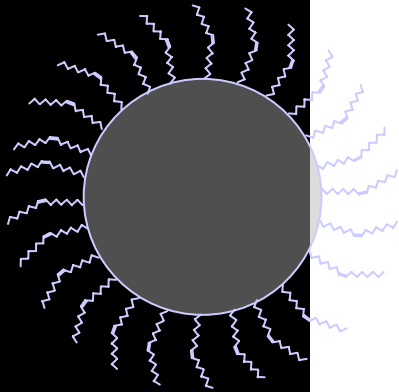


Nanocrystal quantum dots and quantum dot solids



QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Soft Condensed Matter

20 April 2007

Daniël Vanmaekelbergh

Nanocrystal quantum dots and quantum dot solids

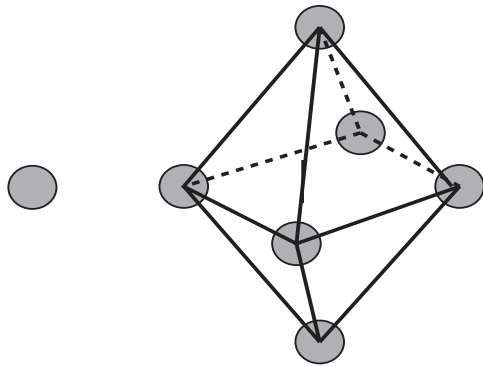
Nanocrystals and assemblies of nanocrystals: An overview

Chemical preparation

Electronic structure, optical and electrical properties

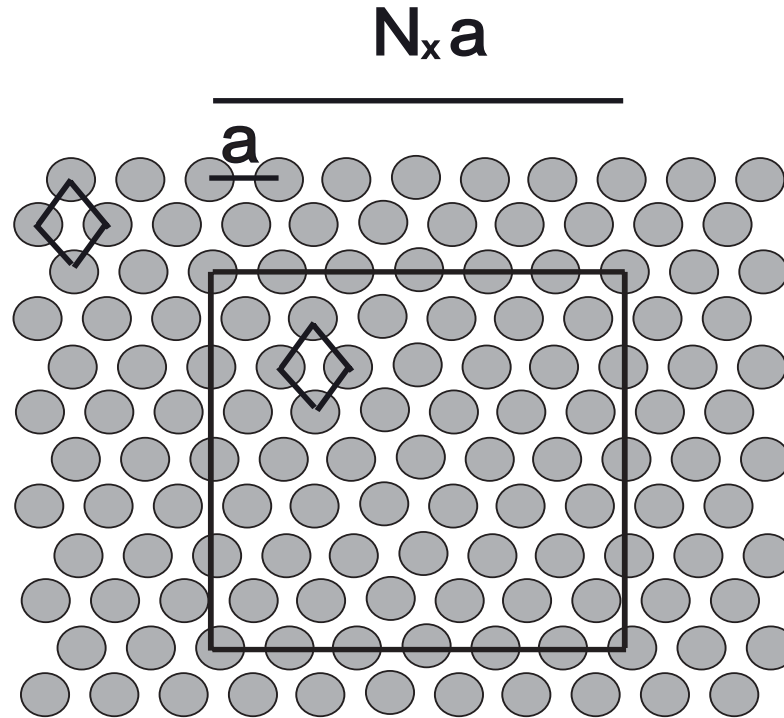
Self-assembly of NC into solids

1.1 Clusters and nanocrystals



cluster: 1- 100 atoms
Thermodynamic stability and structure depends on N :

Mono-disperse **Au 55**

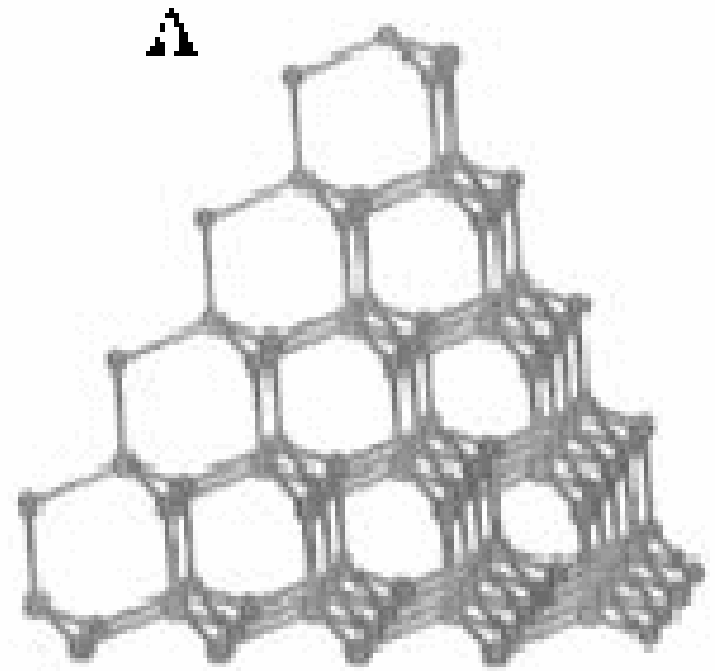
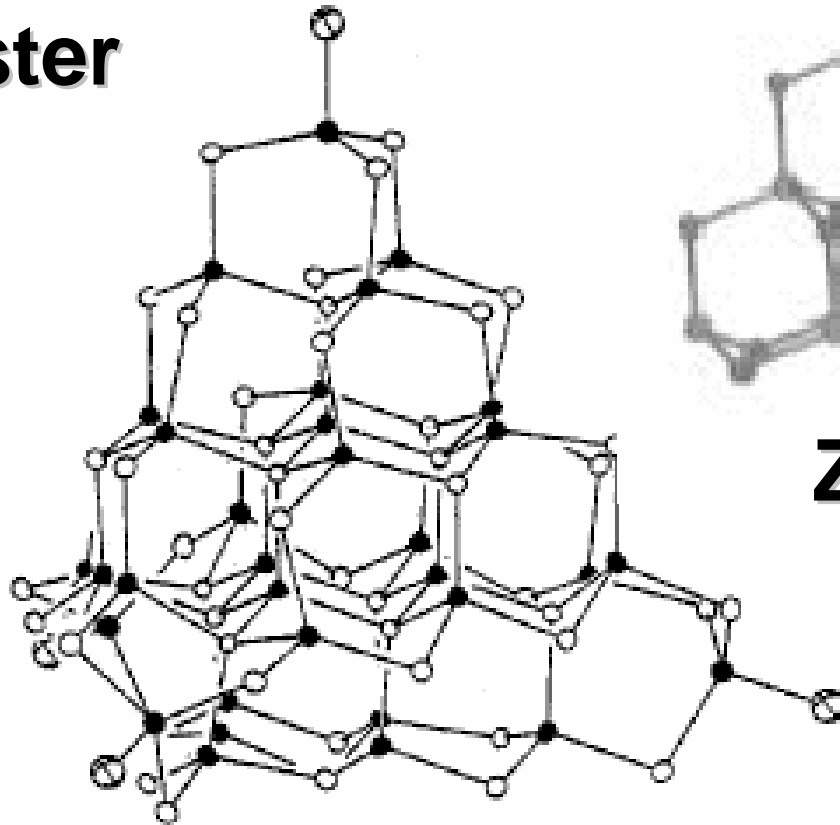


Nanocrystal:

Thermodynamic stability is independent of N :

↓
distribution in size and shape

CdS - cluster

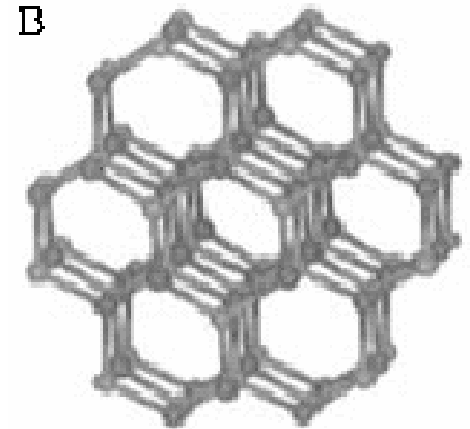
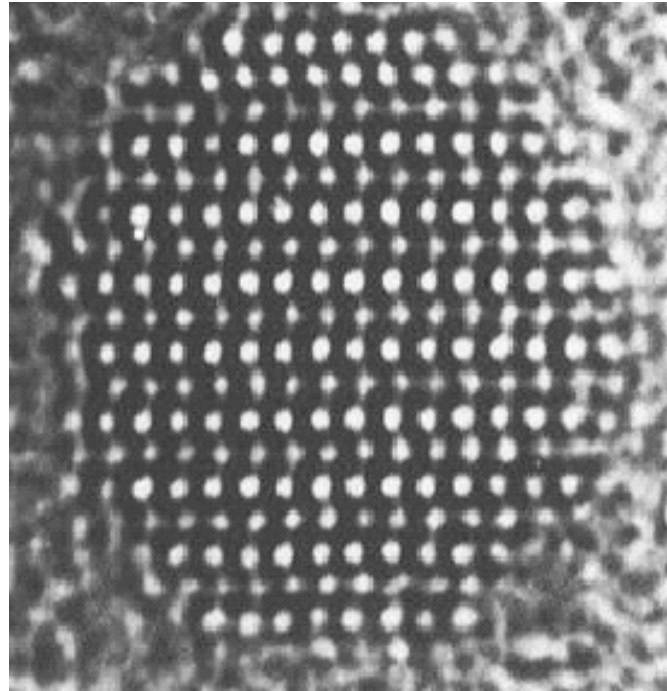
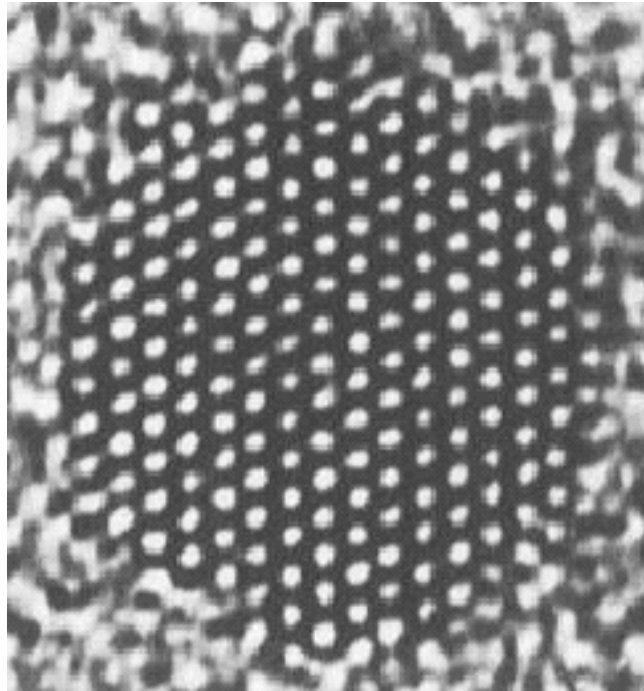


Zinc-blende

Figure 3. Ball and stick model of a $\text{Cd}_{32}\text{S}_{55}$ molecule recently synthesized and structurally characterized by Herron and Wang.²² The organic ligands are omitted for clarity. This molecule is a fragment of the CdS zinc blende lattice.

Colloidal nanocrystals

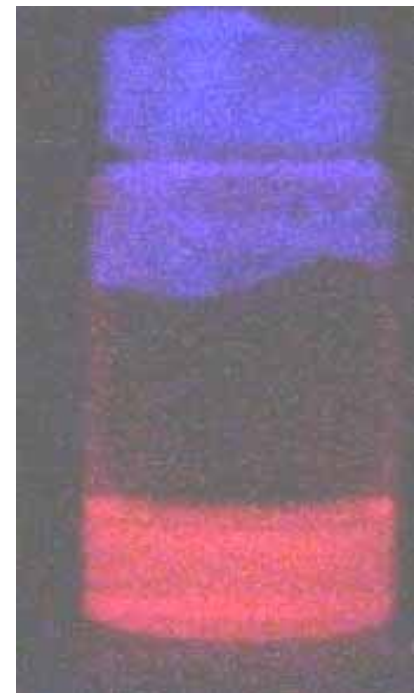
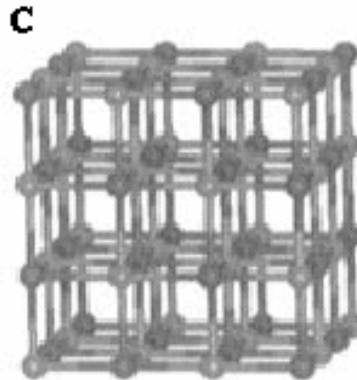
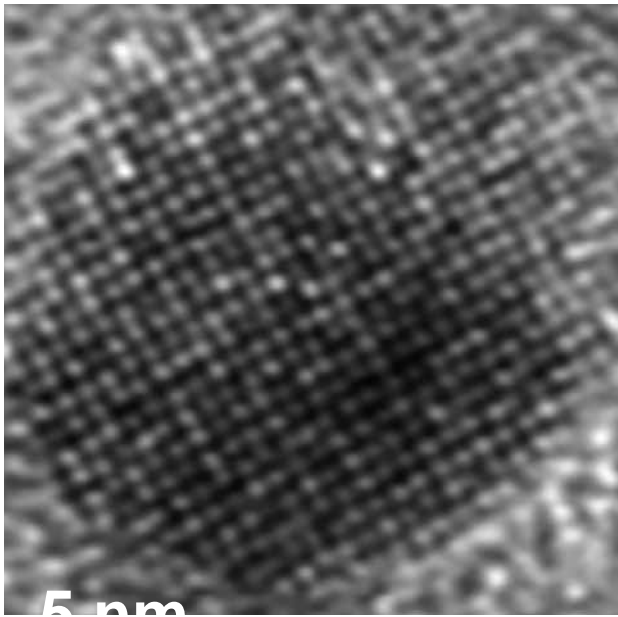
CdSe: wurtzite



Nearly spherical shape, crystal facets

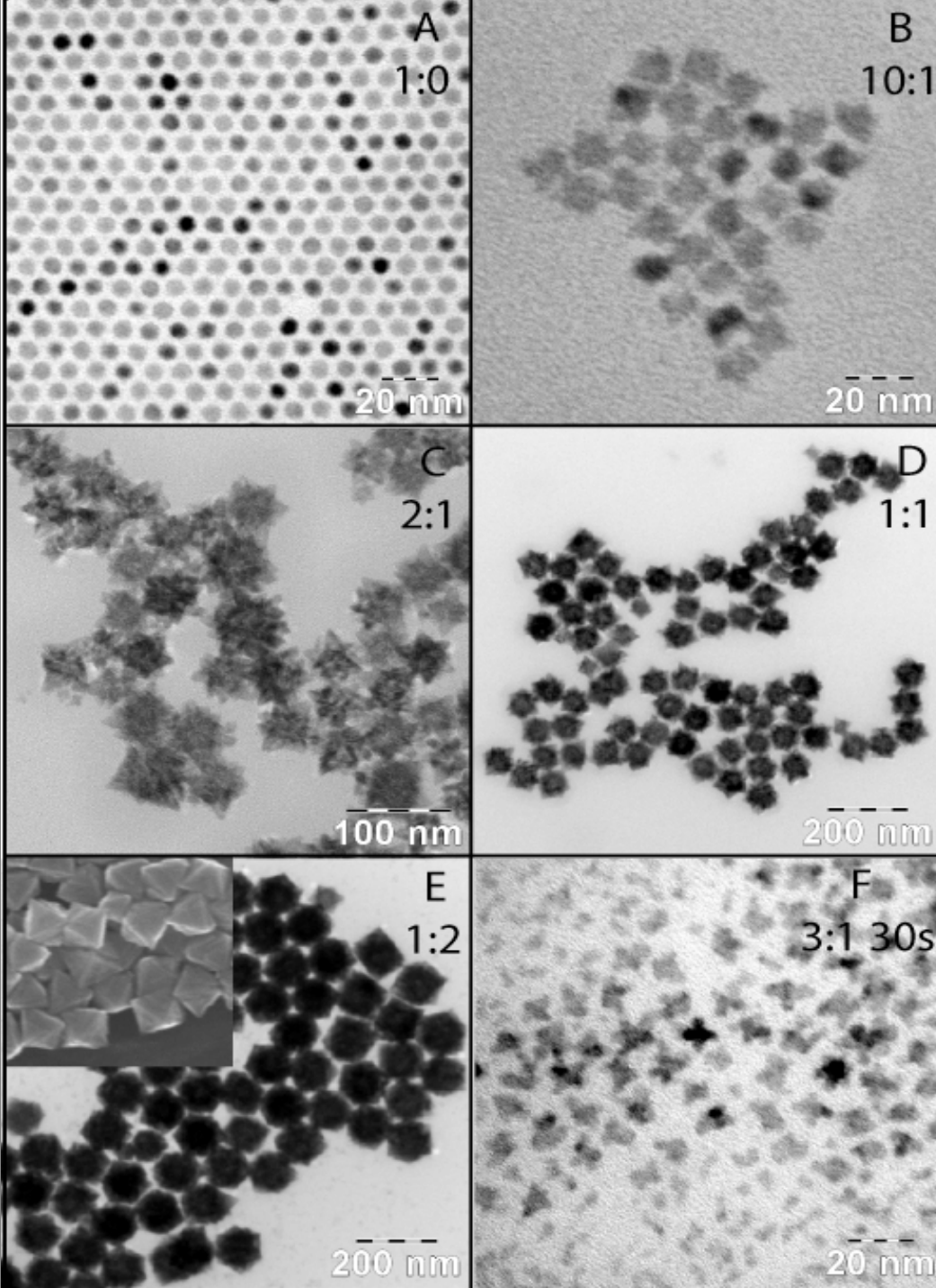
1.1 Colloidal nanocrystals

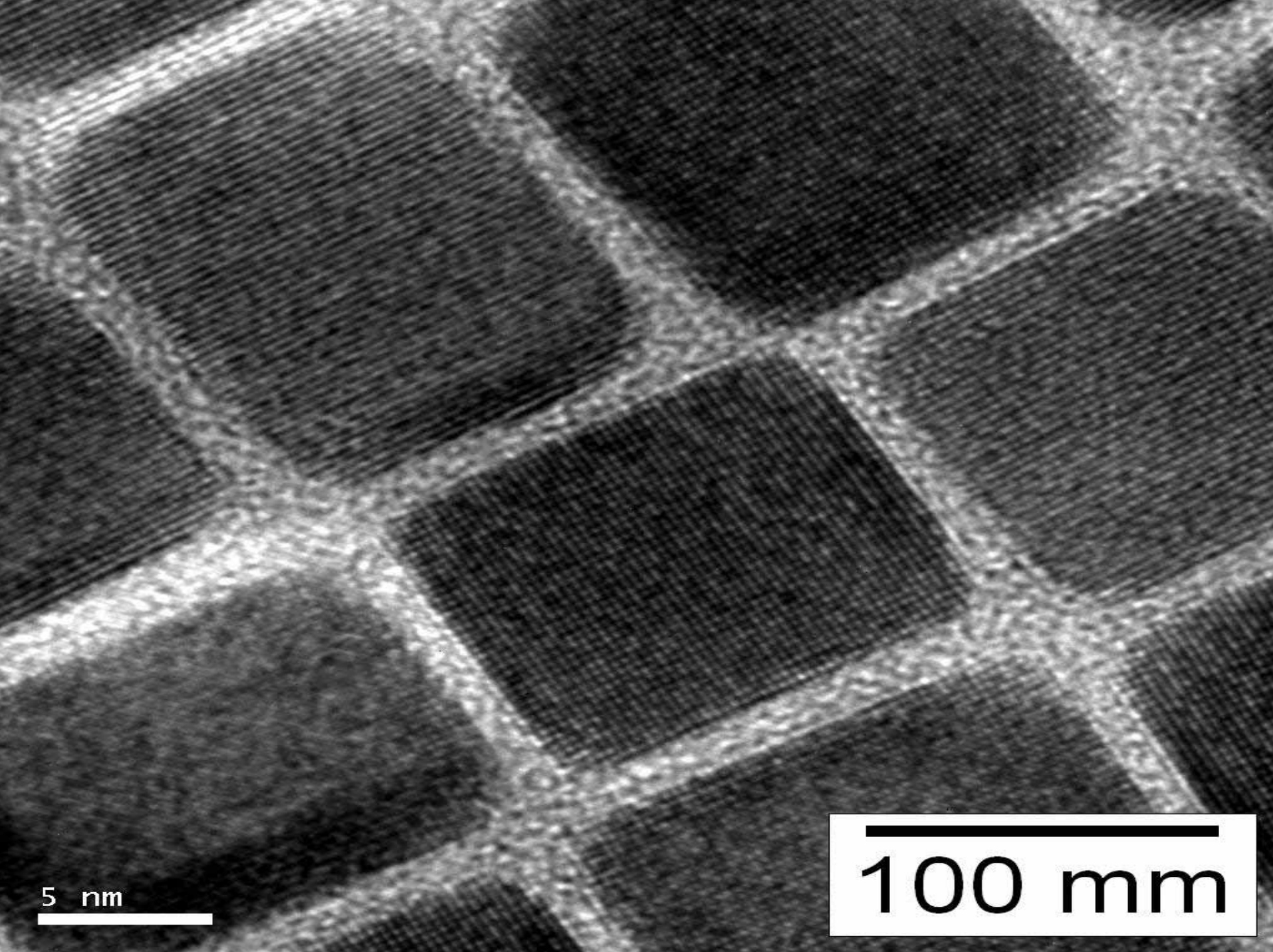
PbS: rock-salt structure



Nearly spherical shape, crystal facets

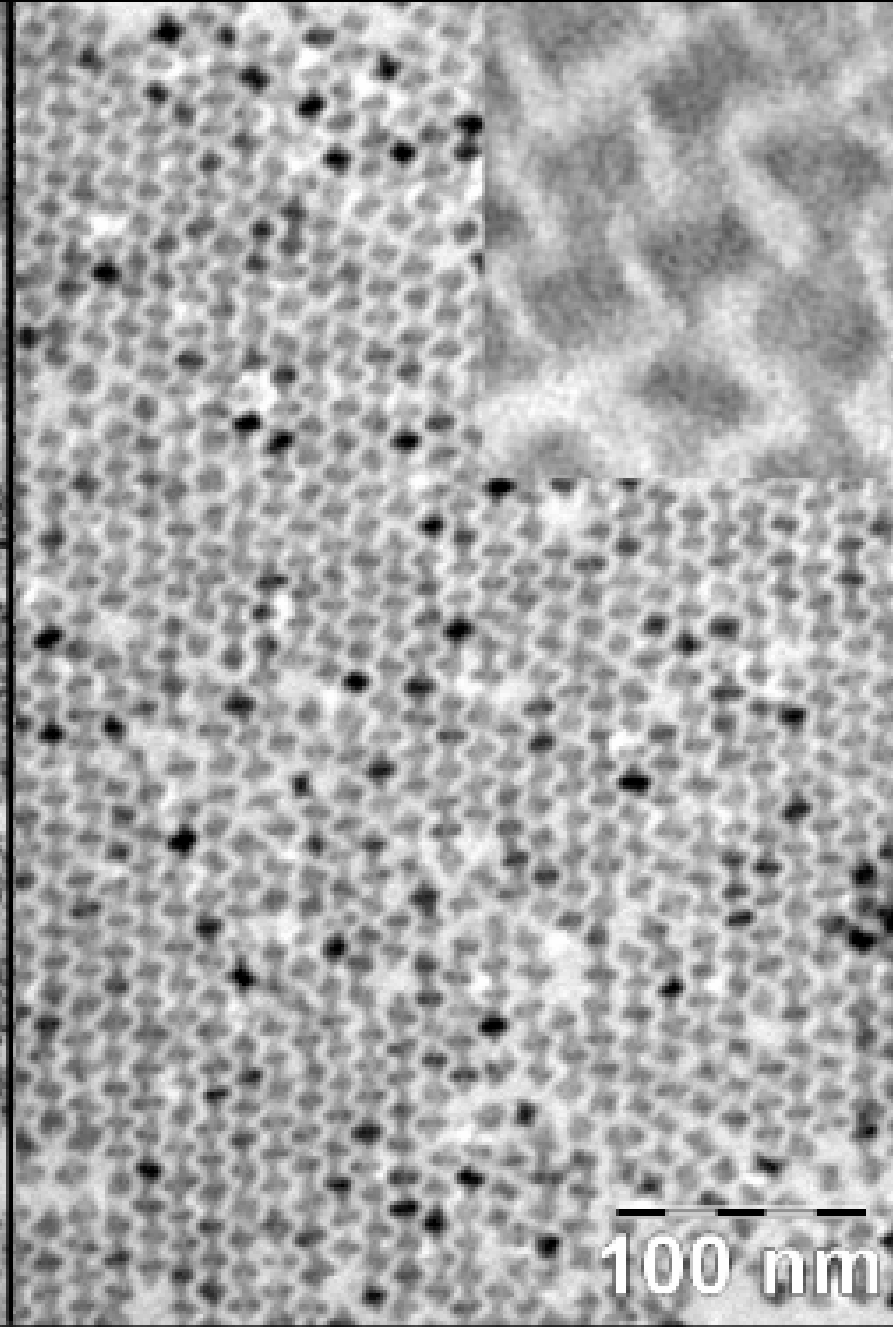
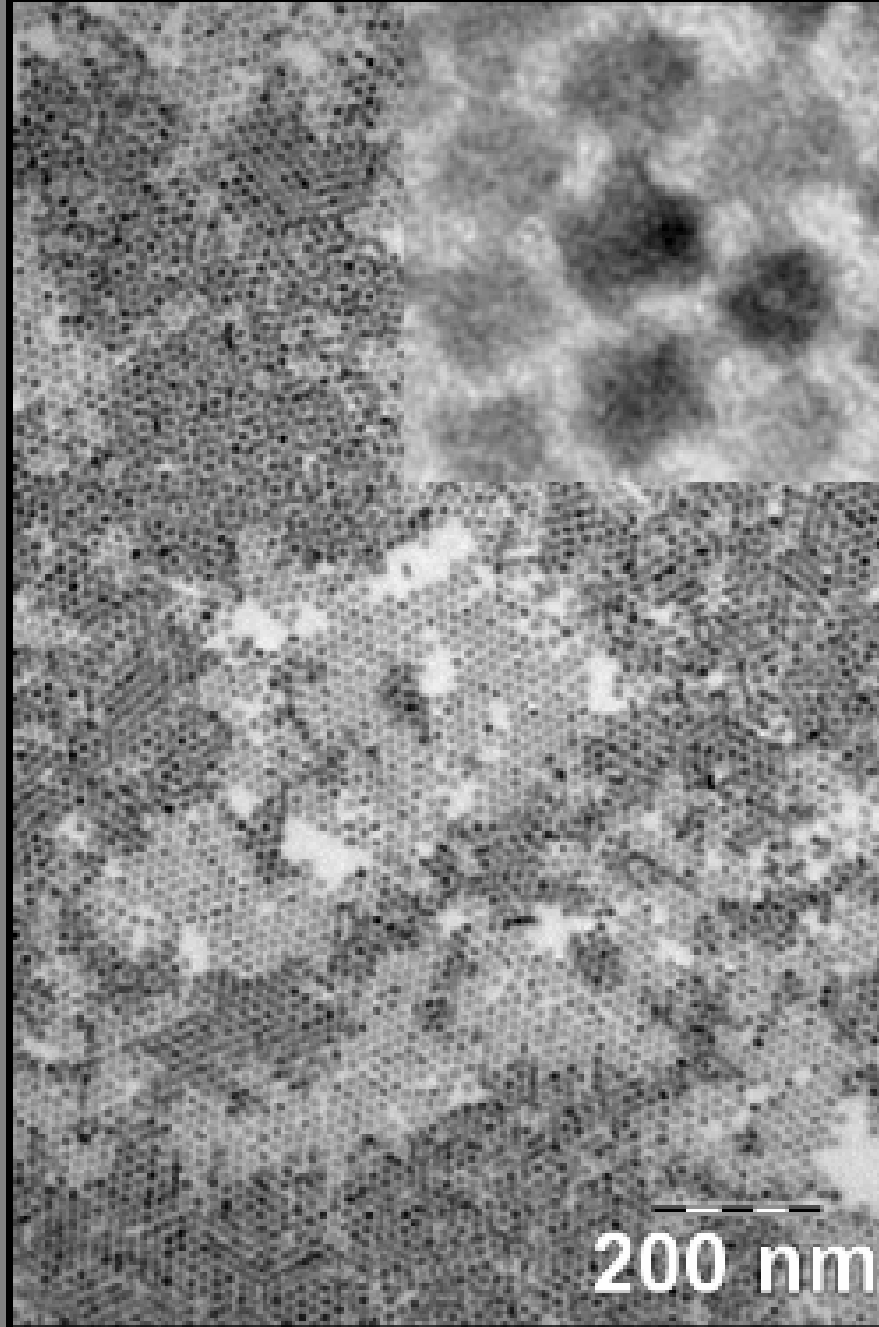
Different shapes of colloidal PbSe nanocrystals





5 nm

100 mm



Self-organization of non-spherical nanocrystals

First conclusions:

Nanocrystals same crystal structure as big crystals

No thermodynamic selection of size and shape

Uniform size and shape can be obtained by “clever” chemistry (kinetics of growth)

Nanocrystal quantum dots and quantum dot solids

Nanocrystals and assemblies of nanocrystals: An overview

Chemical preparation

Electronic structure, optical and electrical properties

Three principles of making nanostructures

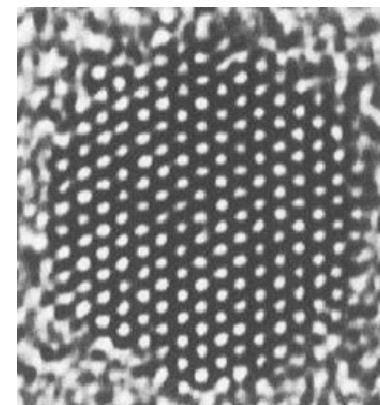
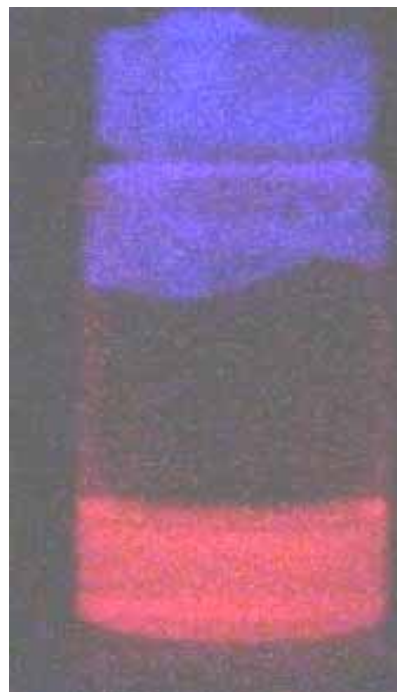
1

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Top-down: lithography >50 nm

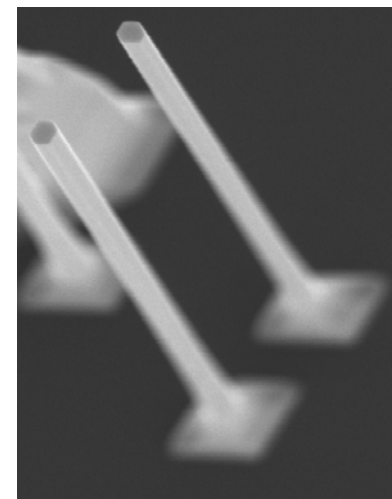
Fabrication in small numbers

2



Bottom-up (>1nm):

Synthesis of mole-
fraction numbers



Three principles of making nanostructures

- 3 STM -manipulation: placing atom by atom (R. Feynman)

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

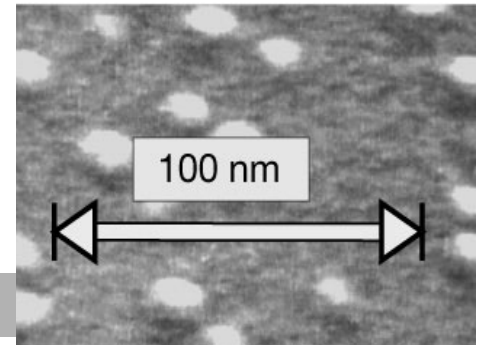
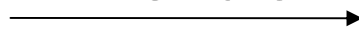
**Synthesis starting from
molecular precursors
“chemistry”**

Heterogeneous chemical preparation

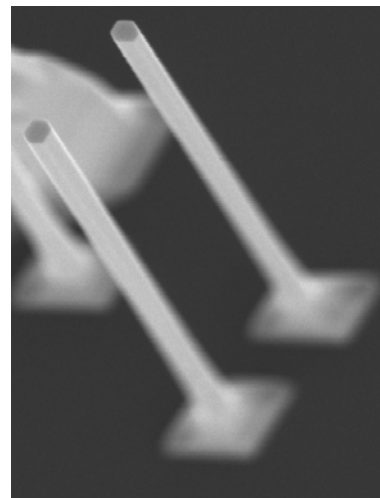
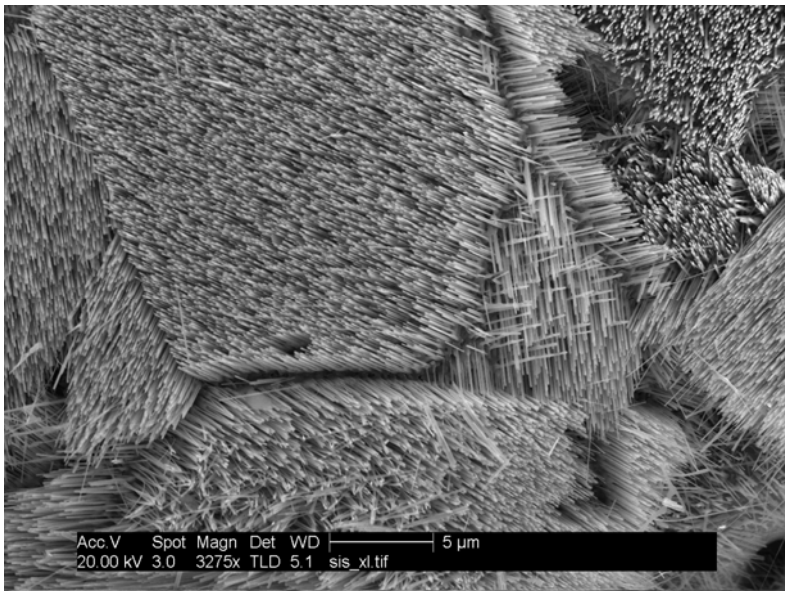
Chemical vapor deposition InAs on GaAs



Lattice mismatch

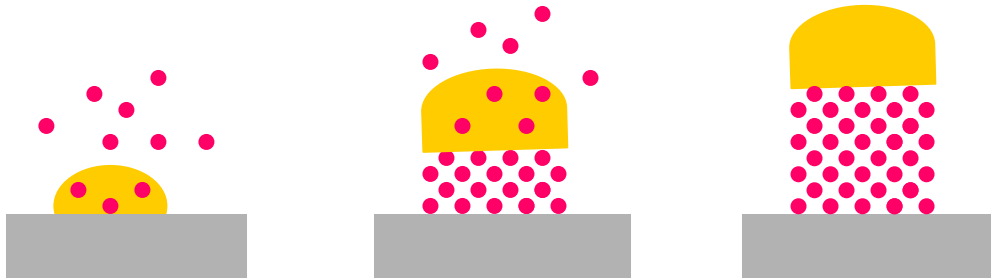


Chemical vapor deposition: ZnO epitaxial on sapphire (Al_2O_3)

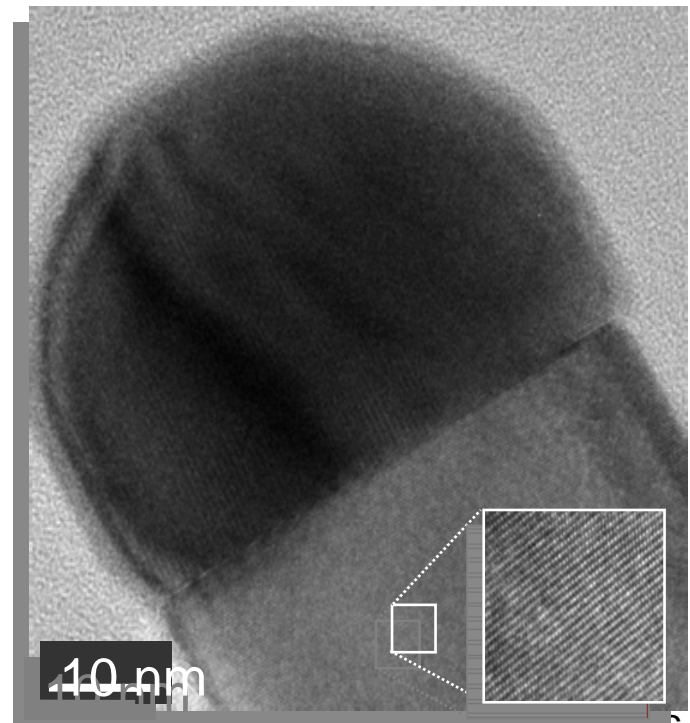
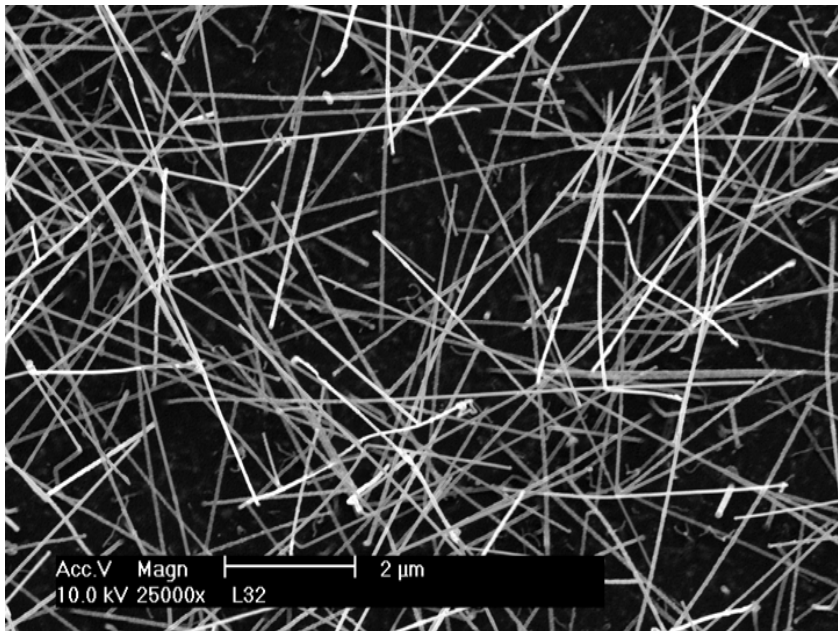


Heterogeneous chemical preparation

Metal-catalysed deposition: Vapor-Liquid-Solid method



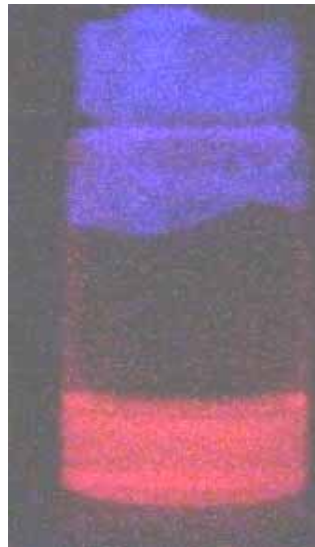
Si, InP, InAs, GaP,
GaAs, GaN, ...



Homogeneous chemical preparation: colloidal suspensions

Solutes \Leftrightarrow solid

Solutes \Leftrightarrow nanocrystal suspension \Leftrightarrow solid



Homogeneous chemical preparation: colloidal suspensions

Synthesis in aqueous solution

$\text{Cd}(\text{ClO}_4)_2$ in water + H_2S (gas) + surfactant: $\text{Na}(\text{PO}_3)_n$

Organo-metallic synthesis at high temperature

$\text{Cd}(\text{CH}_3)_2$ + TOP-Se in TOP-TOPO-HDA

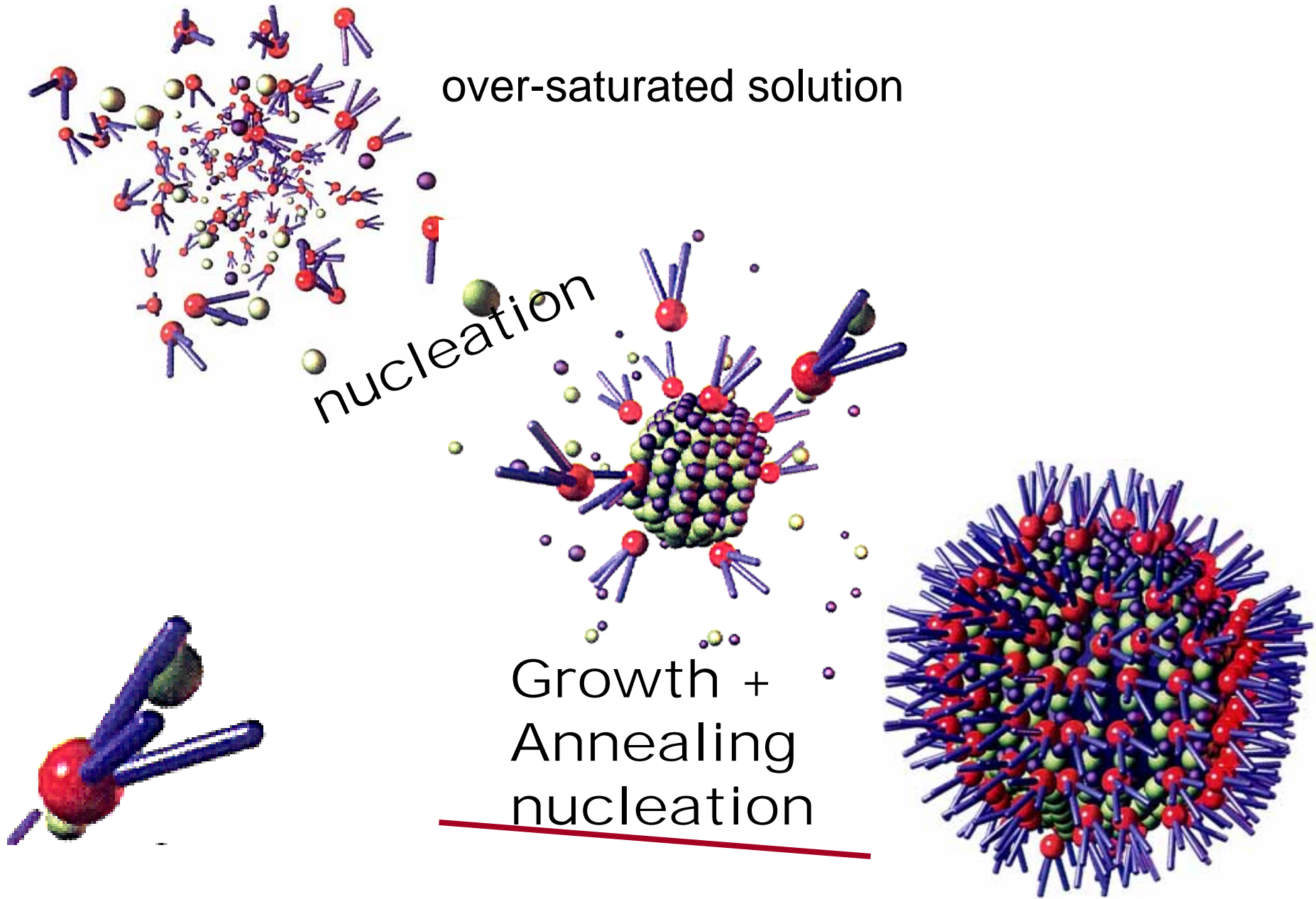
nucleation - growth + surface annealing

C. B. Murray, JACS 115, 8706 (1993)

1500 citations!



Homogeneous chemical preparation: colloidal suspensions

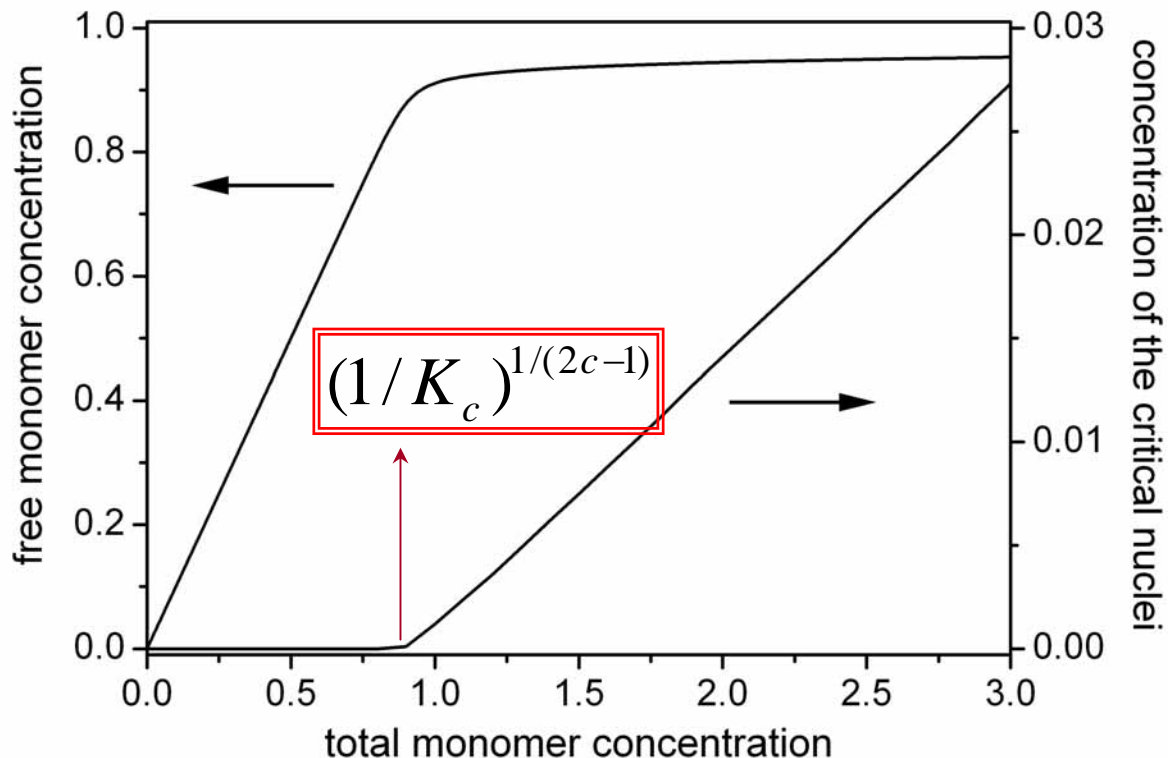


PHYSICO-CHEMICAL EVALUATION: TEMPORAL SEPARATION OF NUCLEATION AND GROWTH

Debye (1949): quantitative formation of critical nuclei starting from a critical monomer concentration (micelles)



$$K_c = \frac{[(\text{CdSe})_c]}{[\text{Cd}]^c [\text{Se}]^c}$$



2.3 Surface chemistry

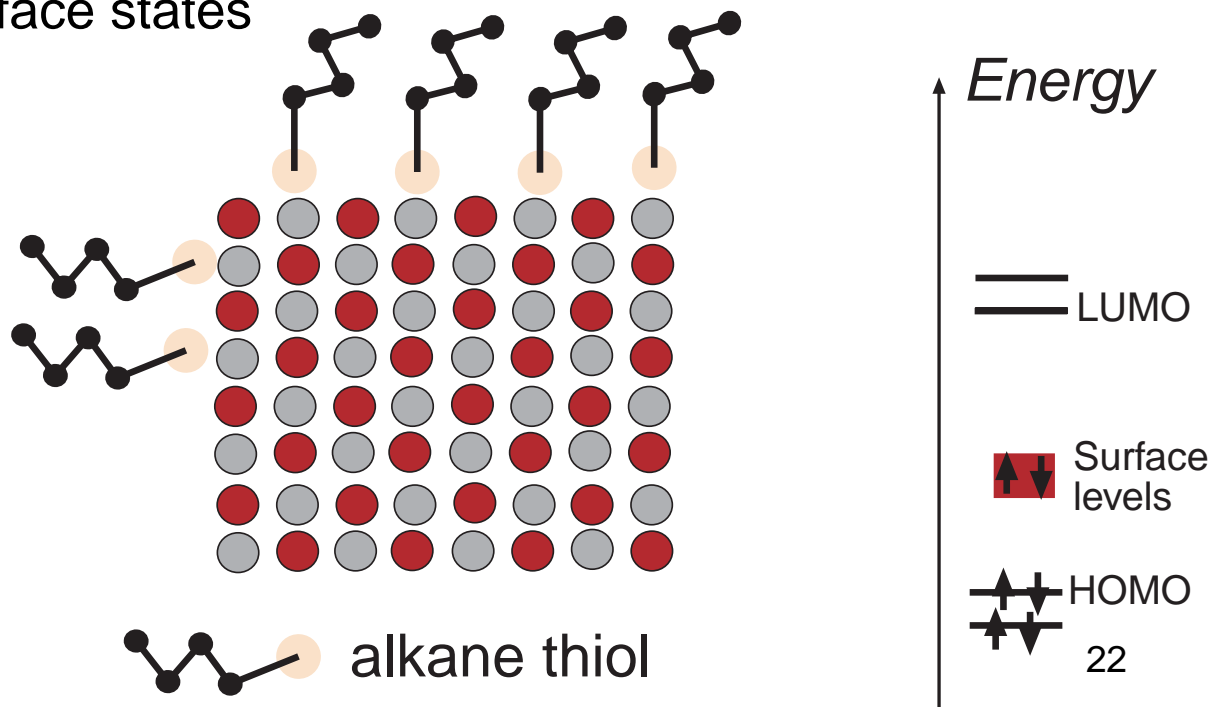
Organic surfactant molecules

strong influence on kinetics of growth

stabilise colloidal dispersion *how?*

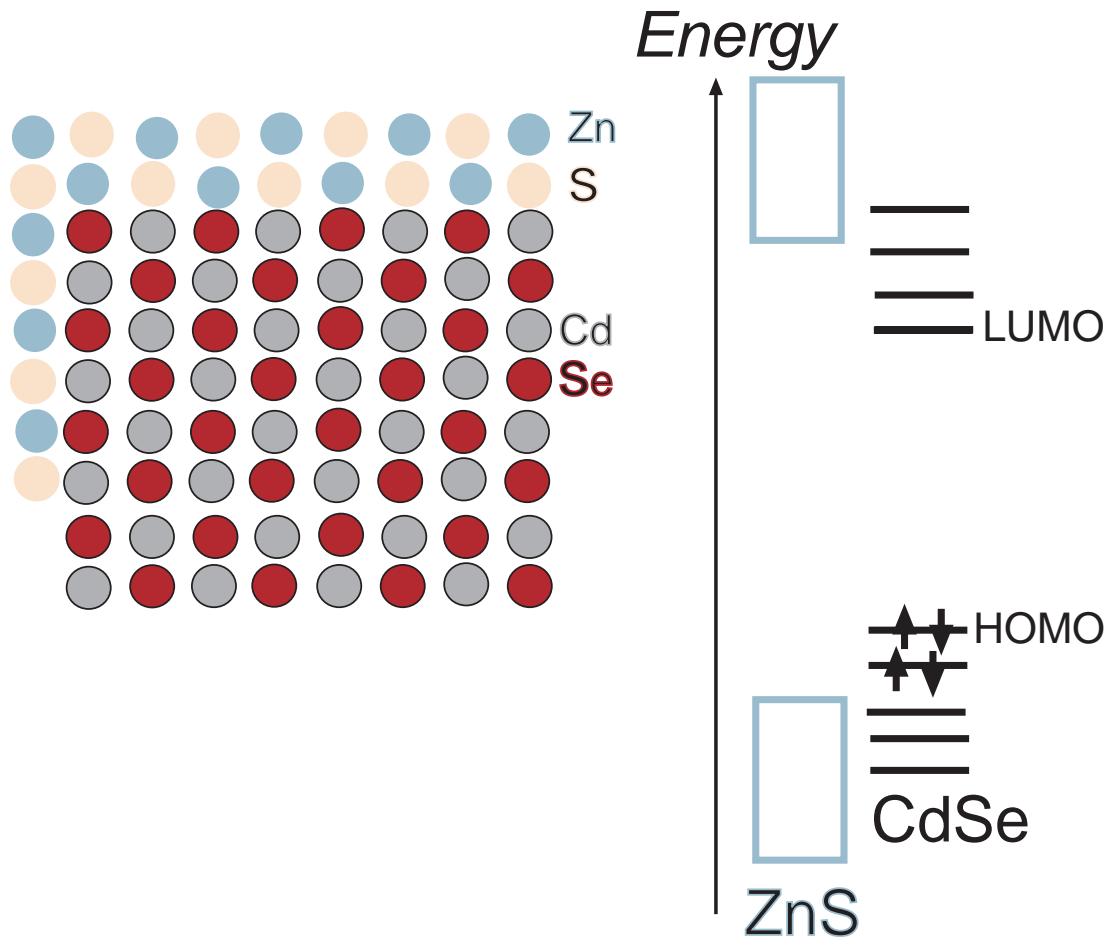
prevent chemical surface reactions with H_2O , O_2

passivate electronic surface states



2.3 Surface chemistry

Inorganic surface molecules



Summary:

Three principles of fabrication

Chemical synthesis

- deposition on substrate**
- nucleation and growth in solution: colloidal nanocrystals**
- colloidal nanocrystals are ideal building blocks for new “supercrystals”**

3 Electronic properties of nanocrystalline quantum dots

3.1 Energy levels: a qualitative understanding

3.2 Energy levels: More sophisticated models

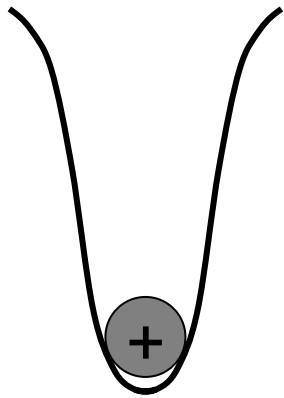
3.3 Charge (and spin) interactions

3.4 Comparison with experimental results

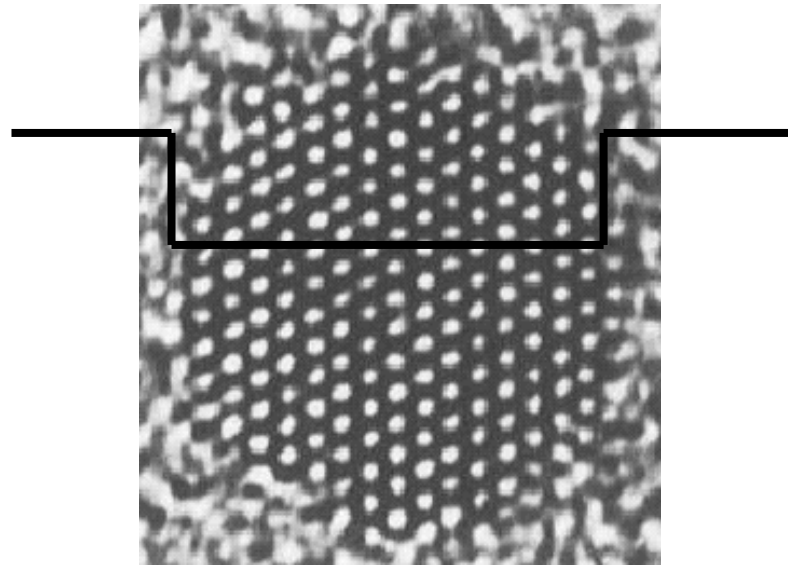


What do you know about the electronic structure of solids?

Potential wells

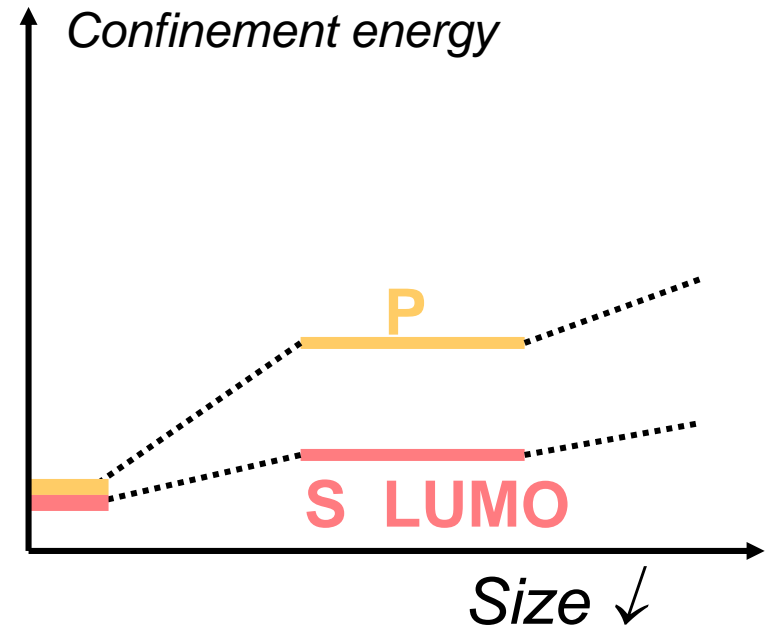
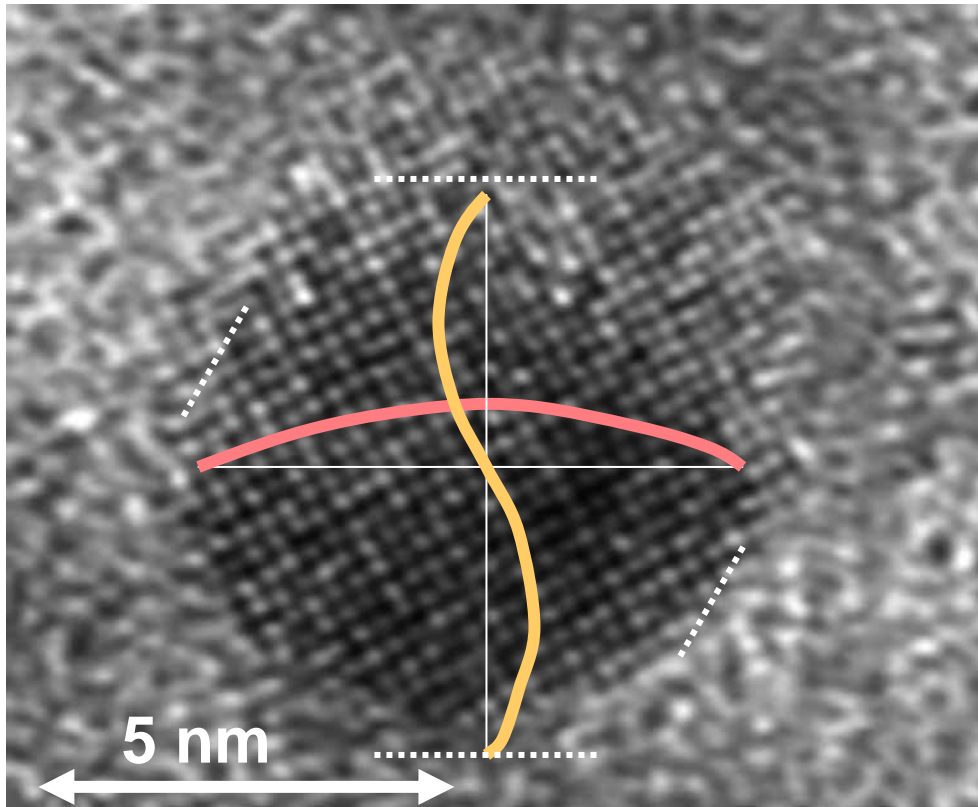


atom



nanocrystal artificial atom

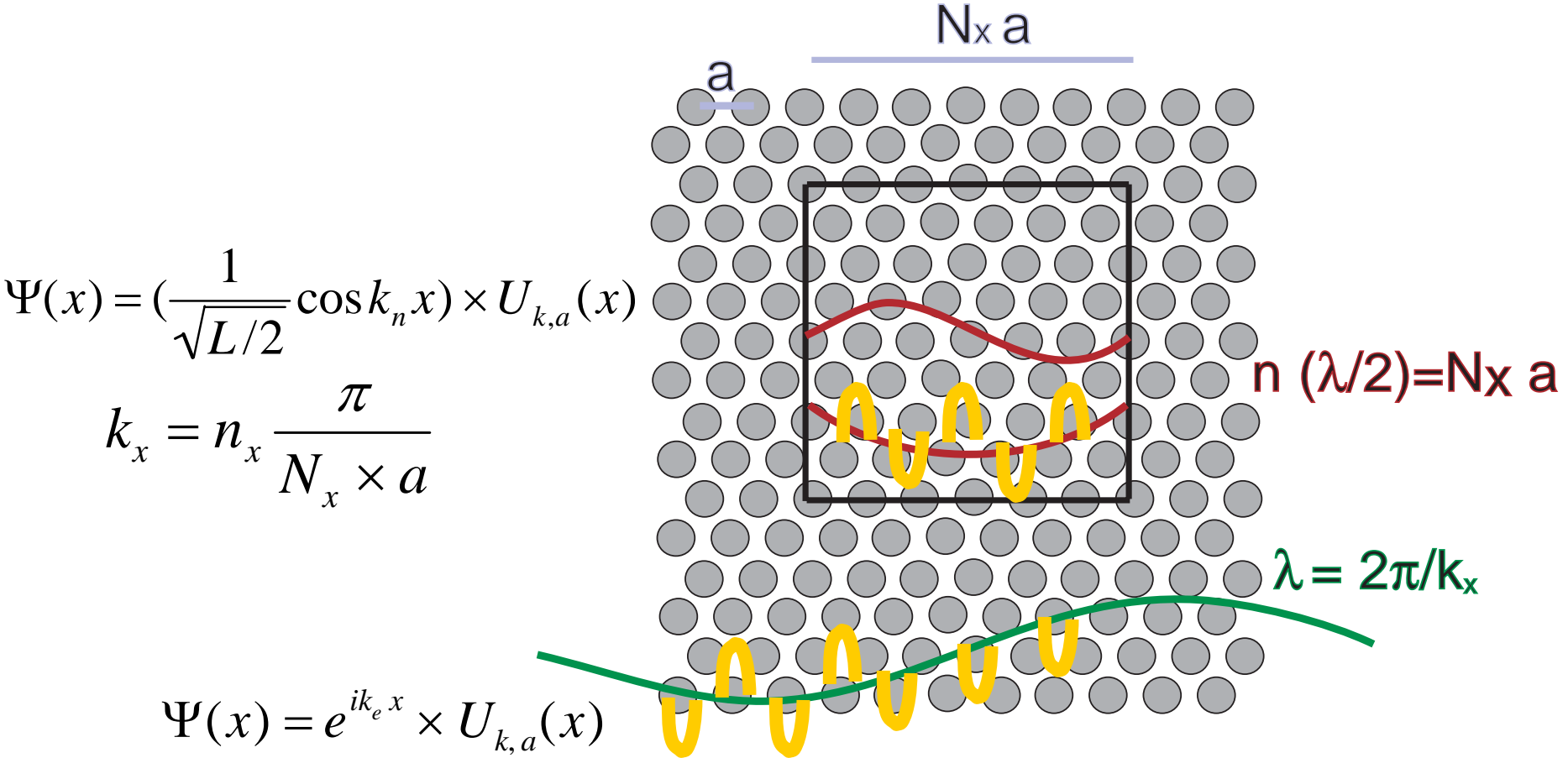
3.1 One electron in empty box



zie opgave!

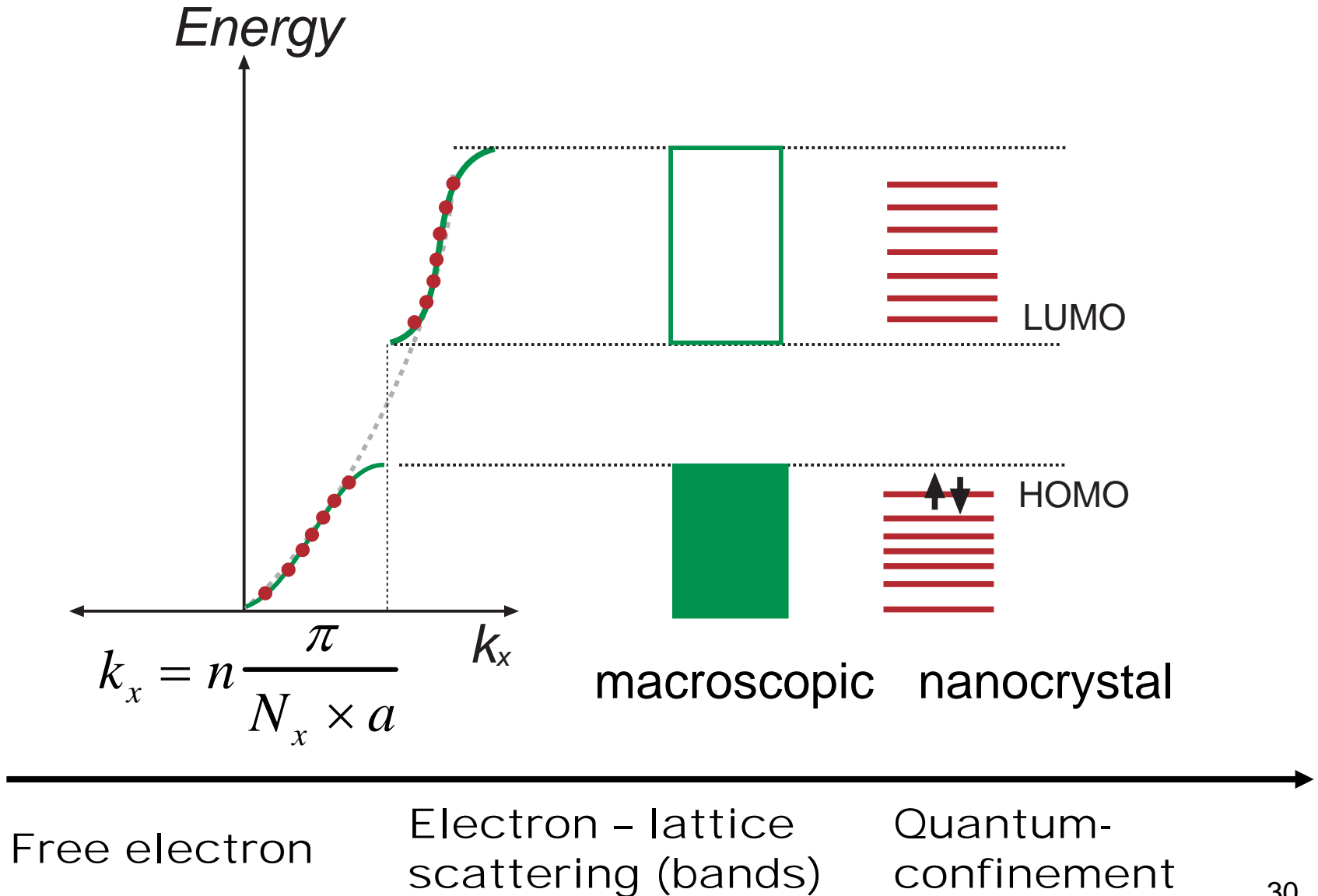
Excess electrons in an insulating nanocrystal: bound conduction states
Excess holes : valence states

One electron in a box filled with crystal lattice

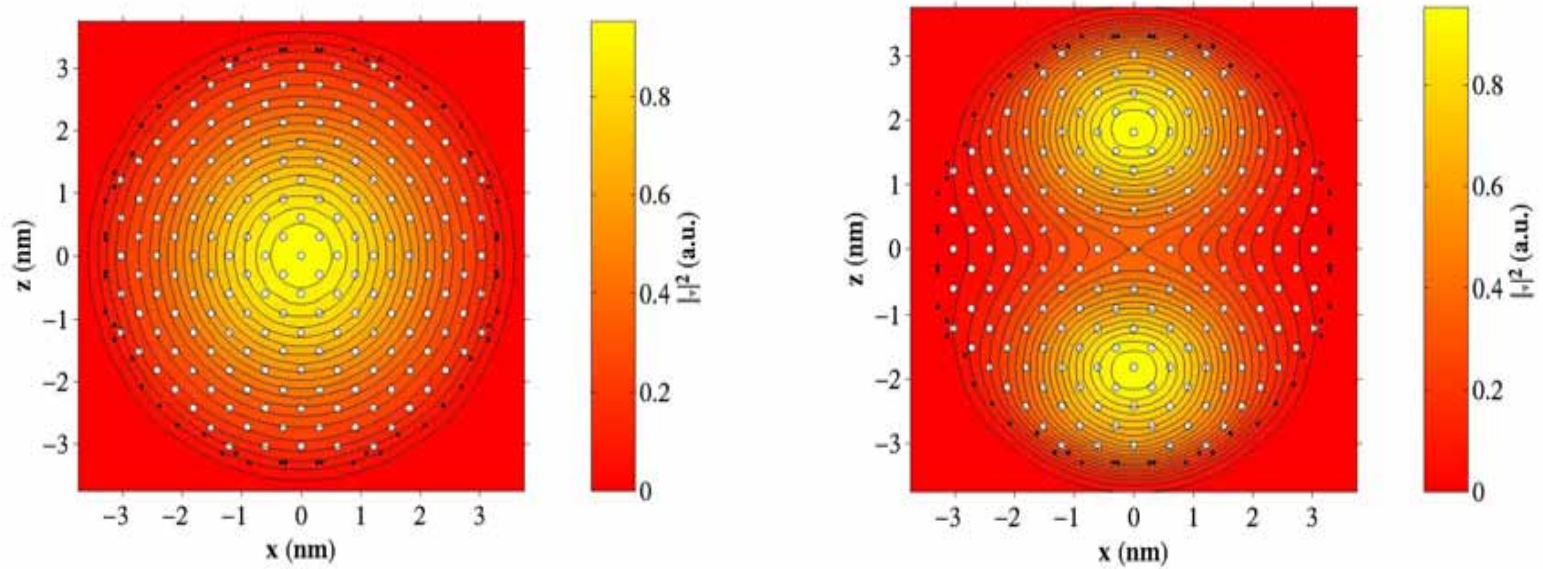


Bloch function U_k determines band structure of macroscopic crystal and forms the basis for the energy levels in a nanocrystal

One electron in a box filled with crystal lattice



3.2 More sophisticated models: Tight-binding



Linear Combination of Atomic Orbitals

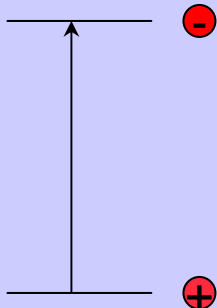
CAN WE PROBE THE ELECTRONIC STRUCTURE ?

Optical spectroscopies

Transition between two levels
(creation - annihilation of an
electron and hole)

Selection rules

Limited spatial resolution

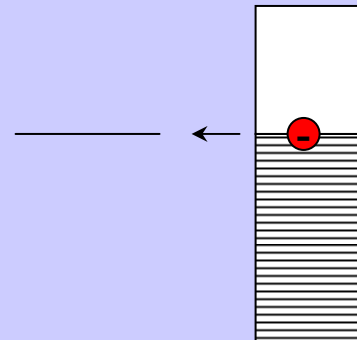


Resonant tunneling spectroscopy

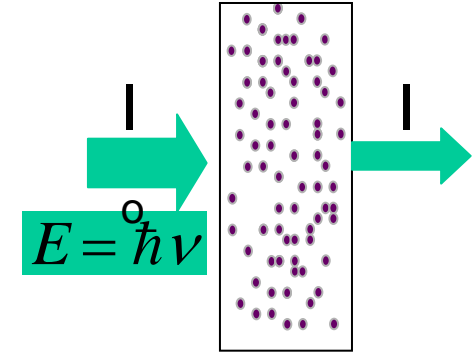
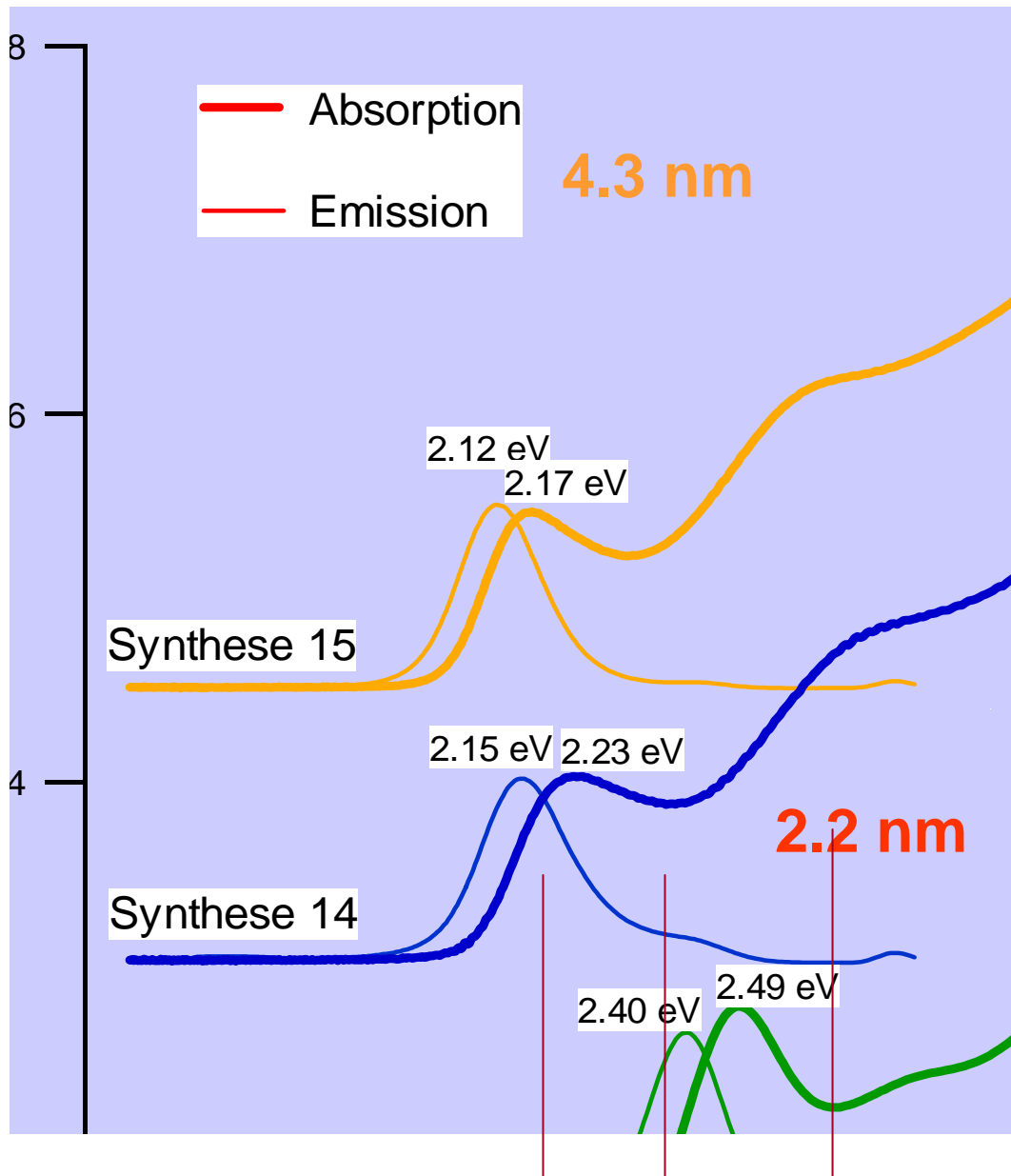
Single level in QD involved

k - selection rules do not play a role :
density of states can be probed

Atom-scale spatial resolution



3.4 Light absorption - luminescence



Discrete inter-band transitions

Selection rules: Bloch part

Inhomogeneous line-broadening

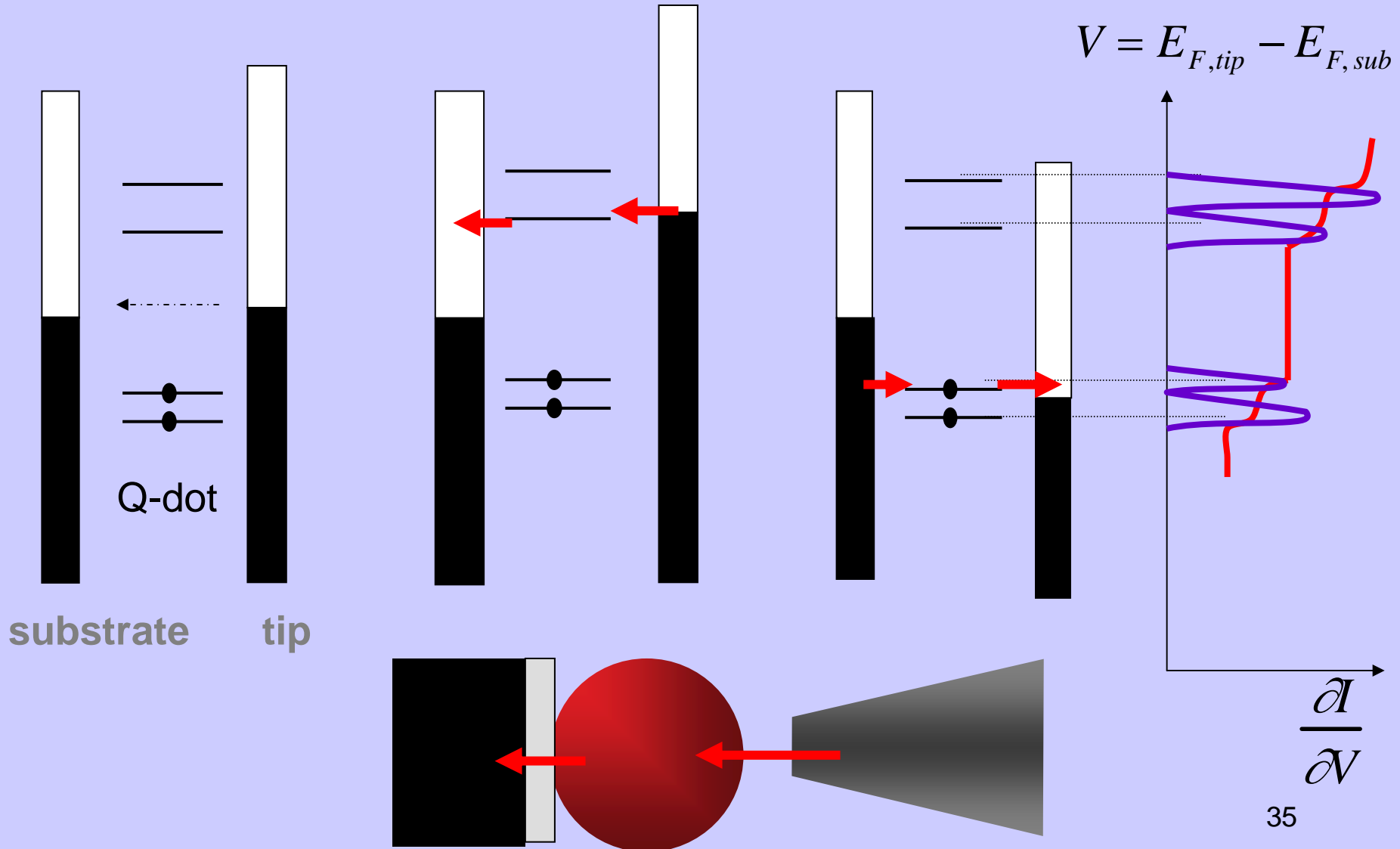
Quantum confinement

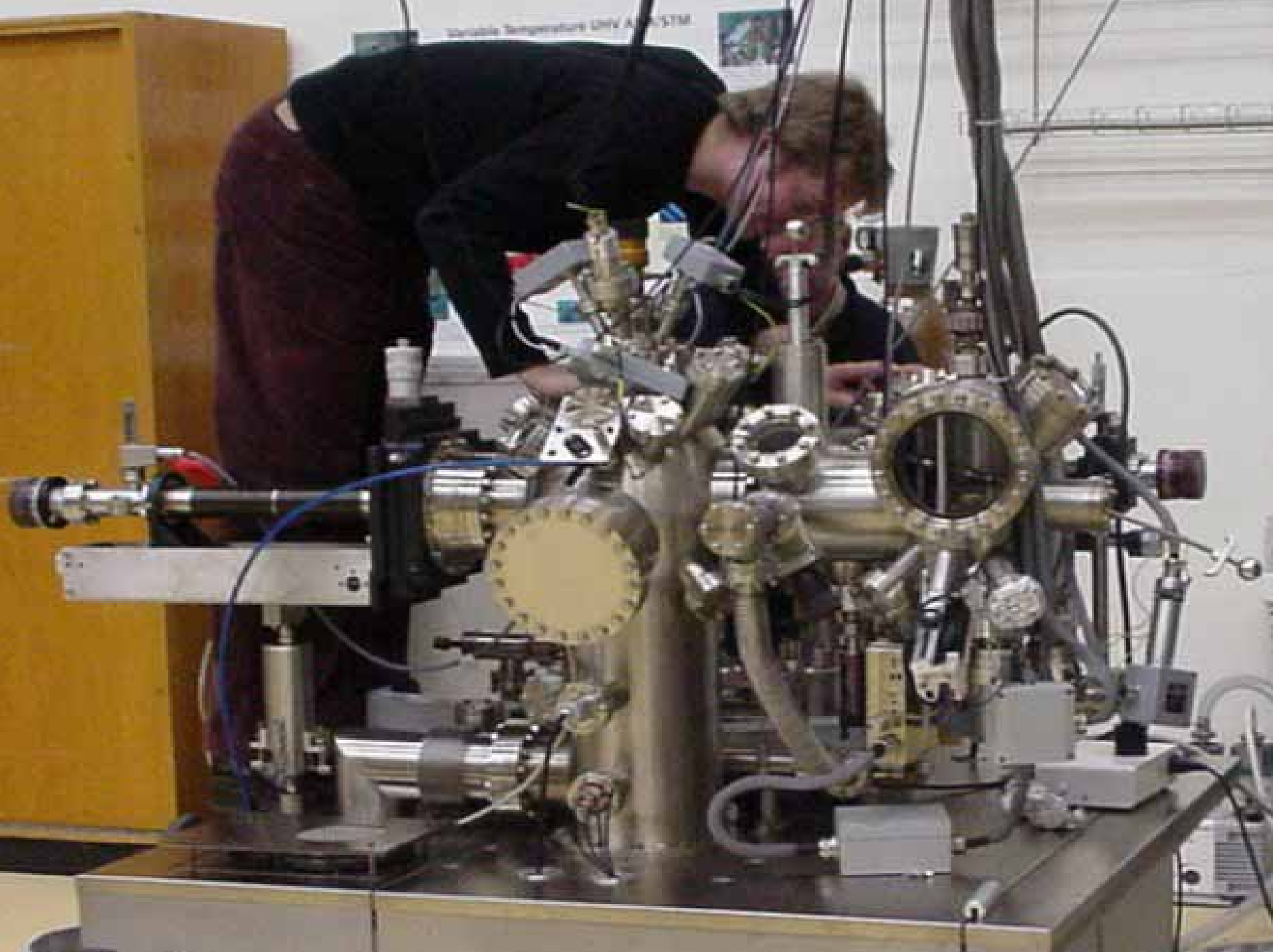
Photoluminescence
quantum yield

3.4 bright luminescence - strongly size-dependent: applications?

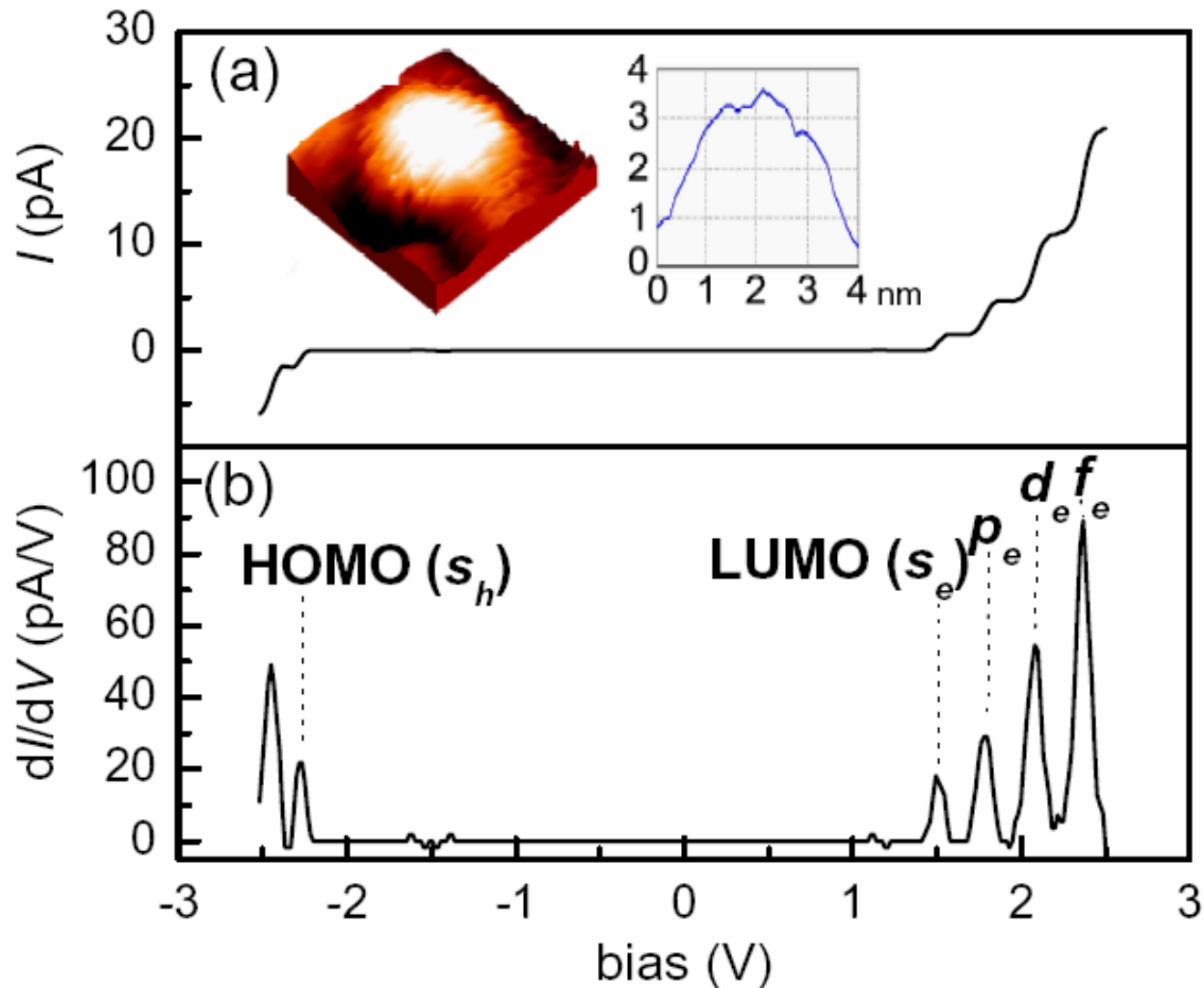


Resonant Tunneling





3.4 shell-tunneling of 3.5 nm CdSe



Summary: Electronic structure

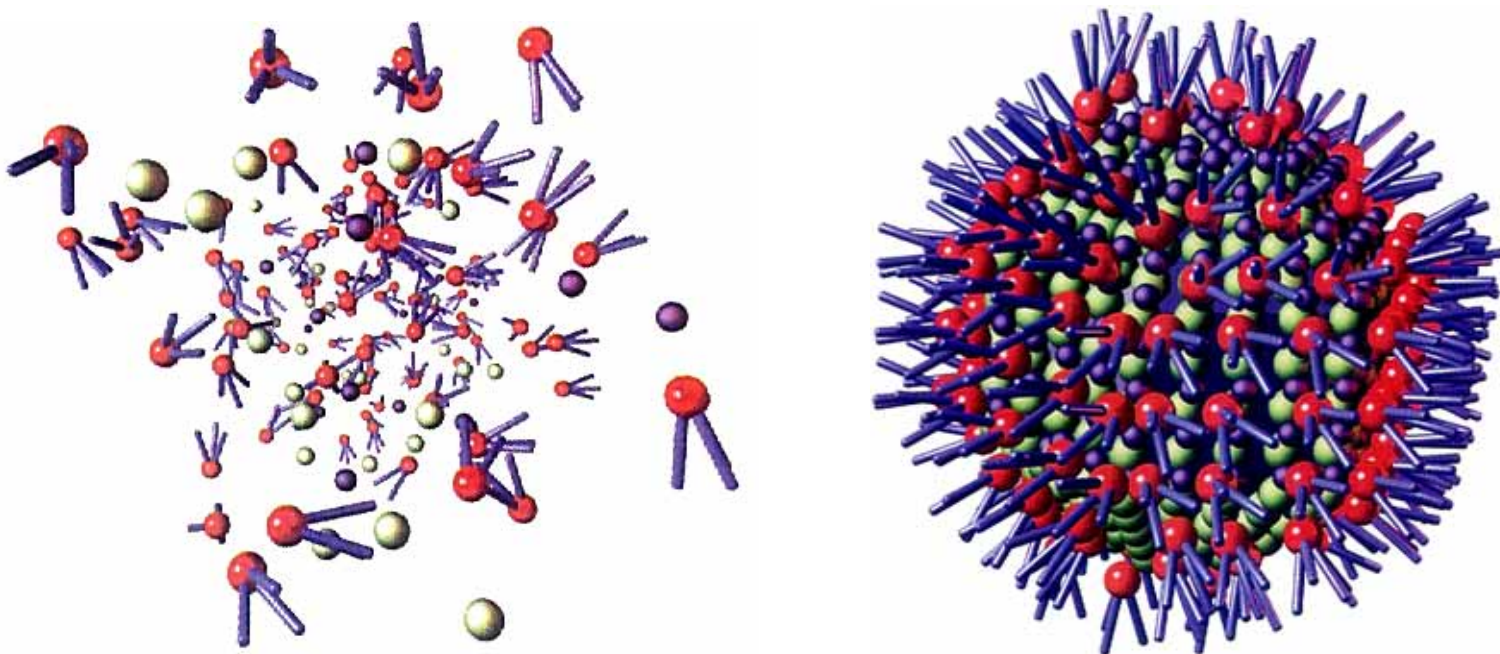
Quantum confinement: discrete energy levels determined by the nature and size of crystal

Ensemble optical spectroscopy

Optical and electrical spectroscopy on single Nan crystal possible

SECTION 5:
SELF-ASSEMBLY OF
MONOLAYER-PROTECTED
NANOCRYSTALS

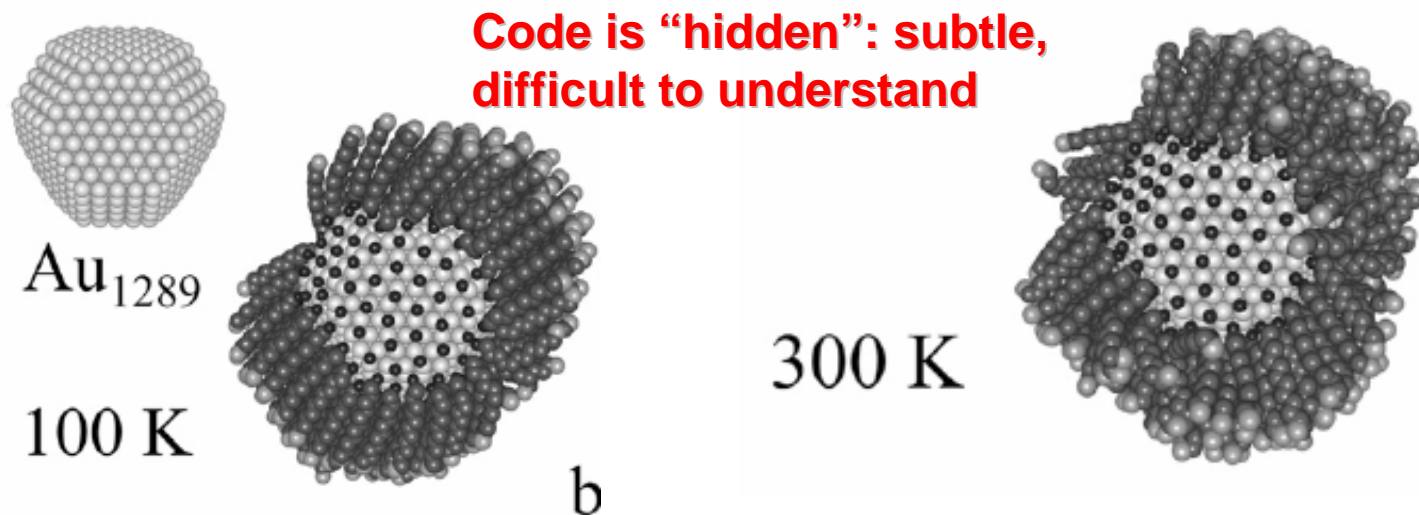
Chemical synthesis of MPNC is an interesting topic on itself
(see Mastercourse TOPICS IN NANOSCIENCE)



From the viewpoint of self-assembly:

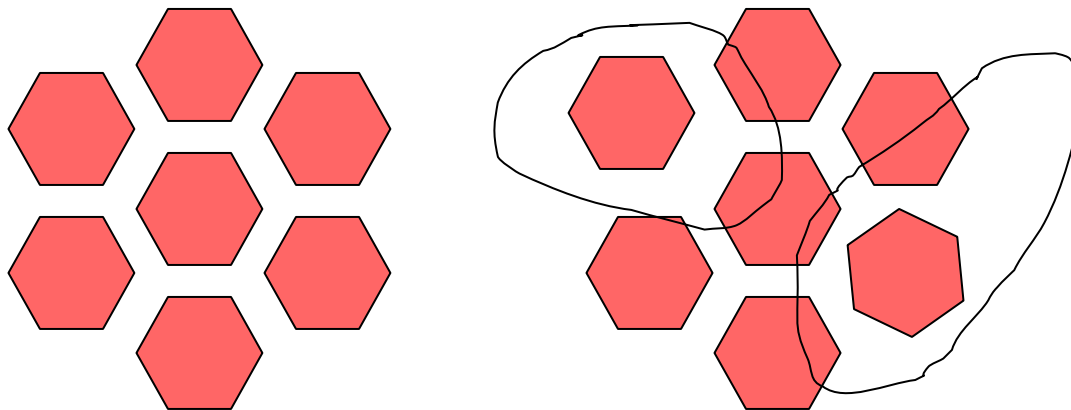
Building blocks have dimensions one order of magnitude larger than molecules, much smaller than the “usual” colloids (> 100 nm)

“Spherical” building blocks have a simple geometry (on the first sight!), there are often considered as “large atoms”....but...the crystal facets, and the organization of capping molecules around the nanocrystal provide new degrees of freedom and lead to new phenomena

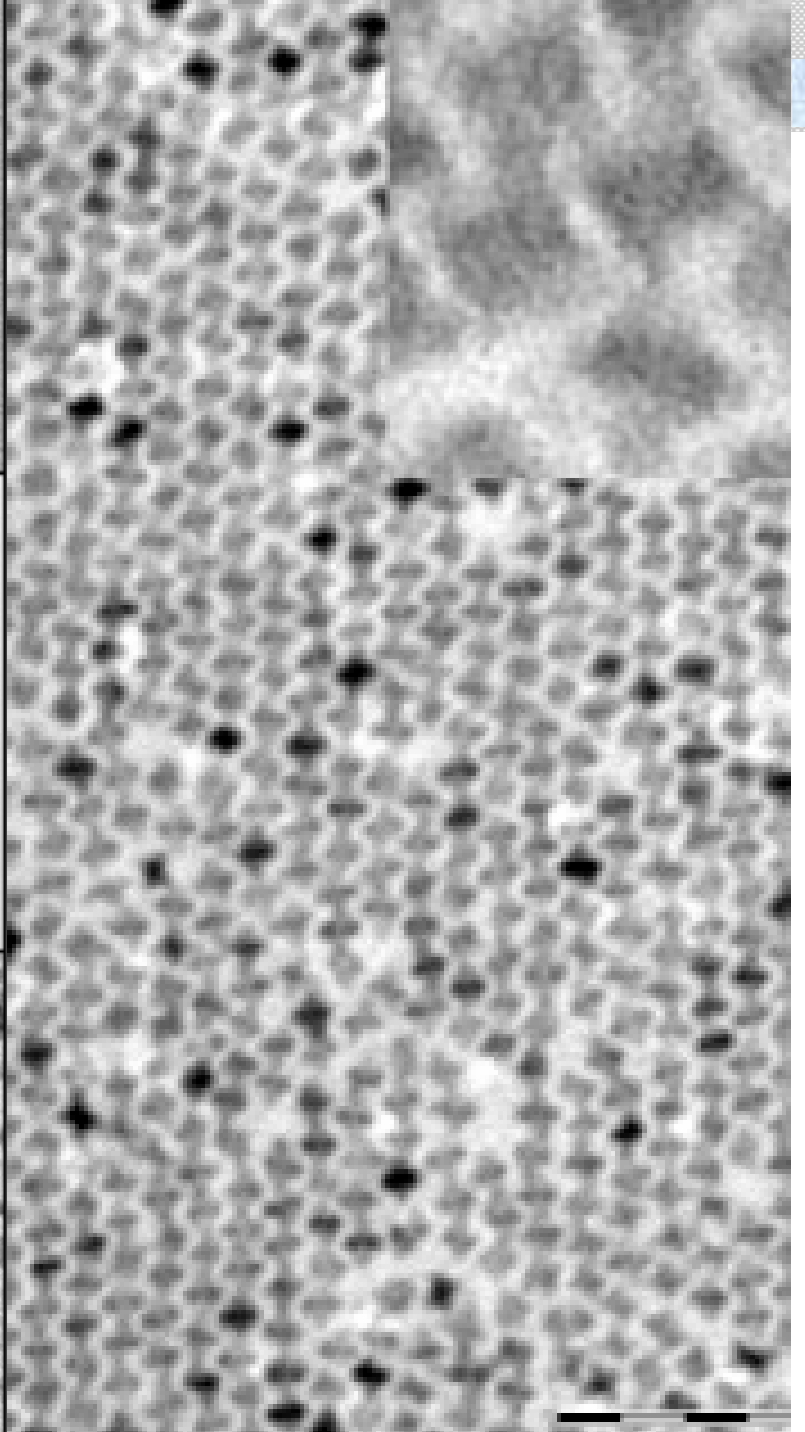
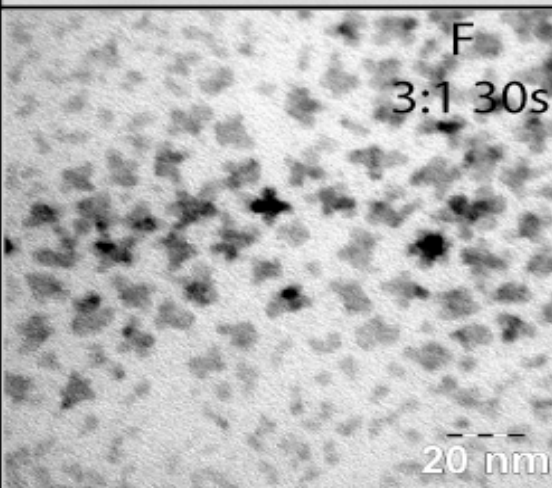
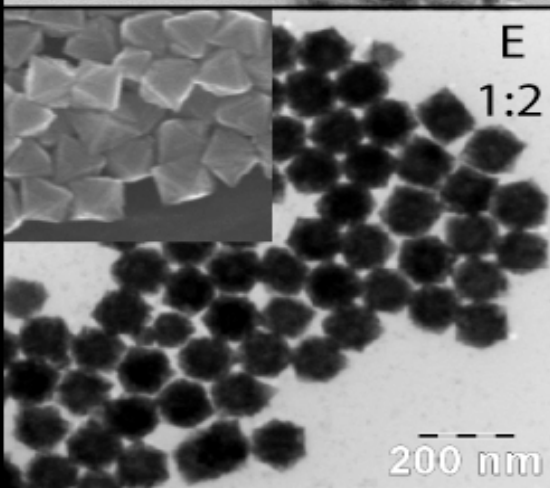
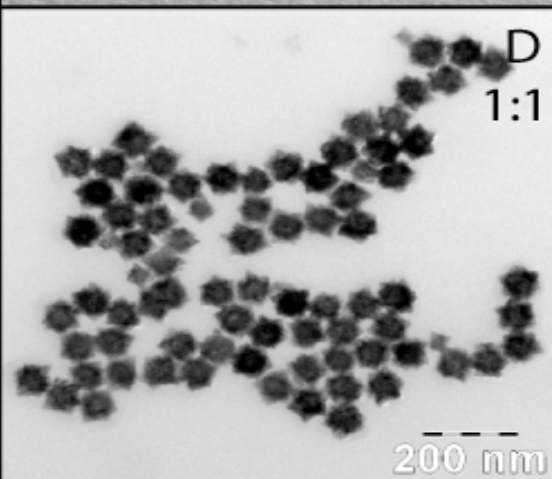
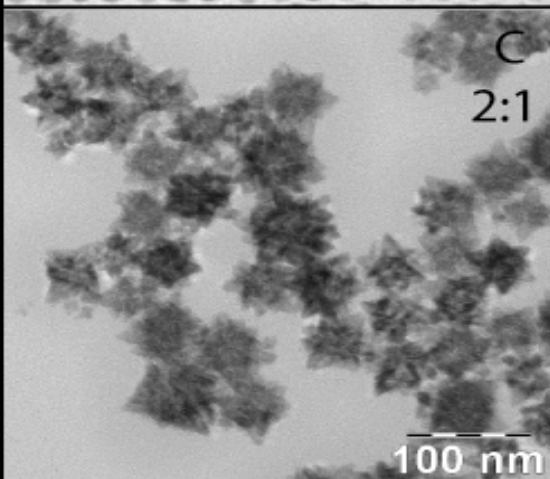
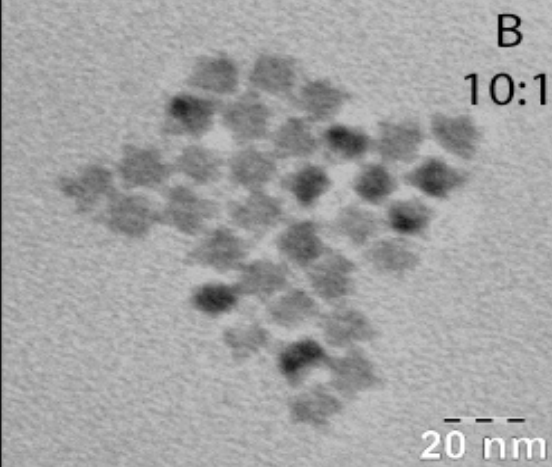
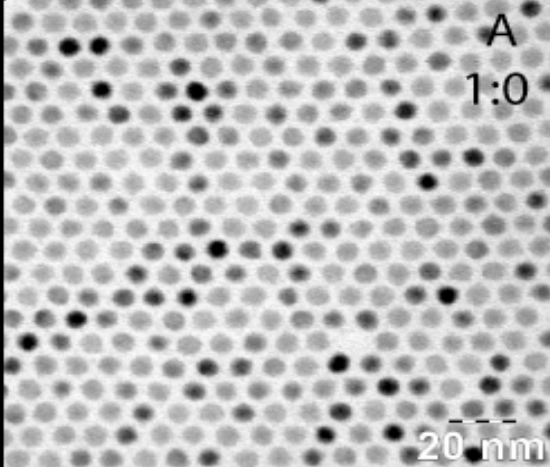


From the viewpoint of self-assembly:

Non-spherical building blocks lead to new degrees of freedom and new disorder effects with respect to an ordinary atomic solid



Strength of bonding between building blocks (pair potential) is not directly related to the electronic coupling unlike for ordinary atoms



Importance for nanophysics and material science:

Nanocrystals are metallic, magnetic, semiconductor compounds with size - tunable properties

Electron (hole) wave confinement

Dielectric confinement

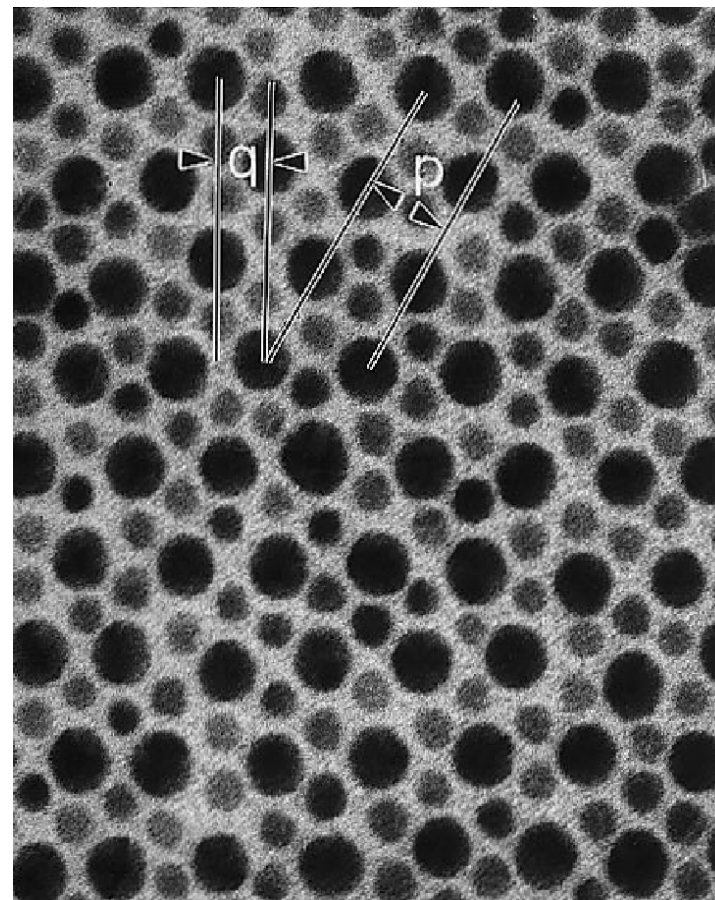
Volume-dependent magnetic moment (particle-size smaller than magnetic domain)



Importance for nanophysics and material science:

Solids of “artificial atoms” can be prepared; the electronic properties of these “artificial solids” compared to ordinary atomic solids are of huge interest for physical sciences.

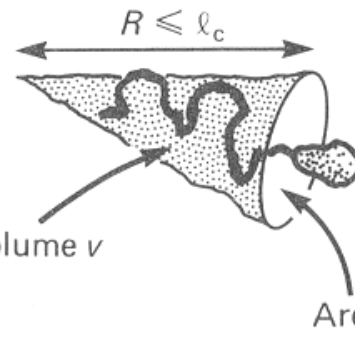
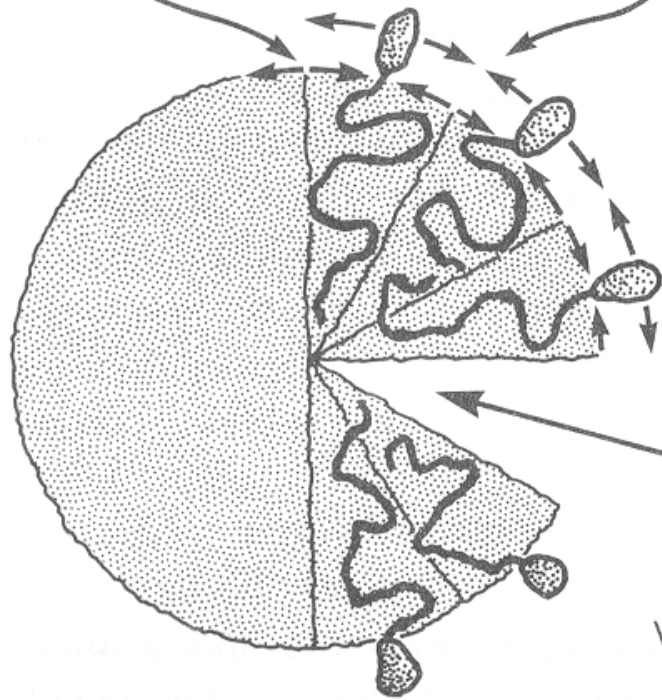
Examples: dipolar (Förster) energy transfer, exchange energy transfer, distance-dependent electronic coupling, metal-insulator transitions...



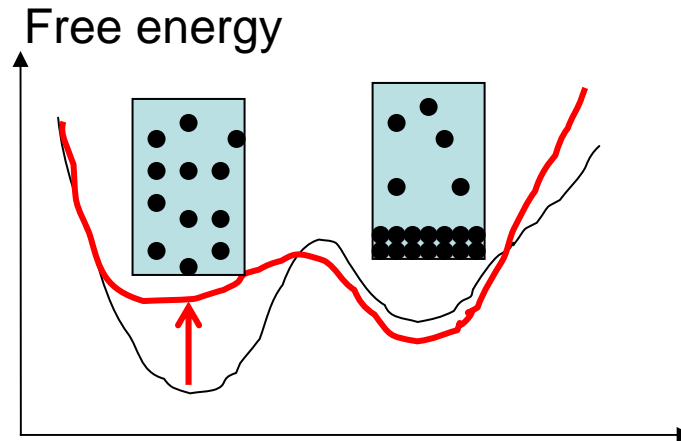
Applications: Materials with novel opto-electrical and magnetic functions that depend on the nature of the building block and the interactions between them in the condensed phase

Interfacial
(hydrophobic)
attraction

Head-group (hydrophilic) repulsion



Principle: “destabilization” means increasing the chemical potential of the nanocrystal building blocks in the solution. In such a way a spontaneous assembly can occur until equilibrium between the solution and the solid is reached



Two methods of destabilization:

$$\mu = \mu^o + kT \ln \frac{c}{c_{Ref}}$$

- increasing the concentration of NC by thermal evaporation of solvent
- Increasing external pressure (Langmuir-Blodgett trough)
- addition of a non-solvent to a colloidal solution
- **other methods? Why is T-increase not working?**

Exercise: can we understand the surface pressure vs. area diagrams? (see section 2)

3-D system

Gas-pressure (exerted by molecules on the walls of container)

$$p = -\left(\frac{\partial F}{\partial \mathcal{V}}\right)_{T,N} = -\left(\frac{\partial U}{\partial \mathcal{V}}\right)_{T,N} + T\left(\frac{\partial \mathcal{S}}{\partial \mathcal{V}}\right)_{T,N}$$

2-D system

Surface-pressure - exerted by units of assembly on the edges of the system

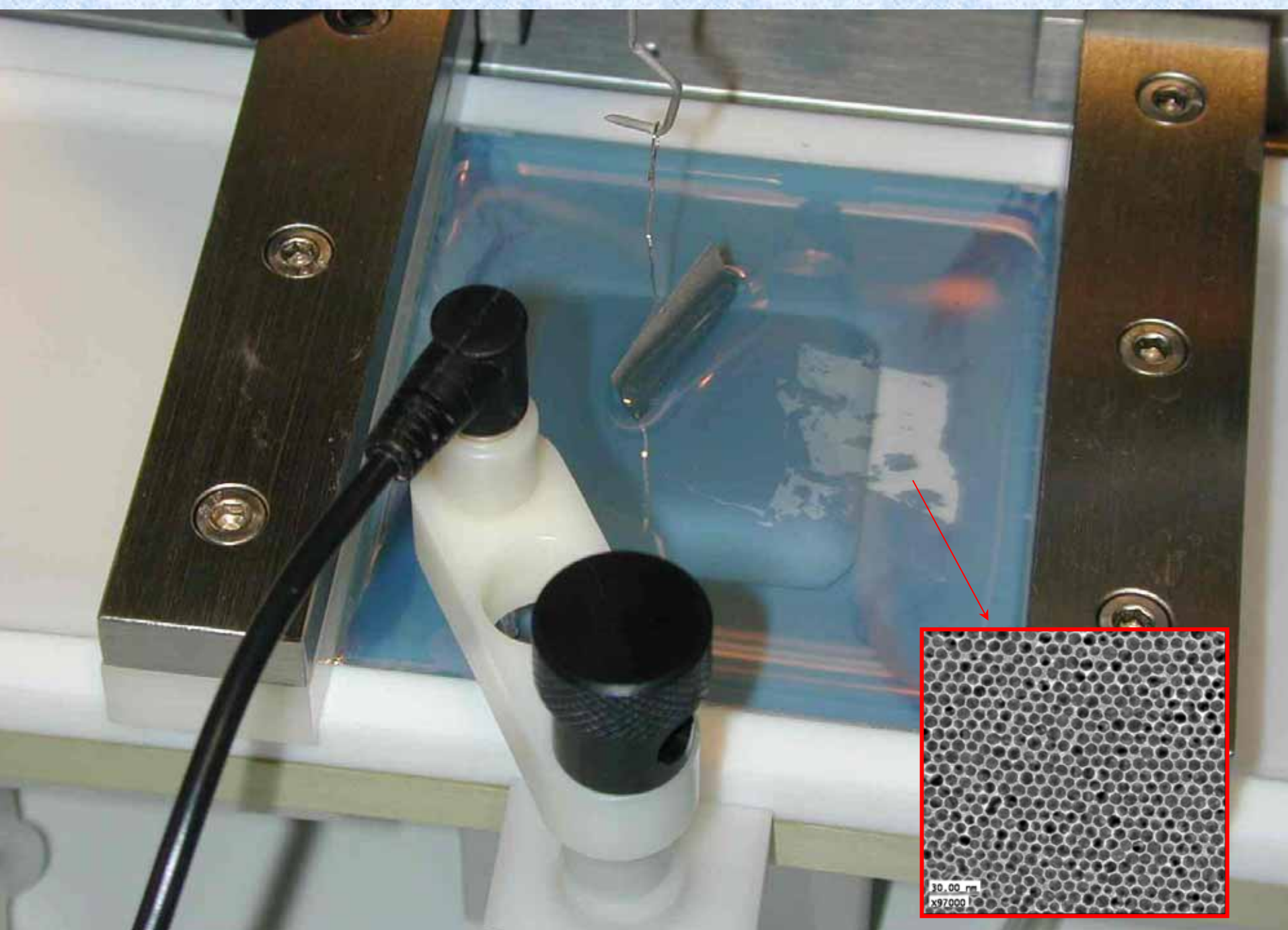
$$\pi = -\left(\frac{\partial F}{\partial A}\right)_{T,N} = -\left(\frac{\partial U}{\partial A}\right)_{T,N} + T\left(\frac{\partial \mathcal{S}}{\partial A}\right)_{T,N}$$

Surface-tension: change of free energy with change of area

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{T,N} = -\pi$$

In a Langmuir-trough the “surface pressure” [$\gamma(\text{water}) - \gamma(\text{particles})$] is measured by pulling on a Welhelminiplate; the meaning of this result is thus $\pi(\text{particles}) - \pi(\text{pure water})$ (pure water is the reference)

ASSEMBLY IN A LANGMUIR-BLODGETT TROUGH



Geometry of am MP NC:

Excess volume: (Volume of cone = volume available for ligand) determined by footprint (f) of ligand on surface, radius (R) of NC and length L of Molecule: V_e scales with L^3/R^2

(p,A) Phase diagram and structure

The phase behavior and structure of two-dimensional MPNC layers must be determined by entropy effects and by dispersion interactions between capping molecules and between NC cores. The geometry of the MPNC building blocks is essential, especially L vs. R and V_e determine phase behavior and structure

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Case I: $V_e > 350 \text{ \AA}^3$

Case II: $150 \text{ \AA}^3 < V_e < 350 \text{ \AA}^3$

Case III: $V_e = 30 \text{ \AA}^3$

nanocrystals have facets - effect on ordering of molecules!

Pressure/temperature phase diagrams and superlattices of organically functionalised metal nanocrystal monolayers. J. R. Heath et al., JPC B 101, 189 (1997).

Langmuir-Blodgett manipulation of size-selected CdSe nanocrystallites. B.O. Dabbousi et al., Chem. Mater. 6, 216 (1994).

Case II: $150 \text{ \AA}^3 < V_e < 350 \text{ \AA}^3$

Condensed phase with order,
repulsions between capping
molecules, distance between
NC can be controlled

Low-density
gas phase

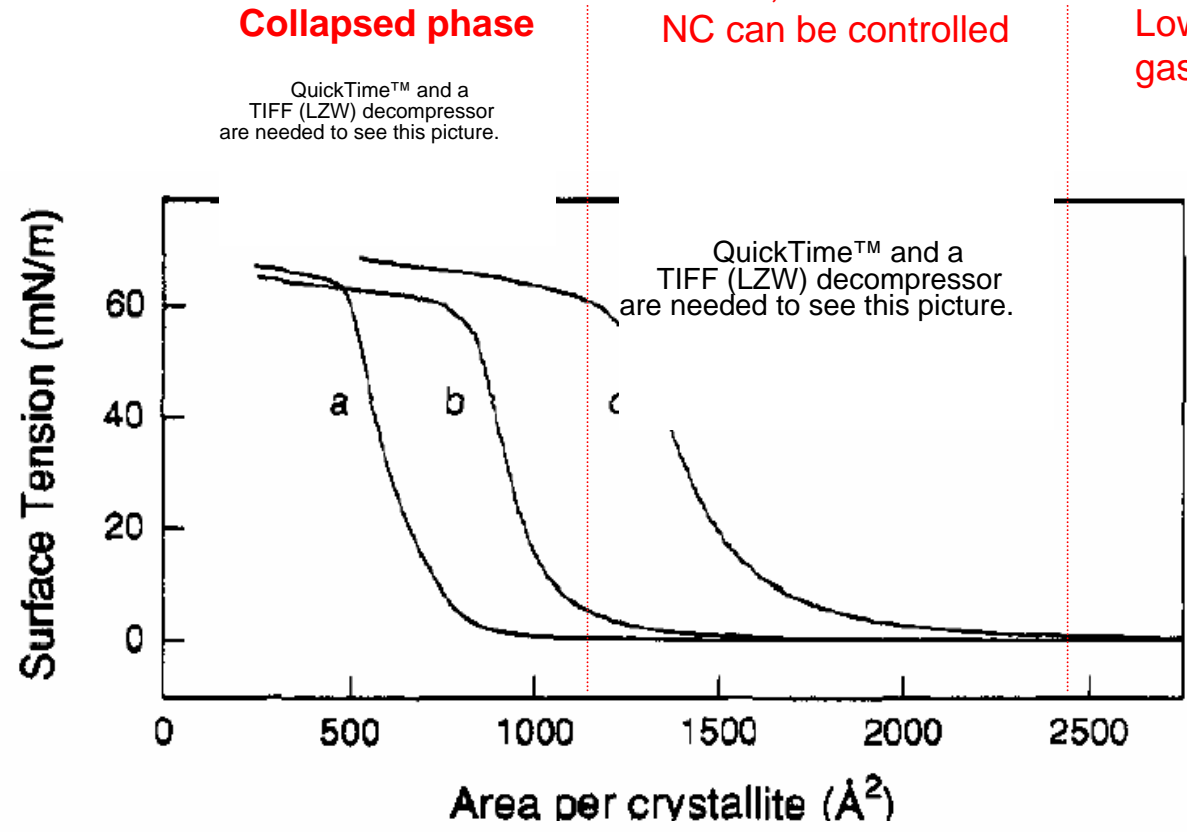
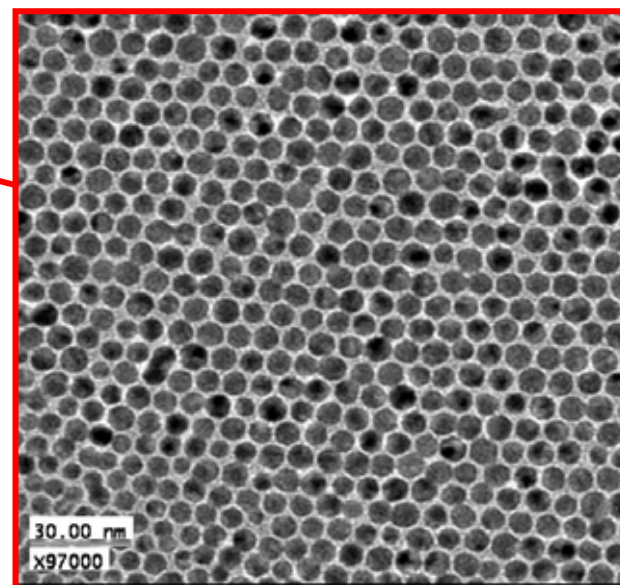
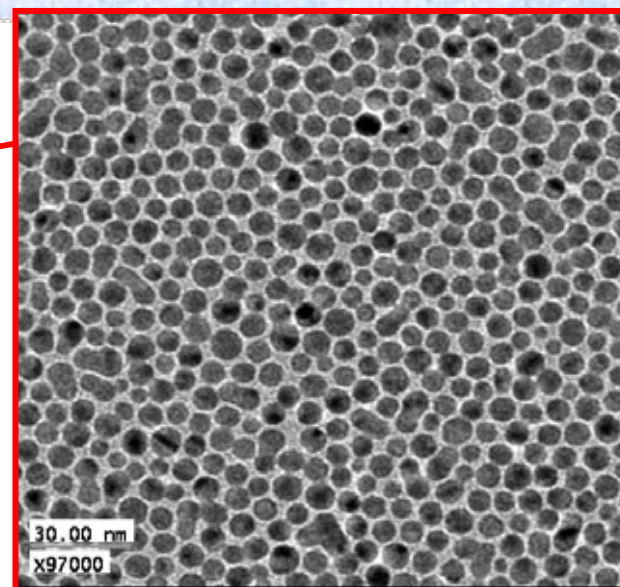
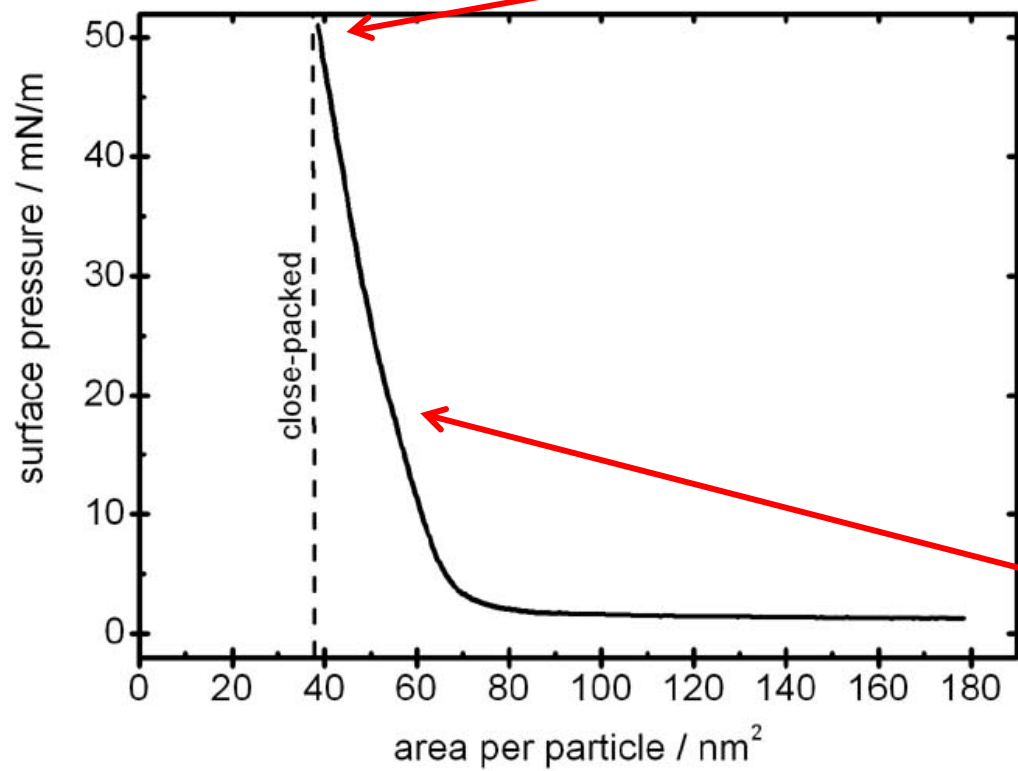
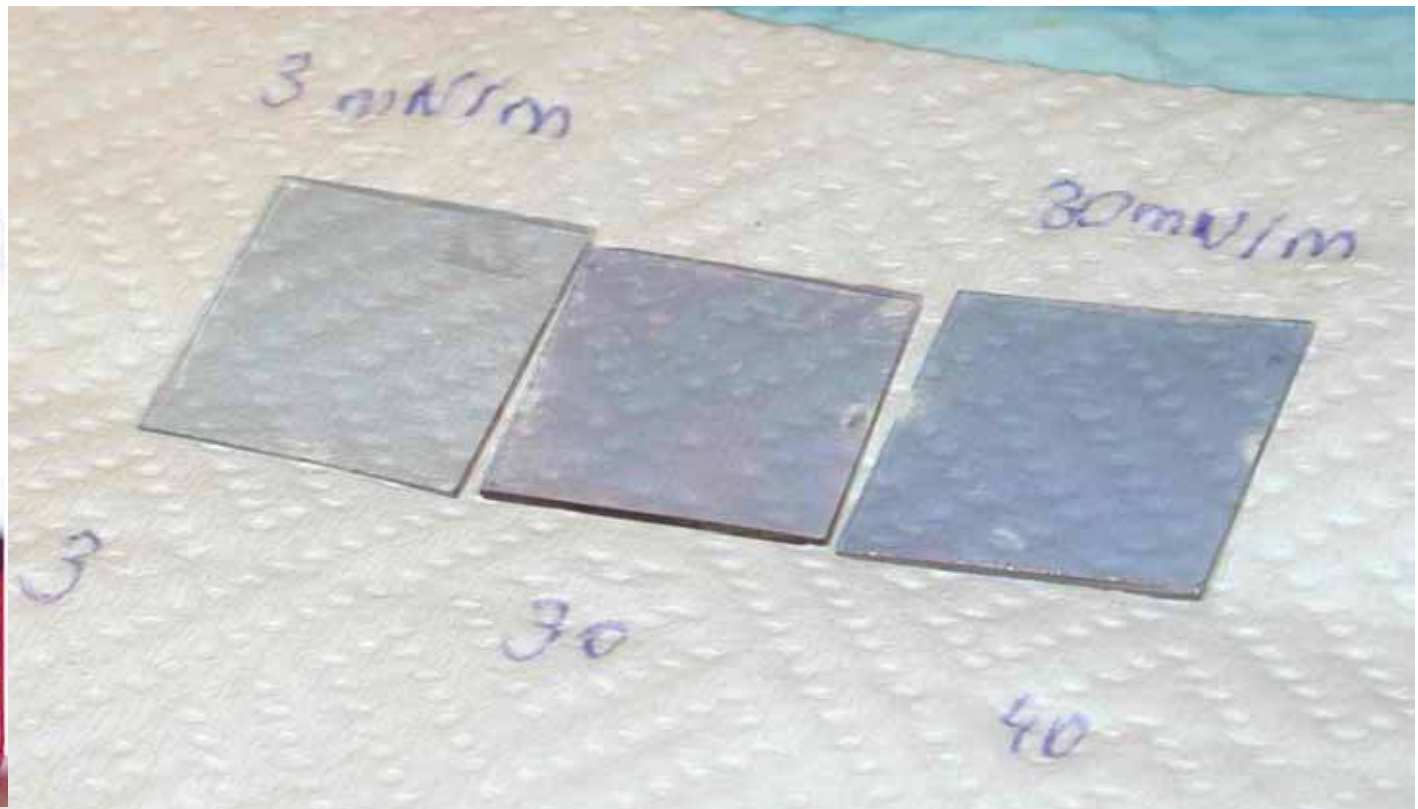


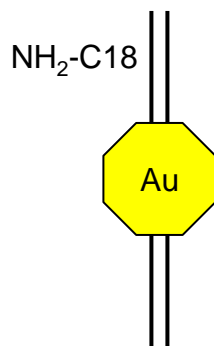
Figure 1. Surface pressure–area (π - A) isotherms for Langmuir monolayers of CdSe nanocrystallites. Diameters are (a) 25, (b) 30, (c) 36, (d) 43, and (e) 53 Å. The area per crystallite is obtained by dividing the total area available during compression by the estimated number of crystallites applied onto the water surface.

Case II: $150 \text{ \AA}^3 < V_e < 350 \text{ \AA}^3$ 



Case I: $V_e > 350 \text{ \AA}^3$

London forces between capping molecules are dominant, leading to low density phases with order and decreasing disorder at higher densities



QuickTime™ and a
 GIF (LZW) decompressor
 are needed to see this picture.

Easy compressible

Weakly
 compressible at low
 surface coverage

“gas-phase”

Case I: $V_e > 350 \text{ \AA}^3$

London forces between capping molecules are dominant, leading to low density phases with order and decreasing disorder at higher densities

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

$d\pi/dT < 0$

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Pressure/temperature phase diagrams and superlattices of organically functionalised metal nanocrystal monolayers. J. R. Heath et al., JPC B 101, 189 (1997).

Langmuir-Blodgett manipulation of size-selected CdSe nanocrystallites. B.O. Dabbousi et al., Chem. Mater. 6, 216 (1994).

Case I: $V_e > 350 \text{ \AA}^3$

London forces between capping molecules are dominant, leading to low density phases with order and decreasing disorder at higher densities

$$\pi = -\left(\frac{\partial F}{\partial A}\right)_{T,N} = -\left(\frac{\partial U}{\partial A}\right)_{T,N} + T\left(\frac{\partial S}{\partial A}\right)_{T,N}$$

$$\frac{\partial \pi}{\partial T} = \frac{\partial S}{\partial A}$$

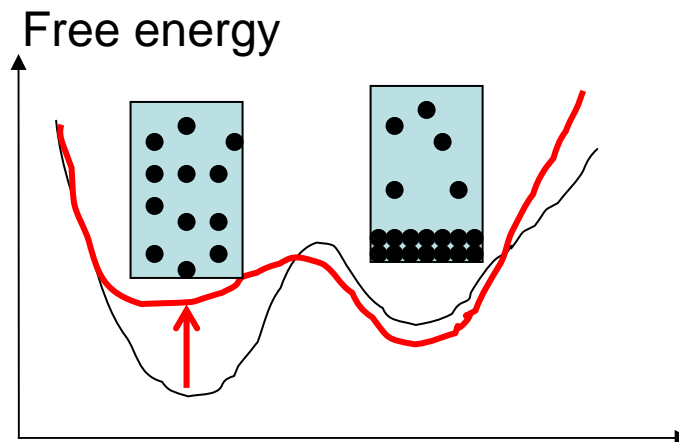
Normally positive, but here negative!

Pressure/temperature phase diagrams and superlattices of organically functionalised metal nanocrystal monolayers. J. R. Heath et al., JPC B 101, 189 (1997).

Langmuir-Blodgett manipulation of size-selected CdSe nanocrystallites. B.O. Dabbousi et al., Chem. Mater. 6, 216 (1994).

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Principle: “destabilization” means increasing the chemical potential of the nanocrystal building blocks in the solution. In such a way a spontaneous assembly can occur until equilibrium between the solution and the solid is reached



Two methods of destabilization:
$$\mu = \mu^o + kT \ln \frac{c}{c_{Ref}}$$

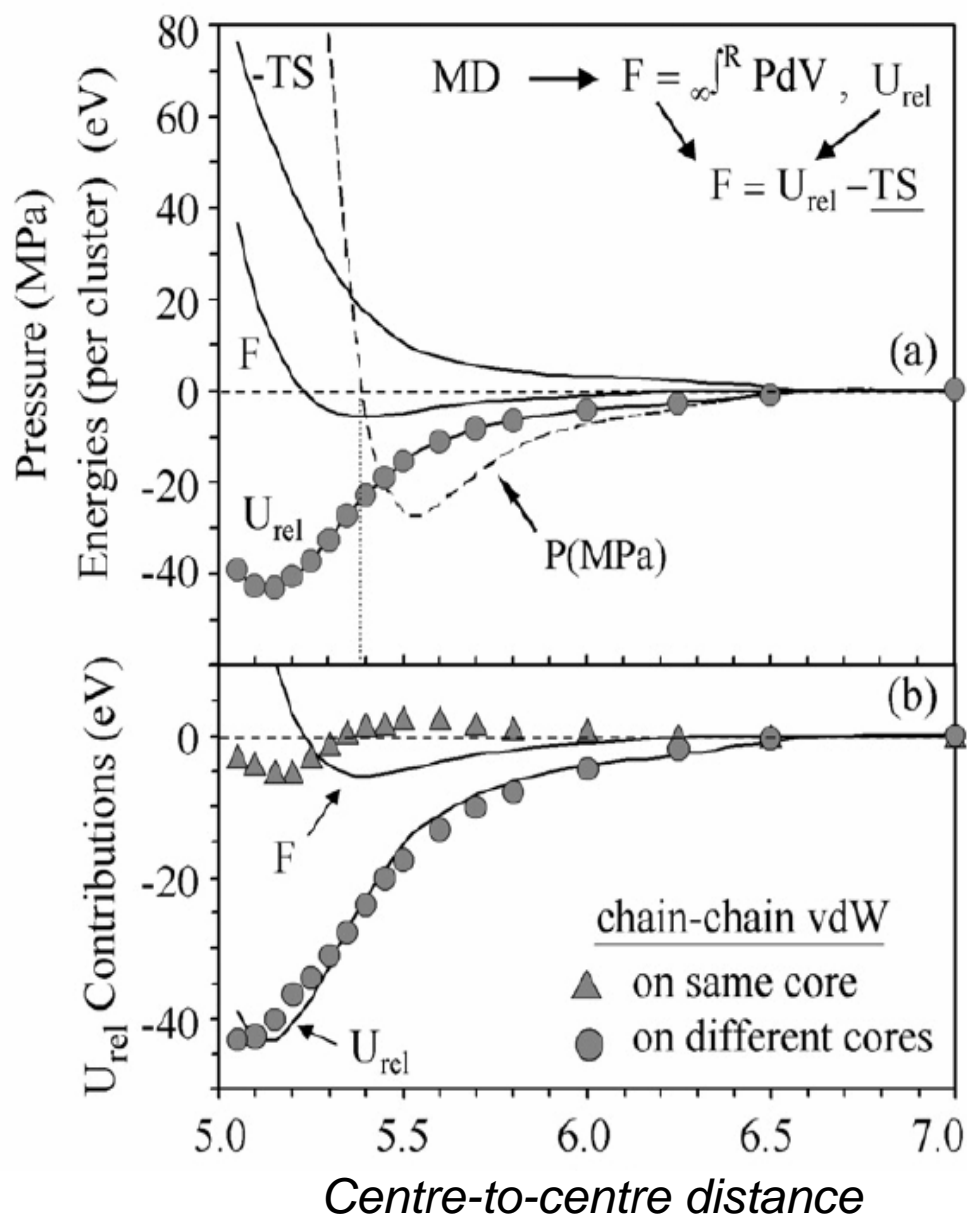
* increasing the concentration of NC by thermal evaporation of solvent

** addition of a non-solvent to a colloidal solution

*** other methods? Why is T-increase not working?

Homogeneous nucleation: formation of 3-D micrometer large superlattices

Heterogeneous nucleation on a substrate: formation of 2-D monolayers, bilayers etc. by dropcasting and thermal evaporation



Reduce V - Calculate P and U

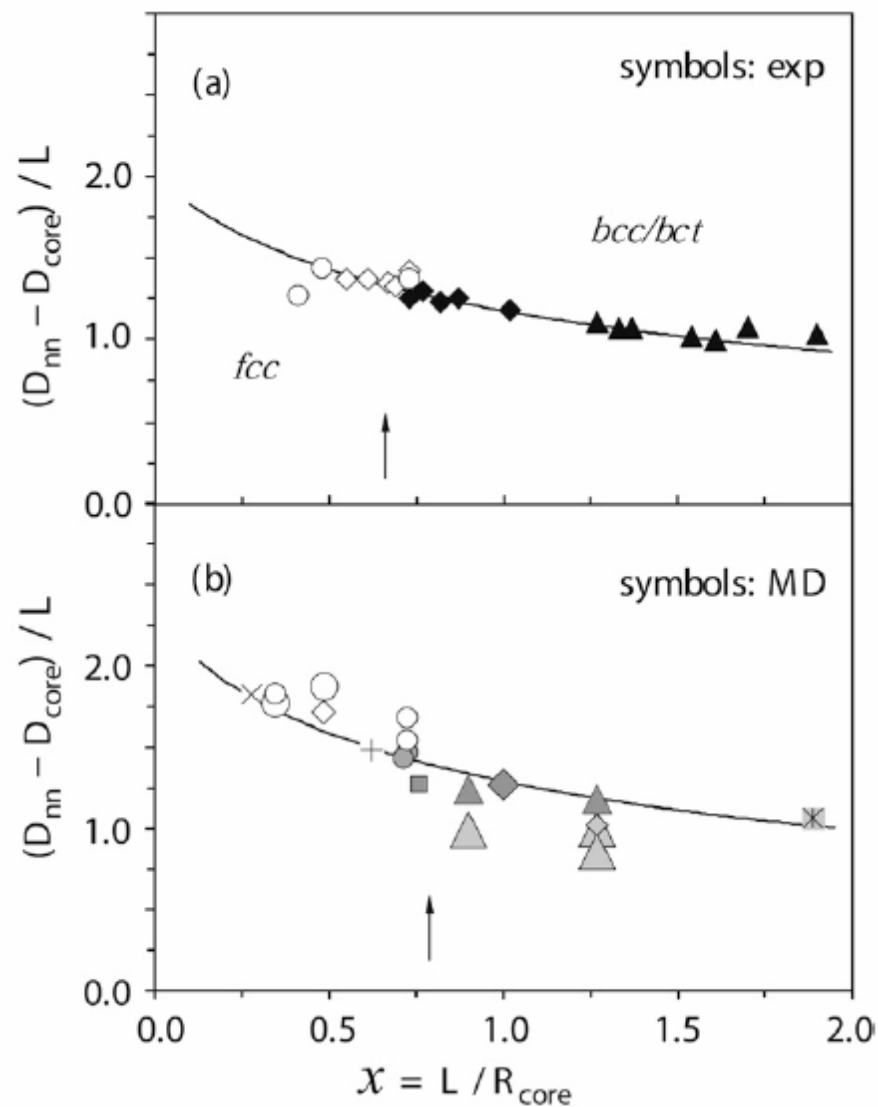
Free energy can be calculated from:

$$p = - \left(\frac{\partial F}{\partial \mathcal{N}} \right)_{T,N}$$

From F and U, -TS can be calculated
 (increase of entropy due to reduction
 of volume)

L/R is important part of the code

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.



“First” example was the formation of three-dimensional 5 to 50 micrometer colloidal crystals of CdSe

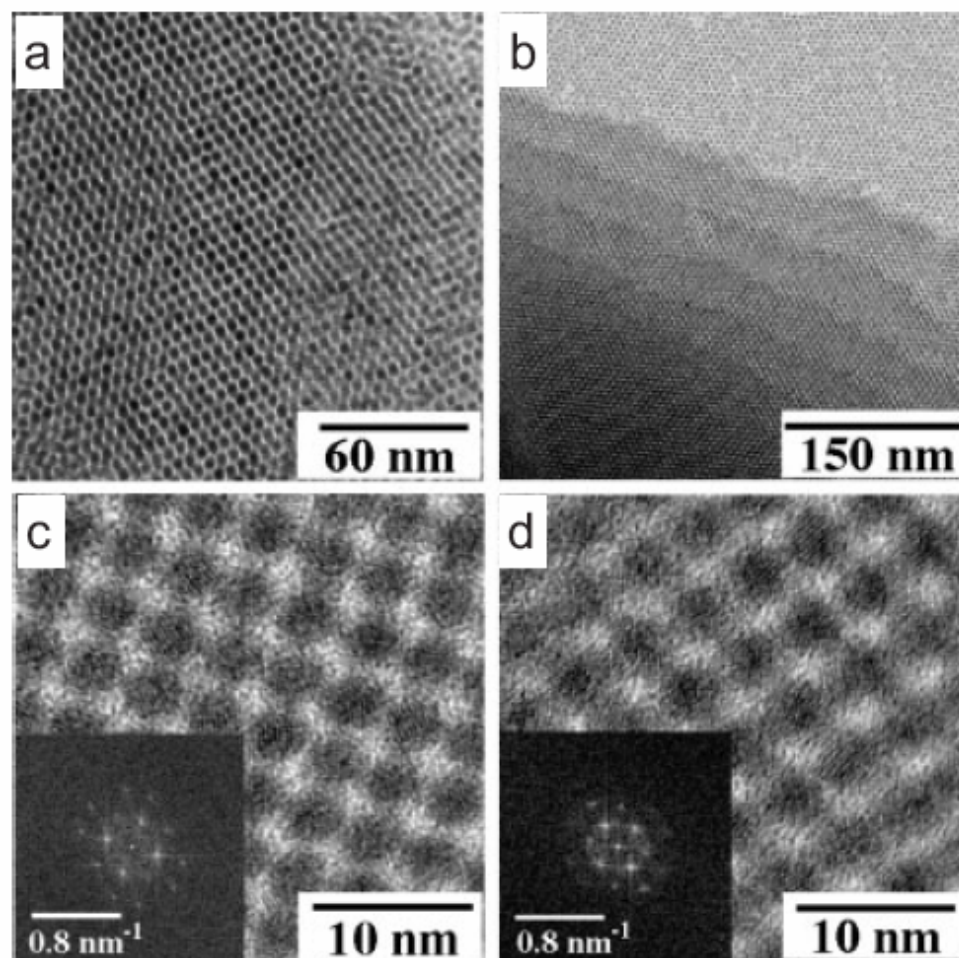
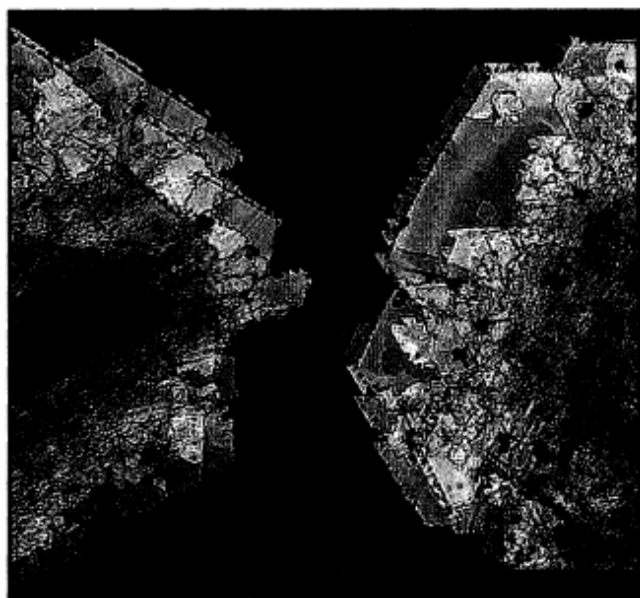
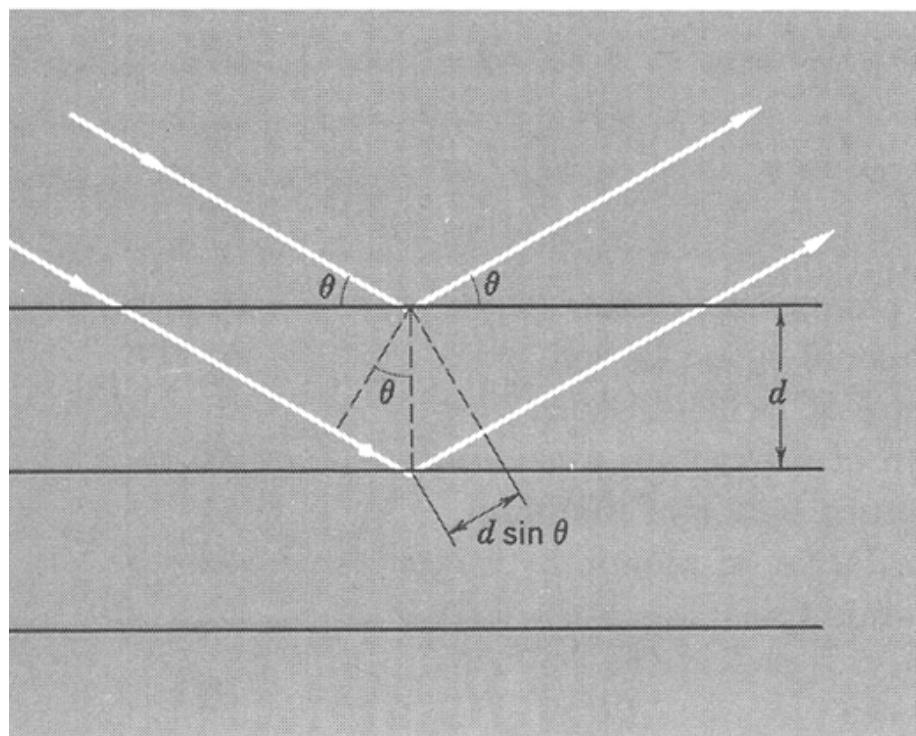


Fig. 12. TEM images of 3D arrangements of CoPt₃ (a) and CdSe (b) nanocrystals, and HRTEM images of (100) (c) and (110) (d) projections along the CdSe superlattice with corresponding FFTs.



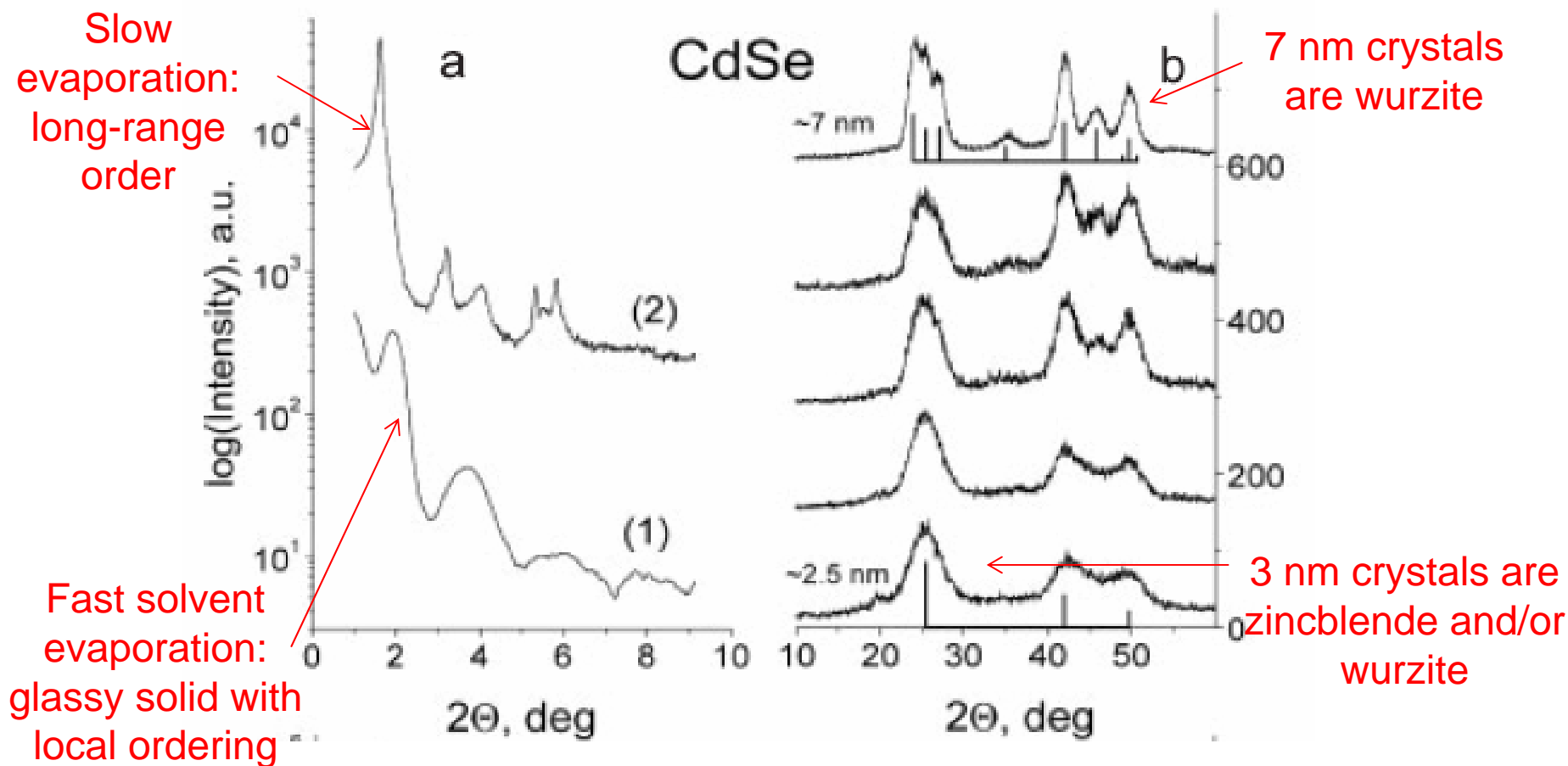
Small angle XRD spectra: structure of superlattice of NC building blocks

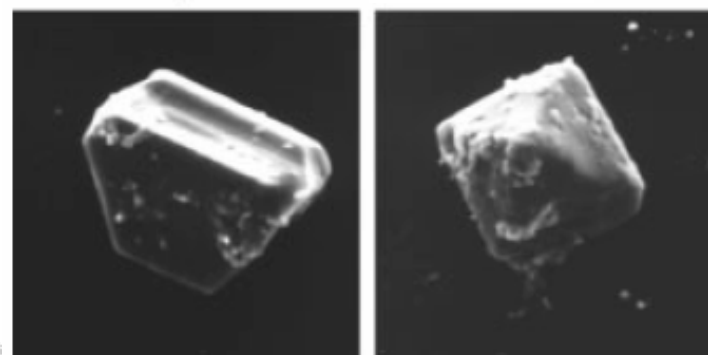
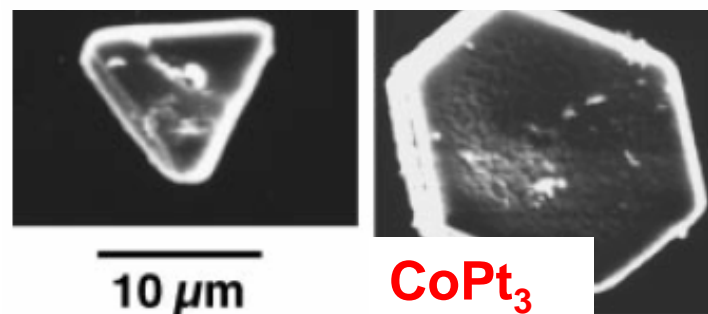
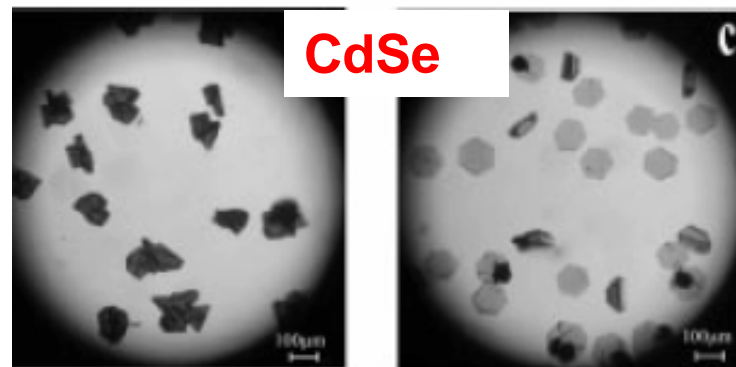
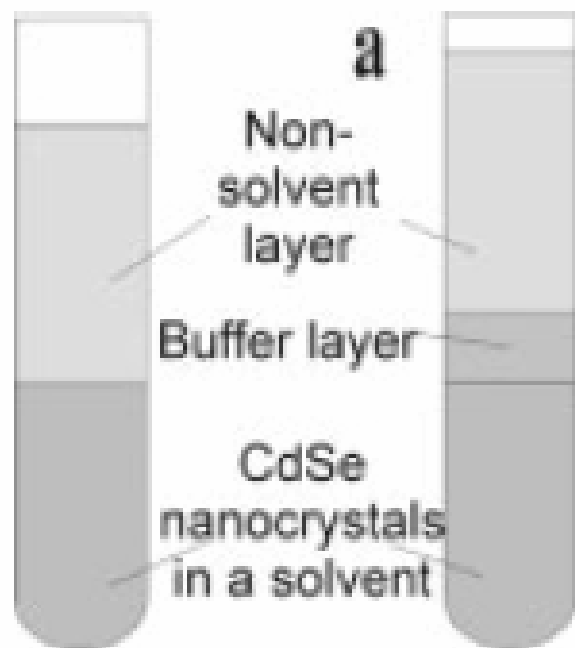
Wide-angle XRD spectra: atomic structure of nanocrystal and nanocrystal orientation in superlattice

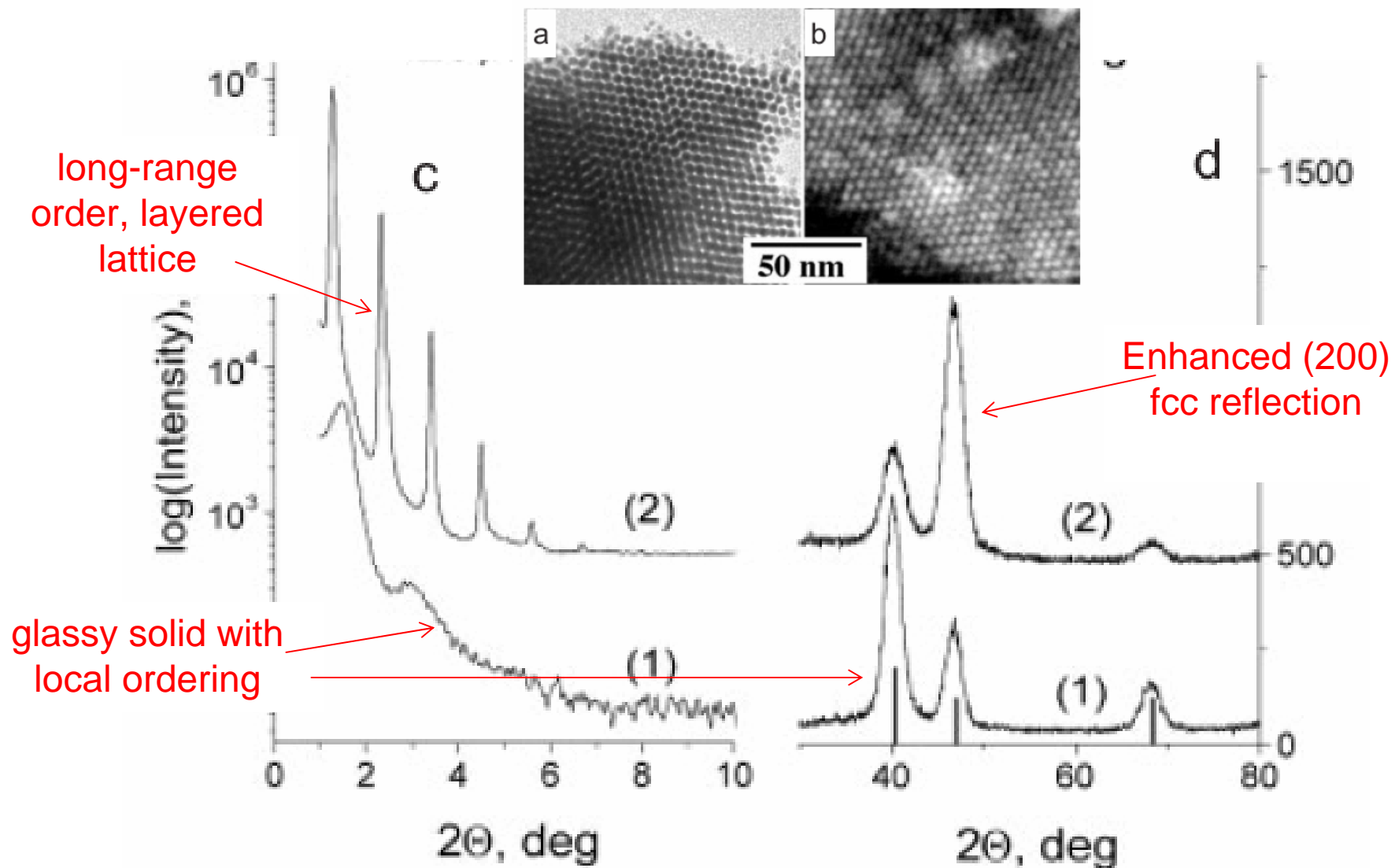
2 Derivation of the Bragg equation $2d \sin \theta = n\lambda$; here d is the spacing of parallel atomic and $2\pi n$ is the difference in phase between reflections from successive planes. The reflecting have nothing to do with the surface planes bounding the particular specimen.

Small angle XRD spectra: structure of superlattice of NC building blocks

Wide-angle XRD spectra: atomic structure of nanocrystal and nanocrystal orientation in superlattice

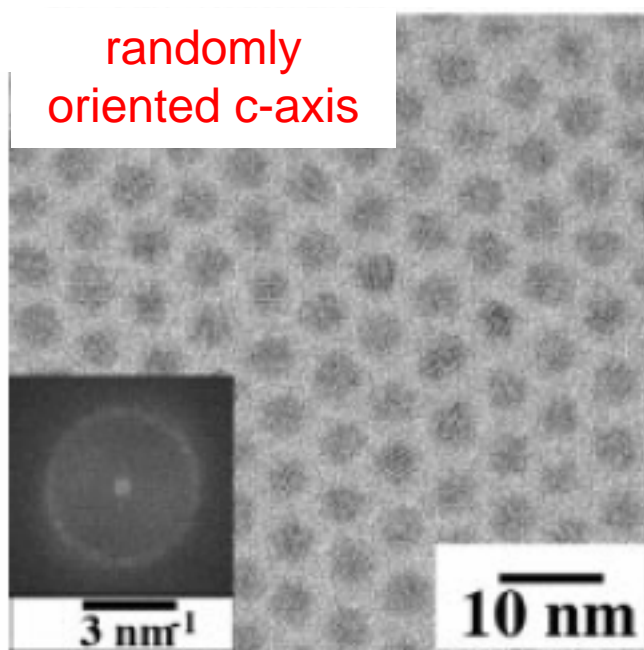




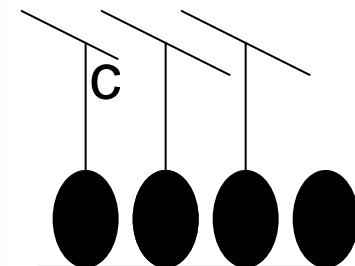
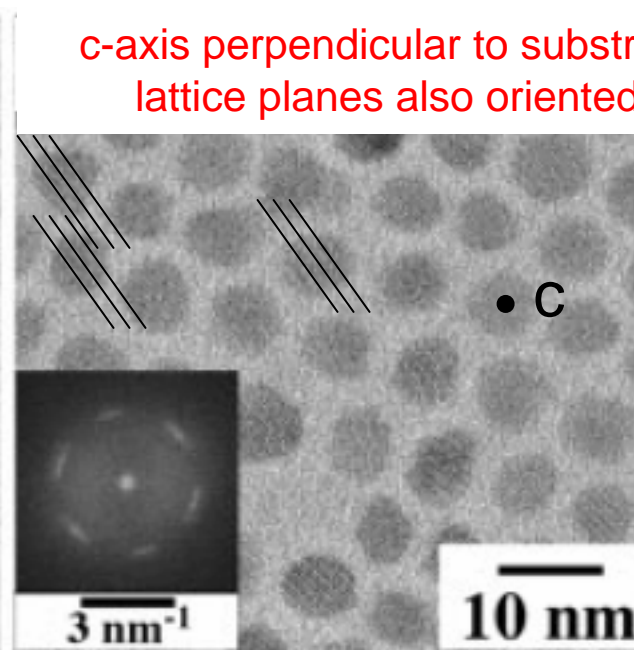


TEM

randomly oriented c-axis

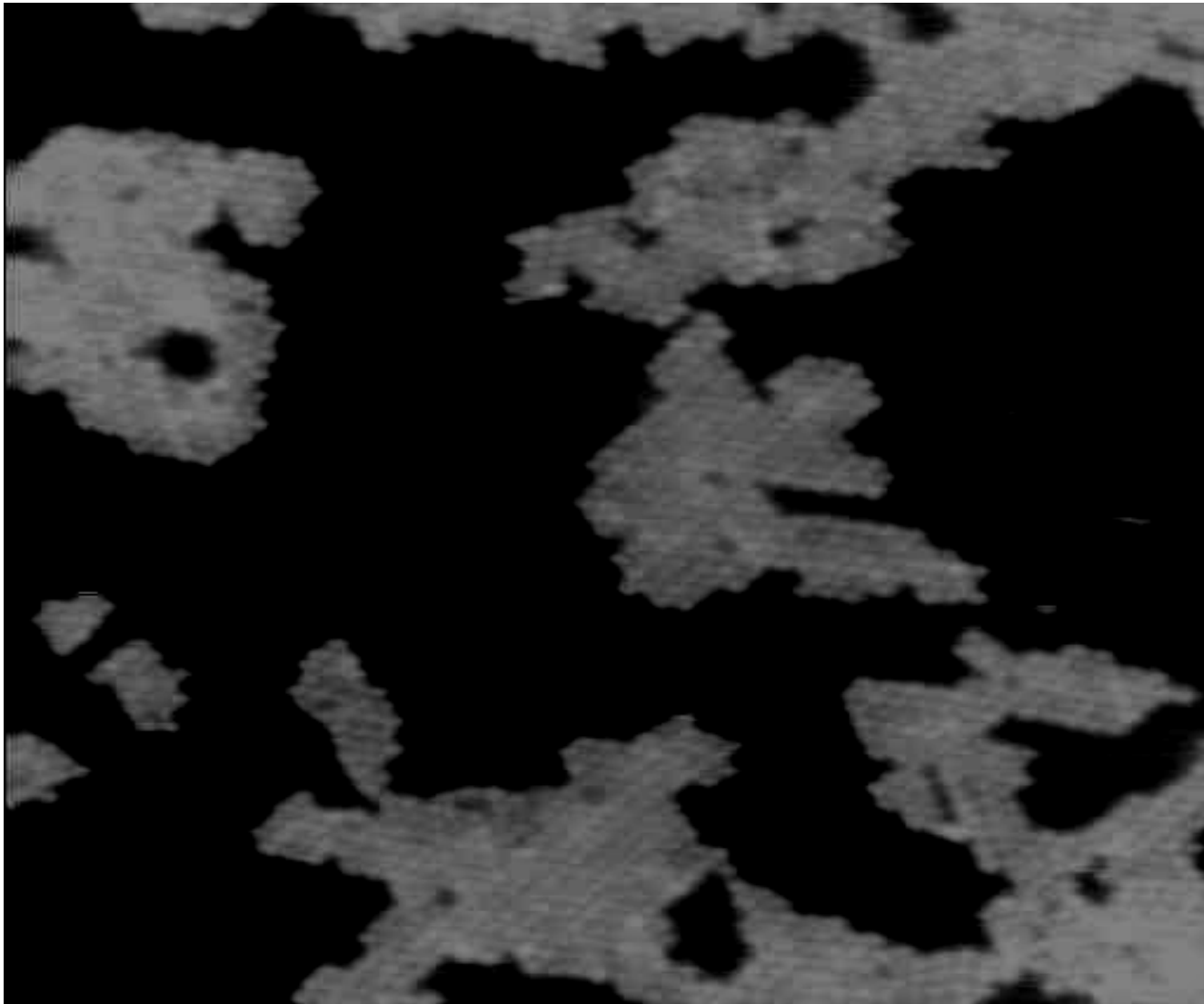


c-axis perpendicular to substrate, lattice planes also oriented!

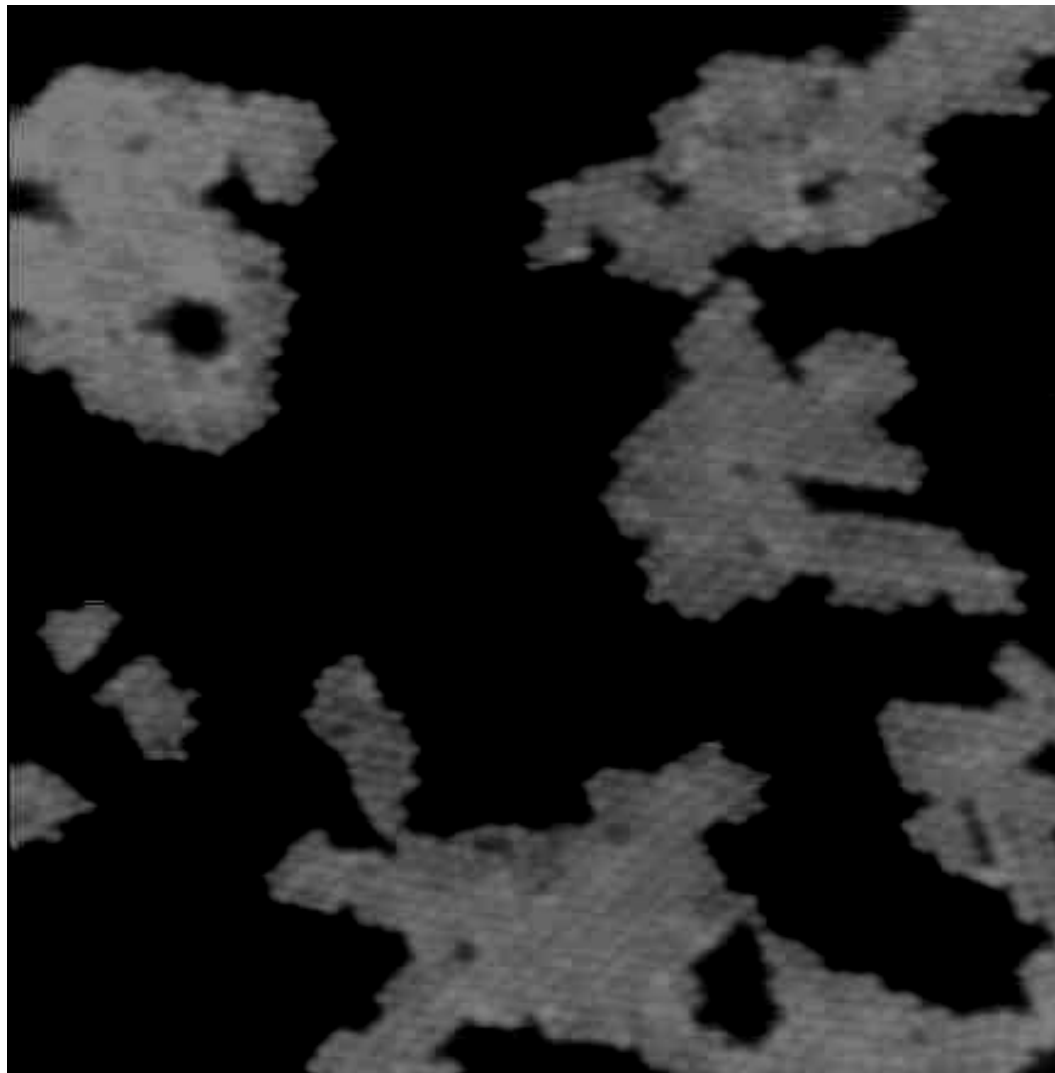


Subtle effects of secret parts of the “code”

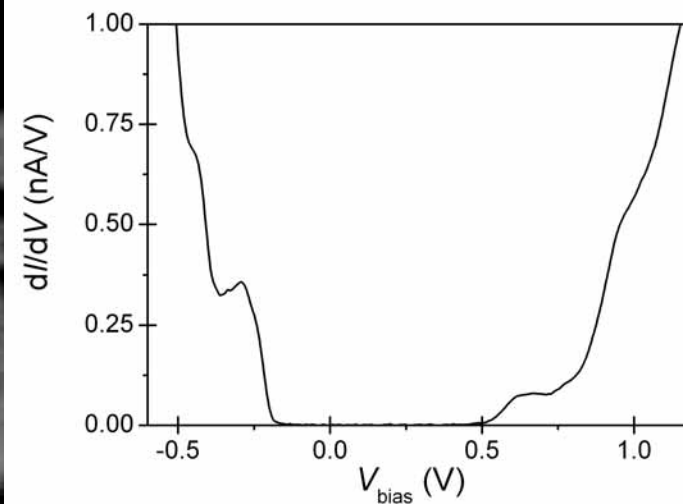
Is it the crystal dipole moment?



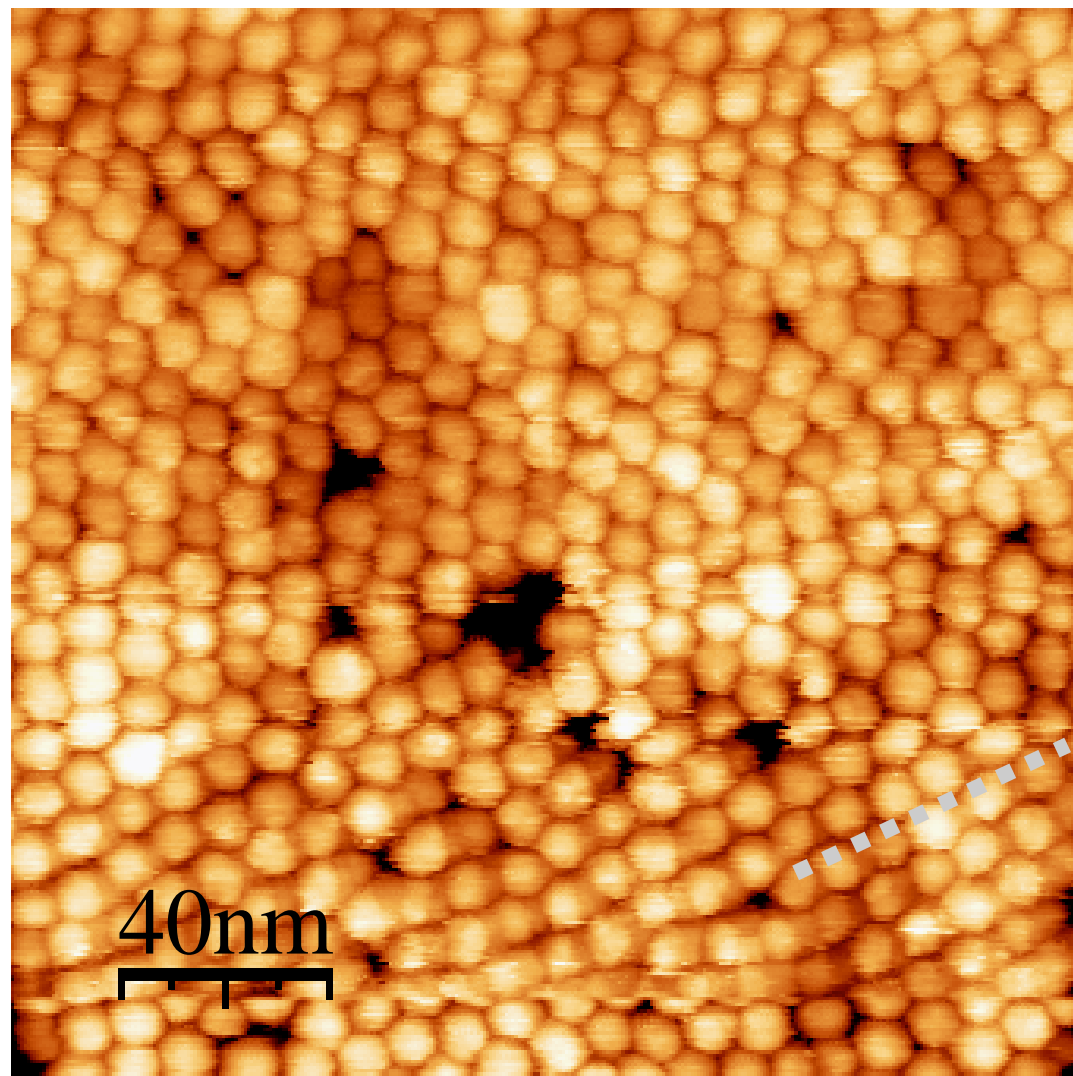
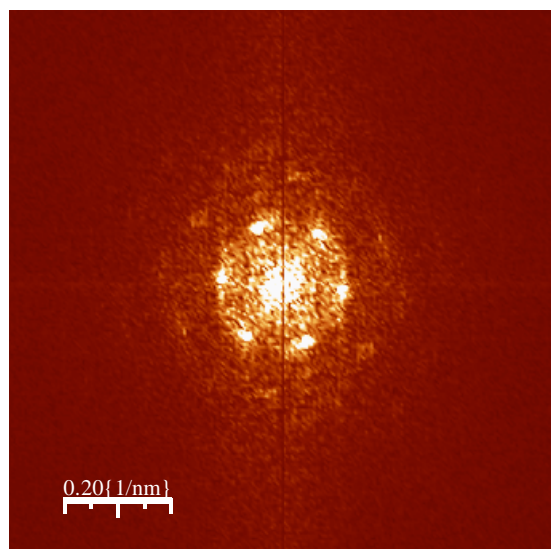
AFM: orientation due to HOPG substrate?



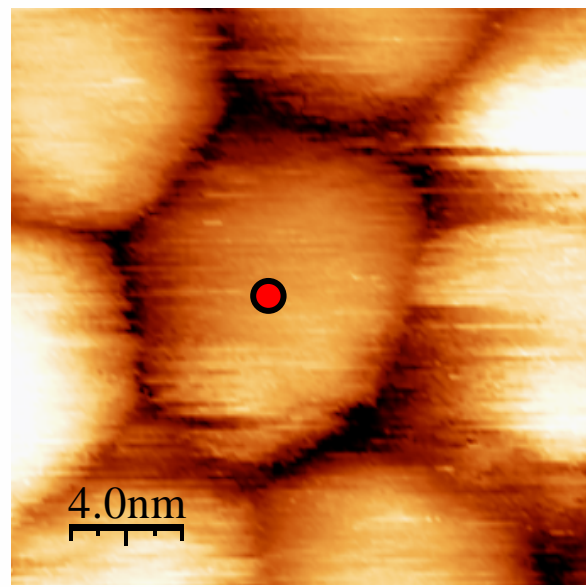
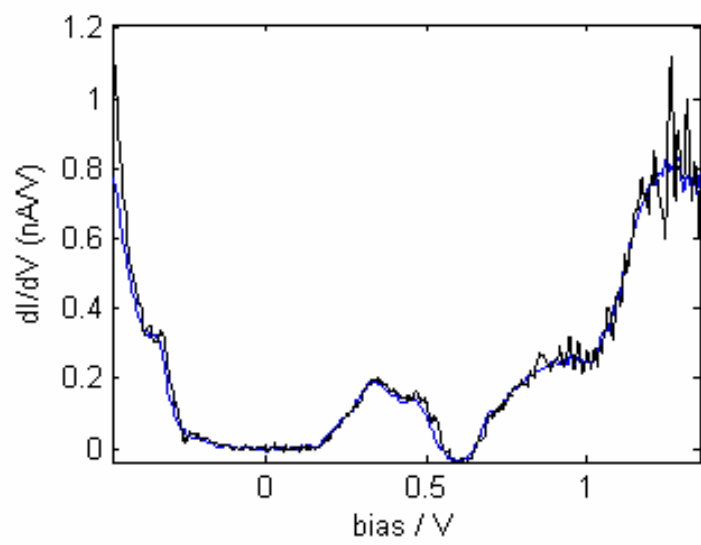
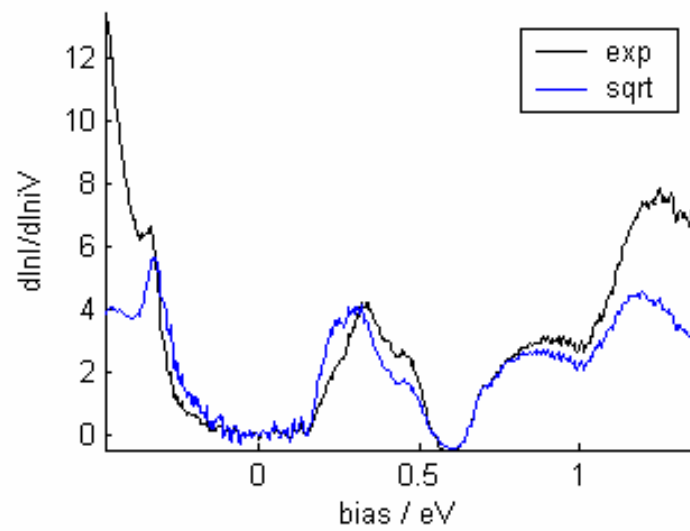
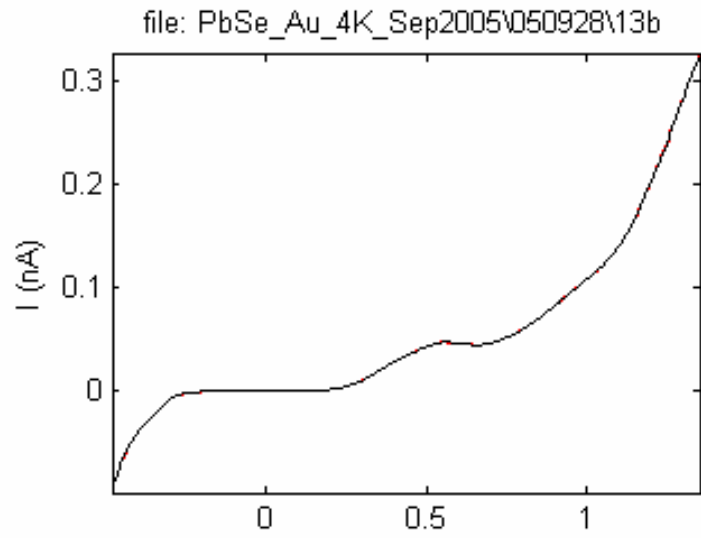
STM and spectroscopy



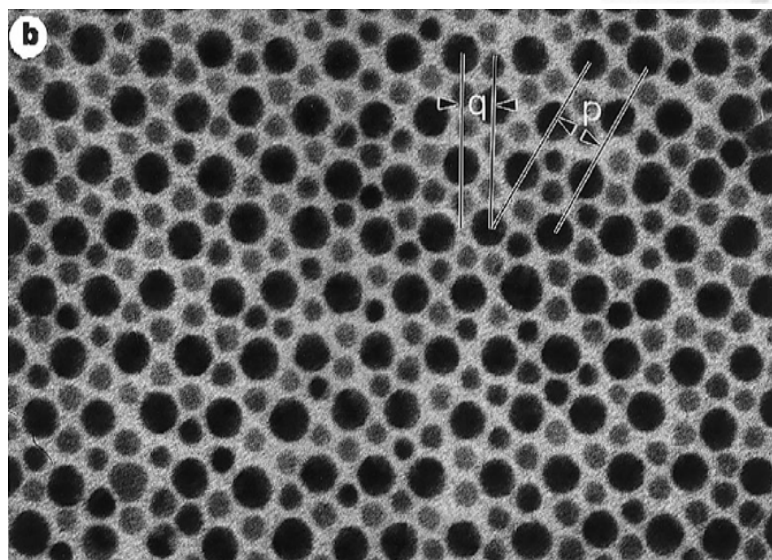
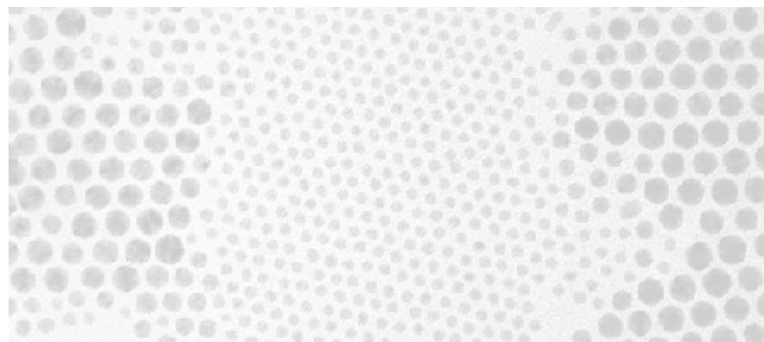
STM and spectroscopy



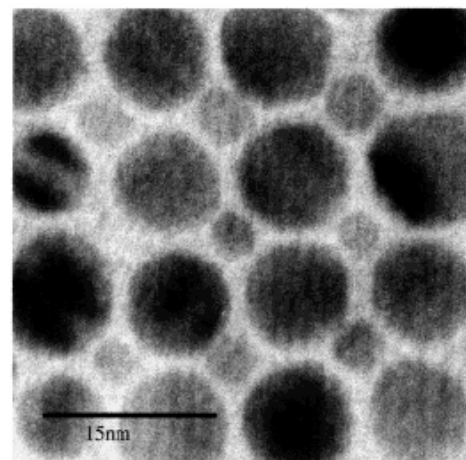
STM and spectroscopy



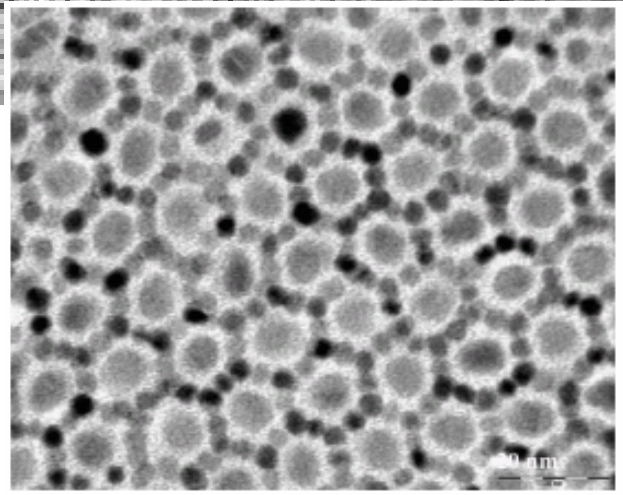
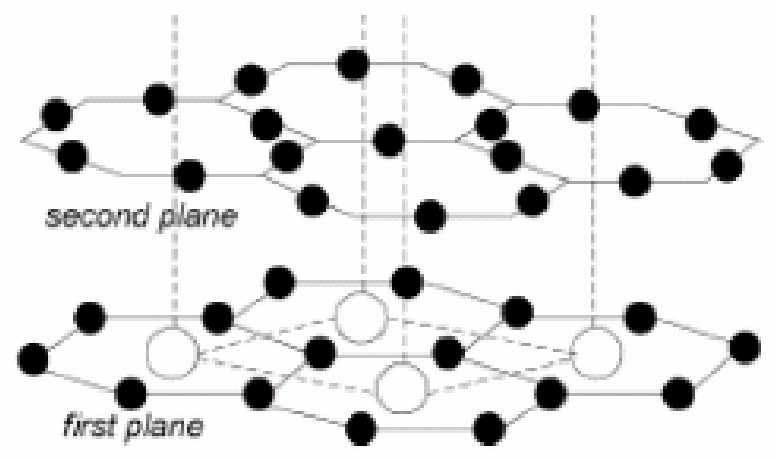
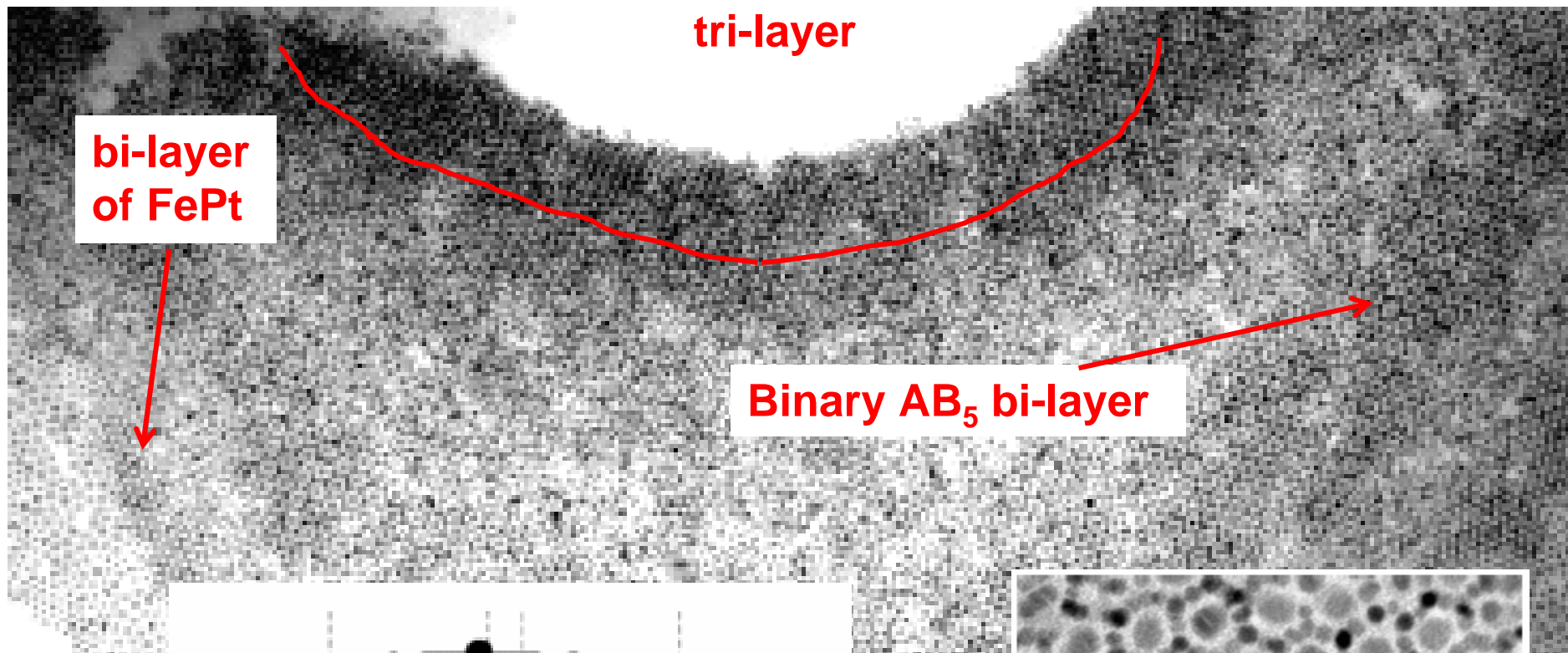
If size ratio is far from suitable,
nanocrystals do not mix!



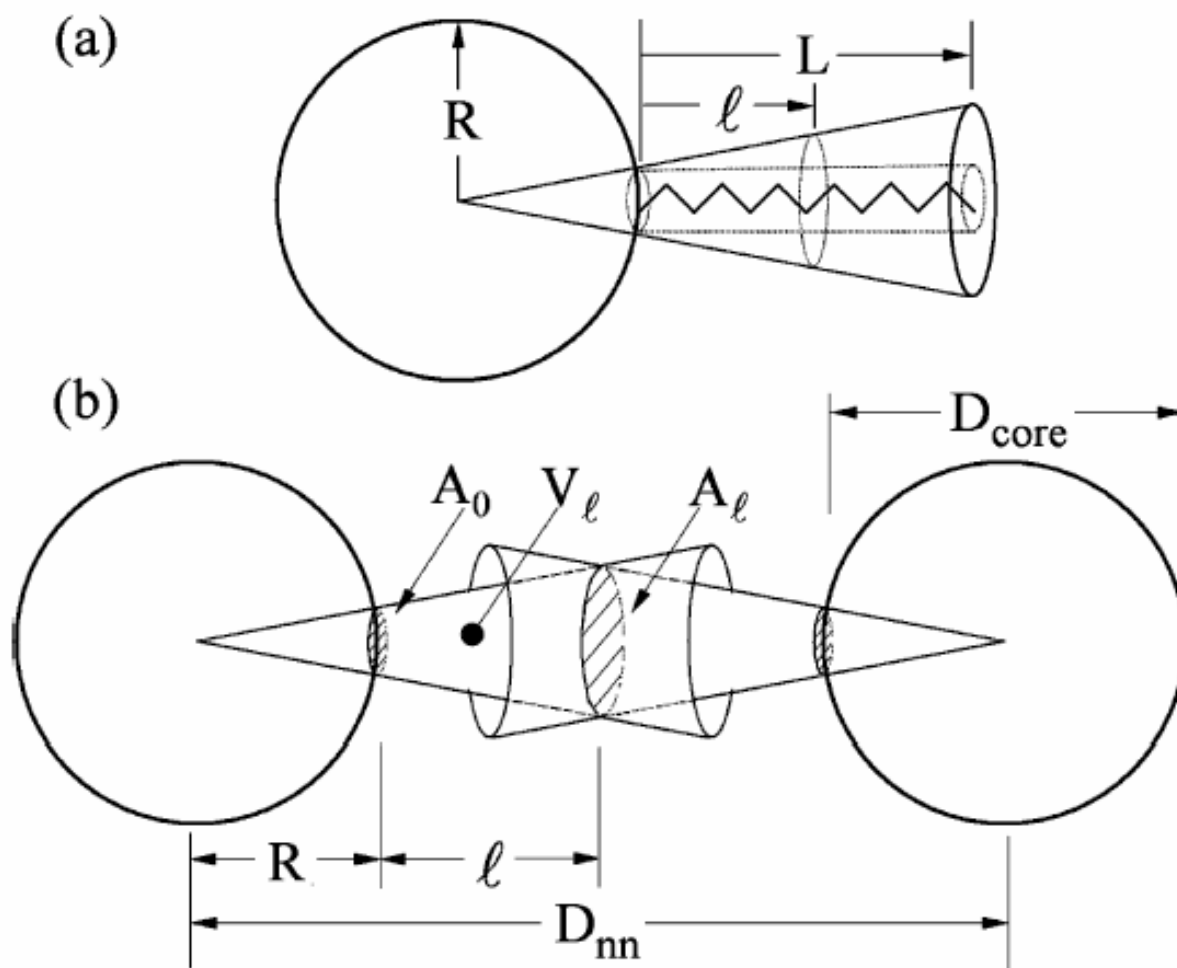
Gold nanocrystals with size ratio
between 0.48 and 0.63 leads to
AB₂ structures

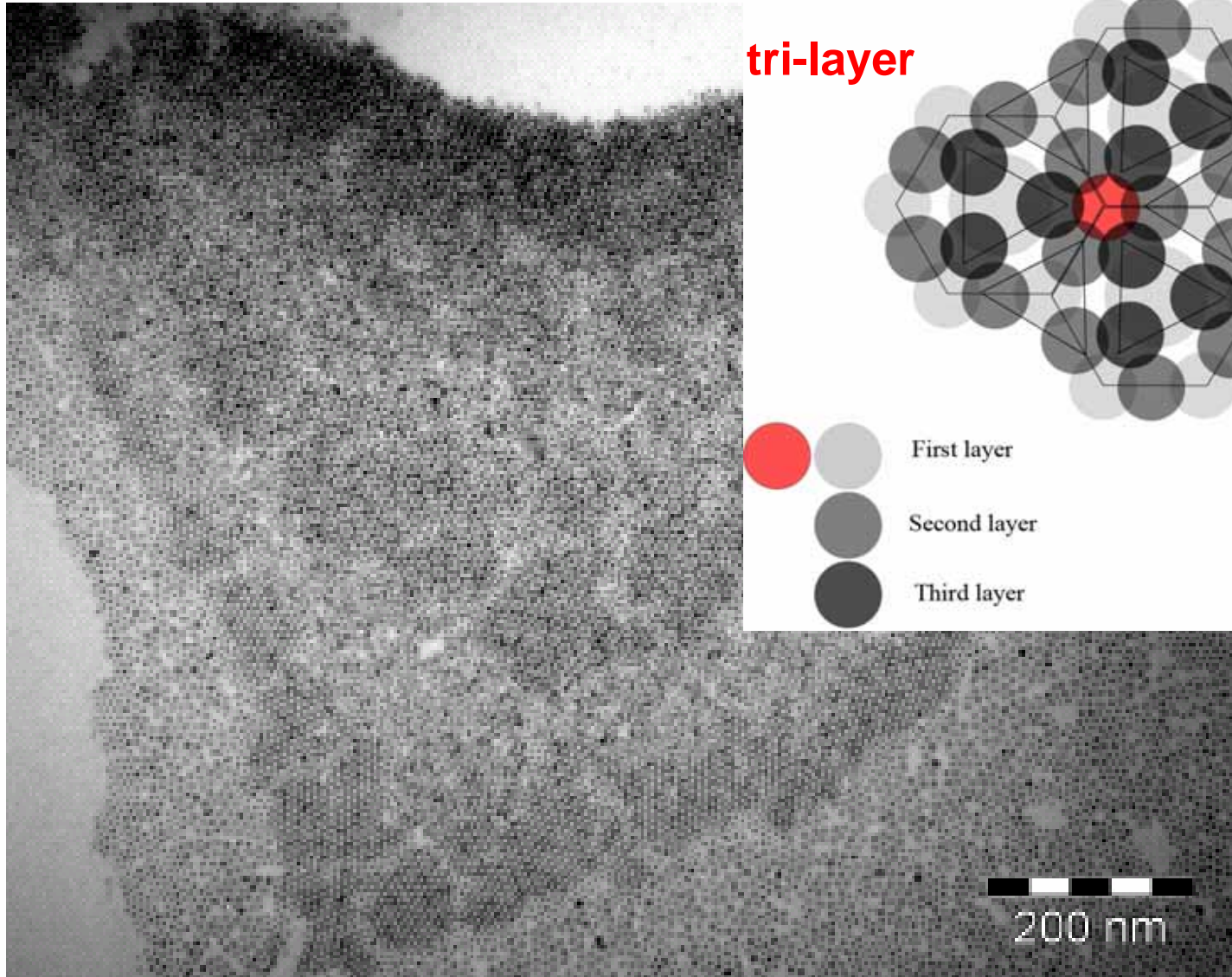


Gold nanocrystal with size ratio
between 0.24 and 0.48 leads to
AB structures



The code in parameters: L/R , excess volume, ...





Disordered layers form if solvent evaporates too fast

