Synchrotron studies of nanocrystal thin film self-assembly

D. Pontoni,[1] K. J. Alvine,[1] A. Checco,[3] O. Gang,[4] B. Ocko,[3] P. S. Pershan,[1,2] & F. Stellacci.[5]
[1]Division of Engineering and Applied Sciences and [2]Department of Physics, Harvard University; [3]Department of Physics and [4]Center for Functional Nanomaterials, Brookhaven National Lab; [5]Department of Materials Science and Engineering, MIT;

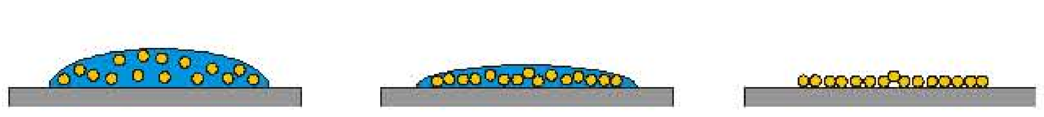
Motivation

Investigate fundamental aspects of nanocrystal self-assembly on solid substrates with particular attention to:

1. Intermediate thermodynamic equilibrium states rather than final products of irreversible non-equilibrium processes.
2. Effect of thin wetting solvent films on the assembly microstructure.
3. Nanocrystals with complex size distributions and stabilizing layers.
4. Influence of nanocrystal size and solvent quality.
5. In-situ determination of nanocrystal-substrate separation and in-plane nearest-neighbor distance.

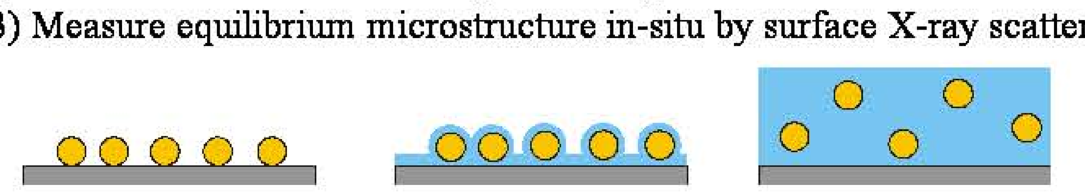
Conventional investigative approach

(a) Deposit a droplet of nanocrystal solution on substrate.
(b) Let solvent evaporate.
(c) Study final local microstructure by imaging techniques.



Our alternative approach

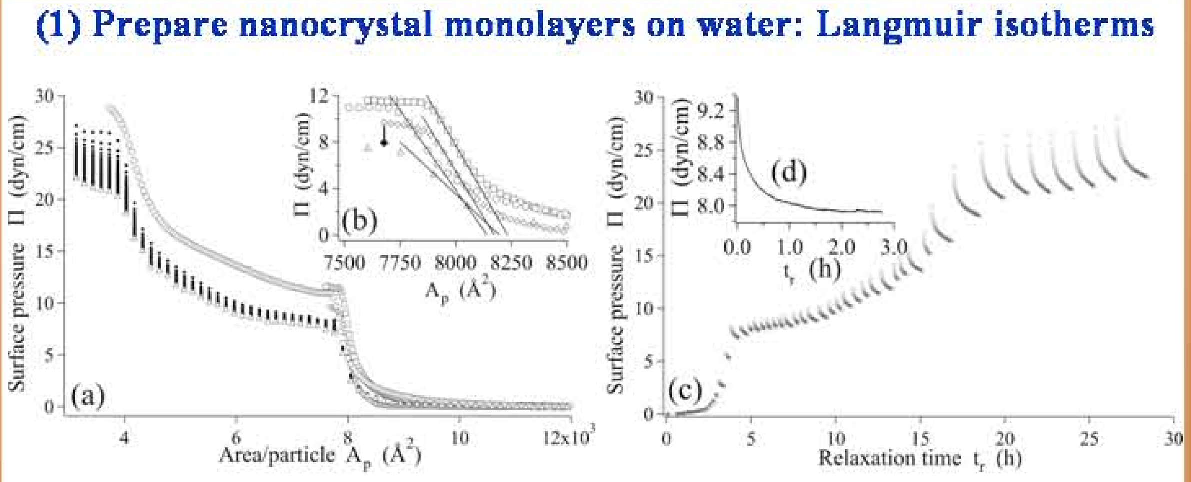
(1) Prepare dry nanocrystal layers on substrates.
(2) Generate stable nano-thin liquid wetting films.
(3) Measure equilibrium microstructure in-situ by surface X-ray scattering.



Typical particle size range: ~ 10-100 Å
Typical wetting film thickness range: ~ 1-100 Å

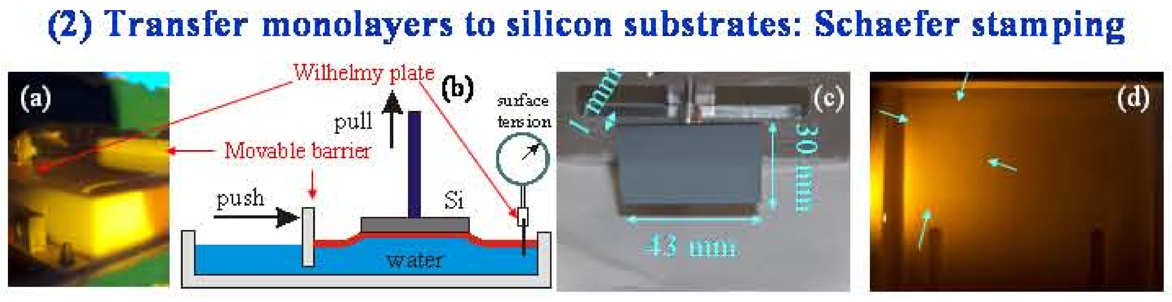
Methods

(1) Prepare nanocrystal monolayers on water: Langmuir isotherms



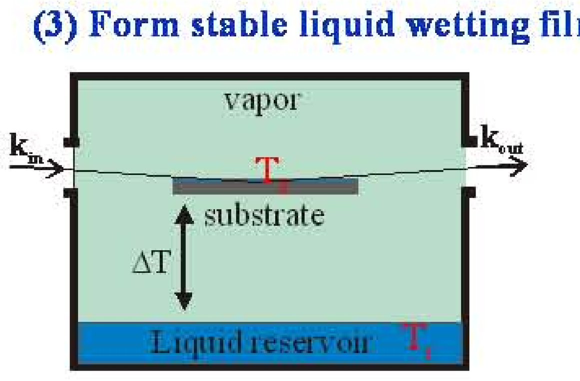
(a) Different types of isotherms: ○ continuous; △ relaxation; □◊ stamping preparation.
(b) Isotherms enlarged near monolayer plateau and linear extrapolation of equilibrium area per particle.
(c) Complete time history of a relaxation isotherm (● in (a)).
(d) Monolayer relaxation before stamping (▼ in (b)).

(2) Transfer monolayers to silicon substrates: Schaefer stamping



(a) Picture of teflon trough and Wilhelmy plate (filter paper) immersed normal to water surface.
(b) Schematic of trough and Schaefer stamping procedure (horizontal lift-off method).
(c) Typical dimensions of Si(100) substrates onto which the nanocrystal monolayer is transferred.
(d) Picture of the water surface after stamping. Arrows indicate edges of stamped rectangle.

(3) Form stable liquid wetting films: controlled nano-wetting



The thickness of the liquid film adsorbed on the substrate from vapor is controlled through the positive temperature offset ΔT.

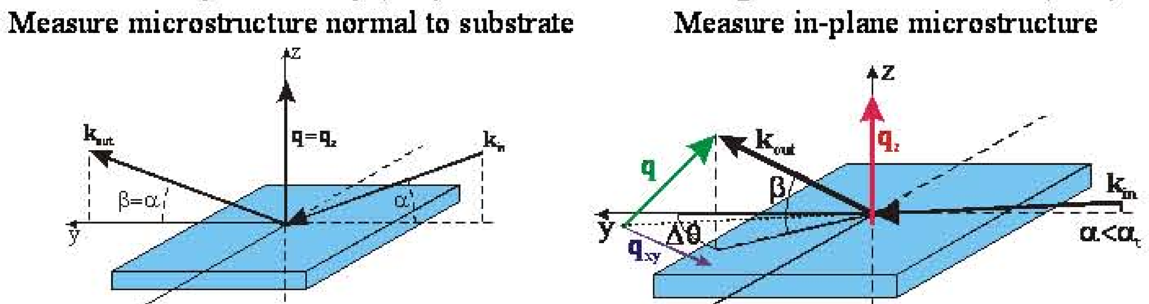
$$\Delta T = T_s - T_r \geq 0$$
$$t \sim (\Delta T)^{-1/3}$$

T_s : substrate temperature
T_r : liquid reservoir (ambient) temperature
t : thickness of the adsorbed liquid layer

(4) Measure average microstructure by surface X-ray scattering

X-ray reflectivity (XR) — Measure microstructure normal to substrate

Grazing incidence diffraction (GID) — Measure in-plane microstructure

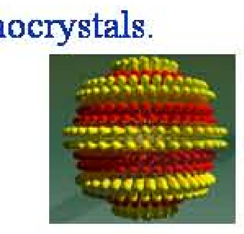


Results

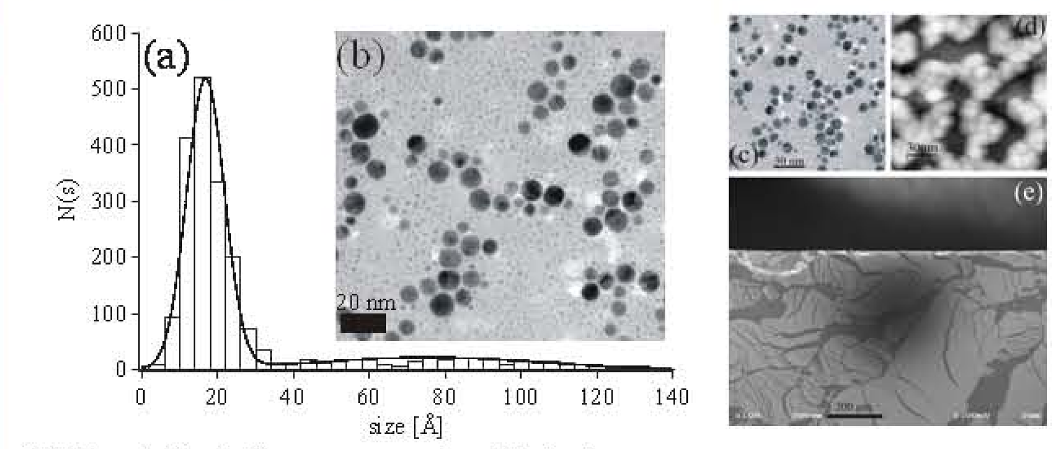
(A) Sample preparation and characterization.

(A1) Particles: bifunctional thiol-stabilized gold nanocrystals.

Stabilizing layer = 2:1 mixture of OT:MPA
OT = octanethiol = CH_3-$(CH_2)_7$-SH
MPA = mercaptopropionic acid = HOOC-$(CH_2)_2$-SH
Chain lengths: OT ~ 6 Å ; MPA ~ 12 Å



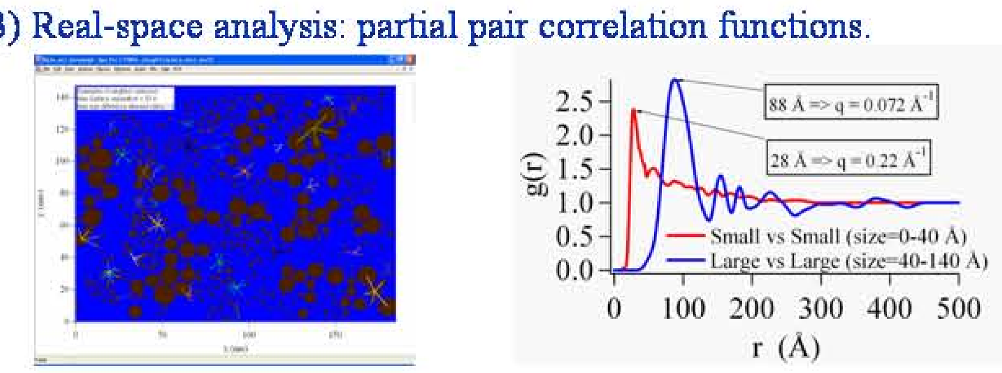
(A2) Microscopy: nanocrystal size and monolayer stamping quality.



(a) bimodal/polydisperse core size distribution.
(b),(c) TEM of monolayer portions from water surface
(d) AFM of monolayer on stamped Si(100) substrate.
(e) Low resolution SEM of substrate edge showing monolayer cracks (dark)

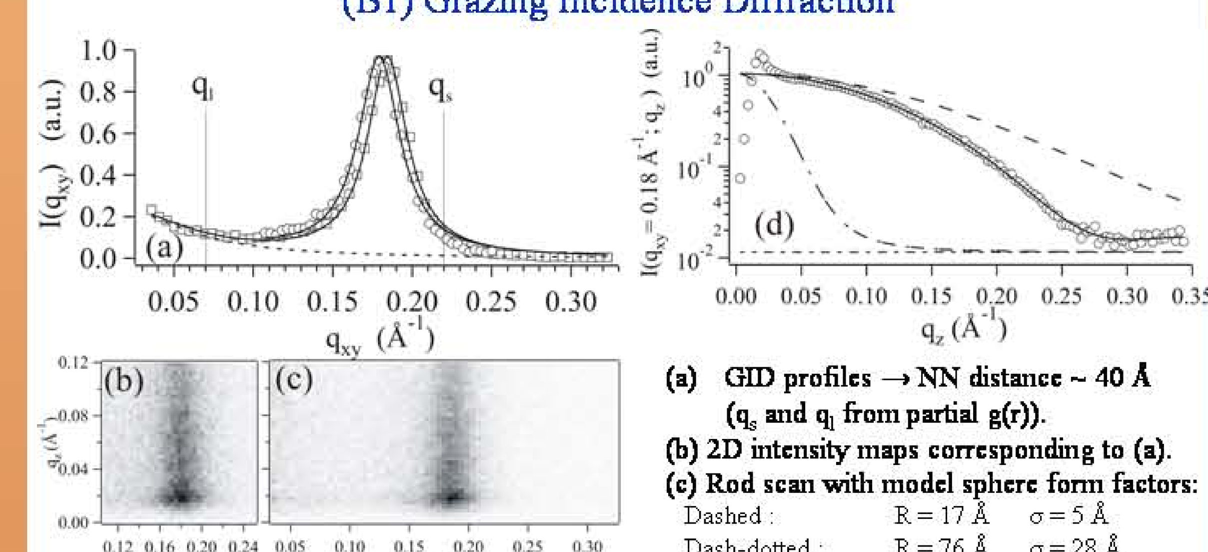
Small = 17 ± 5 Å
Large = 76 ± 28 Å

(A3) Real-space analysis: partial pair correlation functions.



(B) Dry nanocrystal monolayers on silicon: X-ray results

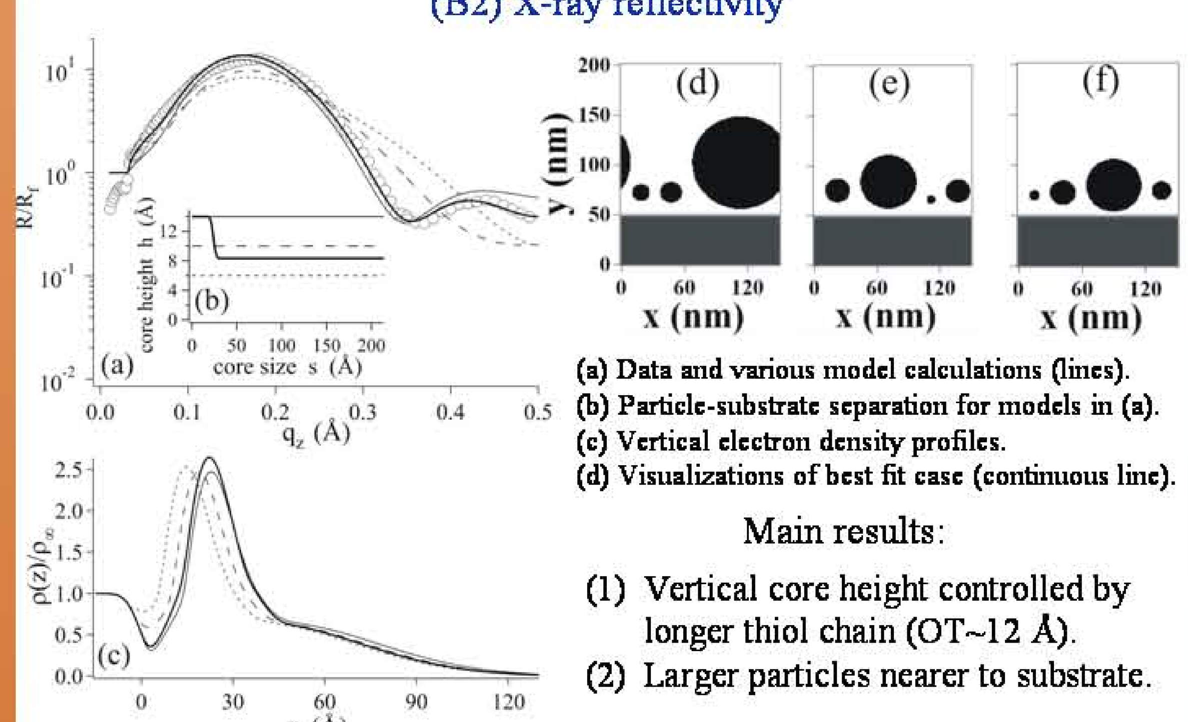
(B1) Grazing Incidence Diffraction



(a) GID profiles → NN distance ~ 40 Å (q_s and q_l from partial g(r)).
(b) 2D intensity maps corresponding to (a).
(c) Rod scan with model sphere form factors:

Dashed :	R = 17 Å	σ = 5 Å
Dash-dotted :	R = 76 Å	σ = 28 Å
Continuous :	R = 30 Å	σ = 4 Å

(B2) X-ray reflectivity



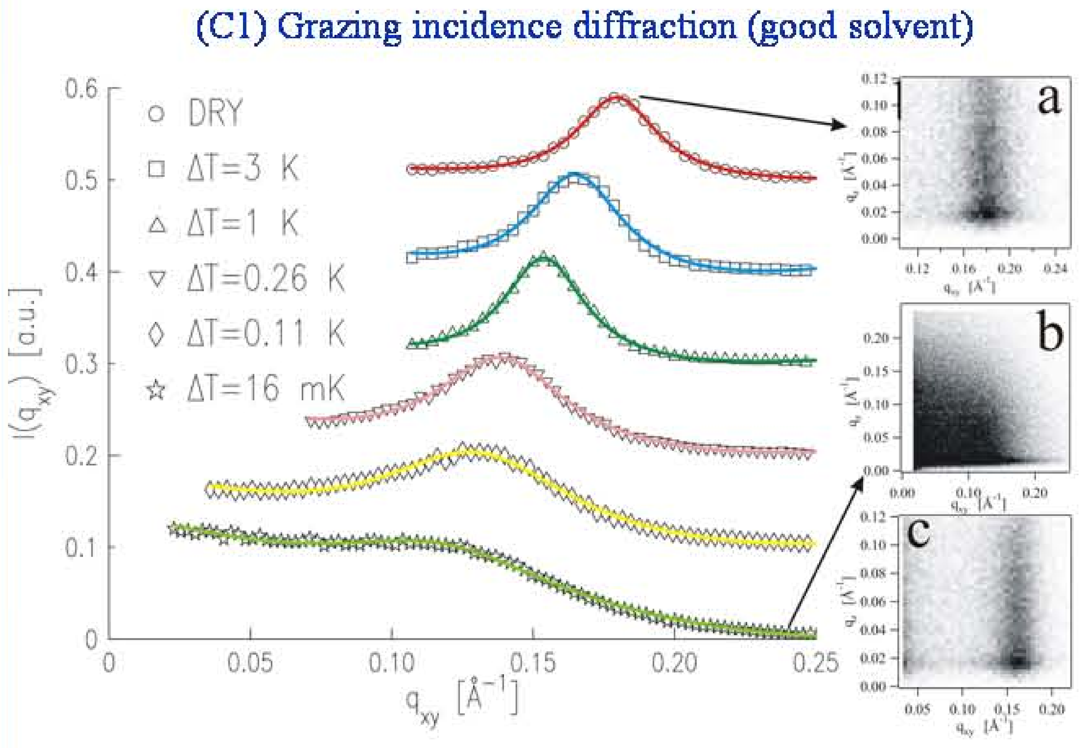
(a) Data and various model calculations (lines).
(b) Particle-substrate separation for models in (a).
(c) Vertical electron density profiles.
(d) Visualizations of best fit case (continuous line).

Main results:

(1) Vertical core height controlled by longer thiol chain (OT~12 Å).
(2) Larger particles nearer to substrate.

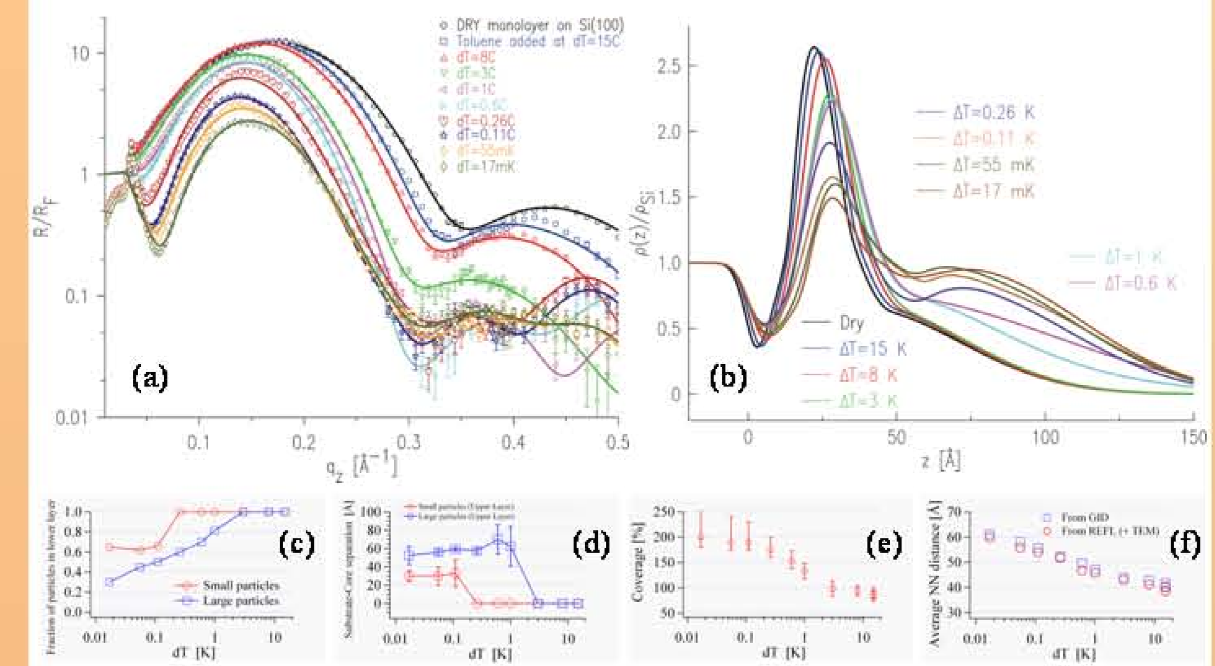
(C) Controlled nano-wetting with a good solvent (toluene)

(C1) Grazing incidence diffraction (good solvent)



Thin wetting liquid (large ΔT) → increasing NN distance, monolayer expansion.
Thick wetting liquid (small ΔT) → increased disorder, dissolution.
Invert ΔT (back to large) → monolayer re-assembly (panel (c)), reversible process, monolayer annealing.

(C2) X-ray reflectivity (good solvent)



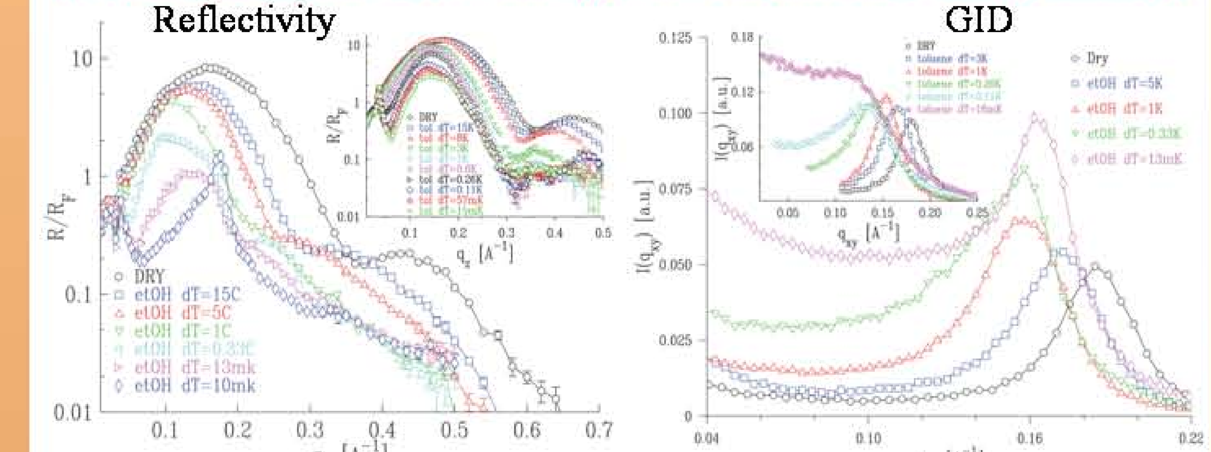
(a) XR data with box model fits
(b) Density profiles from physical XR model
(c) Fraction of particles in lower layer
(d) Height of the particles in upper layer
(e) Substrate coverage
(f) In-plane nearest particle distance

Main results

- Monolayer expansion up to ~100% coverage
- Further evolution resembles a bilayer transition
- Large particles are first promoted to upper layer

(D) Controlled nano-wetting with a poor solvent (ethanol)

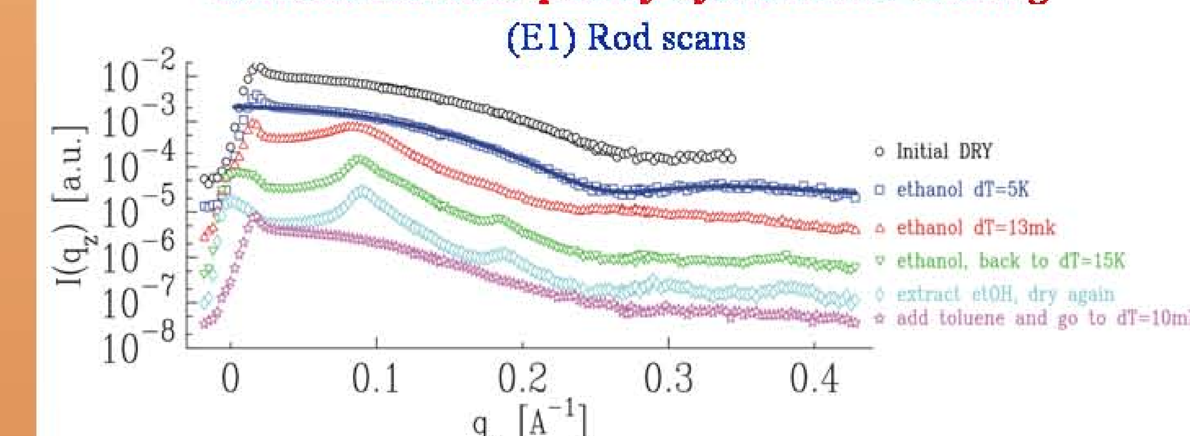
Reflectivity — GID



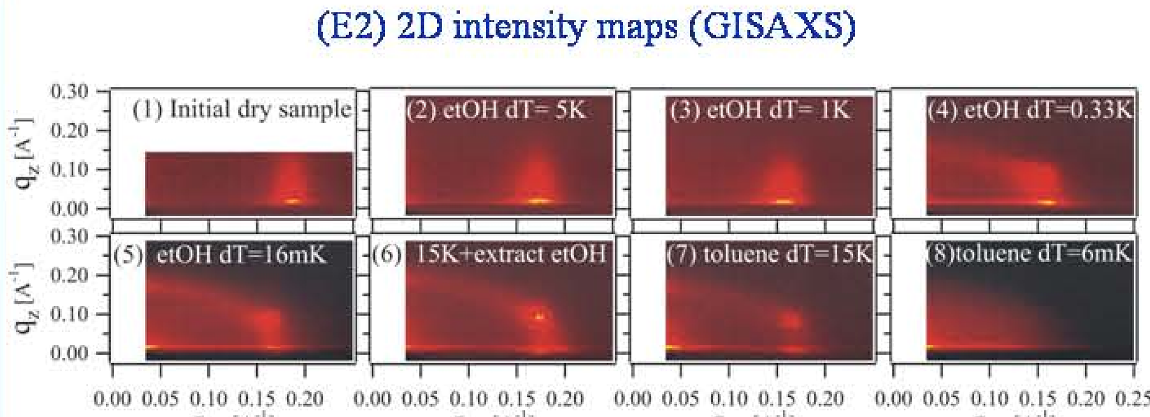
Thin film regime similar to good solvent case
Thick film regime very different: monolayer "destruction" and signature of 3D nanocrystal aggregates

(E) From 2D to 3D assembly and return: variable solvent quality cyclic nano-wetting

(E1) Rod scans



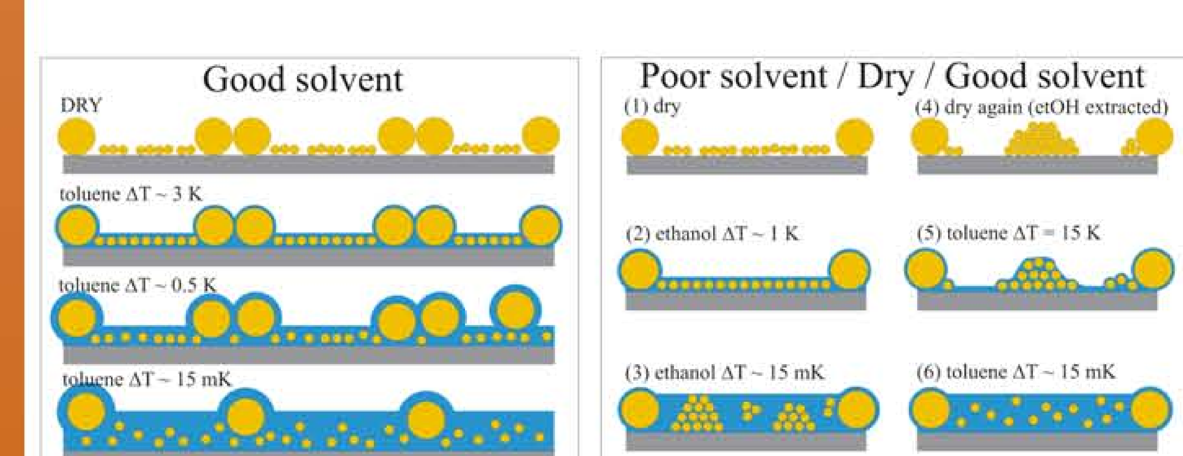
(E2) 2D intensity maps (GISAXS)



Main results

- Aggregates compacted and annealed by ethanol thinning and drying.
- Aggregates loosened by exchange to toluene and dissolved by toluene thickening.
- Initial monolayer can be re-assembled by final toluene thinning.

Pictorial Summary



Acknowledgements

This work was supported in part by the National Science Foundation Grant No. 03-03916.