WORKSHOP ON MESOSCOPIC AND NANOSCOPIC SCIENCE USING X-RAY TECHNIQUES

Eric Isaacs (ANL/U of C)

Sunil Sinha (UCSD/LANL)

Thanks to Gopal Shenoy (ANL)

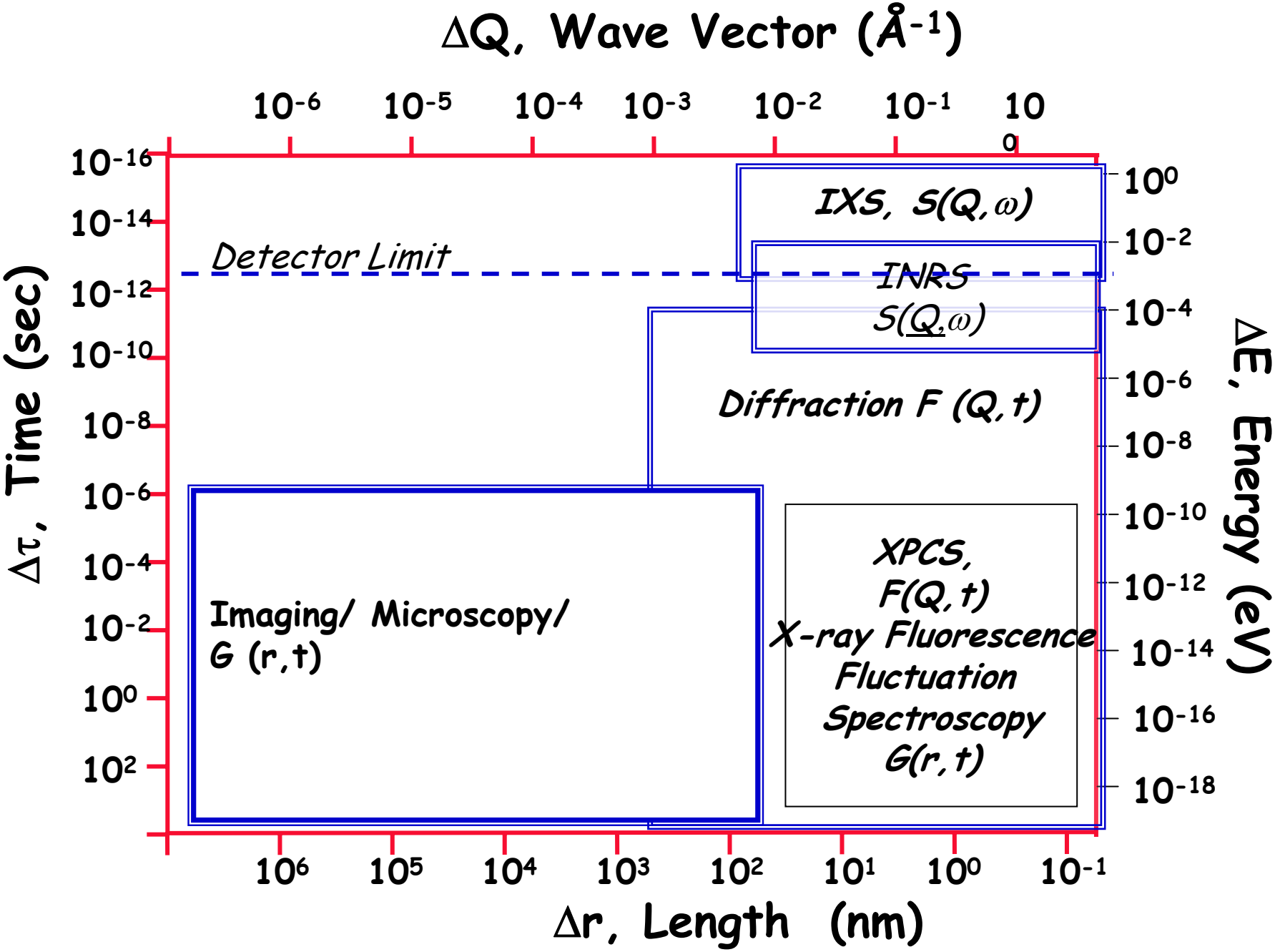
Workshop Chairs

August 29 – September 1, 2004, The Abbey, Fontana, Lake Geneva Area, WI

Grand Challenges In Understanding Mesoscopic and Nanoscopic Materials Properties and Opportunities for X-ray Techniques to Address them

Generic Challenges . . .

To explore and develop new approaches to the fabrication, characterization, and understanding of *nanoscale confined materials*, including but not limited to patterned, self-assembled and hierarchically assembled heterostructures, with *new functionality.*


ΔQ, Wave Vector (Å-1)
10-6
10-5
10-4
10-3
10-2
10-1
100
Δτ, Time (sec)
10-16
10-14
10-12
10-10
10-8
10-6
10-4
10-2
100
102
ΔE, Energy (eV)
100
10-2
10-4
10-6
10-8
10-10
10-12
10-14
10-16
10-18
Detector Limit
IXS, S(Q,ω)
INRS
S(Q,ω)
Diffraction F (Q,t)
Imaging/ Microscopy/
G (r,t)
XPCS,
F(Q,t)
X-ray Fluorescence
Fluctuation
Spectroscopy
G(r,t)
106
105
104
103
102
101
100
10-1
Δr, Length (nm)

DOE BES Initiative for Nanoscience & Nanotechnology: NSRCs and Facility Integration

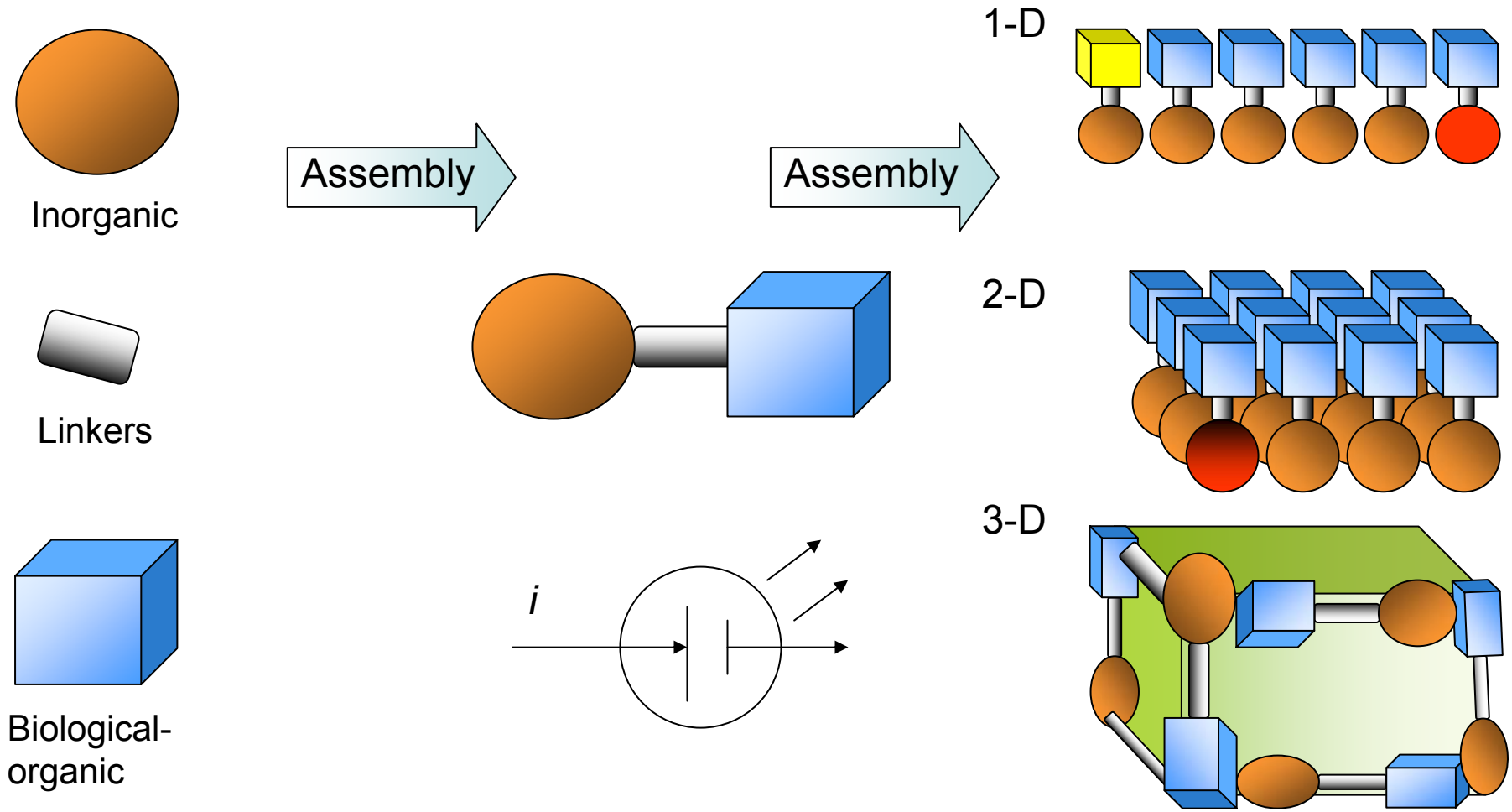
- DOE's 5 NSRCs
  - The Center for Nanophase Materials Sciences (ORNL)
  - The Molecular Foundry (LBNL)
  - The Center for Functional Nanomaterials (BNL)
  - The Center for Integrated Nanotechnologies (SNL-LANL)
  - Center for Nanoscale Materials (ANL)

Workshop Focus

- Controlled synthesis
- Directed Assembly
- New properties

Principles: Design, synthesis, assembly

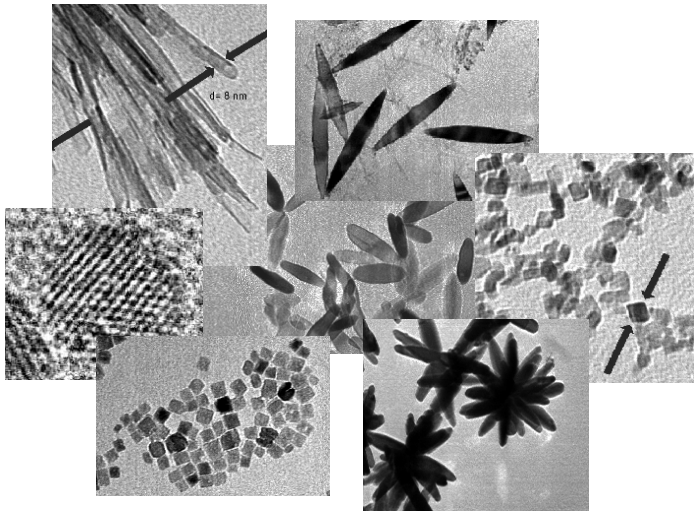
Building Blocks **Functional Units** **Functional Assemblies**



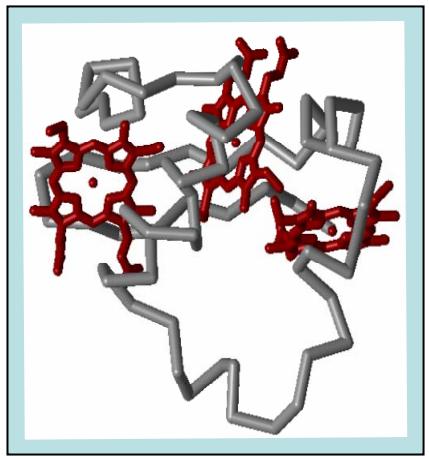
Synthesis of Building Blocks

Building Blocks: Nanoparticle Libraries

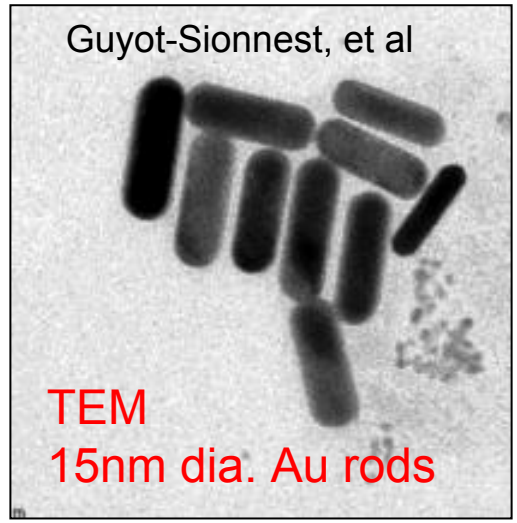
Rajh, et al

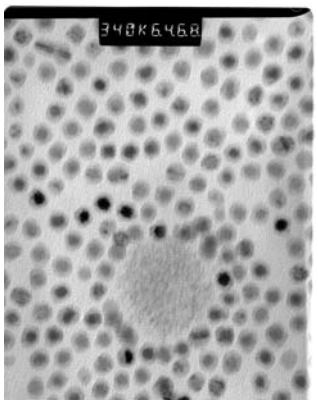


TiO_2 semiconductor

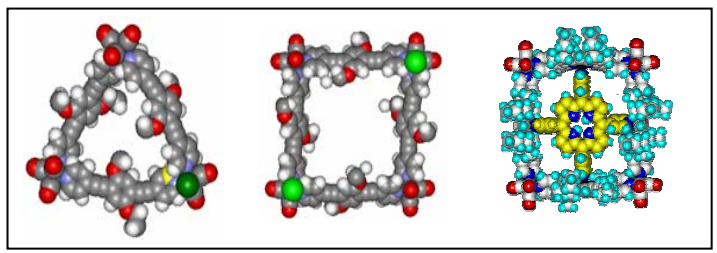


bio-molecules, eg.
cytrochrome c7





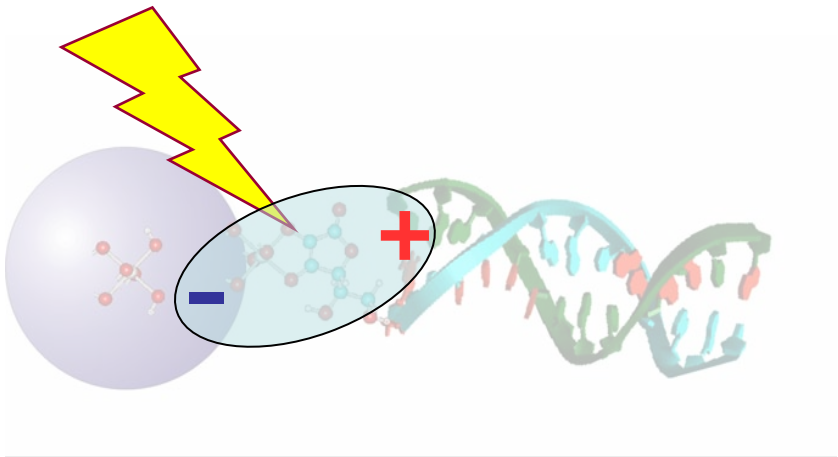
Co-CoPt
core-shell magnetic
nanoparticles
X.-M. Lin, et al



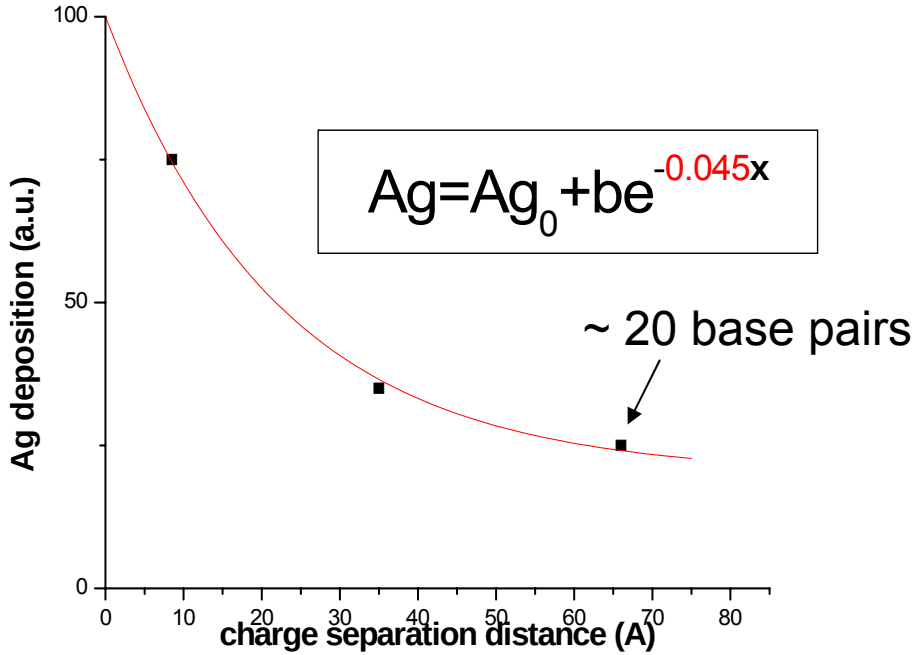
synthetic molecular assemblies
J. Hupp, et al.

Can we improve on Nature?
Bio-inorganic Functional Unit:

T. Rajh, et al, ANL



DNA-TiO_2- nanoparticle assembly



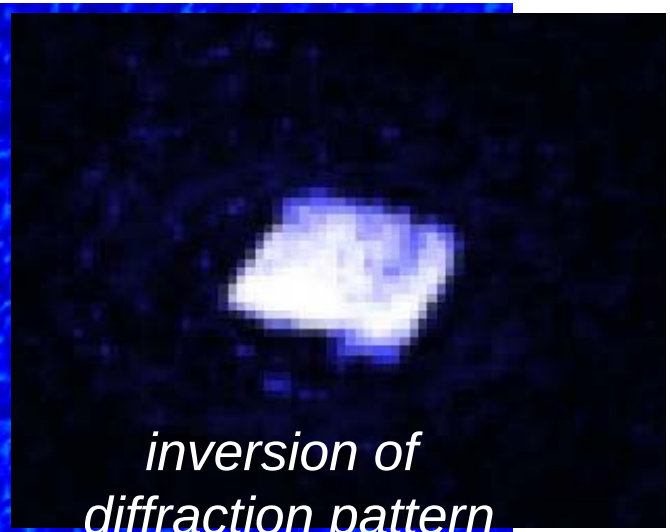
charge separation over large distances (~ 60 Å)

- photo-conversion
- in-vivo gene surgery
- catalysis, …

Imaging of individual nanoparticles at the APS

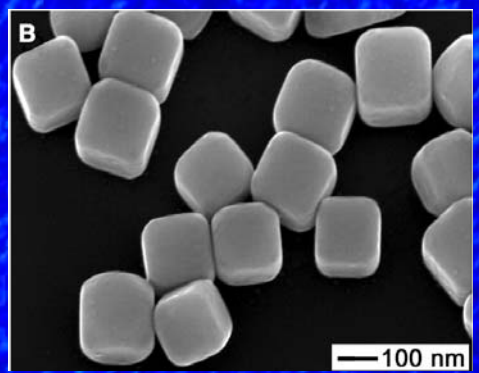
Ross Harder, University of Illinois, Champaign

Coherent diffraction pattern from 170 nm Ag particle



inversion of diffraction pattern 'lensless imaging'

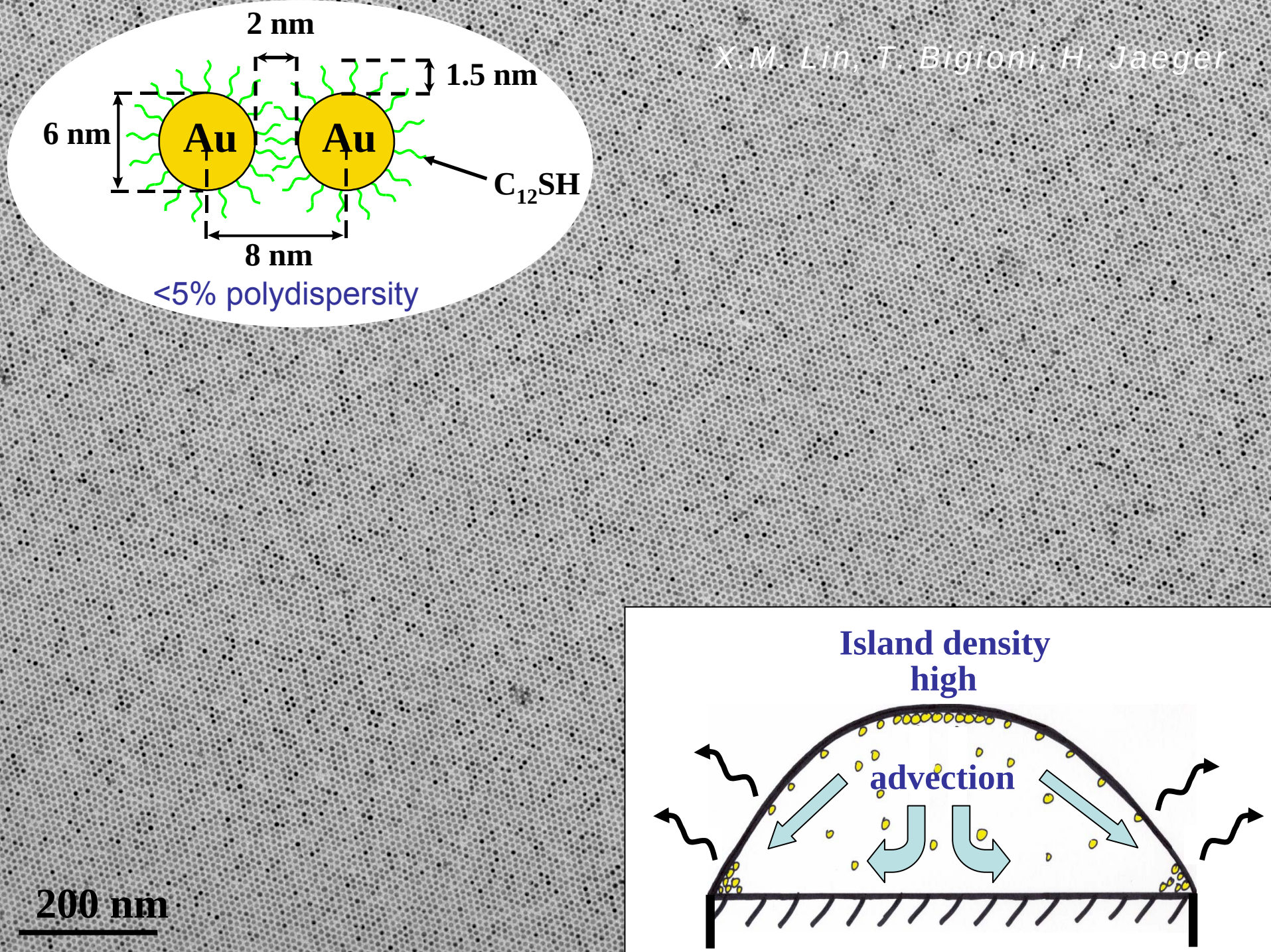
170 nm silver cubes



5×10^{-2} nm^{-1}

I.K. Robinson, et al., Science 298 2177 (2003)

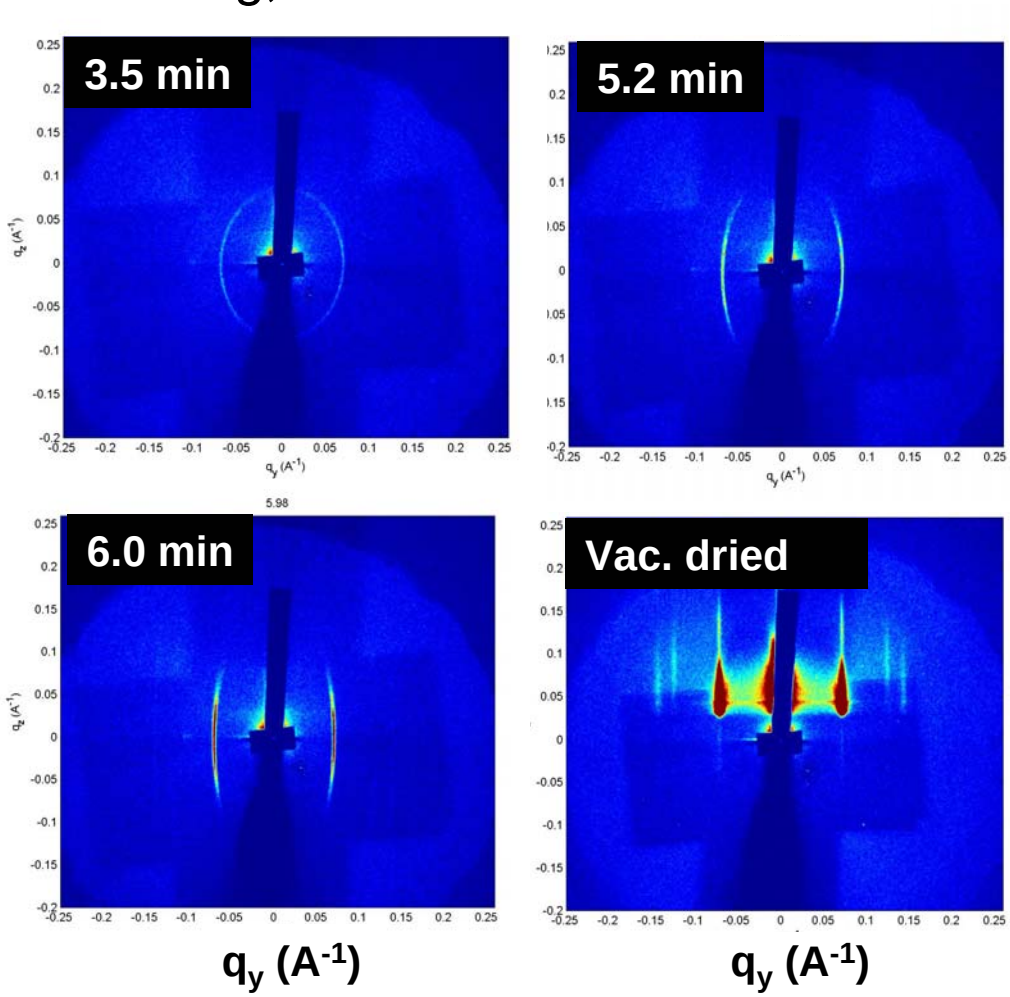
Self-assembly &
Directed Self-assembly

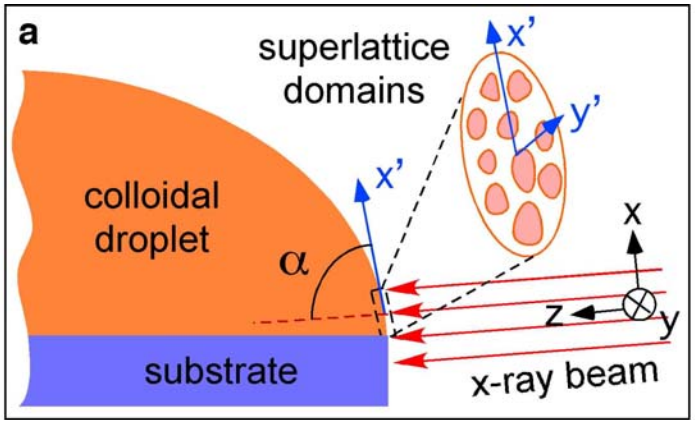

X.M. Lin, T. Bigioni, H. Jaeger
2 nm
1.5 nm
6 nm
Au
Au
$C_{12}SH$
8 nm
<5% polydispersity
200 nm
Island density
high
advection

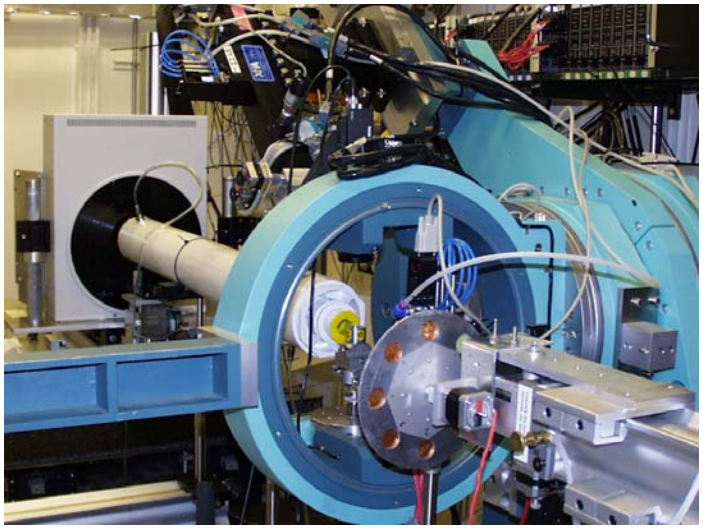
In-situ monolayer growth with GISAXS at APS

key feature: lattice assembles at droplet's *top surface*

Jin Wang, APS





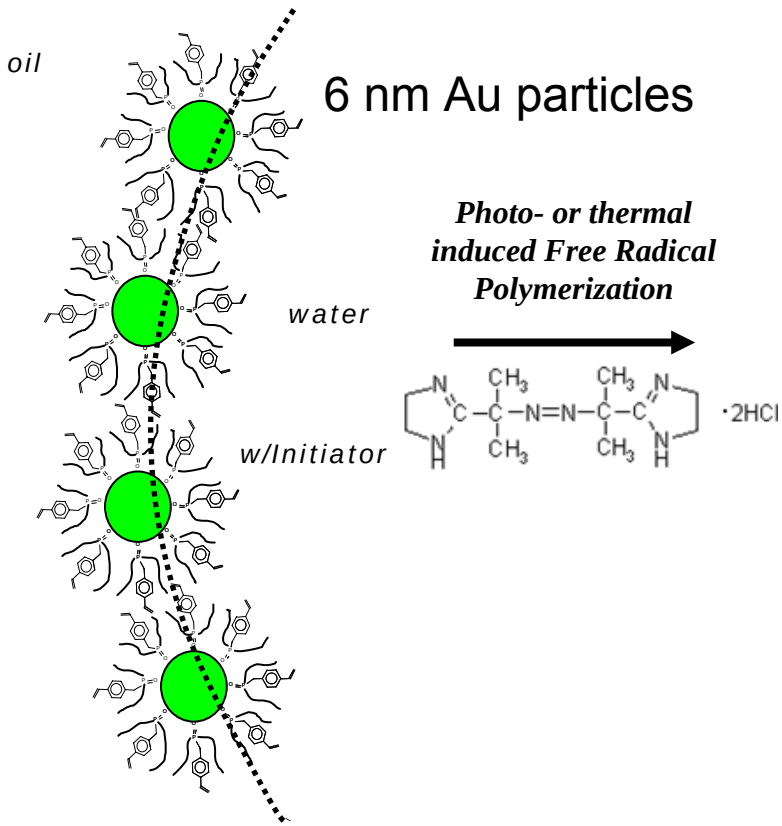


Narayanan, Wang & Lin, PRL (2004)

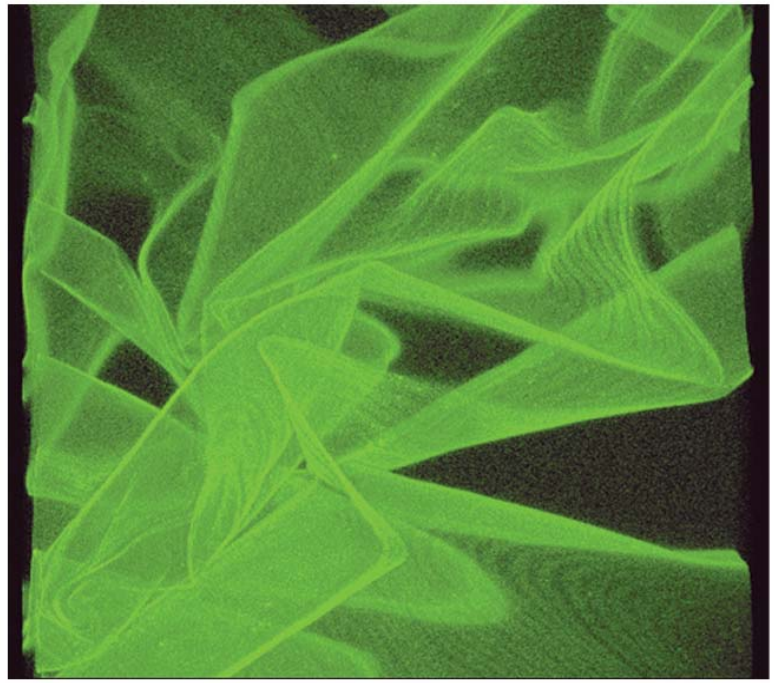
Exp't /theory/simulations: Kinetics versus Energetics

Ultra-thin Membranes

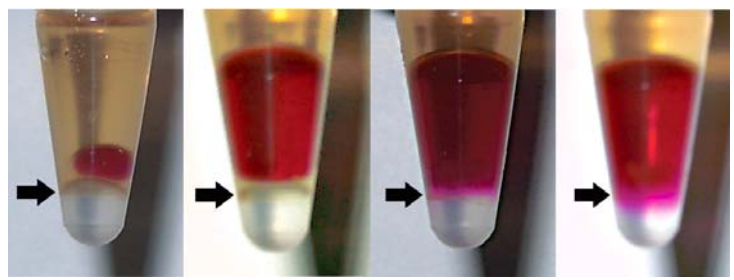
Yao Lin, U Mass, Amherst



Membrane taken out from flat interface



Membrane as a diffusion barrier

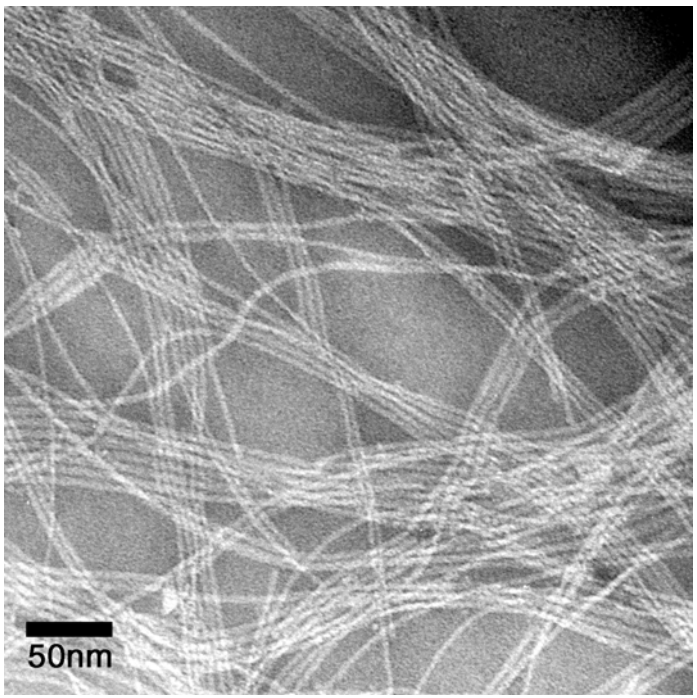


Goal: membranes with specified nanopores.

Simulating Self-Assembly

Mark Ratner, Northwestern

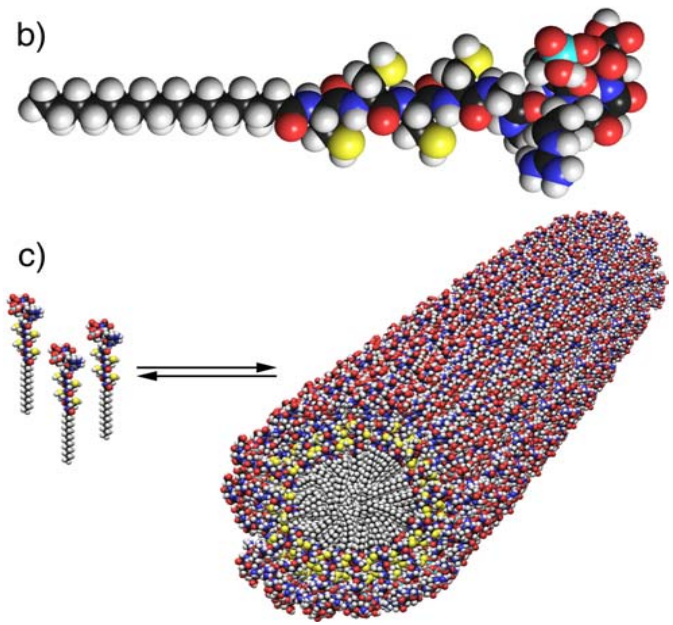
- Monte-carlo
- Molecular dynamics
- Rule based (agent) models



***Stupp et al, Science*, 294, 1684 (2001).**

self-assembled bioactive nanofiber – cylindrical micel

hydrophobic hydrophilic



What is the actual structure?
What are pathways of growth?
New growth pathways
e.g., SAXS, WAXS.

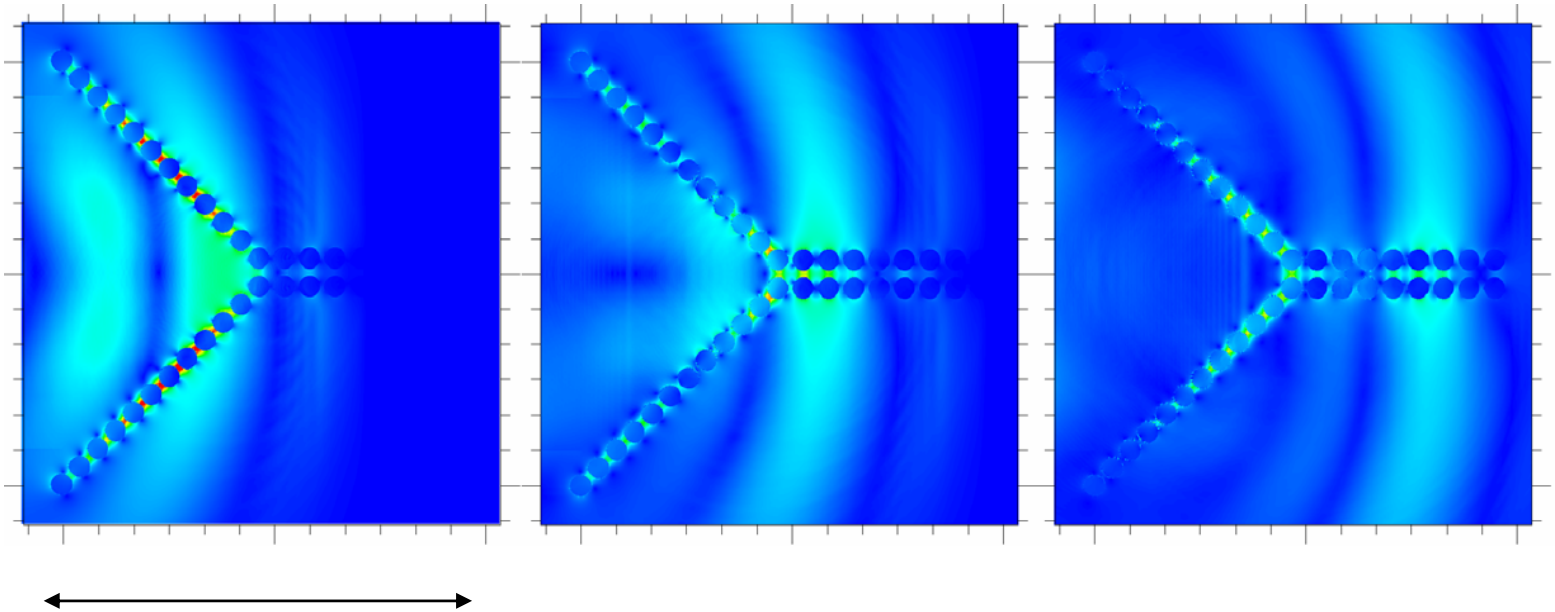
Nanomaterials with New Properties

- New behaviors
- Quantum liquids
- Nanobio medical

Silver Nanoparticle Optical Waveguides

Stephen Gray, ANL

E field at 0.5 fs time intervals:



600 nm

Can achieve sub-100 nm confinement of 1 μm light.

[Gray and Kupka, Phys. Rev. B** 68**, 045415 (2003)]

Finite Size effects in Ferroelectrics

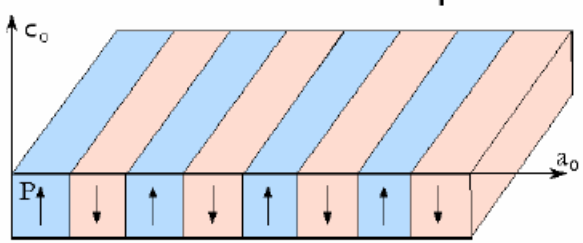
Carol Thompson, Northern Illinois University

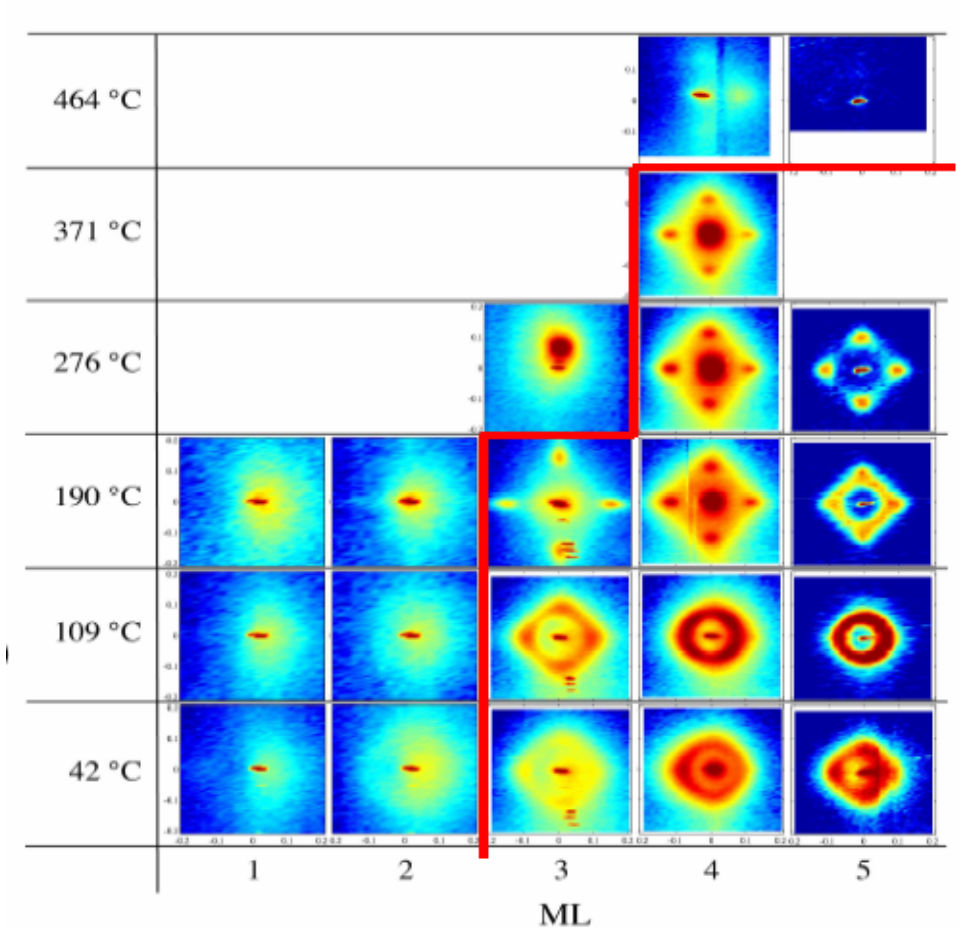
How thin is too thin?

In-situ diffraction studies of $PbTiO_3$ at the APS, BESSRC (12ID).

Striped domains

– 10nm film ~ 10nm period



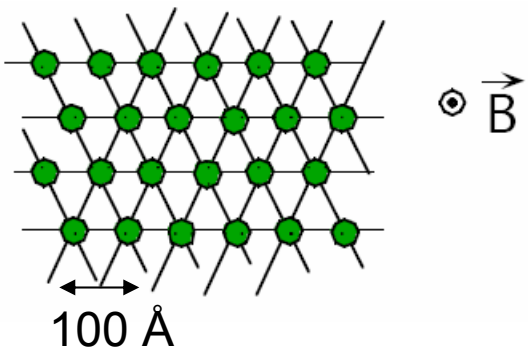


Fong, et al., Science 304, 1650 (2004)

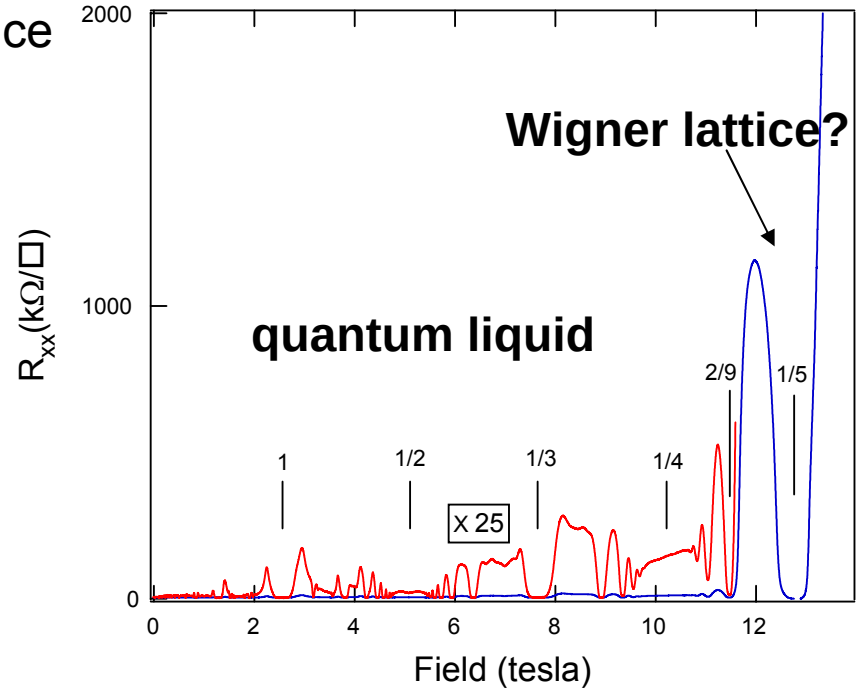
Mesoscopic Phases in Two-Dimensional Electron Systems

Woowon Kang, U of Chicago

- Wigner lattice – electrons form 2D lattice in a large magnetic field



- Quantum liquid, integer and fractional quantum Hall (B intermediate)
- Striped phases?

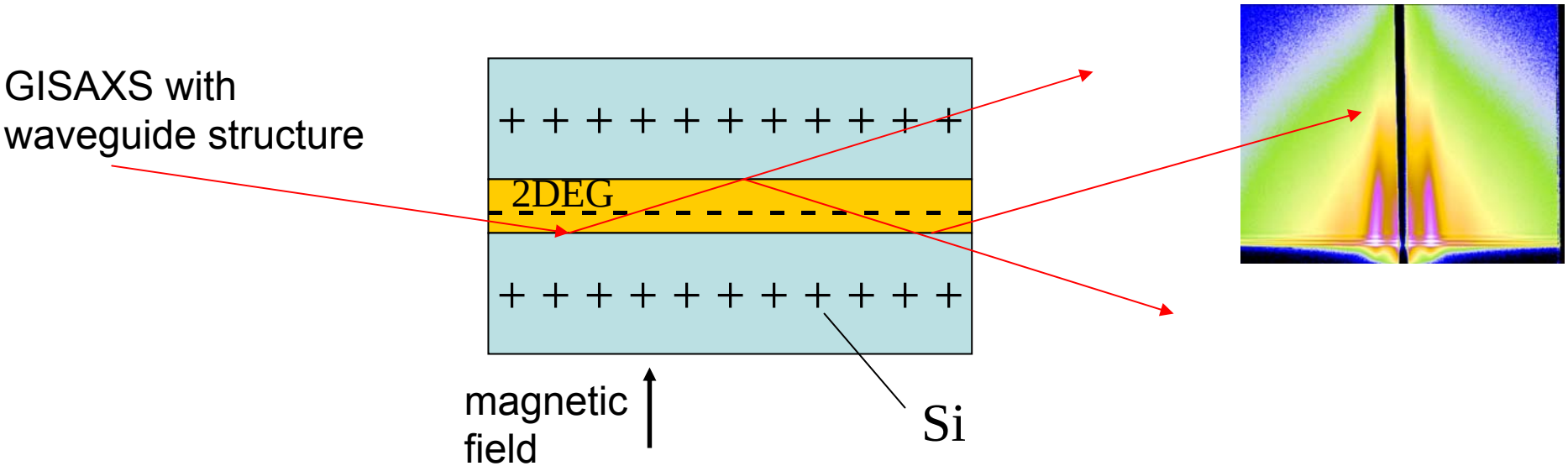


Transport: inadequate to prove electron crystallization

Missing: diffraction pattern & S(q)

X-ray Study of 2D Electron Systems

2D electron gas in GaAs or multilayer 2DEG

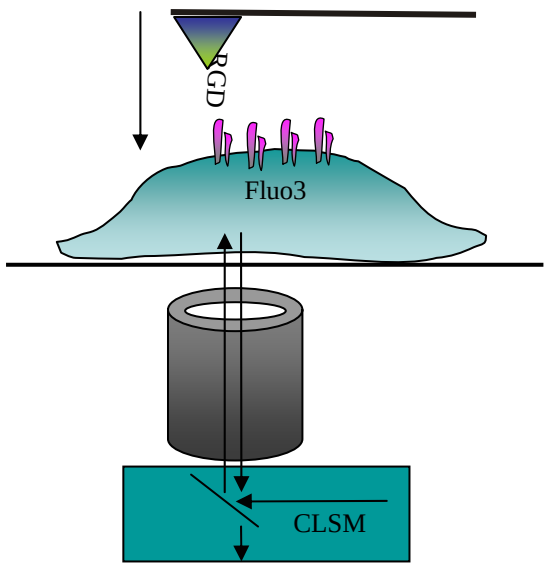


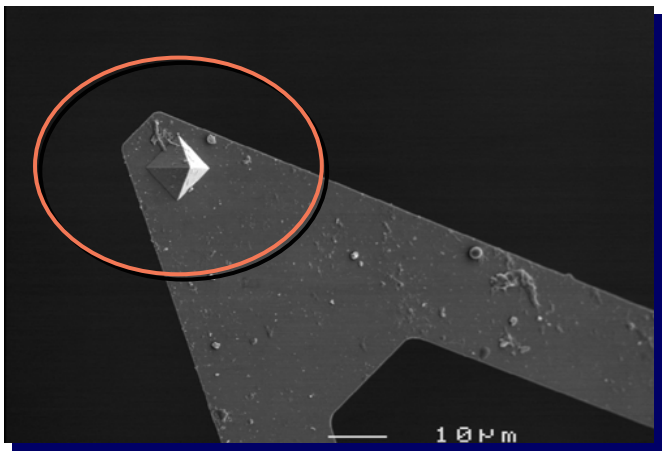
- Challenge: low T, high B; low density of electrons
  Adequate beamtime (tour-de-force experiment)
- Measure S(q) in Wigner crystal/FQHE/Stripe phases
- Resonance enhanced GISAXS at atomic resonance.

Nano-bio Medical

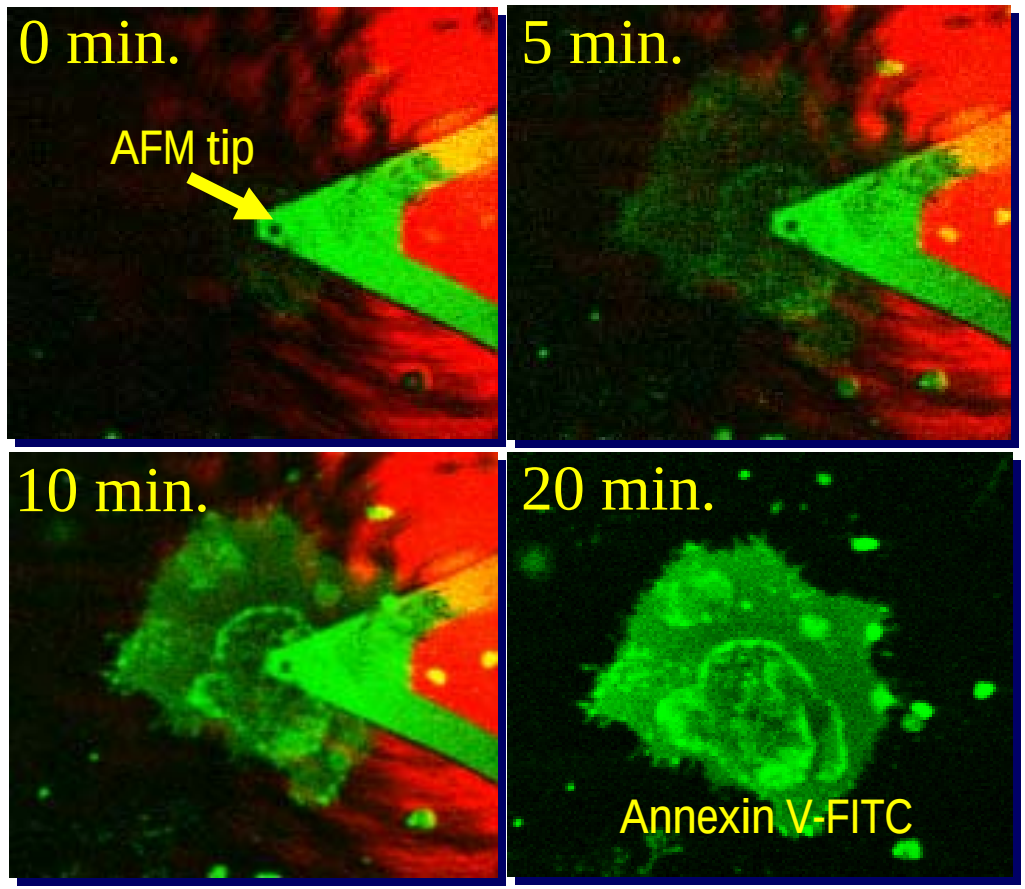
Towards Treatment and Disease Dynamics – direct drug delivery to live cells

Gabriel Aeppli, London Center for Nanotechnology





Combines AFM w/confocal microscopy



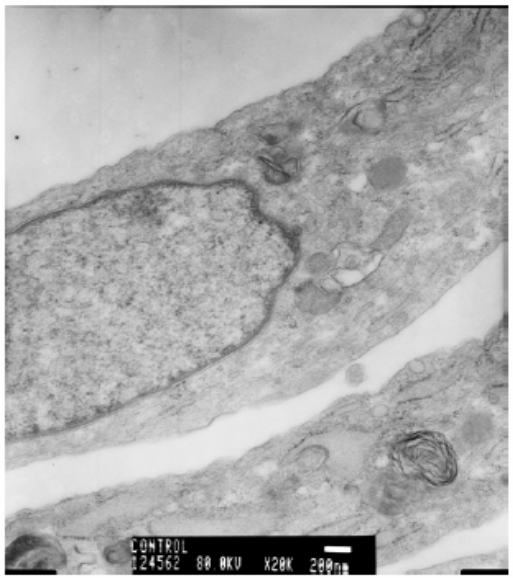
Example of nanomanipulation

Societal and Health issues

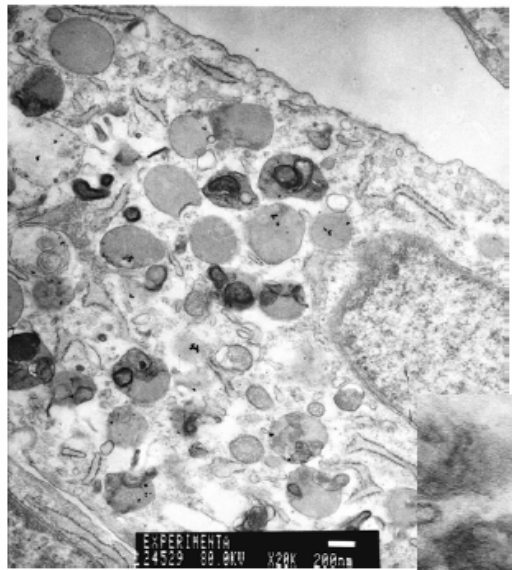
Miriam Rafailovich, SUNY Stony Brook

Effect of 10 nm gold particles on living tissue.
Au is FDA approved for internal medical use.

Human dermal fibroblast.



6days-Control



6days-Nano

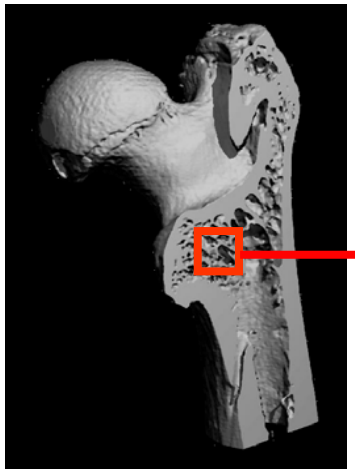
Vesicles with nanoparticles

From the cross-section image of cells under TEM, nanoparticles were found inside of cells and clustered in vacules.

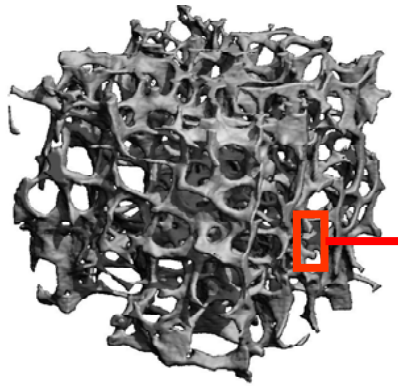
OSTEOPOROSIS NEEDS NANOTECHNOLOGY

Gabriel Aeppli, London Center for Nanotechnology

Whole bone

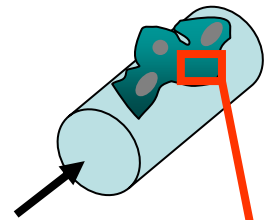


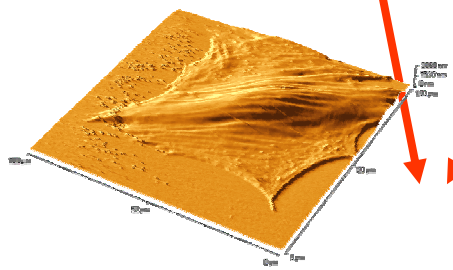
Trabecular bone



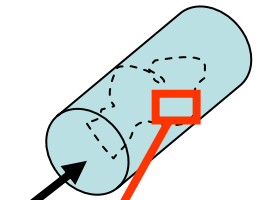
Cellular level

Surface osteoblasts





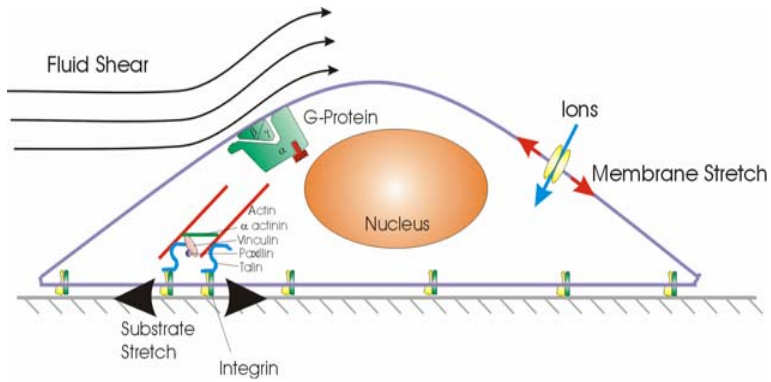
Osteocyte



if sufficiently large …
detection, reaction to,
propagation of signal …

and adaptation
- new bone added or removed

Deformation of cell membrane



Nanocharacterizations

- ***GISAXS***
- ***microbeam***

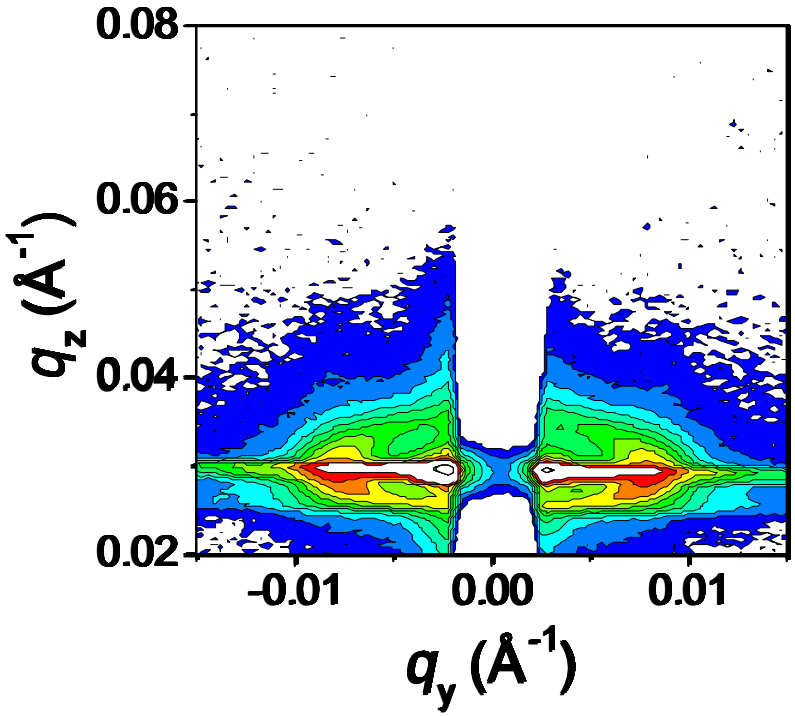
- ***coherent techniques***
- ***ensemble characterization***

In-situ & real time GISAXS: Diblock copolymer film exposed to solvent vapor

Detlef Smilgies, CHESS, Cornell University

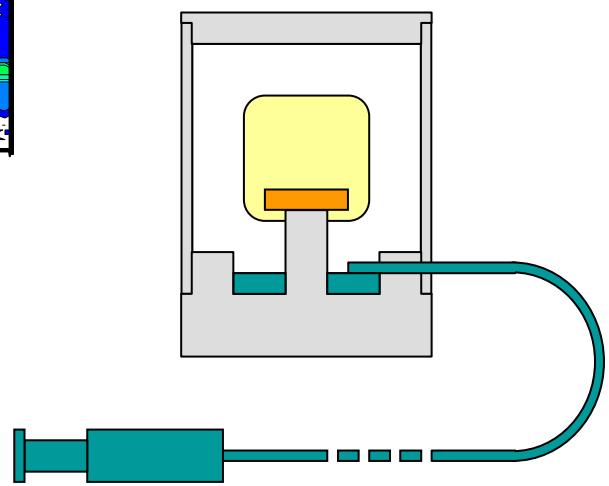
→ 1 image per 40 sec

→ 0.75 -17 min after exposure



183 kg/mol,
D_{lam}= 836 Å,
D_{film} = 2340 Å

sample cell



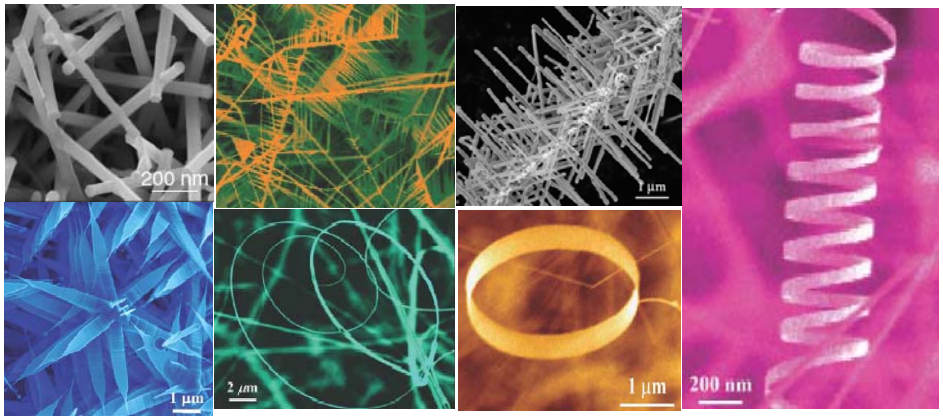
Bragg rods shorten and bend:

- increase of lamellar thickness
- change of lamellar orientation during vapor treatment

Smilgies, Busch, Posselt & Papadakis, SRN 15(5), pp. 35-41 (2002).

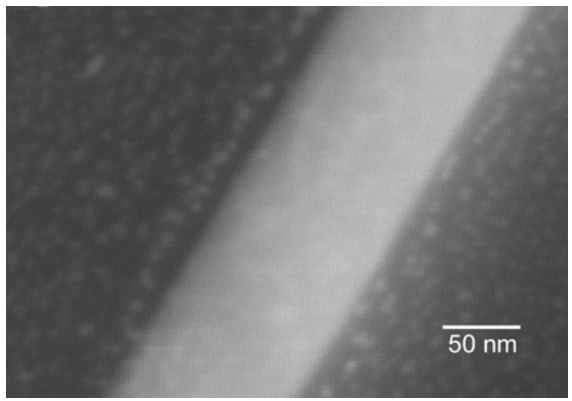
Structures of tin oxide nanobelts with microbeams

Metal oxide nanobelts with rich morphologies

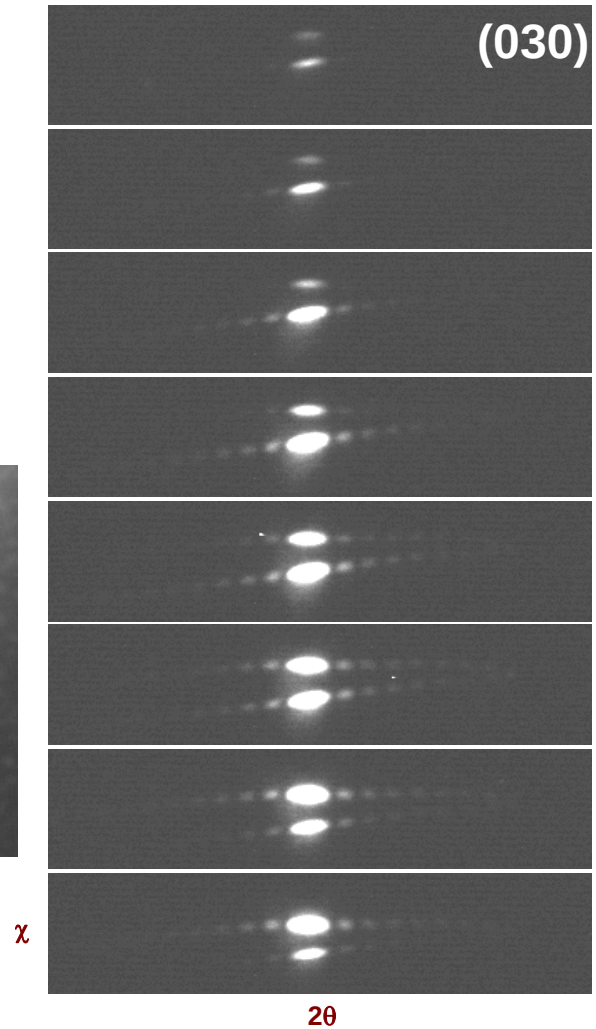


Sensitivity today:
20 nm x 20 nm x 200 nm

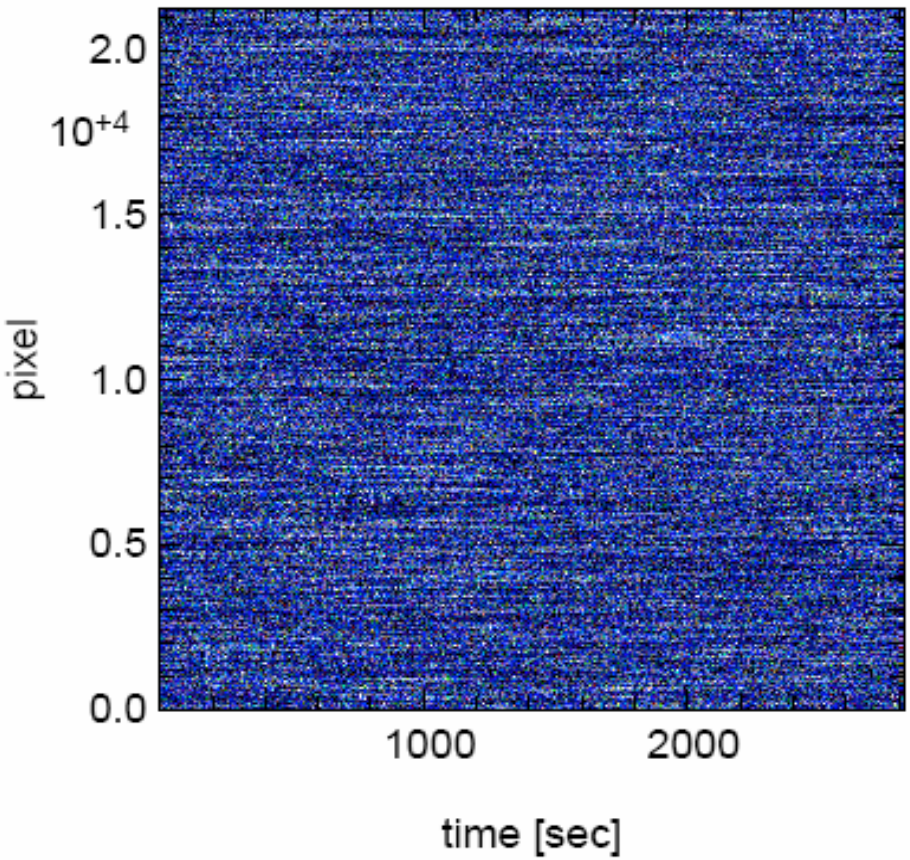
Ultimate at APS:
< 10 nm x 10 nm x 10nm



Single grain boundary in Sn_2O_3 nanobelt



Equilibrium fluctuations of Gold nanoparticles (Brownian Motion) with XPCS



Time fluctuations in coherent scattering

Gold nanoparticles in polystyrene matrix

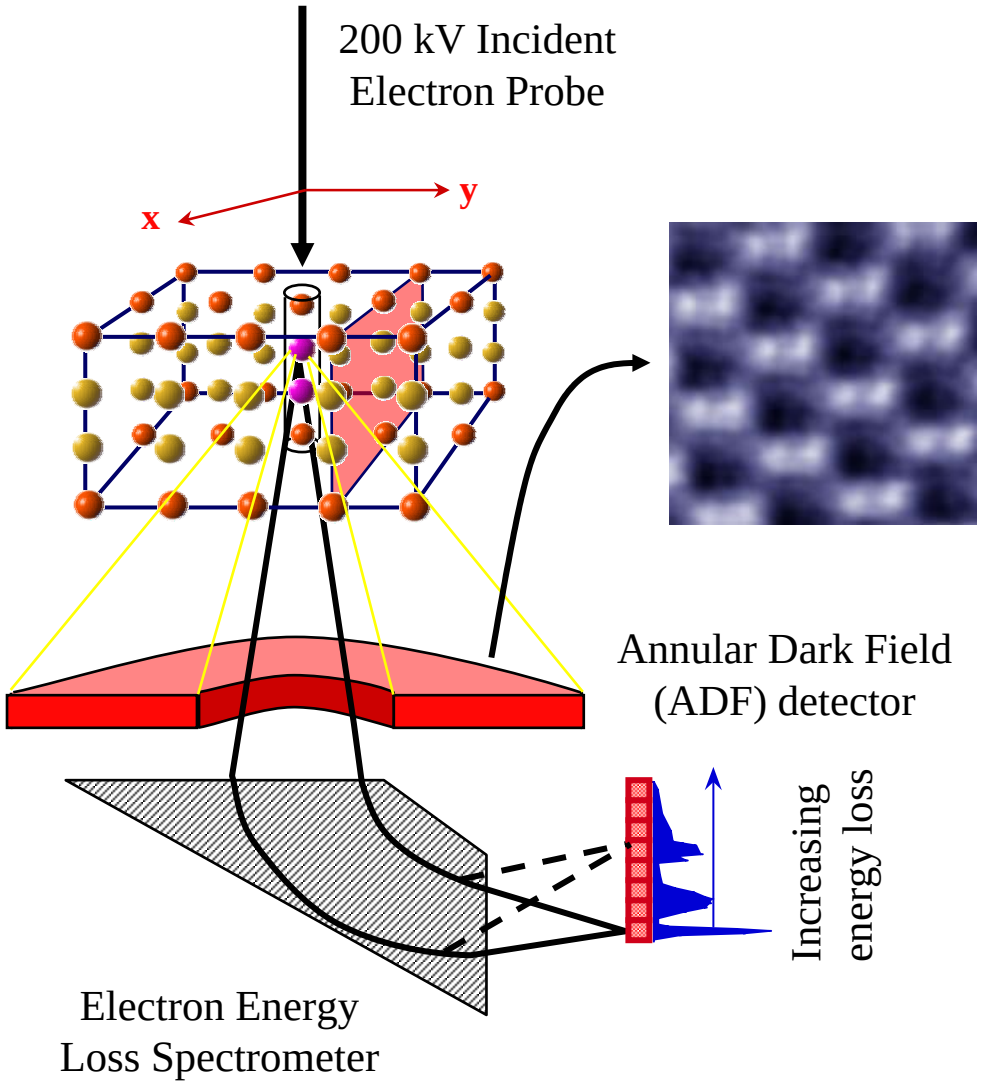
$$g_2(\vec{q},t) = 1 + \beta\left[\frac{S(\vec{q},t)}{S(\vec{q},0)}\right]$$

Complementary characterizations

- Develop APS tools that complement, not compete, with better alternatives.
  - eg., electrons, neutrons, optical, scanning probes.
  - Advantages of x-rays
    - In-situ, high resolution, penetration, generally non-destructive, trace element sensitivity, polarization, finite-q, global statistical averages, time domain, structure.

Scanning Transmission Electron Microscope

Paul Voyles, UW, Madison

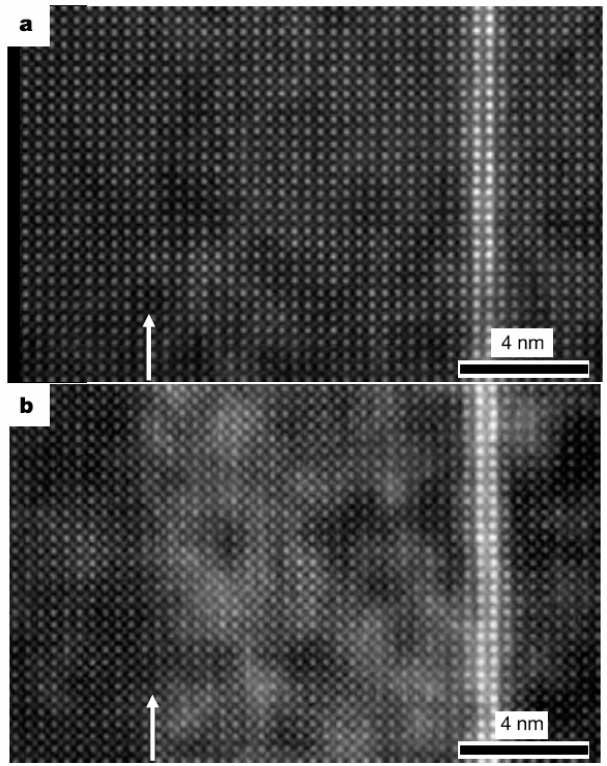


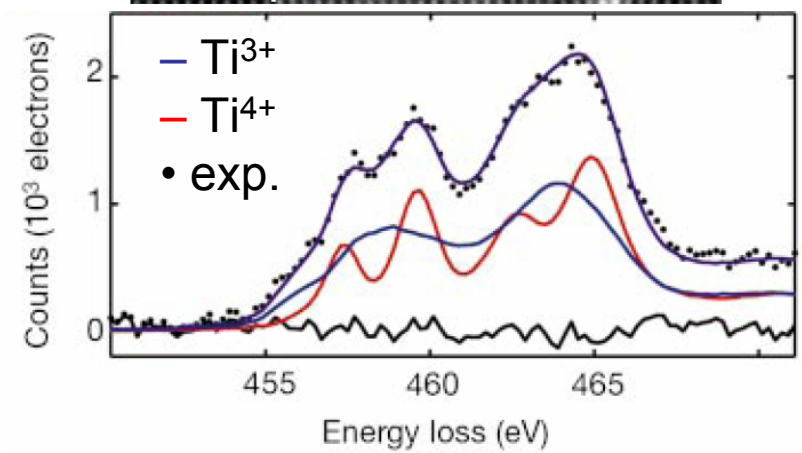
Capabilities:

- sub-Ångstrom resolution imaging
- <0.15 eV spectroscopy at 2 Å real-space resolution
- diffraction from volumes sub-nm to a few μm in diameter.
- imaging of large, localized strains associated with extended defects

O Vacancies in $SrTiO_3$

- Muller et al., Nature **430,** 657 (2004).
- PLD homoepitaxial $SrTiO_{3-\delta}$; δ varied by O partial pressure
- Vacancies appear in
  - O K-edge fine structure directly
  - Ti $L_{2,3}$ edge, which is sensitive to Ti valence
  - LAADF image via strain-induced dechanneling
- Detection limit 1-4 O_V





Recommendations for Nanoscience at the APS

Nanoscience at the APS

It is recognized that the APS already supports and develops many of the tools required for nanoscience….

- Microprobe, coherent diffraction (proof of principle, so far), GISAXS, SAXS.
- Extensive experiments impacting nanoscience.

… and should continue to do so at a high level.

APS should continue to explore and support development of new techniques as they become possible and to nurture the evolution of demonstration experiments to routine application, eg., coherent imaging.

'High-throughput' characterization

- **Expect a big demand for GISAXS, SAXS, reflectivity**
- **Workshop recommends a dedicated instrument (e.g., sector 8).**
- Powder diffraction (APS)
- Nanoprobe (CNM)

- Predominantly Users w/o synchrotron experience requires User friendly, beamline support/instrumentation.

- Coordination of access and tool development.

In-Situ Experiments

- In-situ and real-time experiments clearly spans the full range of synthesis, assembly and properties characterization.
- Workshop recognized that in-situ often requires extended setup and characterization time, substantial support, adequate hutch space.
- Recommendations:
  - Dedicated programs for in-situ studies.
  - Hardware that resides in-place for extended periods.
  - Adequate access time.

Scientific Environment at APS

- APS scientists who do world-class science and develop new techniques are critical.
- APS resident theorists, e.g., with interests in nanoscience.
- Coordinate with CNM, e.g, Virtual Fab Lab for theory.

- Develop community codes for data analysis.
  - e.g., inversion of coherent diffraction.
  - Like to do this during beamtime.

Instrumentation

- Optics development.
  - High numerical aperture focusing optics.
    - 80 nm today, want < 30 nm (CNMs Nanoprobe).
    - Zone-plates, mirrors, & refractive lenses.

- Sample manipulation technique development.
  - Positioning 30 nm particle in 30 nm beam.
  - Scanning sample – e.g., piezos.
  - Orientation (e.g., ‘sphere of confusion’)
  - All of the above with environment control (in-situ).
  - Optical tweezers?

Instrumentation

- High resolution area detector development.
  - XPCS, coherent diffraction, GISAXS, high res diffraction/scattering, …
  - Megapixel CCD.
  - 20 μm pixels.
  - Full frame per microsecond (10^{12} bits/sec!).
  - Unit quantum efficiency.

Outreach

- Building a Nanoscience User community at the APS.
  - High impact scientists.
  - Education: nanoscience representation at N/X summer school.
- CNM will bring many non-x-ray expert users to ANL and the APS.
- Infrastructure for occasional or even one-time Users.
  - User shows up with a sample and leaves with data.

Some Grand Challenges for Nanoscience with X-rays

- Imaging with x-ray wavelength resolution.
- 3D structural, electronic, magnetic and chemical properties at the nanoscale.
  - Single and ensembles of nanoparticles.
- Dynamics of nanoparticles.
- Structure of single macromolecule.
- Theory and modeling.
- Coherent manipulation of nanoparticles.
- Nonlinear x-ray processes.

Workshop participants

Gabriel Aeppli, UCL
Mike Bedzyk, Northwestern
Zhonghou Cai, APS
Massimiliano Di Ventra, UCSD
Stephen Gray, ANL
M. Grimstitch, ANL
Alex Groisman, UCSD
Ross Harder, UIUC
Eric Isaacs, ANL/U of C
Heinrich Jaeger, U of C
Jackie Johnson, ANL
Woowon Kang, U of C
Hyungjung Kim, Sogang U, Korea
Jyotsana Lal, IPNS
Xuefa Li, APS
Yao Lin, U. Mass
Derrick Mancini, ANL
Denis Mills, APS
Miriam Rafailovich, SUNY, Stony Brook
Mark Ratner, Northwestern
Miquel Salmeron, UCSD
Ivan Schuller, UCSD
Sunhil Sinha, UCSD
Detlef Smilgies, CHESS
Brian Stephenson, ANL
Mark Sutton, McGill
Carol Thompson, NIU
Vijay Tirumala, ANL
Avi Ulman (Brooklyn Polytech)
Paul Voyles, UW, Madison
Jin Wang, APS
Yanan Xiao, APS
Hoydoo You, ANL