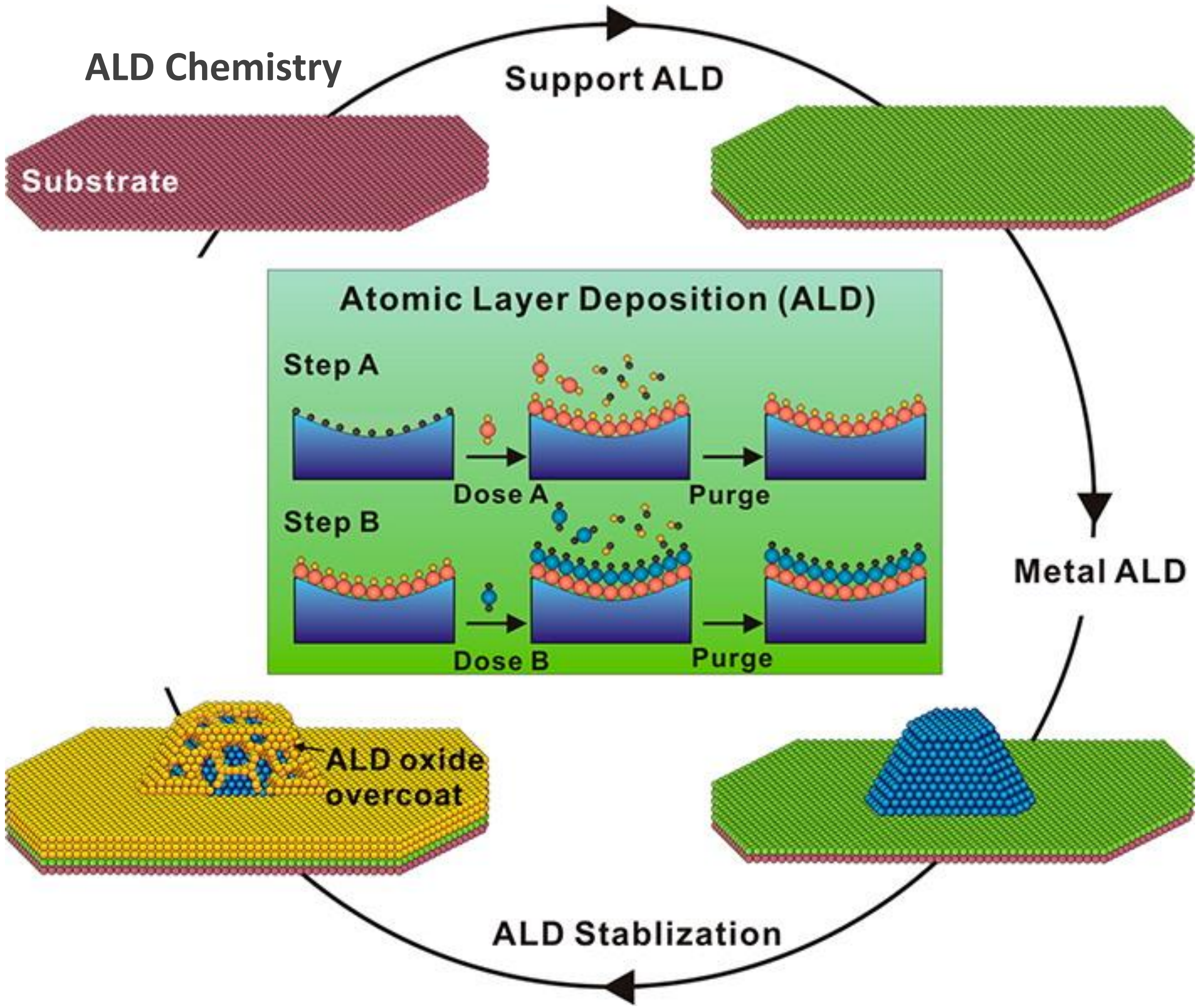

**Correlation peaks** indicative of redoxmer clustering are observed in concentrated solutions of some redoxmers but not the others, depending on *subtle* structural variations.

- **SAXS studies demonstrate aggregation and microscopic phase separation in crowded redoxmer solutions**
- **Aggregation is shown to affect stability of charged redoxmers**
- **It strongly affects viscosity and conductivity**

*Tao and Erik as co-author*

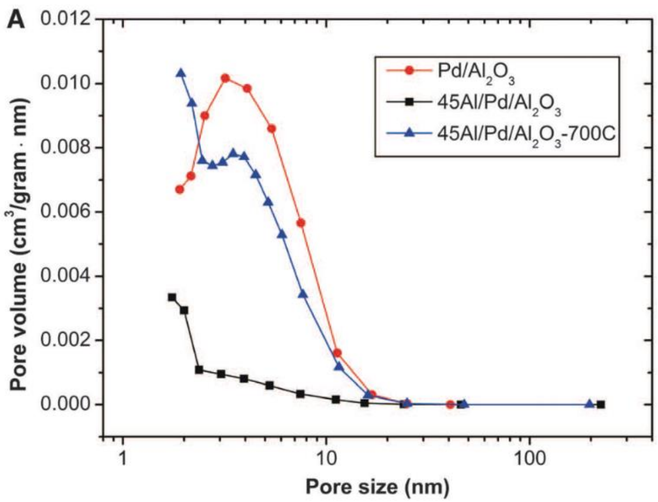
1. *Journal of Physical Chemistry B*, **2020**, *124*, *45*, 10226-10236;
2. *Journal of Physical Chemistry B*, **2020**, *124*, *46*, 10409-10418;
3. *Journal of Molecular Liquid*, **2021,** *334*, 116533.
4. *Journal of Power Sources*, **2021**, *491*, 229506.

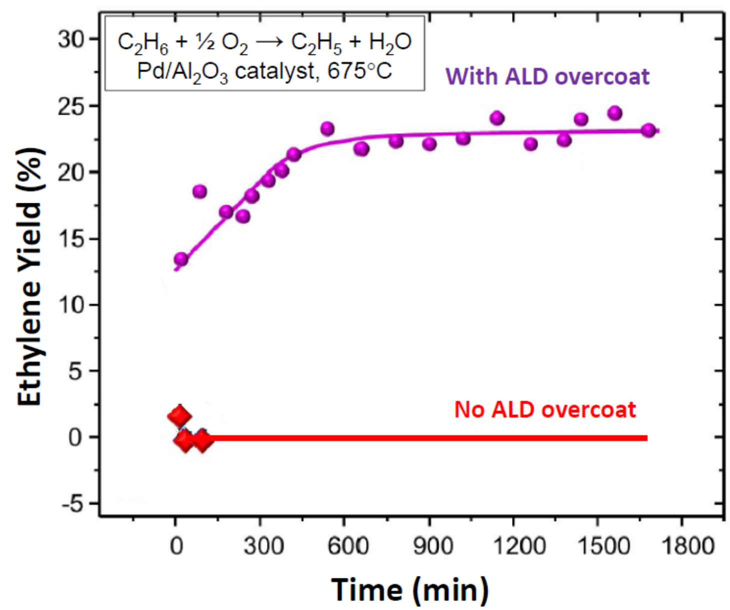
# Supported Metal Catalysts by Atomic Layer Deposition

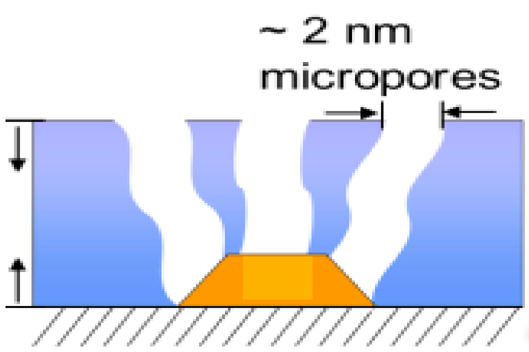



Lu, Junling; Elam, Jeffrey W.; Stair, Peter C. Accounts of Chemical Research (2013), 46(8), 1806-1815

# ALD Overcoated Catalyst with Enhanced Stability



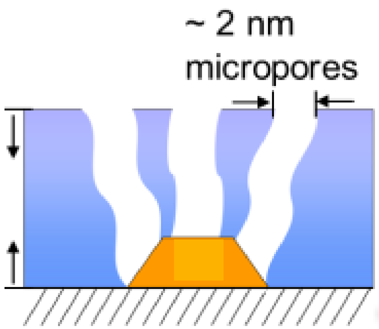



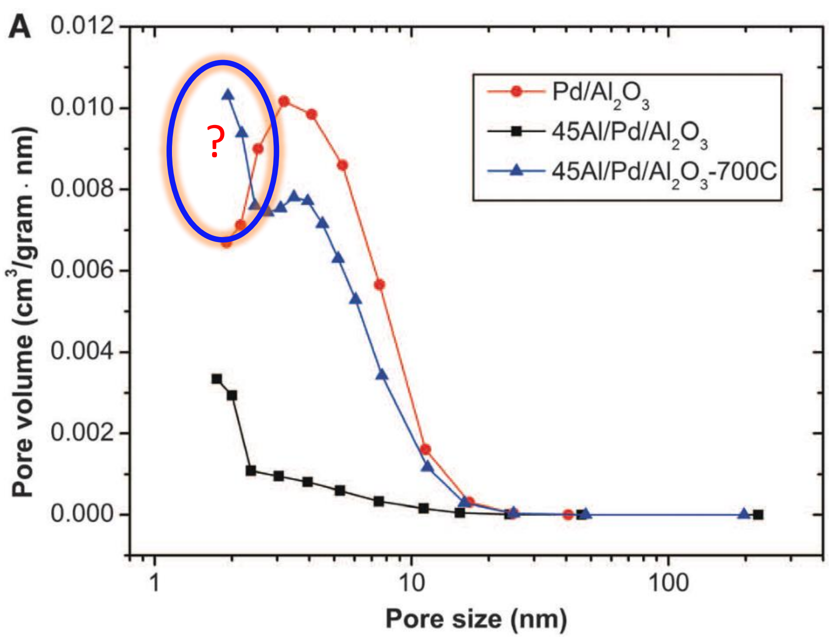

Lu J, et al. Science, 2012, 9, 1205–1208

Lu J, et al. Chem. Mater. 2012, 24, 2047–2055

- Dramatically improved yield and lifetime with ALD overcoat
- Without overcoat, coke formed in <30 min, zero yield
- With overcoat, virtually no coking, >20% yield
- Lifetime enhancement: >100x

# 45c $Al_2O_3$ Over-coating on $Pd/Al_2O_3$ Catalyst

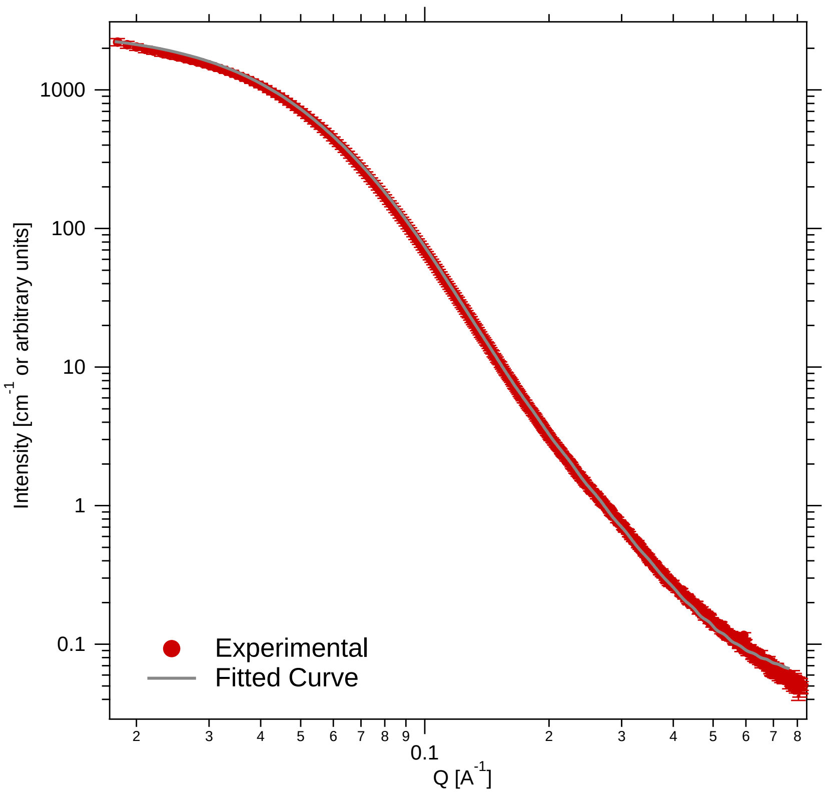


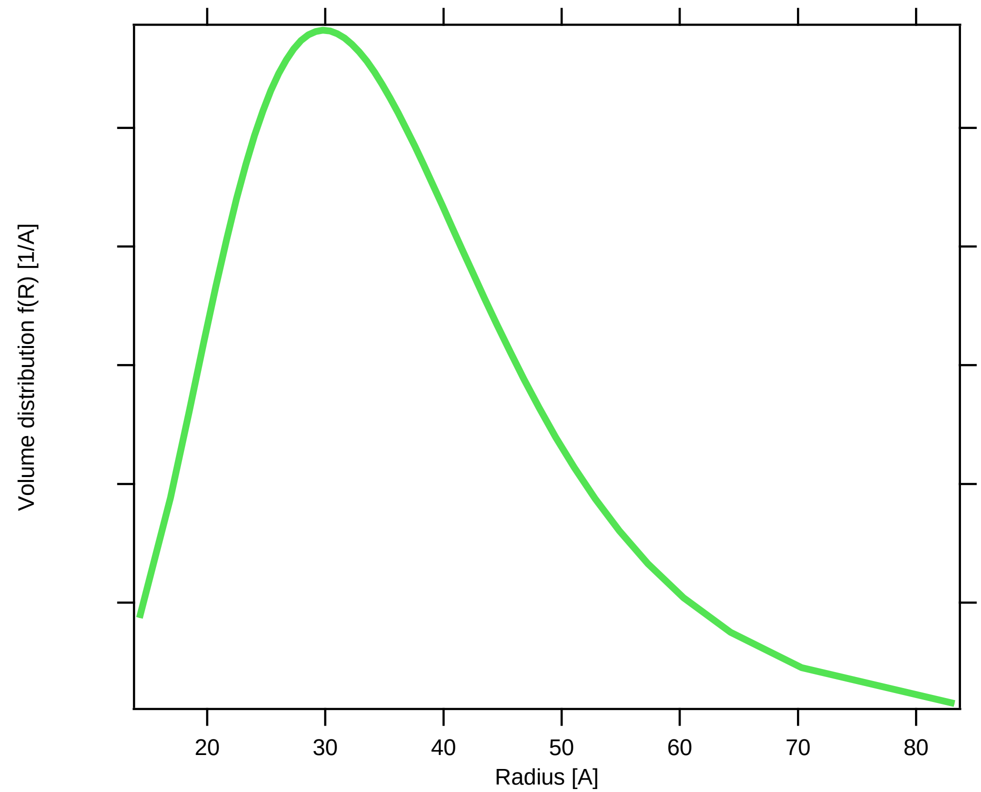




Collaborated with Peter Stair, Northwestern University

**Science, 2012, 9, 1205–1208**

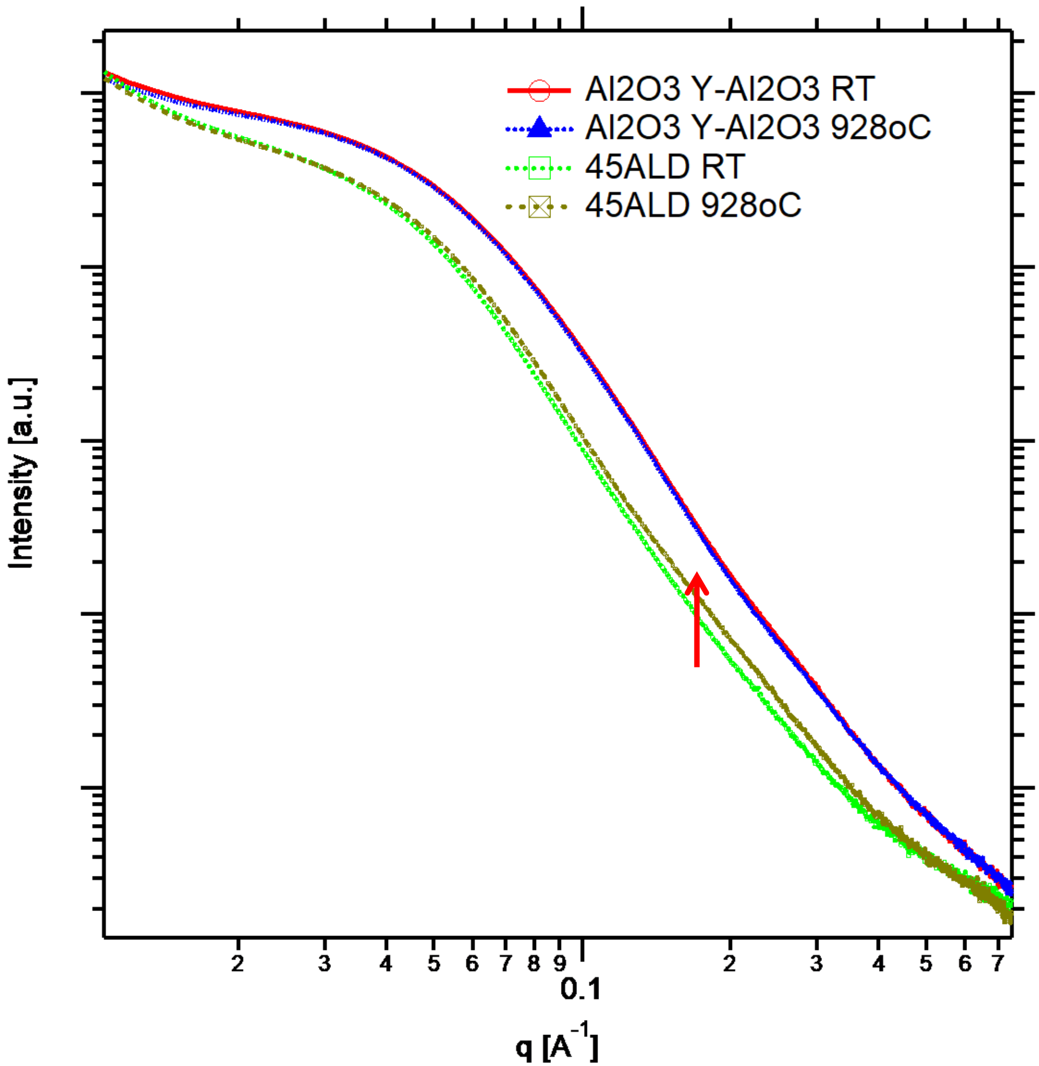
# Pore Size of γ-$Al_2O_3$ Support from SAXS

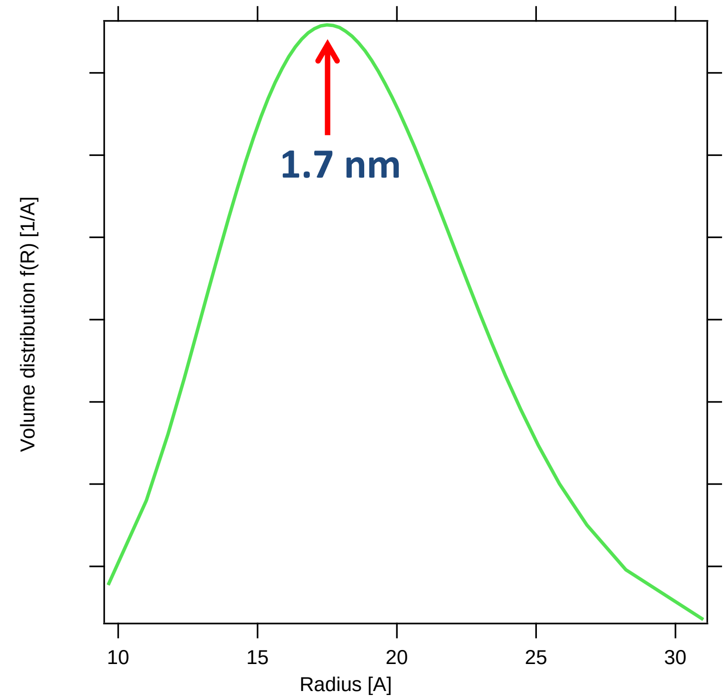



**The fitting shows that the average particle size is 6.7 nm, consistent with BJH Model data 7.1 nm.**

# Pore Size of 45ALD/Cu/ γ-$Al_2O_3$ -700 Support



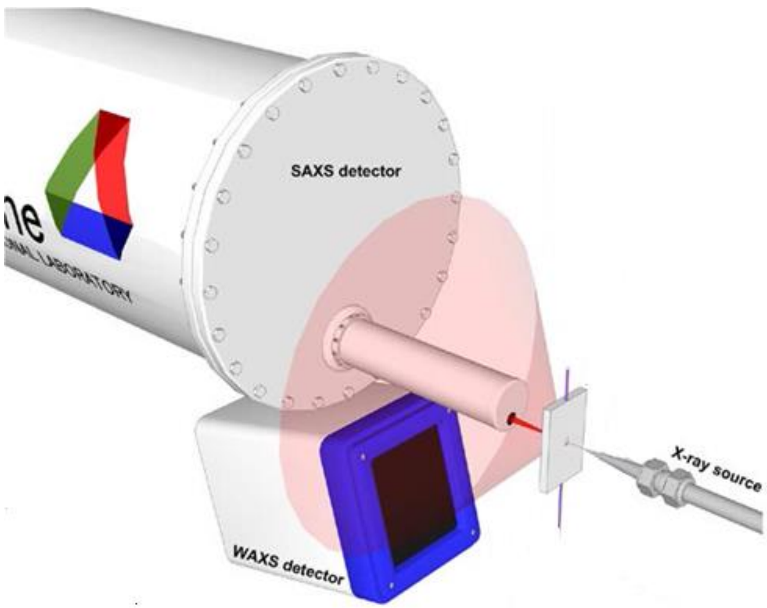



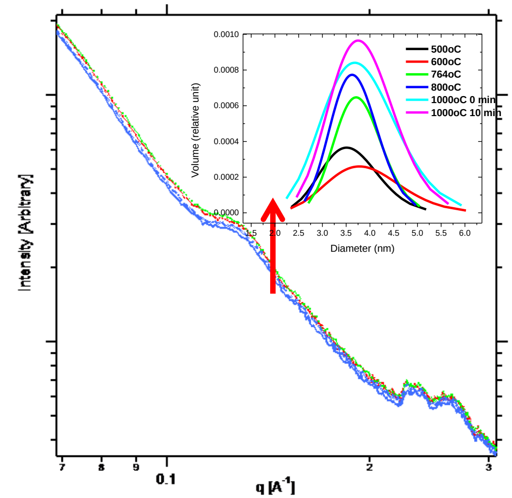

- Gamma-$Al_2O_3$ support has no change before and after heating.
- For 45ALD coated samples, the intensity Increases, indicating the pore.
- Average pore radius 1.7 nm

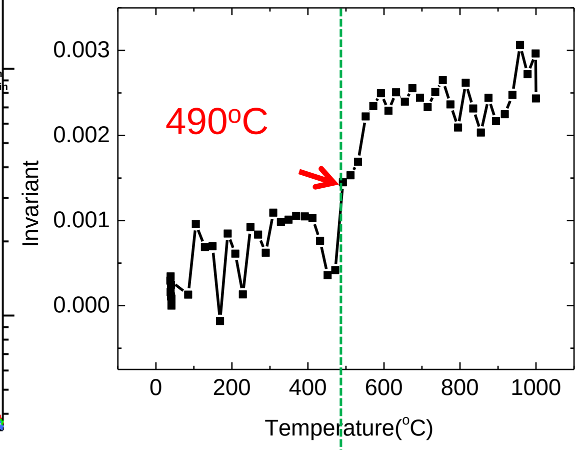
*Tao Li as co-author. ACS Catalysis,* **2020**, *10 (23),* 13957-13967.

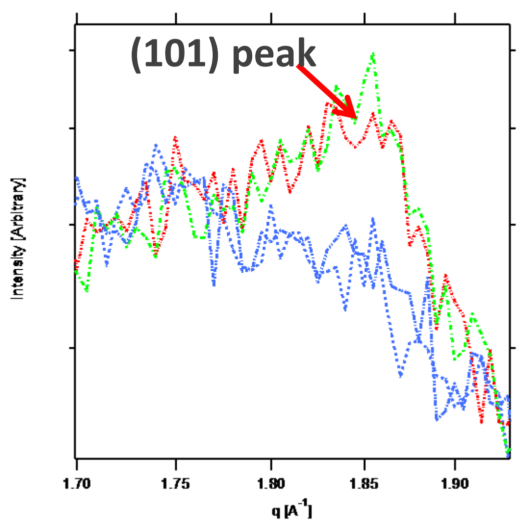
# Combined SAXS/WAXS of $TiO_2$ Overcoat

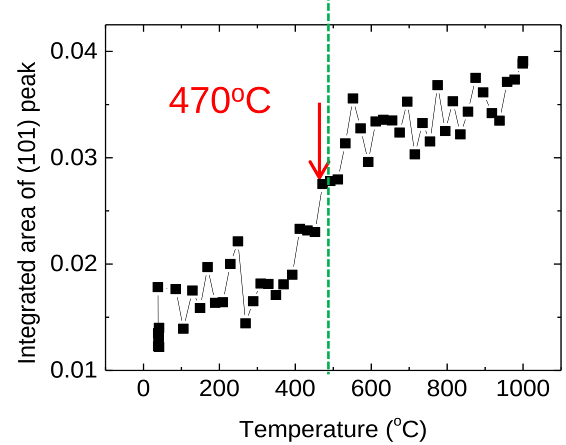
## 5 nm ALD $TiO_2$ overcoat on spherical nanodur   Heat in air 20°C/min to 1000°C



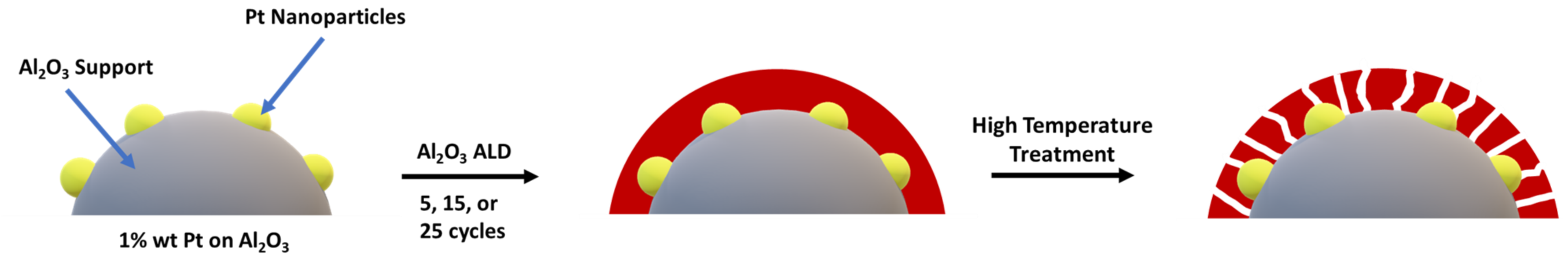



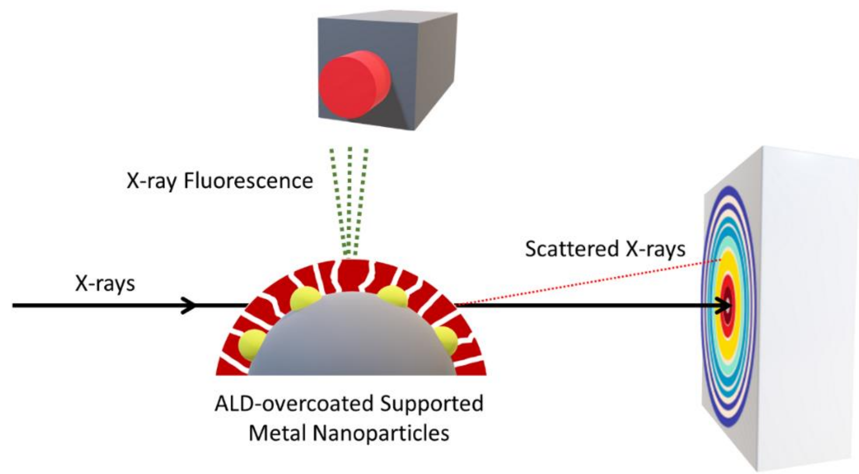

- **APS (12 ID-B)**
- **Linkam stage (RT to 1500 ˚C )**

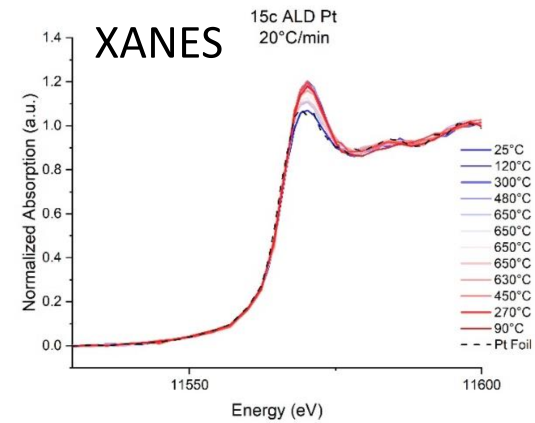
  - SAXS: pore size.
  - WAXS: crystallization.

E. Sarnello, Z. Lu, S. Seifert, R. Winans, **Tao Li***. *ACS Catalysis*, **2021**, *11*, 2605-2619.

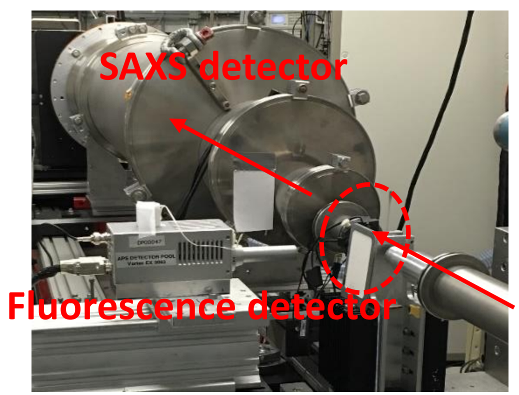
# In Situ SAXS/XAS of $Al_2O_3$ Overcoat on Nanodour

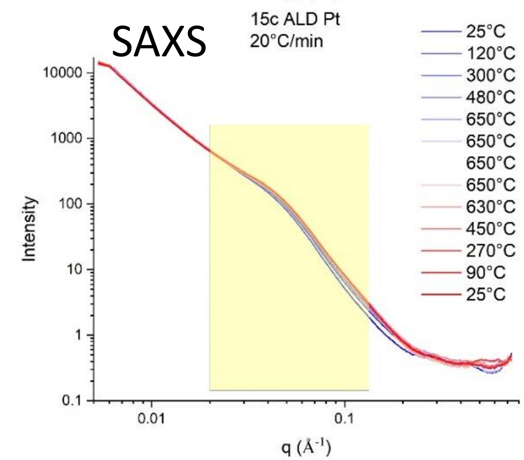


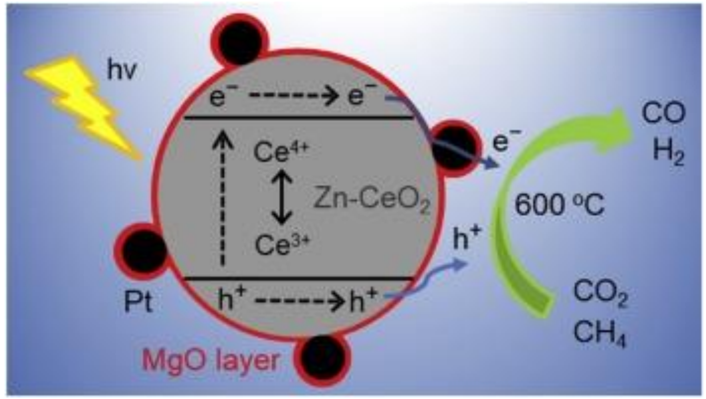



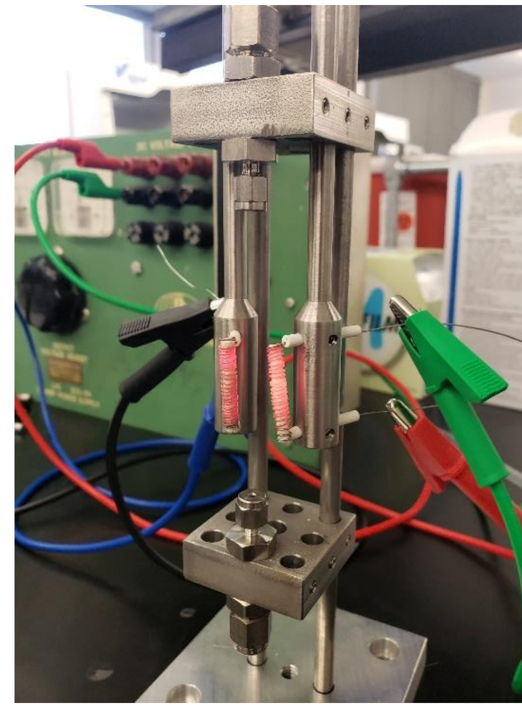

12 ID-C

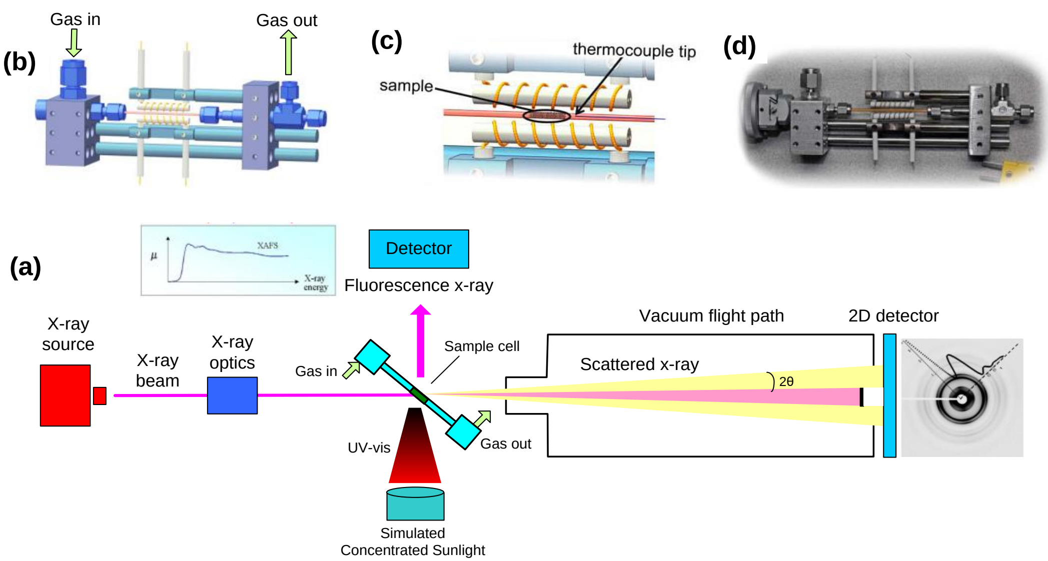


# Integrating Photocatalysis and Thermocatalysis to Enable Efficient Dry Reforming of Methane (DRM)



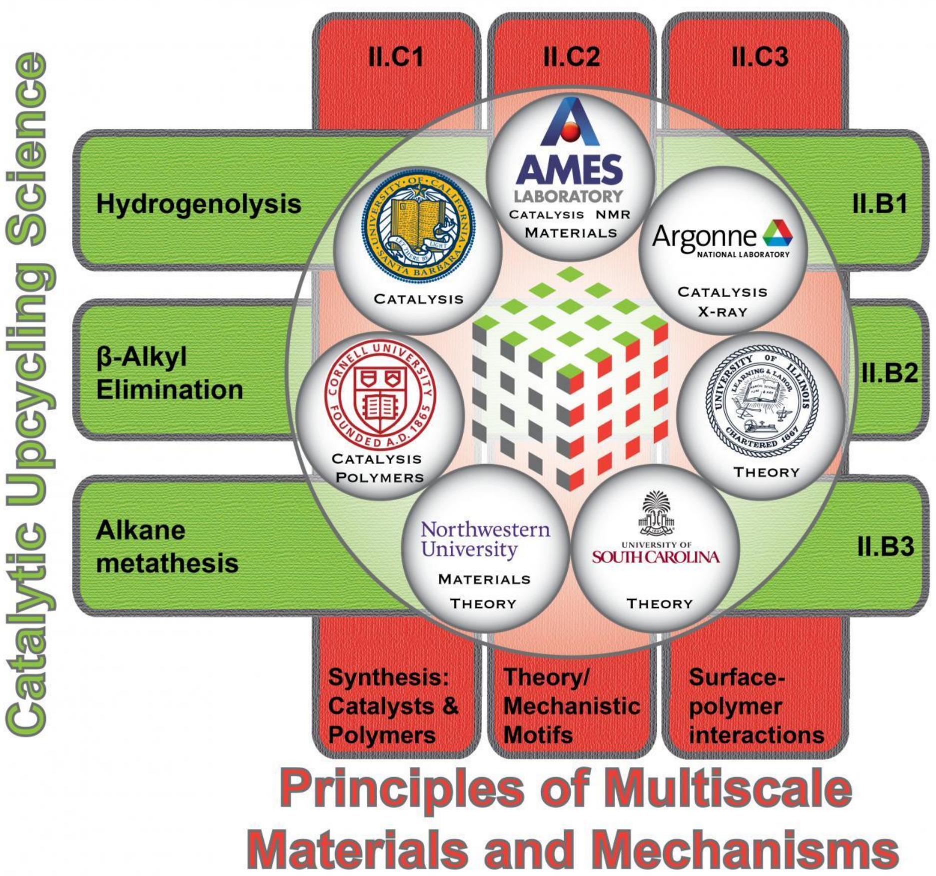



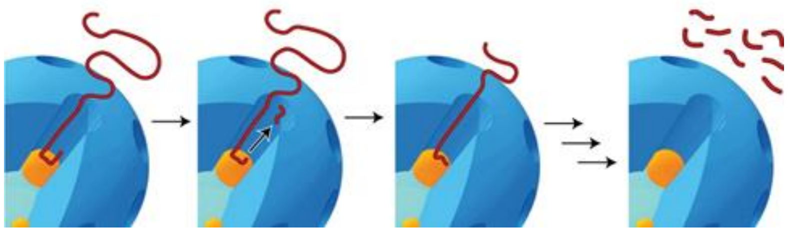


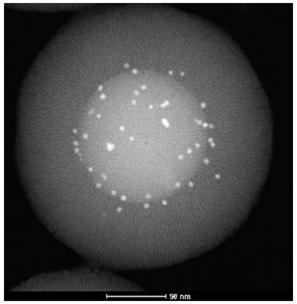

Collaborator: Ying Li (TAMU)

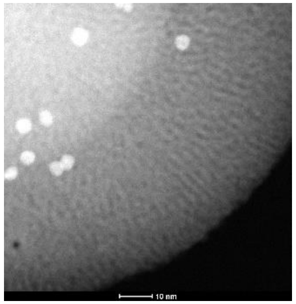
P. Fu, E. Sarnello, **Tao Li***, Y. Li*. *Appl. Catal. B.*, **2020**, *260*, 118189.
L. Fang, Z. Feng, L. Cheng, R. Winans, **Tao Li***. *Small Methods*, **2020**, 2000315.
Z. Du, F. Pan, E. Sarnello, X. Feng, Y. Gang, **Tao Li**, Y. Li*. *Journal of Physical Chemistry C* **2021**, in press

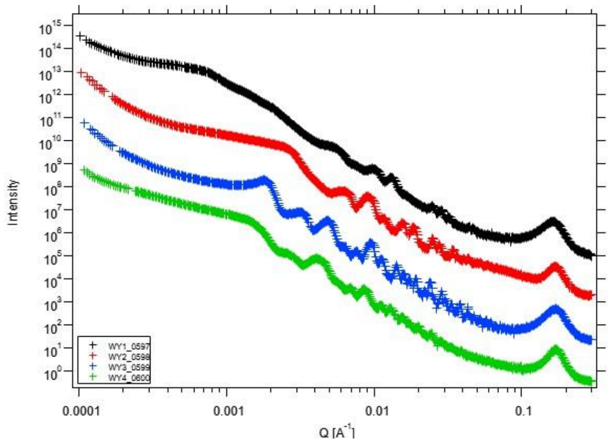
# Polymer Recycling










Collaborator: Byeongdu Lee (ANL), Wenyu Huang (ISU/Ames)

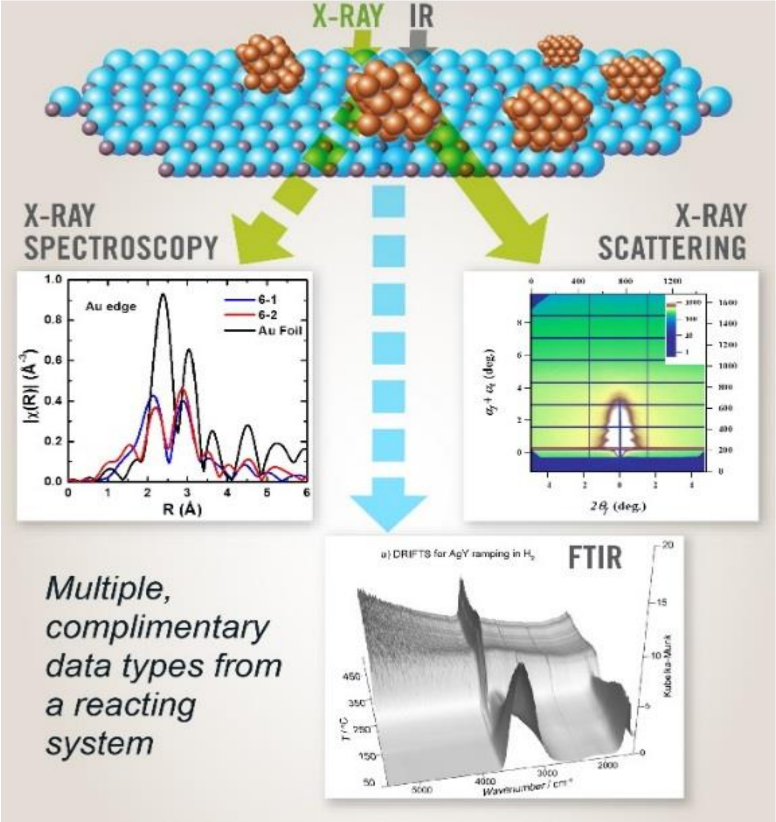
# Multiple Techniques to Observe Structure under Real Conditions

*(If you can do it in the lab, we can do it on the beamline)*

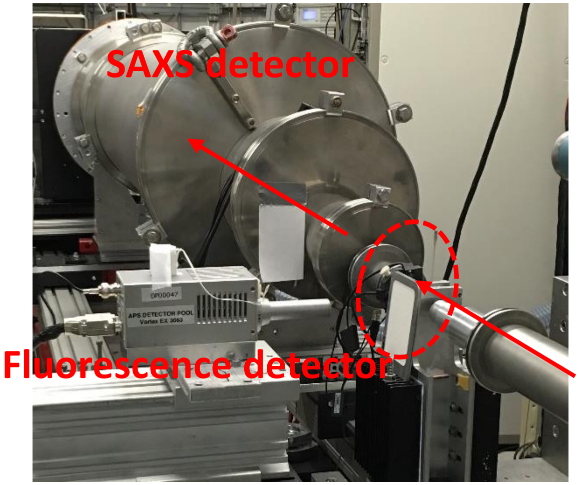
Five sectors provide a suite of in-situ techniques including X-ray scattering and spectroscopy at:

1-ID (high energy SAXS/WAXS (PDF))
9-ID-D(USAXS/SAXS)
9-BM, 20-BM (XAS)
10-ID (XAS)
11-BM (Hi res powder diff)
11-ID-B,C (PDF)
12-BM (XAS/SAXS)
12-ID-B, C (SAXS/WAXS, and GISAXS/GIWAXS)
Also - Imaging and Microscopy (2-BM, 32-ID-BC)

Upgraded
Upgrading




12 ID-C




X-ray scattering and spectroscopy combined with FTIR and Raman to study in situ catalysis on a flat surface.

# Software and useful website

http://smallangle.org/content/Software

- Fit2D or Nika for data reduction.
- SASfit, Irena, SasView
- Crysol
- GIXSGUI and FitGISAXS

Irena and Nika software course
Beyond Rg Materials
Beyond Rg Bio
BioSAS: Advanced Applications

# THANK YOU