Introduction to Small Angle X-ray Scattering for Nanomaterials

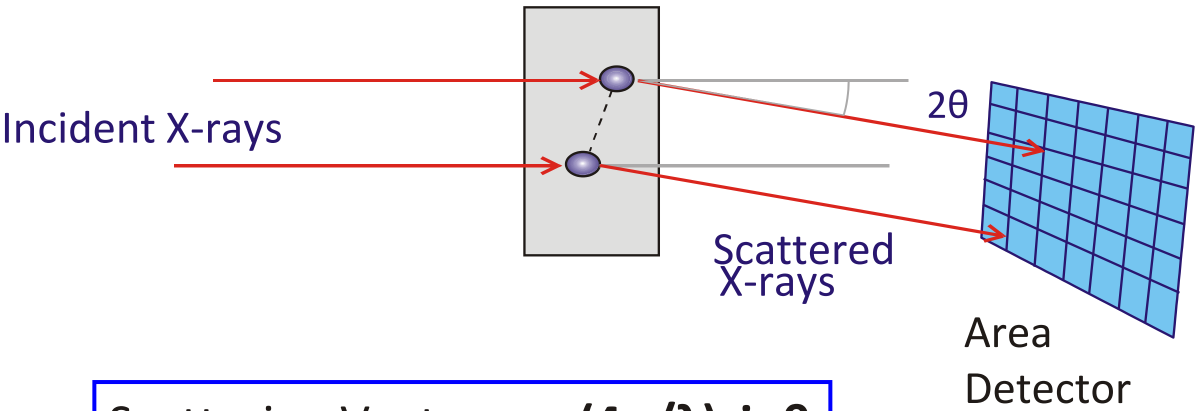
Tao Li (tli4@niu.edu; taoli@anl.gov)
Chemistry Department of Northern Illinois University
Advanced Photon Source of Argonne National Laboratory (joint)

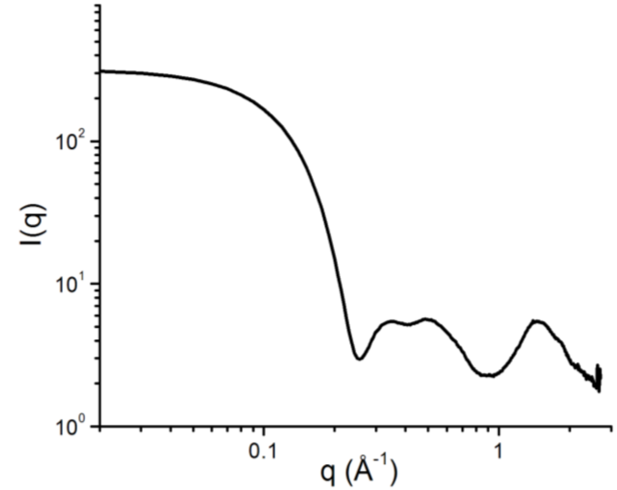
Thanks to Xiaobing Zuo, Byongdu Lee, Pete Jemian, Jan Ilavsky, Randall Winans for some slides.

Outline

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

What Does Small Angle Scattering Measure?



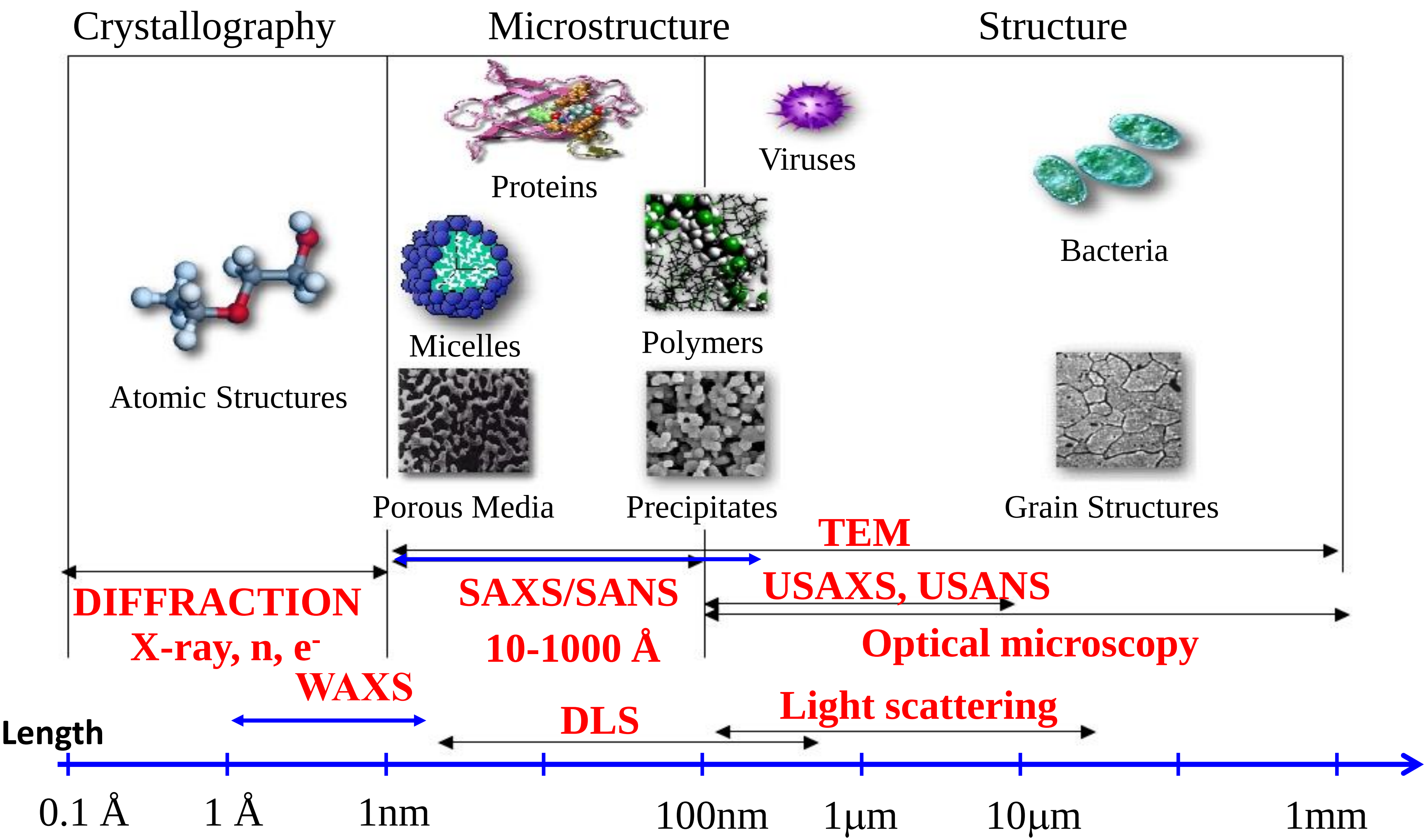


Scattering Vector: $\mathbf{q = (4\pi/\lambda)\sin\theta}$

- Measuring the size range from 1 to 100 nm
- Size and distribution, shape, particle distance, compositions, volume fractions

Tao Li, A. Senesi, B. Lee* *Chem. Rev.*, **2016**, *116*, 11128 - 11180.

Length Scales Probed by SAS and Other Characterization Techniques



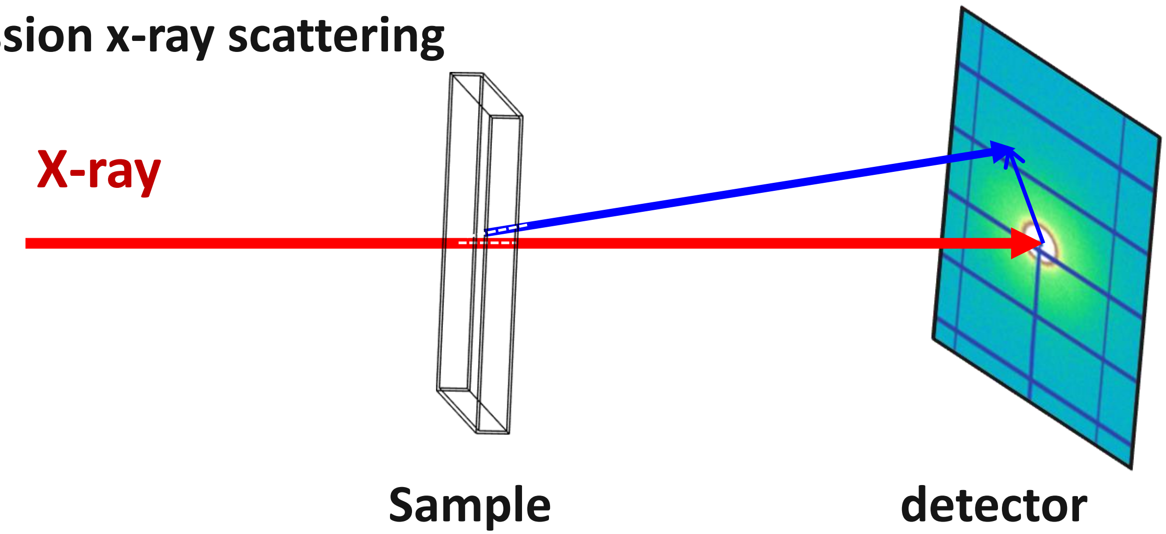
1. X-ray Scattering Setup

- Storage-Ring synchrotron
- X-ray scattering setup

X-ray Scattering Setup Configuration

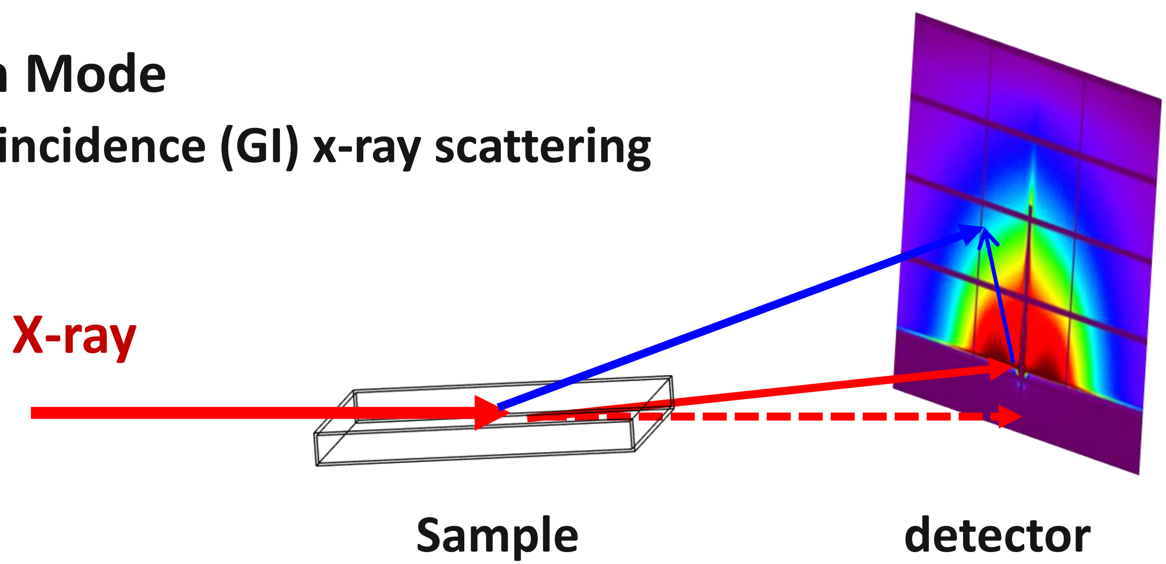
Transmission Mode

Transmission x-ray scattering



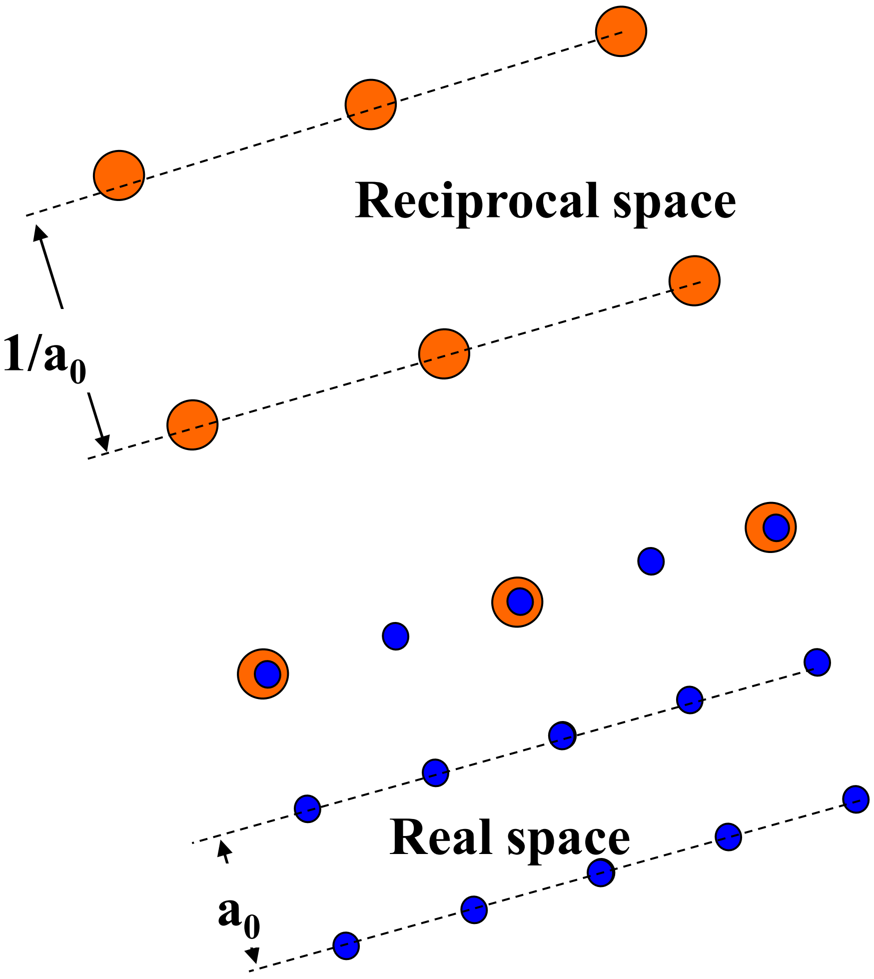
Reflection Mode

Grazing incidence (GI) x-ray scattering

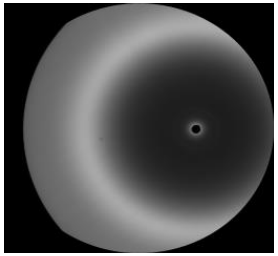


Real space vs Reciprocal space

- 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

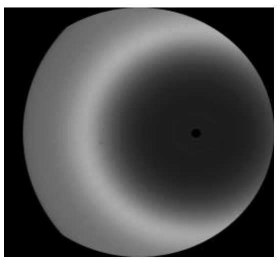


(Solution) X-ray Scattering Data



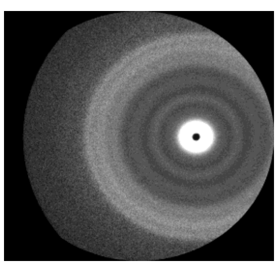
Solution (Solute + Solvent)

−



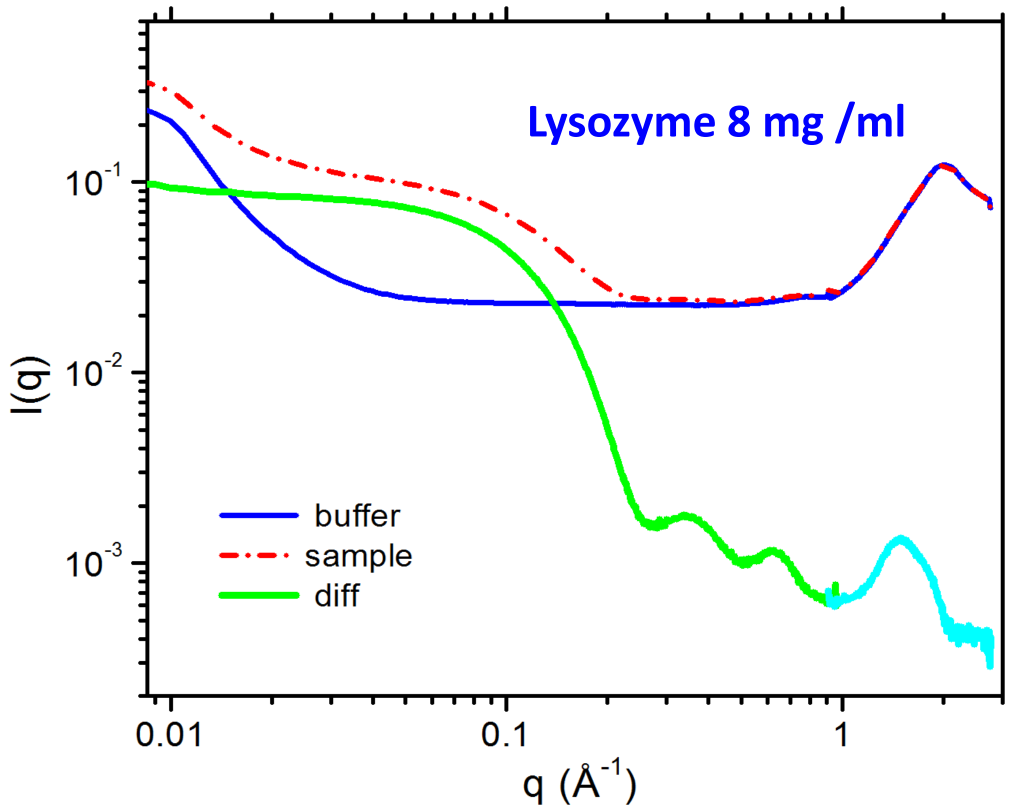
Solvent / Buffer

=



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

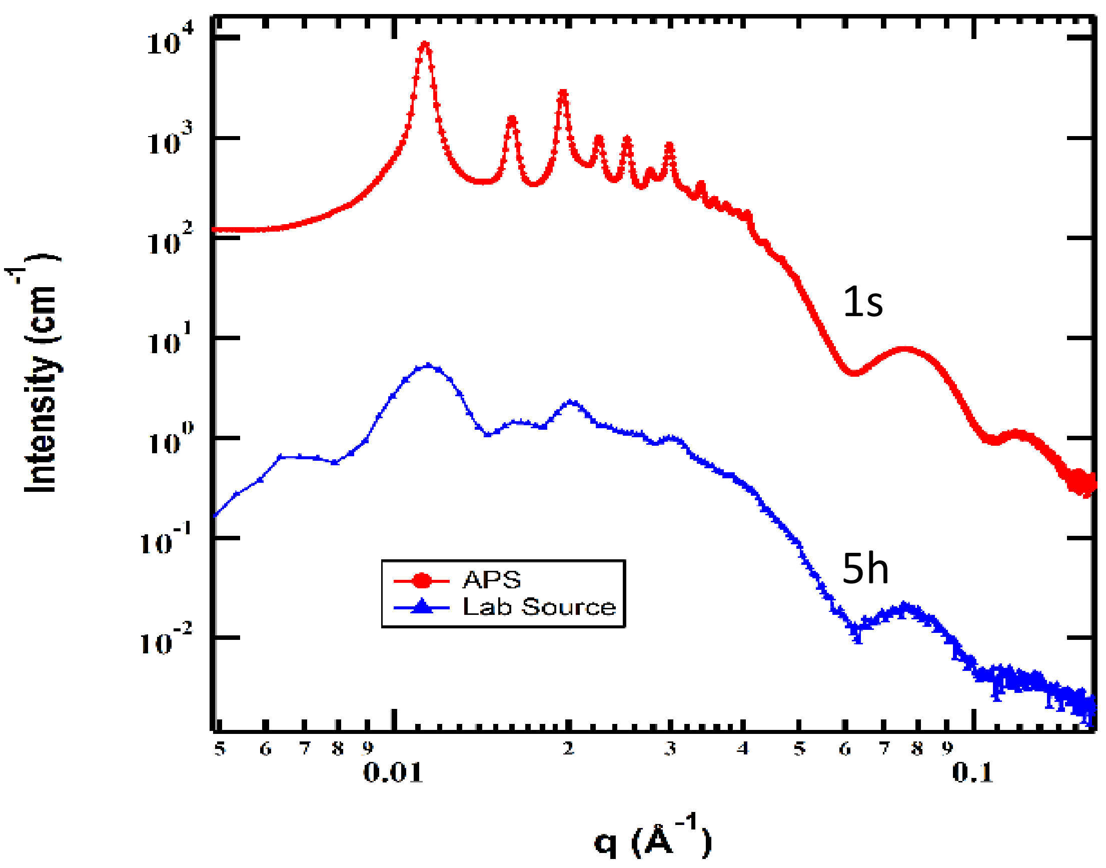
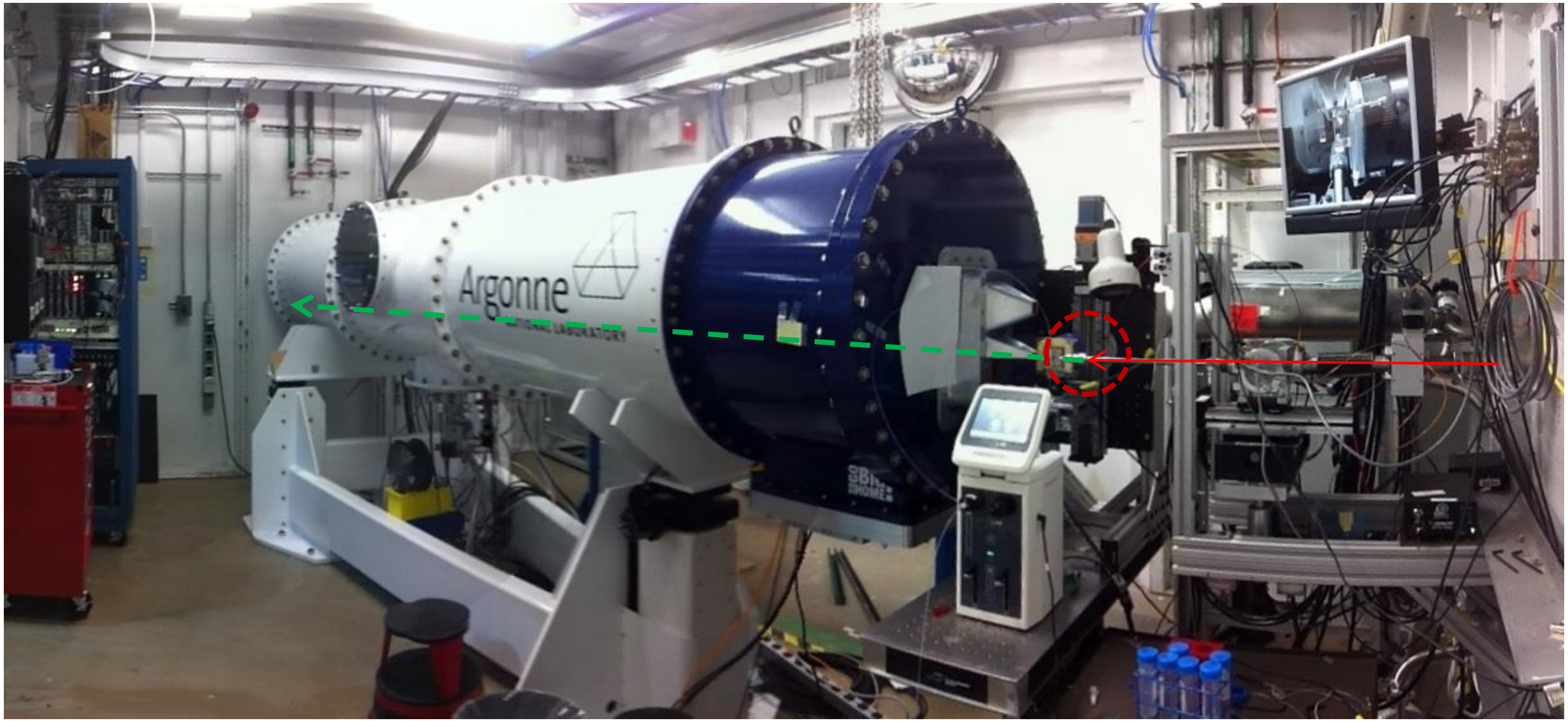


Figure 3. SAXS data of BCC SL of 15nm gold spherical particles linked with DNA. The same sample were measured with APS and Lab sources.

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



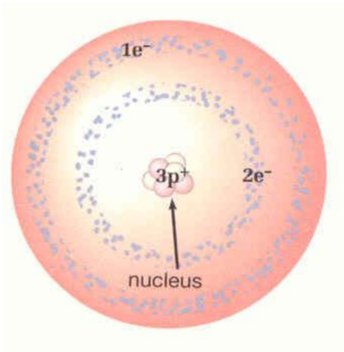
- From 1 to 150 nm
- High flux, one measurement less than 0.1 s
- In situ SAXS study : high temperature (up to 1500^{o}C) and high pressure (up to 20,000 psi)
- Element specific information from ASAXS
- Can be combined with many other techniques such as IR and other spectroscopy

Fundamentals of X-ray Scattering

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

Atomic Form Factor

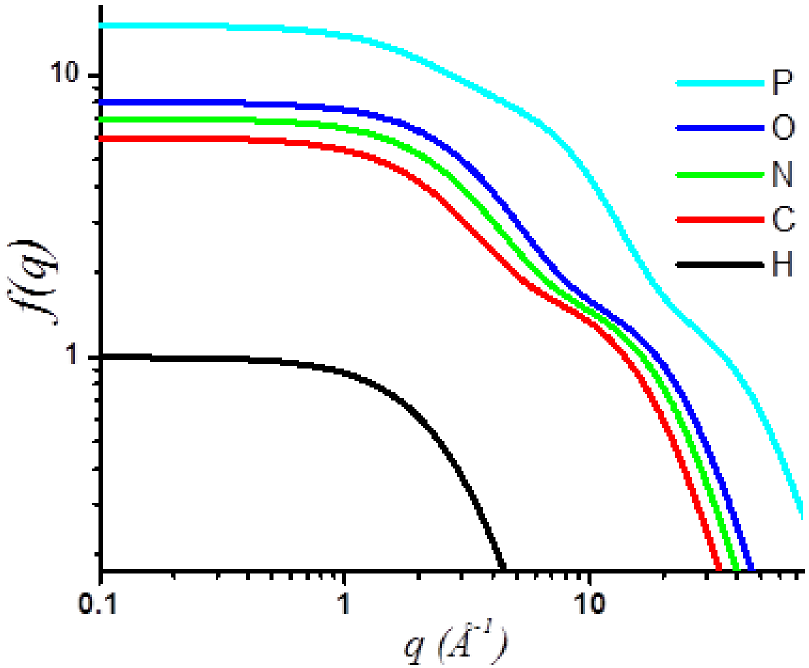
Electron cloud in atoms has radial density distribution $\rho(r)$



Atomic electron cloud

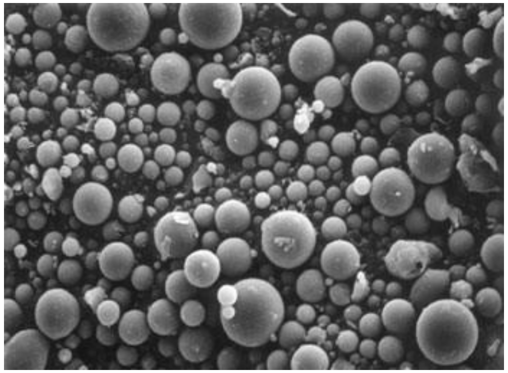
$$f(q) = 4\pi \int \rho(r) r^2 \frac{\sin(qr)}{qr} dr$$

- 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.



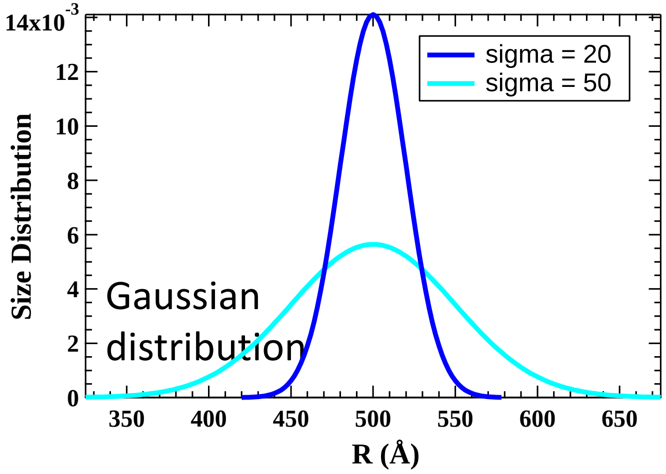
Data taken from **International Tables for Crystallography**, Vol. C, Table 6.1.1.1

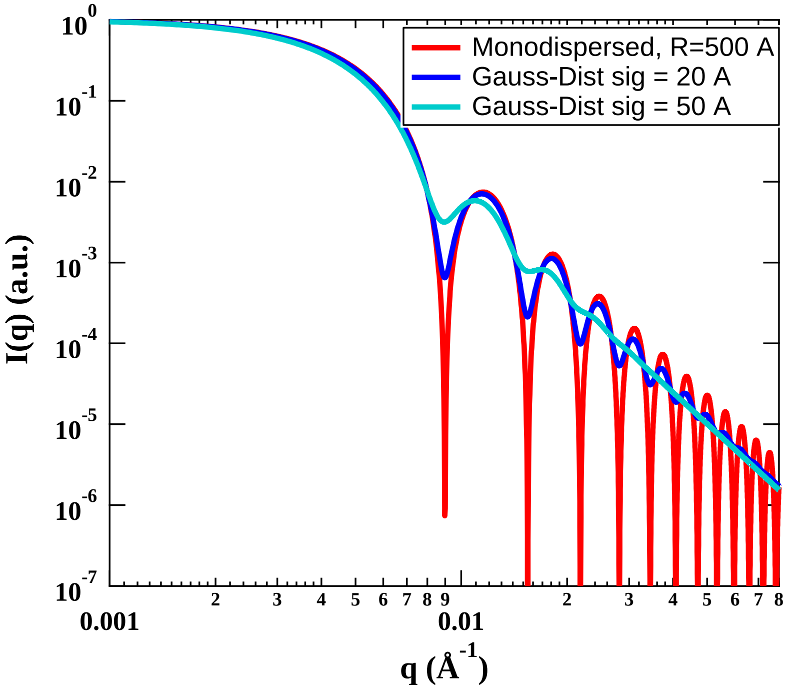
Polydispersity: Size Distribution



Scattering for an ensemble with different sizes:

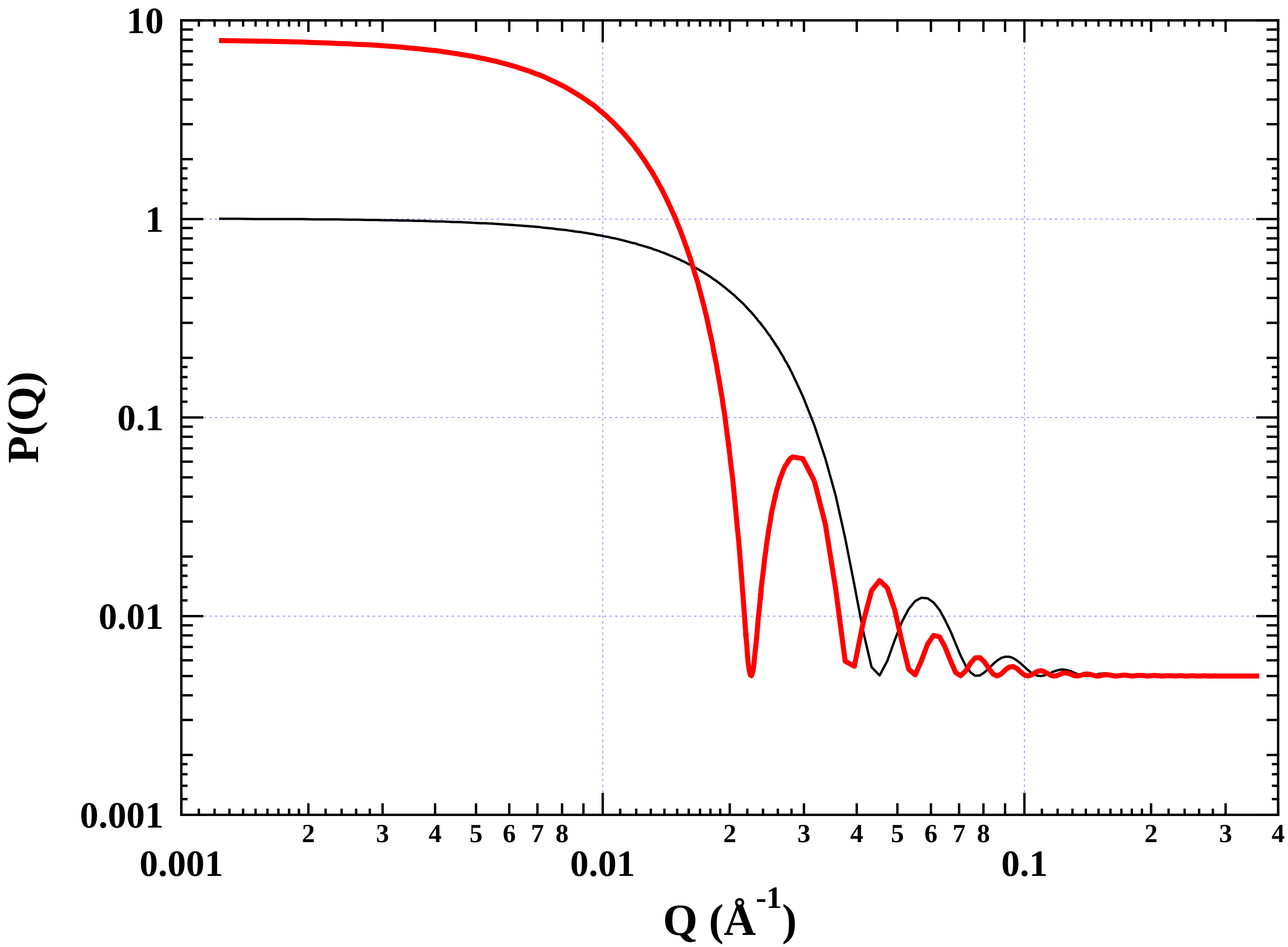
Sphere radii with Gaussian distribution



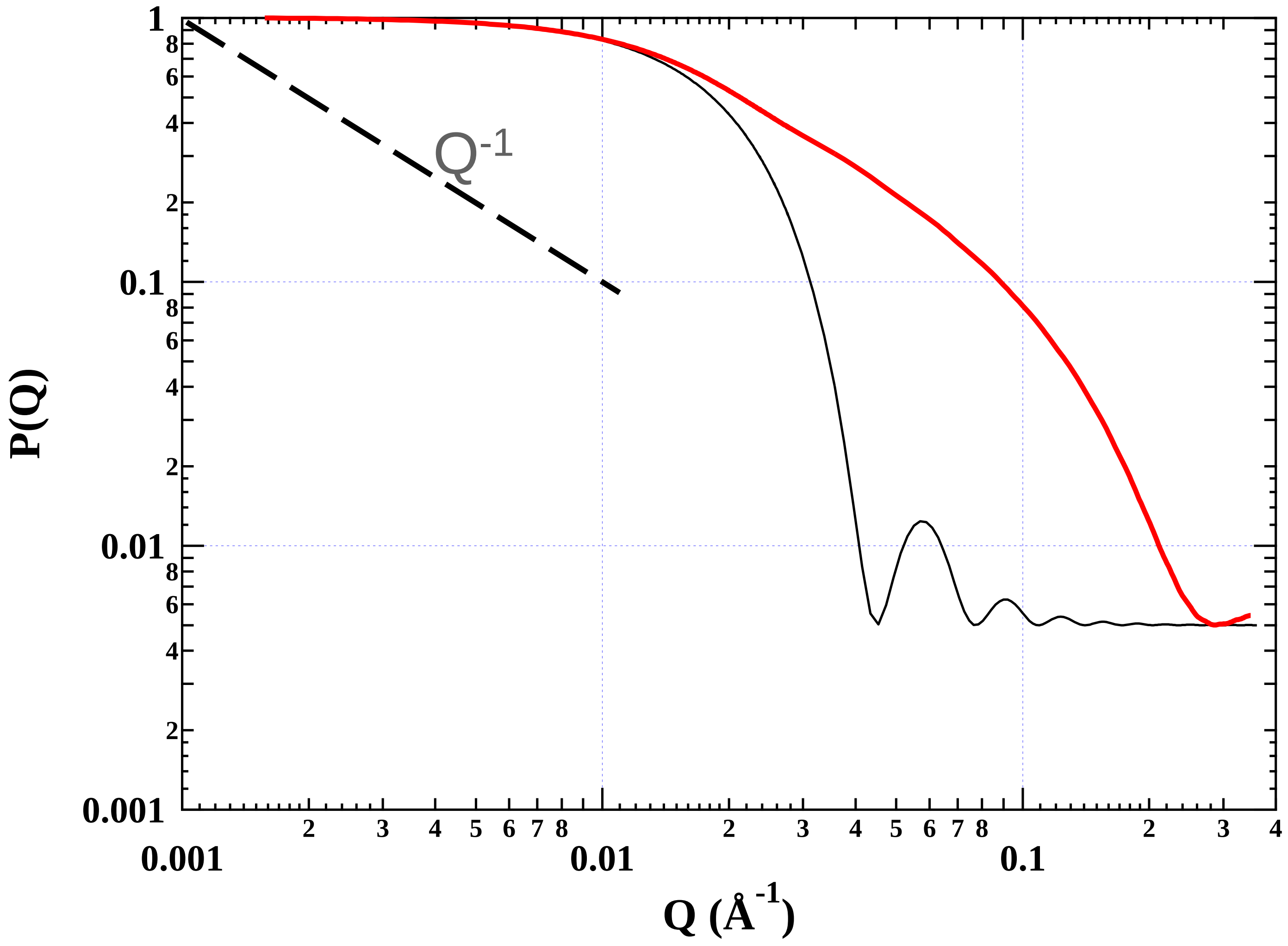


- Size polydispersity smears/dampens fine features in scattering profile.

Spheres of different sizes



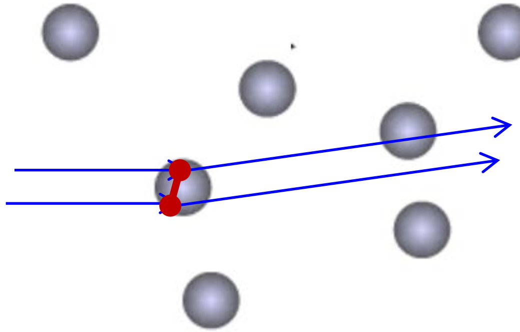
“Long & thin” cylinder



Particle Correlation: Structure Factor

Dilute, randomly distributed particles:

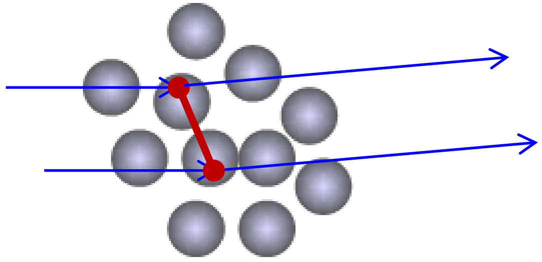
$$I(q) = NP(q)$$



Correlated particles:

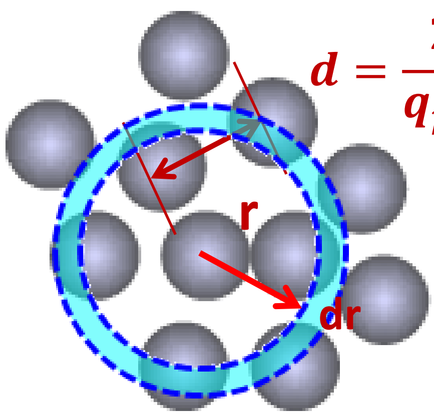
$$I(q) = NP(q)S(q)$$

S(q) structure factor

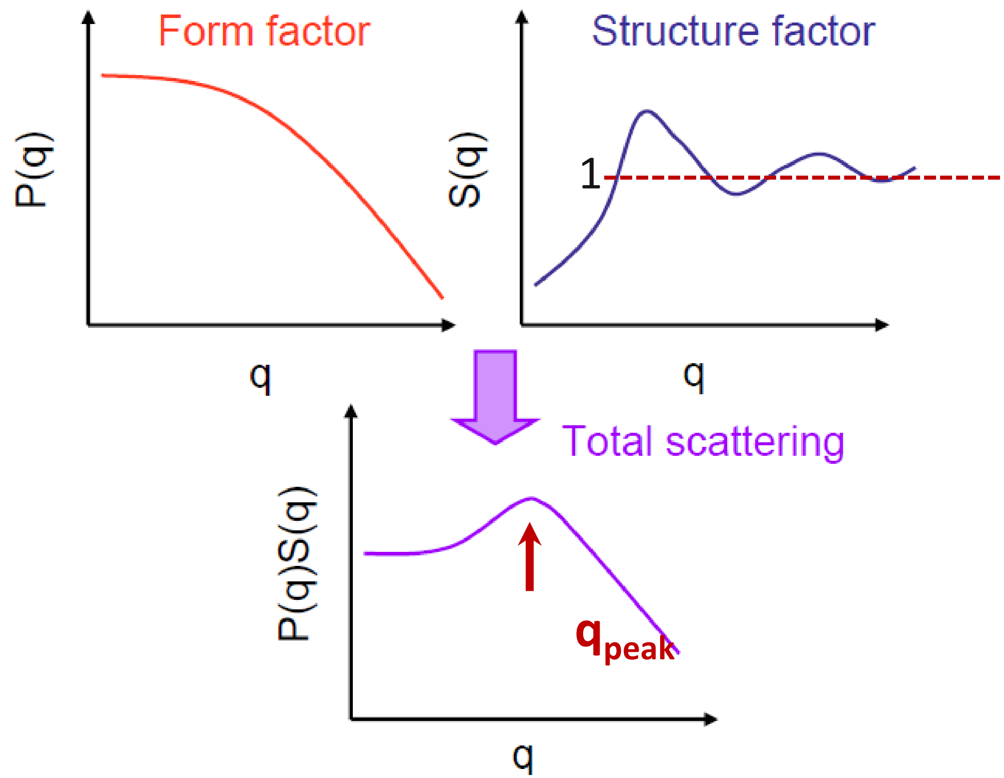


Structure Factor: Common Spacing(s) between Scatterers

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



$$d = \frac{2\pi}{q_{peak}}$$



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

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

Theory and Applications of SAXS

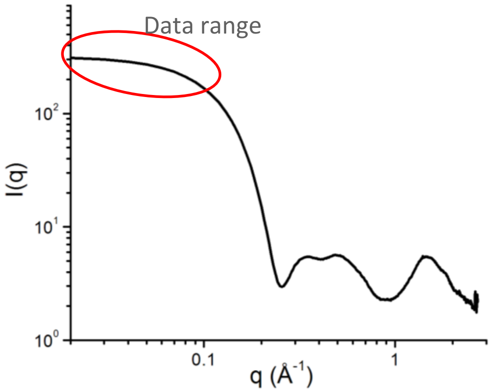
- Guinier Approximation
- Porod Law
- Invariant
- Hierarchical structural Information

Guinier Equation

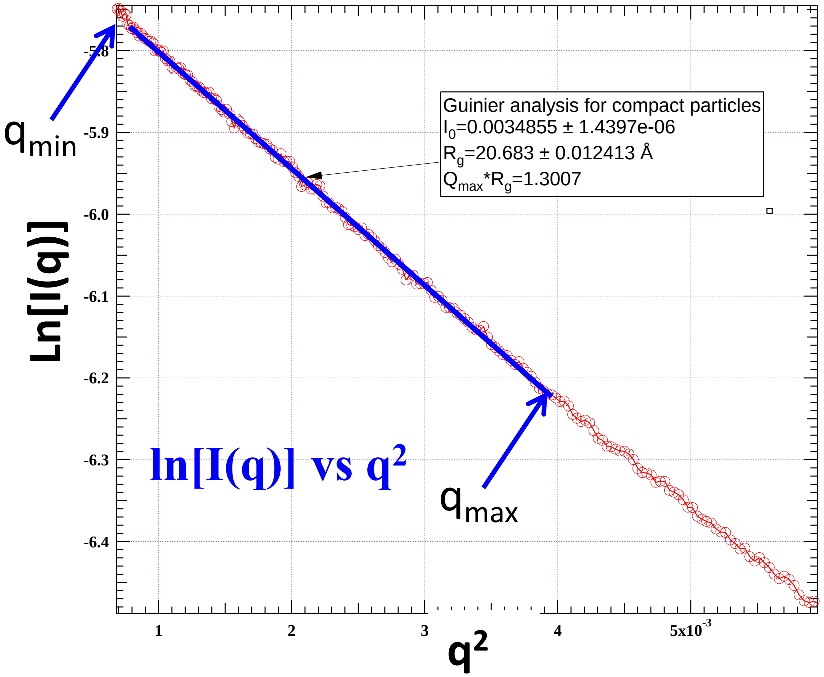
When $q \rightarrow 0$,

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

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



André Guinier (1911-2000)



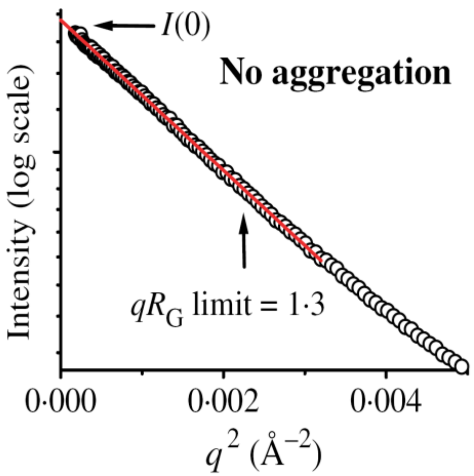
<u>To get reliable Guinier plot / R_g analysis:</u>

- 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

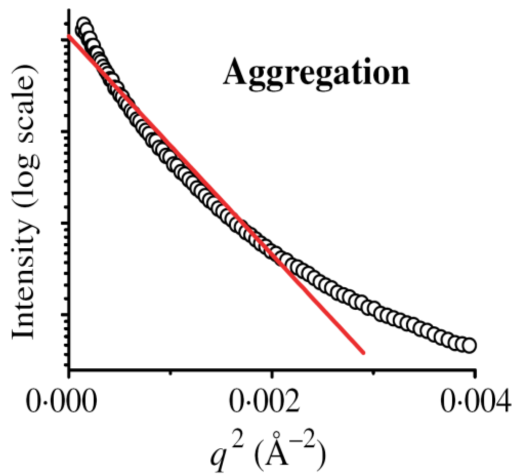
Mono-dispersed

Normal / linear



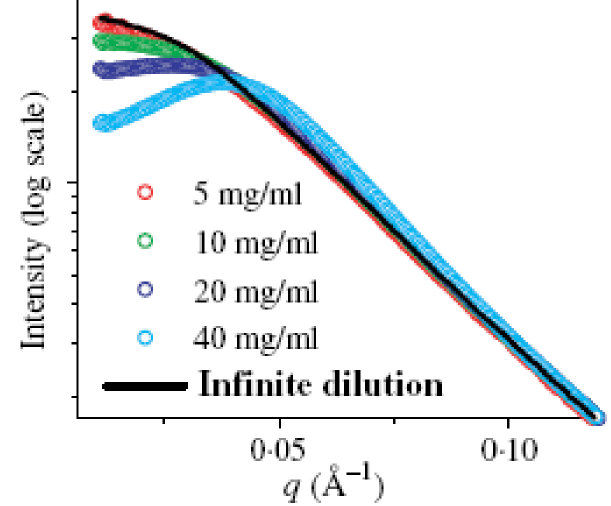
Poly-dispersed aggregates

Curve-up



Repulsion

Curve-down



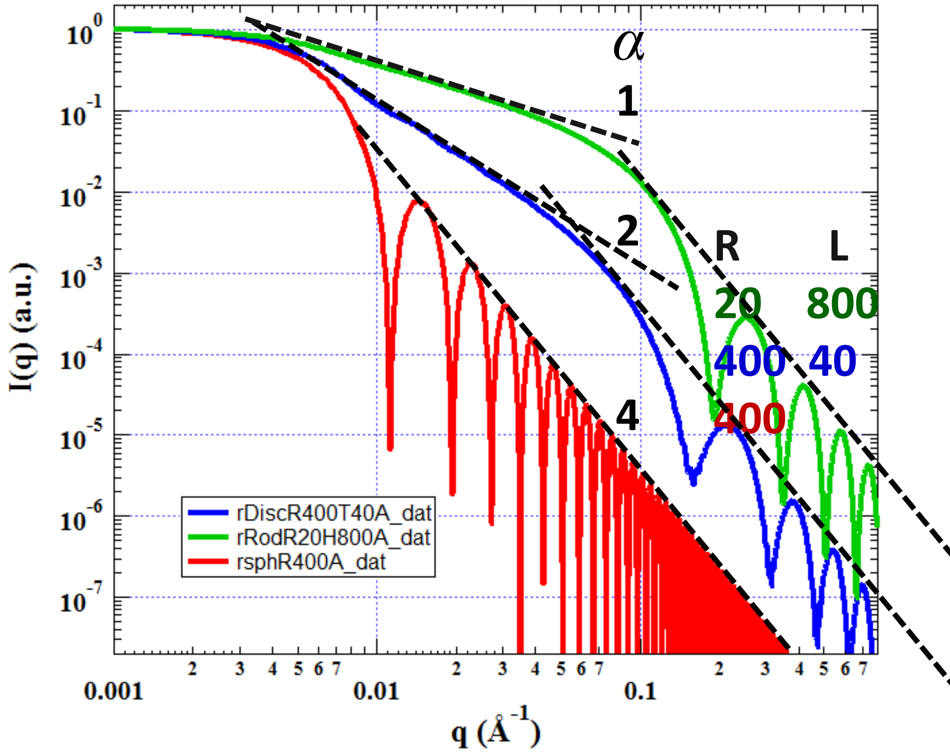
Putnam, D., et al. (2007) Quart. Rev. Biophys. 40, 191-285.

Porod Law

Generalized form:

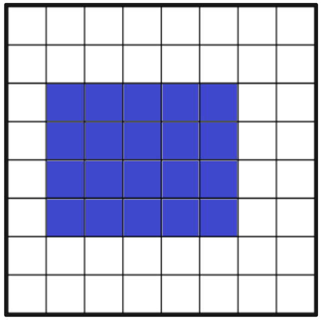
$$I(q) \propto q^{-\alpha}$$

α = 1 rod-like
2 lamellar/disc
4 sphere
fraction: fractals



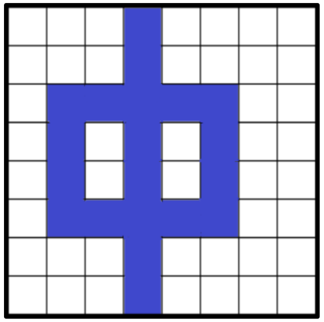
- Can provide morphology information
- May not be valid in atomic length region
- Could be misled by inaccurate background subtraction

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:

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

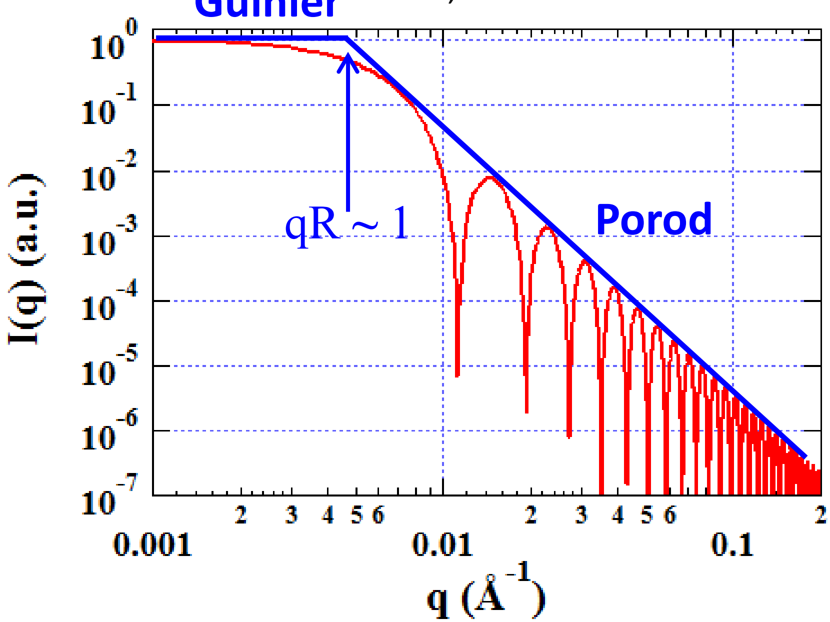
Porod volume:

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

- 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.

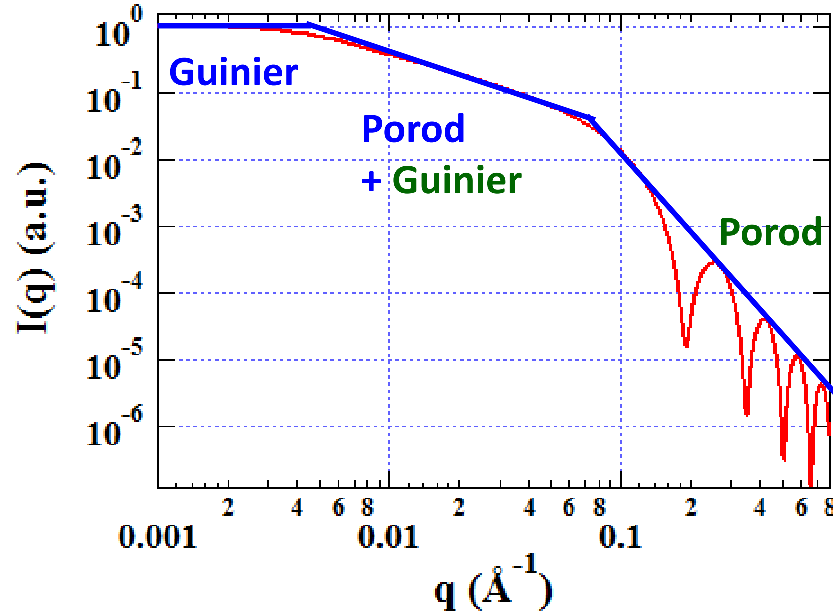
Anatomy of SAXS Profile

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



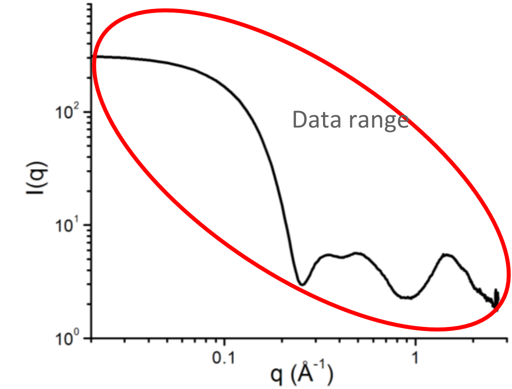
R=20 A, L = 800 A

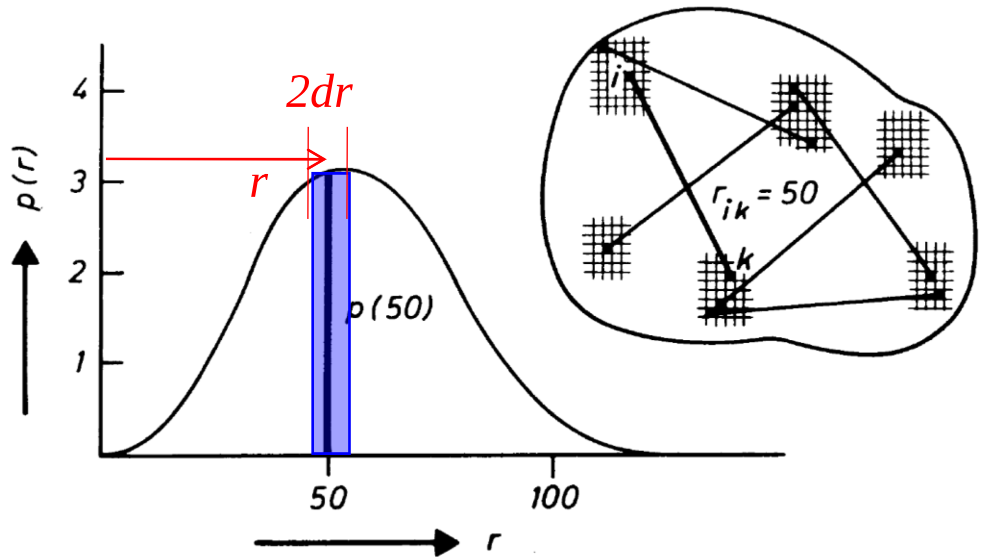
Two characteristic lengths:
L >> 2R



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)



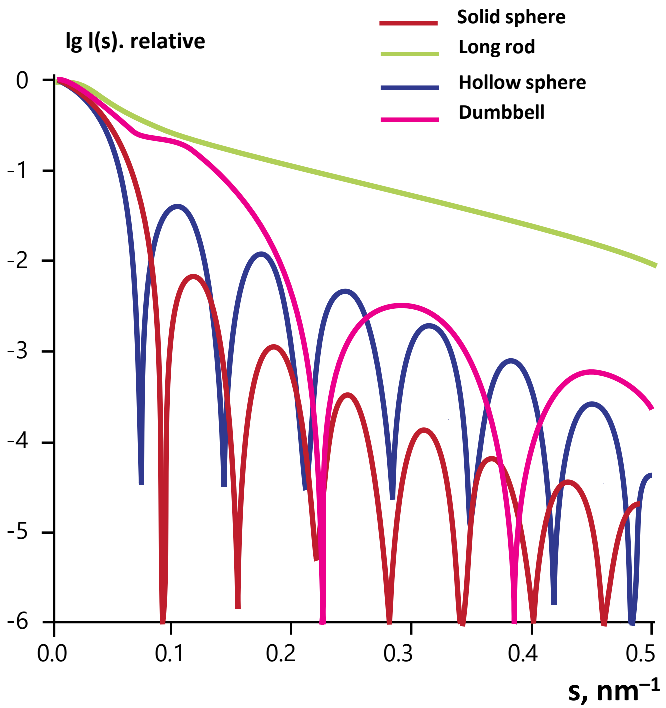


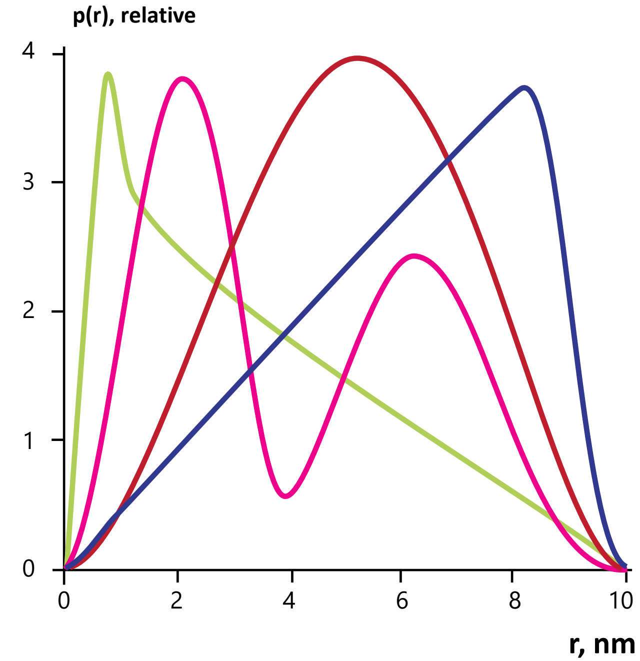
$$p(r) \sim \sum_{|\vec{r}_j - \vec{r}_k| < r+dr} 1 \times \Delta n(\vec{r}_j) \times \Delta n(\vec{r}_k) \times r^2$$

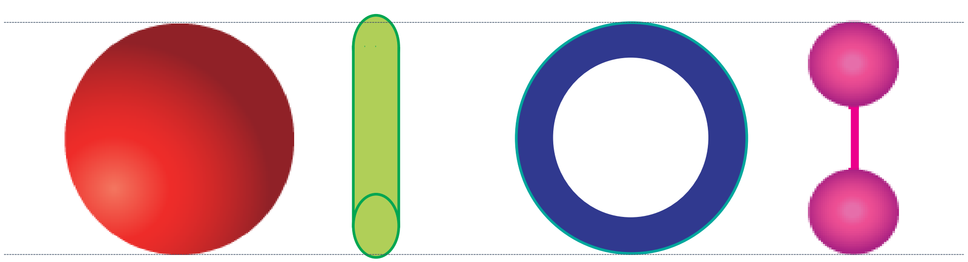
excess electrons of atom *j* over solvent

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

Combination of SAXS & PDDF for Shape Determination

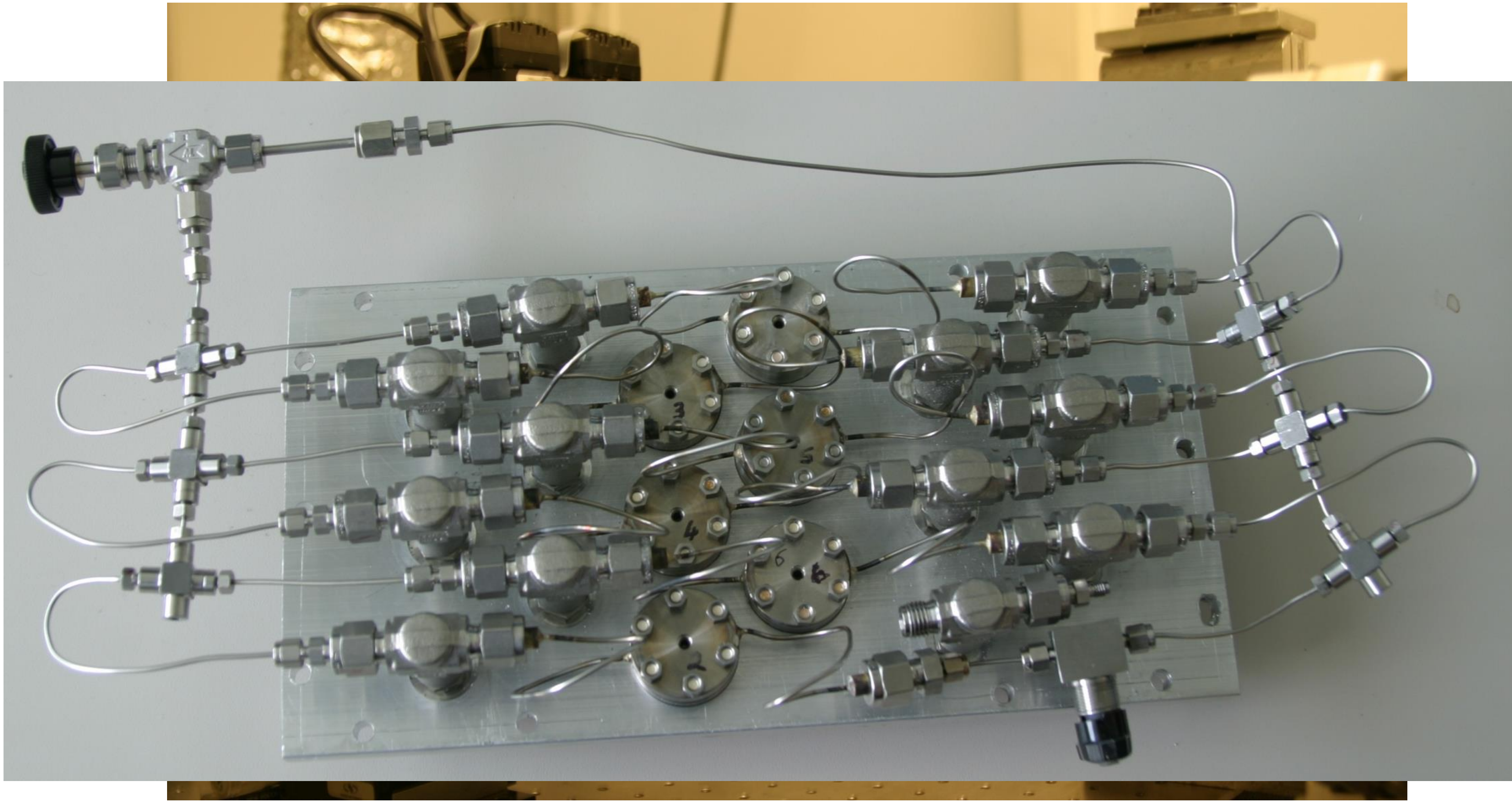




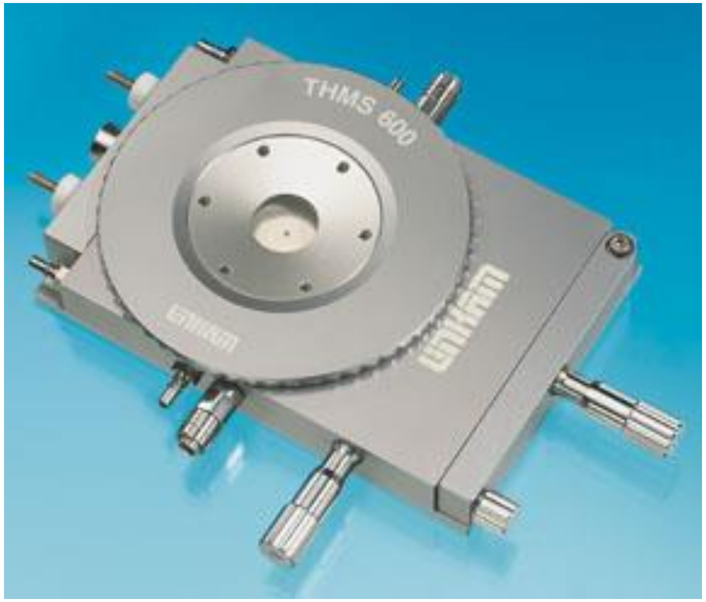


Adopted from: Svergun, D., Koch, M. (2003) Rep. Prog. Phys. 66, 1735-1782.

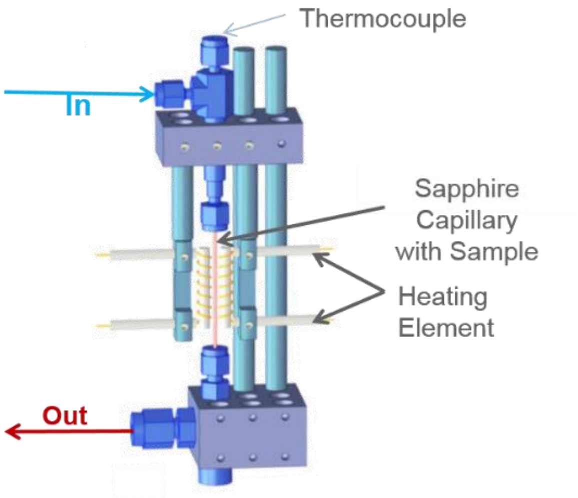
SAXS Instruments at 12ID



Setup



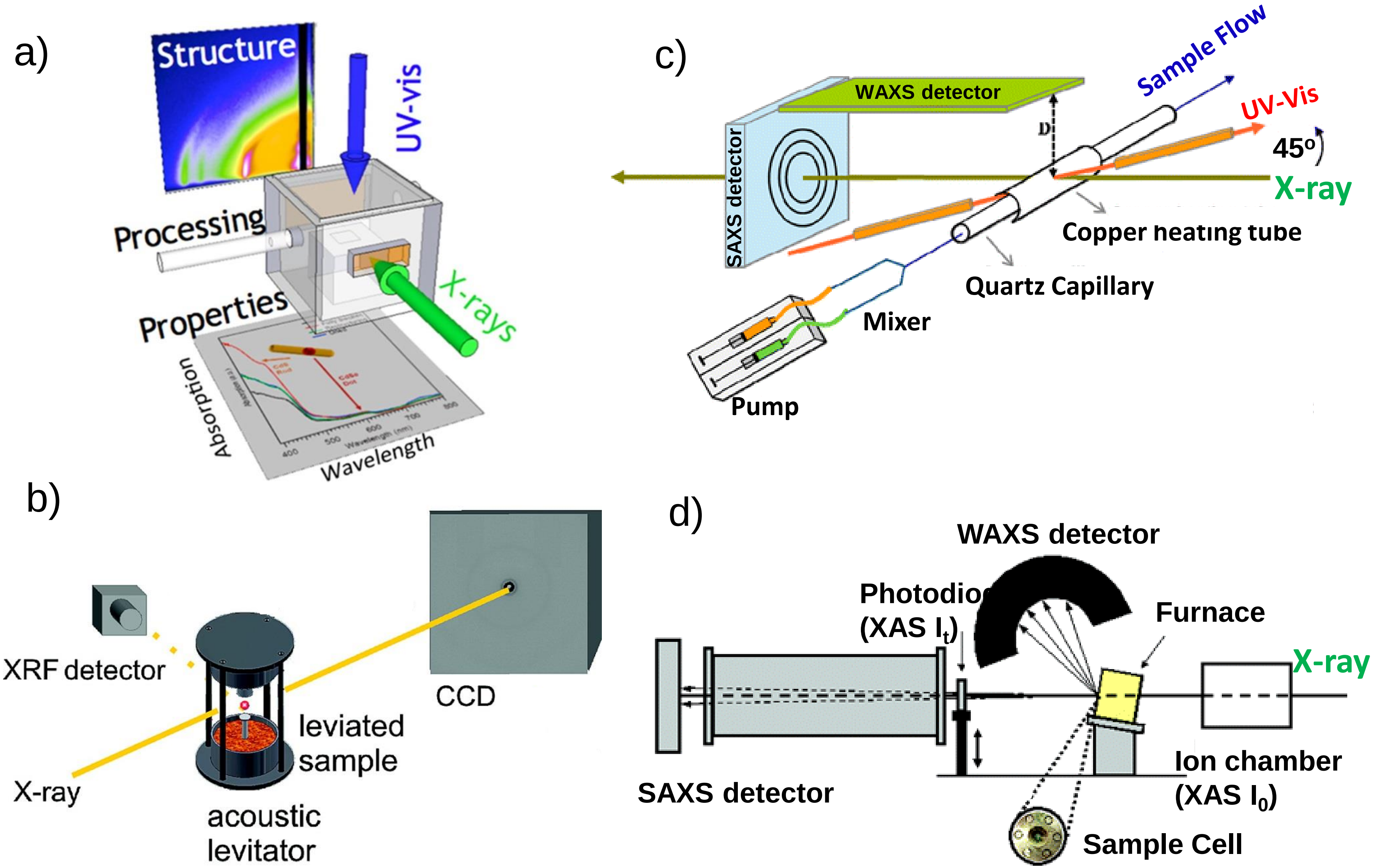
Heating up to 1500 ^{o}C



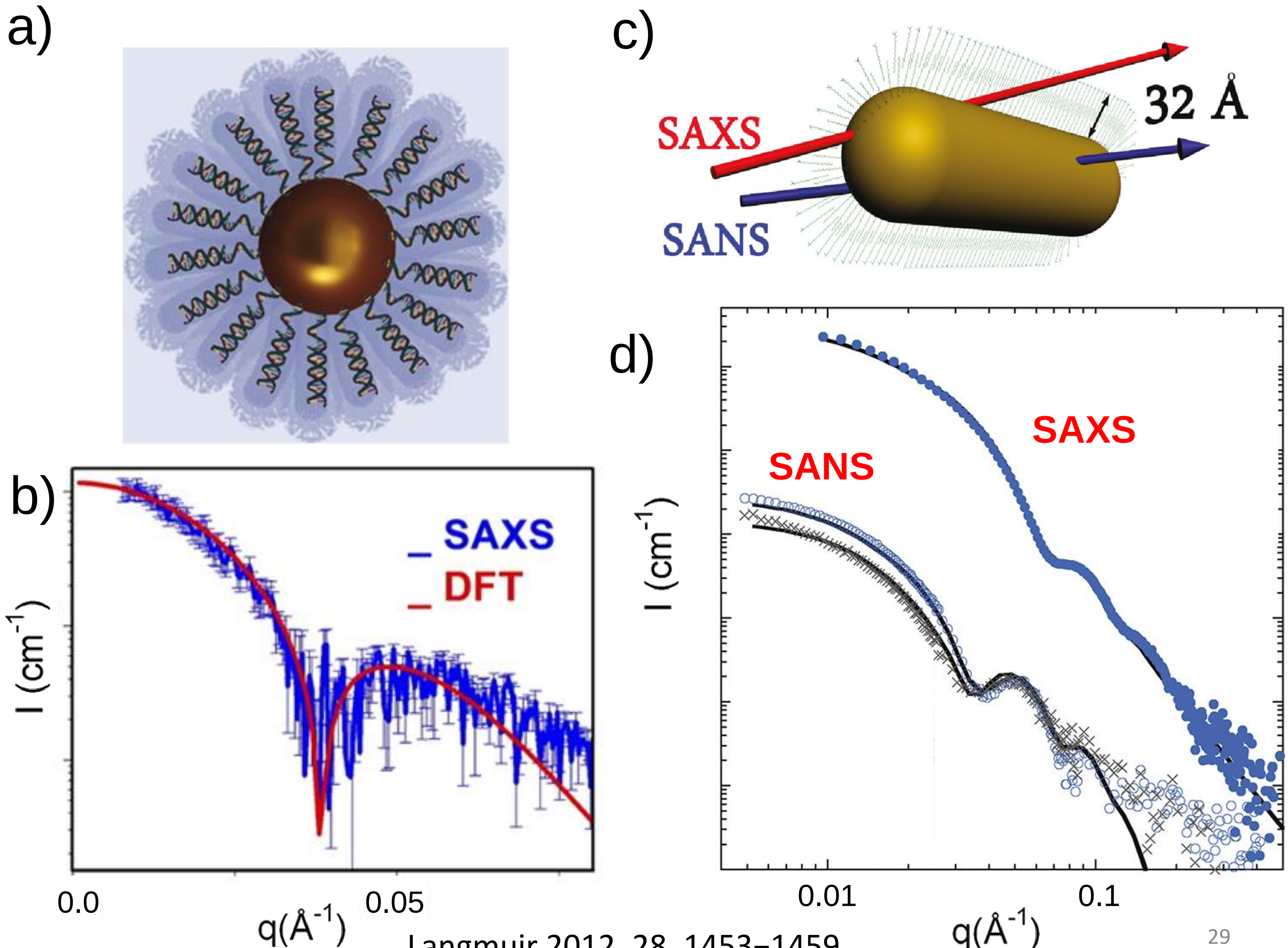
Heated capillary flow cell

GISAXS cell for high temperature and pressure reactions

Combined SAXS with other technique

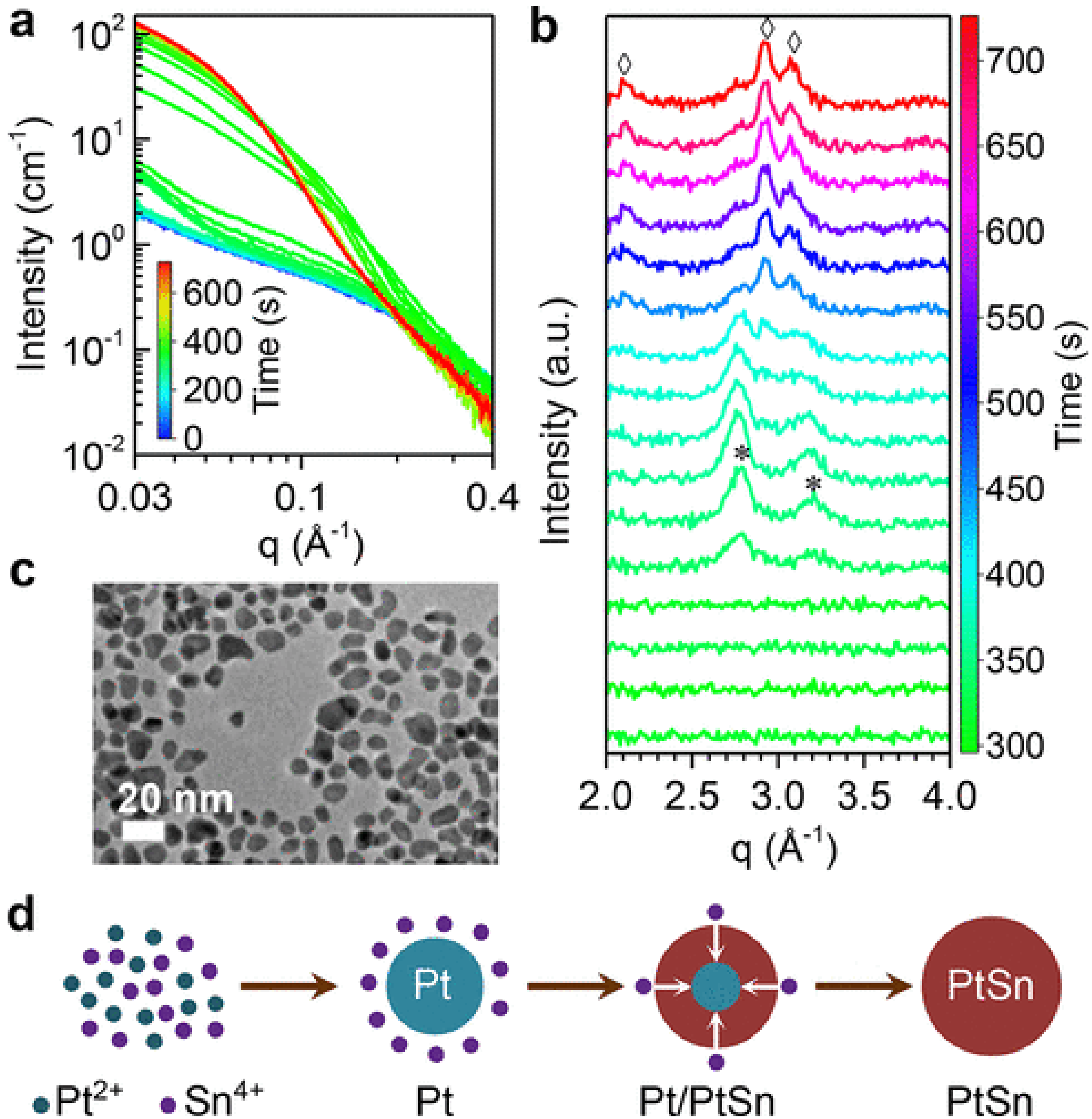


SAXS and SANS



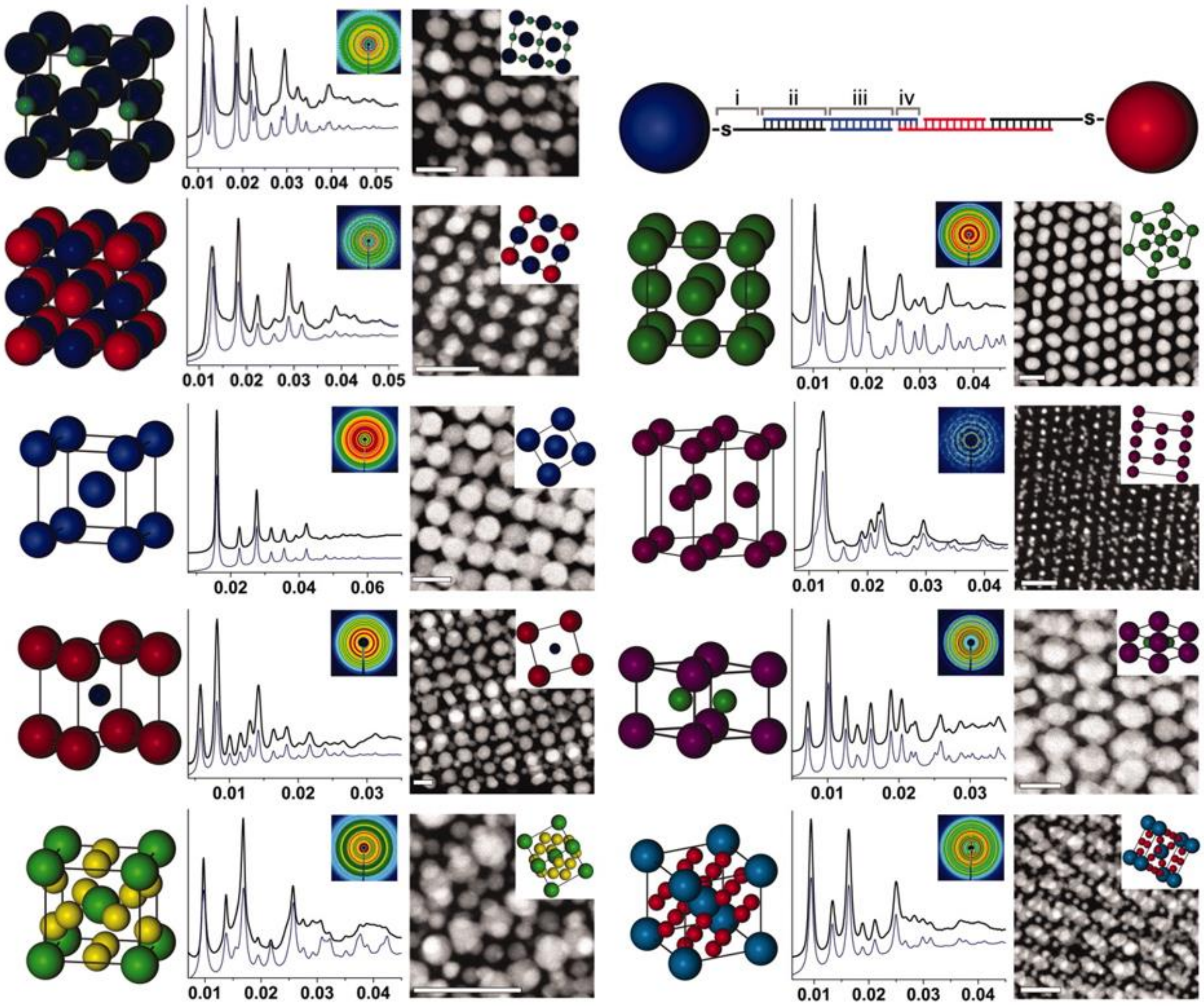
Langmuir 2012, 28, 1453−1459.

In situ SAXS/WAXS



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

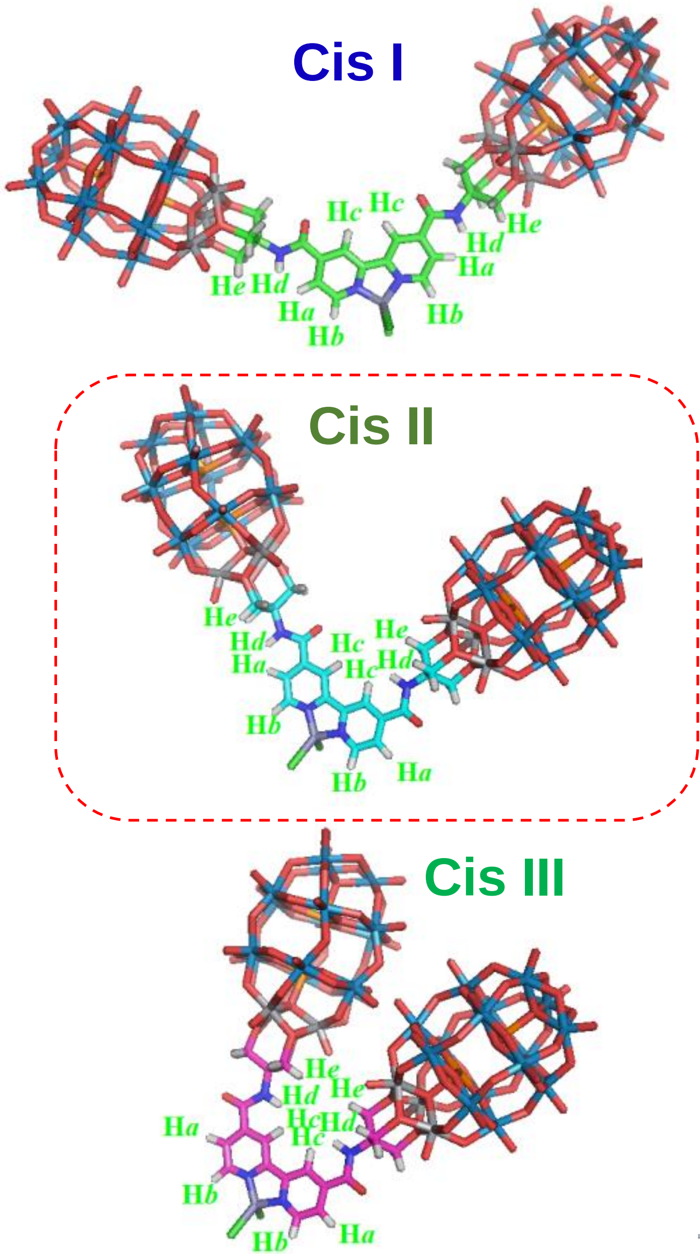
SAXS of Au-DNA Superlattice

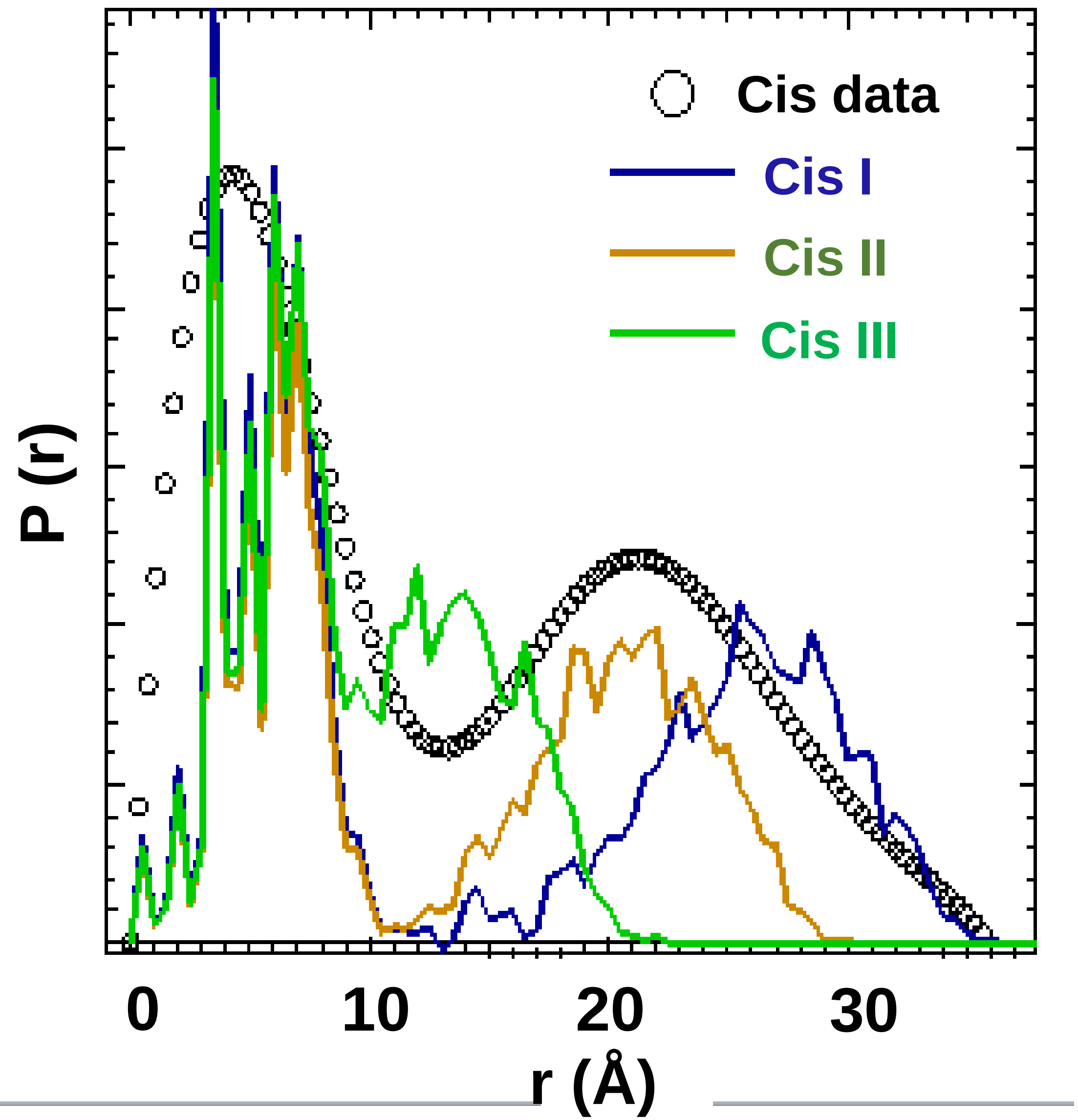


Science **2011**,334, 204– 208

P(r) of dimmer structure

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

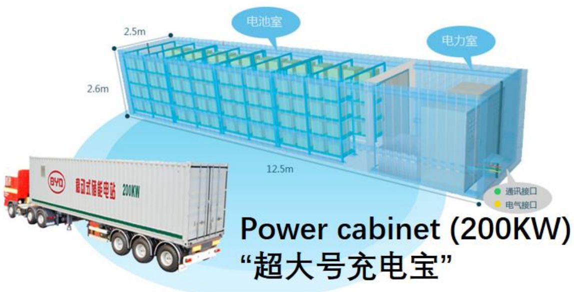




Lithium Ion Battery

Lithium ion batteries are powering the world.

Consumer electronics → **New applications**



Northern Illinois University

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

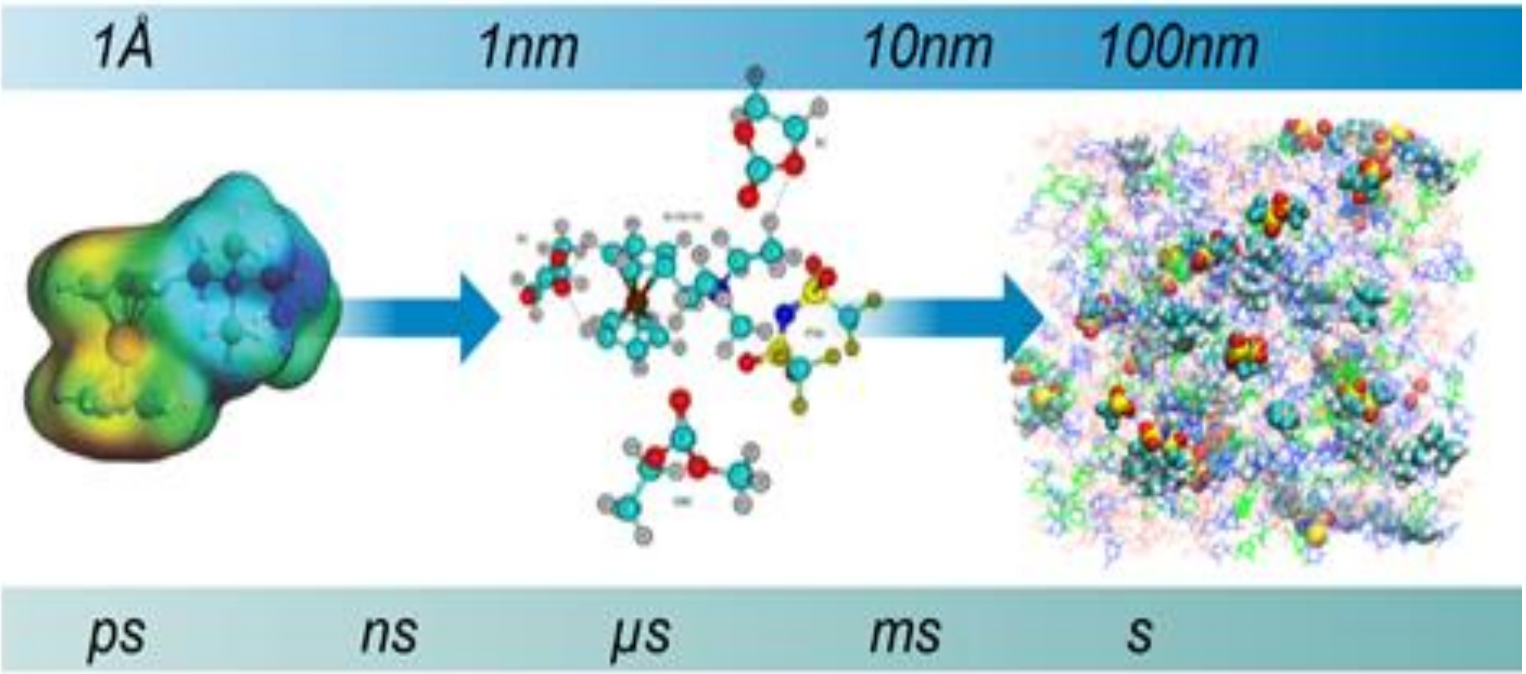
Ill. Niklas Elmedhed. © Nobel Media.

Akira Yoshino

Prize share: 1/3

Northern Illinois University

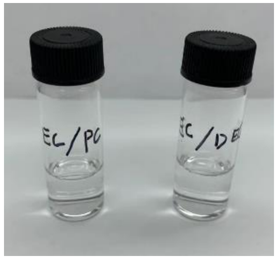
Electrolytes



How to characterize the electrolyte in the solution?

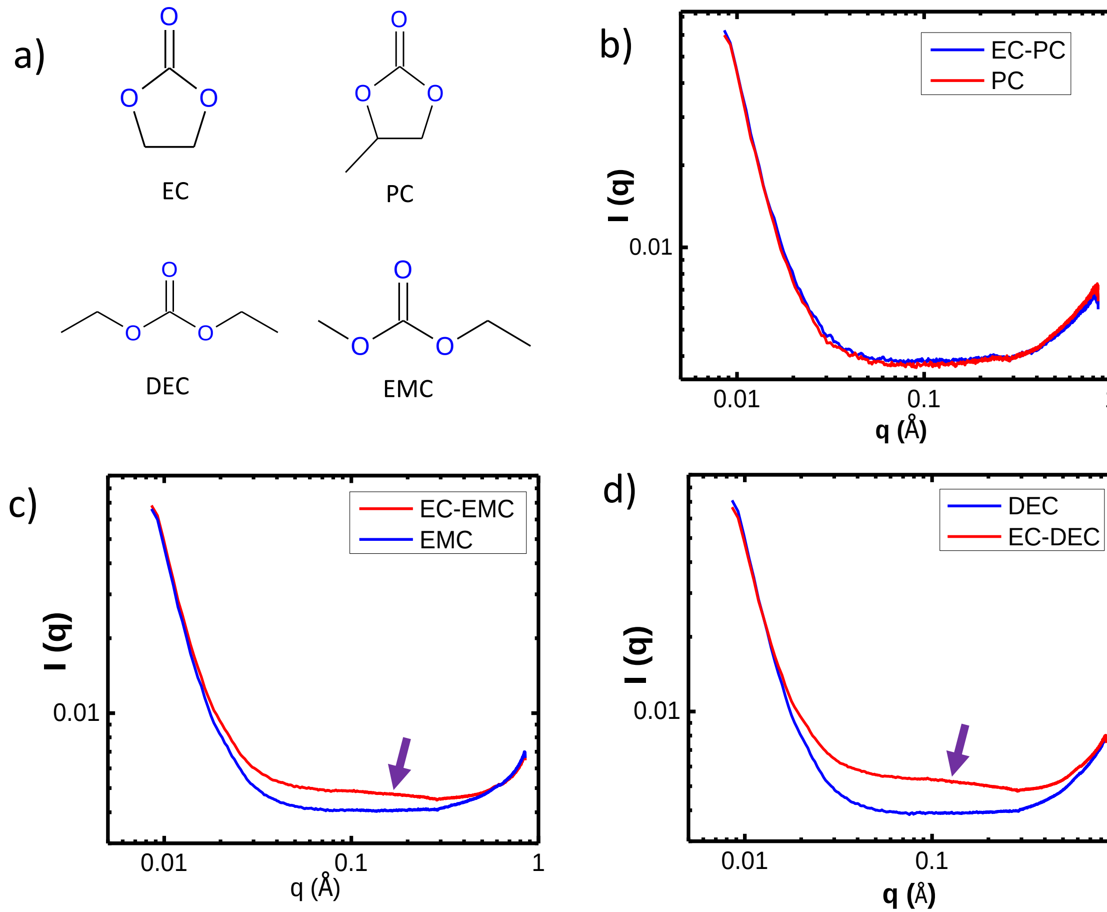
K. Qian, R. Winans, **Tao Li*.** *Advanced Energy Materials,* **2021**, 2002821.
K. Qian, Y. Liu, D. Gosztola, H. Nguyen, **Tao Li***. *Energy Storage Materials,* **2021**, *41,* 222-229.

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

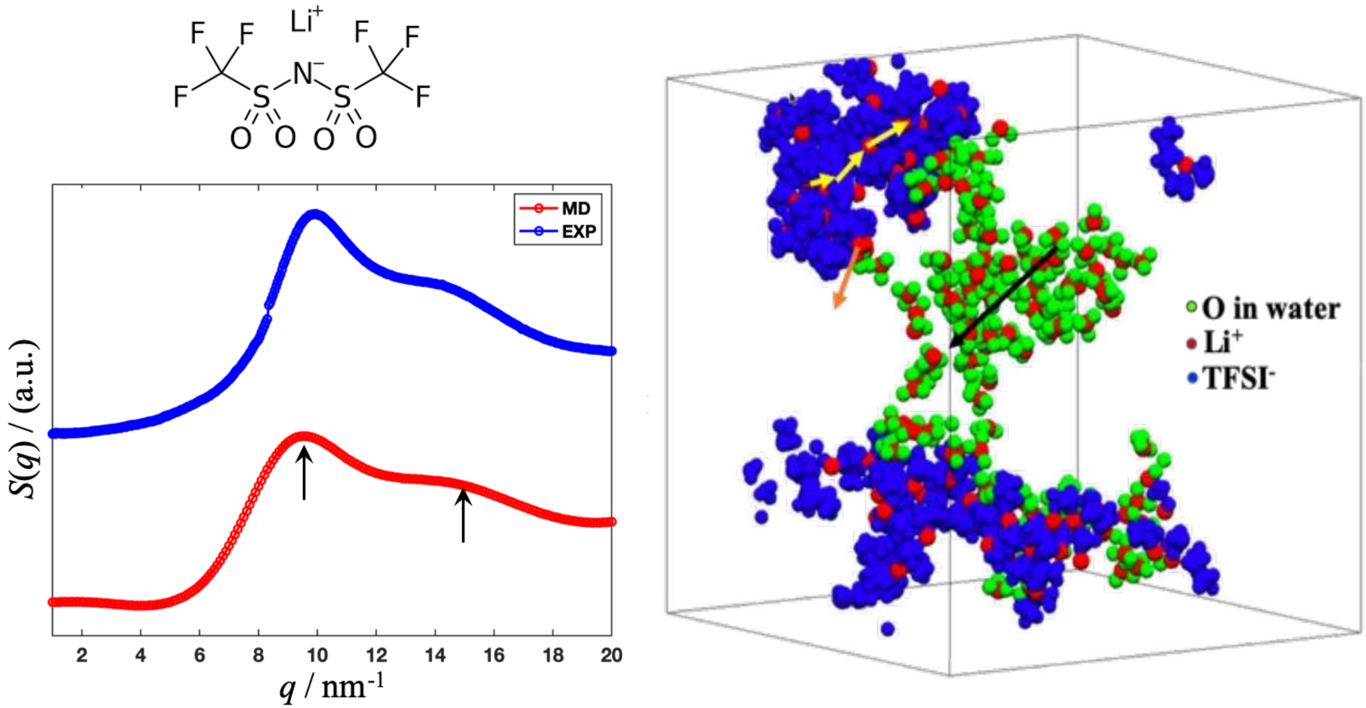
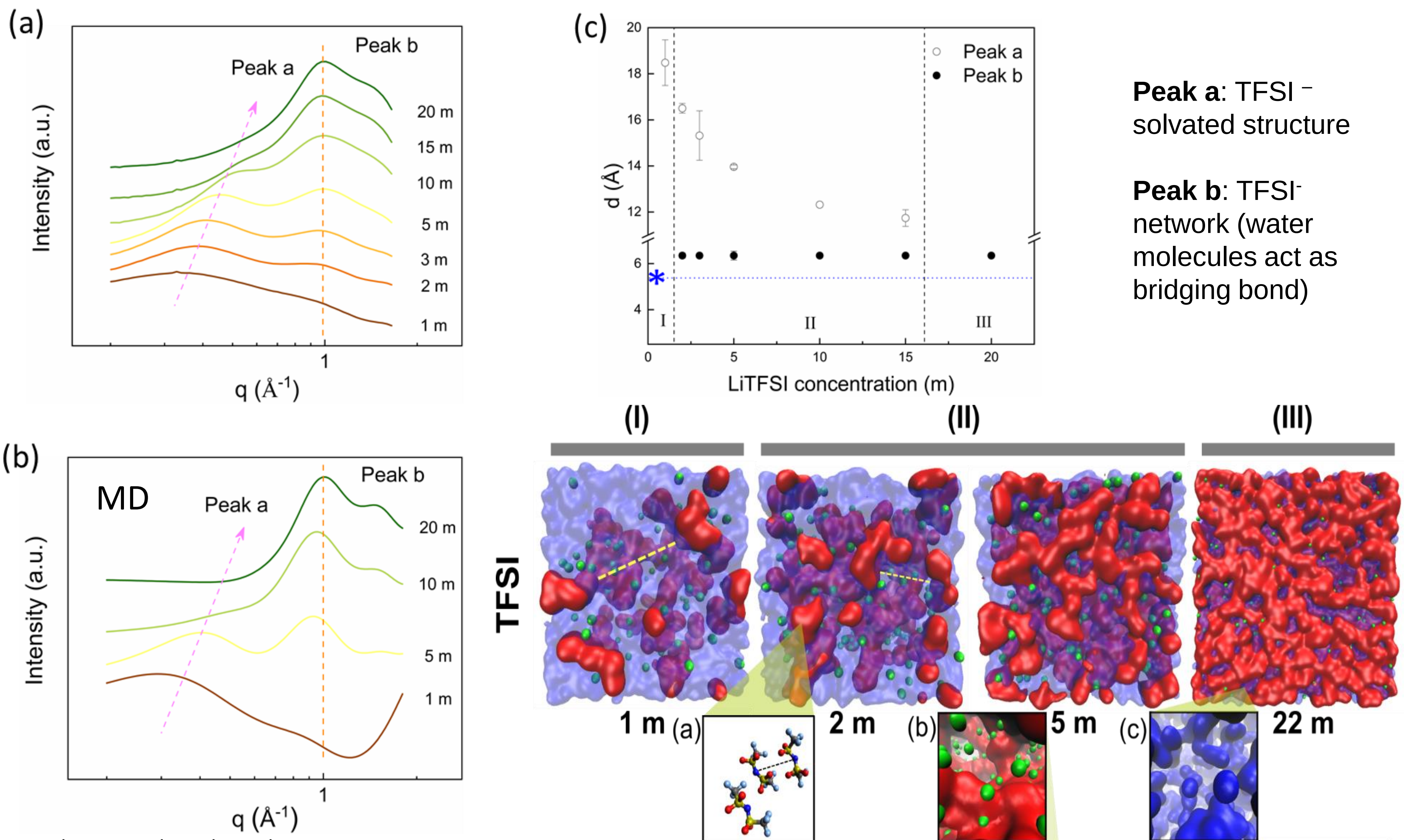


Figure. **Experimental** **and** **calculated** **SAXS data for 20 m LiTFSI in water.**

(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

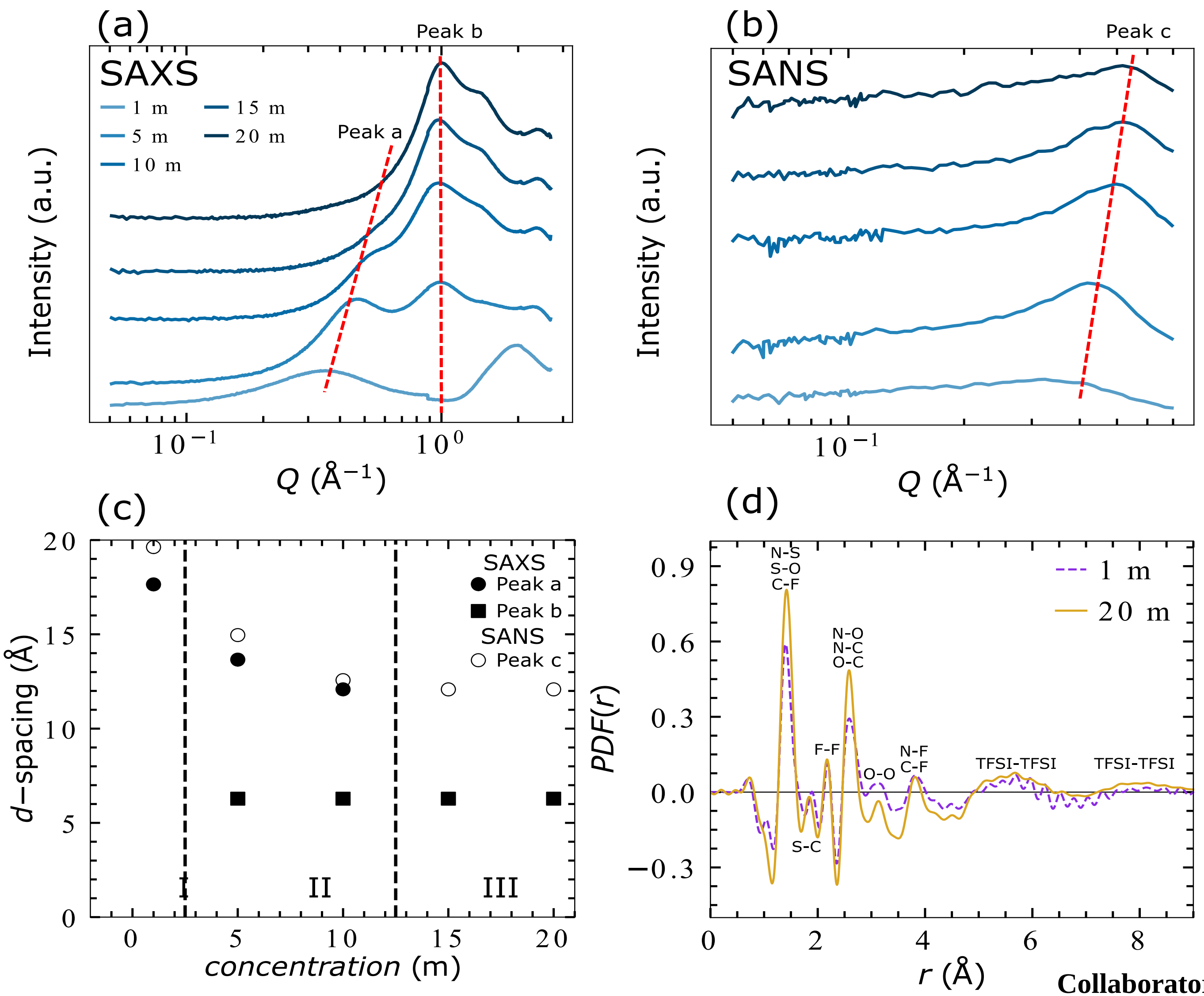
Peak b: TFSI^{-} network (water molecules act as bridging bond)

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 and SANS Study of LiTFSI Solvation Structure



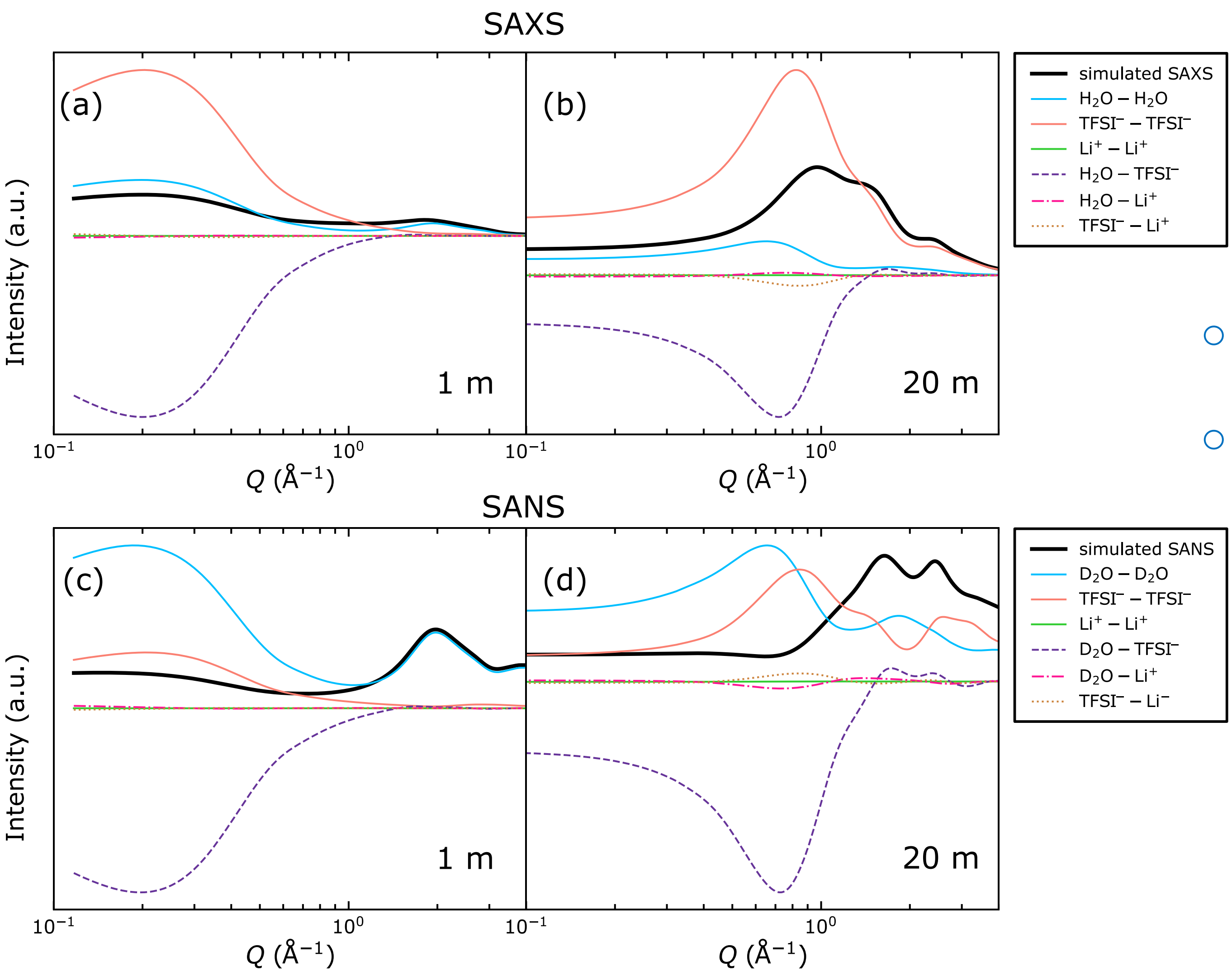
Peak a,c: TFSI $^{-}$ solvated structure

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

Collaborator: Yang Zhang (U of Michigan)

X. Liu,# S.-C.Lee,# S. Seifert, L. He, R. E.Winans, C. Do, Y Z,* **Tao Li.*** *Chemistry of Materials,* **2023**, 35,2, 2088-2094.

SAXS and SANS: Decomposition

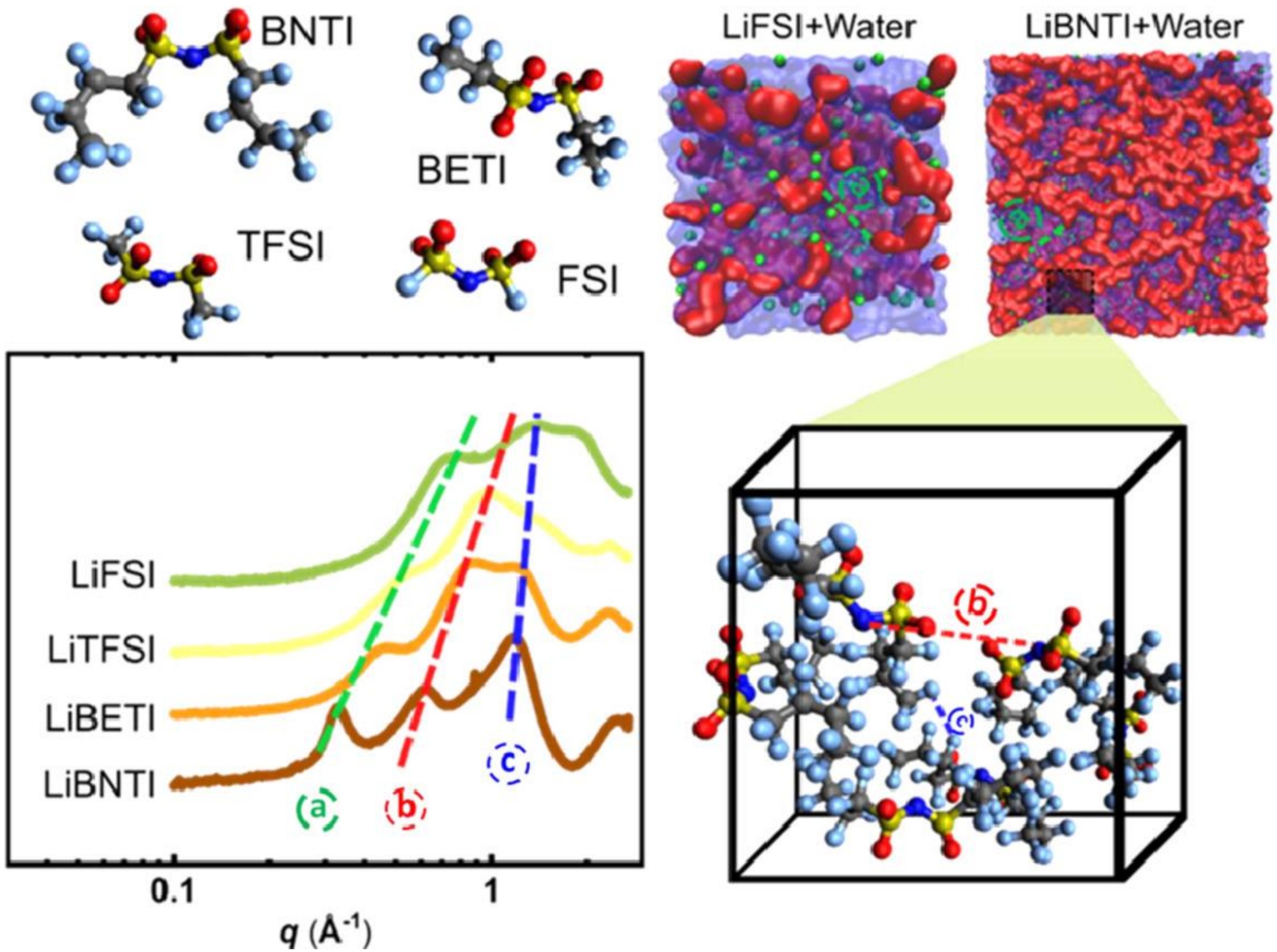


- Feature in SAXS is mainly due to TFSI-TFSI
- Feature in SANS is mainly due to D_2O-D_2O

Collaborator: Yang Zhang (U of Michigan)

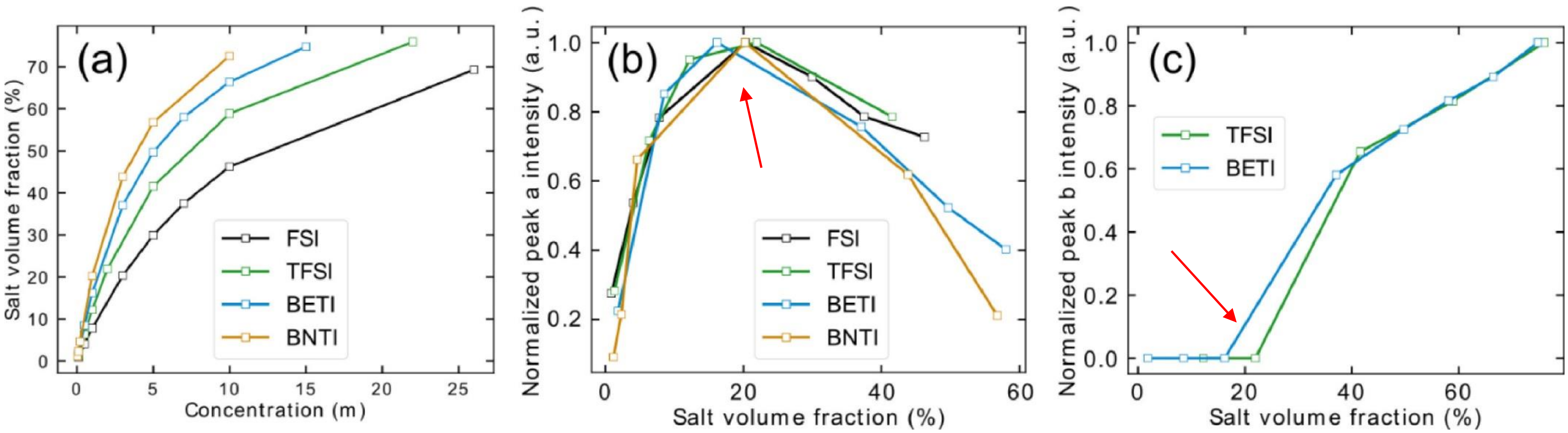
X. Liu,# S.-C.Lee,# S. Seifert, L. He, R. E.Winans, C. Do, Y Z,* **Tao Li.*** *Chemistry of Materials*, **2023**, 35,2, 2088-2094.

SAXS/WAXS Study of Different Anions



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

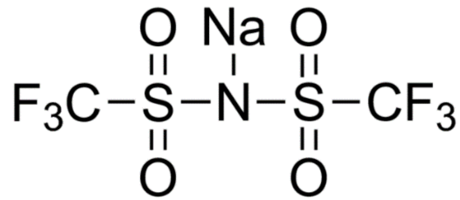
SAXS/WAXS Study of Different Anions

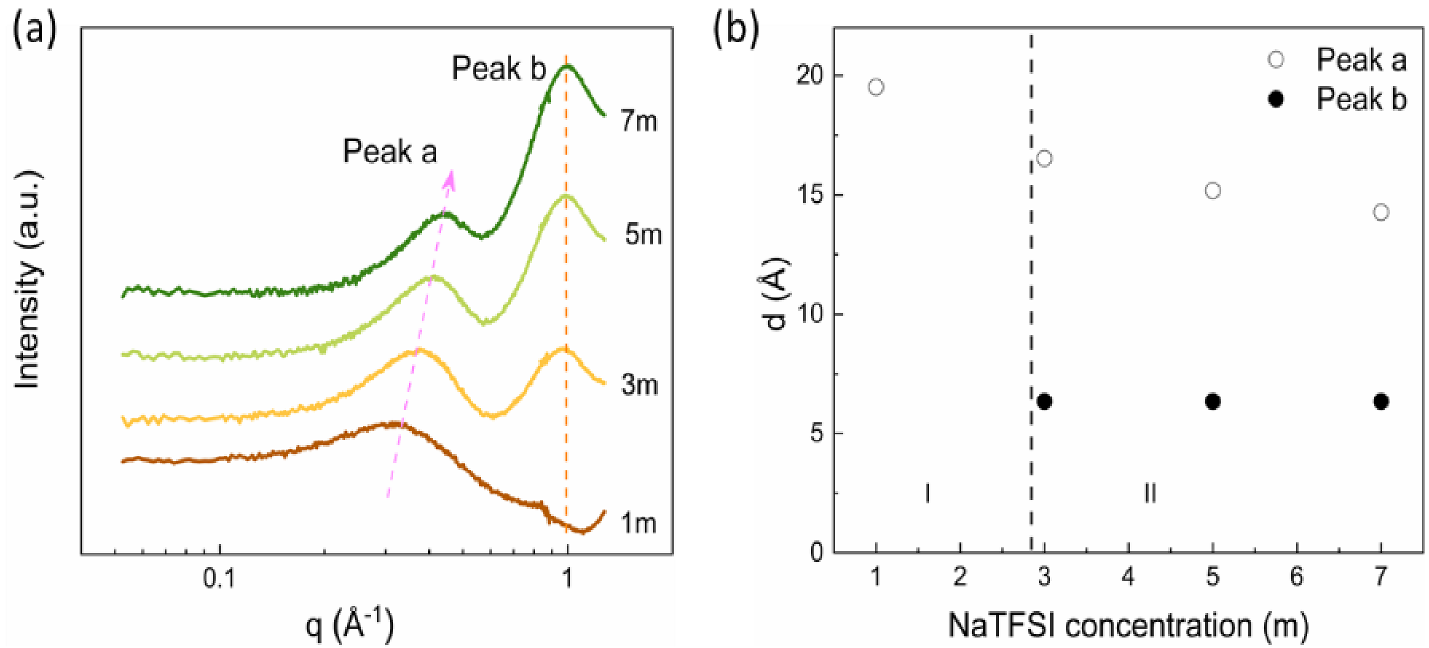


MD simulation results reveal that the formation of anion networks starts at around 20% of the salt volume fraction for all imide-based lithium salts aqueous solutions.

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

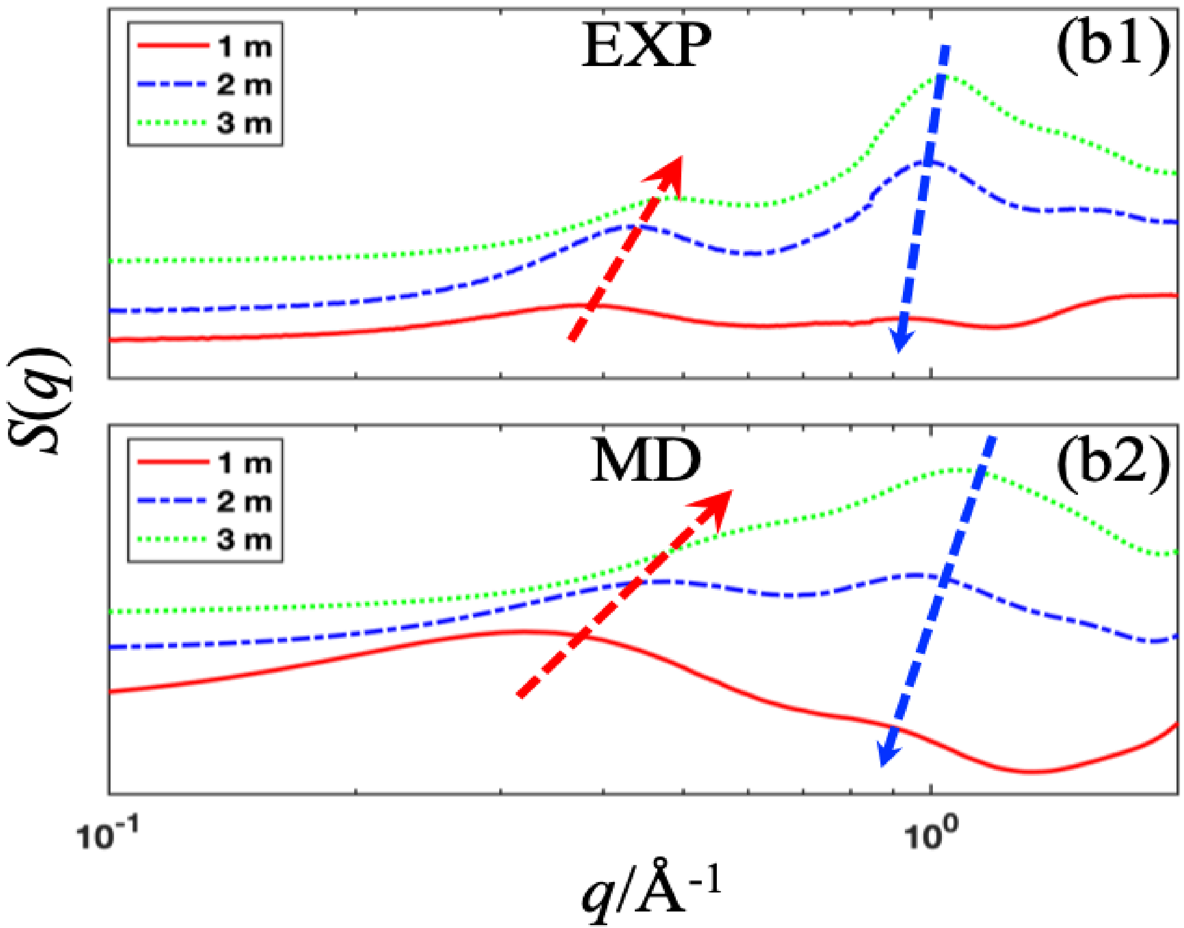
SAXS/WAXS Study of NaTFSI in Water

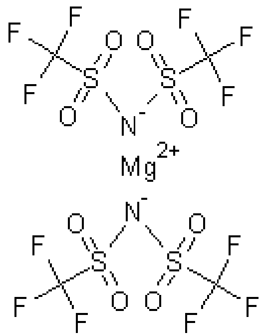




X. Liu, Z. Yu, E. Sarnello, K. Qian, S. Seifert, R. E. Winans, L. Cheng*, **Tao Li**.* *Energy Materials Advances*, **2021**, 7368420.

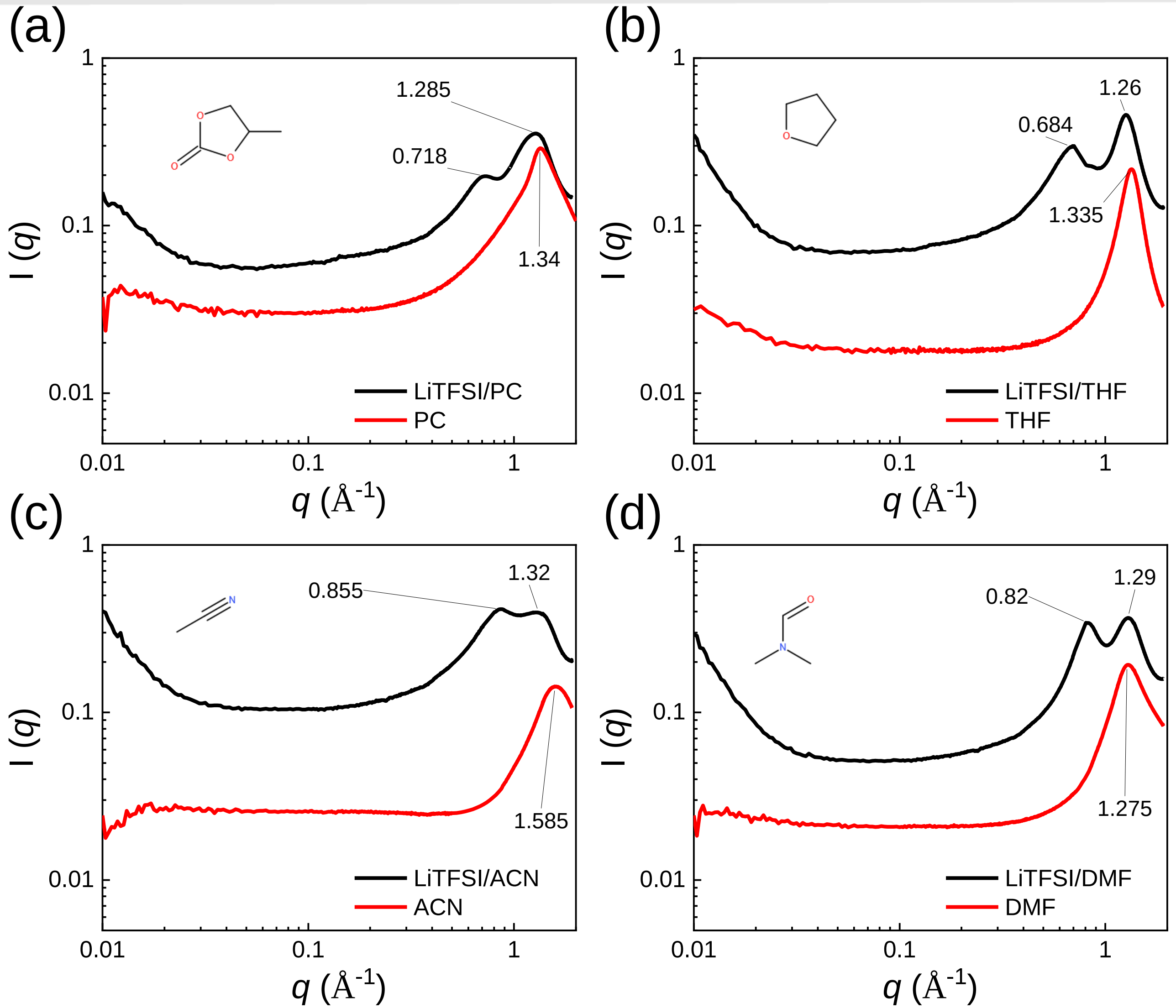
SAXS/WAXS Study of $Mg(TFSI)_2$ in Water





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.

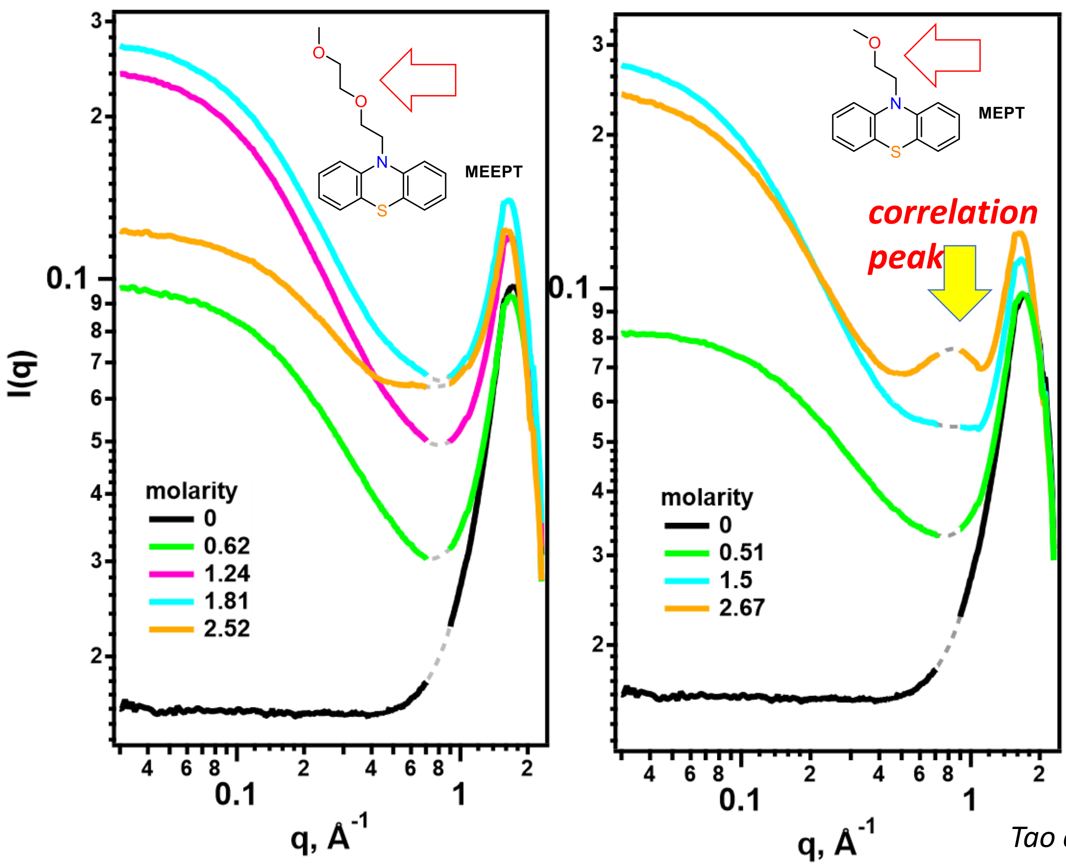
SAXS of LITFSI in Different Solvents



K. Qian, 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**

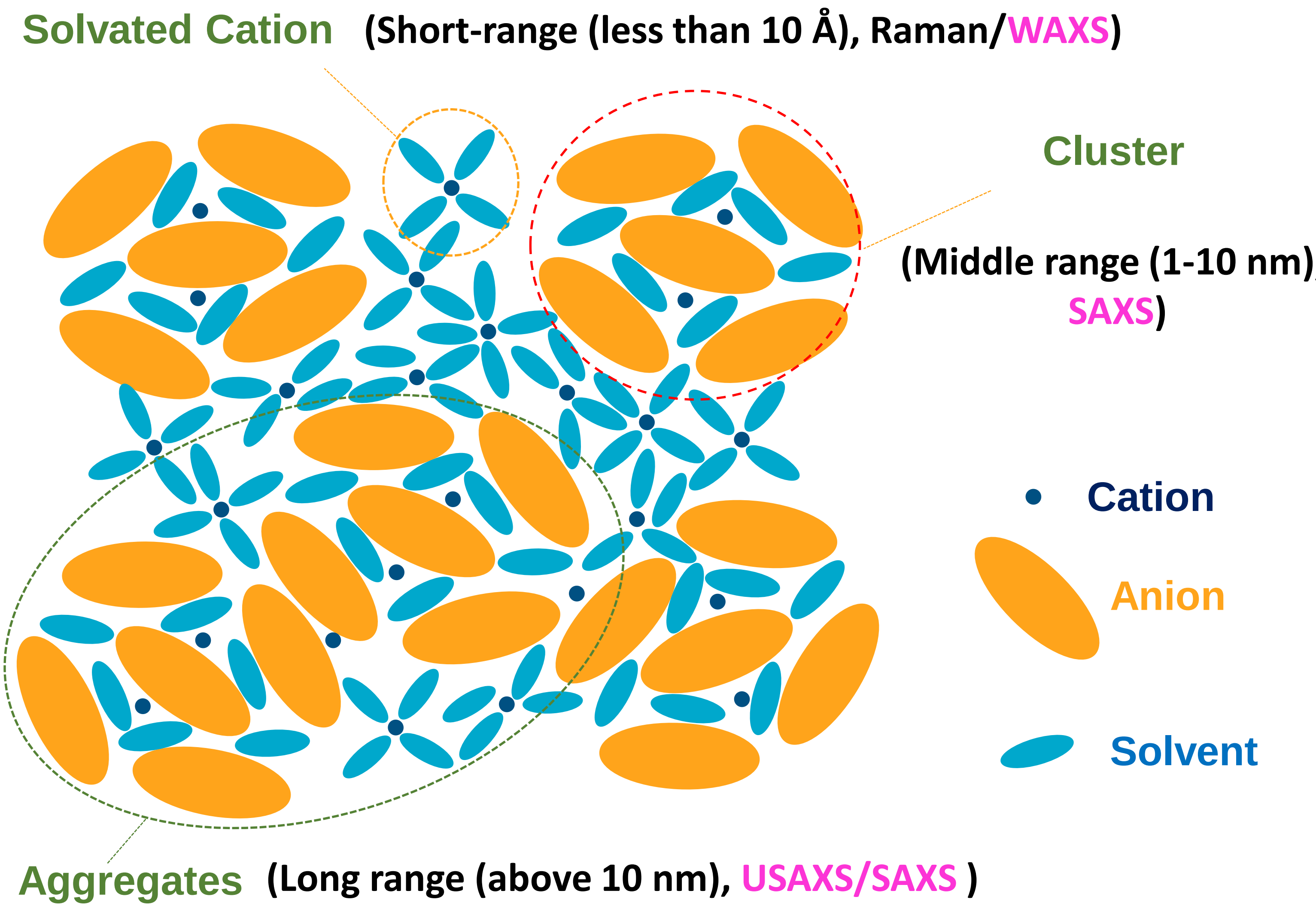
Tao and Erik as co-author

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.

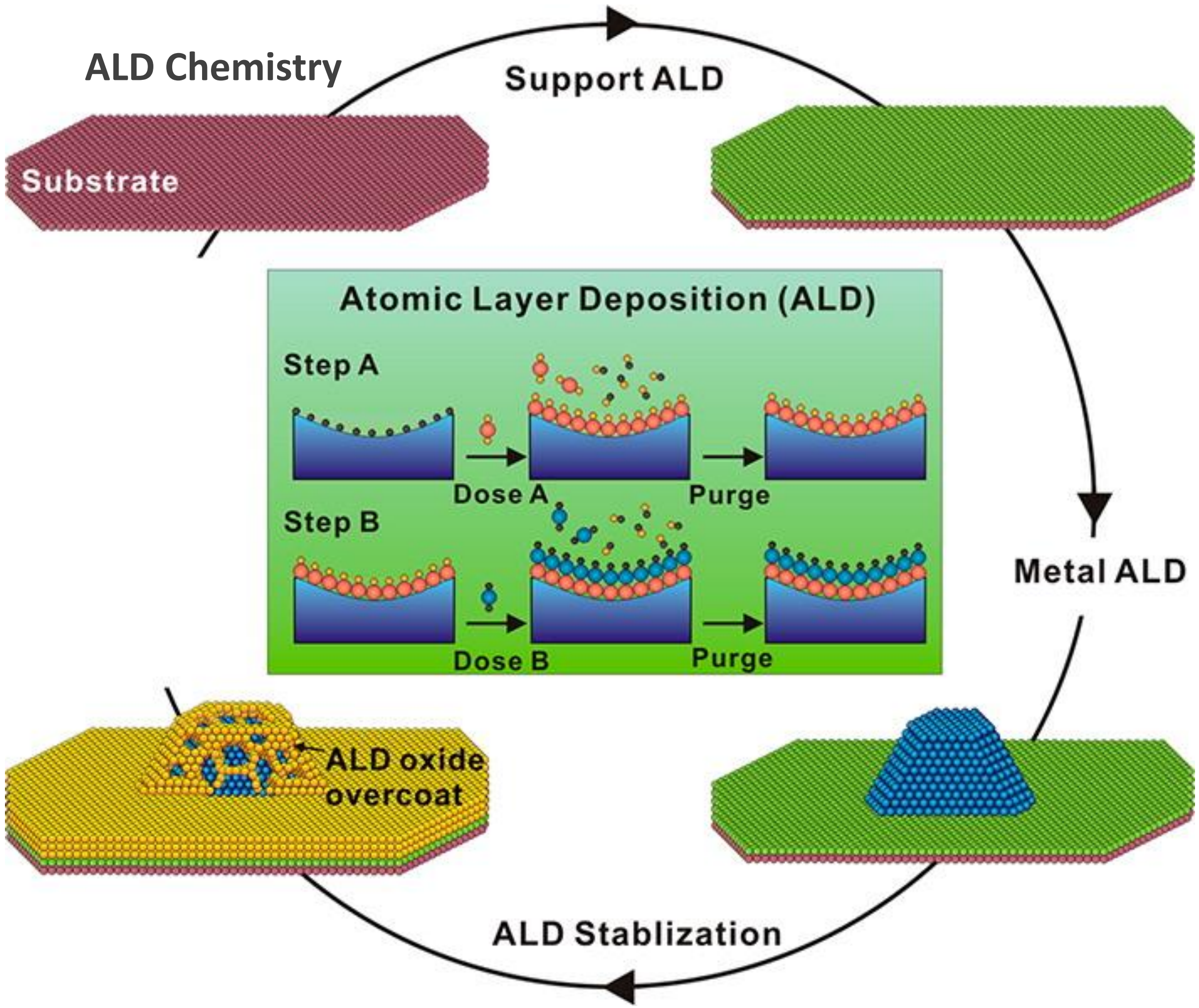
Electrolytes

Northern Illinois University

What we have learned about solvation structures of electrolytes with X-ray scattering

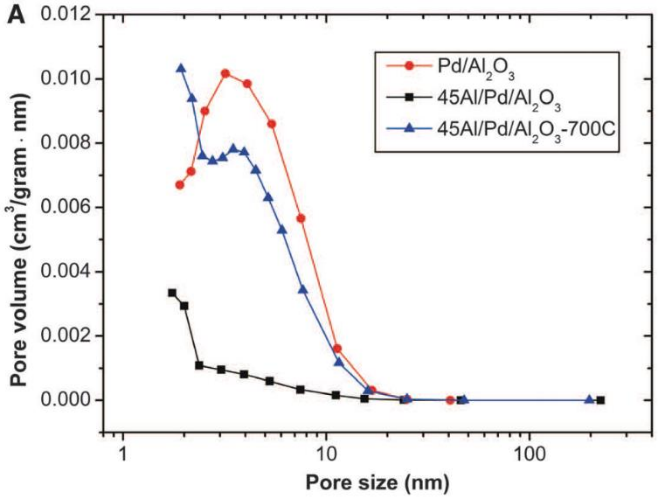


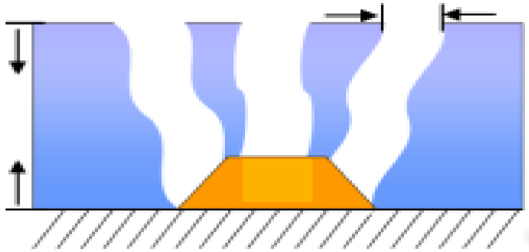
Supported Metal Catalysts by Atomic Layer Deposition

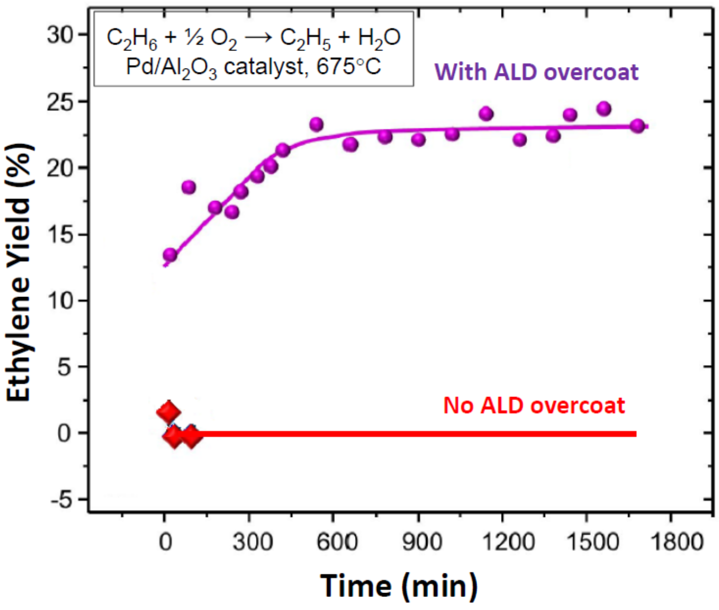


Lu, Junling; Elam, Jeffrey W.; Stair, Peter C. Accounts of Chemical Research (2013), 46(8), 1806-1815

ALD Overcoated Catalyst with Enhanced Stability





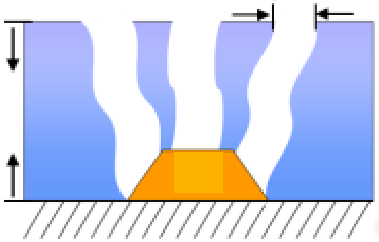


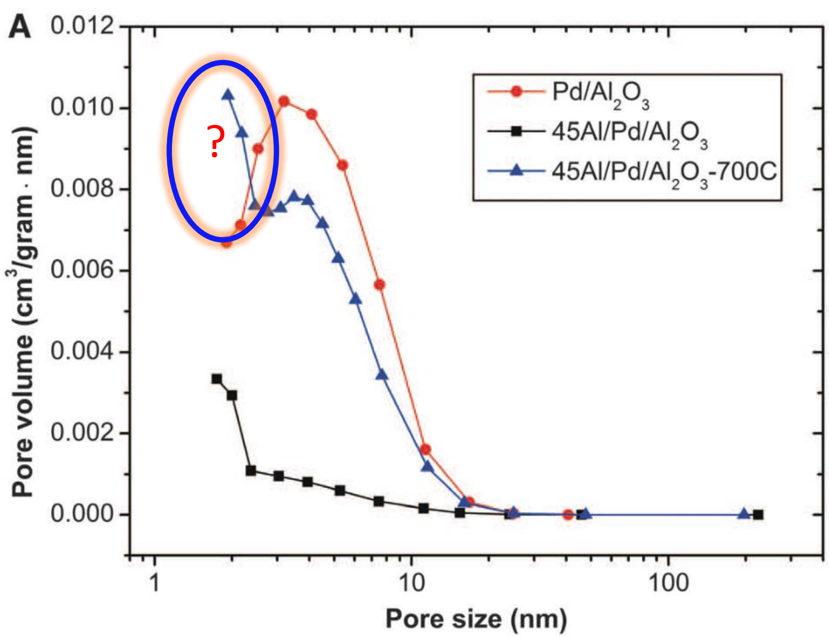
- **Dramatically improved yield and lifetime with ALD overcoat**
- **Without overcoat, coke formed in <30 min, zero yield**
- **With overcoat, virtually no coking, >20% yield**
- **Lifetime enhancement: >100x**

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

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

45c Al_2O_3 Over-coating on Pd/Al_2O_3 Catalyst

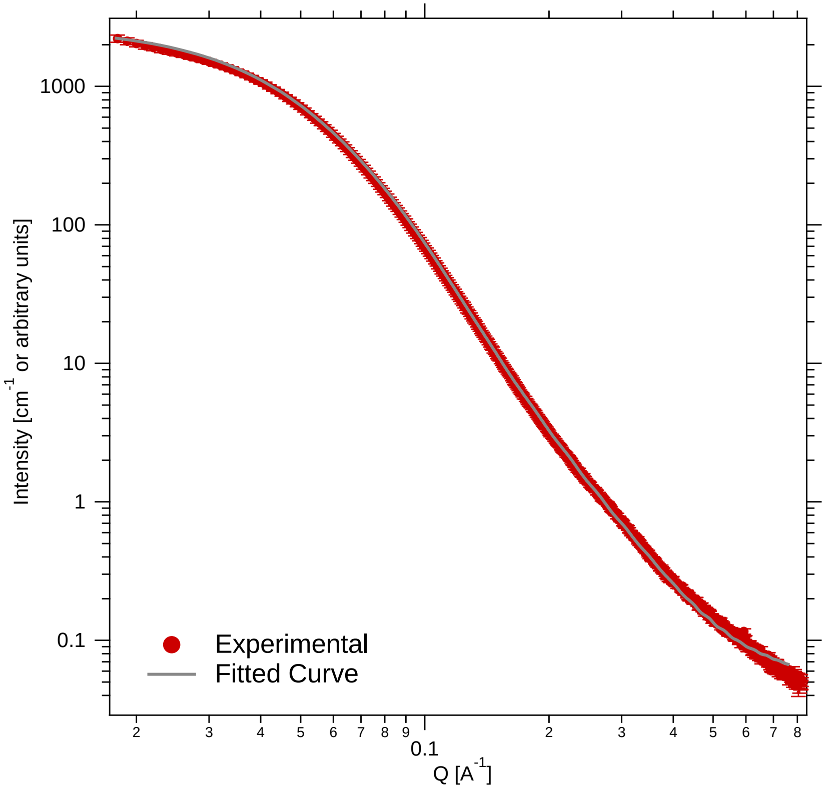


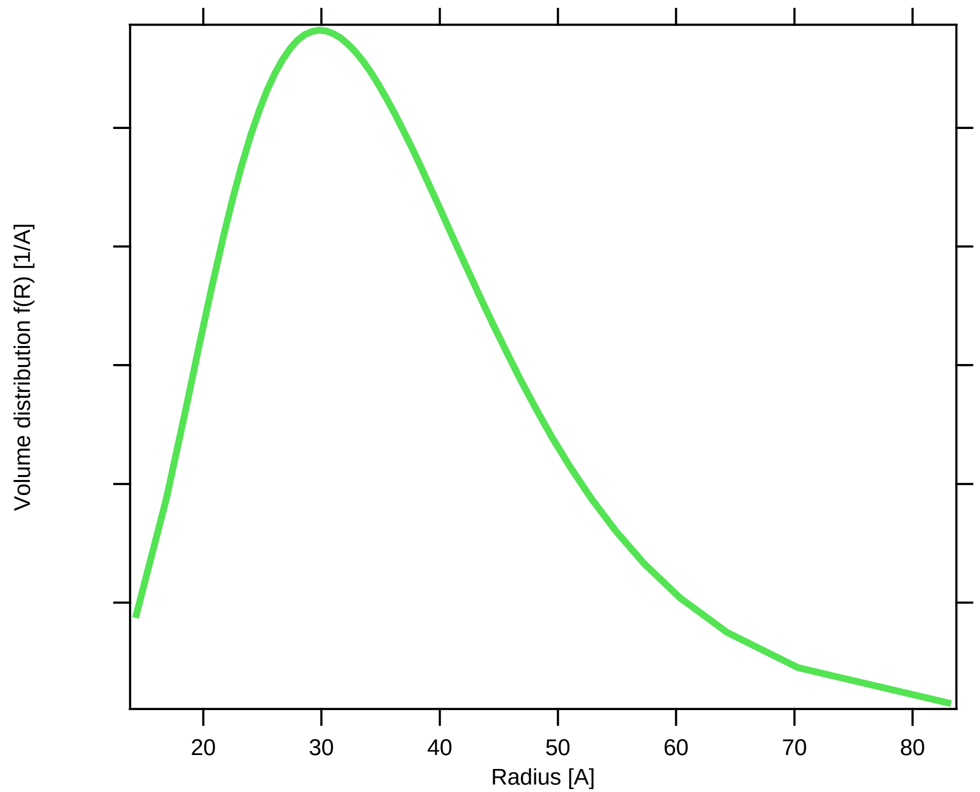


Collaborated with Peter Stair, Northwestern University

Science, 2012, 9, 1205–1208

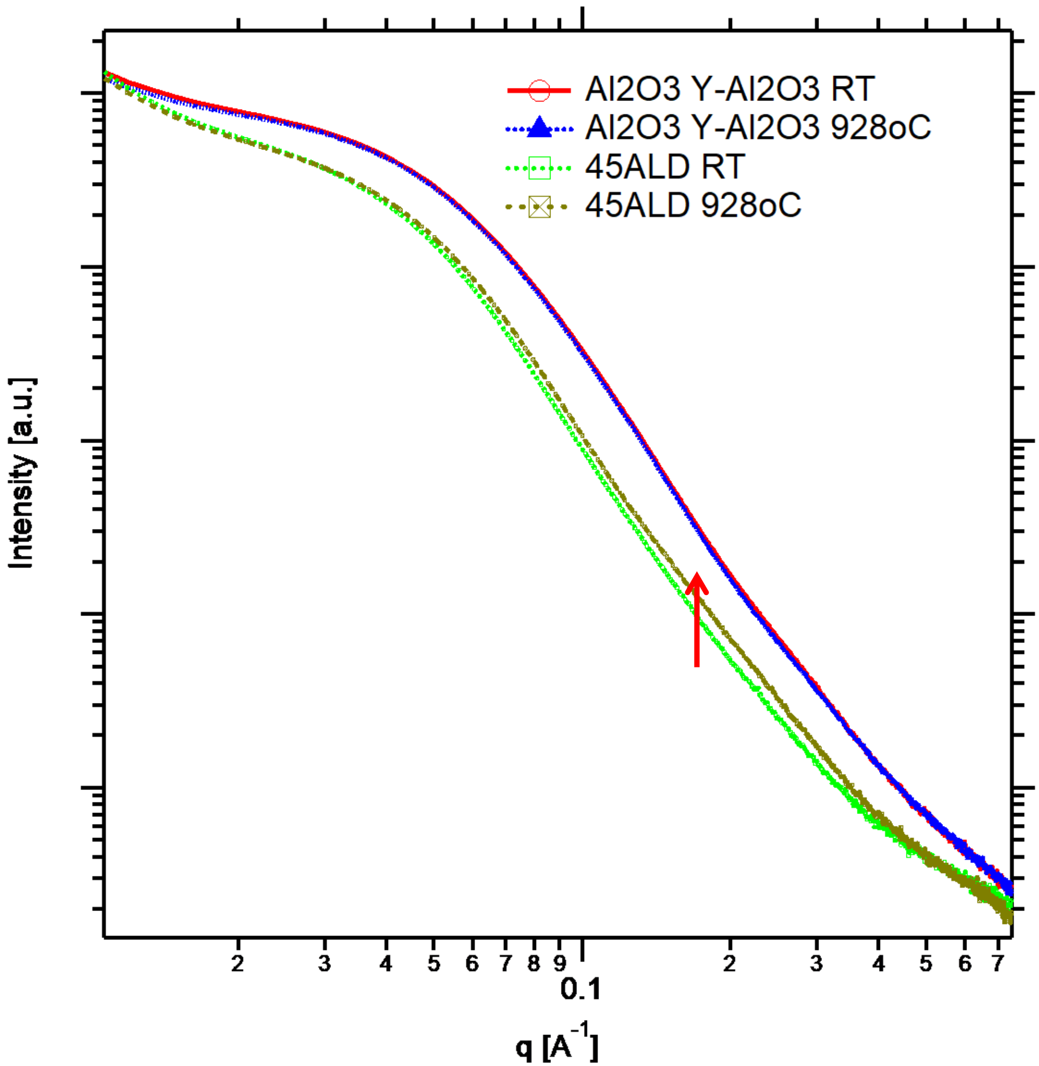
Pore Size of γ-Al_2O_3 Support from SAXS

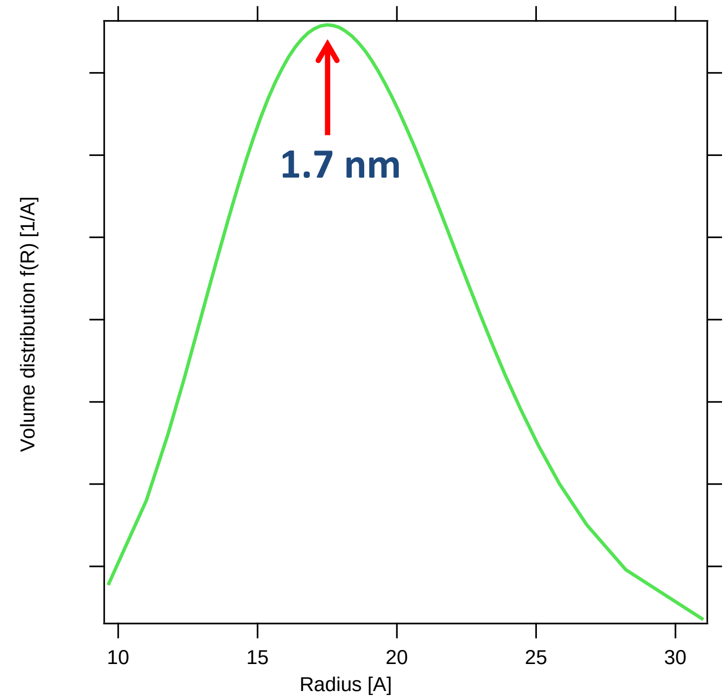




The fitting shows that the average particle size is 6.7 nm, consistent with BJH Model data 7.1 nm.

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



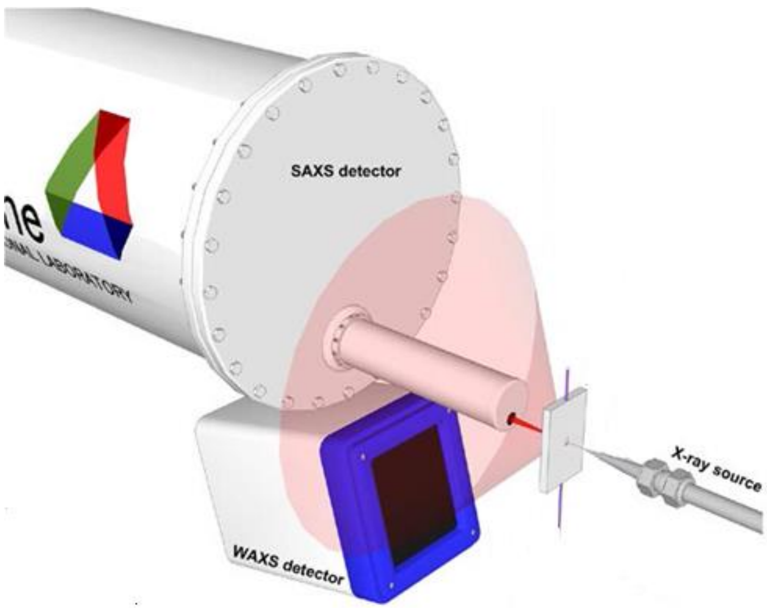


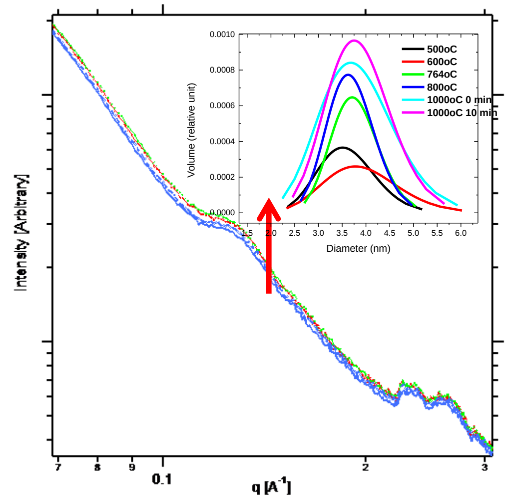
- Gamma-Al_2O_3 support has no change before and after heating.
- For 45ALD coated samples, the intensity Increases, indicating the pore.
- Average pore radius 1.7 nm

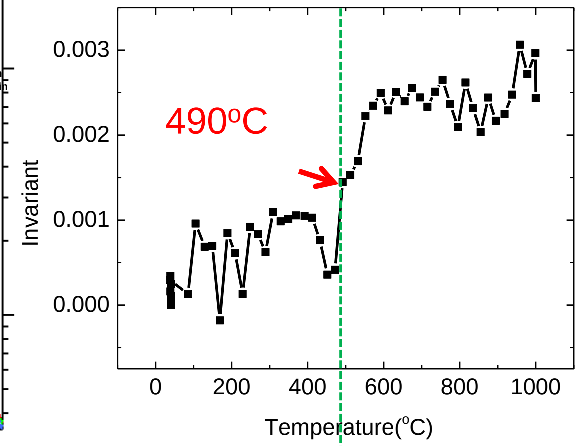
Tao Li as co-author. ACS Catalysis, **2020**, *10 (23)*, 13957-13967.

Combined SAXS/WAXS of TiO_2 Overcoat

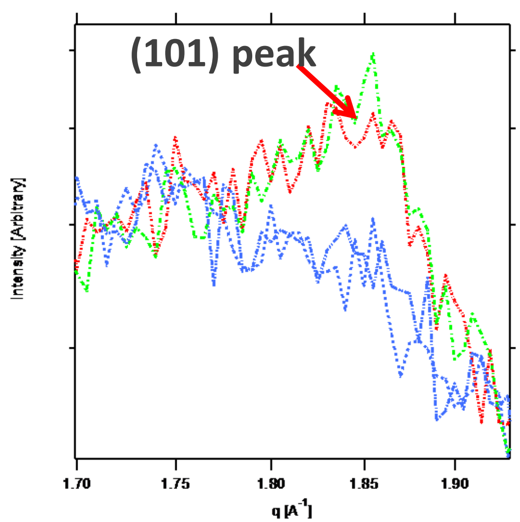
5 nm ALD TiO_2 overcoat on spherical nanodur   Heat in air 20°C/min to 1000°C

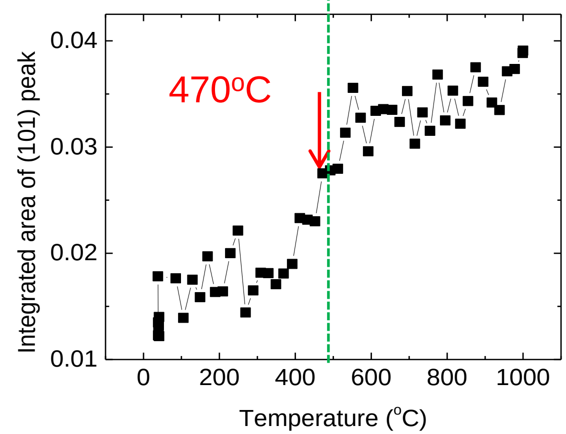






- APS (12 ID-B)
- Linkam stage (RT to 1500 ˚C)

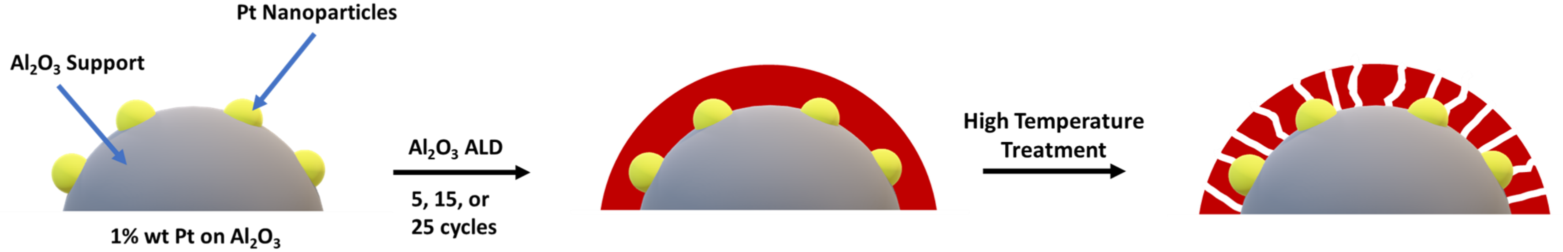


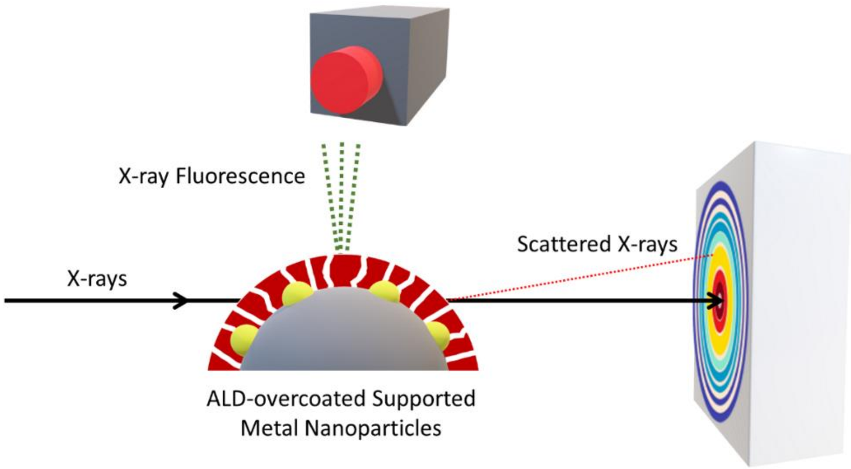


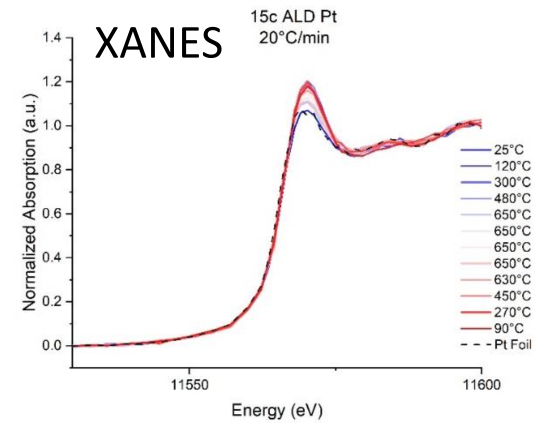
- SAXS: pore size.
- WAXS: crystallization.

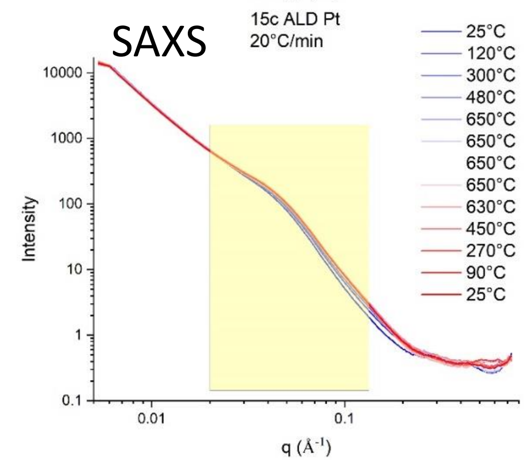
E. Sarnello, Z. Lu, S. Seifert, R. Winans, **Tao Li***. *ACS Catalysis*, **2021**, *11*, 2605-2619.

In Situ SAXS/XAS of Al_2O_3 Overcoat on Nanodour

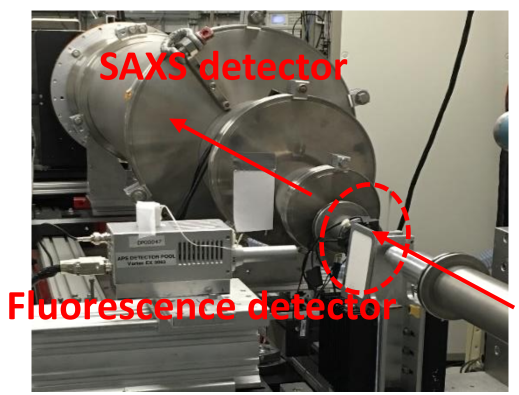




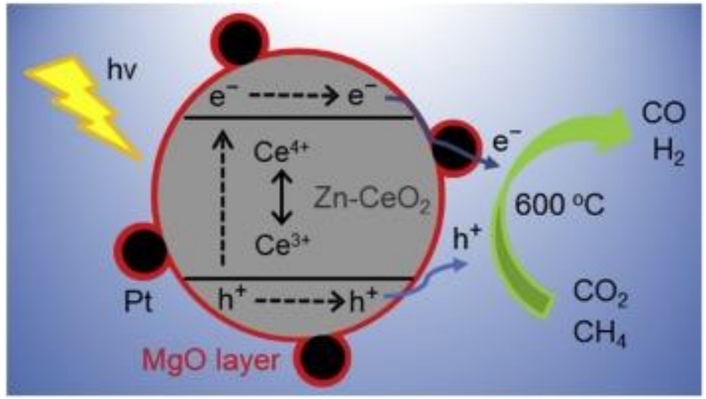


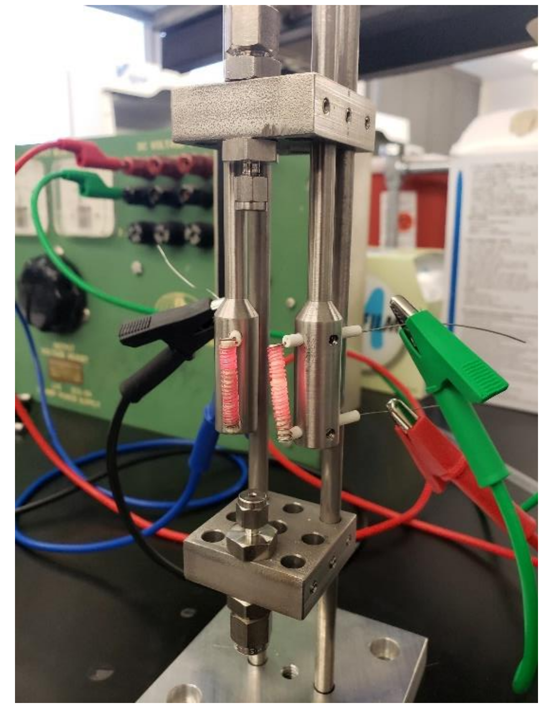


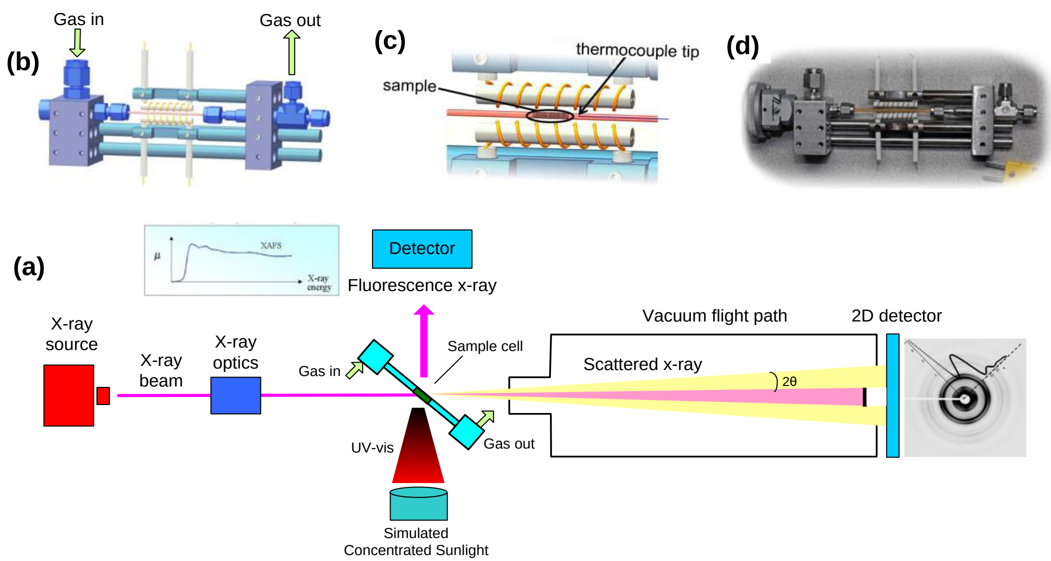
12 ID-C



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

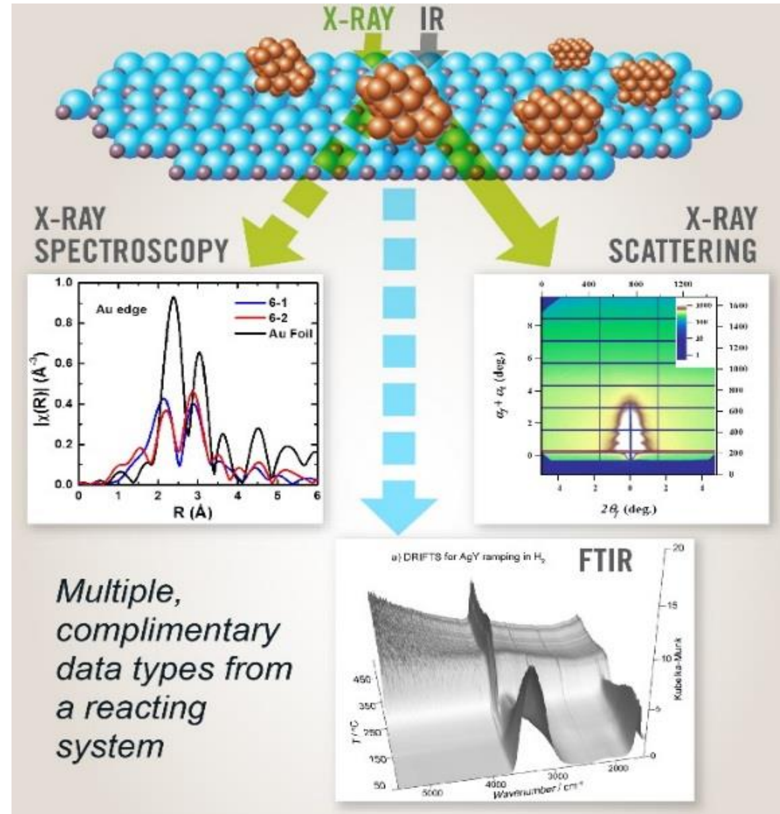
Multiple Techniques to Observe Structure under Real Conditions

(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:

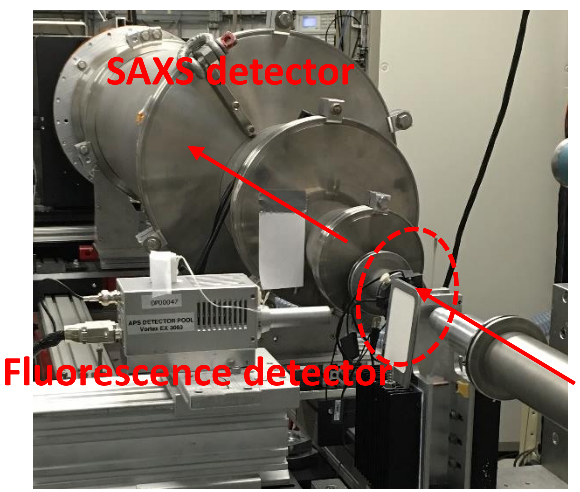
1-ID (high energy SAXS/WAXS (PDF))
9-ID-D(USAXS/SAXS)
9-BM, 20-BM (XAS)
10-ID (XAS)
11-BM (Hi res powder diff)
11-ID-B,C (PDF)
12-BM (XAS/SAXS)
12-ID-B, C (SAXS/WAXS, and GISAXS/GIWAXS)
Also - Imaging and Microscopy (2-BM, 32-ID-BC)

Upgraded
Upgrading



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

12 ID-C



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