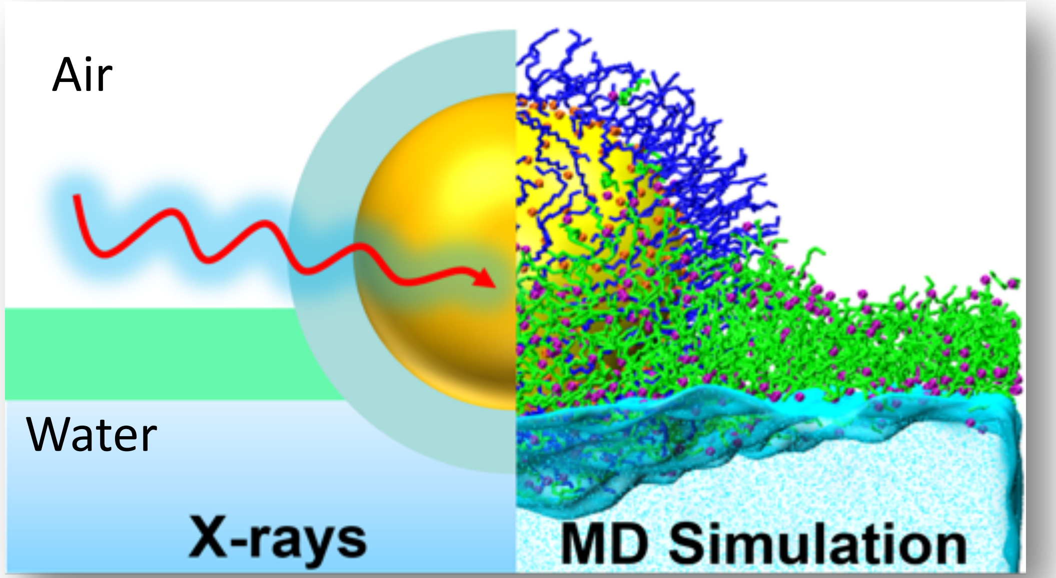
Free Thiols Regulate the Interactions and Self-assembly of Thiol-passivated Metal Nanoparticles

Pan Sun, Linsey Nowack, Wei Bu, Mrinal Bera, Sean Griesemer, Morgan Reik,

Joshua Portner, Stuart A. Rice, and Binhua Lin, *University of Chicago*

Mark L. Schlossman, *University of Illinois at Chicago*



NSF's ChemMatCARS UCHICAGO

ORSO Annual Workshop, June 14-18, 2021

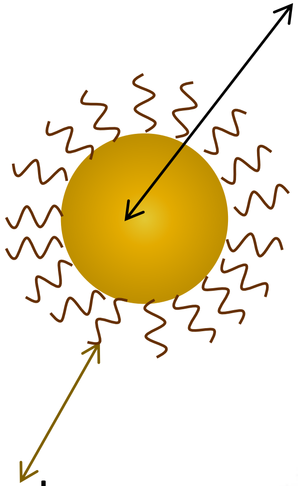
System

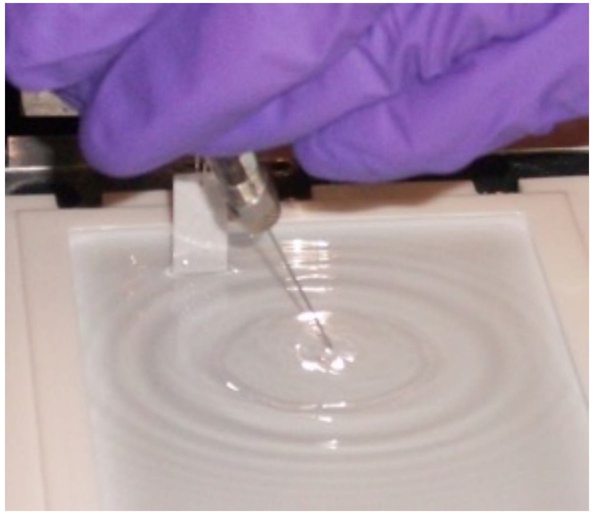
2D Self-assembly of Au Nanoparticles (AuNPs) at the Air-Water Interface

Xiaomin Lin
ANL

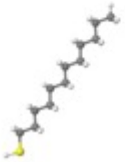
Josh Portner
U of Chicago

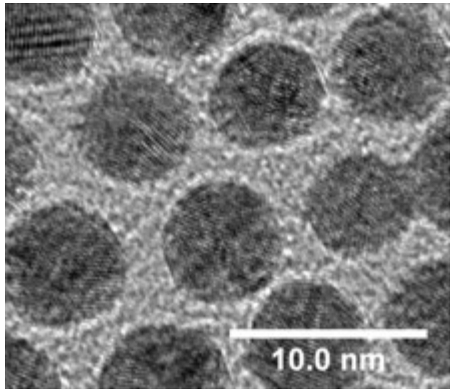
Au nano-crystal core: ~5.2 nm (polydispersity <10%)



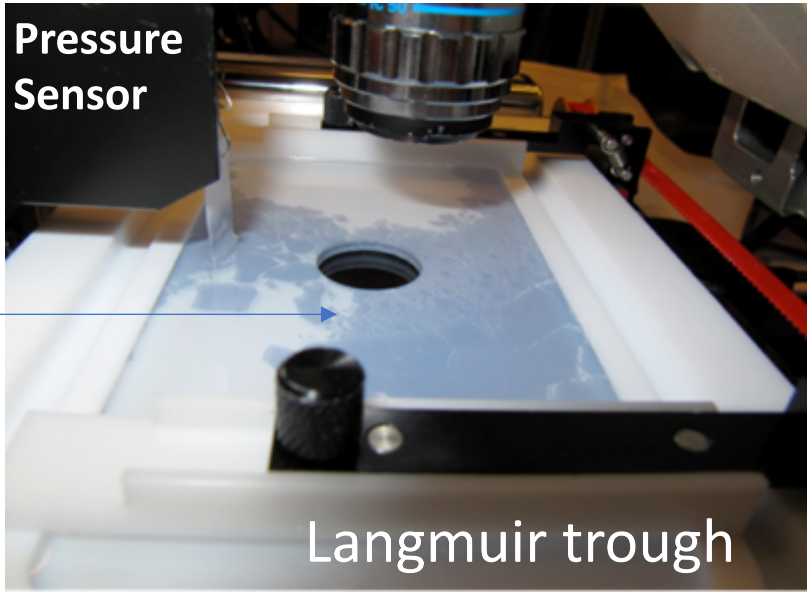


Ligands:
Dodecanethiols: ~1.8nm

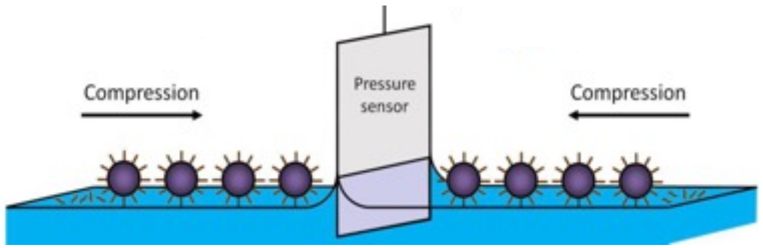




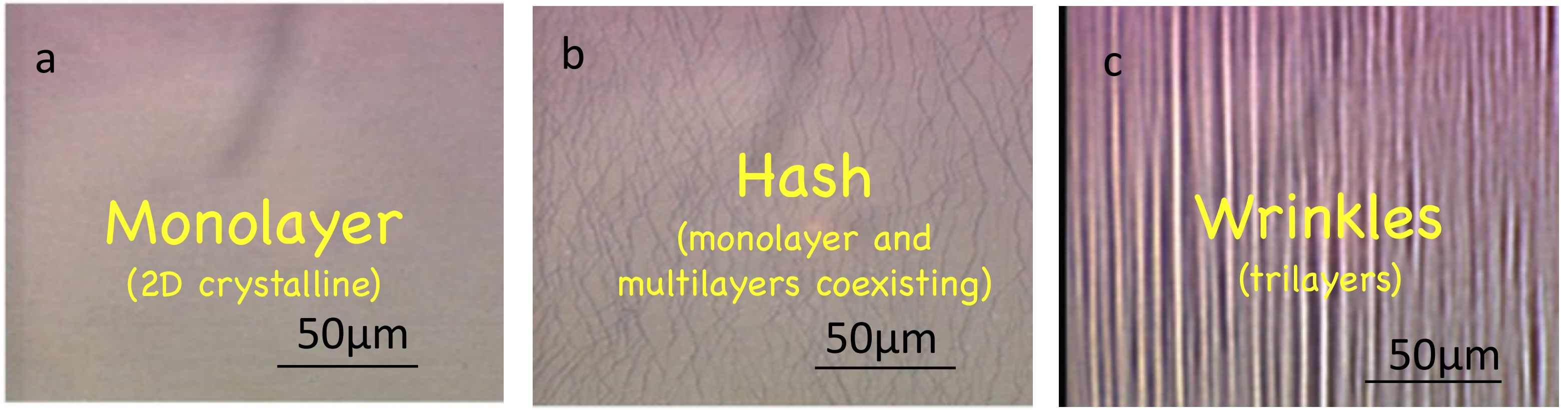
Self-assembled into ultra-thin elastic membranes (monolayers of AuNPs)



Intriguing Elastic Properties of Self-assembled AuNP Membranes

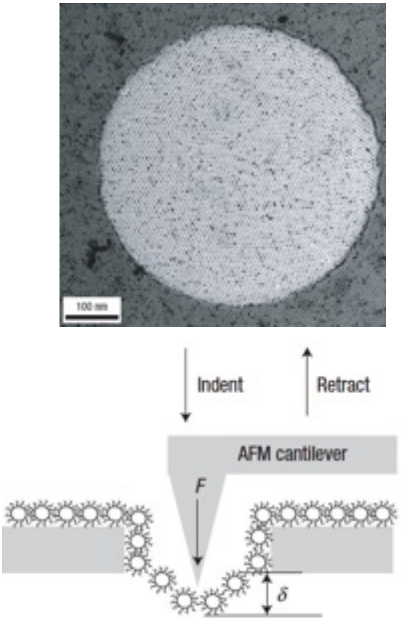


Elastic Response of a Nanoparticle Film on the Surface of Water

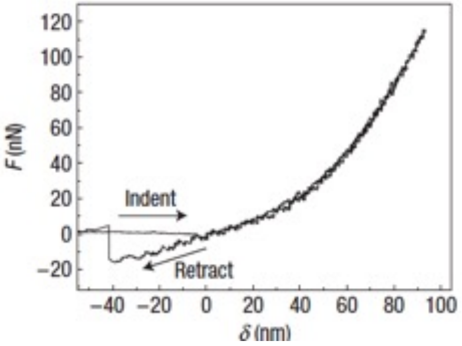


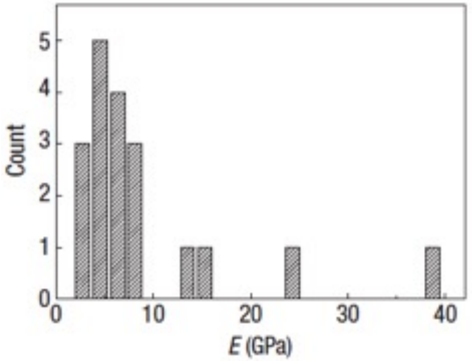
Leahy, et al, *PRL*, **105**, 058301 (2010)

Pocivevsek, et al, *Science* **320**, 912 (2008)



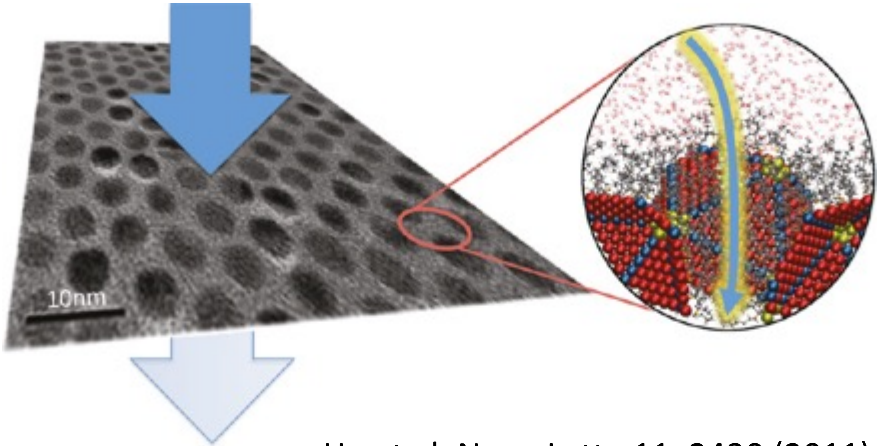
High Young's Modulus of Free Standing AuNP monolayers





Mueggenburg et al, *Nat. Mat.,* 6, 656 (2007)

Diffusion and Filtration Properties



He et al, Nano Lett., 11, 2430 (2011)

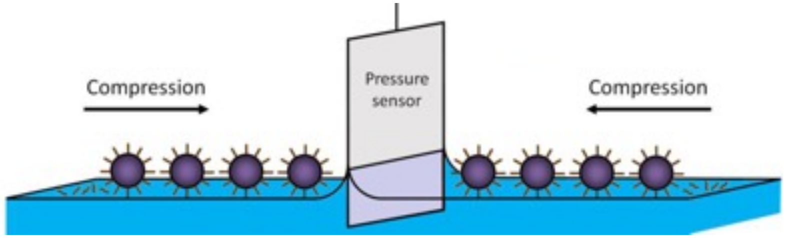
Jaeger's group, U of Chicago

Tuning the Elastic Properties of AuNP Films with Ligands

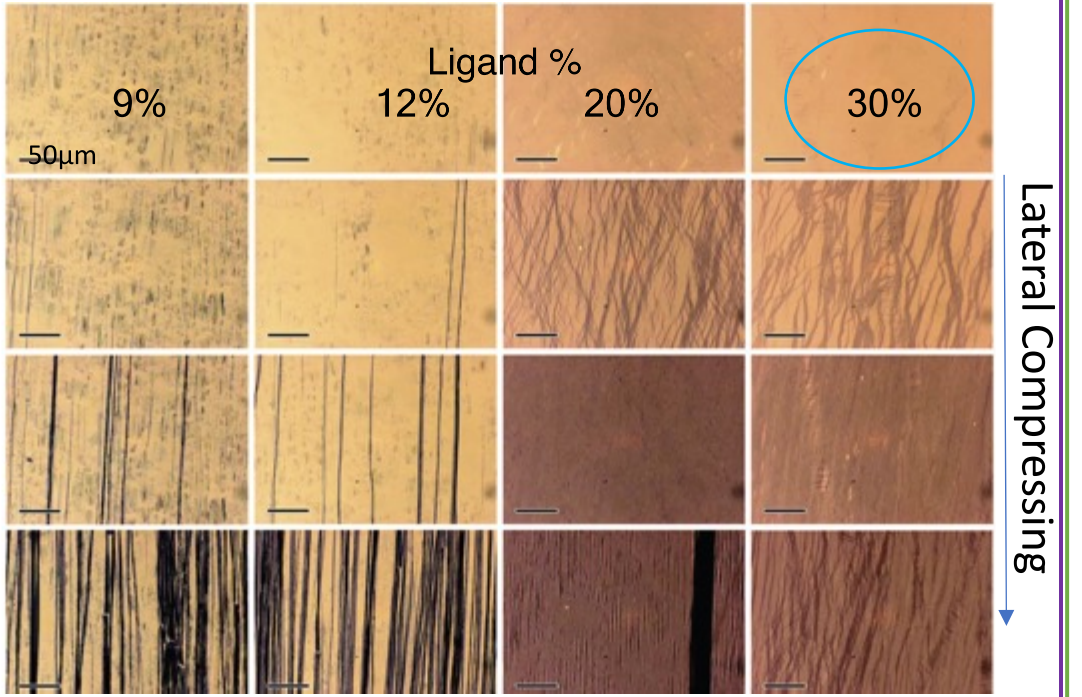
1. Masses of S (ligand), M_L, and Au, M_{au}, of the *extensively washed* AuNP solution were measured by ICP-MS

2. Ligands were back added to the AuNP solution to reach different Ligand %

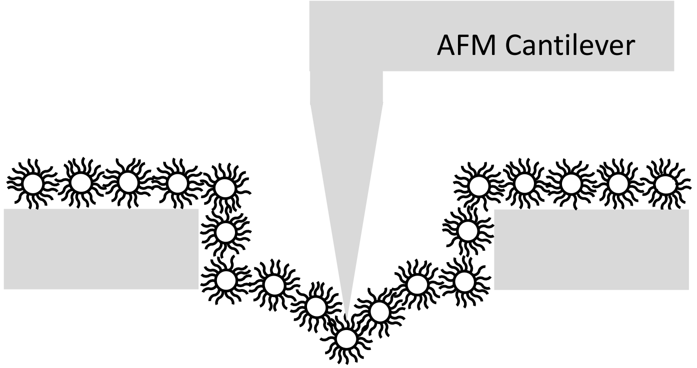
Ligand % = $\frac{M_L}{M_L+M_{au}}$

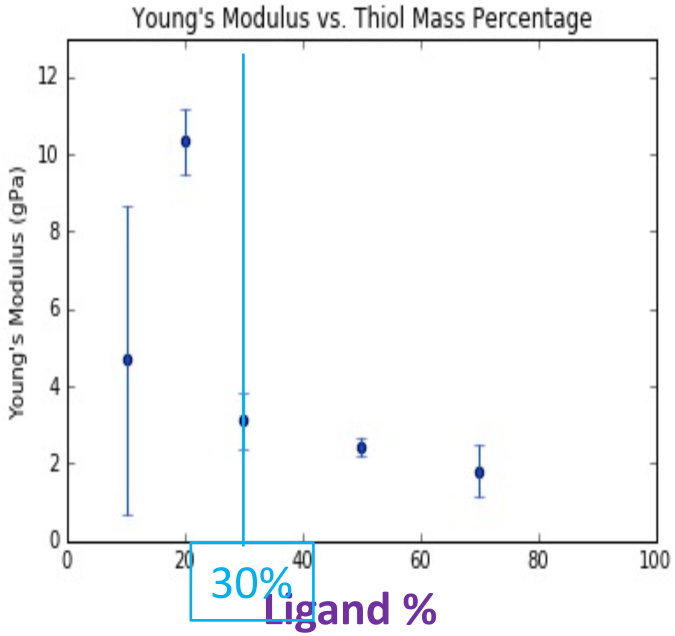


Increasing the ligand % past a threshold value inhibits monolayer wrinkling and folding



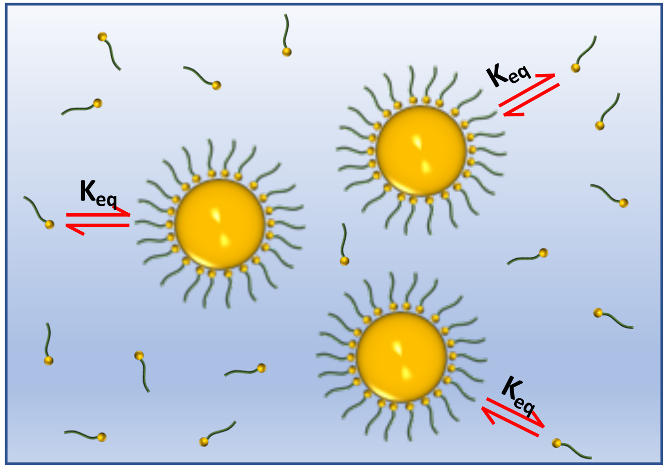
Griesemer, *et al*, *Soft Matter*, 2017, **13**, 3125





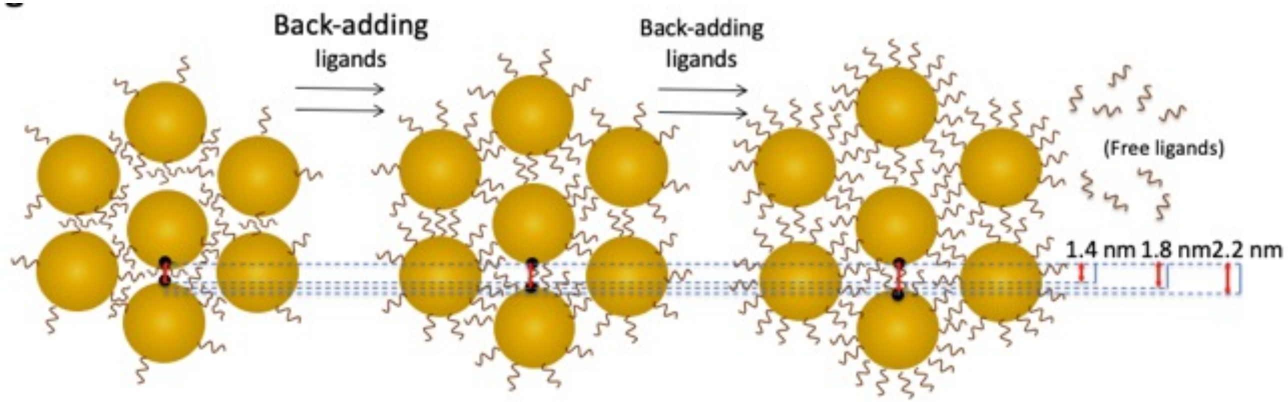
MacFarland et al, *unpublished*

Where Have All the Thiols Gone?



Equilibrium between **free thiols** and **bounded thiols**

Au-S: *40-50 kcal/mol*, weak enough that Langmuir kinetics is applicable to the kinetics of thiol adsorption.
Hintervirth et al, ACS Nano. 7 1129 (2013)



Equilibrium bounded thiols on AuNPs

Langmuir Adsorption Kinetics

$$\theta = \frac{C_1}{C_1 + \left(\frac{1}{K_{eq}}\right)} = \frac{C_2}{C_{satuate}}.$$

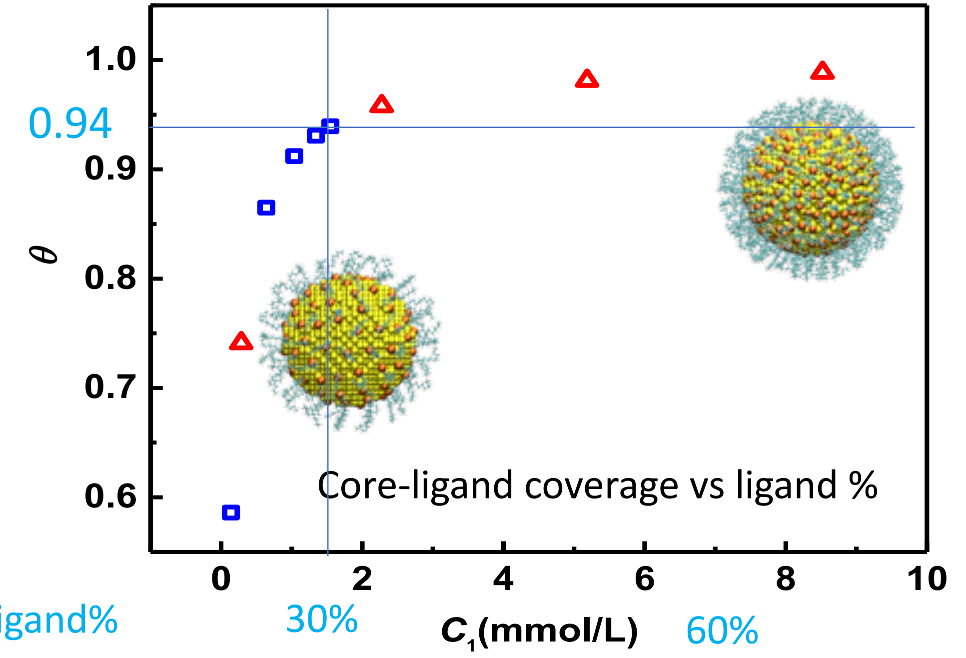
C_1: Free thiols concentration

C_2: Bounded thiols concentration

$C_{satuate}$ => 21.7Å²/ligand

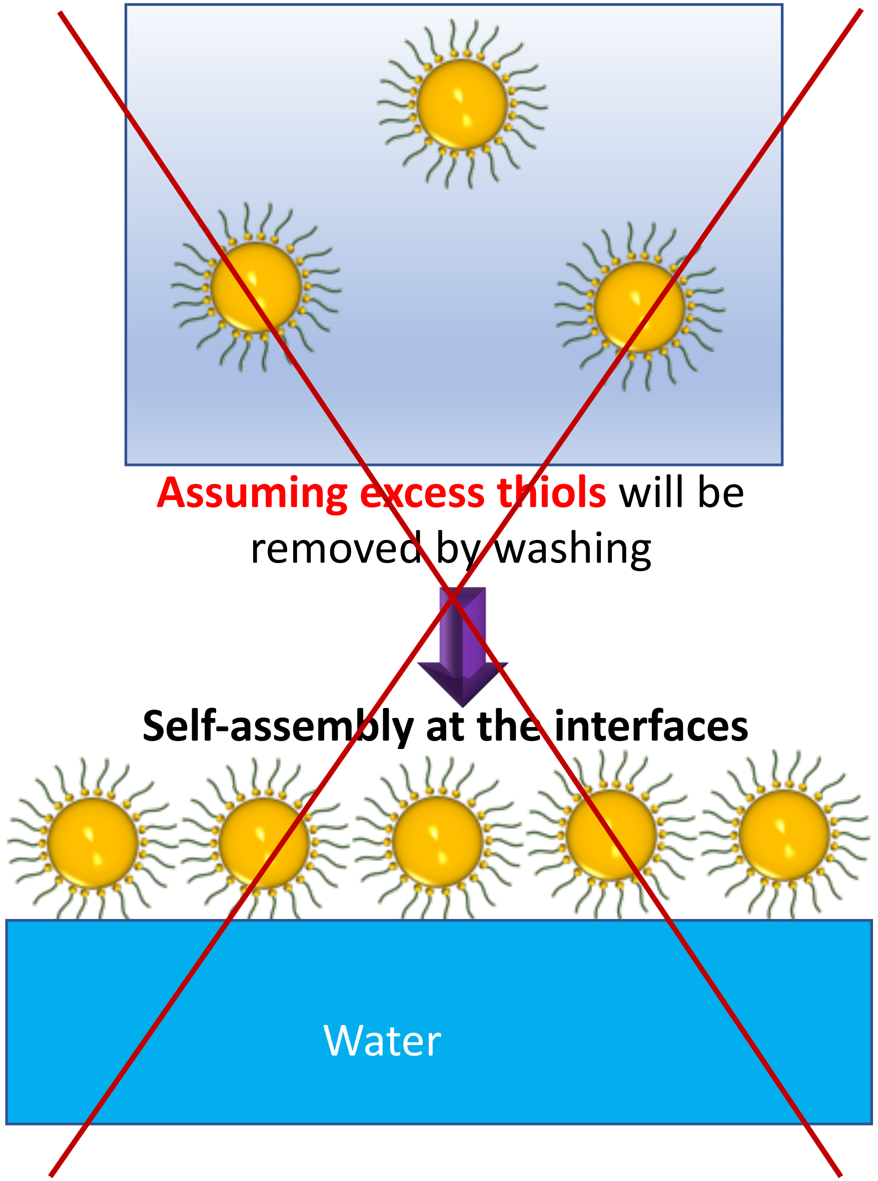
C_1+C_2 ⟷ **Ligand%**

θ, Core-Ligand Coverage

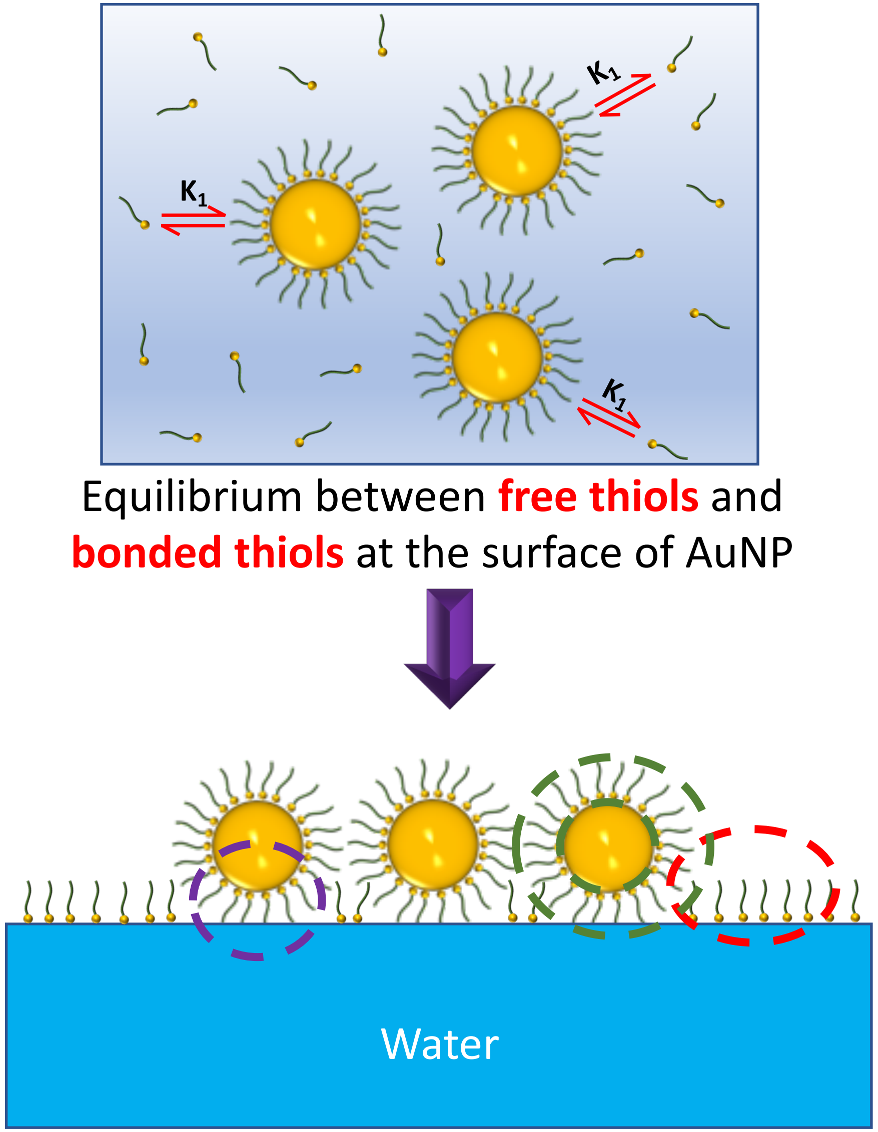


* Reik, M. *Soft Matter* **2019,** *15* (43), 8800-8807.

Where Have All the Free Thiols Gone?



Assuming excess thiols will be removed by washing



Equilibrium between **free thiols** and **bonded thiols** at the surface of AuNP

Main Question:

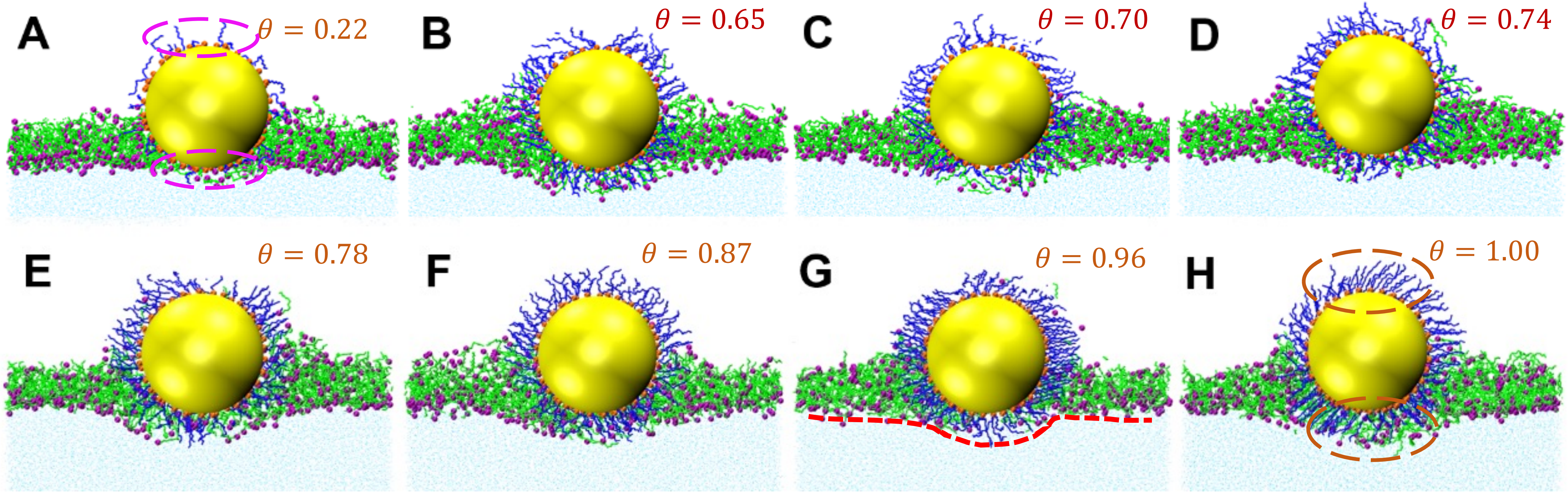
How do free thiols affect the self-assembly of AuNPs at the interface?

1. How do free thiols affect the structure of AuNP ligand shells and their environment?
2. How do free thiols affect the location of AuNPs on the water surface?

Linsey Nowack

MD Simulations: Ligand Structure of a AuNP in the Presence of Free Thiols on the Surface of Water

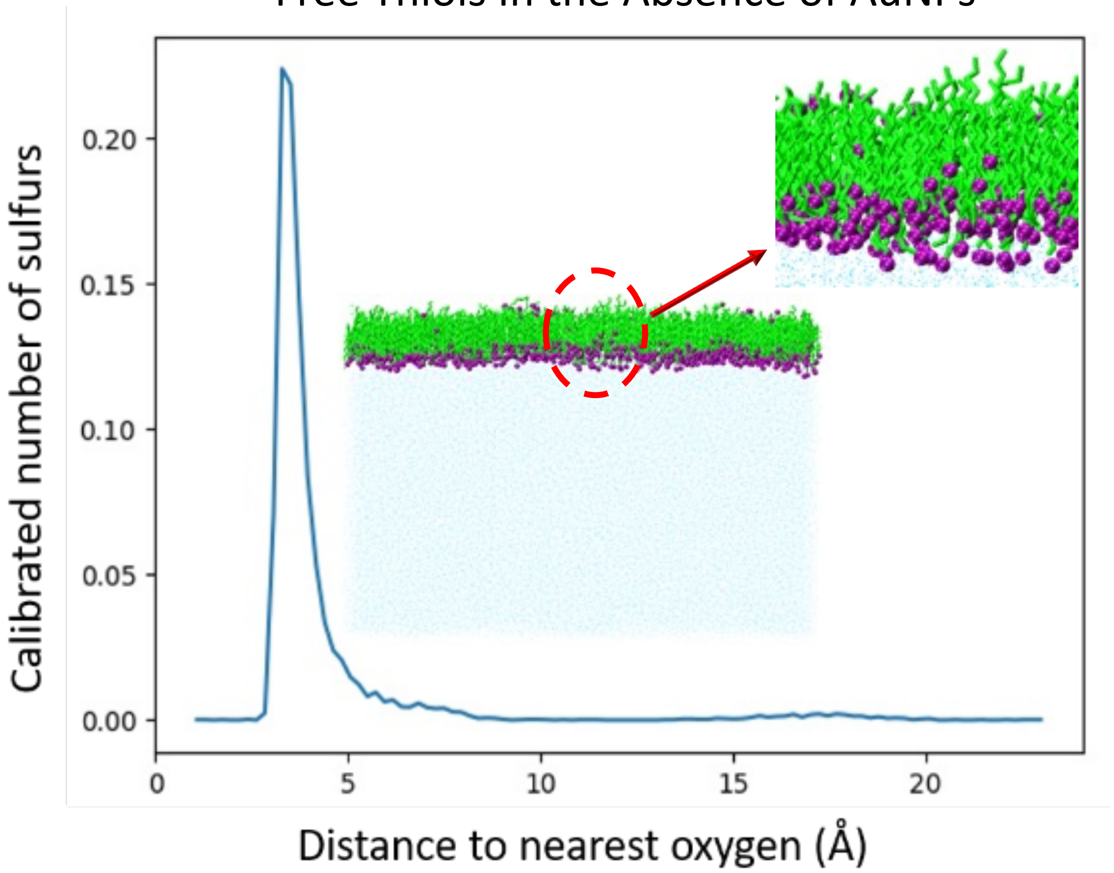
Snapshots from MD simulations of different core-ligand coverage θ (θ=1 => 21.7Å^2/ligand)



Ligand shell is asymmetric at very low θ and symmetric as θ is increased

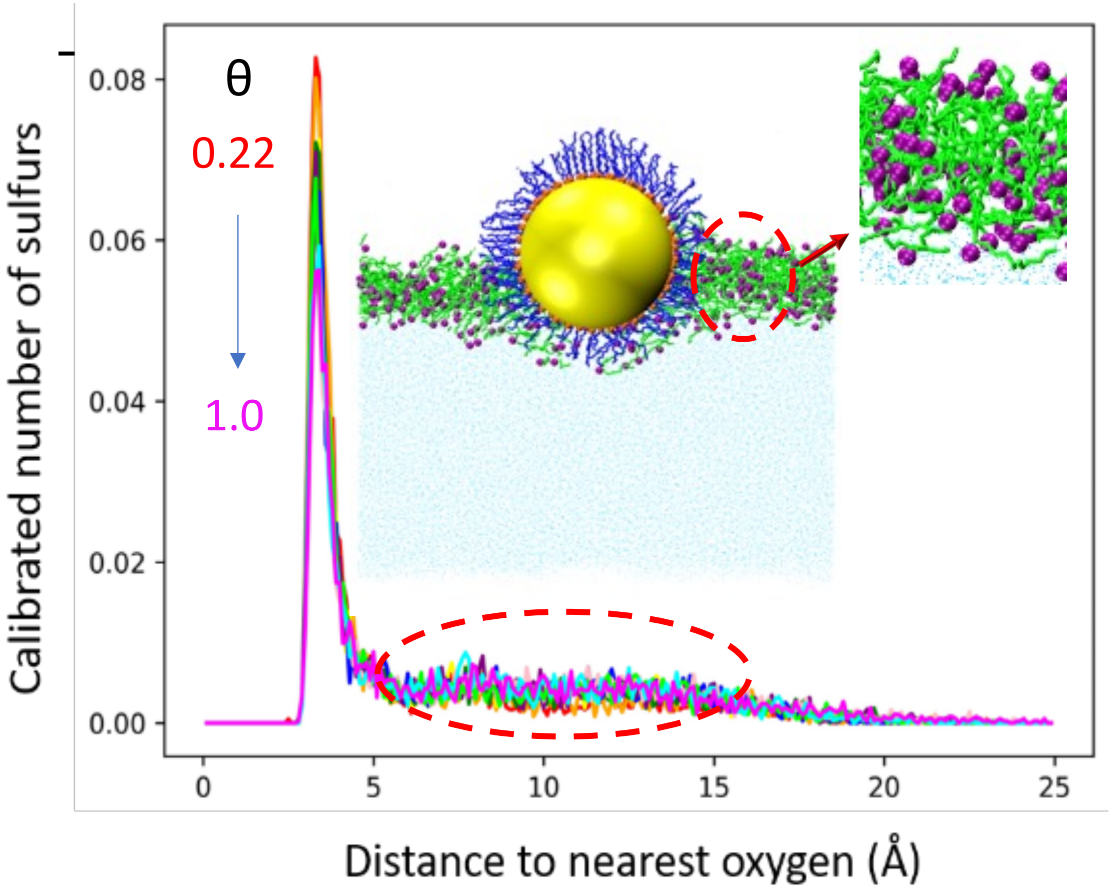
The Free Thiol Layer in the Absence and Presence of a AuNP

Free Thiols In the Absence of AuNPs



Distribution of sulfur atoms in the pure thiol monolayer

Free Thiols In the Presence of a AuNP

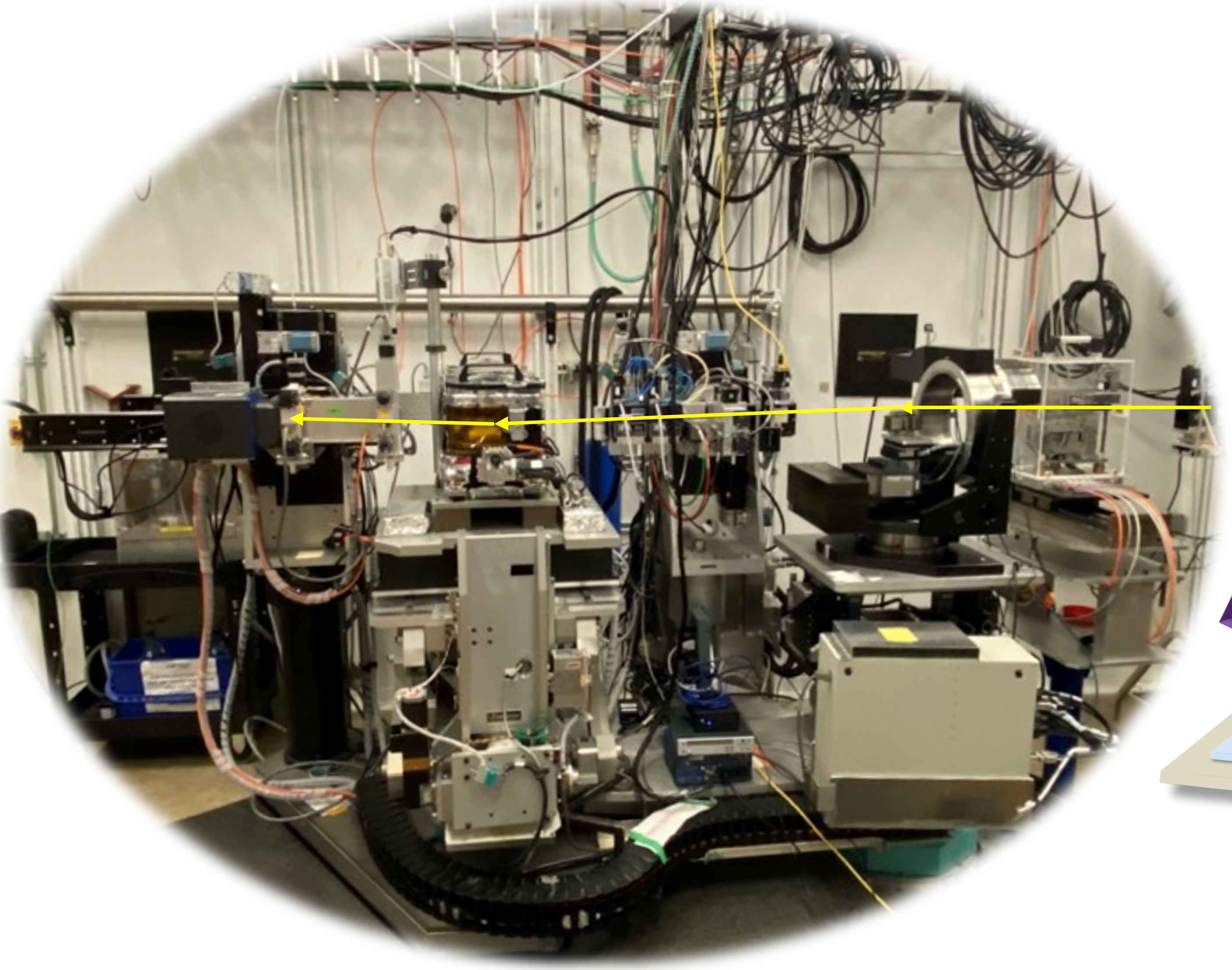


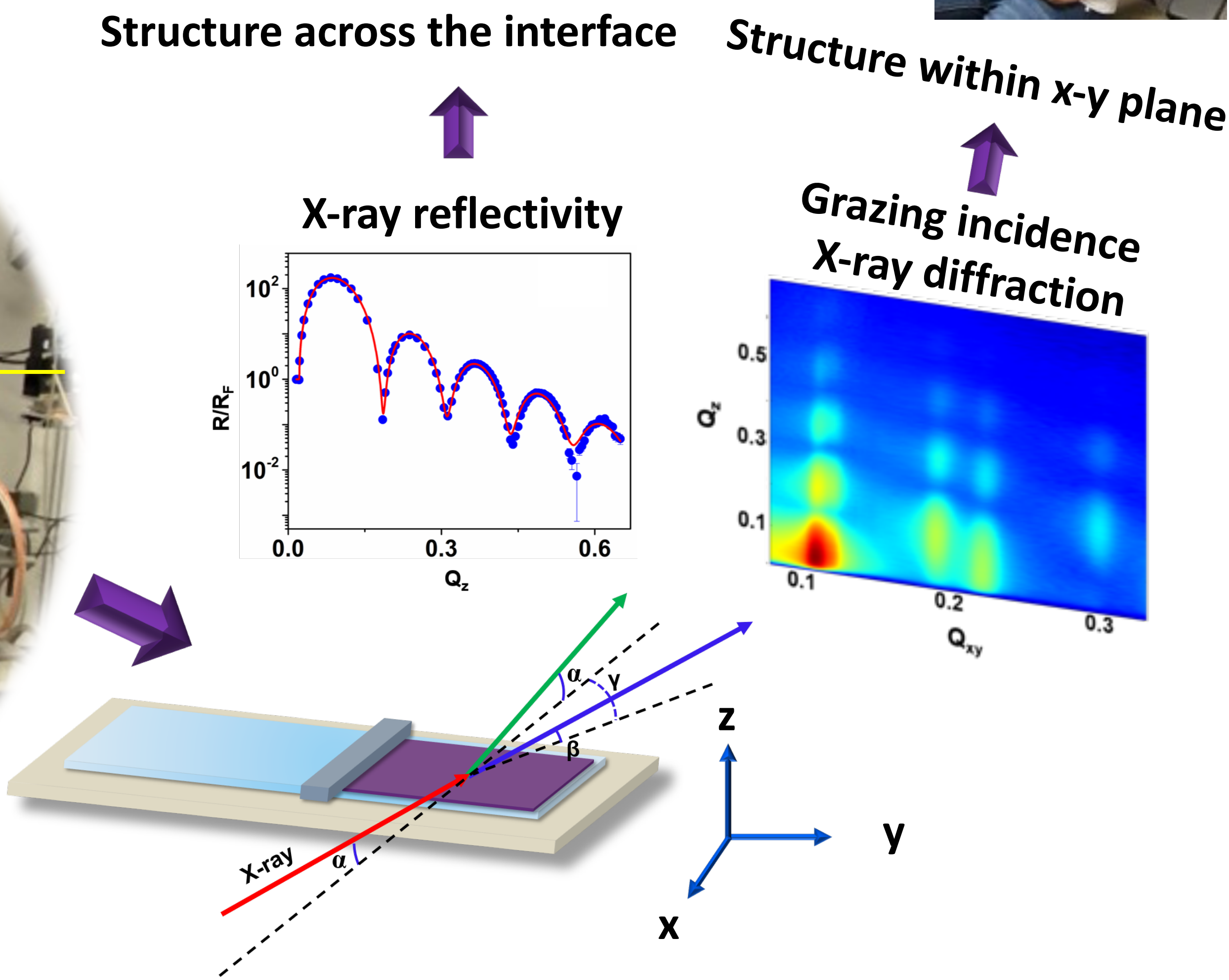
Distribution of sulfur atoms in the thiol film of AuNP system

Liquid Interface X-ray Scattering Experiments

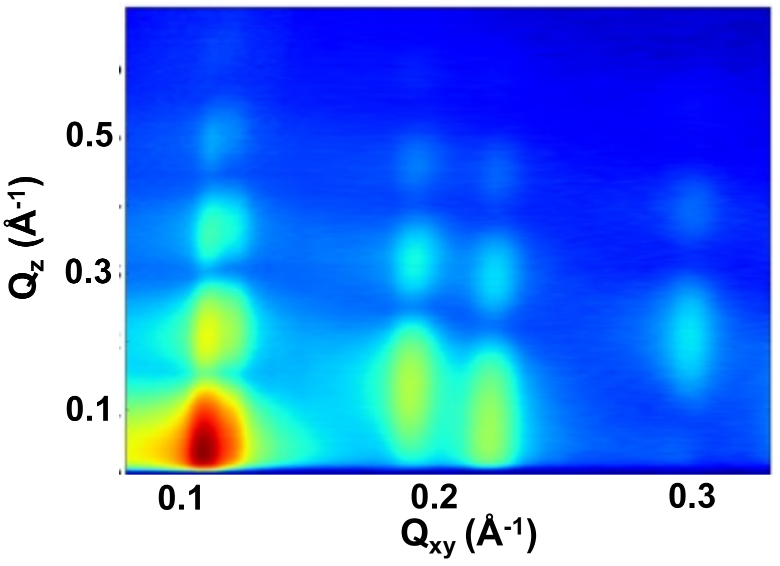
Liquid interface scattering instrument at
NSF's ChemMatCARS, Sector 15, Advanced Photon Source, USA

Pan Sun

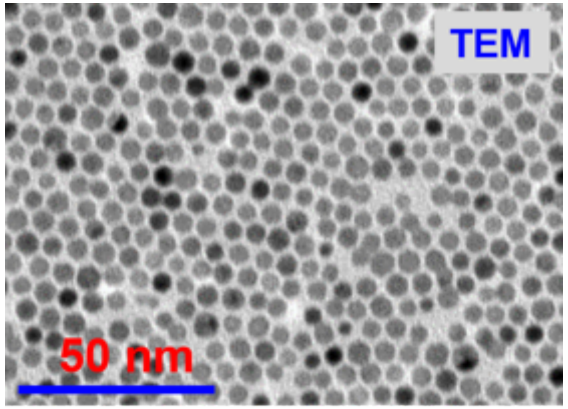




Free Thiols Regulate 2D Packing of AuNPs at the Interface



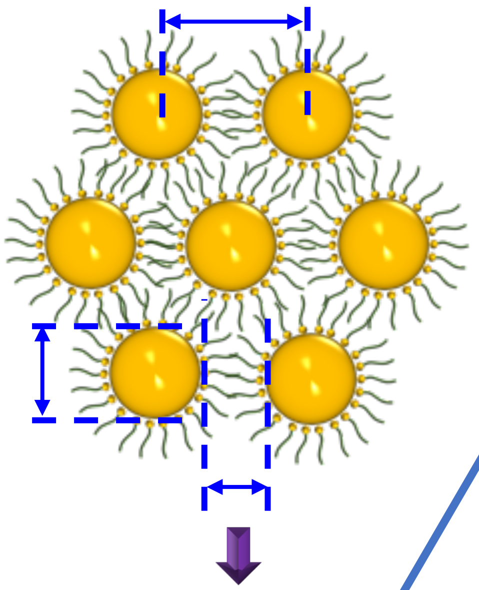
Typical Bragg Rod Diffraction Pattern



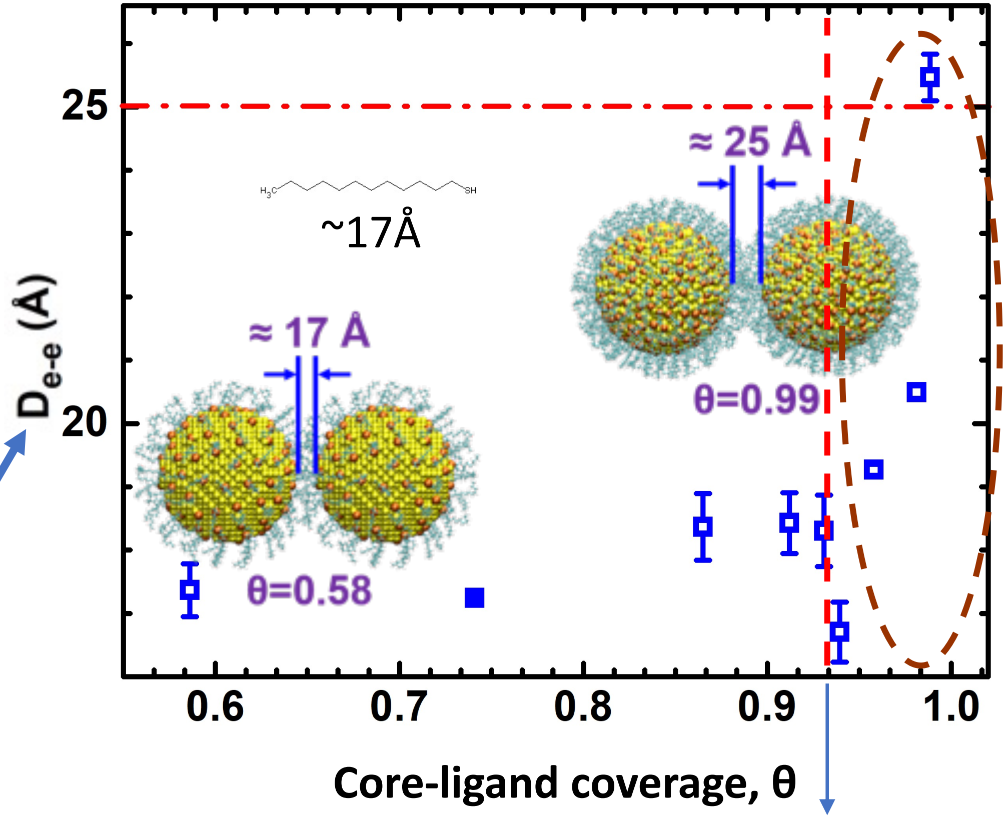
Core size D_c

- Hexagonal packing
- At θ > 94%, the edge-to-edge distance ($D_{e\text{-}e}$) increases very fast

Center-to-center distance ($D_{c\text{-}c}$)

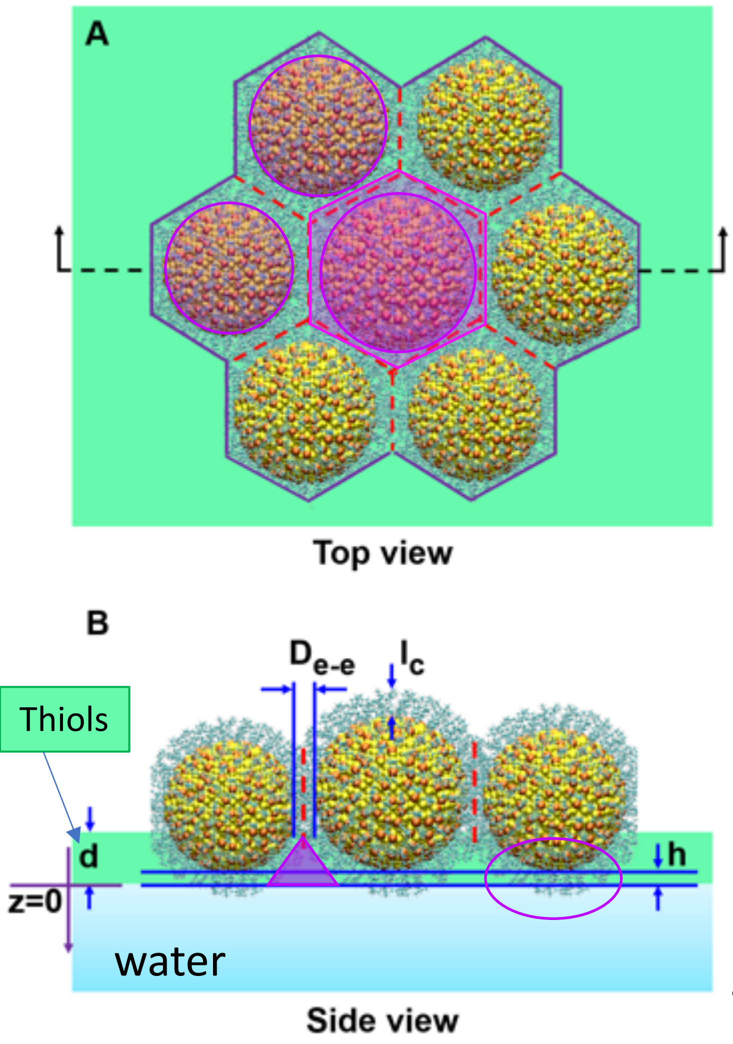


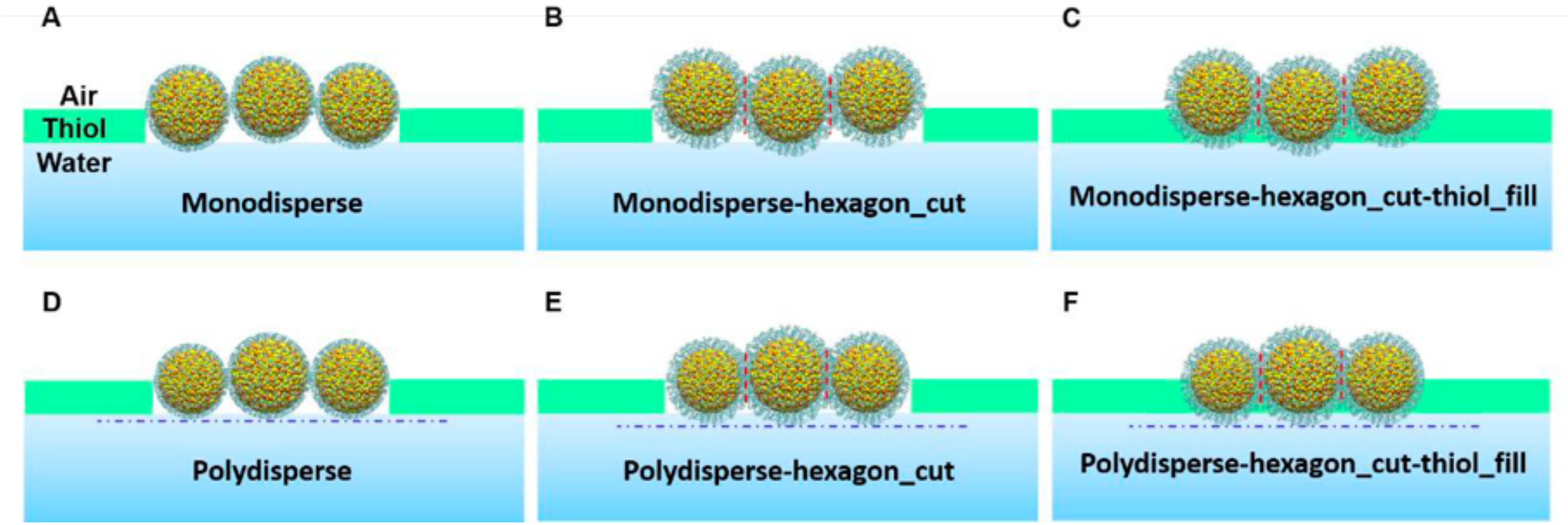
Edge-to-edge distance ($D_{e\text{-}e}=D_{c\text{-}c}-D_c$)



Ligand % ≈ 30%

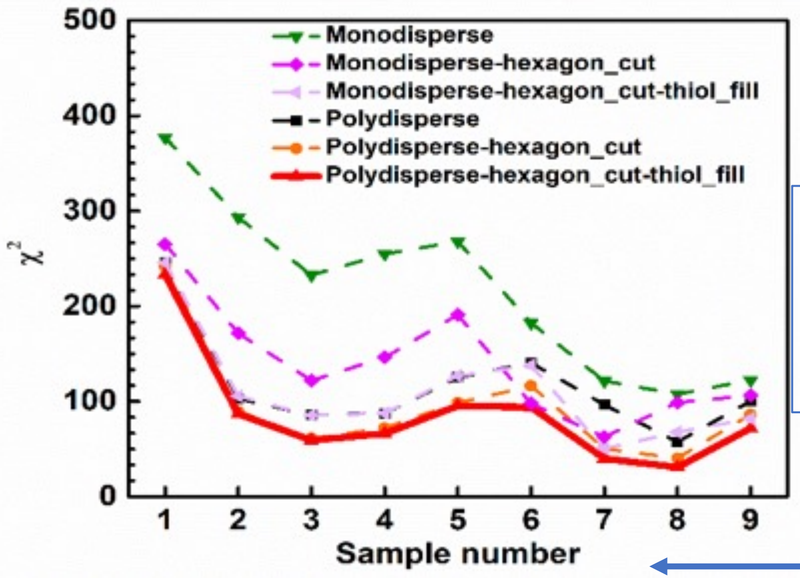
Fitting Model for X-ray Reflectivity





Model for fitting X-ray reflectivity

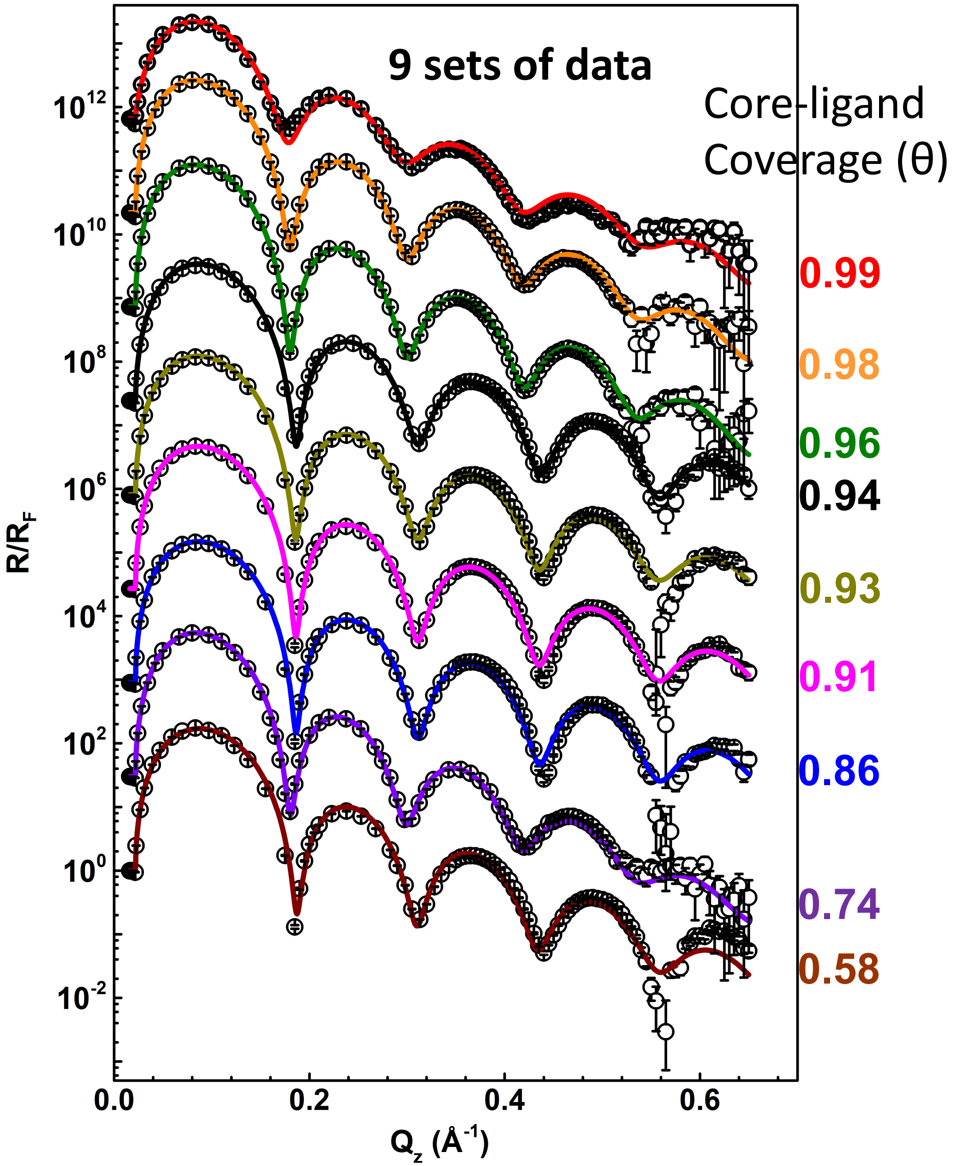
1. NP size distribution
2. Free thiols fill in between NPs
3. NPs make dimples on the surface of water
4. Hexagonal ligand shells
5. Disordered free thiol film with a variable thickness, *d*.



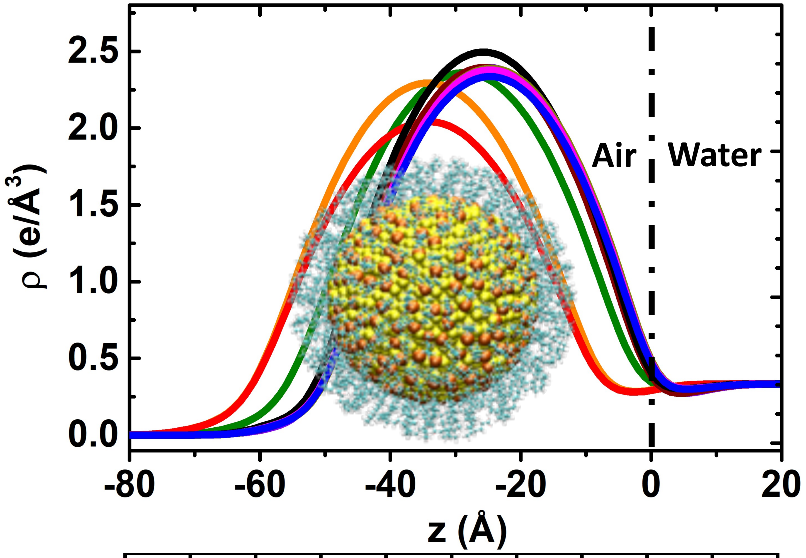
9 sets of samples with different core-ligand coverage (θ)

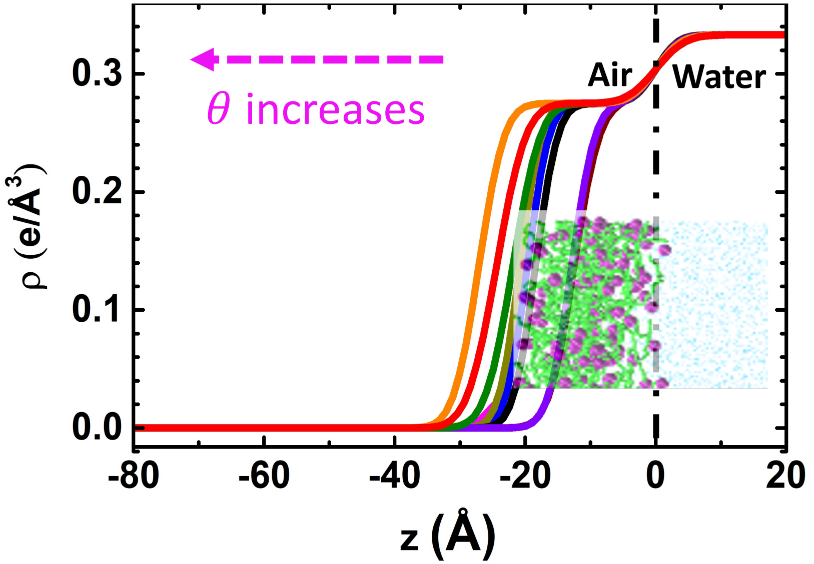
Model of AuNPs Normal to the Interface

X-ray reflectivity data and fitting



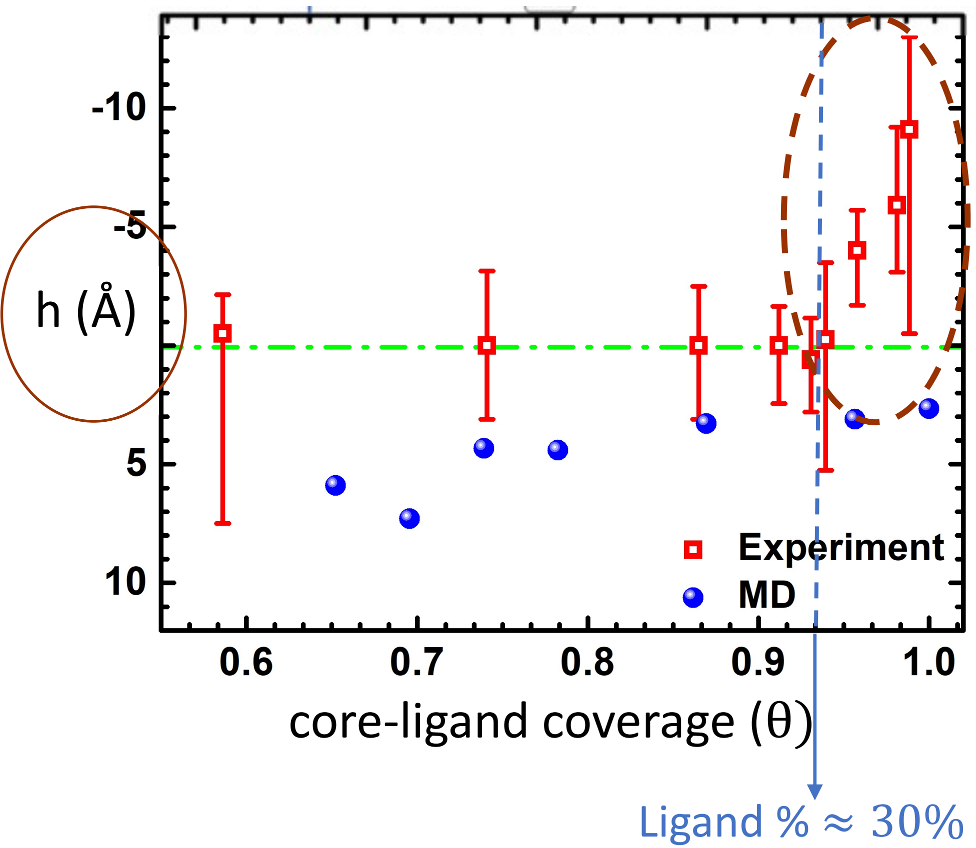
Electron density profile for AuNPs (Top) and thiol film (Bottom)





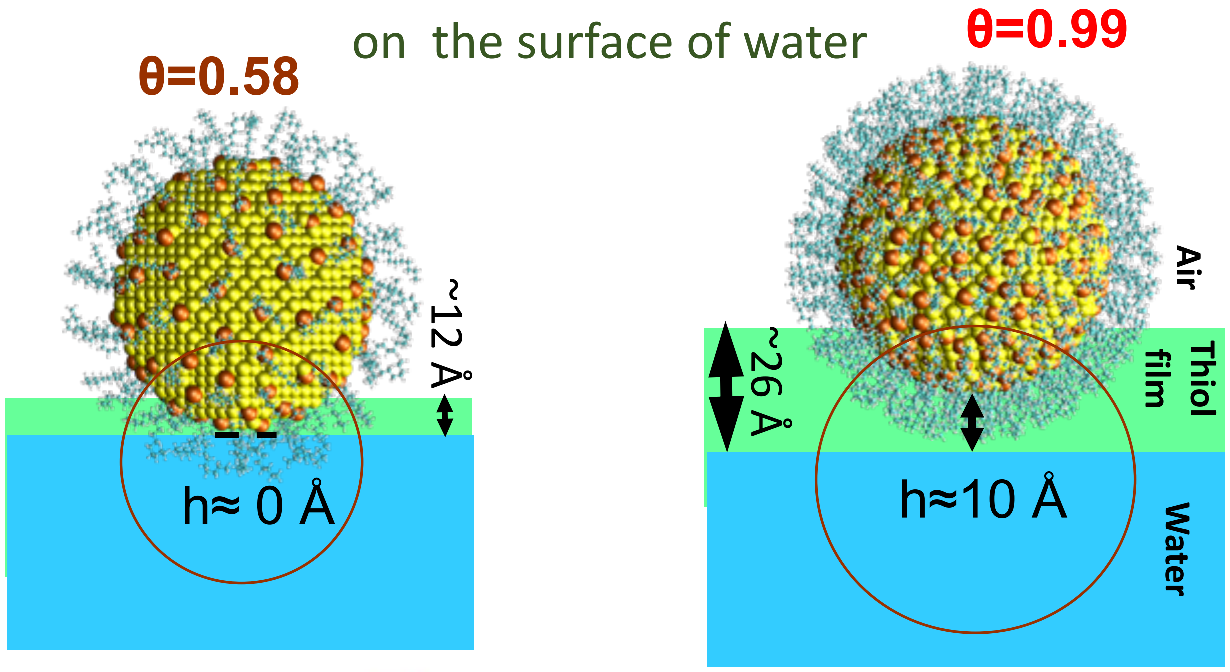
Free Thiols Regulate the Height of AuNPs at the Interface

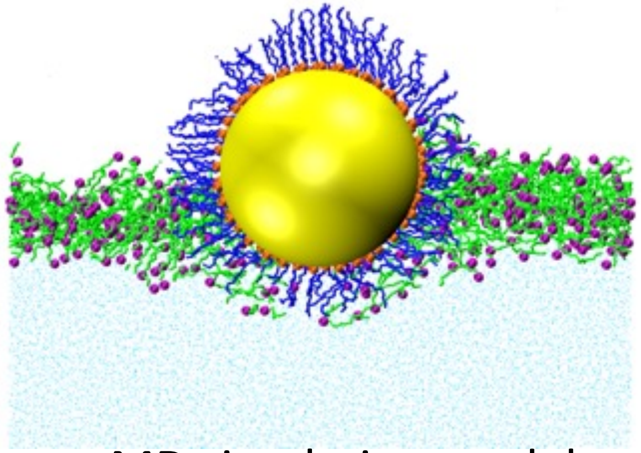
AuNP height as a function of θ



The height of AuNPs (h) increases at $\theta > 0.94$

Model of AuNPs with free thiols on the surface of water



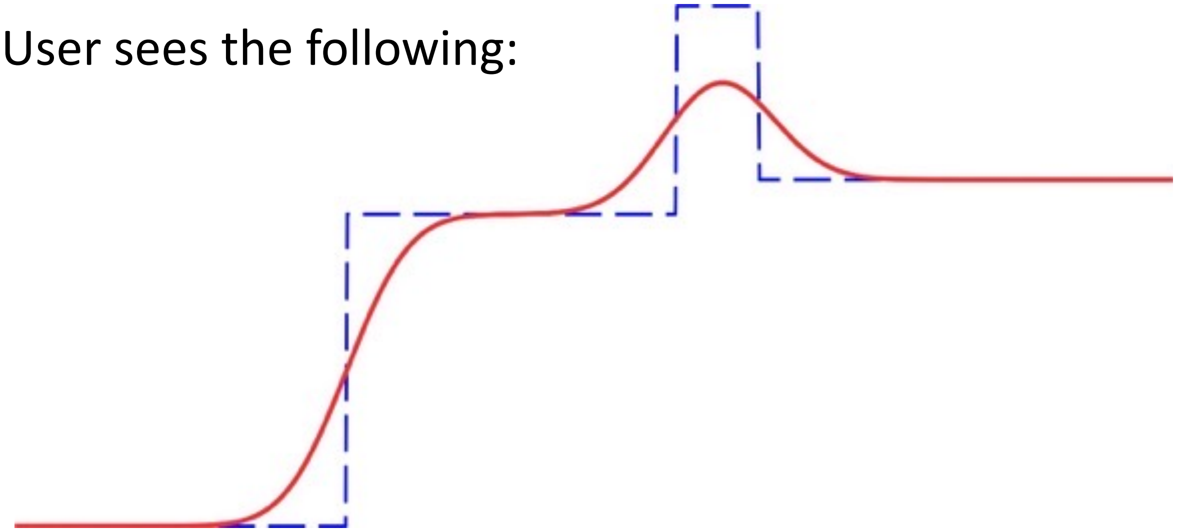


MD simulation model

Au core was modeled as a sphere instead of a *polyhedral Au crystal* with flat facets.

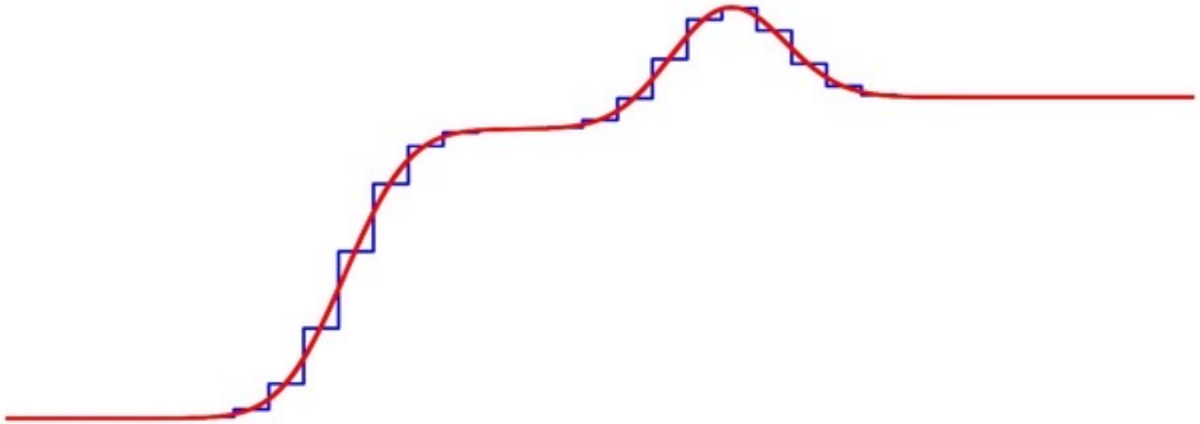
X-ray Reflectivity Calculation Engine is Exact

User sees the following:



- User constructs model of electron density profile with a few slabs and interfacial roughness.
- User fits the model at this level.
- Interfacial roughness included with error functions (equivalent to convolution of zero-roughness model with gaussians).
- Many alternative functions available in addition to the slab model.

Calculations are exact with original Parratt algorithm

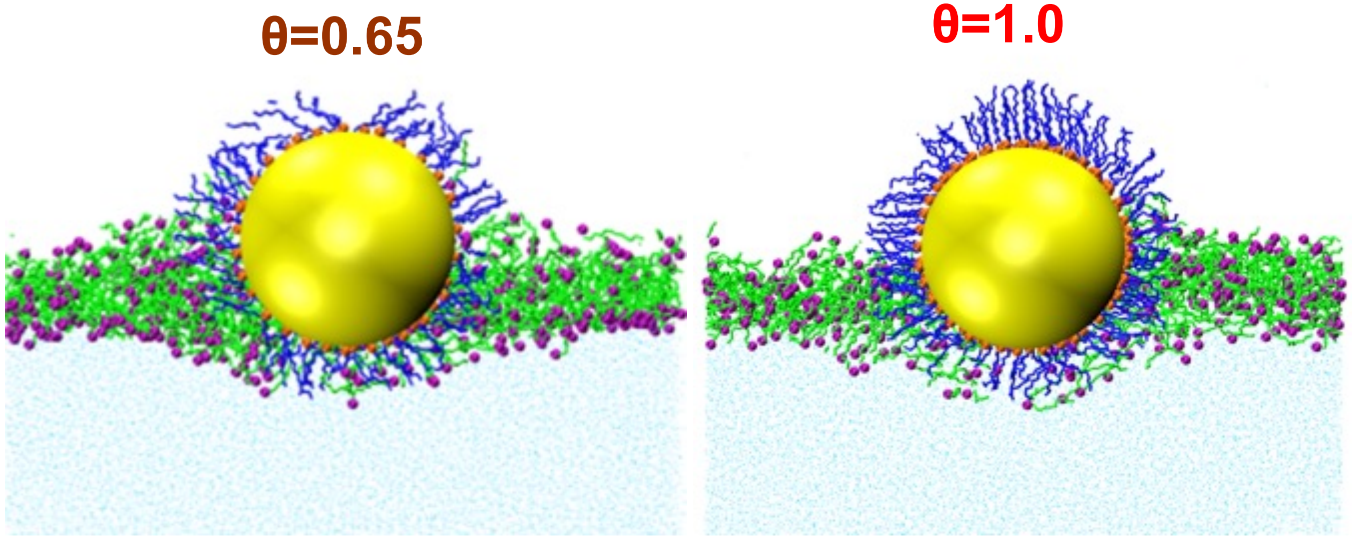


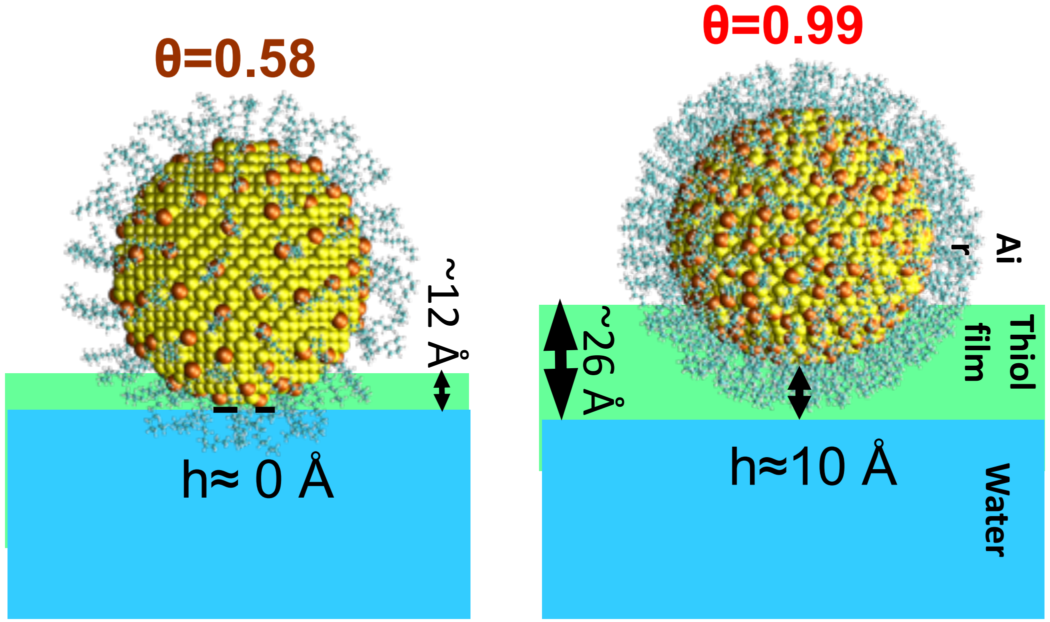
- Calculation engine operates on user-selected model for electron density profile.
- Electron density profile sliced into hundreds of thin, uniform layers with equal thickness (< 1Å).
- Reflectivity calculated *exactly* for many layers by original Parratt algorithm.
- Works for arbitrary (slab or non-slab) models.
- Difficulties with Nevot-Croce approximation bypassed!

Summary

- **MD simulations and X-ray scattering:** In the presence of free thiols, bounded thiols on the Au cores and free thiols interdigitate and produce a symmetric ligand shell.
- **X-ray scattering:** Above a critical value of core-ligand coverage $\theta \approx 94\%$, AuNP cores rise above the water surface quickly, and the AuNP spacing increases rapidly as well (at $\theta > 94\%$, AuNP films loose elasticity).

Free thiols regulate the organization of bounded thiols on the core and the interactions of nanoparticles with their surroundings

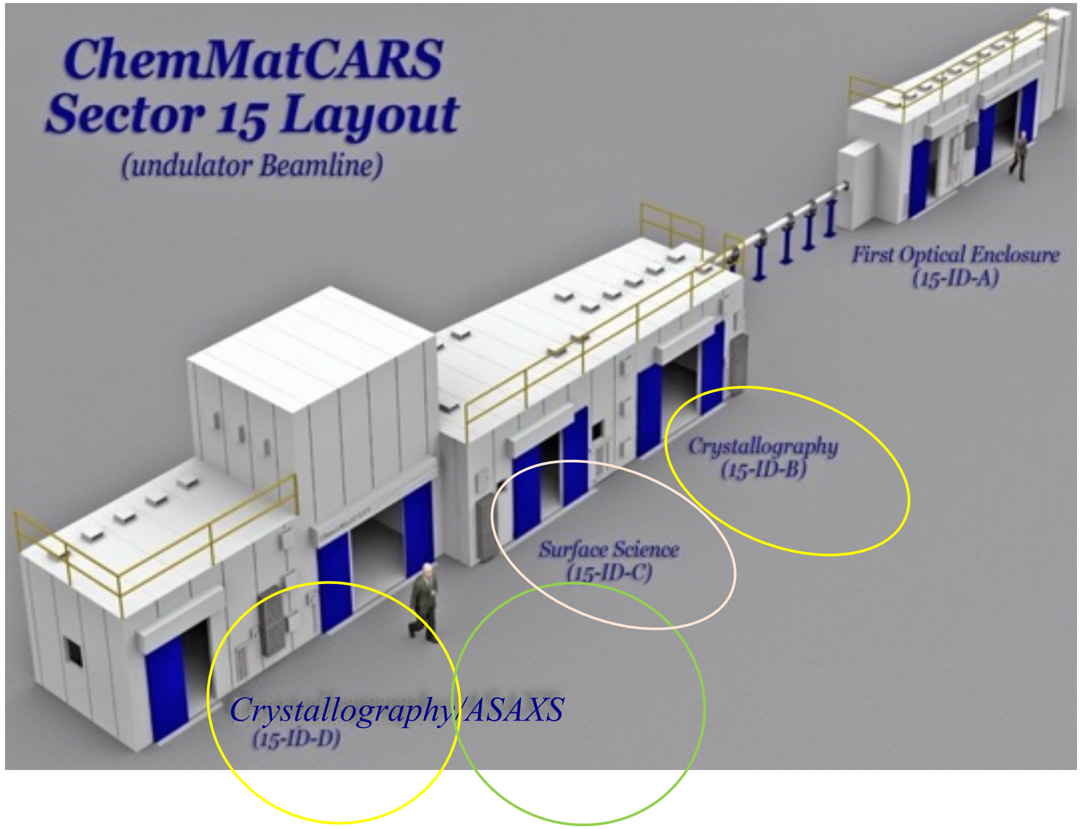


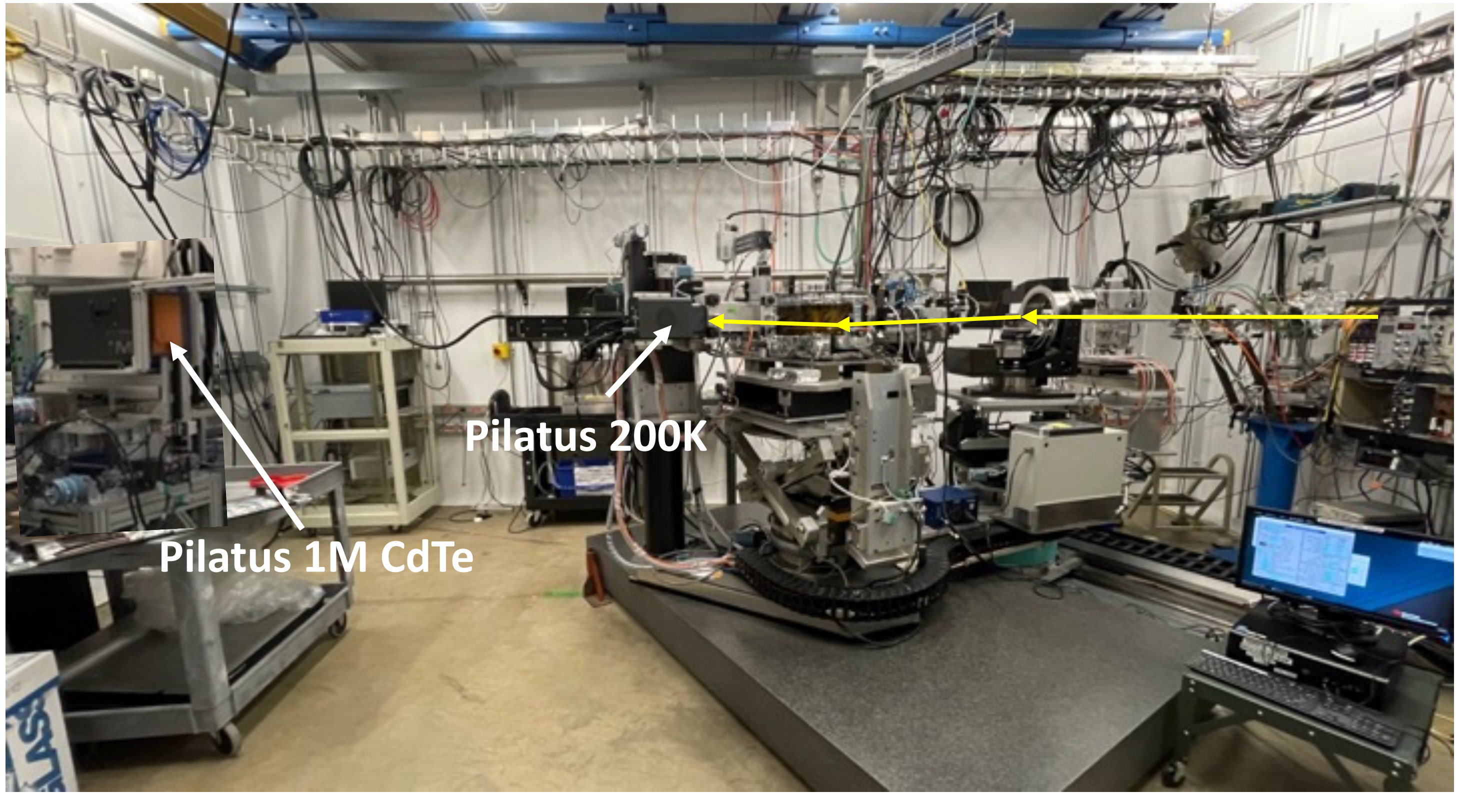


Sun et al., Nano Lett., **21**, 1613 (2011)

NSF/CHE- 1834750 NSF/DMR-2011854 DE-AC02-06CH11357

Liquid Interface Scattering at NSF's ChemMatCARS Sector 15, APS, ANL, Chicago, USA





Tunable energy from 5 – 70 keV

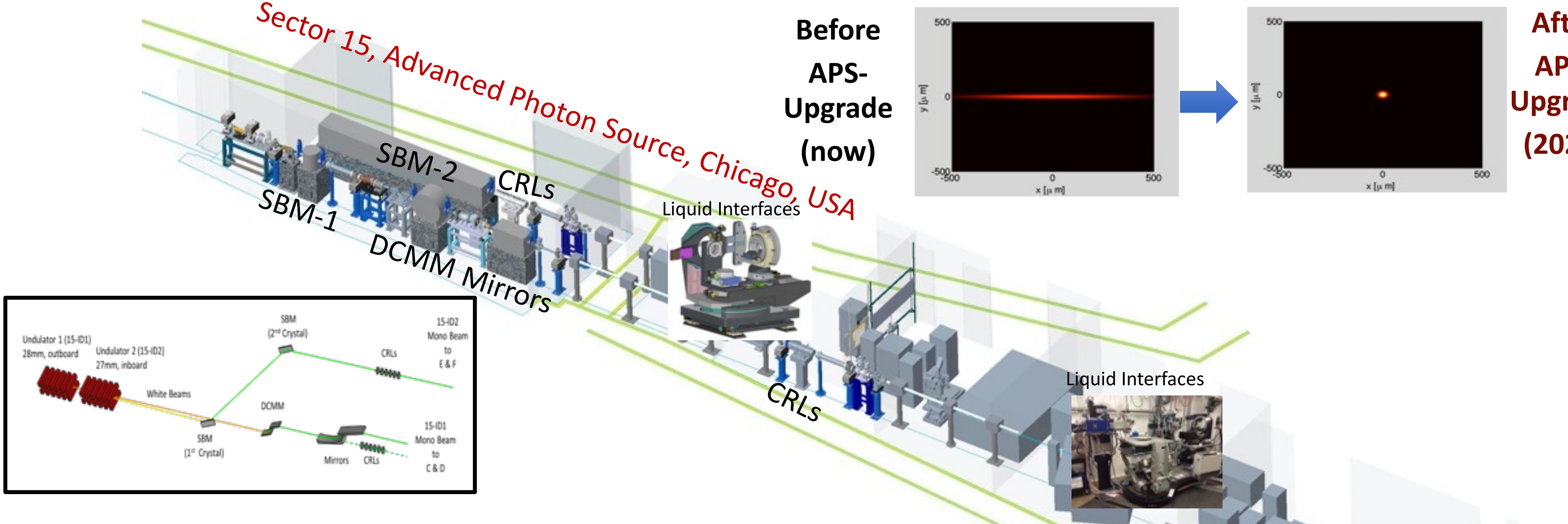
- Single steering crystal geometry
- Large Q-range ($Q_{z\text{-max}}$ of ~3.8 Å^{-1}, in-plane rotation ~ 90˚)
- High spatial resolution

Sector Upgrade: Second, Independent Beamline at NSF's ChemMatCARS

2 independent beams to serve 2 concurrent experiments

Before APS-Upgrade (now)

After APS-Upgrade (2024)



- ➢ Doubled capacity to expand liquid interface science user community
- ➢ New opportunities for liquid interface community
  - ➢ Scattering from Solid-Liquid Interfaces,
  - ➢ Smaller samples for liquid interfaces
  - ➢ Scanning for heterogeneities and defects at liquid interfaces
  - ➢ Lens-less imaging of surfaces with resolution of several nanometers
  - ➢ Enhanced scattering from buried liquid-liquid Interfaces

Acknowledgment

NSF's ChemMatCARS Team

Funding

(U.S.) National Science Foundation

Divisions of Chemistry and
Materials Research
in Directorate of Math and Physical Science
(NSF/CHE-1834750)
for operations

Divisions of Chemistry in MPS,
CBET in Engineering,
MCB and DBI in Biological Sciences,
(NSF/CHE-1836674)
for construction of a second beamline