Colloidal Crystallization: Nucleation and Growth

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Peter Schall	Harvard	Frans Spaepen	Harvard
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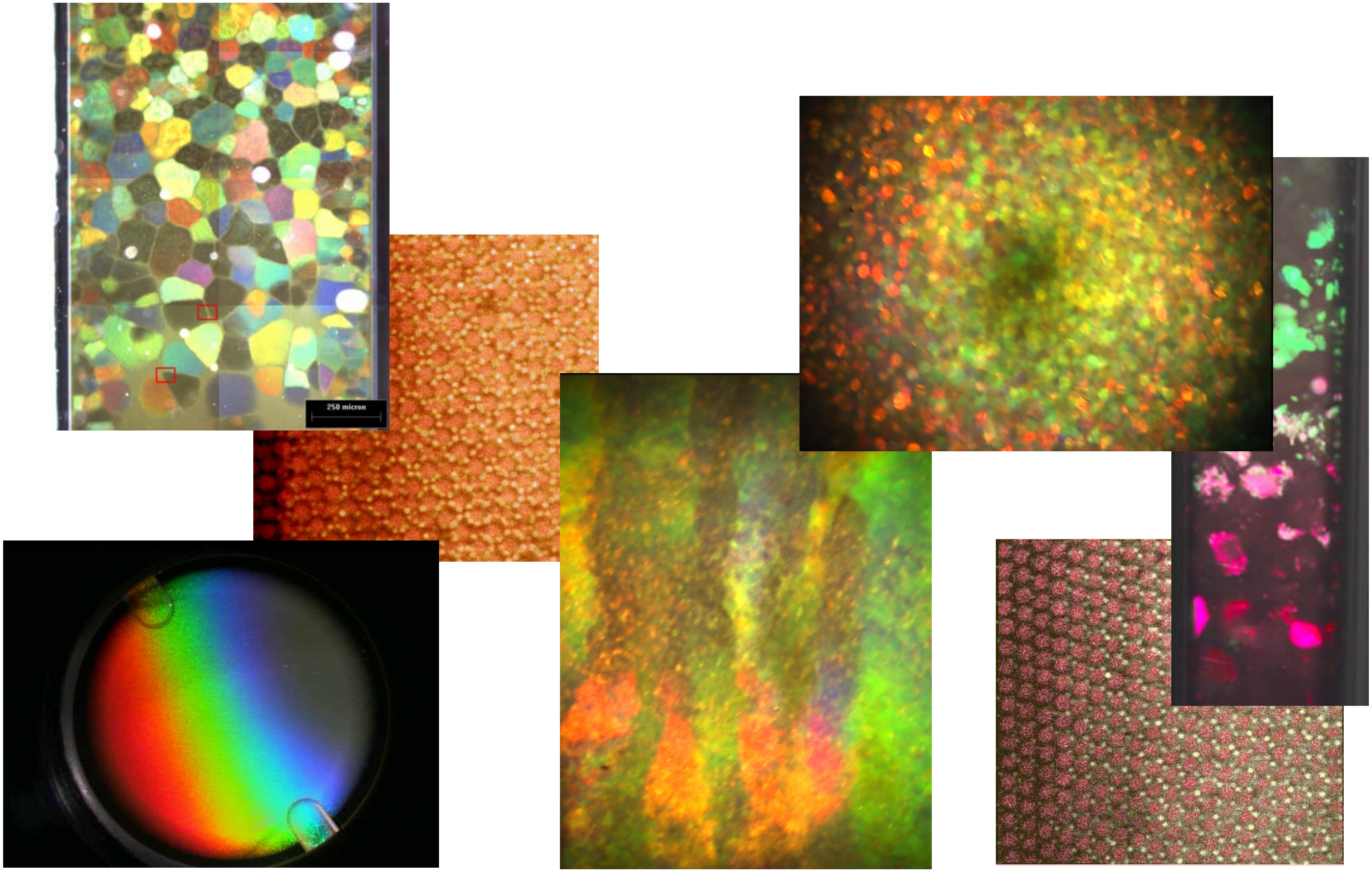
- Colloids as model systems – soft materials
- Nucleation and growth of colloidal crystals
- Defect growth in crystals
- Binary Alloy Colloidal Crystals

NSF, NASA

http://www.deas.harvard.edu/projects/weitzlab

EMU 6/7//04

Colloidal Crystals



Colloids

1 nm - 10 μm solid particles in a solvent

Ubiquitous

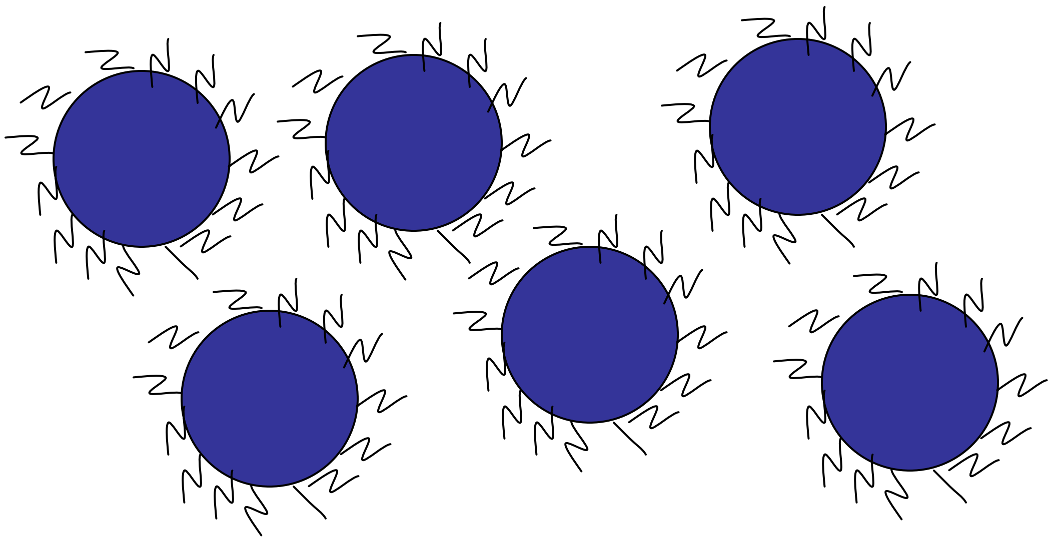
ink, paint, milk, butter, mayonnaise, toothpaste, blood

Suspensions can act like both liquid and solid

Modify flow properties

Control: Size, uniformity, interactions

Colloidal Particles



- Solid particles in fluid
- Hard Spheres
  - Volume exclusion
- Stability:
  - Short range repulsion
  - Sometimes a slight charge

Colloid Particles are:

•Big

- $\sim a \sim 1$ micron
- Can "see" them

Slow

- $\tau \sim a^2/D \sim$ ms to sec
- Follow individual particle dynamics

Model: Colloid → Atom

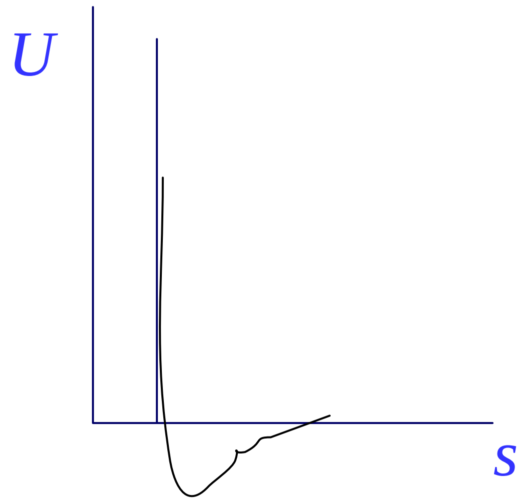
Phase Behavior

Colloids

Hard Spheres
Osmotic Pressure
Centro-symmetric
Thermalized: $k_B T$

- Gas
- Liquid
- Solid

Atomic Liquids



Leonard-Jones
Attraction
Centro-symmetric
Thermalized: $k_B T$

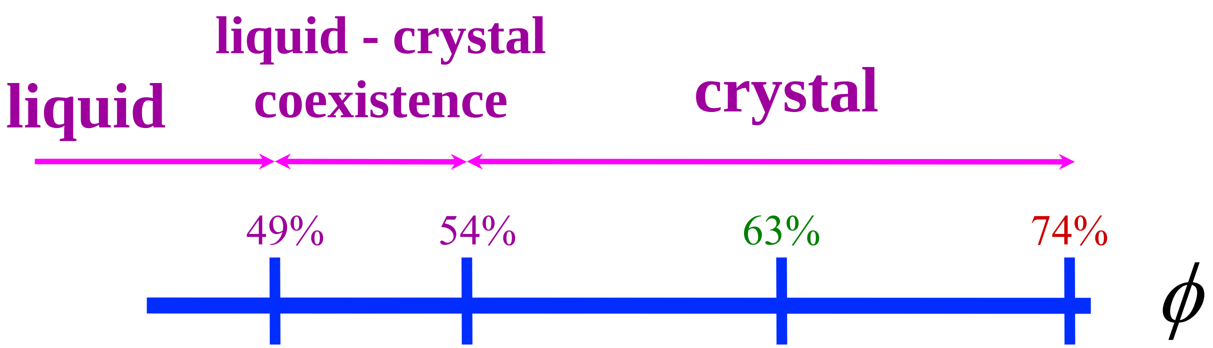
- Gas
- Liquid
- Solid

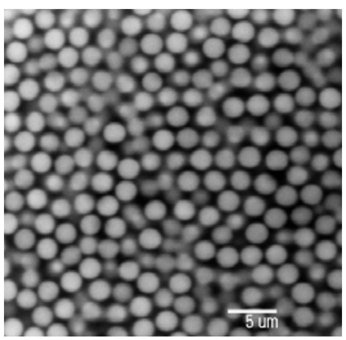
Density

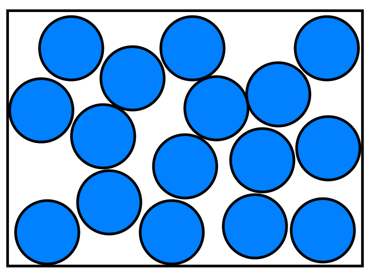
Phase behavior is similar

Hard Sphere Phase Diagram

Volume Fraction Controls Phase Behavior

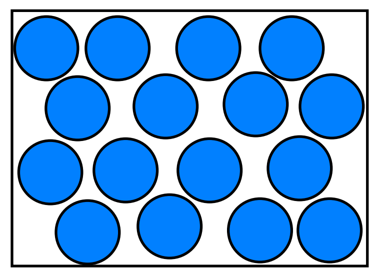






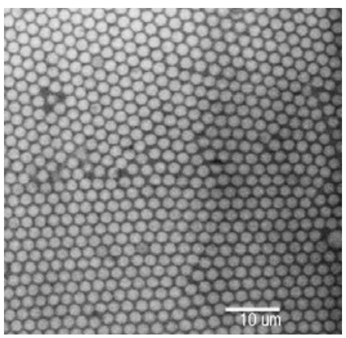
maximum packing

$\phi_{RCP} \approx 0.63$



maximum packing

$\phi_{HCP} = 0.74$



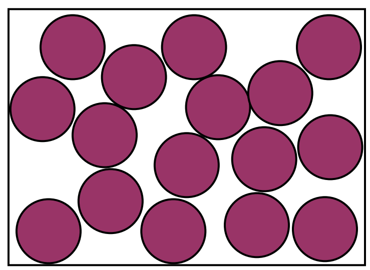
Increase ϕ => Decrease Temperature

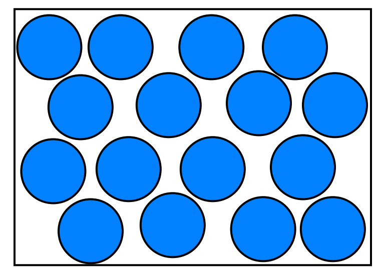
$F = \cancel{U}^{\,0} - TS$

Entropy Drives Crystallization

Entropy => Free Volume

$$F = \cancel{U}^{\,\nearrow 0} - TS$$





Disordered:
- Higher configurational entropy
- Lower local entropy
- Higher Energy

maximum packing
$\phi_{RCP} \approx 0.63$

Ordered:
- Lower configurational entropy
- Higher local entropy
- Lower Energy

maximum packing
$\phi_{HCP} = 0.74$

Soft Solids

Easily deformable → Low Elastic Constant: $\frac{\text{Energy}}{\text{Volume}}$

Atoms: $\frac{eV}{\dot{A}^3}$ ~GPa

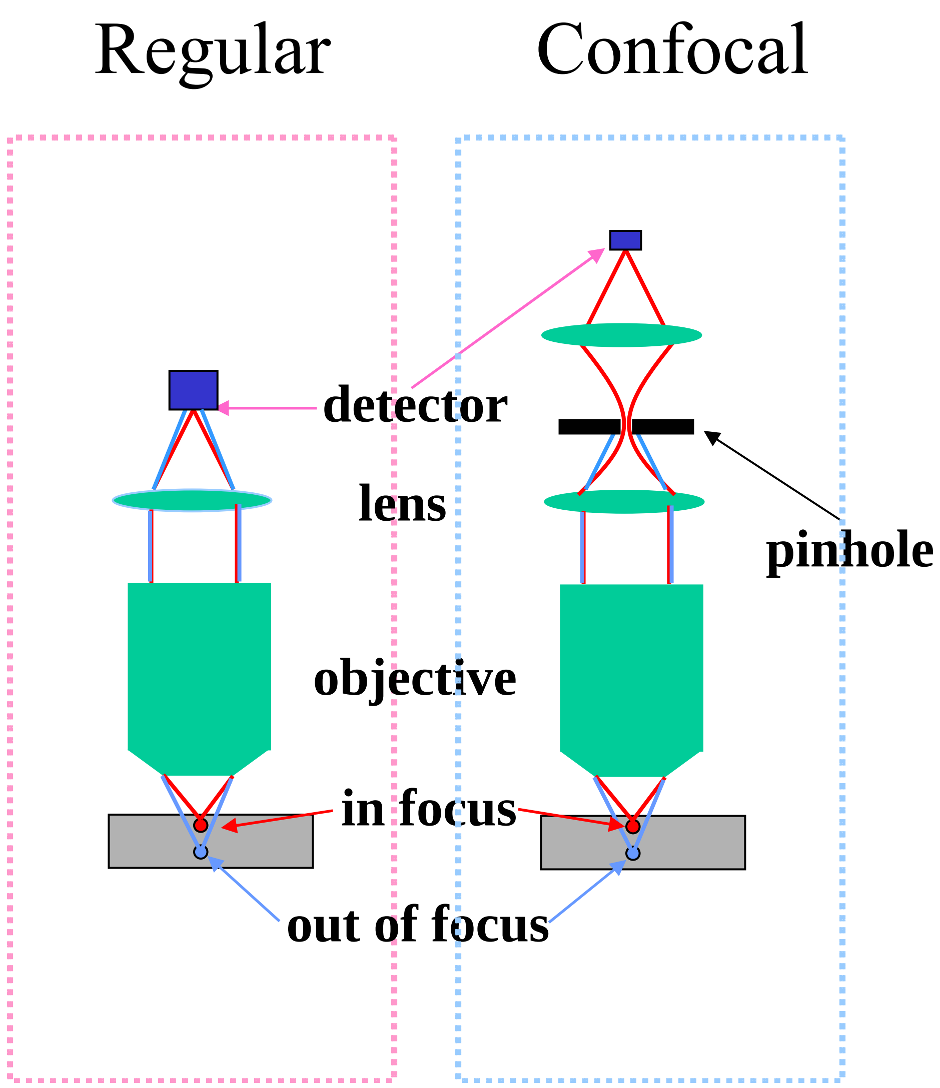
Colloids: $\frac{k_B T}{\mu m^3}$ ~Pa

Easily deformed → Shear melt to randomize

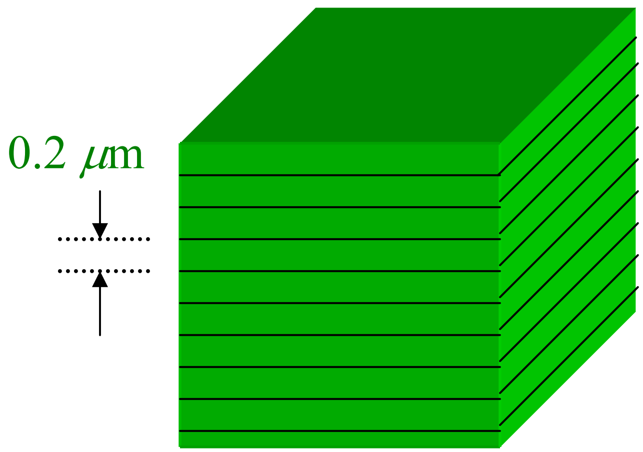
Colloidal Particle → Atom

Watch each atom!

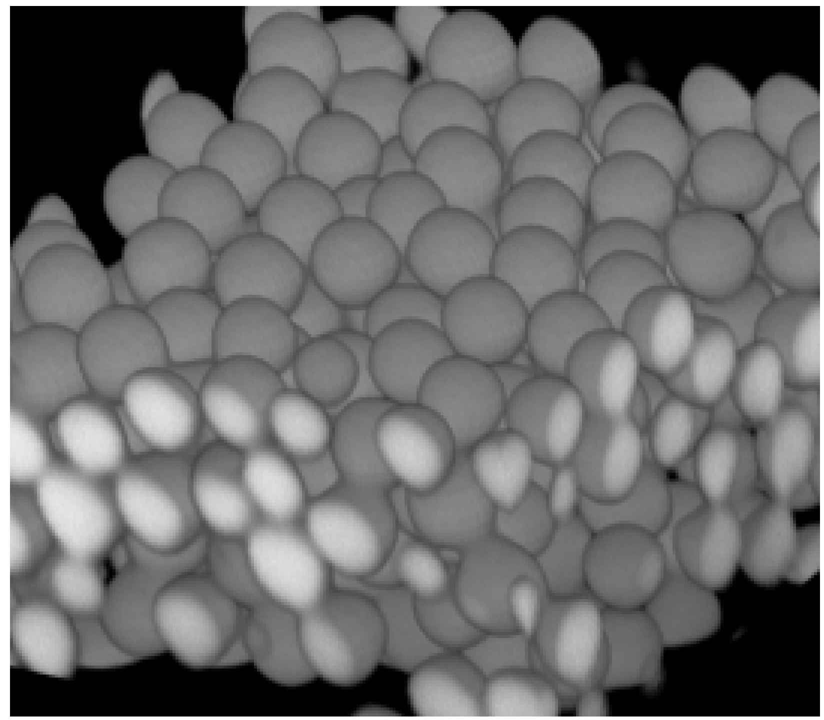
Confocal Microscopy



Confocal microscopy for 3D pictures



Scan many slices, reconstruct 3D image

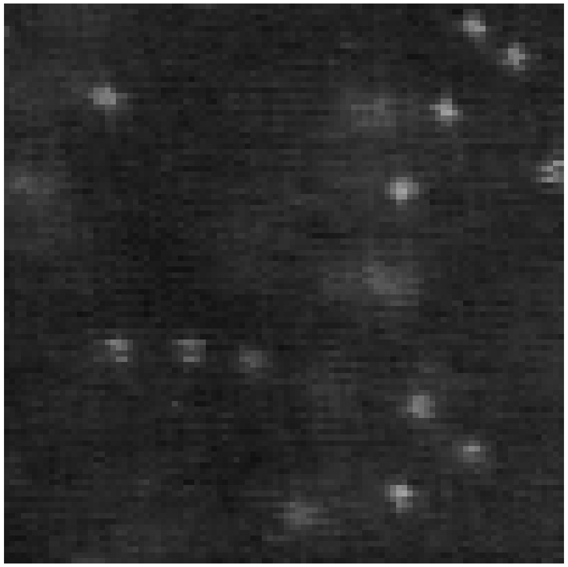


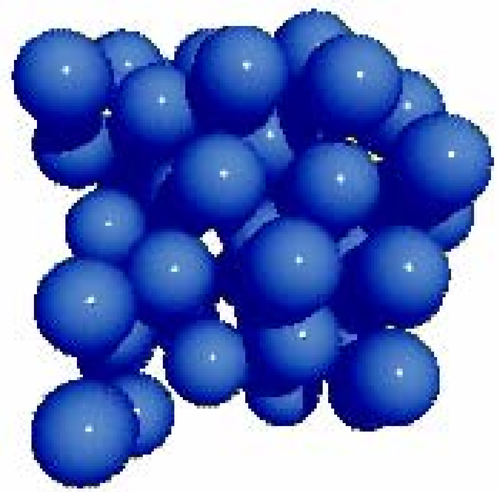
Microscopy and Tracking

Confocal microscopy:	•30 images/s (512×480 pixels, 2D) •one 3D "cube" per 6 s •67 × 63 ×10 μm^3 •100× oil / 1.4 N.A. objective •Identify particles within 0.03 μm (*xy*) 0.05 μm (*z*)
Particle tracking:	•Follow 3000-5000 particles, in 3D •200-1000 time steps = hours to days •≈ 4 GB of images per experiment

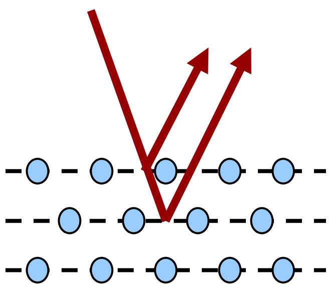
First direct 3D observation of dynamics

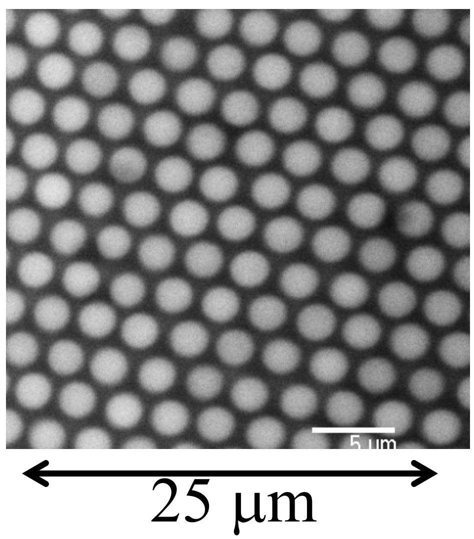
Brownian Motion in Real Time

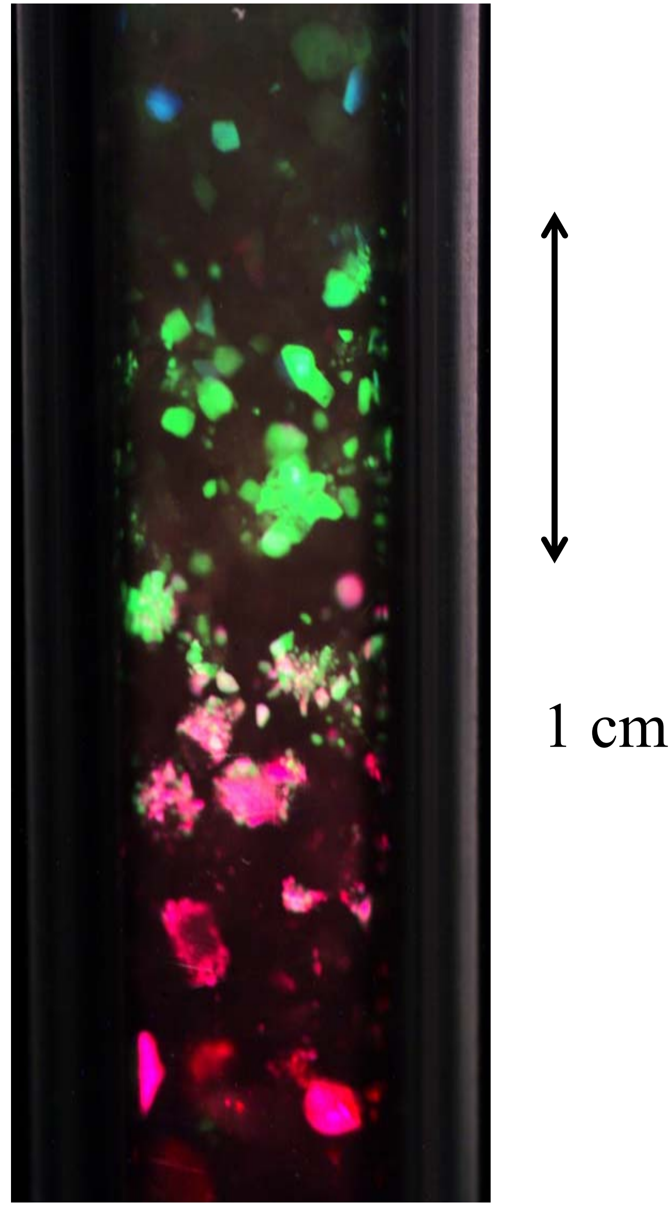




Colloidal Crystals



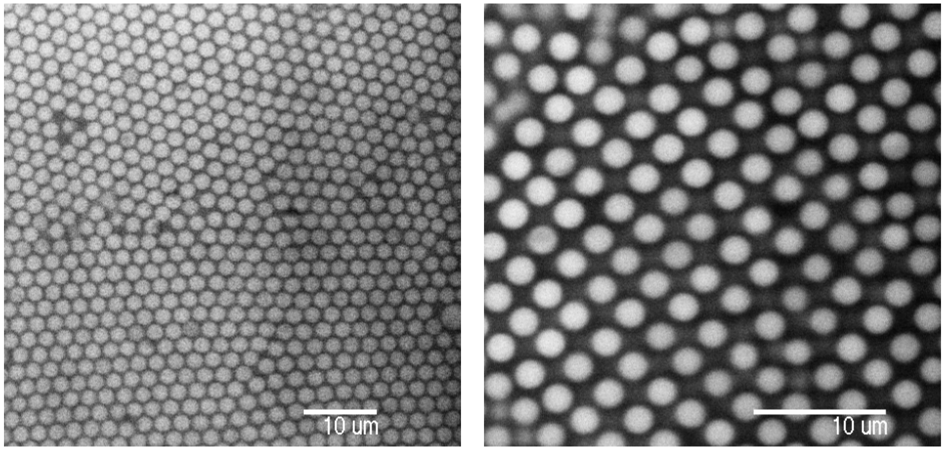




Bragg scattering of visible light

Hexagonal close-packed layers (FCC/HCP)

Nucleation and Growth of Colloidal Crystals



2.3 μm diameter PMMA spheres

Questions:

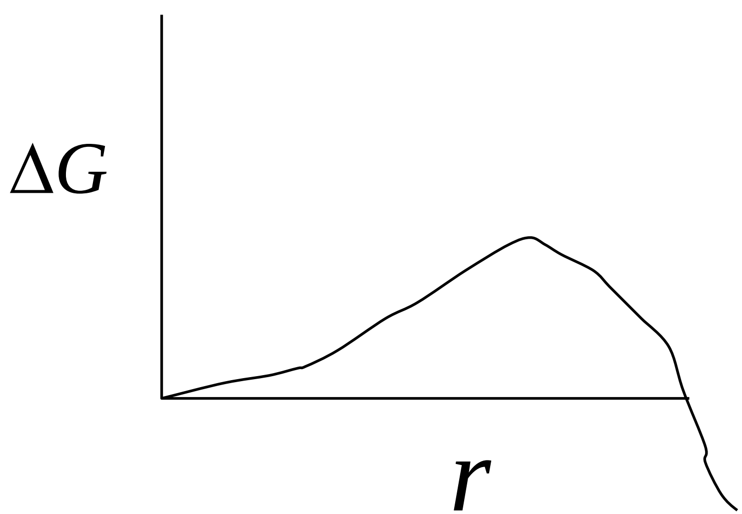
- How do crystals nucleate?
- What is structure of pre- and post-critical nuclei?
- How does structure evolve with time?
- What is free energy barrier?

Crystallization

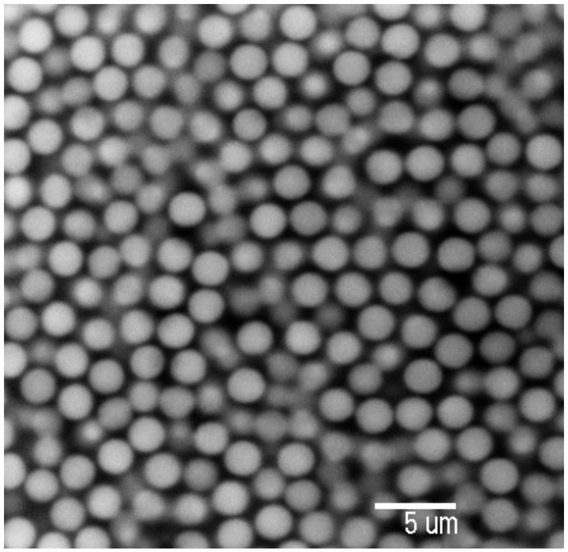
$$\Delta G = \gamma\left(4\pi r^2\right) - \Delta\mu\left(\tfrac{4}{3}\pi r^3\right)$$

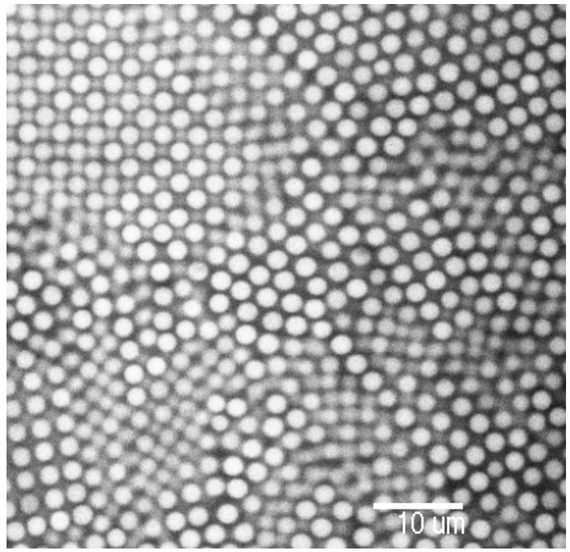
Surface energy

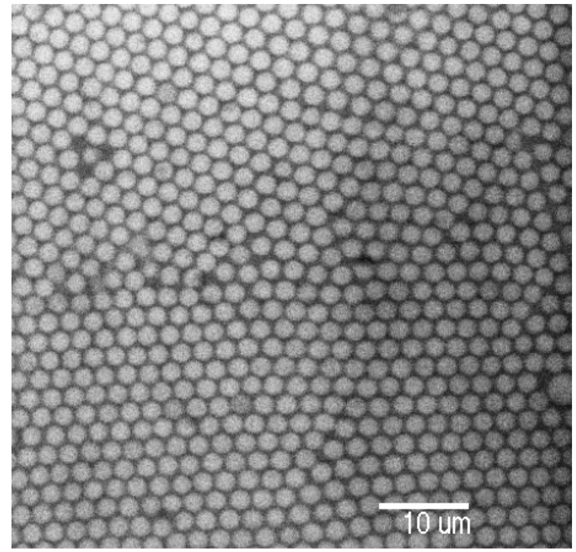
Chemical potential



How to Identify Crystals





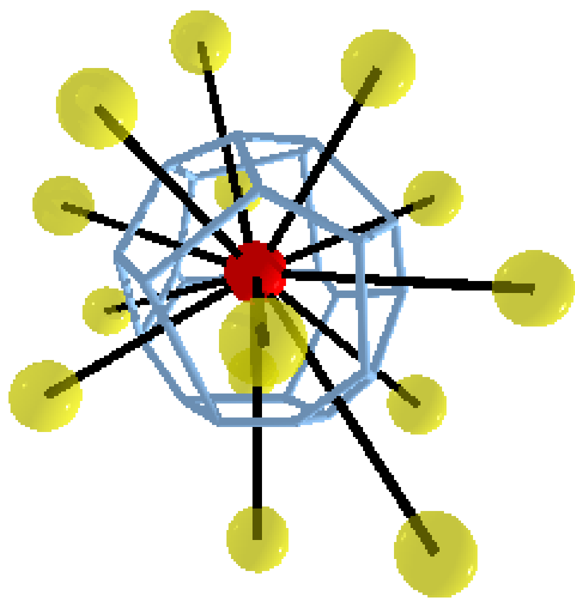


2.3 μm diameter PMMA spheres

Must identify incipient crystal nuclei

Voronoi polyhedra -- Delaunay triangulation

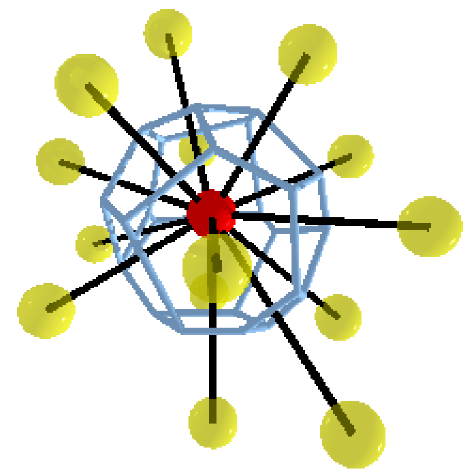
("Wigner-Seitz cell")



defines nearest neighbor particles

Local Crystallization Order Parameter

P. R. ten Wolde, M. J. Ruiz-Montero,
D. Frenkel: *J. Chem. Phys.* **104**, 9932 (1996)



•Find nearest neighbor connections r_{ij}

•Resolve connections in spherical harmonics:

$$q_{lm}(i)=\langle Y_{lm}(r_{ij})\rangle_j$$

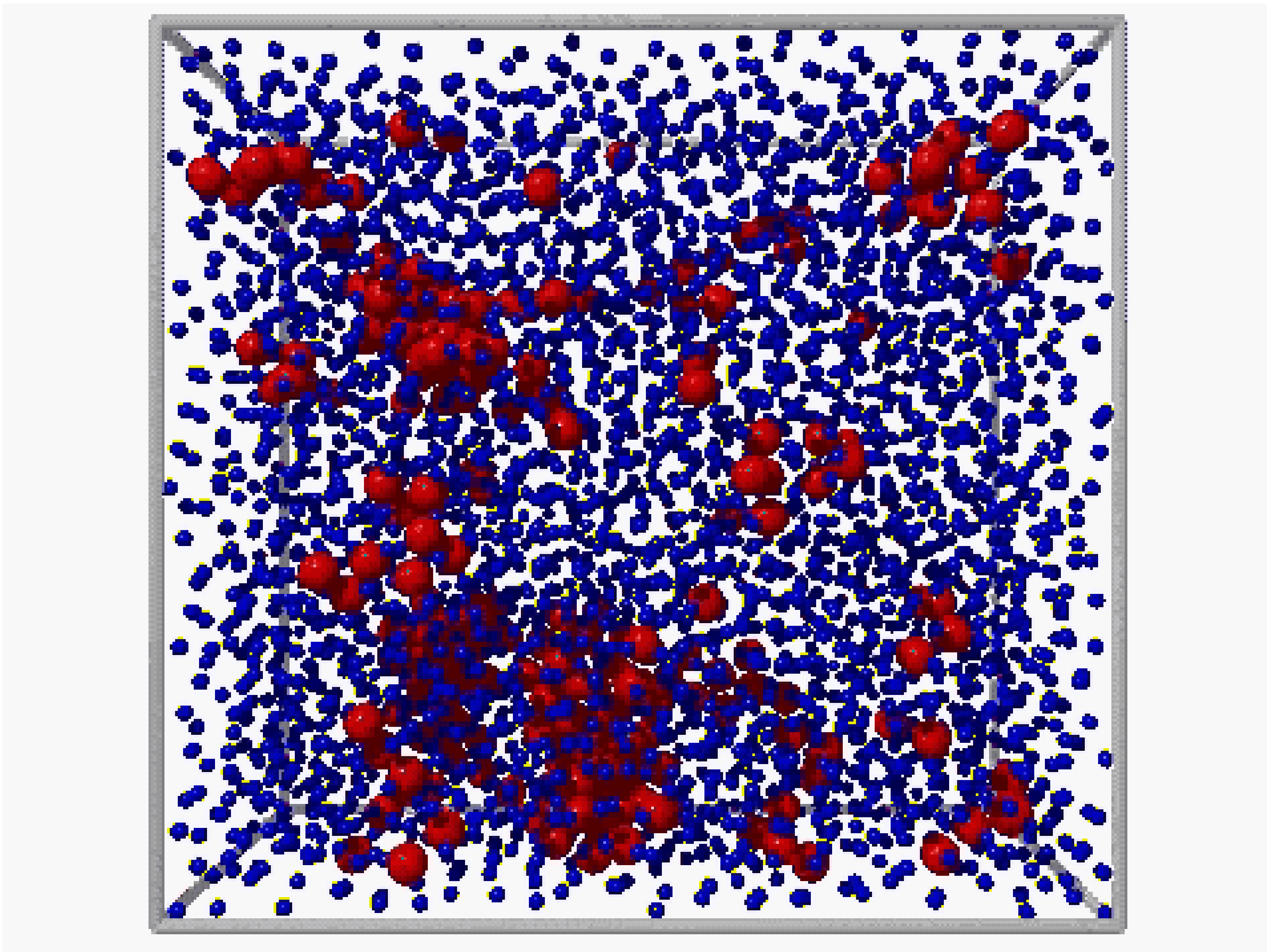
•Examine $l=6$

•Define Order Parameter: $q_{6m}(i) \cdot q_{6m}(j)$

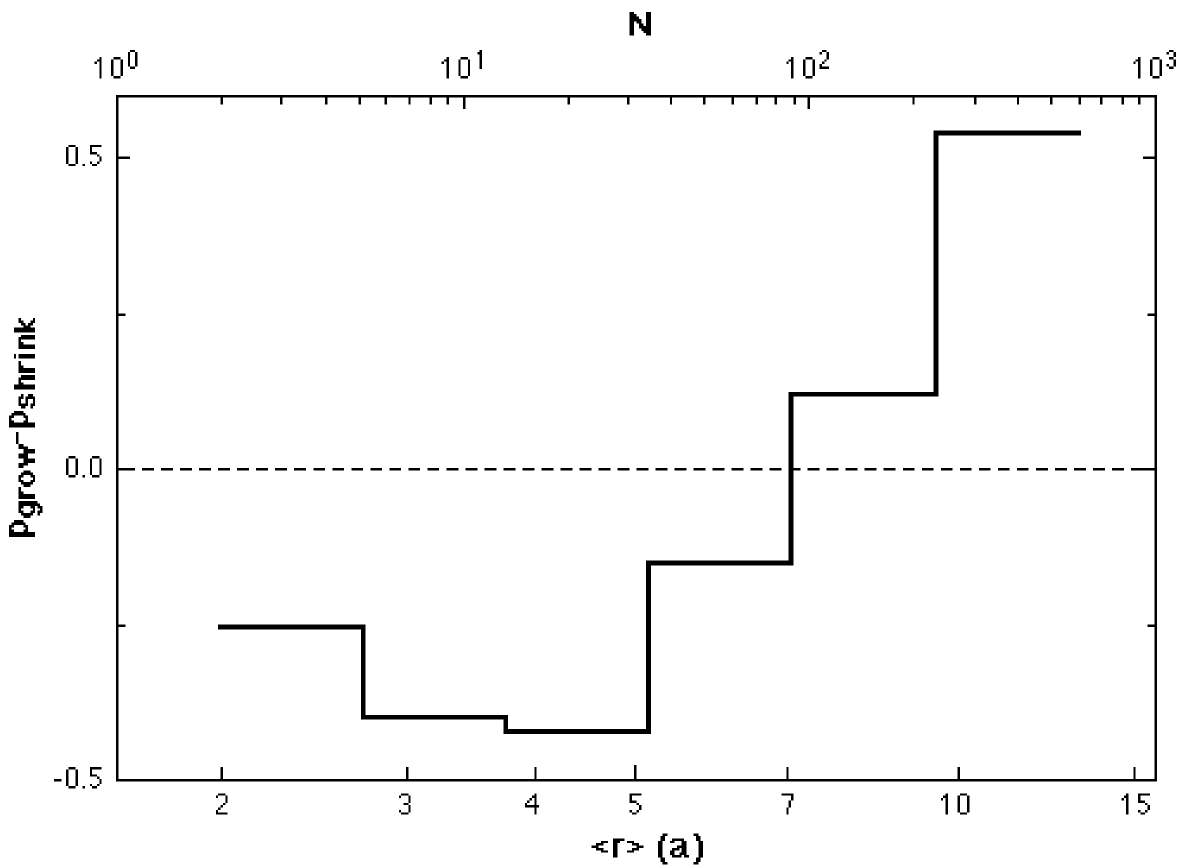
•If $q_{6m}(i) \cdot q_{6m}(j) > 0.5$, then bond (ij) is “crystal-like”

•if particle has ≥ 8 “crystal-like” bonds, it is a **crystal-like particle**

Colloidal Crystallization

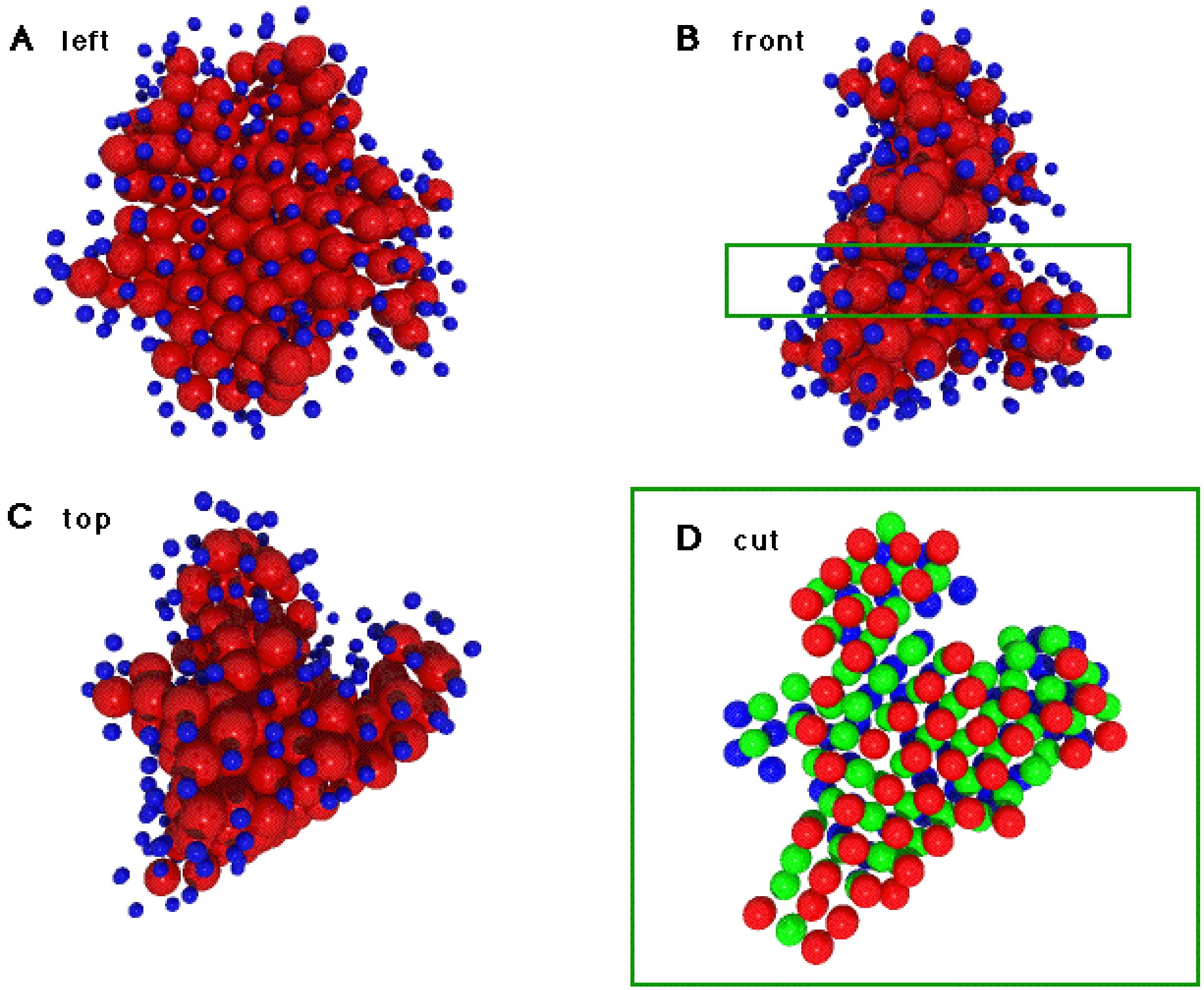


Determination of Size of Critical Nucleus

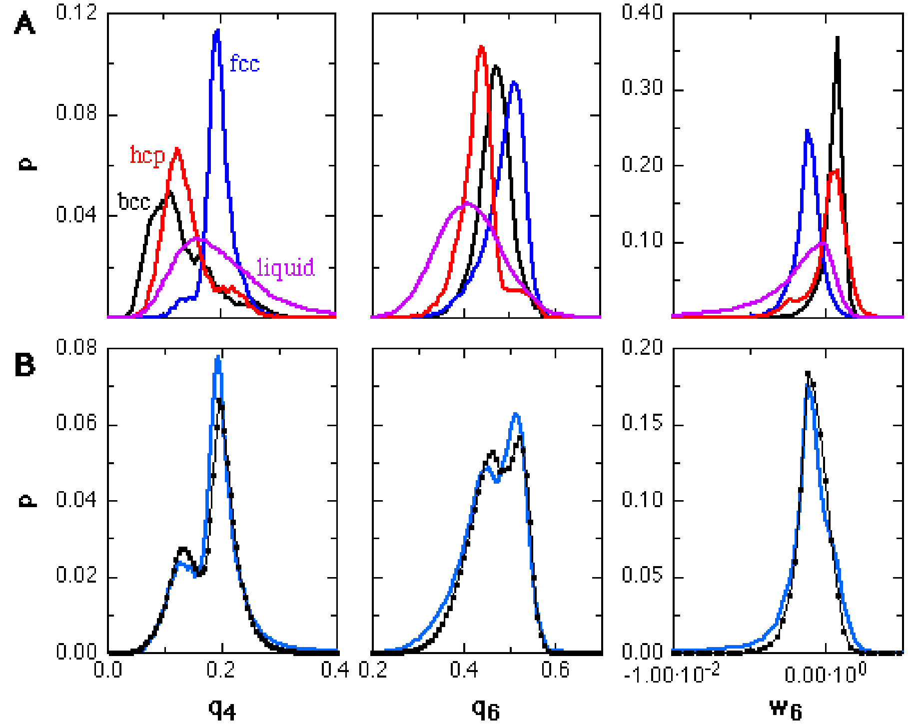


Crystal Nucleus Structure

$R \sim R_c \quad \phi = 0.47$

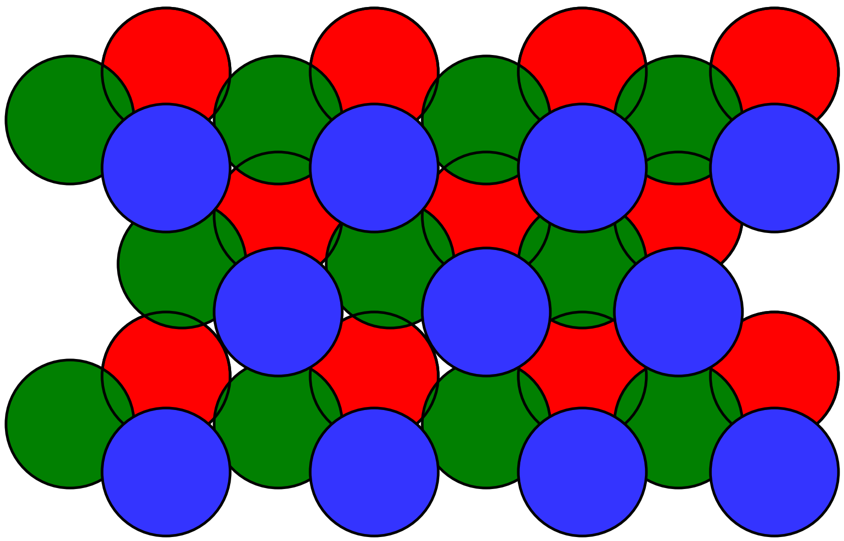


Structure of Crystal Nucleus



ϕ	bcc	fcc	hcp	liquid
0.49	0.00(3)	0.10(3)	0.32(6)	0.58(1)
0.45	0.00(1)	0.58(7)	0.20(3)	0.22(6)
0.43	0.00(3)	0.34(5)	0.25(4)	0.41(1)

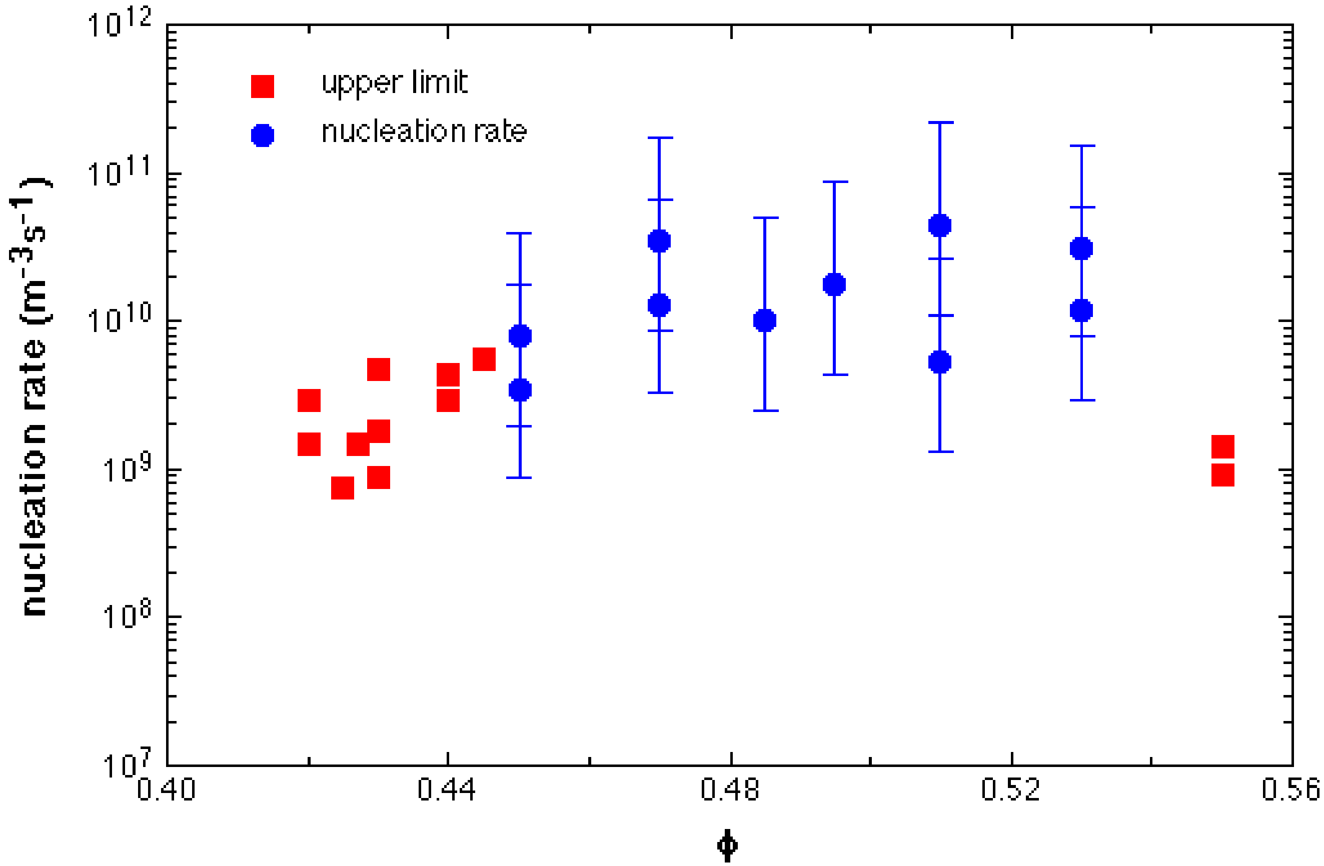
RHCP: Random Hexagonally Close Packed



A B C A

fcc *hcp*

Nucleation Rate



Comparable to light scattering measurements

Faster than simulations

Finding Surface Tension

$$\Delta G = \gamma\left(4\pi r^2\right) - \Delta\mu\left(\tfrac{4}{3}\pi r^3\right)$$

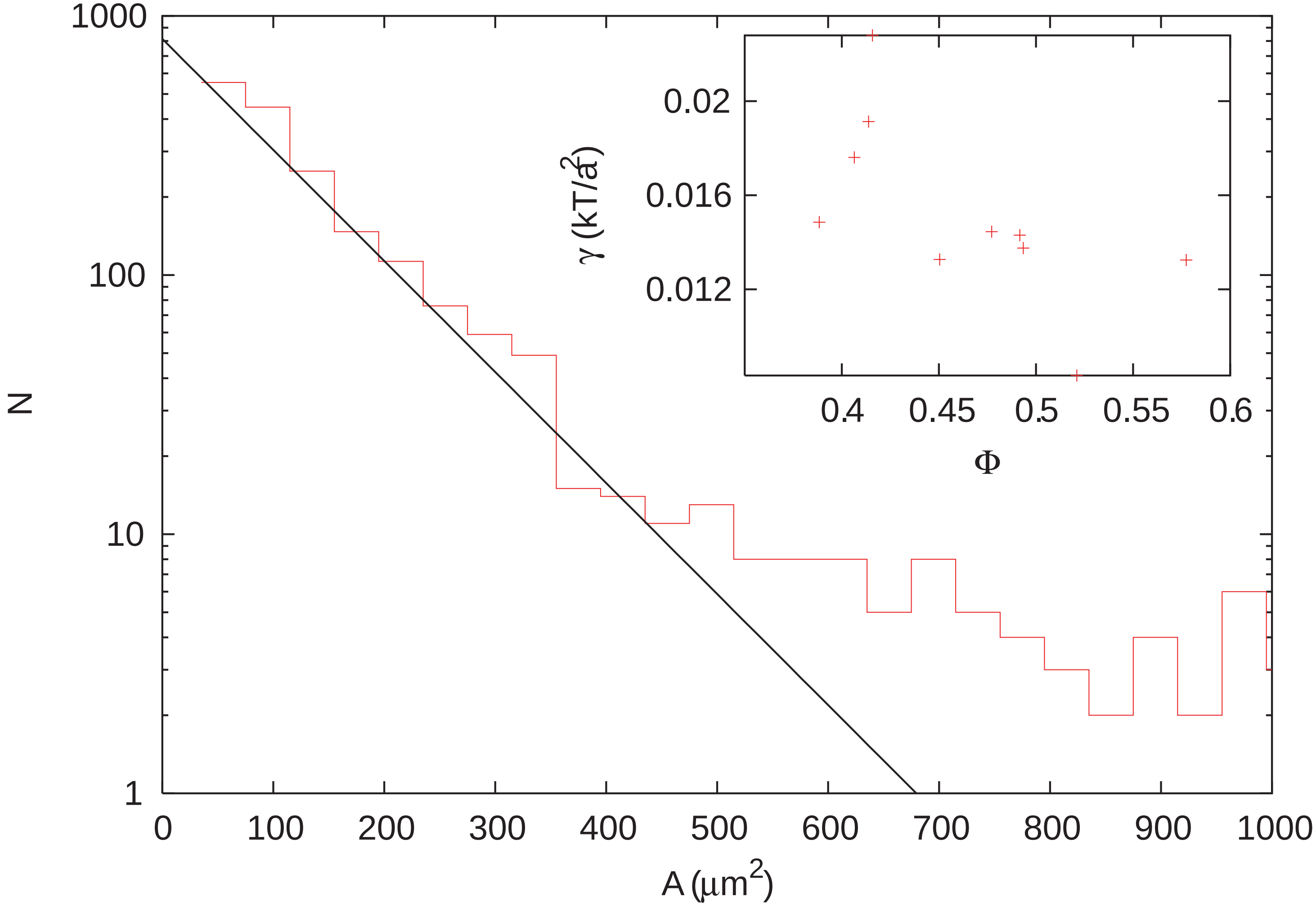
Surface energy

Chemical potential

$$P(r) \approx \exp\left(\frac{-\Delta G}{k_B T}\right) \approx \exp\left(-\gamma r^2\right)$$

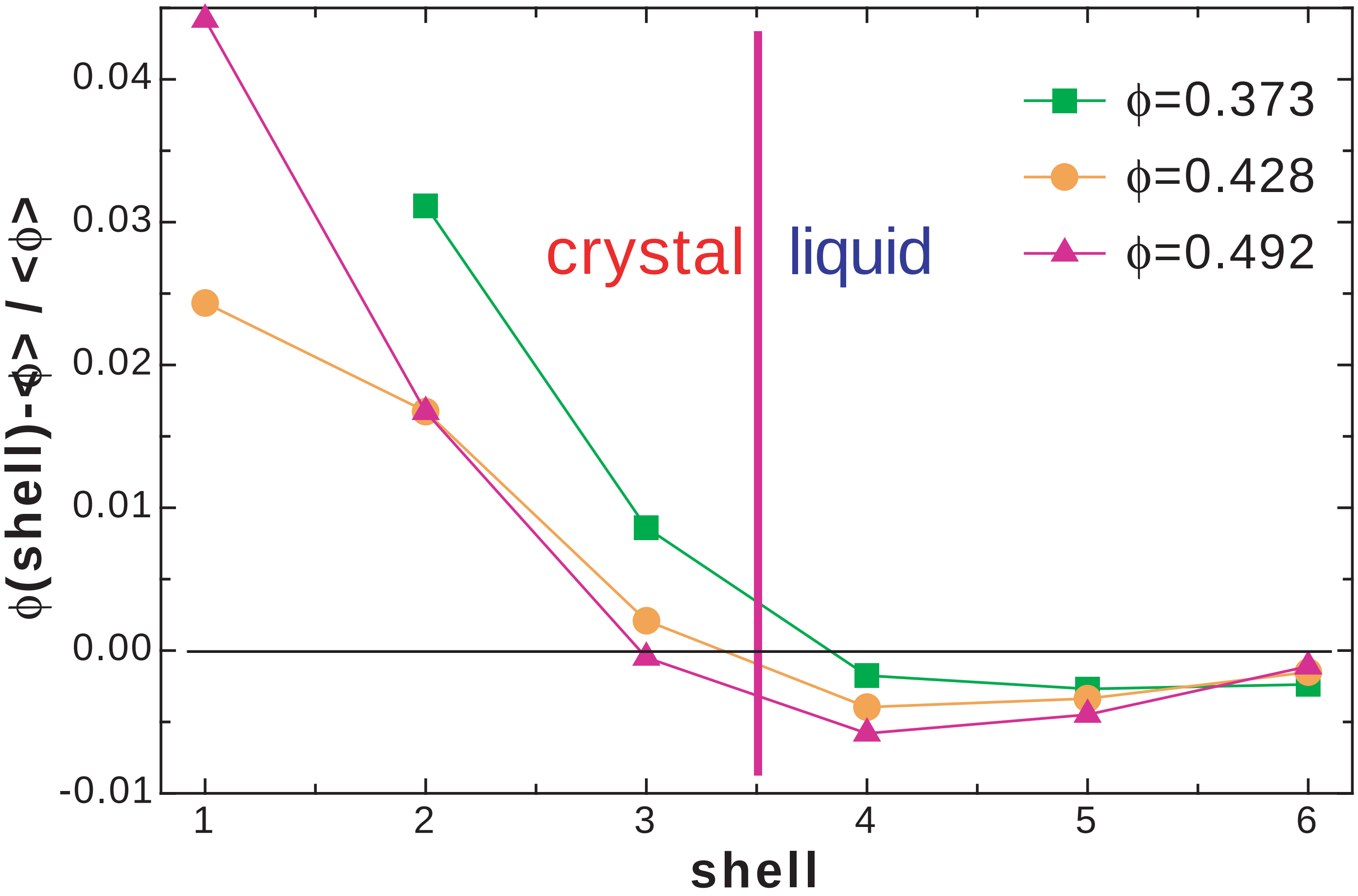
(for small r)

Measurement of Surface Tension

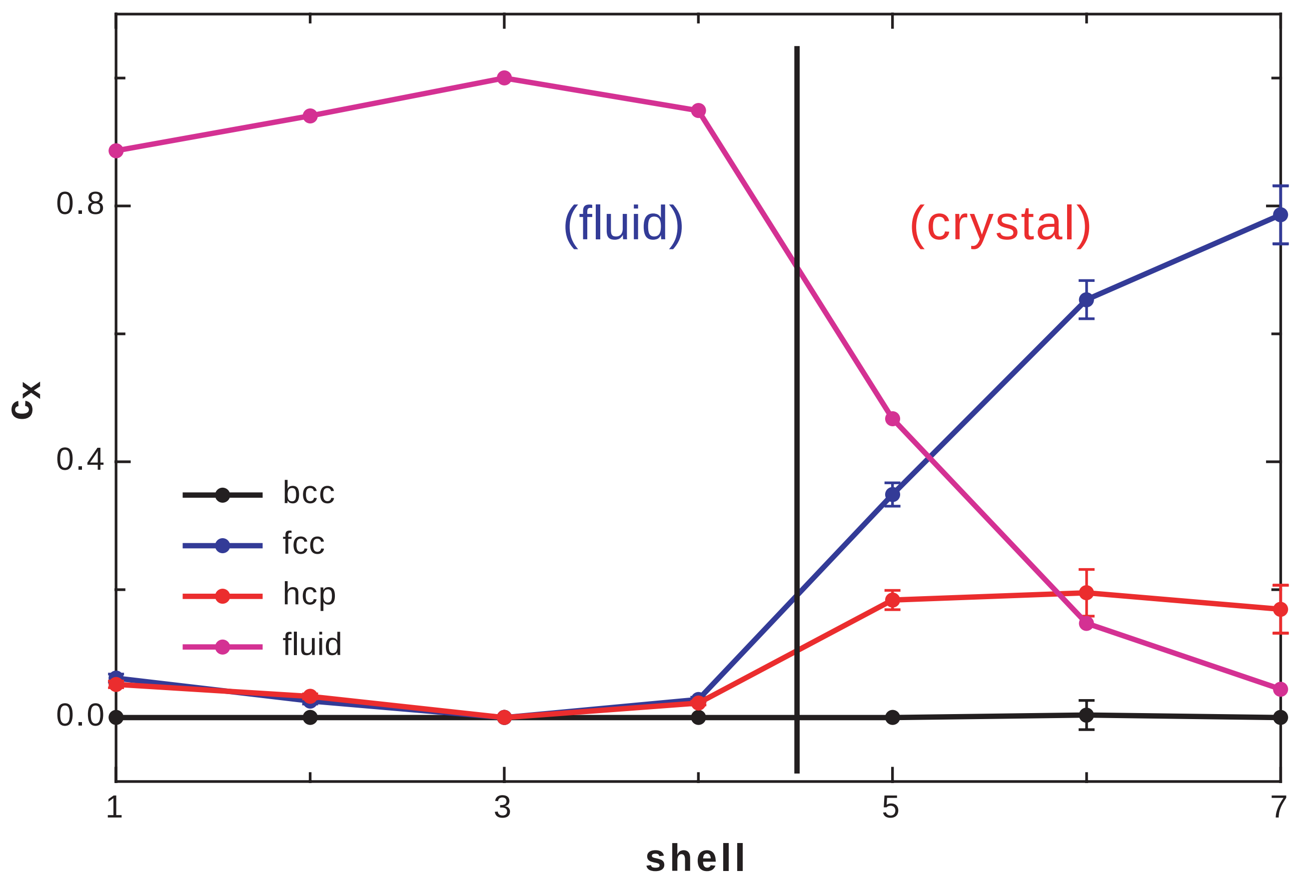


Surface tension is very low

Depletion Zone near Surface



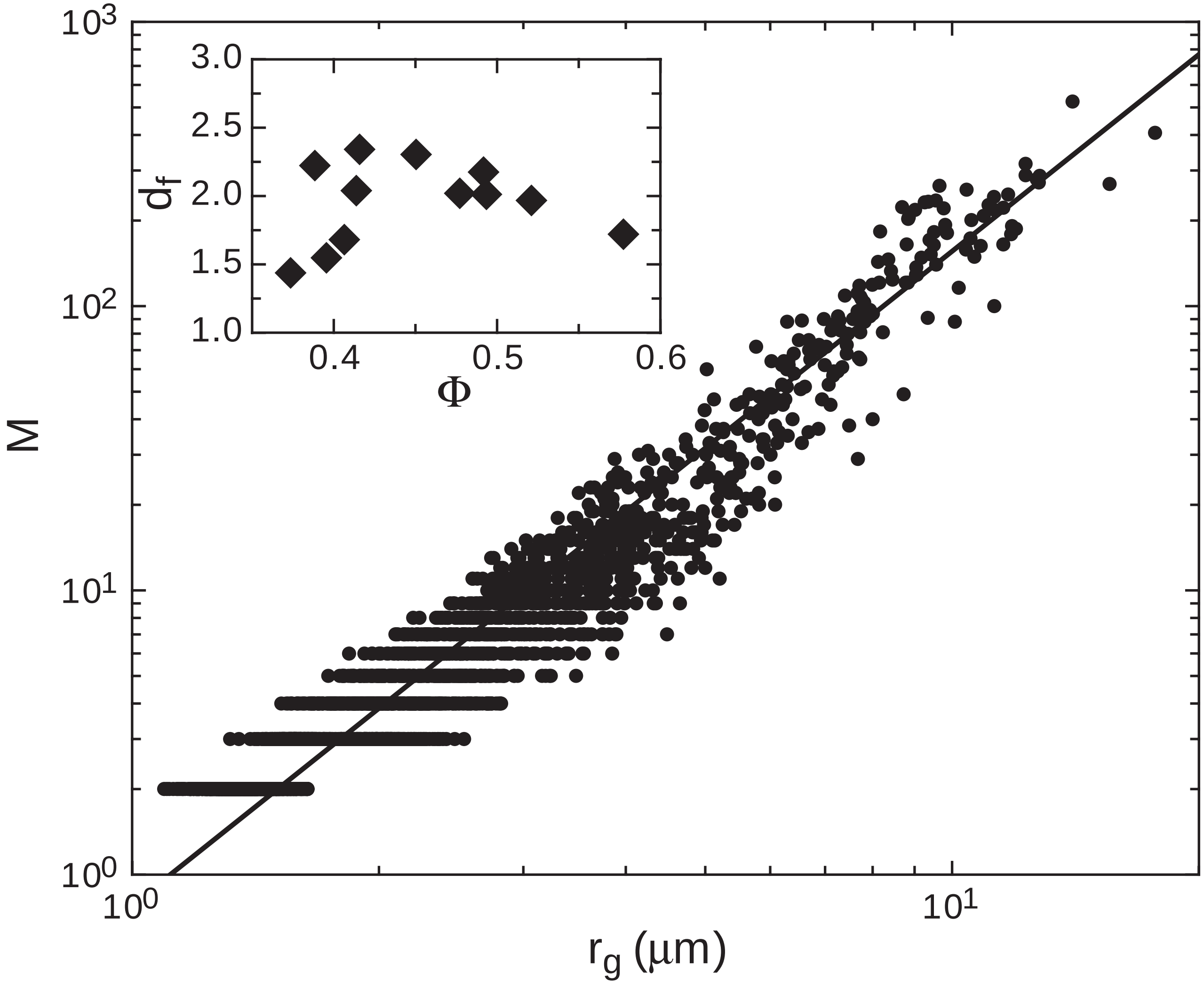
Crystal Structure through Interface



No bcc structure at all

Random stacking of hexagonal planes

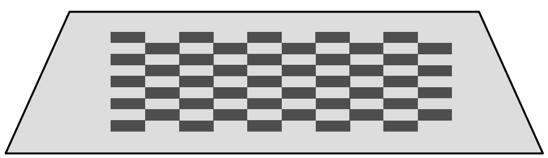
Fractal Structure of Growing Crystallites



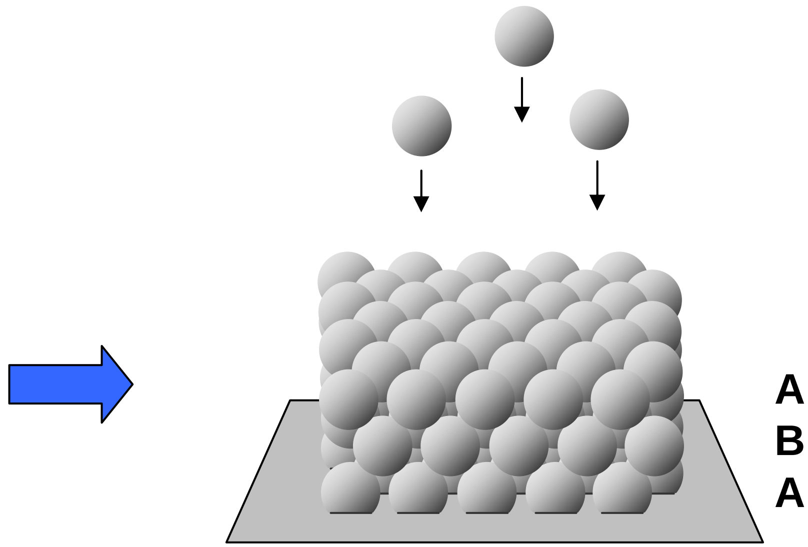
Single Crystal Growth - Principle

Peter Schall and Frans Spaepen

Laser mask writer



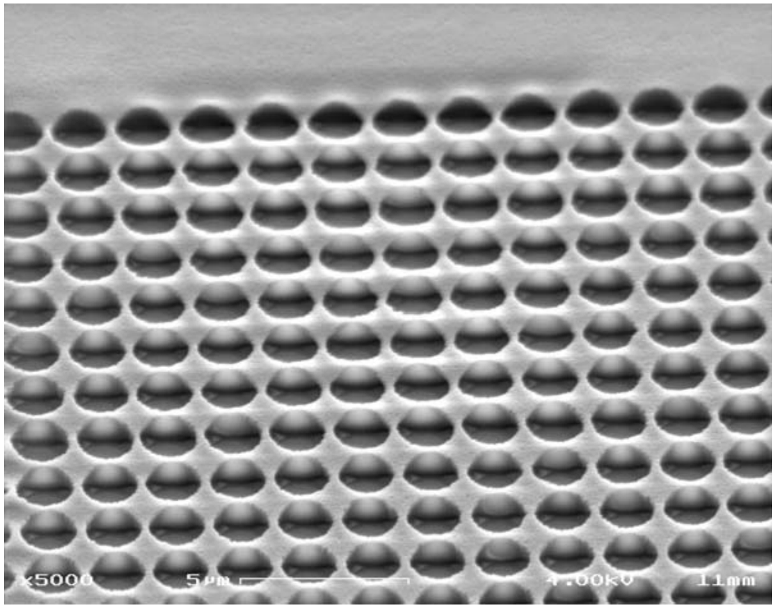
(a)



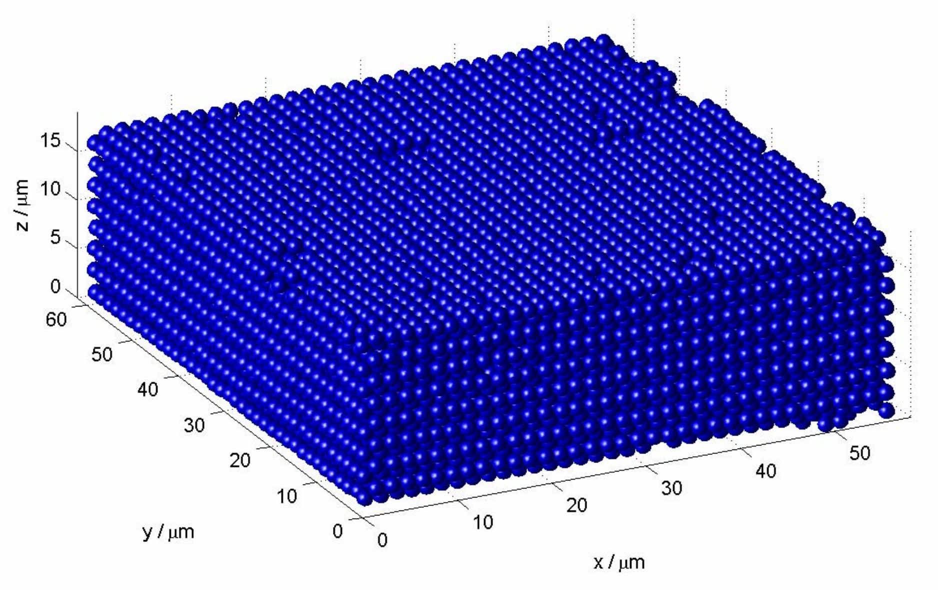
(b)

Fixed stacking sequence → fcc single crystal

Templated Growth of Single Crystals

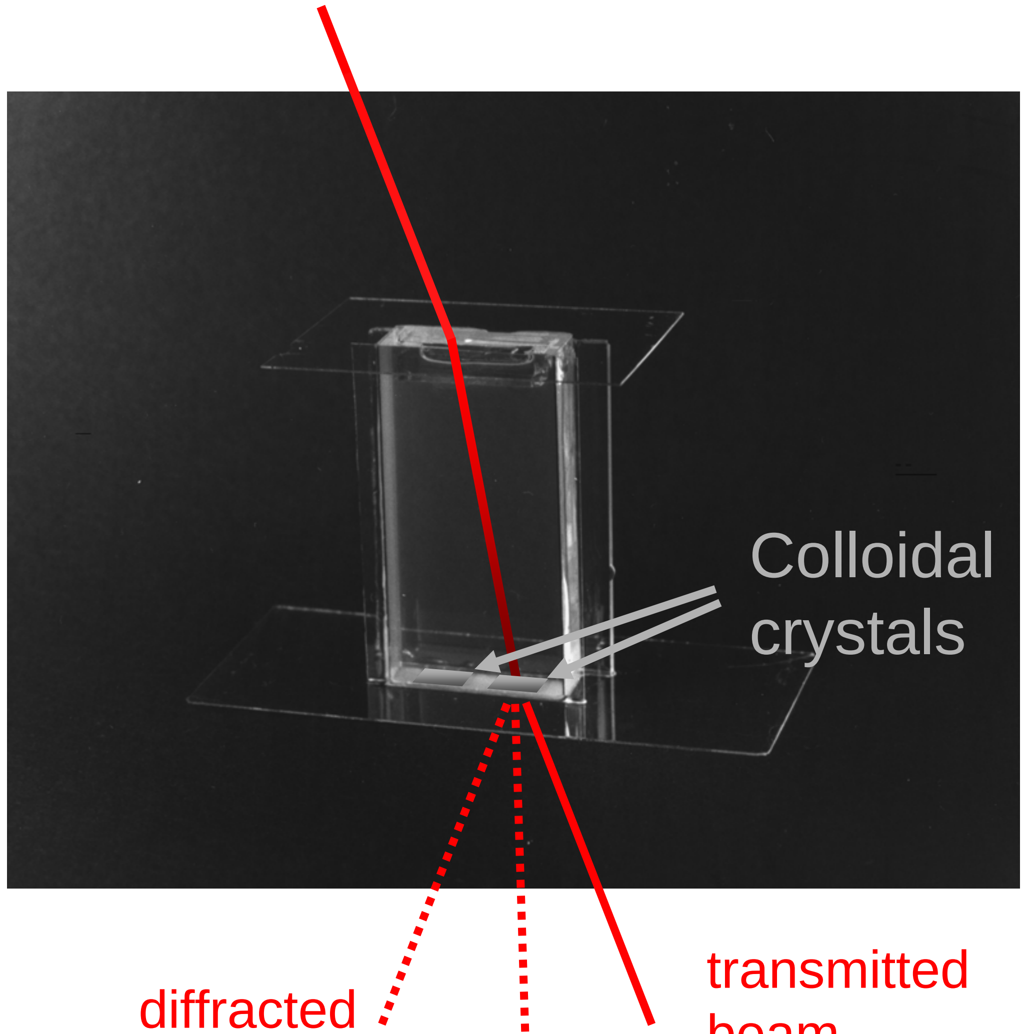


SEM micrograph

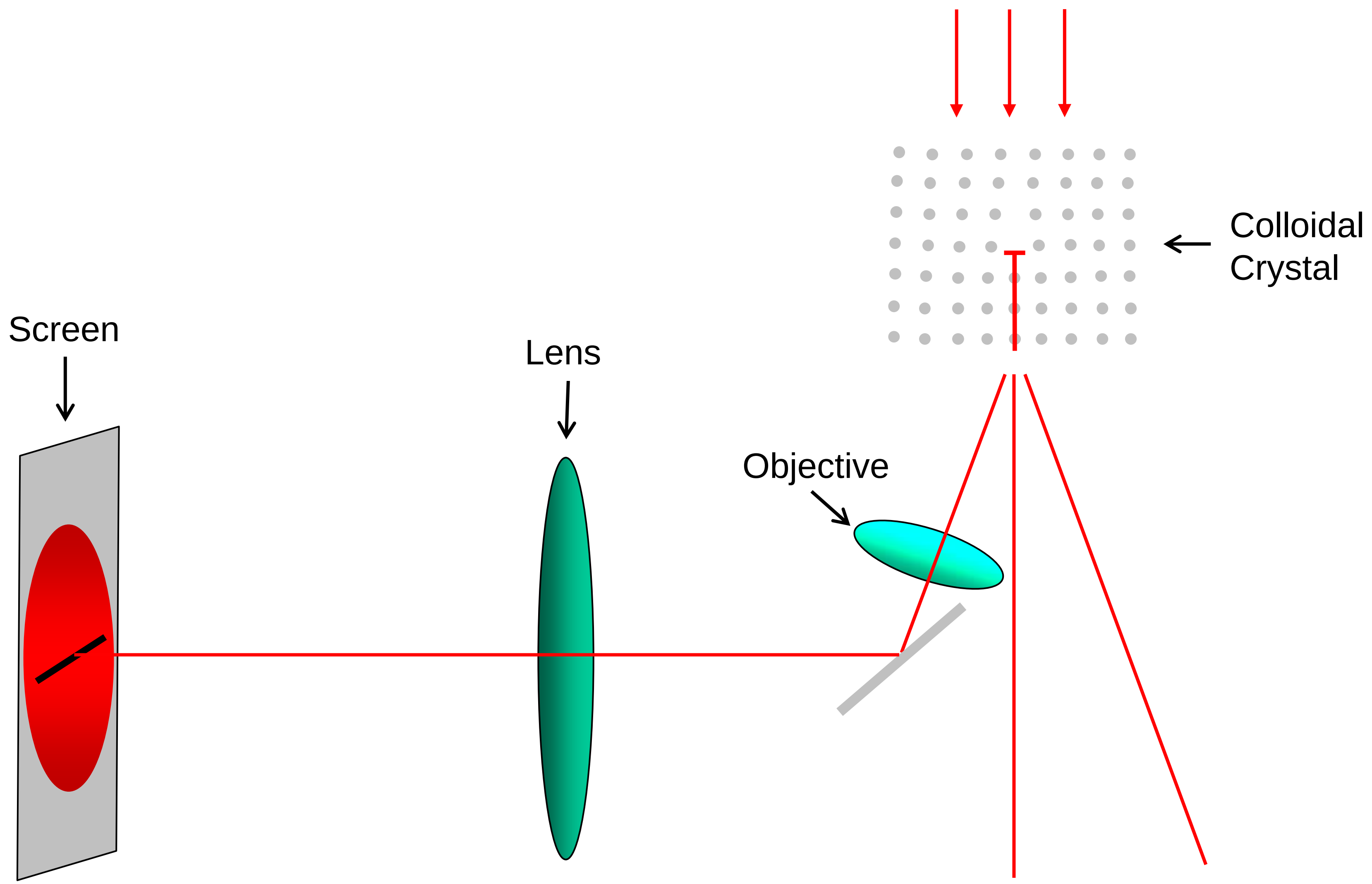


Confocal micrograph

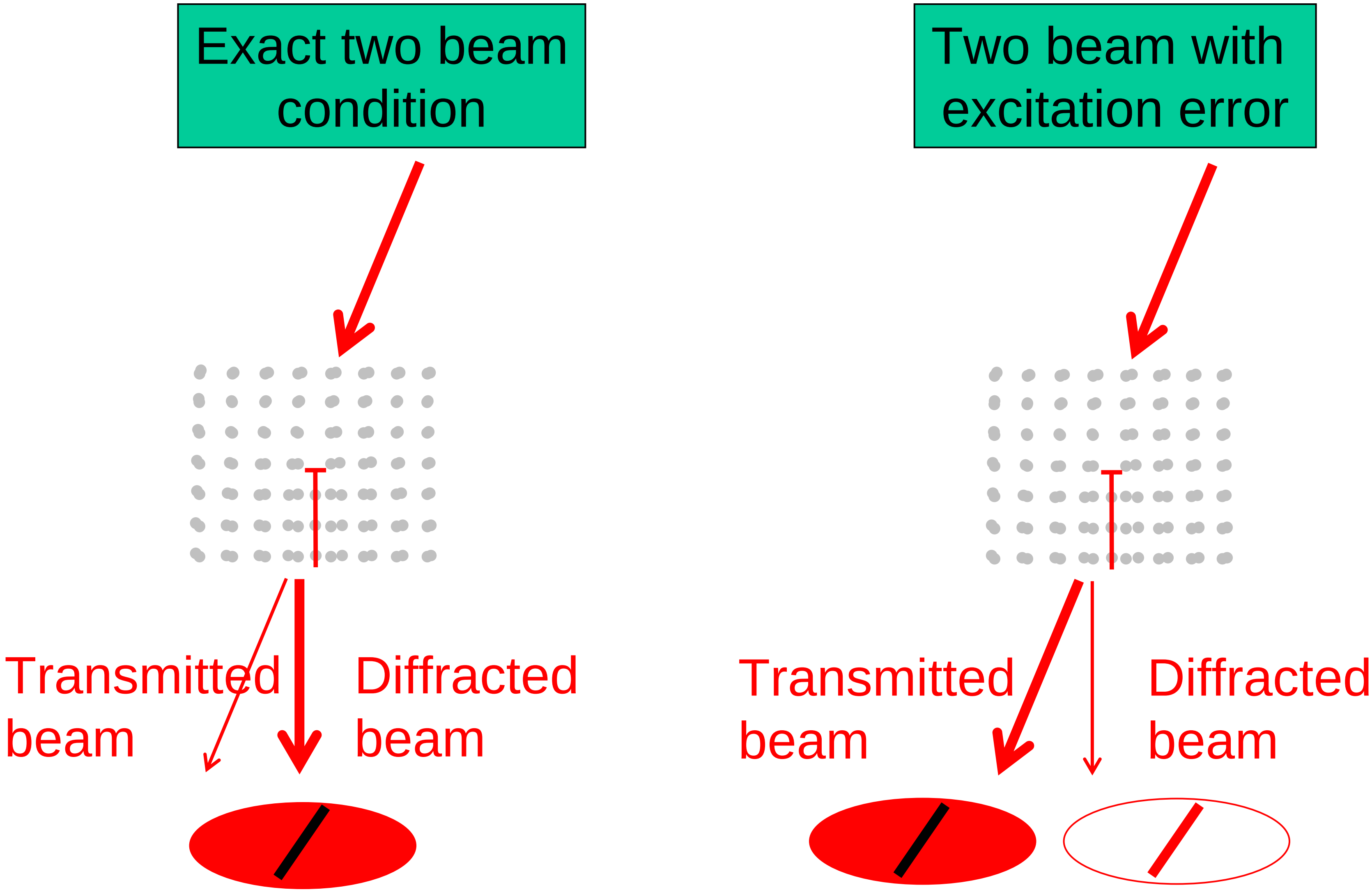
Thin Film of Single Crystal



Imaging Dislocations : Laser Microscope

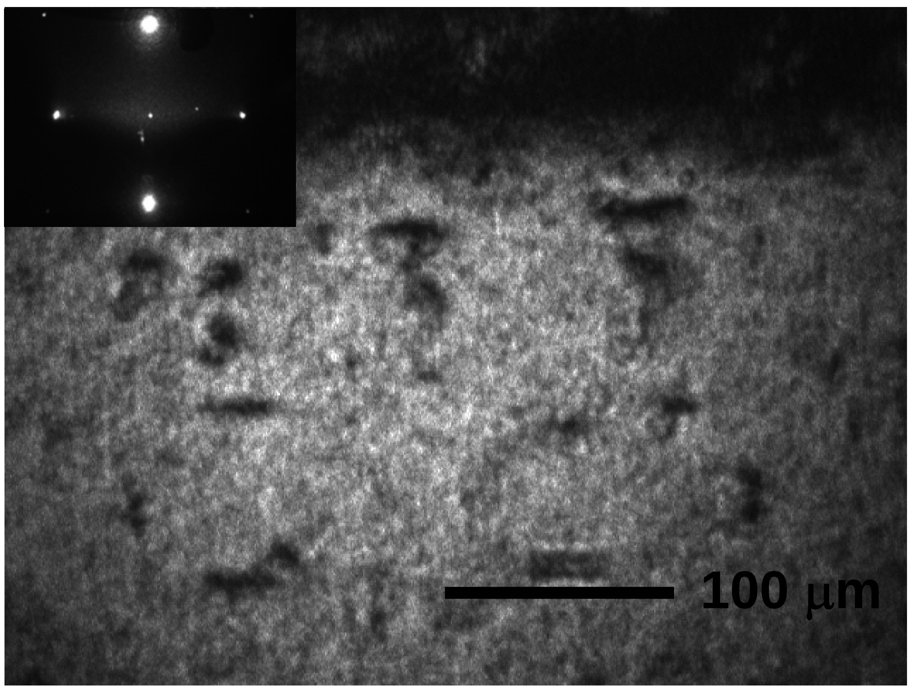


Imaging Dislocations: Excitation Error

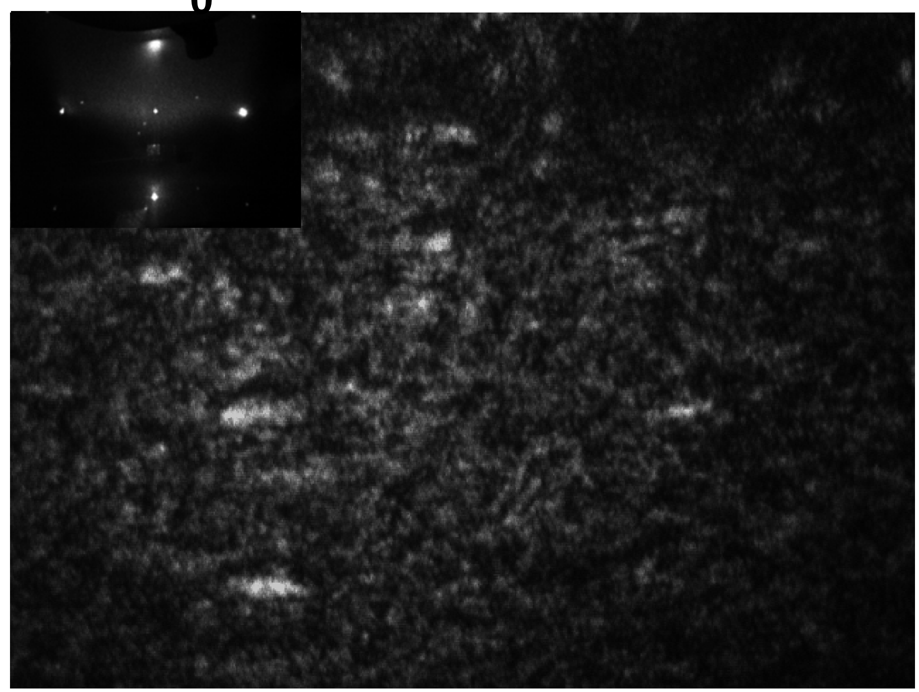


Imaging Dislocations: Nearly perfect crystal

Exact two beam condition



Two beam with excitation error

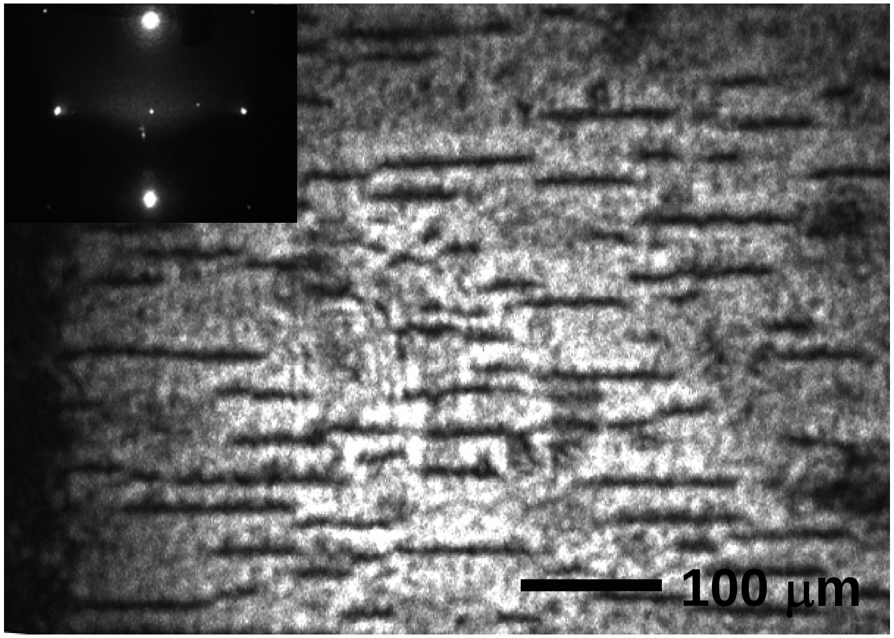


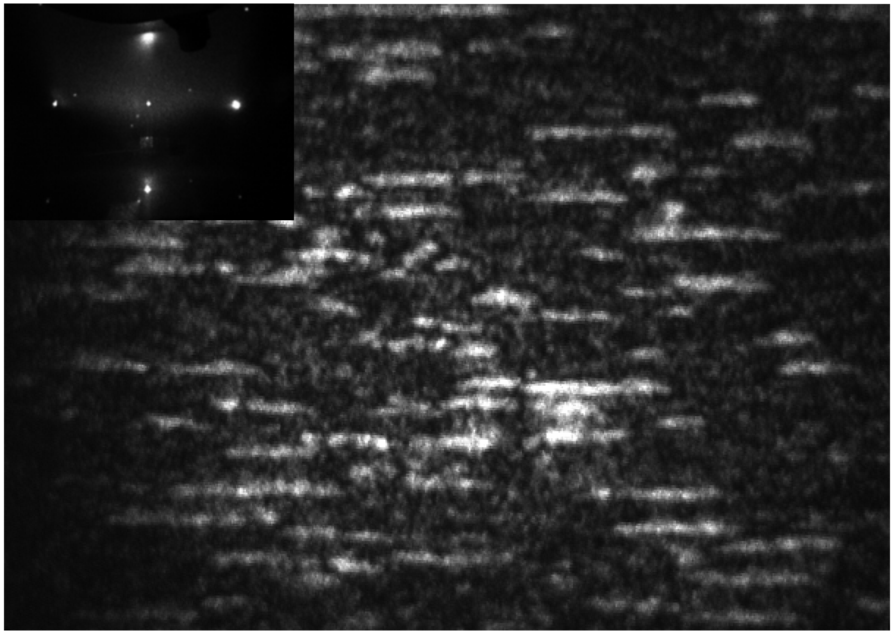
“good“ lattice constant

Imaging Dislocations

Exact two beam condition

Two beam with excitation error

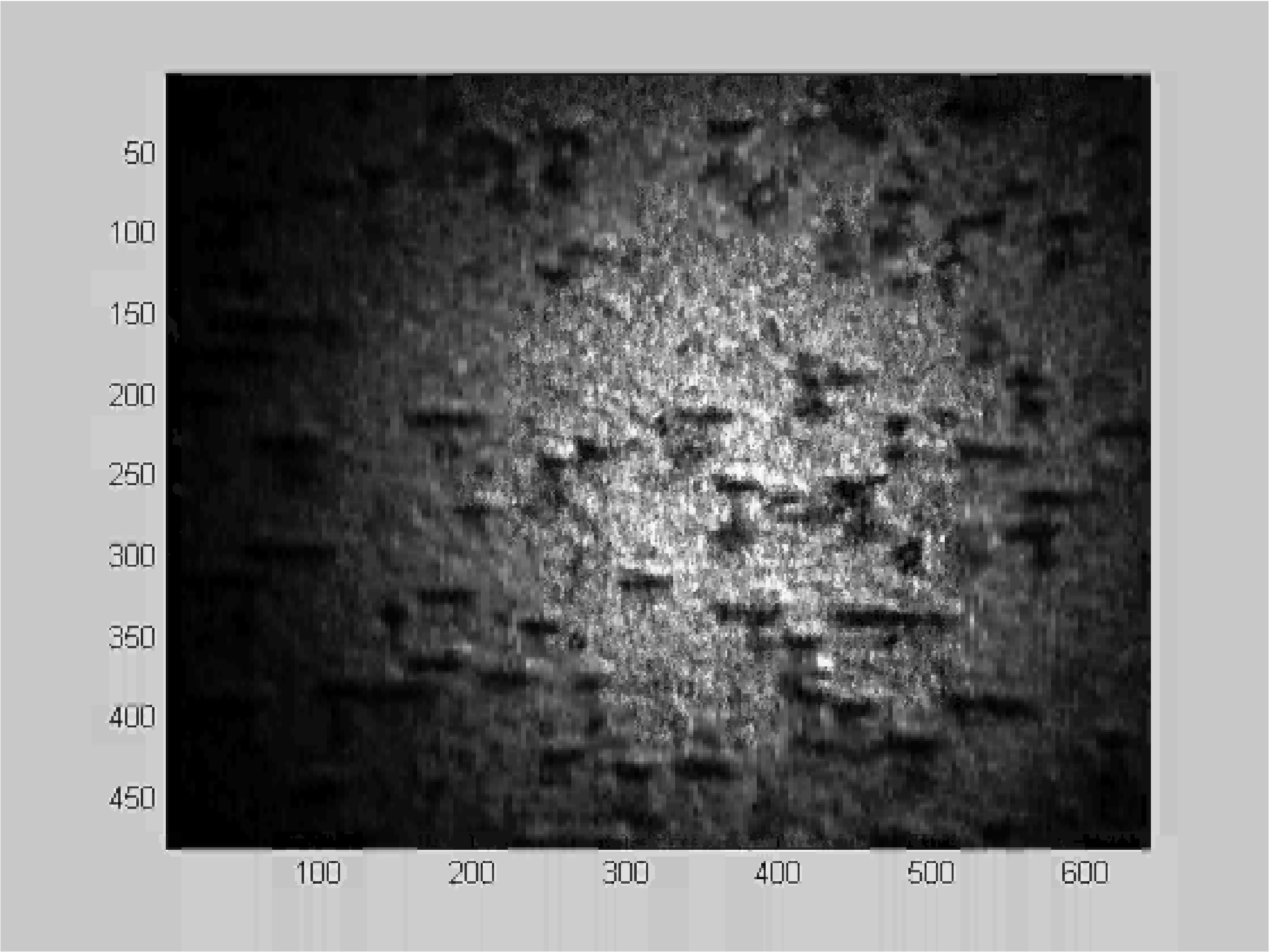




Template stretched by 1.5 %

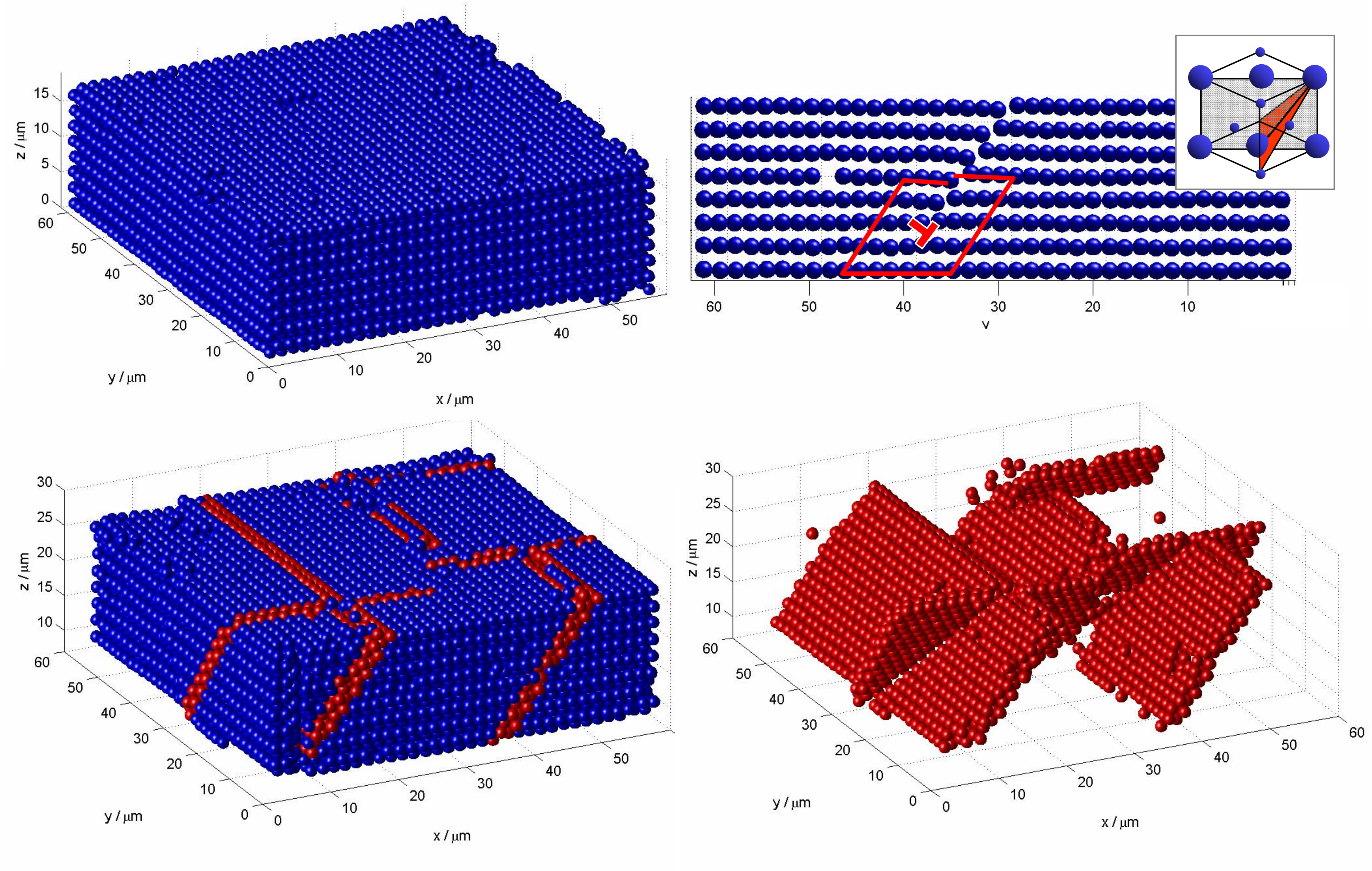
Nucleation and Growth of Dislocations

- template lattice constant off by 1.5 %

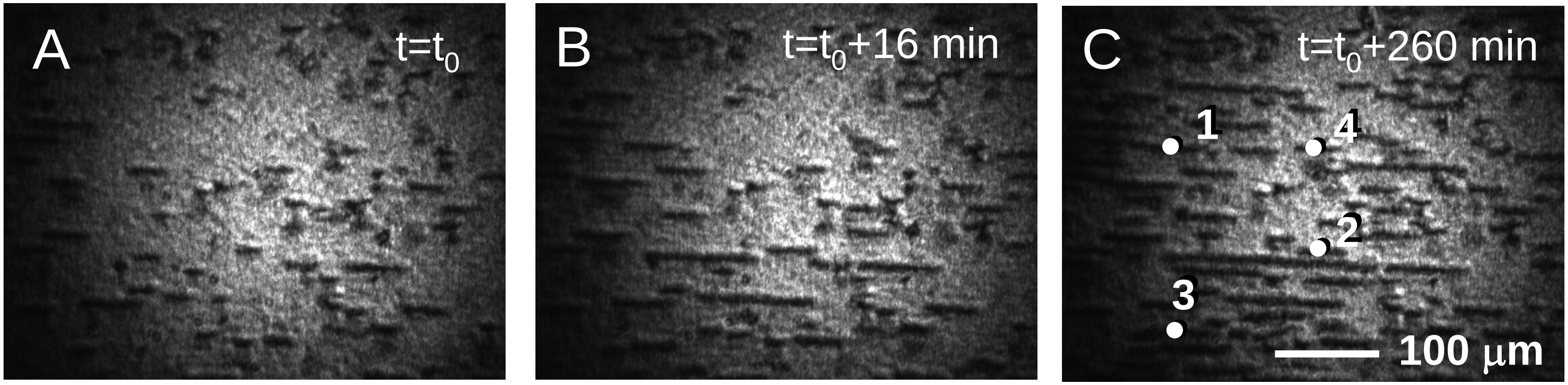


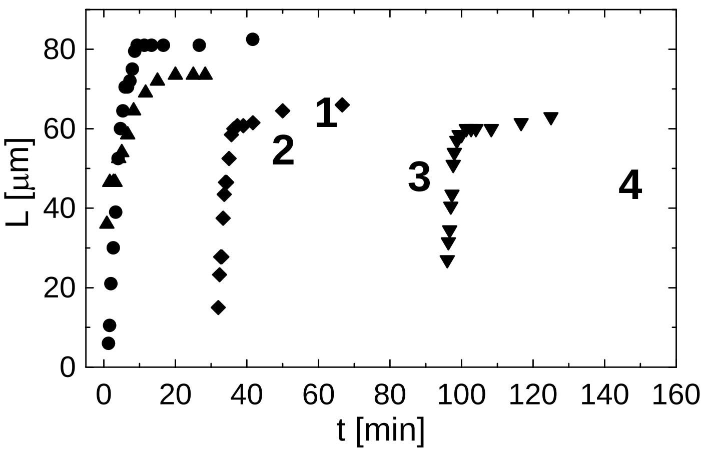
(film recorded immediately after settling of ~ 8 additional crystalline layers
recording time 3.5 hours

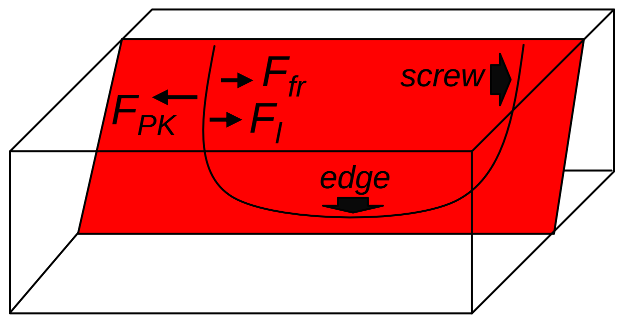
Stacking Faults induced by Lattice Mismatch

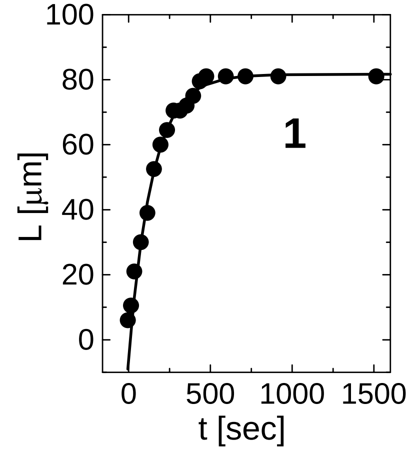


Growth of Defects







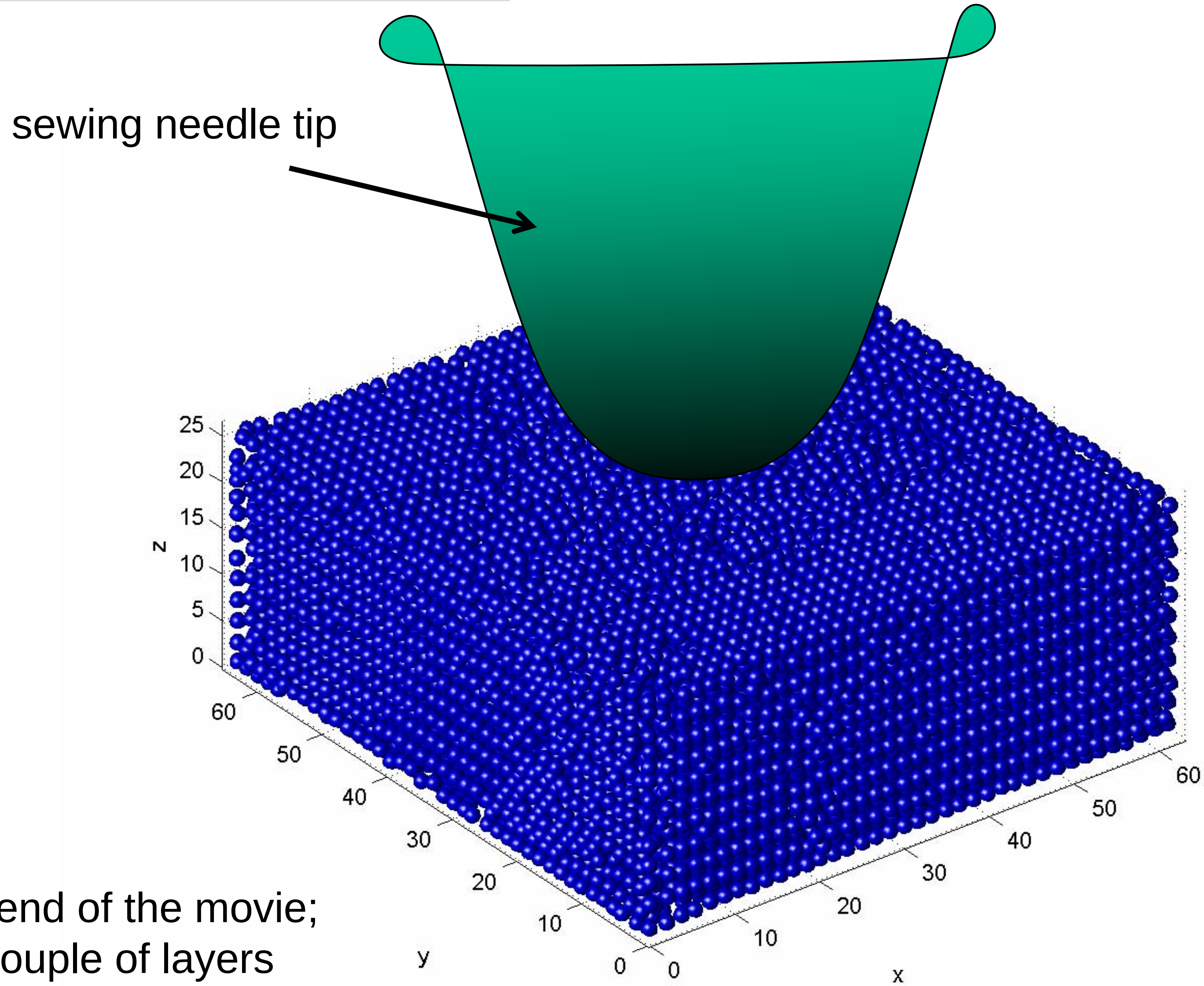


•Balance forces for growth rate

•Elastic force = viscous drag + line tension

•Exponential functional form

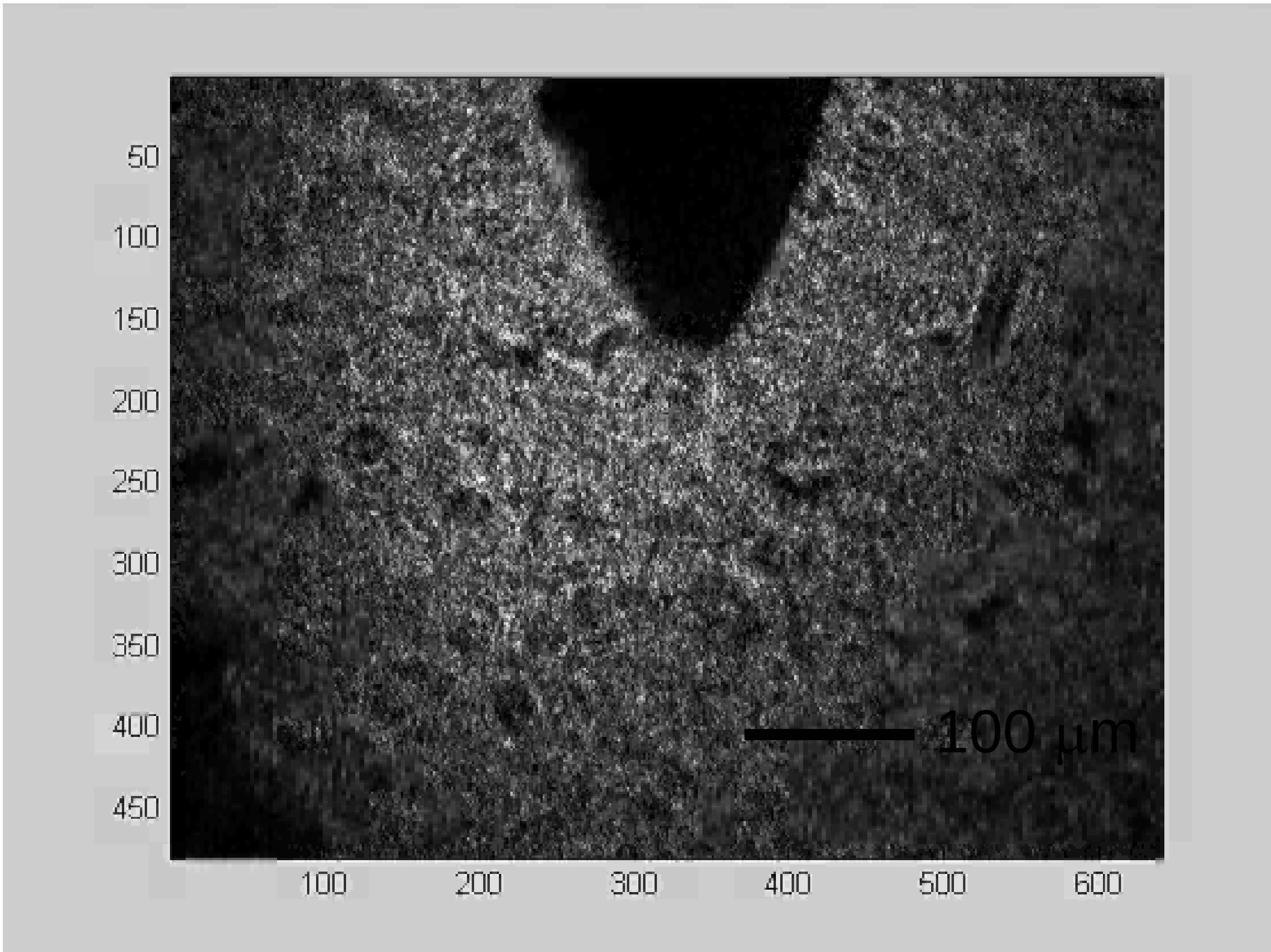
Indentation experiment



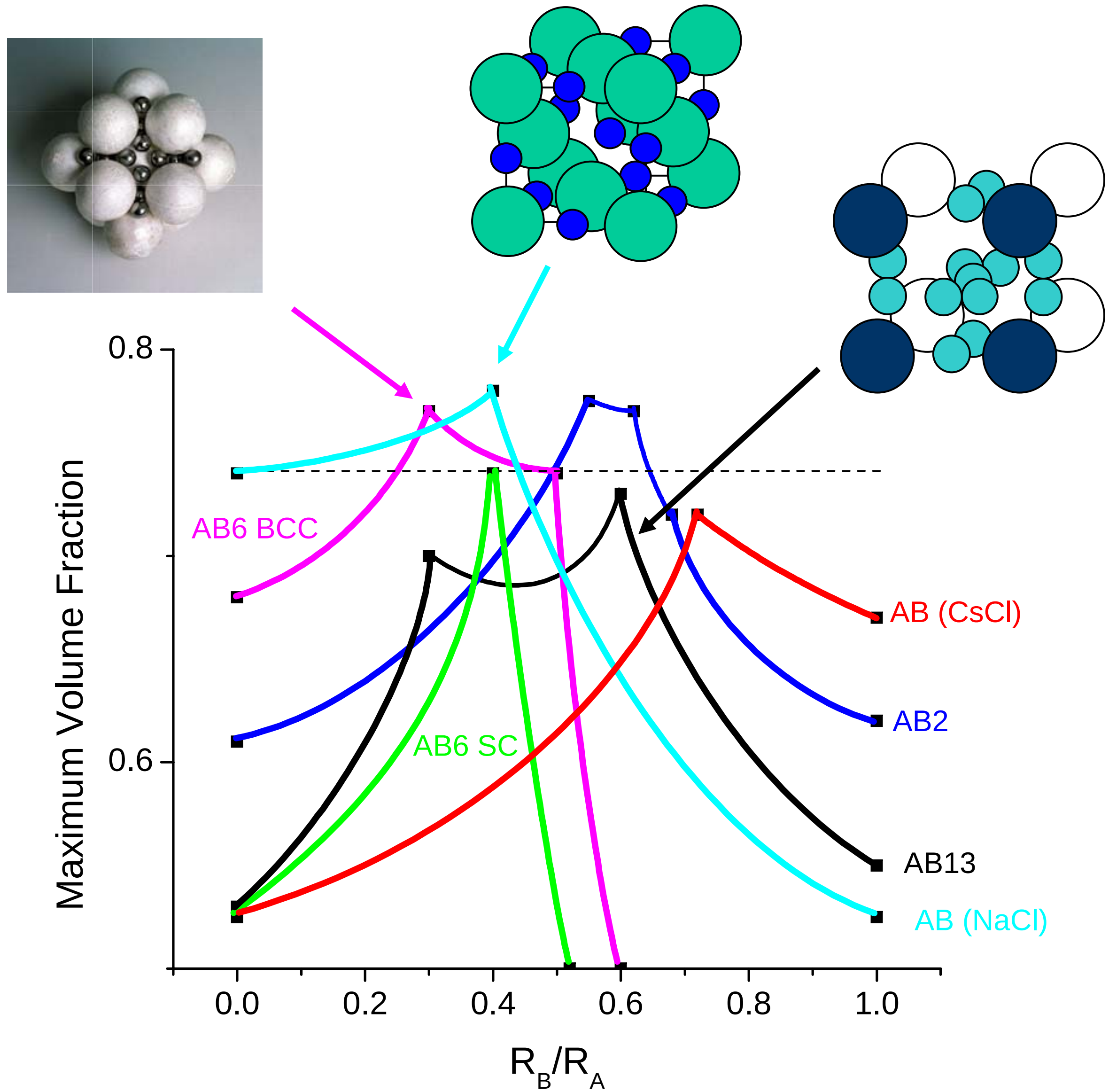
(Crystal at the end of the movie; there is still a couple of layers above the layers shown)

Dislocation Dynamics and Interactions

- Indentation

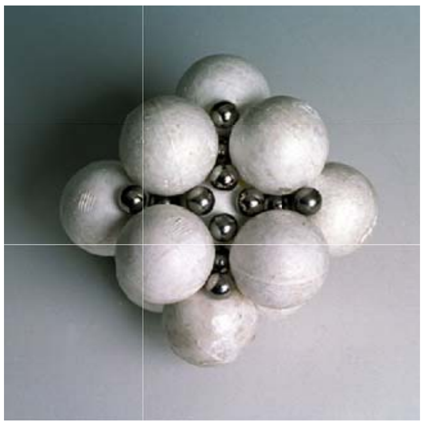


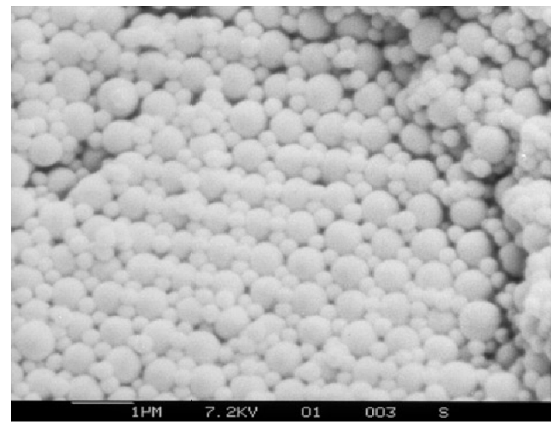
Binary Colloidal Crystals



(Schofield, et al)

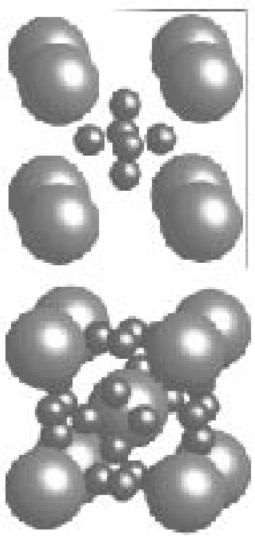
AB_6

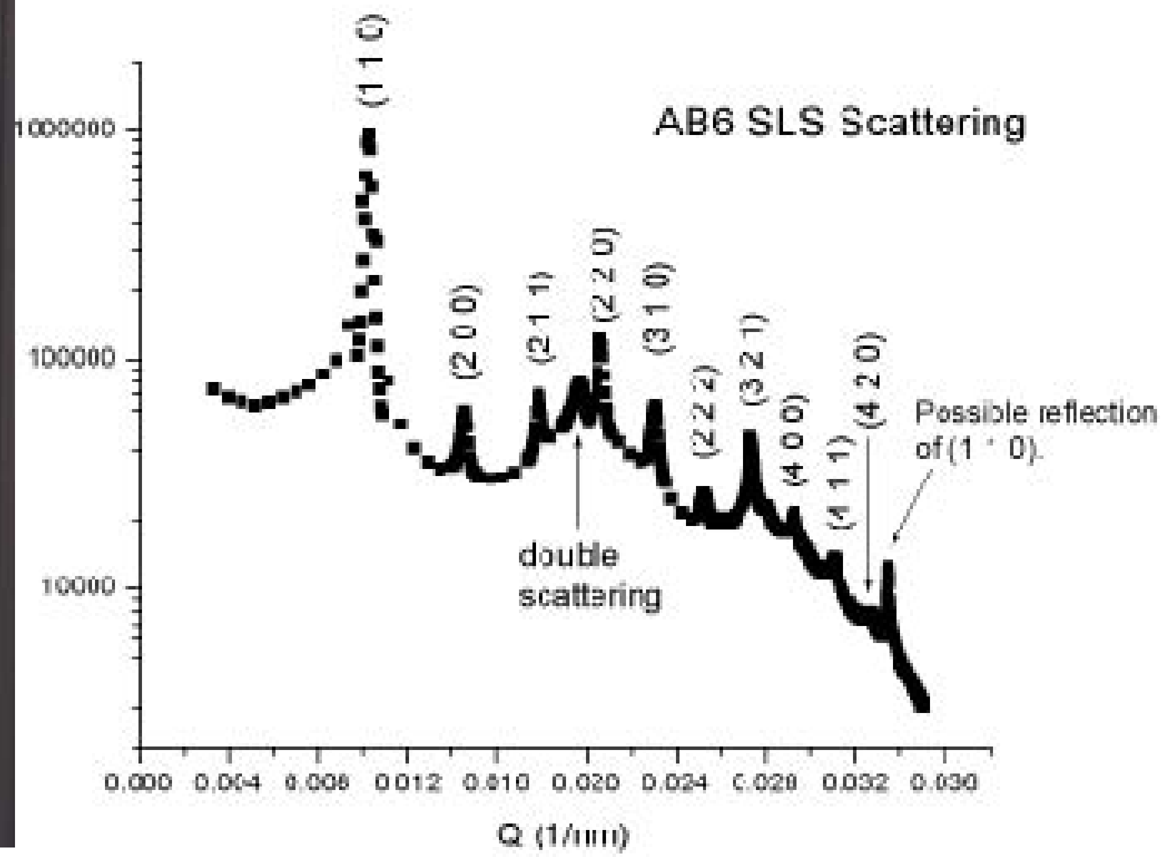




- AB6 occurs in three different structures: simple cubic, BCC and FCC, which occur at different size ratios from 0.3 to 0.4
- BCC is the fastest to crystallize, with crystals forming overnight at the optimal size ratio of 0.4

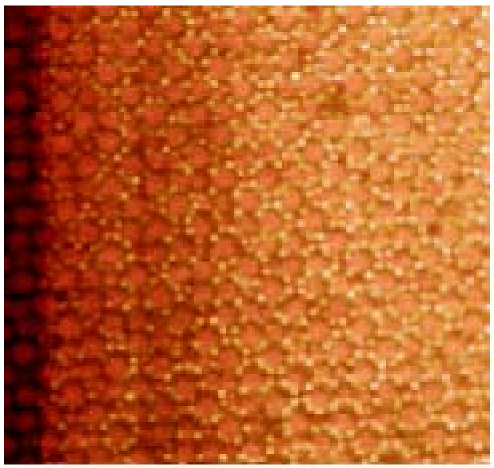
AB$_6$ Binary Alloy Crystal

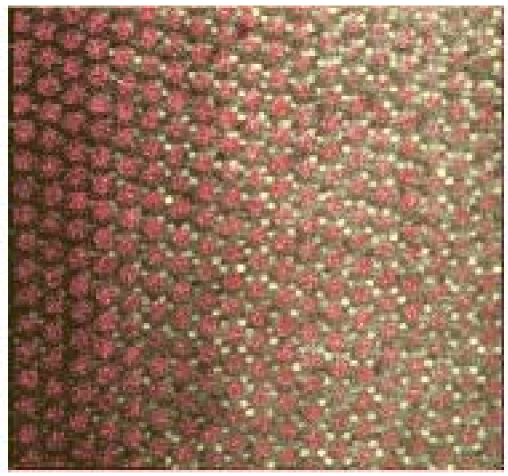


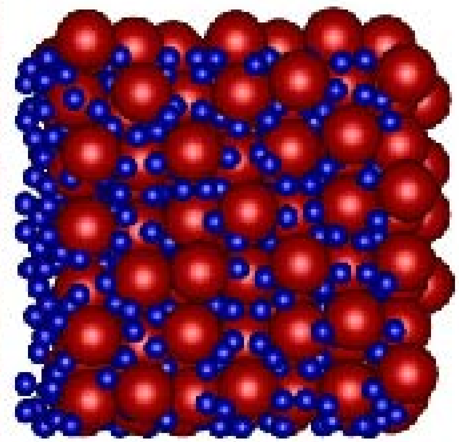


- Very intense Bragg scattering
- Very large crystals

AB_6 Binary Alloy Crystal

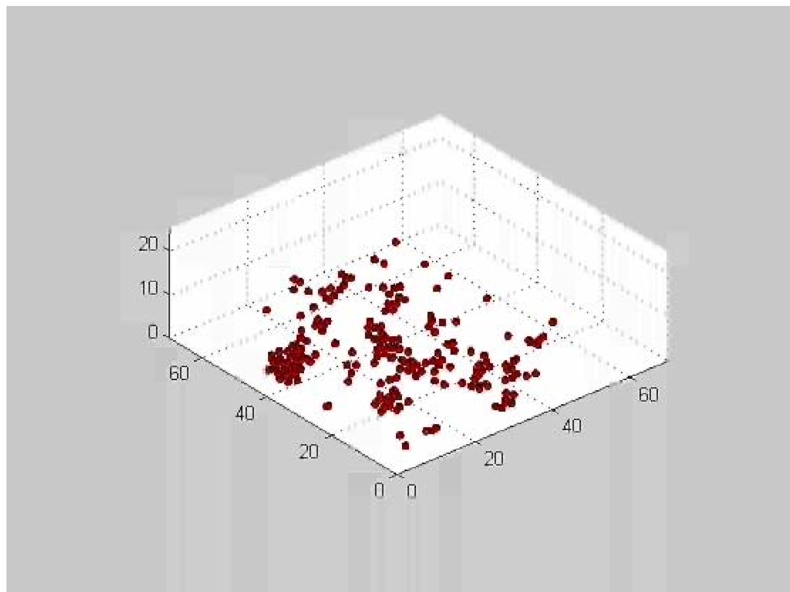






- Very well ordered FCC structure
- Small particles induce effective long-range intereaction
  - Creates highly ordered large particle lattice

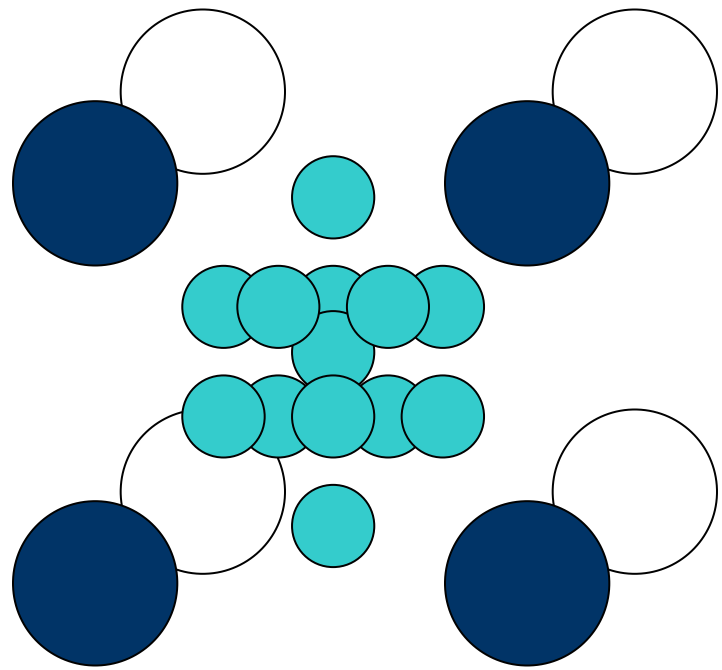
Nucleation and Growth of AB_6



Look only at large particles → perfect BCC lattice

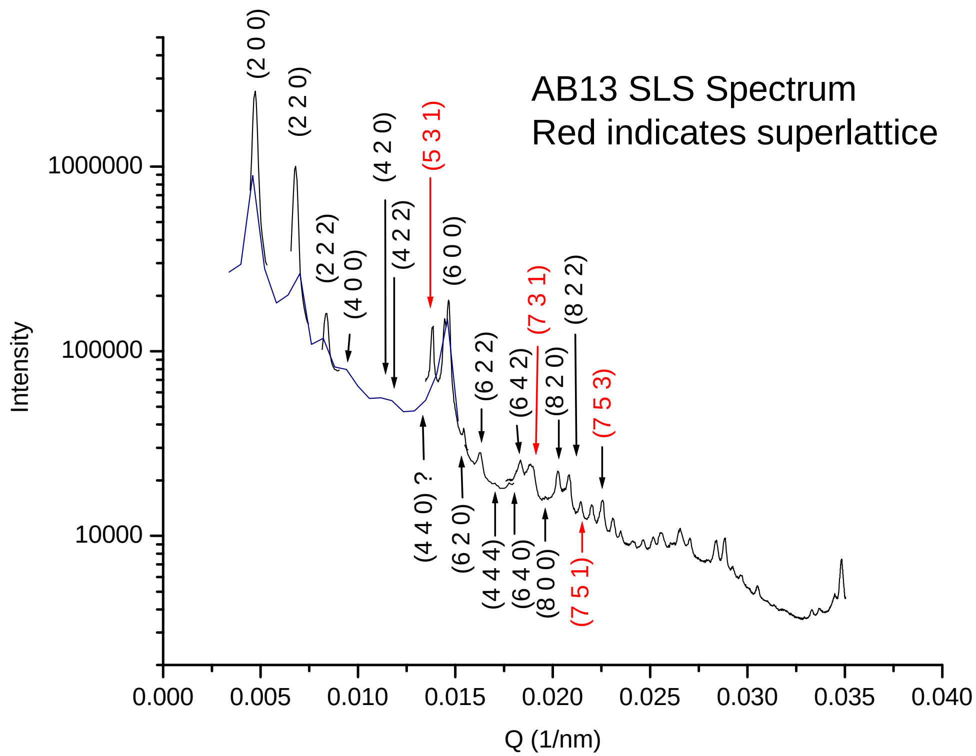
AB_{13}

- Icosahedra of small particles, at center of simple cube of big particles
- Found naturally in bimetallic alloys such as $NaZn_{13}$
- Stable at size ratios from 0.5-0.7

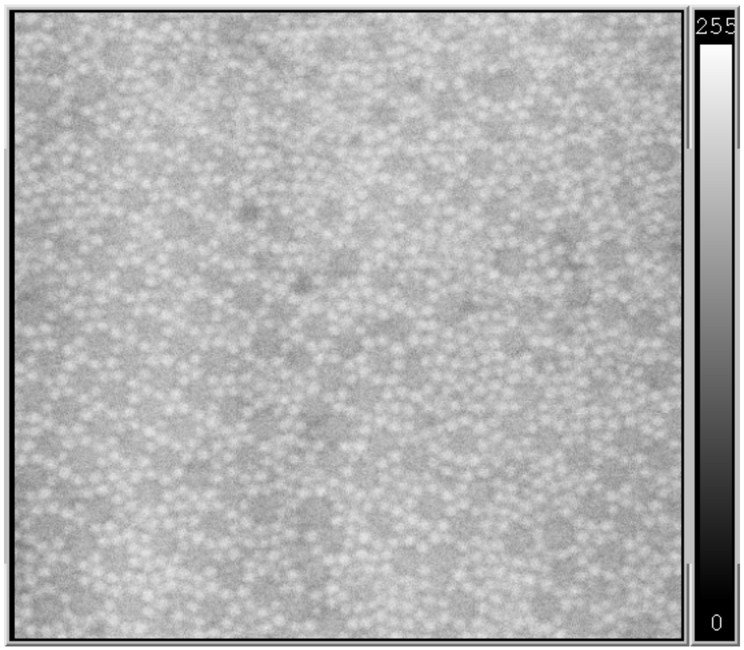


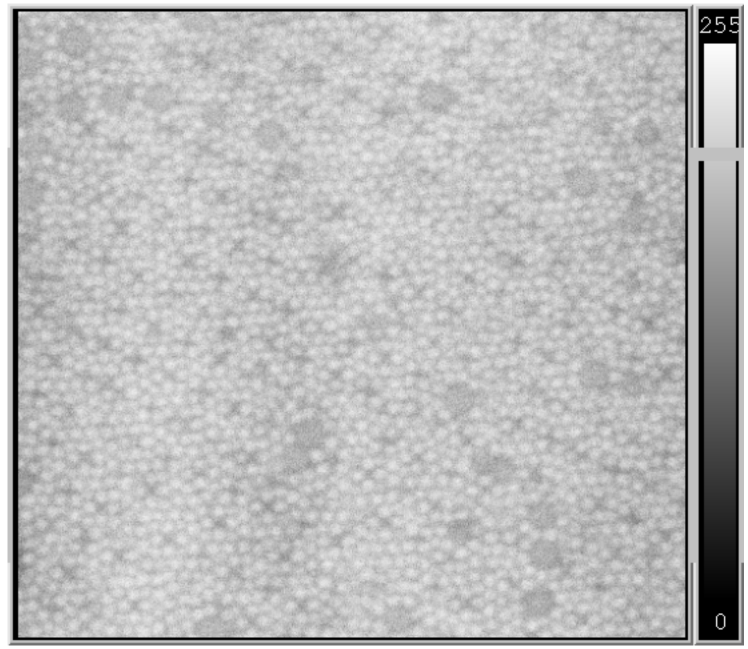
AB_{13} Space Sample

$R_B/R_A = 0.57,\ N_B/N_A = 19$



Mixed Sizes:
AB_{13} Binary Alloy Crystal



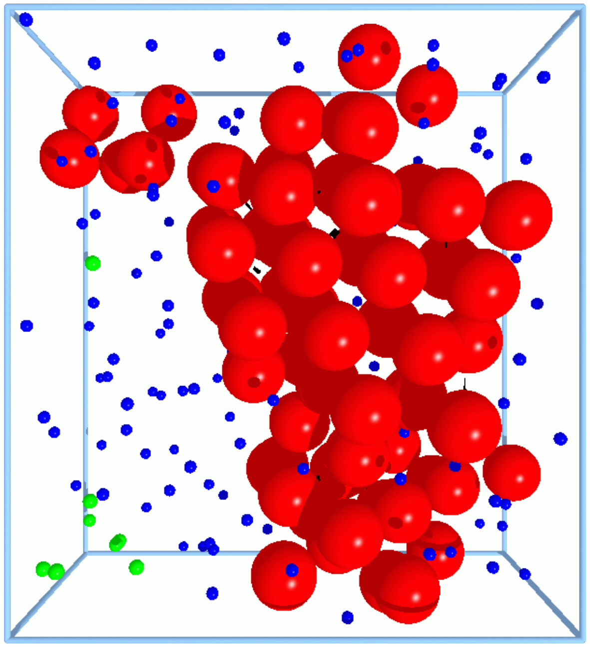


- Very well ordered FCC structure
- Small particles induce effective long-range intereaction
    - Creates highly ordered large particle lattice

Conclusions

Real space imaging of colloidal structure and dynamics

•3D observation of crystallization
•Defect growth in crystal films
•Binary Alloy Colloidal Crystals



http://www.deas.harvard.edu/projects/weitzlab