

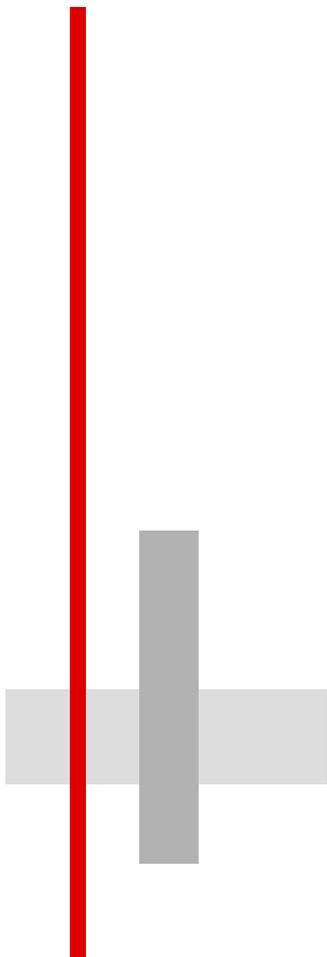
# The Magic of GISAXS:

## Thin Film Kinetics in Soft Materials

Detlef-M Smilgies

CHESS, Cornell University

XIS Workshop, Argonne, Jan 2012



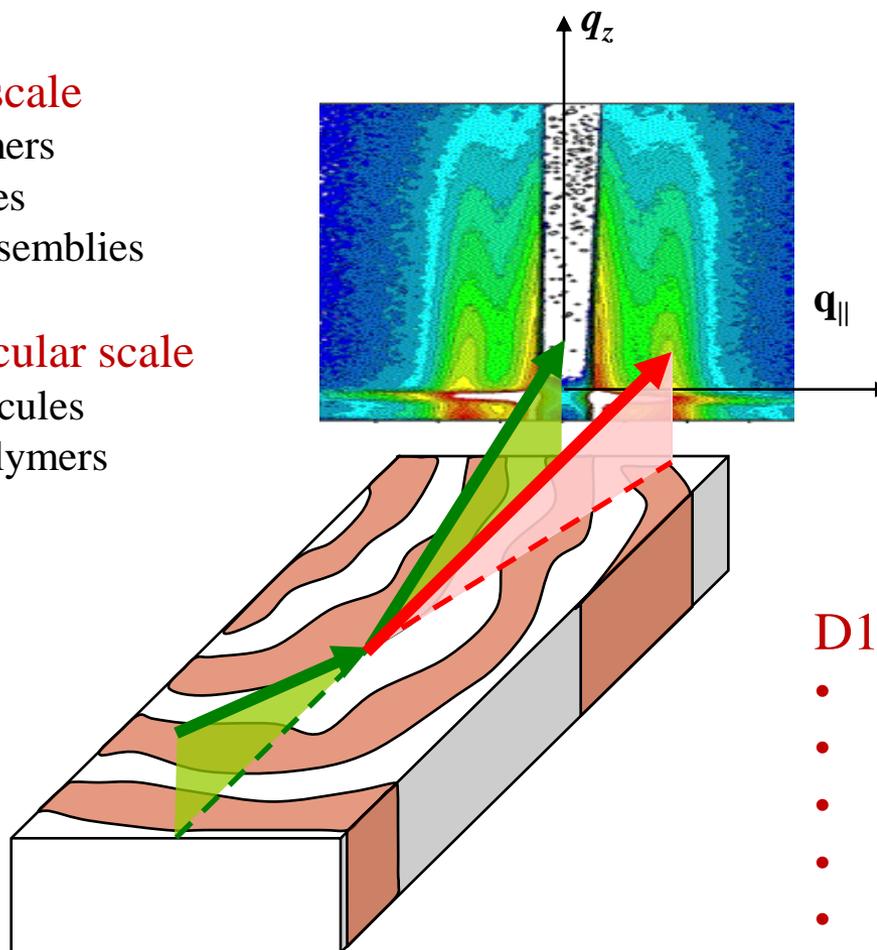
# Grazing Incidence Scattering

## GISAXS > nanoscale

- block copolymers
- nanocomposites
- nanocrystal assemblies

## GIWAXS > molecular scale

- aromatic molecules
- conjugated polymers
- nanocrystals



## D1 in a nutshell

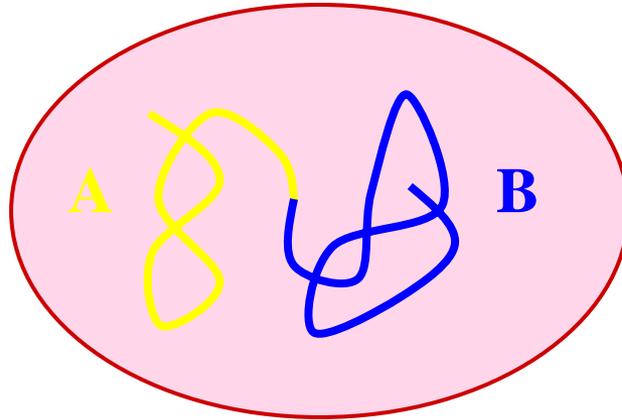
- bending magnet
- multilayer optics
- SAXS slits
- goniometer
- area detector

Smilgies et al., *Synchrotron Radiation News* 15(5), pp. 35-41 (2002).

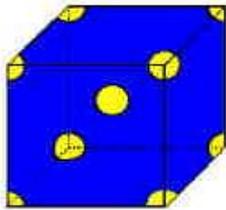
<http://staff.chess.cornell.edu/~smilgies/gisaxs/GISAXS.php>

# Block Copolymer Nanostructures:

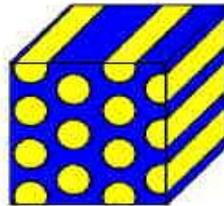
*BCC spheres, HEX cylinders and more*



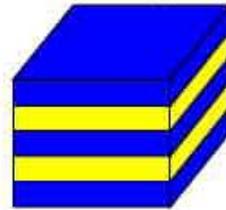
two immiscible polymer chains connected by a chemical bond



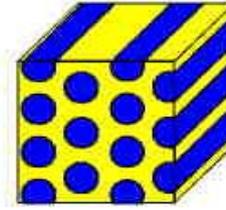
spheres



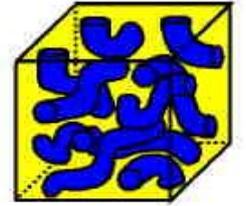
cylinders



lamellae



cylinders

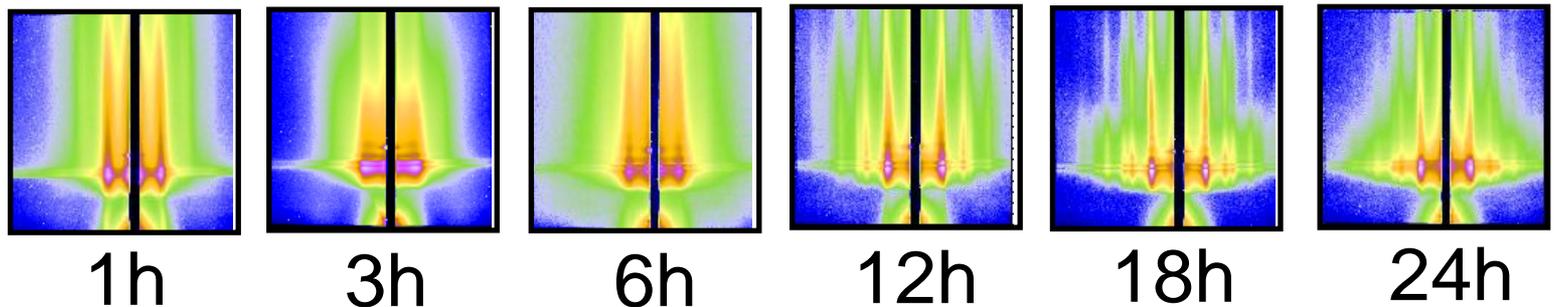


bicontinuous

**>>> Thin Films: Oriented by Substrate <<<**  
**e.g. standing cylinders – lying cylinders**

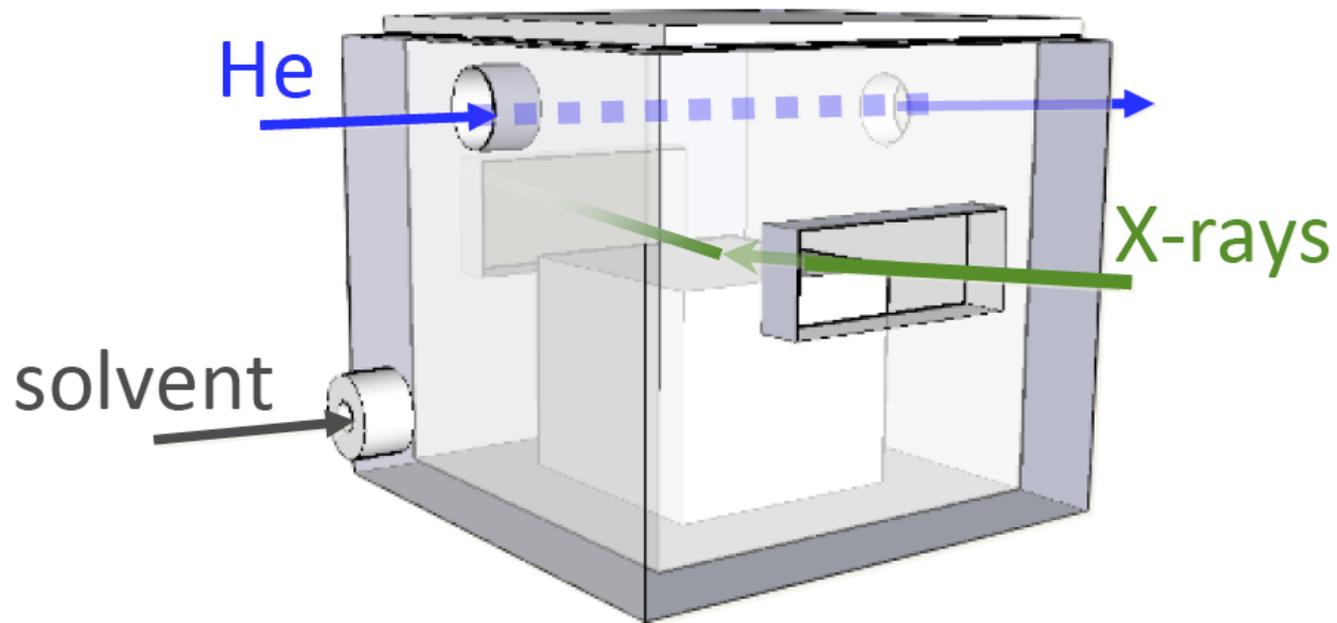
# *Thin Film Dynamics: Solvent Annealing*

spin cast film put in closed container with solvent vapor



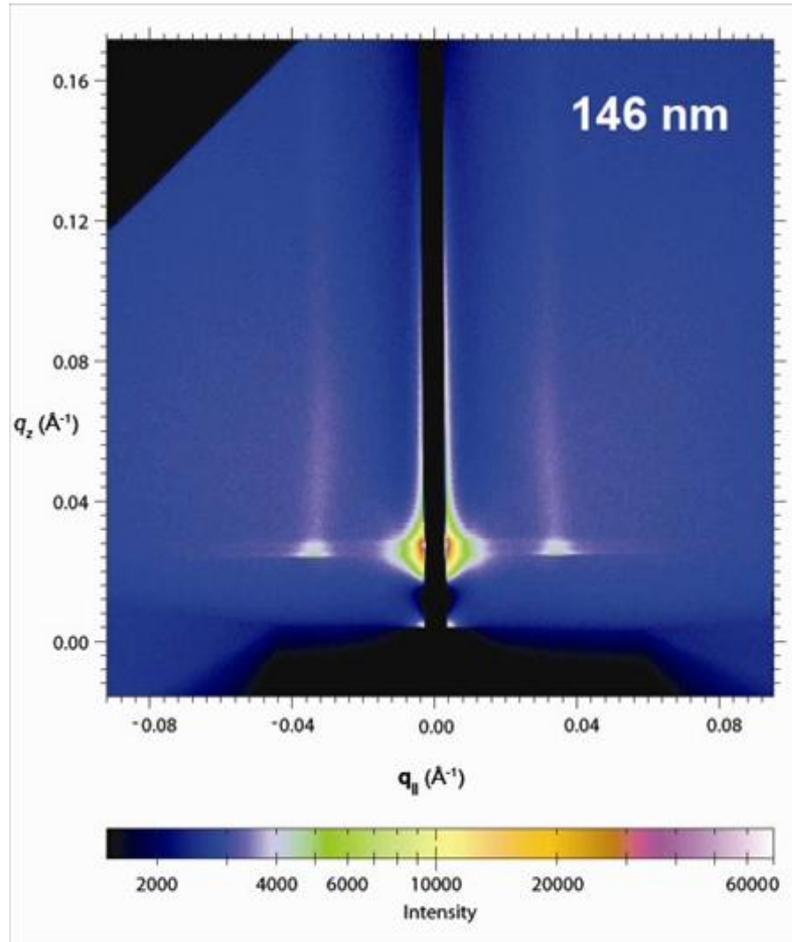
(SBS triblocks: Palta & Bucknall, unpublished)

# *D1 In-situ Vapor Chamber*



- liquid solvent injection
- solvent vapor in purging gas
- rapid drying in purging gas
- optional: film thickness monitor

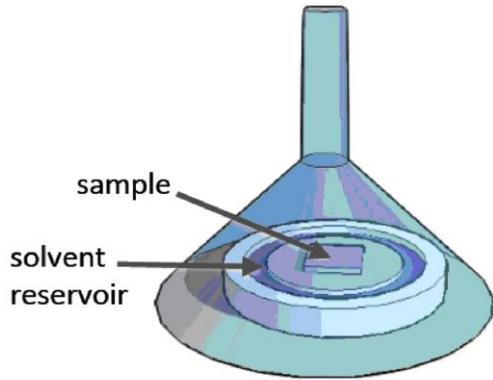
# Selective Solvents: Swelling induced phase transition



PAMS-PHOST  
in acetone vapor

Paik *et al.*,  
Macromolecules 43,  
4253–4260 (2010)

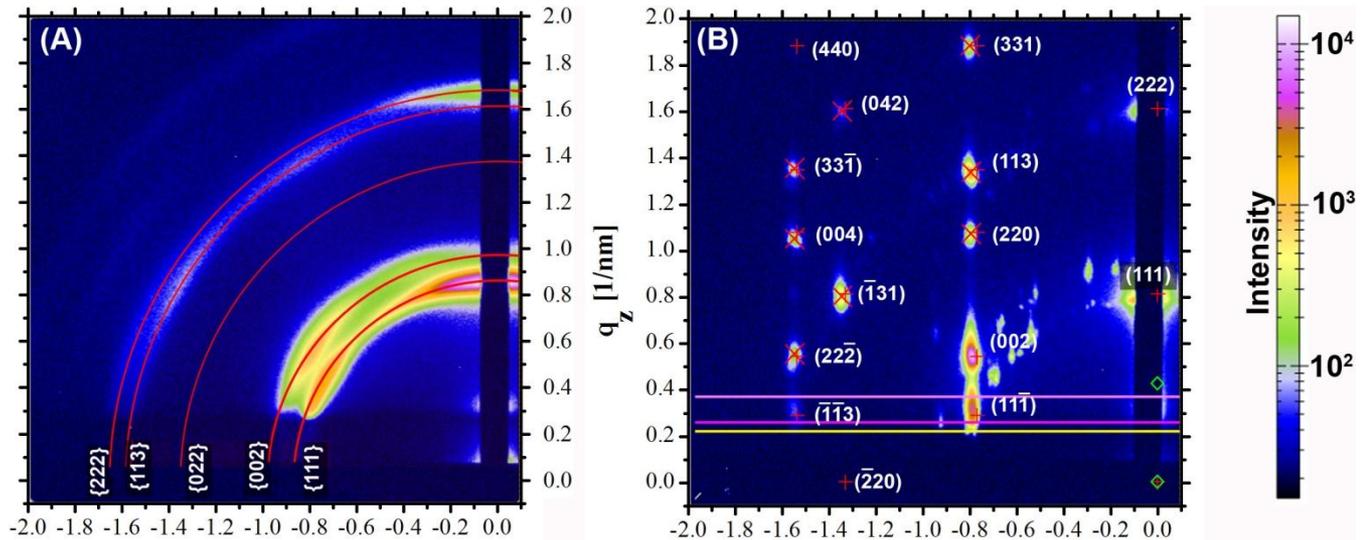
# 3D Nanocrystal Assemblies: Controlled Drying



dropcast PbS NC deposits

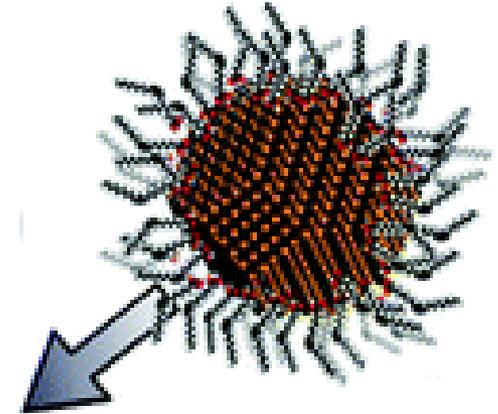
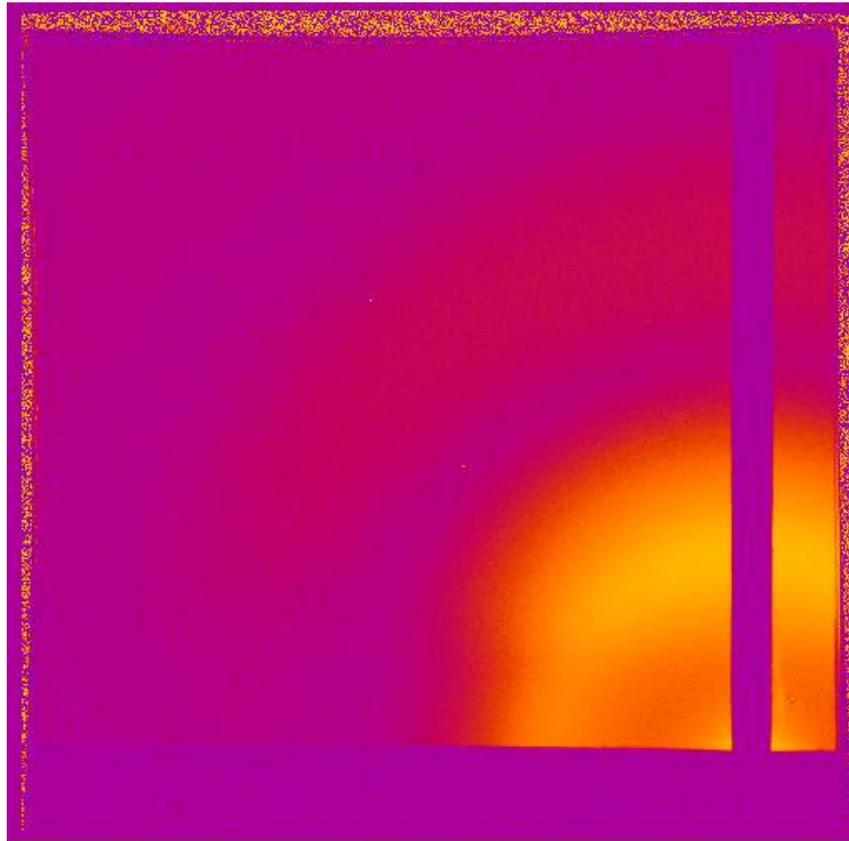
fast drying (4 min)

slow drying (60 min)



Hanrath, Choi & Smilgies, ACS Nano 3, 2975–2988 (2009)

# *Nanocrystal Assembly: in-situ & real-time solvent annealing*

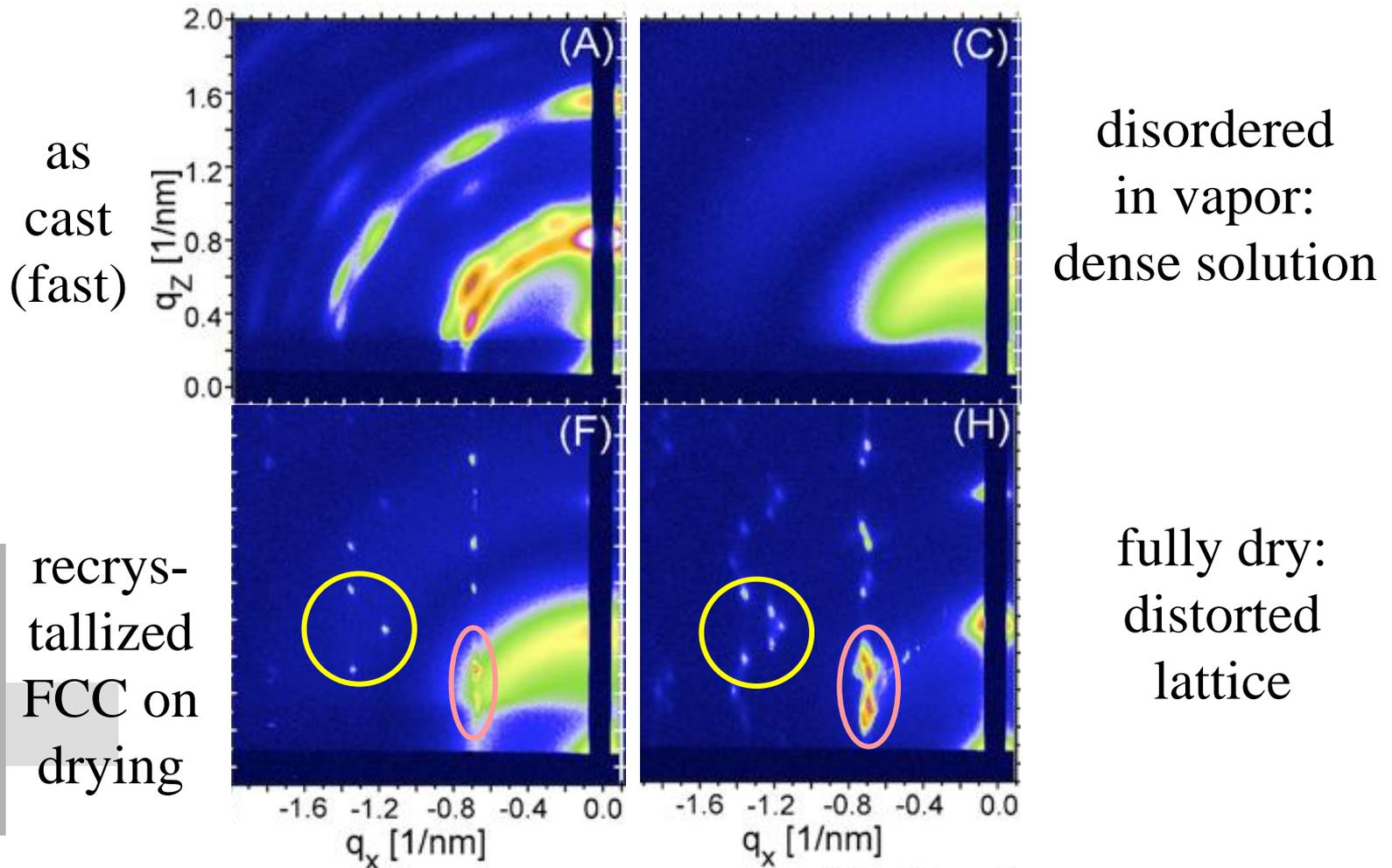


PbS nanocrystals  
dissolved  
in hexane

Drying in  
Nitrogen flow

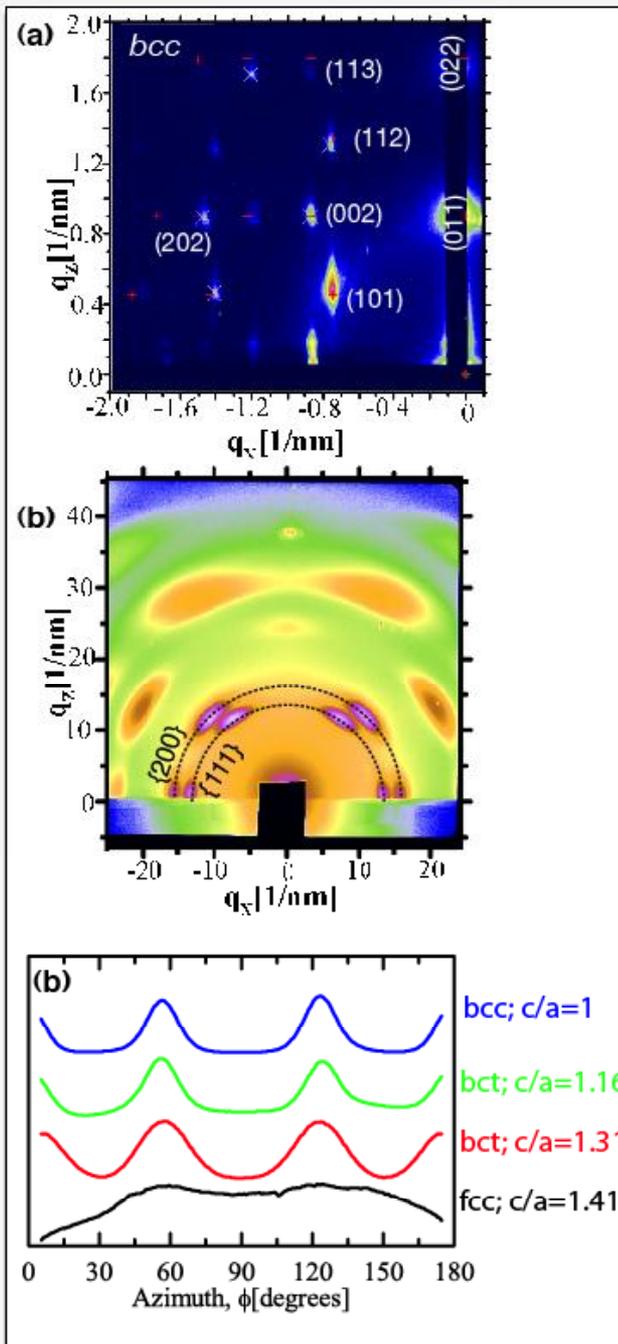
Bian *et al.*, ACS Nano 5 2815–2823 (2011)

# 3D NC assembly: lattice deformation



GISAXS

GIWAXS



The key:

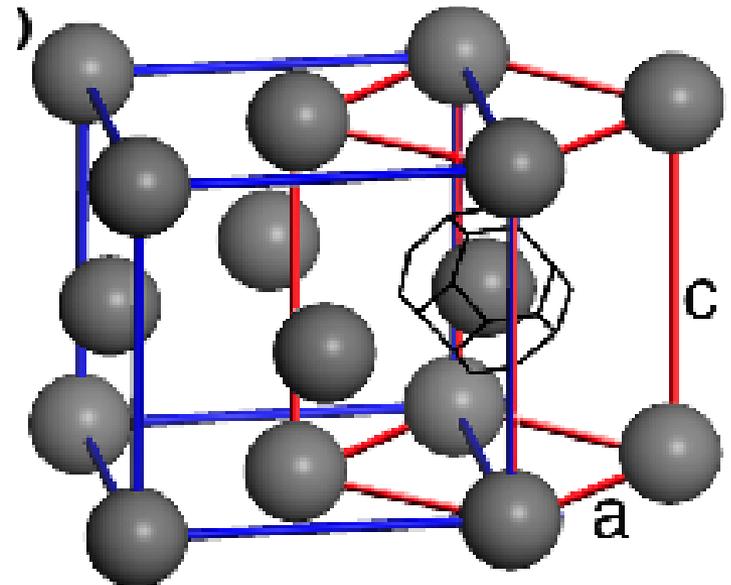
In the BCC phase

NC are oriented  
on SL sites

In the FCC phase

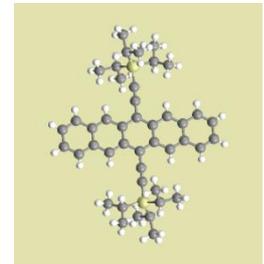
NC are not oriented

>>> Bain Transition



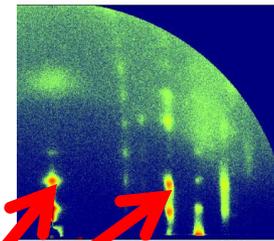
# Laterally Oriented Molecular Films via Solution Shearing

- Controls:
- Gap
  - Speed
  - Temperature
  - Concentration



TIPS-pn

GIXD



Diffacted  
X-ray Beams

Top Plate  
Translates

Solution

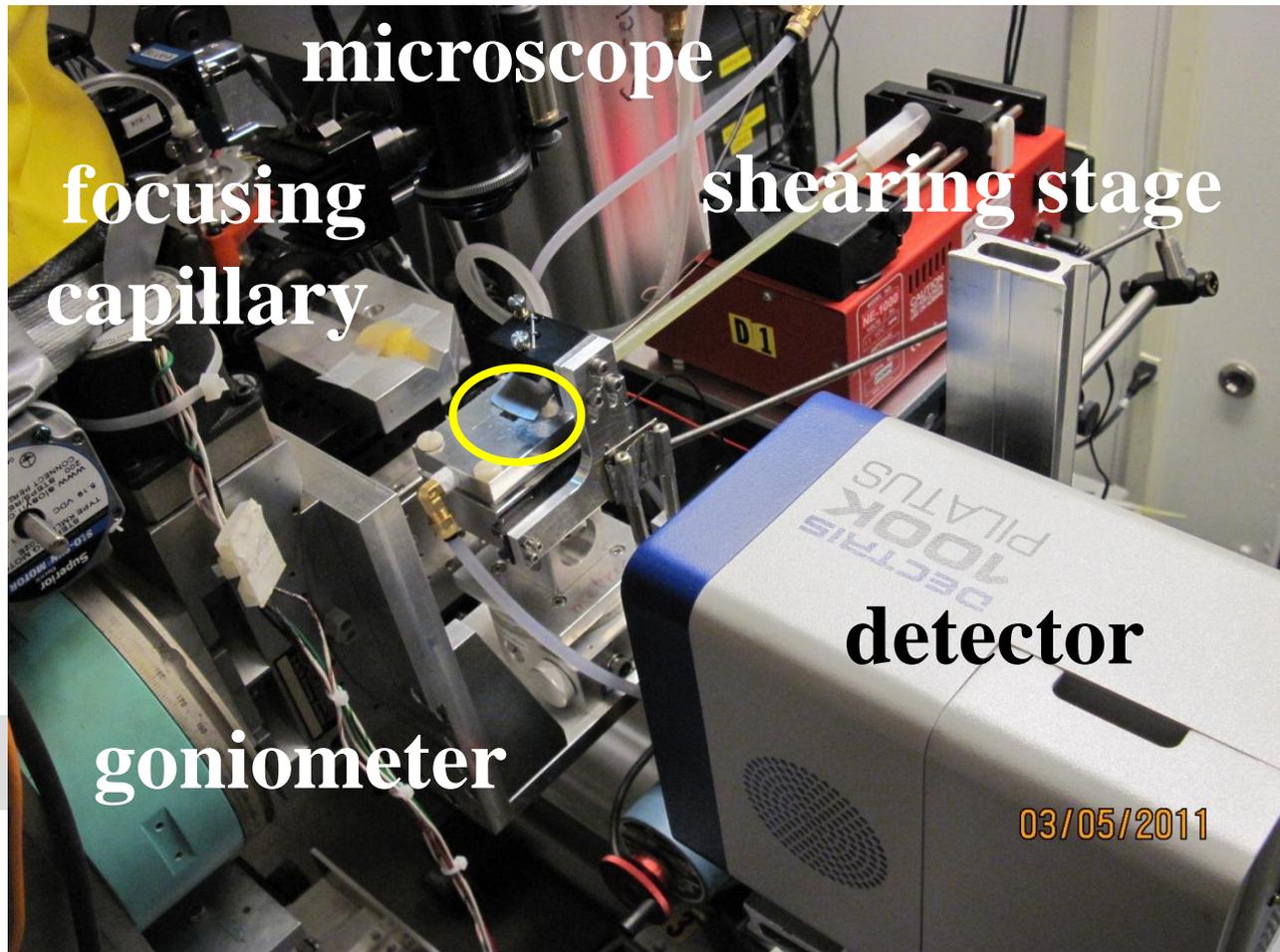
Meniscus

Solid  
Deposit

Heated Substrate

>>> **Roll-to-Roll Processing** <<<

# *In-situ & Real-Time Solution Shearing at D1*



Stanford  
KAUST  
CHESS

# *Conclusions*

Controlled deposition from **solution**  
and **vapor** processing

- Tremendous potential
- Careful attention has to be paid to detail  
**>>> in-situ <<<**
- All processes are diffusion-limited
- Typical time scales: fractions of sec to min

**>> GIXS** is the ultimate tool to study  
**3D self-assembly** in-situ and real time **<<**

# *Acknowledgements*

- Amassian group (KAUST)
- Bao group (Stanford)
- Bucknall group (Georgia Tech)
- Hanrath group (Cornell)
- Ober group (Cornell)

*Funding by NSF & NIH/NIGMS  
KAUST*

