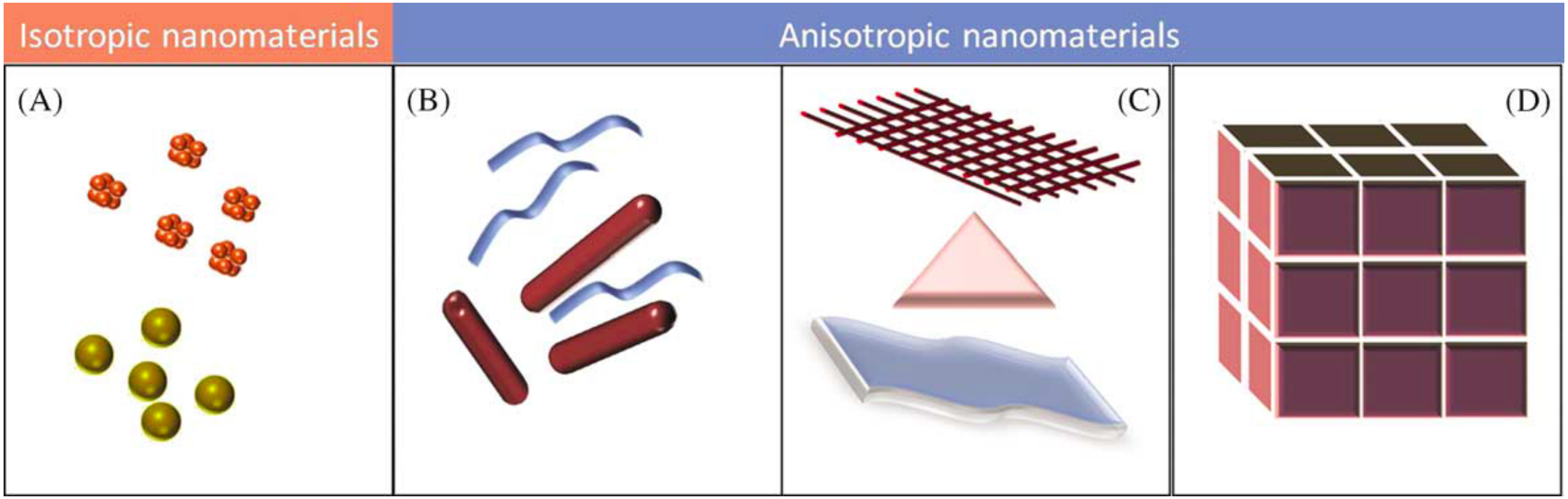
Growth of Nanostructures and Nanomaterials



0D spheres and clusters

1D nanofibers, wires, and rods

2D films, plates, and networks

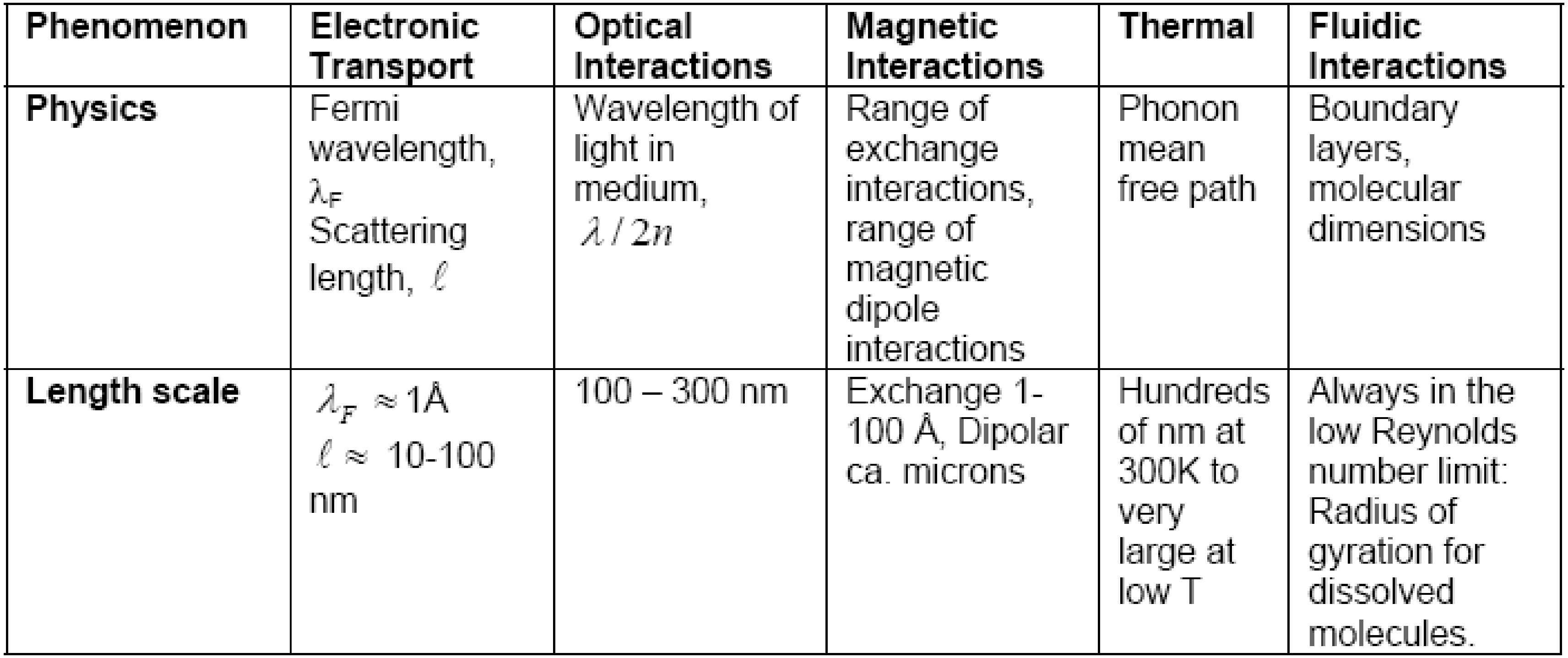
3D nanomaterials

Various kinds of nanomaterials

Panikkanvalappil R. Sajanlal et al., Nano Reviews 2011, **2**: 5883

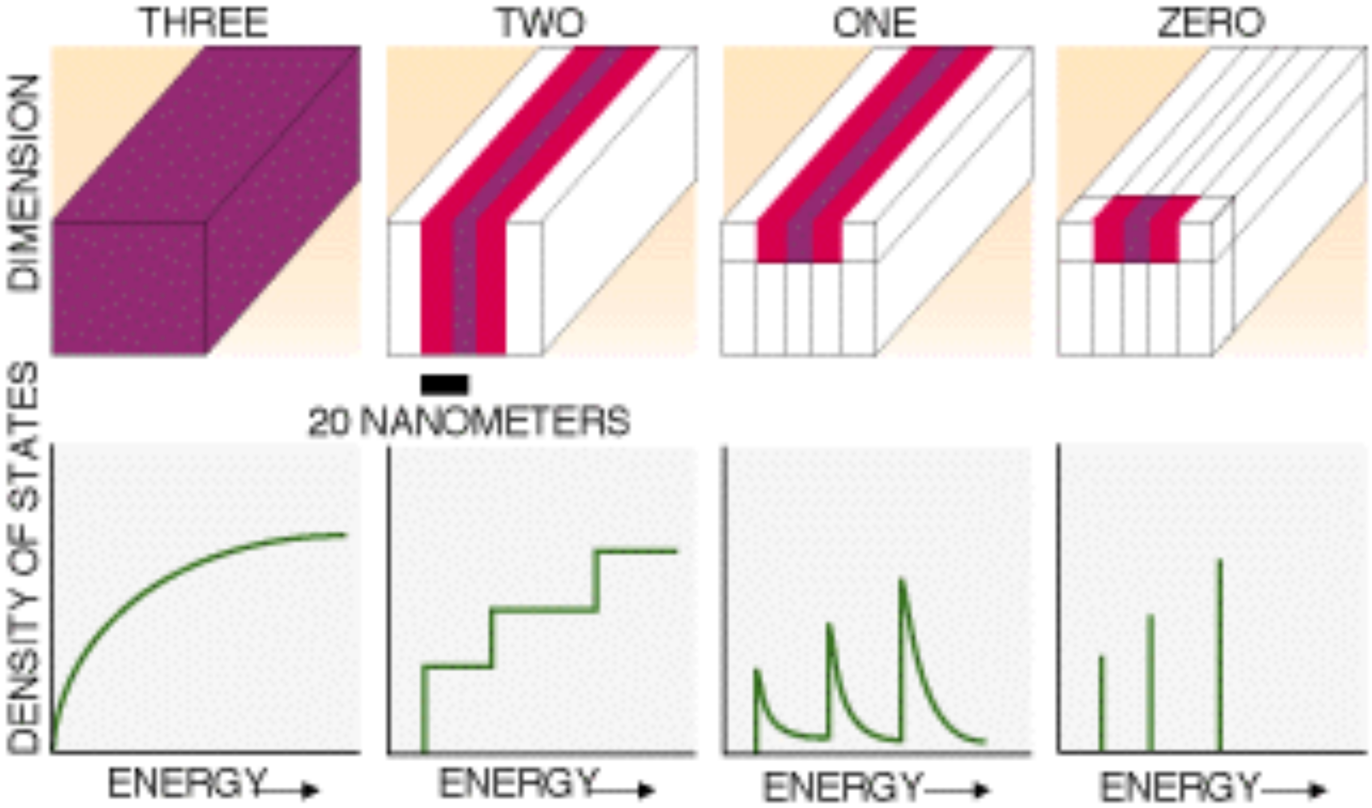
Critical lengthes for Nanostructures

Nanostructured materials derive their special properties from having one or more dimensions made small compared to a length scale critical to the physics of the process.



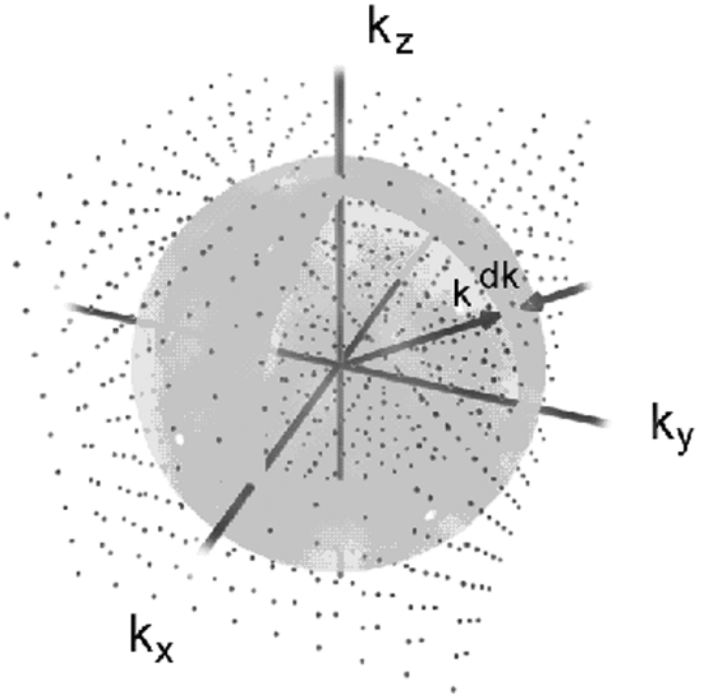
Phenomenon	**Electronic Transport**	**Optical Interactions**	**Magnetic Interactions**	**Thermal**	**Fluidic Interactions**
Physics	Fermi wavelength, λ_F Scattering length, ℓ	Wavelength of light in medium, $\lambda / 2n$	Range of exchange interactions, range of magnetic dipole interactions	Phonon mean free path	Boundary layers, molecular dimensions
Length scale	$\lambda_F \approx 1$Å $\ell \approx$ 10-100 nm	100 – 300 nm	Exchange 1-100 Å, Dipolar ca. microns	Hundreds of nm at 300K to very large at low T	Always in the low Reynolds number limit: Radius of gyration for dissolved molecules.

Quantum confinement



(Scientific American)

Size dependence of density of states



k-space is filled with an uniform grid of points each separated in units of 2π/L along any axis.

The volume (V_k) of k-space occupied by each point is:

$$\left(\frac{2\pi}{L}\right)^3$$

r-space:

$$\frac{4\pi\, r^2 dr}{V}$$

k-space:

$$\frac{4\pi\, k^2 dk}{V_k} = \frac{4\pi\, L^3\, k^2 dk}{8\pi^3}$$

3D DOS

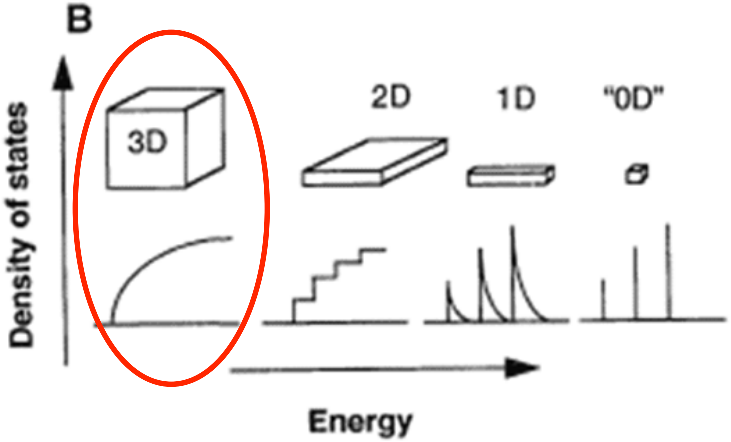
Density of states in a volume V per unit wave vector:

$$\frac{dn}{dk} = \frac{Vk^2}{2\pi^2}$$

For a free electron gas:

$$E = \frac{\hbar^2 k^2}{2m} \qquad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{Vk^2}{2\pi^2}\frac{m}{\hbar^2 k} = \frac{Vm}{\hbar^2 2\pi^2}\sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}$$

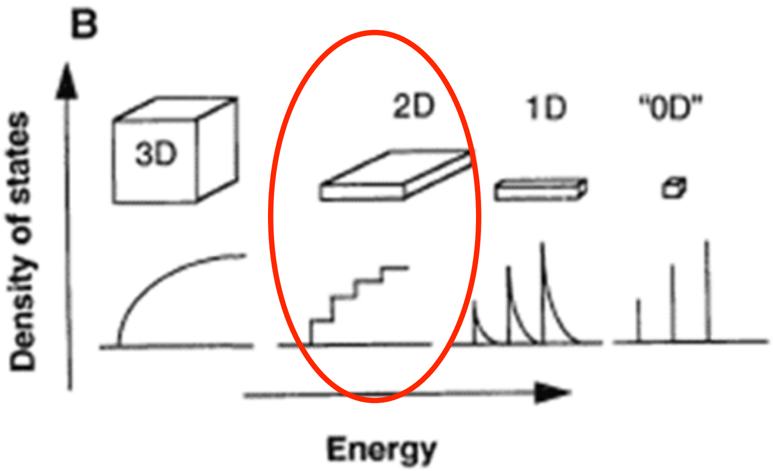


2D DOS

$$\frac{dn}{dk} = \frac{A2\pi k}{(2\pi)^2} \qquad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{Am}{2\pi\hbar^2}$$

Constant for each electronic band

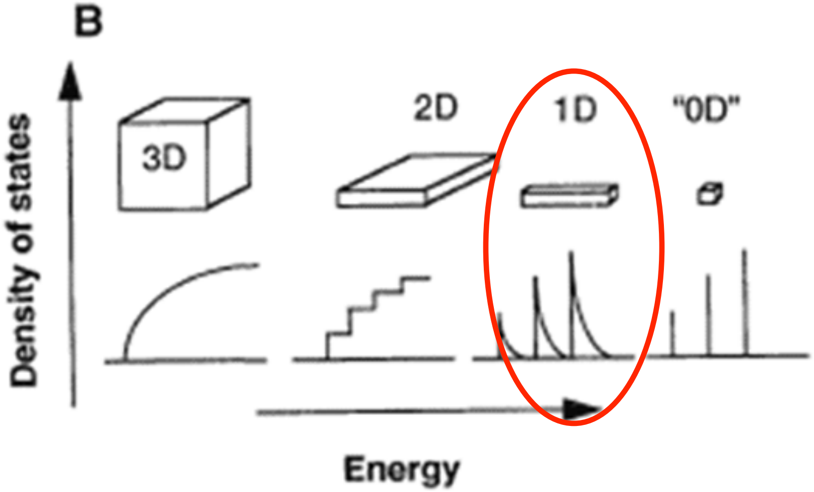


1D DOS

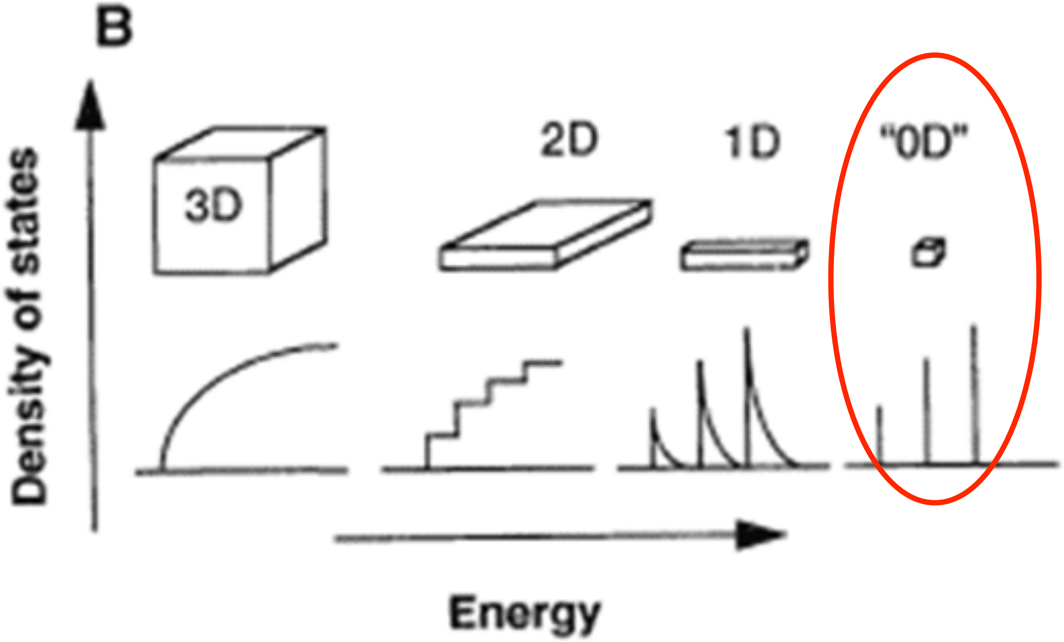
$$\frac{dn}{dk} = \frac{L}{2\pi} \qquad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{Lm}{2\pi\hbar^2 k} \propto E^{-\frac{1}{2}}$$

At each atomic level, the DOS in the 1D solid decreases as the reciprocal of the square root of energy.

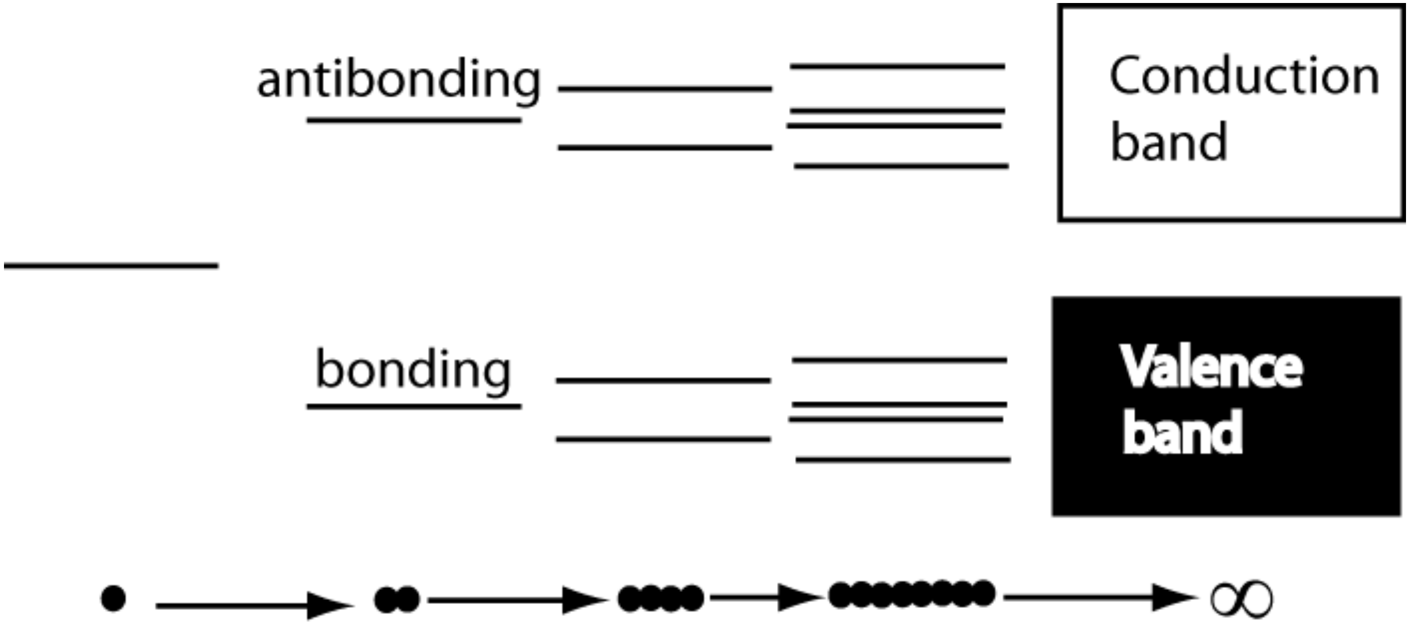


0 D DOS



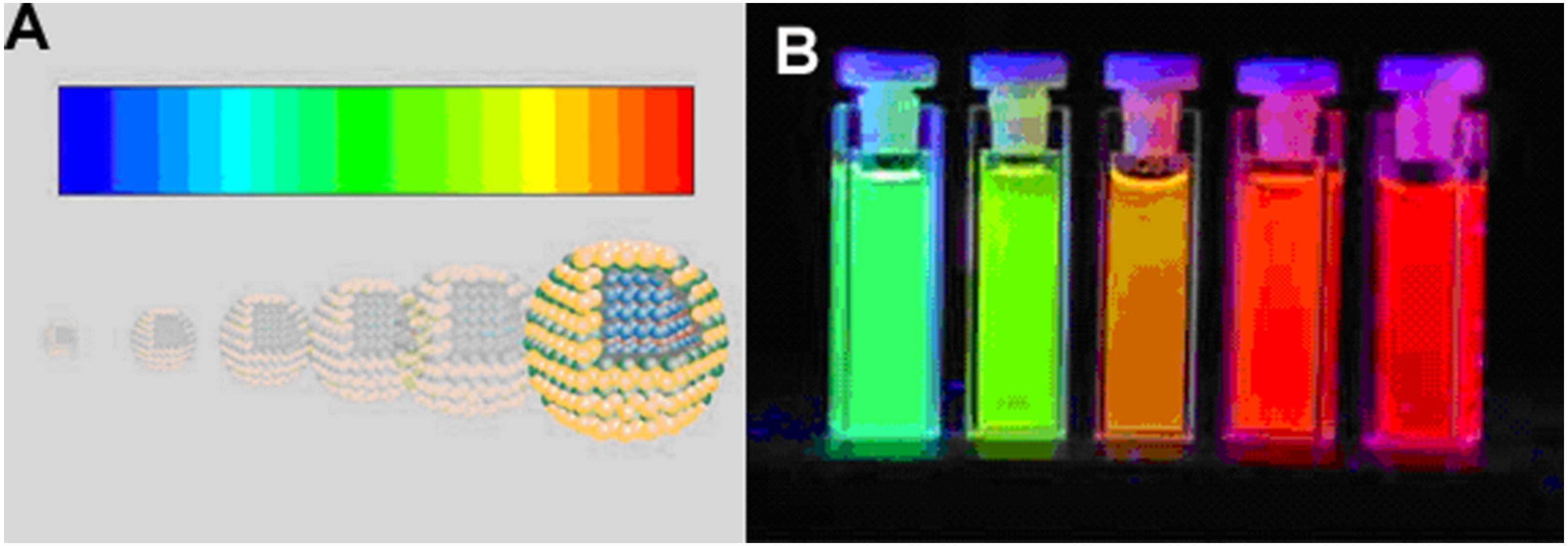
In zero dimensions the energy states are sharp levels corresponding to the eigenstates of the system.

Development of electronic properties as a function of cluster size



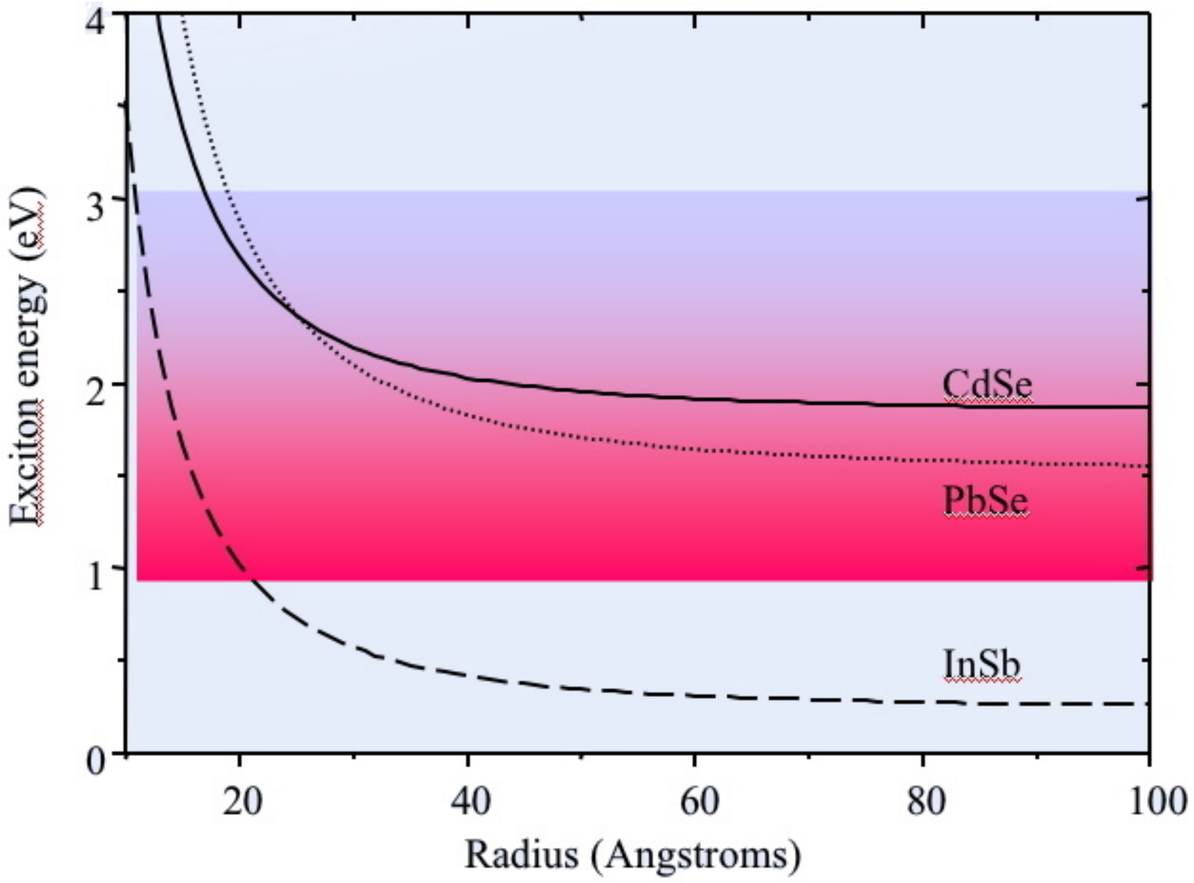
Each band has a width that reflects the interaction between atoms, with a bandgap between the conduction and the valence bands that reflects the original separation of the bonding ad antibonding states.

0D Electronic Structures: Quantum Dots



Light incident on a semiconductor at an energy greater than the bandgap forms an exciton, i.e. an electron-hole quasiparticle, representing a bound state.

Exciton Energy



Nanostructure fabrications

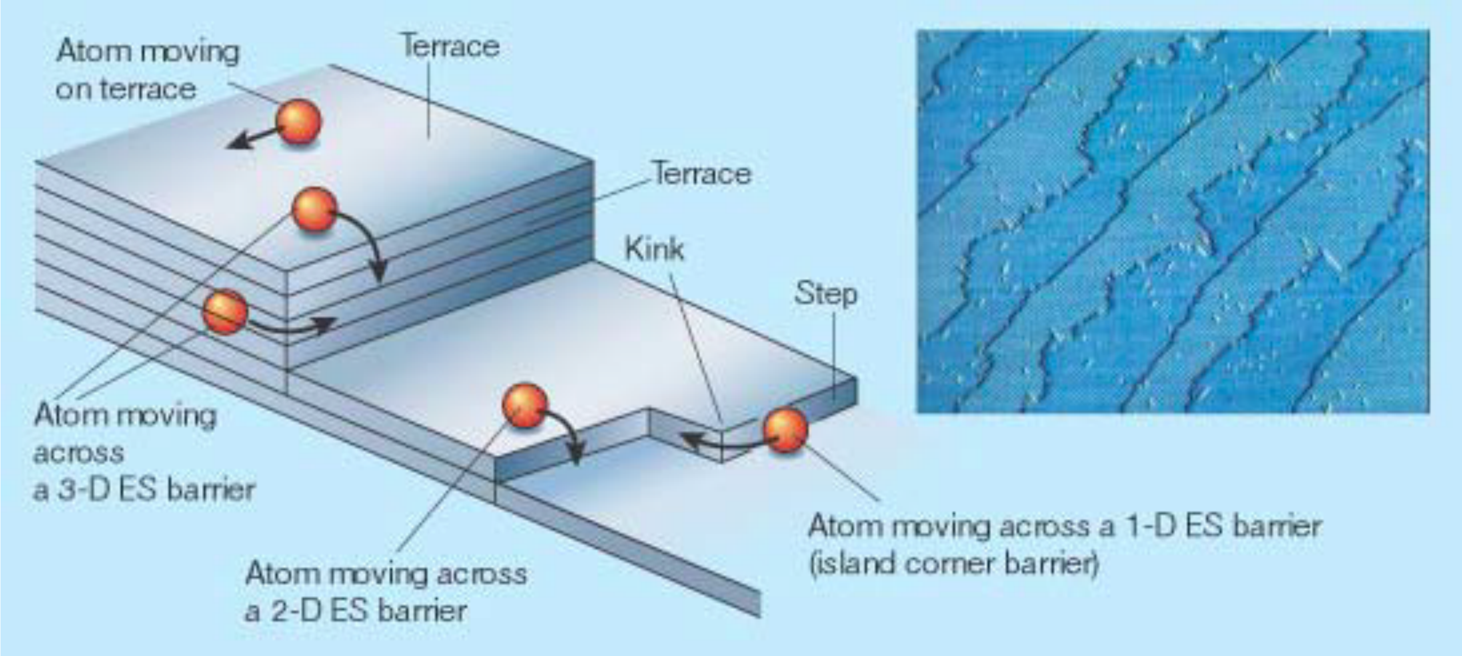
- Bottom-up approach: Growth and self-assembly to build nanostructures from atomic or molecular precursors.
- Top-down approach: Lithographic patterning to structure macroscopic materials at the nanoscale.

Epitaxial Growth

Epitaxial films take on a lattice structure and orientation identical to those of the substrate.

- **Homoepitaxy:** a crystalline film is grown on a substrate or film of the same material.
- **Heteroepitaxy:** a crystalline film grows on a crystalline substrate or film of a different material.

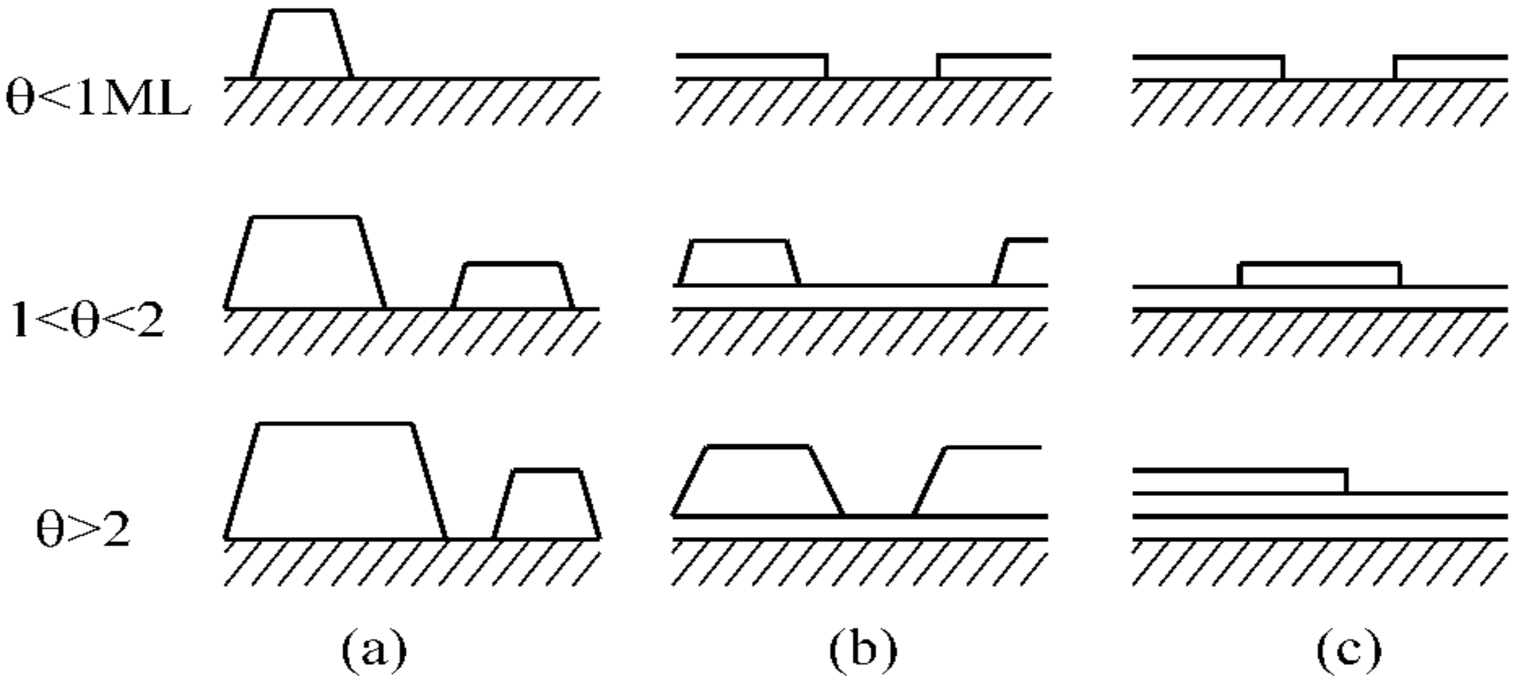
Atomistic Models for Crystalline Surfaces



Terrace Step Kink (TSK) model

Phase growth or transition simply involves the ***bond forming*** and ***bond breaking***

Growth modes



Island

Volmer-Weber

$\gamma_s < \gamma_f + \gamma_i$

Layer + Island

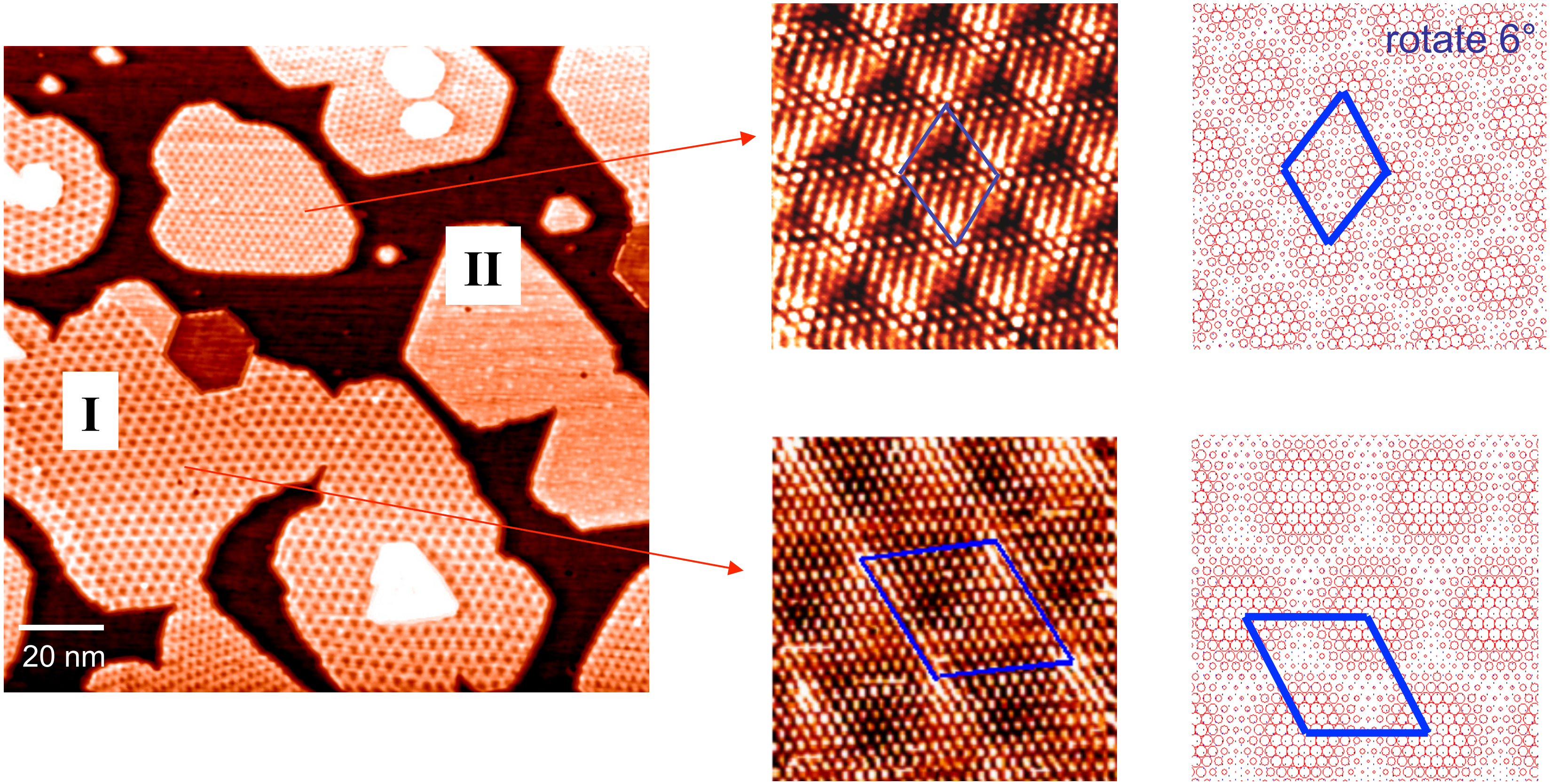
Stranski-Krastanov

Layer

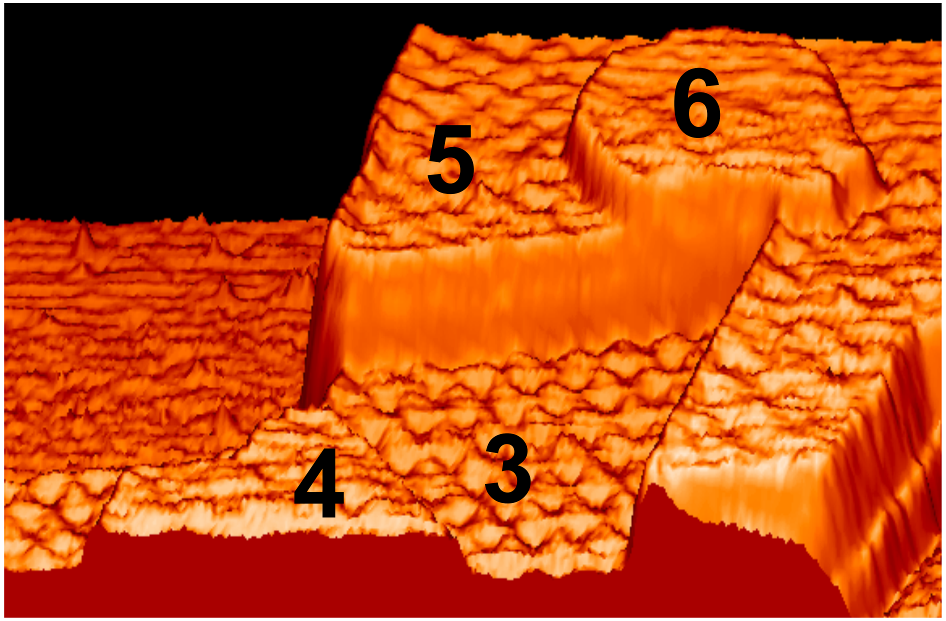
Frank-VdM

$\gamma_s \geq \gamma_f + \gamma_i$

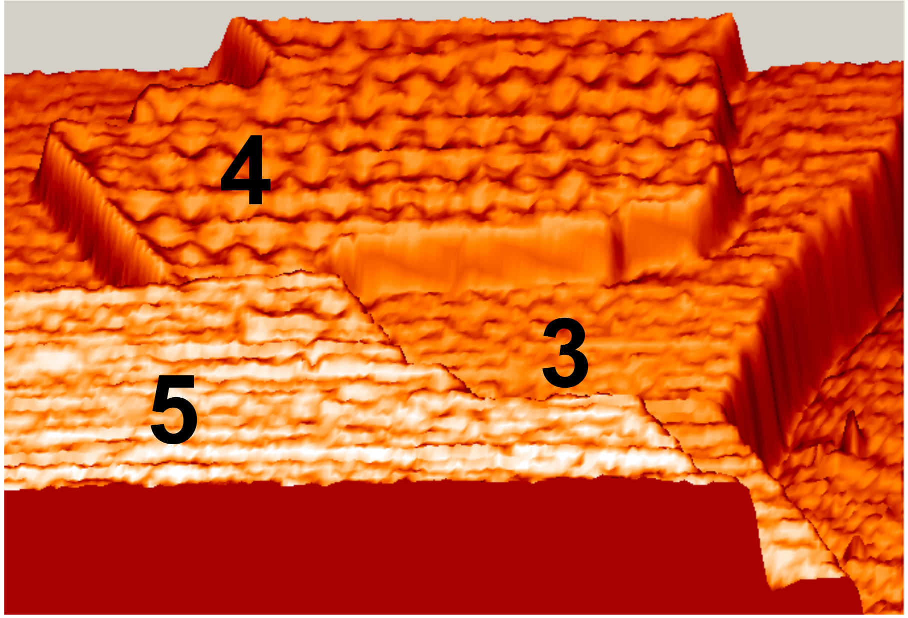
Superstructures of 2D islands



Characteristics of Pb island--- oscillatory and complementary contrast



Type I



Type II

Nanowire preparations

- Specific substrate crystallographic structures.
- Catalytic growth by a liquid droplet in vapor-liquid-solid process.
- Template: Anodic aluminum oxides.
- Self-assembly.
- Lithography.

Techniques for making nanowires

- **Spontaneous growth:**
  - Evaporation condensation
  - Dissolution condensation
  - Vapor-Liquid-Solid growth (VLS)
  - Stress induced re-crystallization
- **Template-based synthesis:**
  - Electrochemical deposition
  - Electrophoretic deposition
  - Colloid dispersion, melt, or solution filling
  - Conversion with chemical reaction
- **Electro-spinning**
- **Lithography** *(top-down)*

General characters for spontaneous growth

- Anisotropic growth is required
- Crystal growth proceeds along one direction, where as there is no growth along other direction.
- Uniformly sized nanowires (i.e. the same diameter along the longitudinal direction of a given nanowire)

Vapor-Solid (VS) technique

- Nanowires and nanorods grown by this method are commonly single crystals with fewer imperfections

- The formation of nanowires or nanorods is due to the anisotropic growth.

- The general idea is that the different facets in a crystal have different growth rates

- There is no control on the direction of growth of nanowire in this method

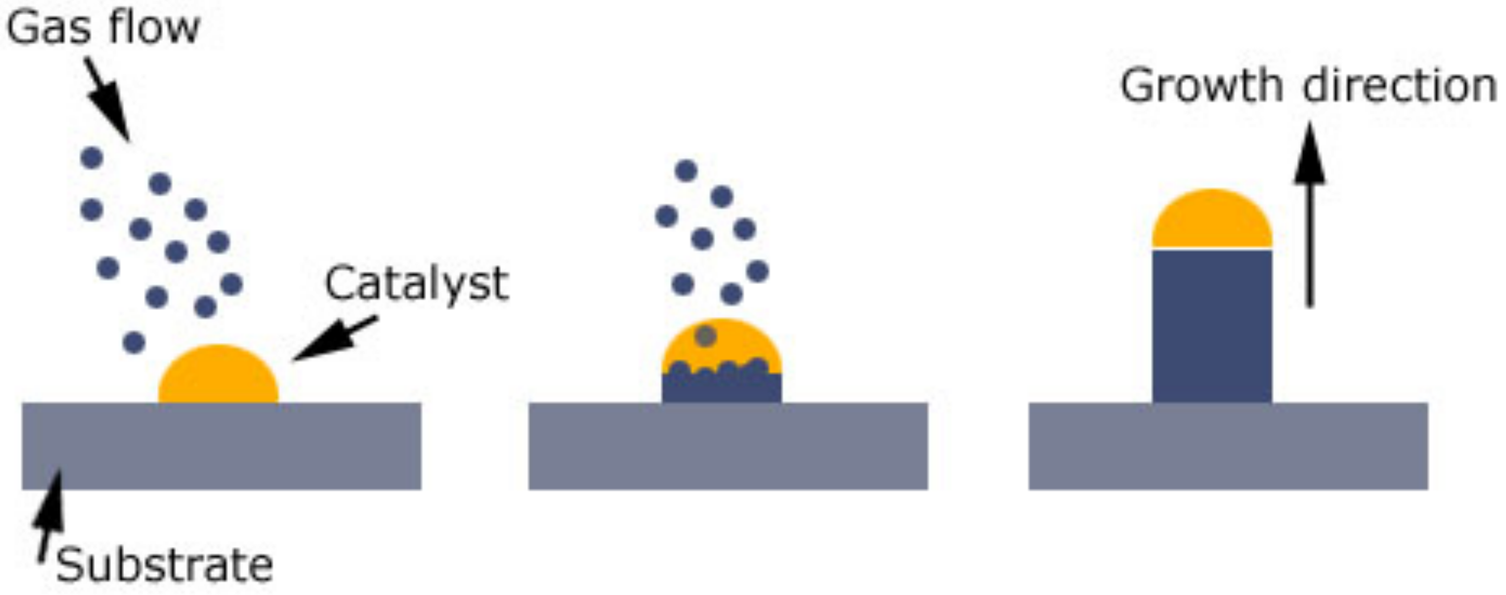
Vapor Liquid Solid Growth (VLS)

General Idea:

A second phase material, commonly referred to as ***catalyst***, is introduces to direct and confine the crystal growth on a specific orientation and within a confined area.

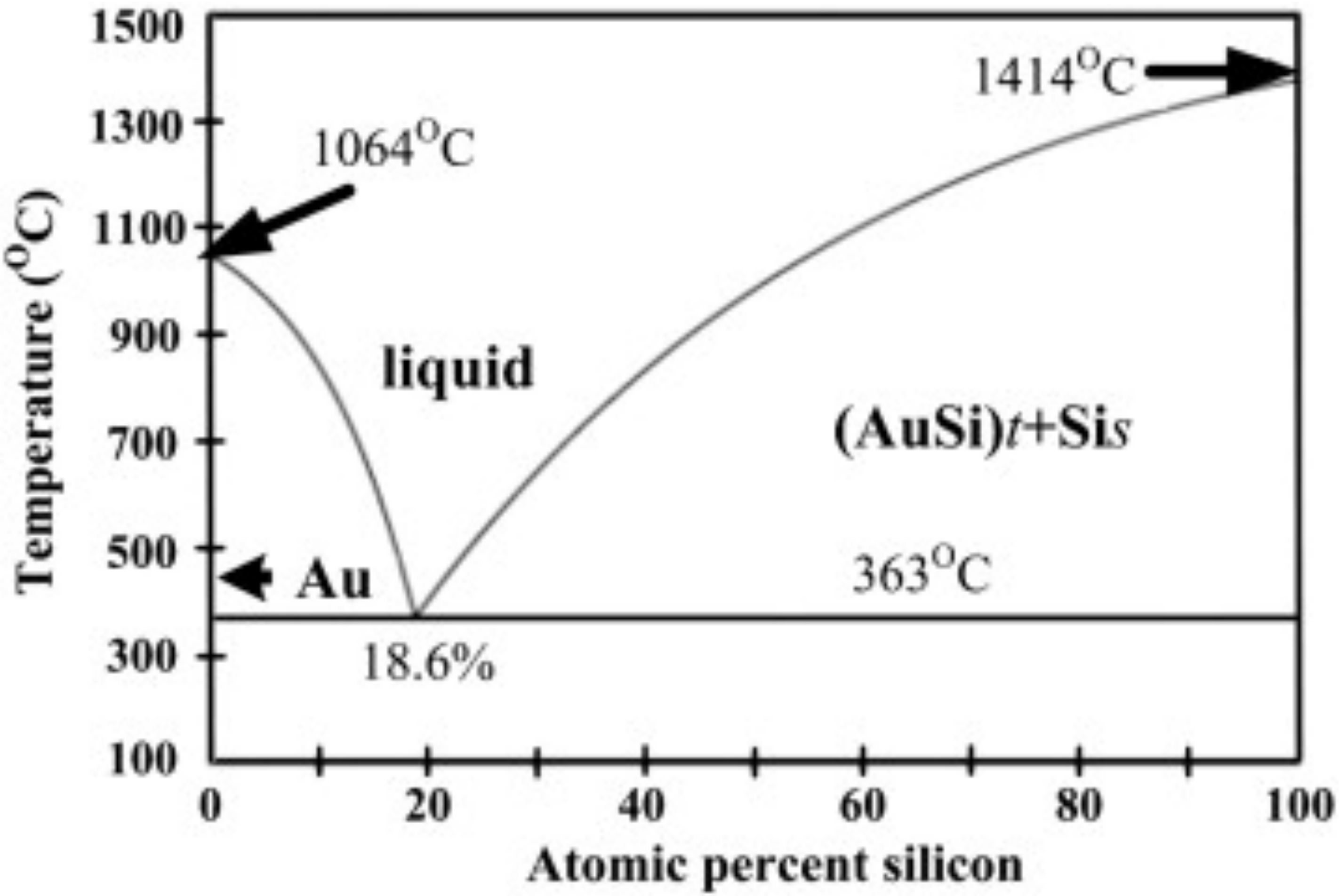
- Catalyst forms a **liquid droplet** by itself
- Acts as a trap for growth species
- The growth species is evaporated first and then diffuses and dissolves into a liquid droplet
- It precipitates at the interface between the substrate and the liquid

VLS Growth

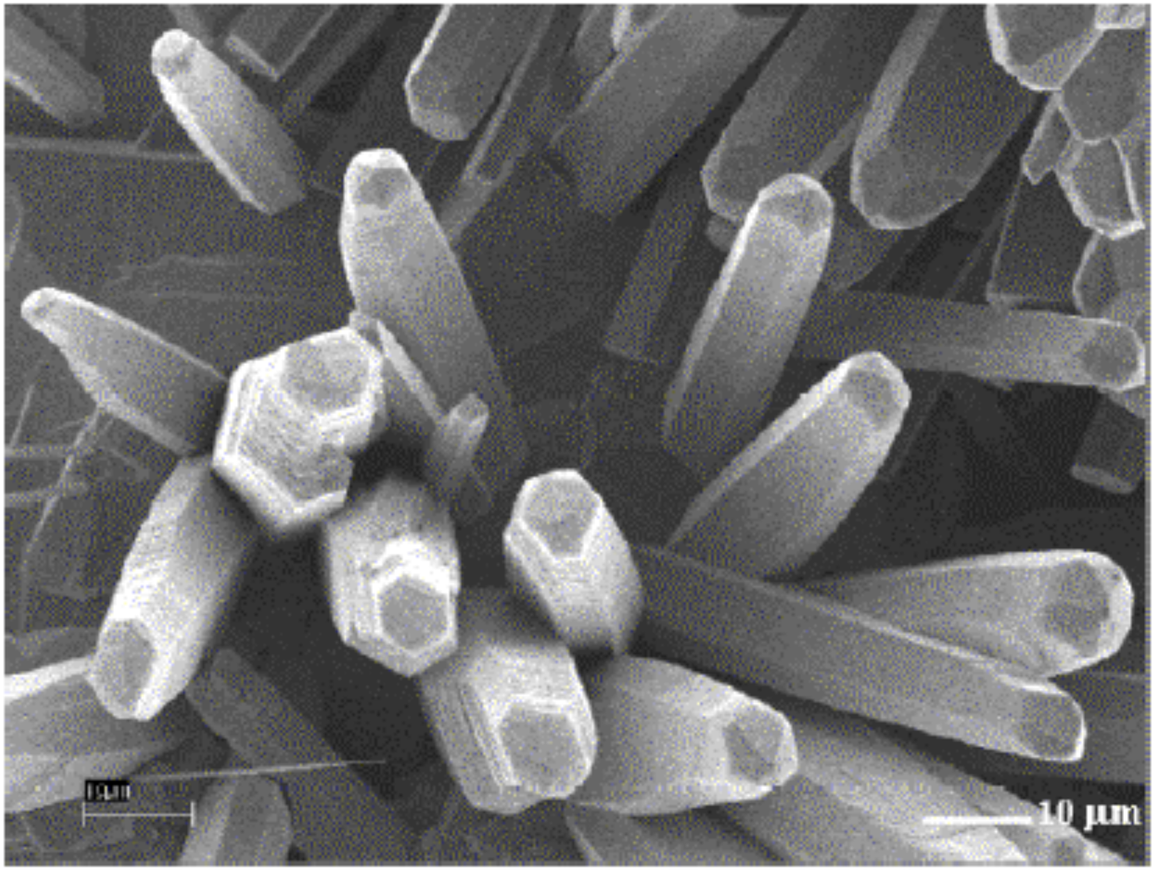


Growth species in the catalyst droplets subsequently precipitates at the growth surface resulting in the ***one-directional growth***

Phase diagram of AuSi

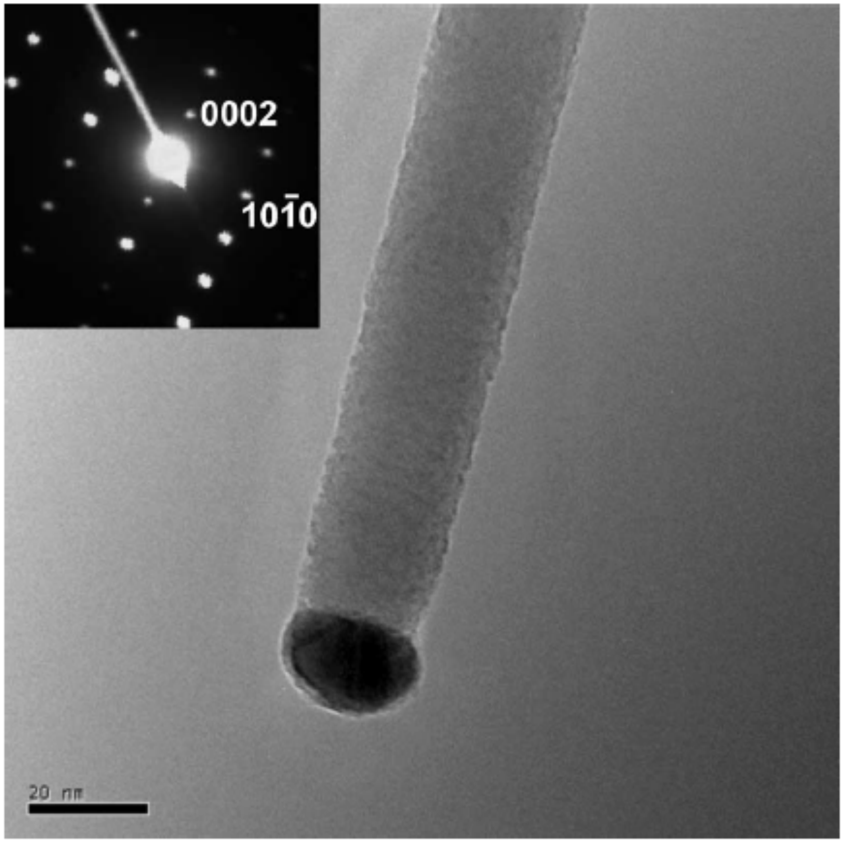


VLS Growth



"A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires," **Shashank Sharma, and Mahendra K. Sunkara**

VLS Growth



TEM and selected area diffraction image of a single crystal ZnO nanorod.(~20 nm width).

"ZnO nanowire growth and devices," **Y.W. Heoa, D.P. Nortona, et al.**

Laser Assisted Catalytic growth

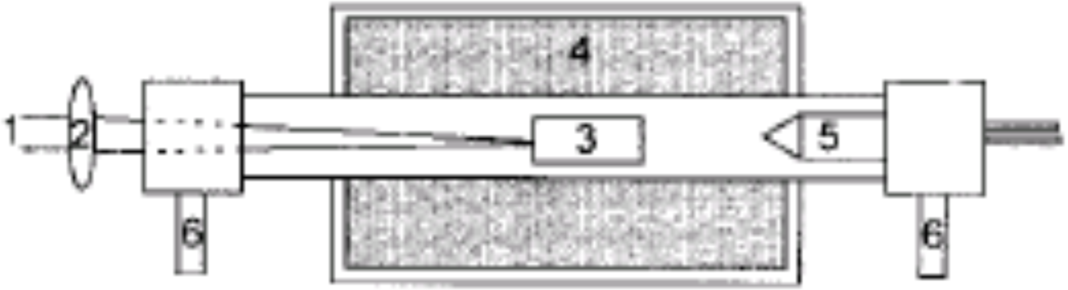


Fig. 2 Schematic of a nanowire growth set up using a combination of laser ablation and vapor-liquid- solid scheme

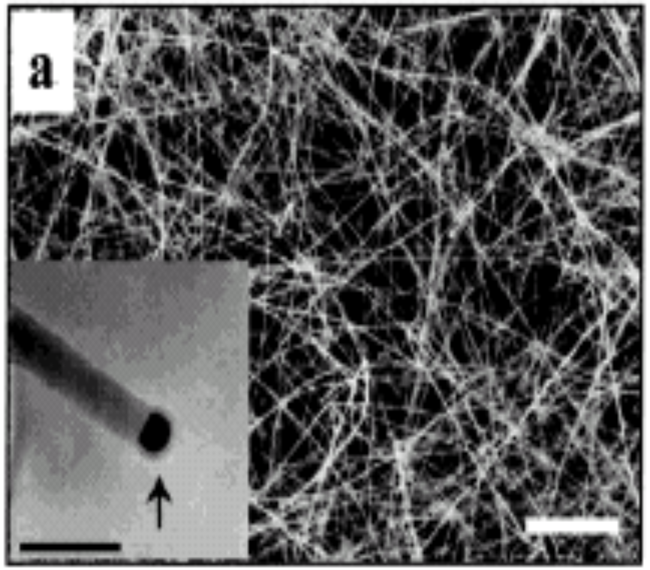
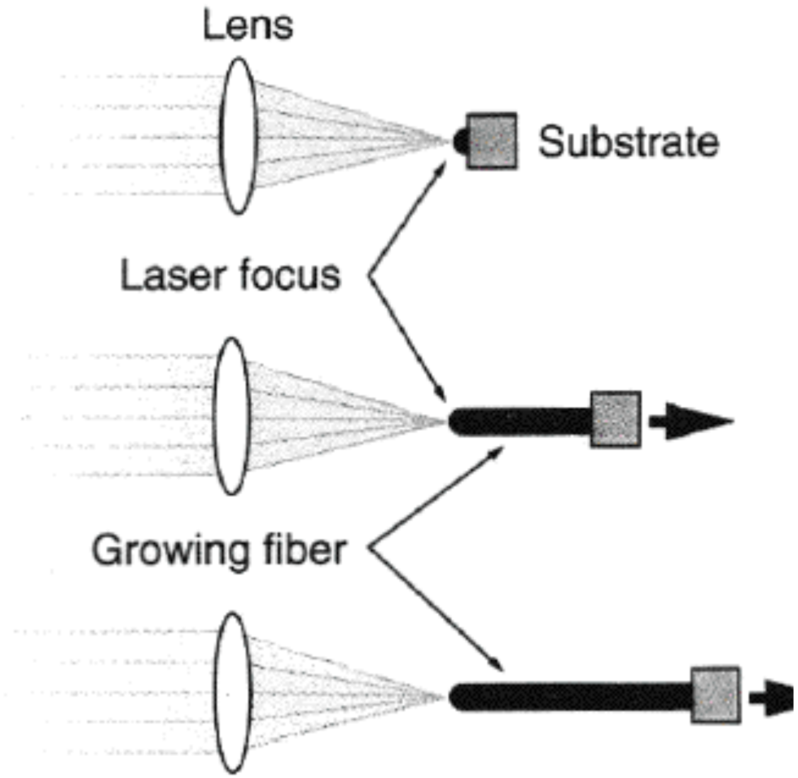


Fig.1 Semiconductor (GaAs) nanowires grown using laser assisted catalytic growth [1ref]. The scale bar corresponds to 50 nm.

Chemical vapor deposition (CVD) : L-CVD

- The L-CVD method is able to fabricate continuous thin rods and fibres by pulling the substrate away from the stationary laser focus at the linear growth speed of the material while keeping the laser focus on the rod tip, as shown in the Figure . LCVD was first demonstrated for carbon and silicon rods. However, fibers were grown from other substrates including silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminium. The L-CVD process can operate at low and high chamber pressures. The growth rate is normally less than 100 μm/s at low chamber pressure ($<<1$ *bar*). At high chamber pressure (>1 *bar*), high growth rate (>1.1 *mm/s*) has been achieved for small-diameter (< 20 μm) amorphous boron fibers.



Nanoparticle preparation

- Vapor condensation: Metallic and metal oxide ceramic nanoparticles. Inert gas condensation, thin film deposition (sputtering, thermal evaporation, chemical vapor deposition etc.).
- Chemical synthesis: In a liquid medium composed of various reactants. Sol-gel, electrodeposition.
- Solid-state processes: Mechanical processes (Grinding or milling) of bulk materials.

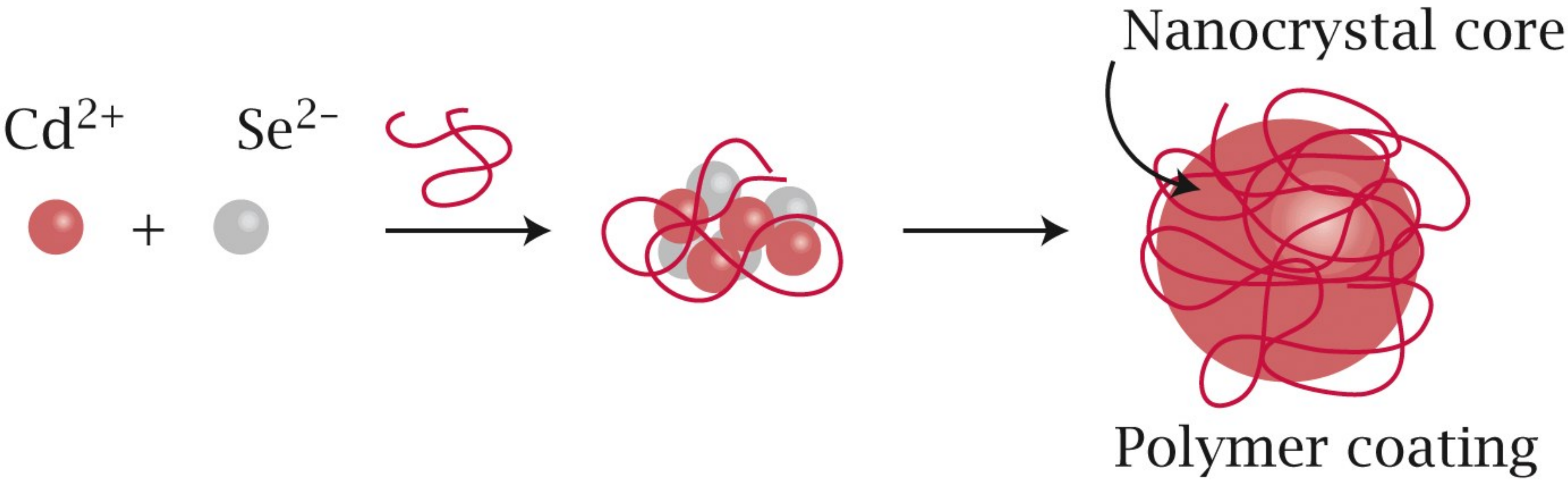


Figure 13.1 Introductory Nanoscience (© Garland Science 2012)

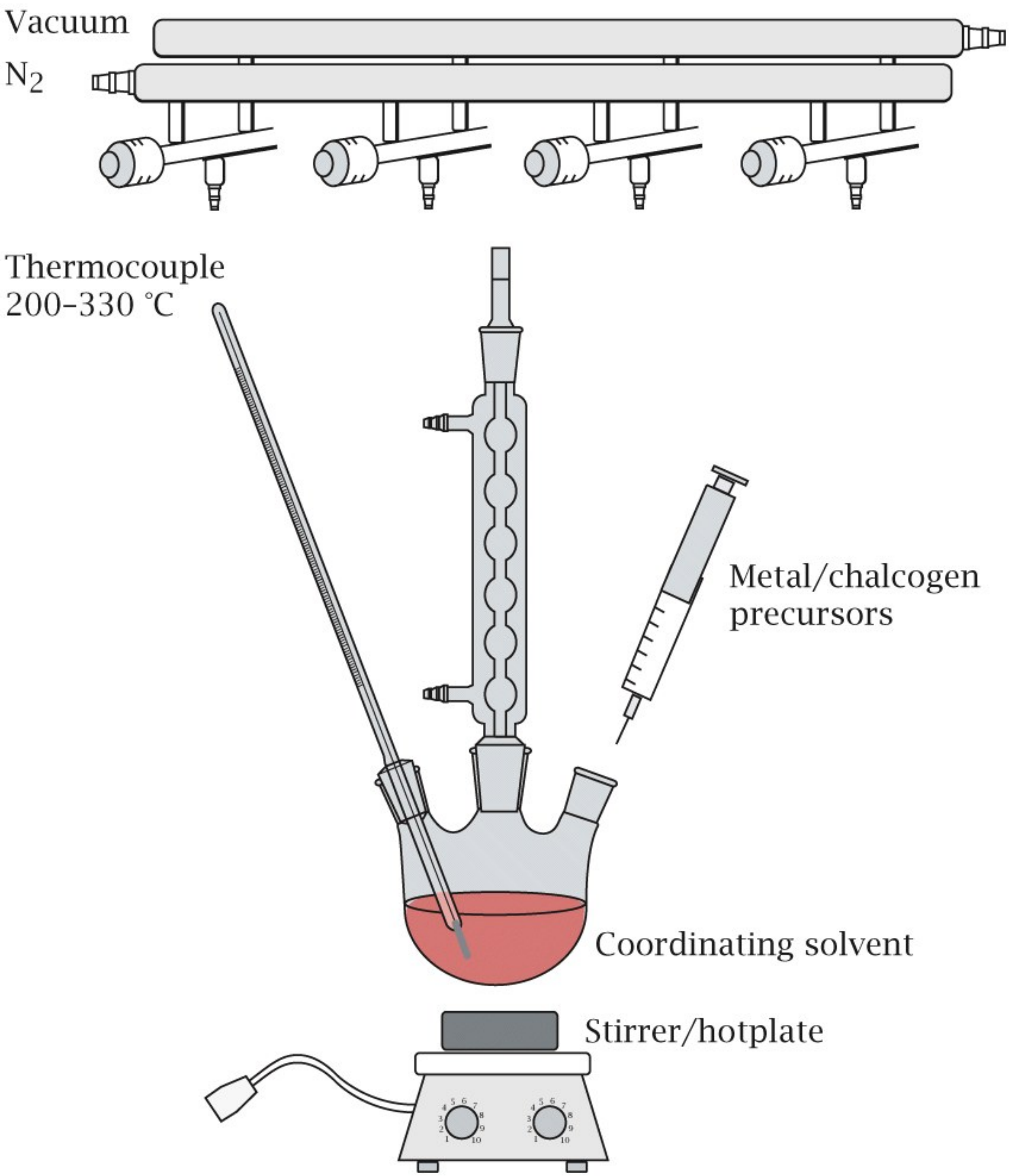


Figure 13.7 Introductory Nanoscience (© Garland Science 2012)

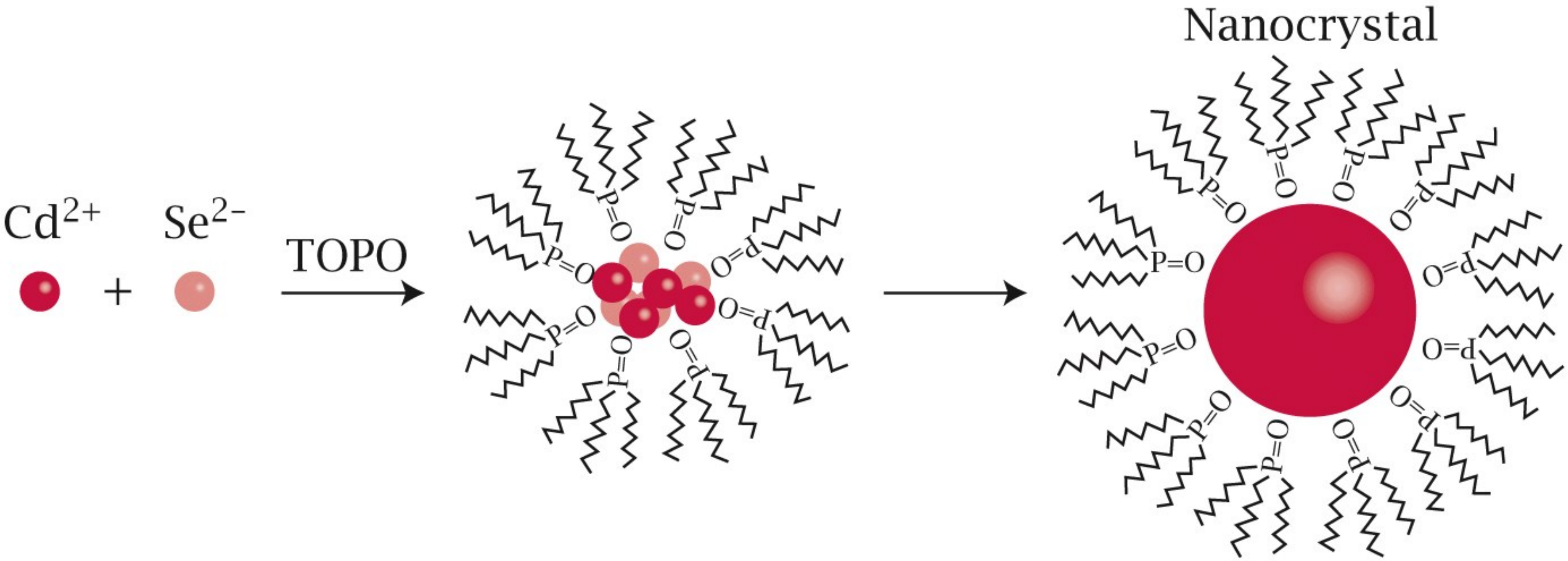


Figure 13.8 Introductory Nanoscience (© Garland Science 2012)

Surface Energy

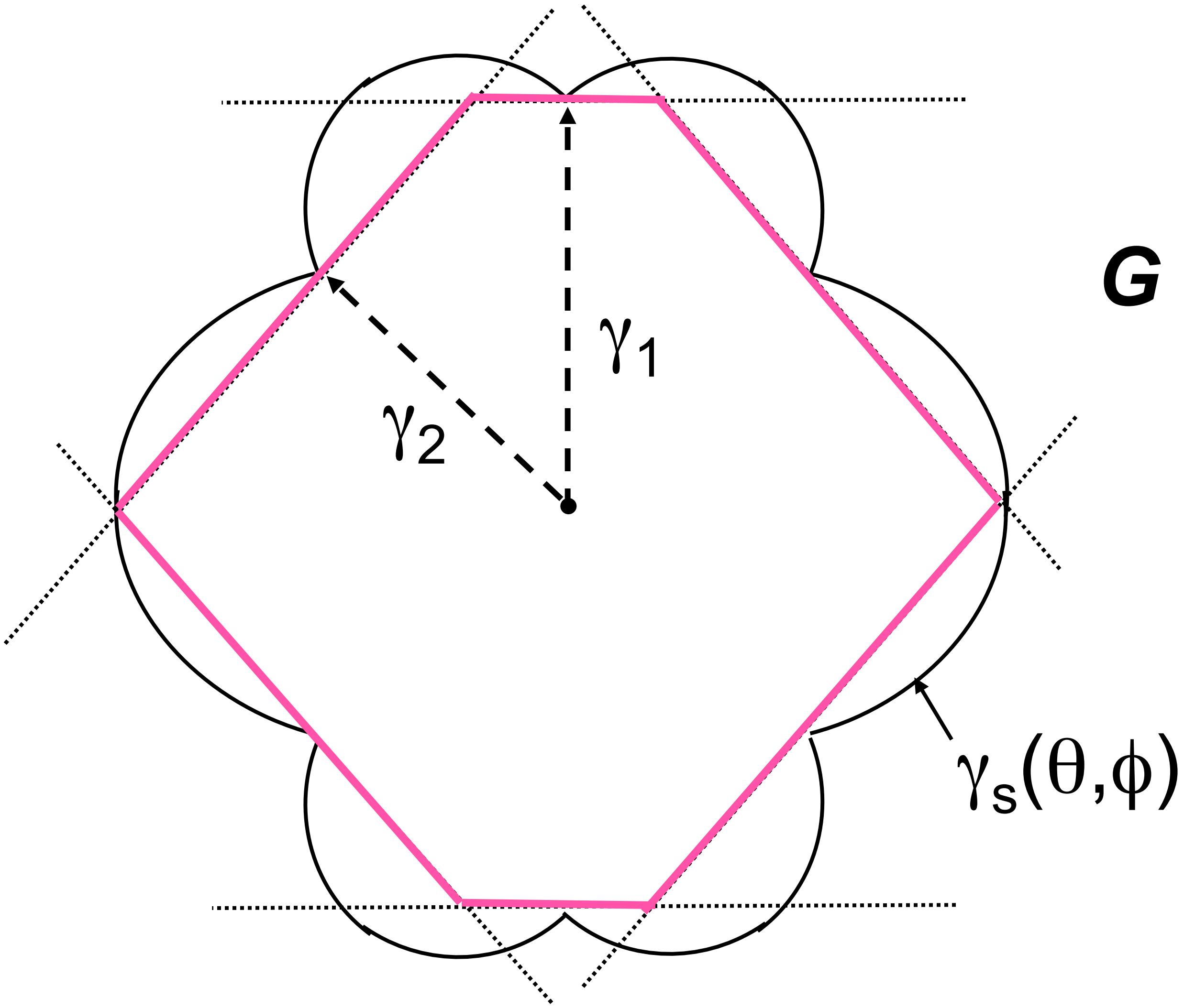
- Surface energy is given by

$$E(\Gamma) = \int_{\Gamma} \gamma \ dS$$

- Standard model for anisotropic surface free energy

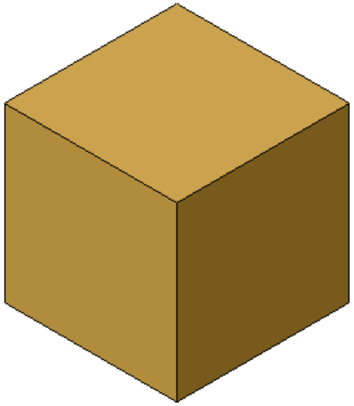
$$\gamma = \gamma_0(n)$$

Wulff construction

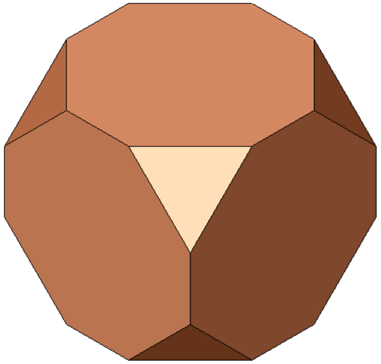


$$G = \int \gamma_s(\theta,\phi)\, dA$$

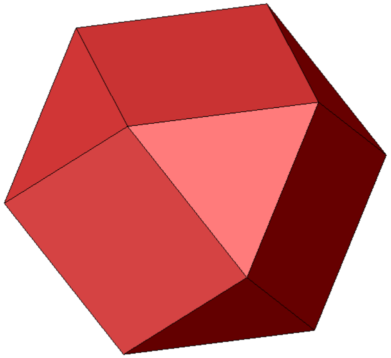
Single crystalline structures



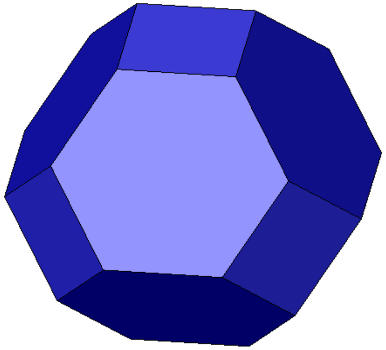
(a) cube



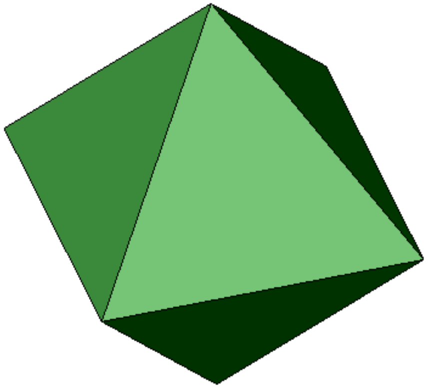
(b) truncated cube



(c) cuboctahedron

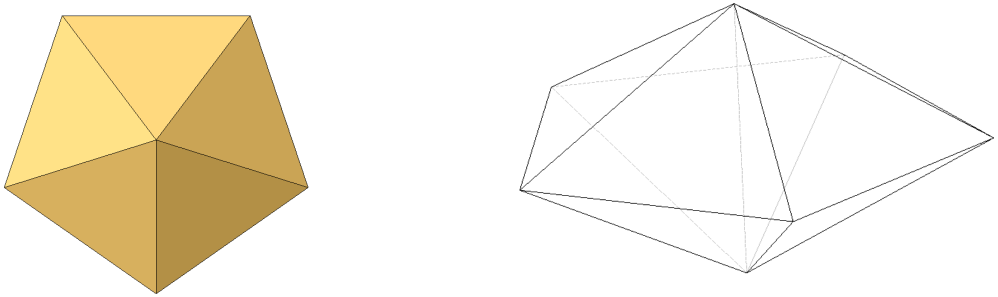


(d) truncated octahedron

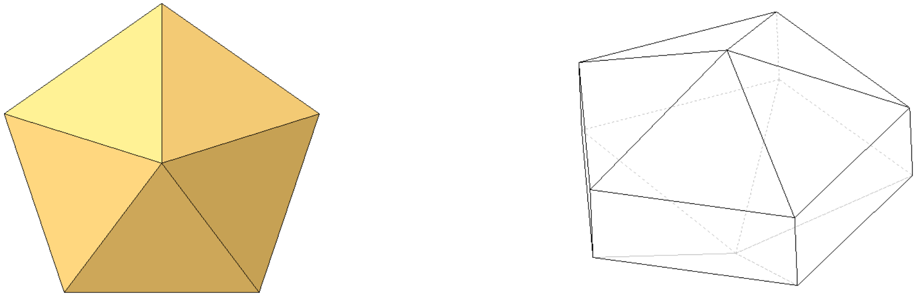


(e) octahedron

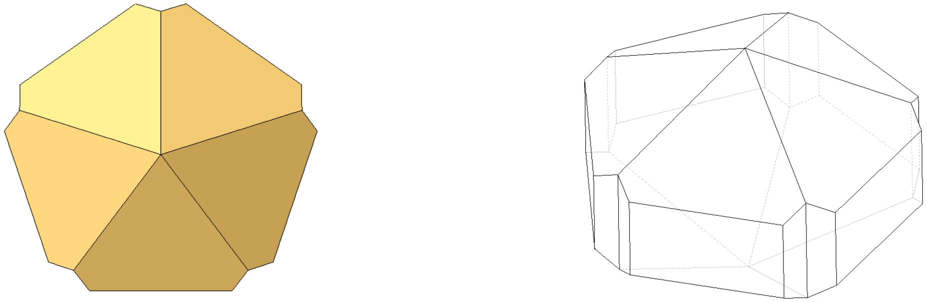
Decahedra



Classic

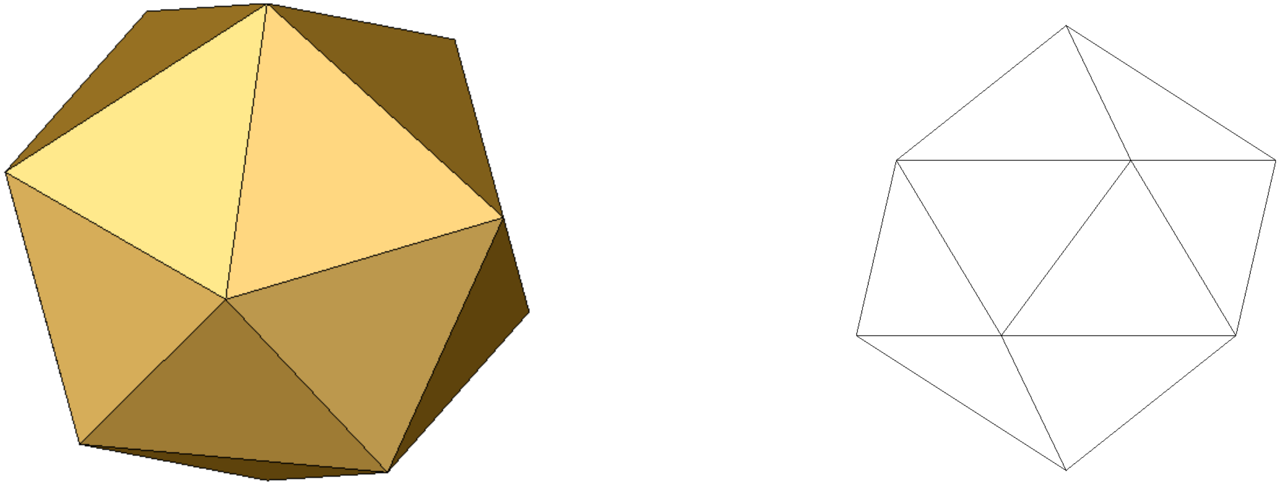


Ino's



Marks'

Icosahedra



Size-dependent structures calculated for Ni clusters:

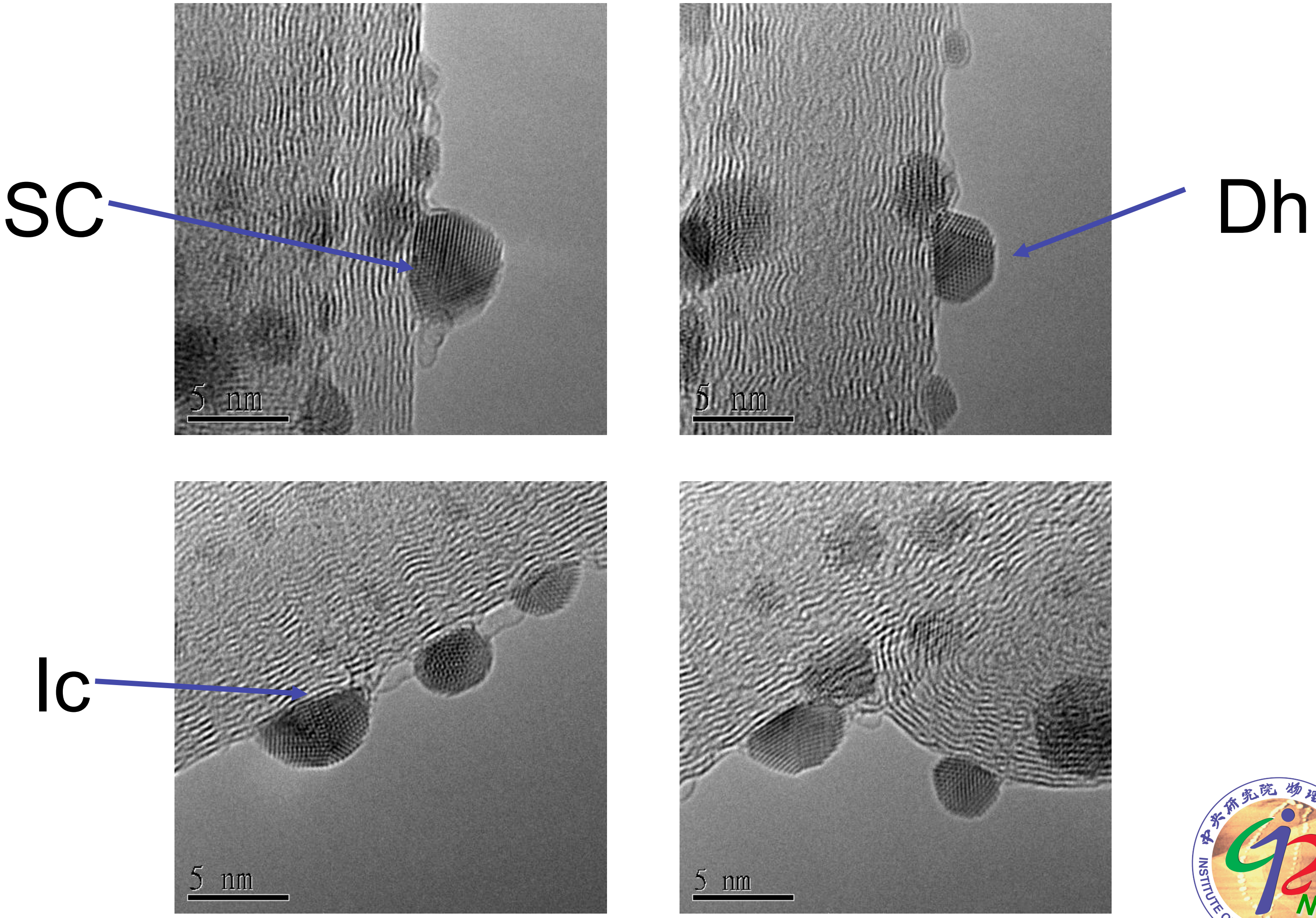
Icosahedra for 142 – 2300 atoms;

Marks’ decahedra for 2300 – 17000 atoms;

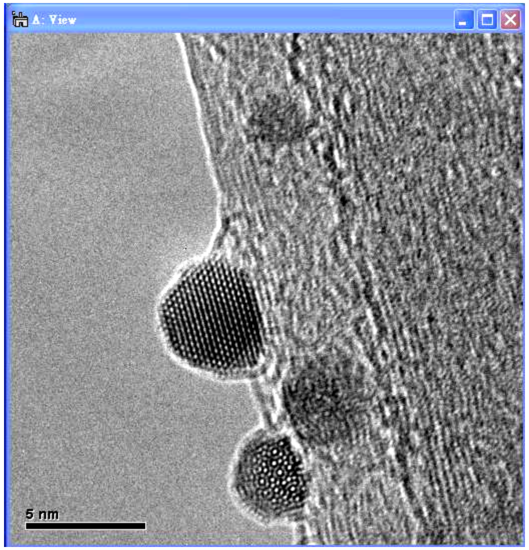
Single crystal for > 17000 atoms.

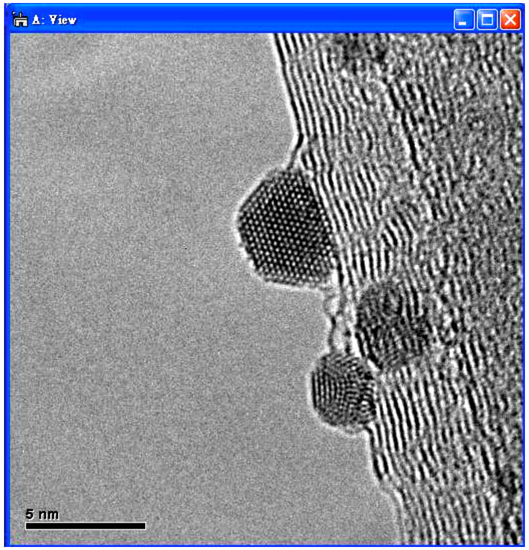
C.L. Cleveland and Uzi Landman, J. Chem. Phys. 94, 7376 (1991)

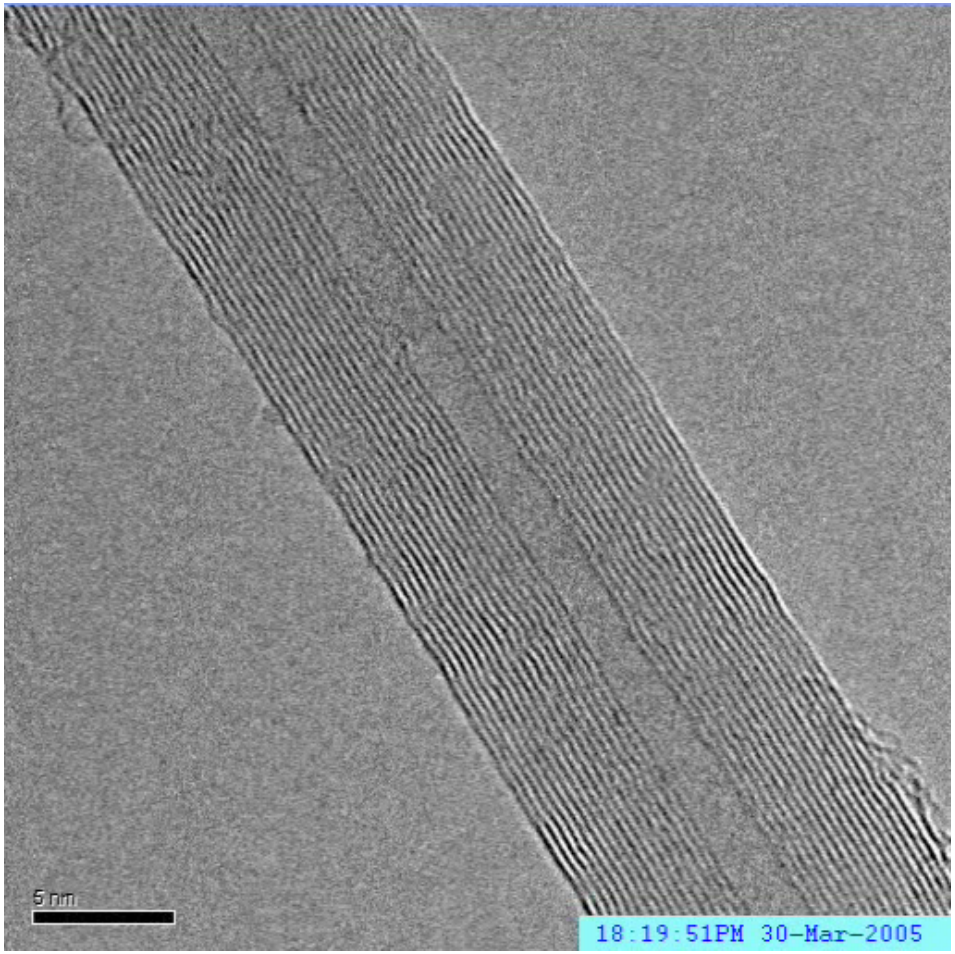
Varying structures of Ag clusters



Atomic motion and recrystallization

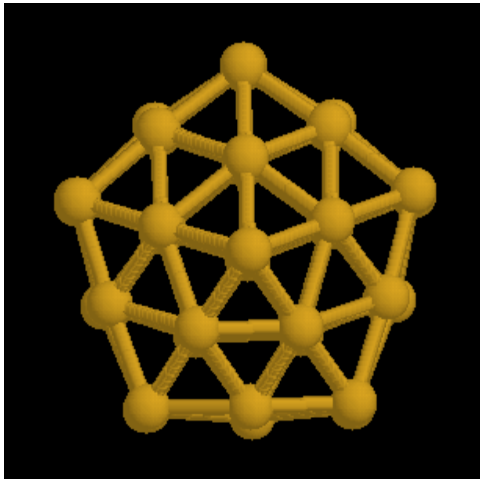




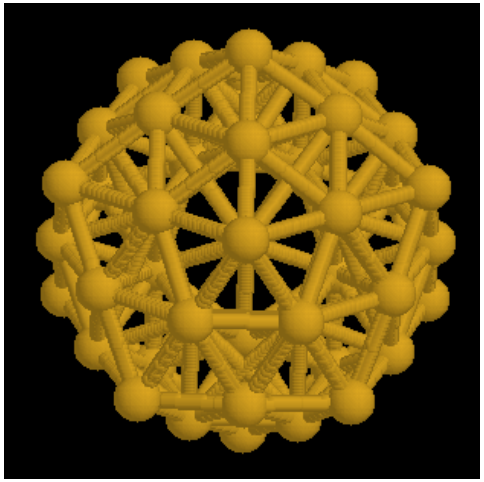


Room temperature

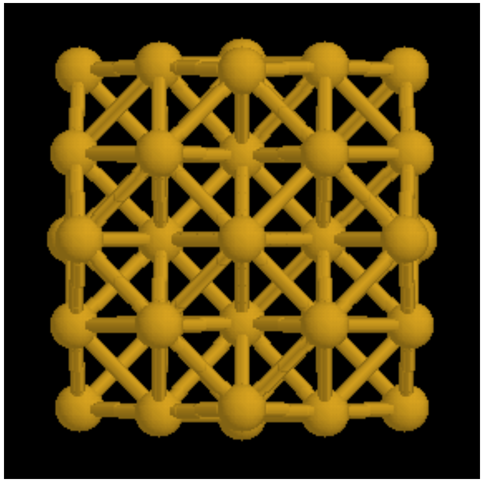
Possible shell structures of nano particles



Decahedral:
10 (111) faces +
5 (100) faces



Icosahedral:
20 (111) faces

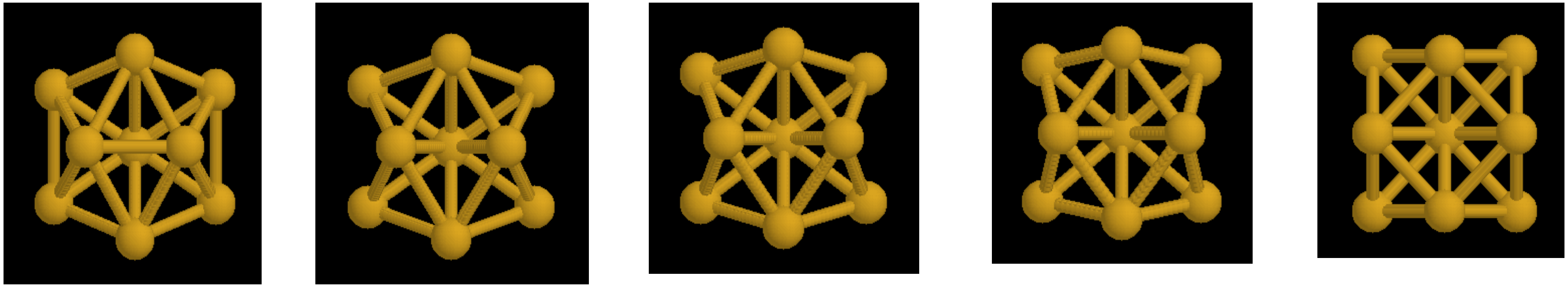


Cuboctahedral:
8 (111) faces +
6 (100) faces

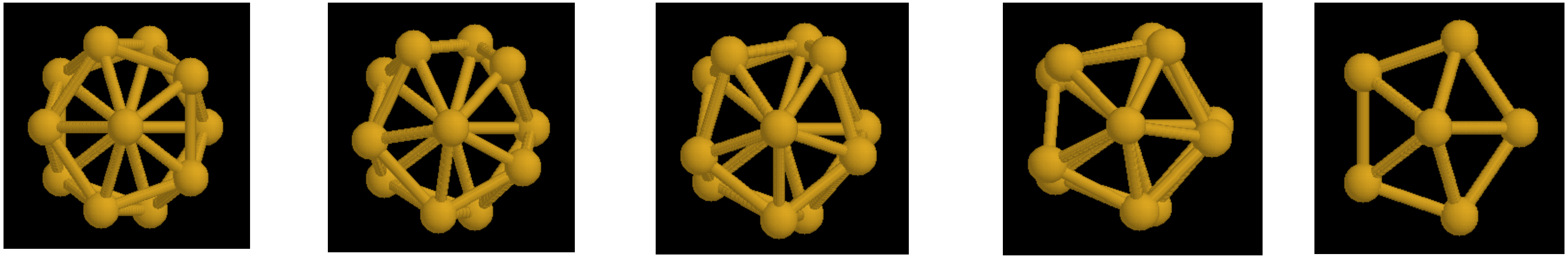
(Courtesy of C.M. Wei)

Structural phase transition

Icosahedral ⇔ Cubotohedral

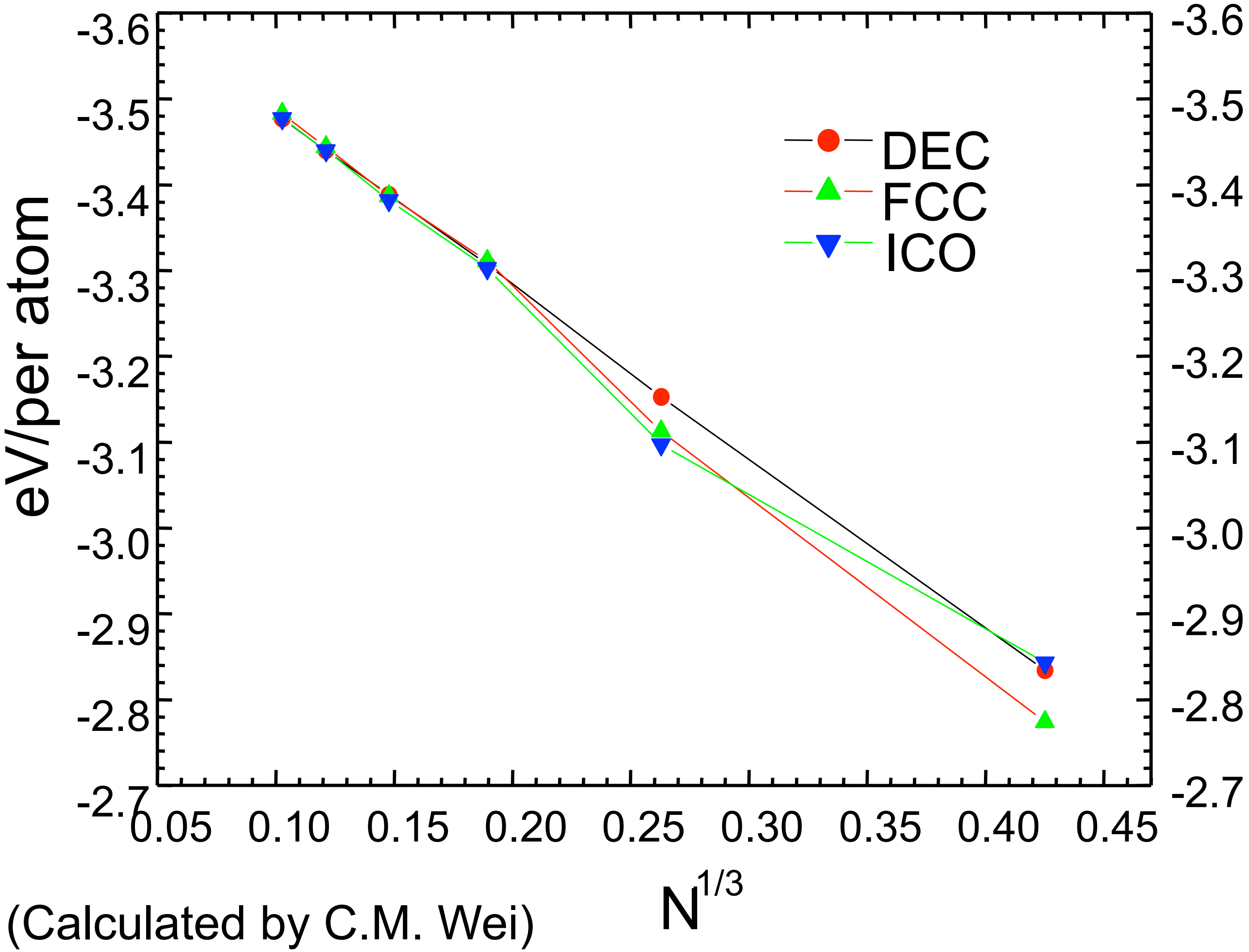


Icosahedral ⇔ Decahedral



(Courtesy of C.M. Wei)

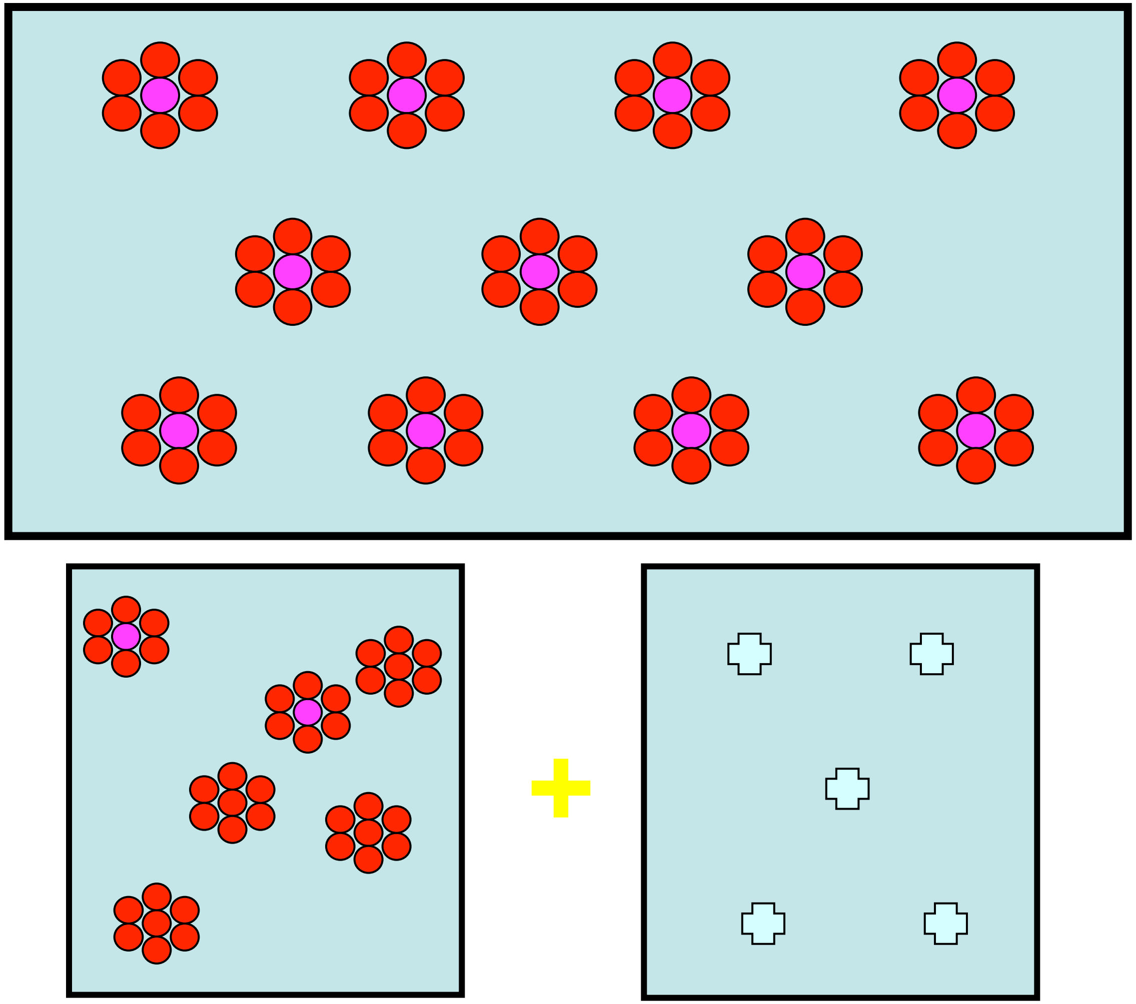
Binding energy for Al nano particles



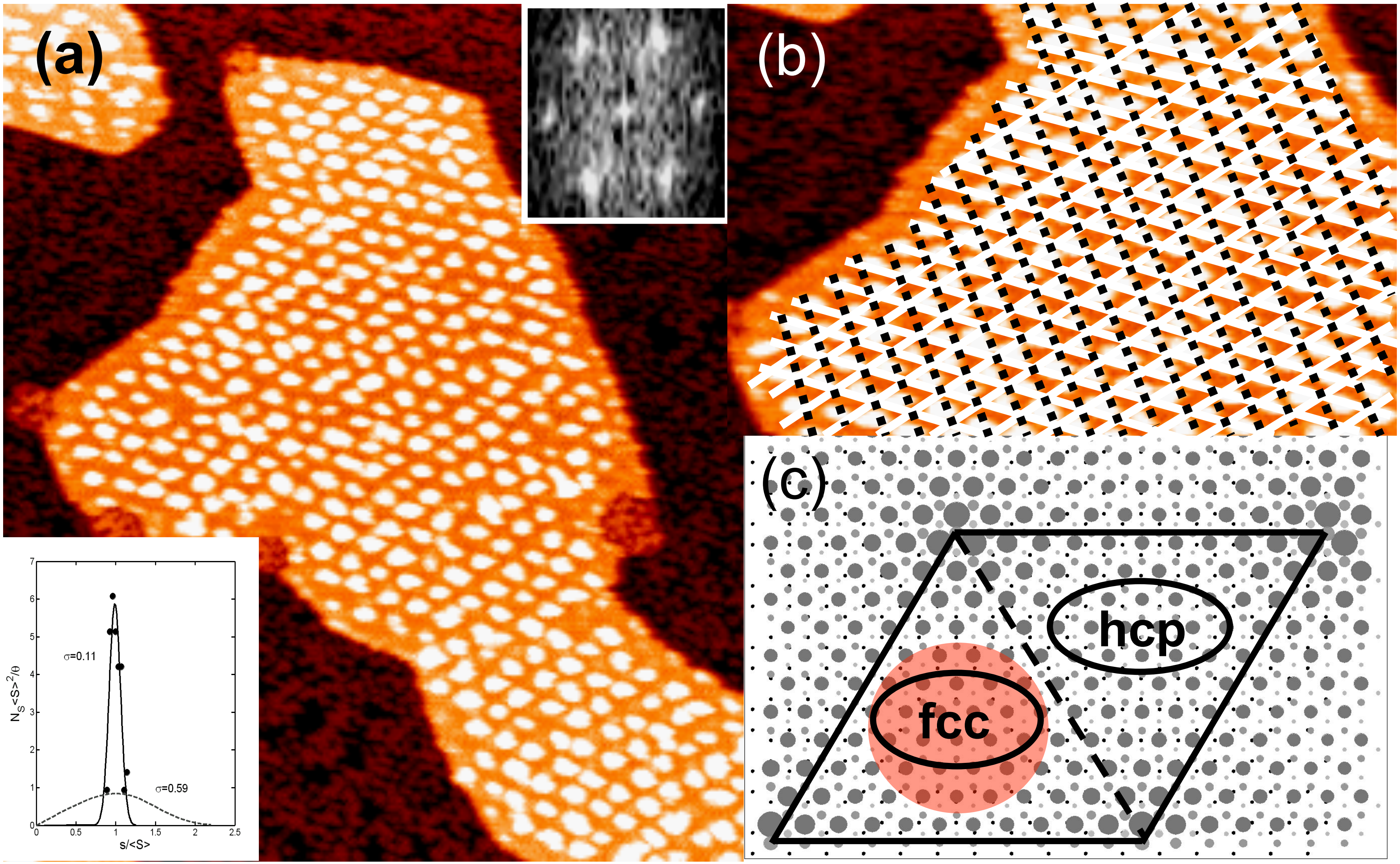
(Calculated by C.M. Wei)

Self-organized growth

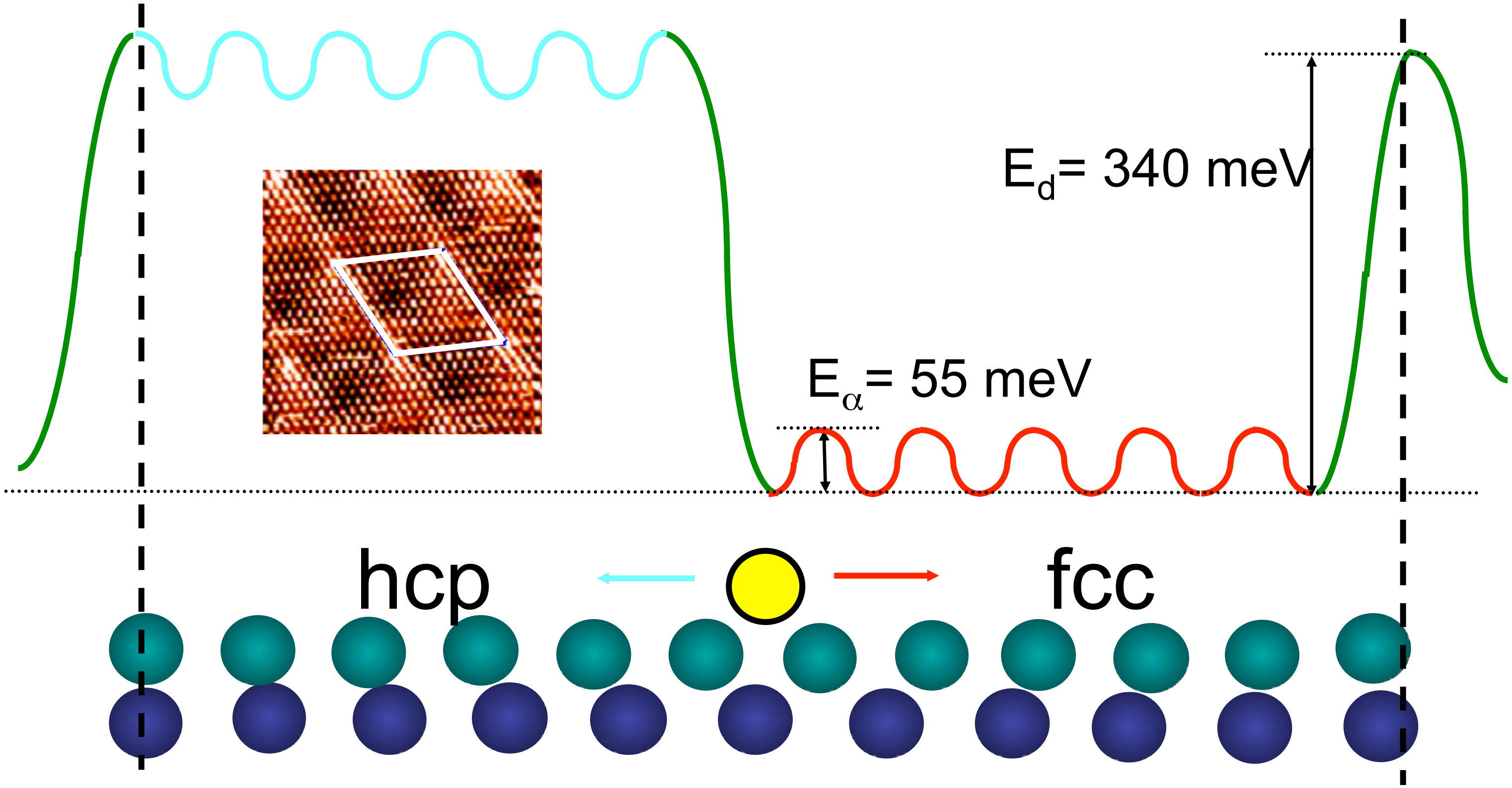
Size uniformity, Shape specification, Spatial orderliness and Functional homogeneity



Properties of nanopucks on Pb islands

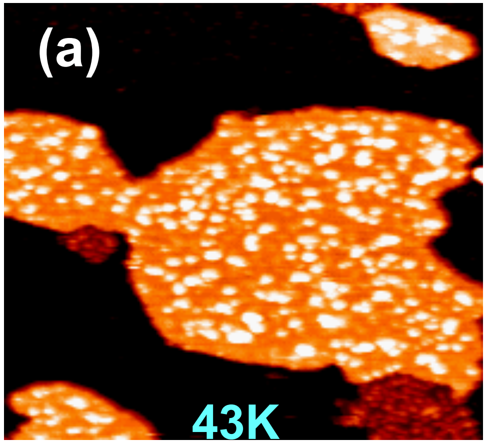


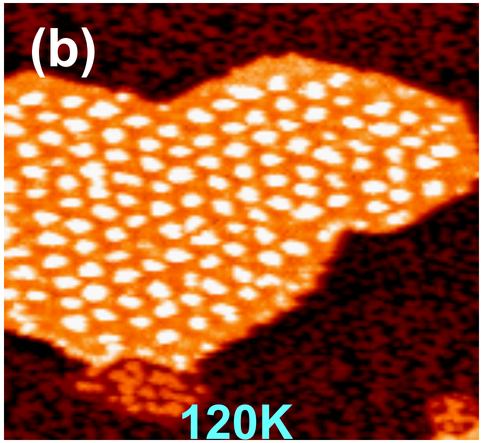
Various diffusion barriers

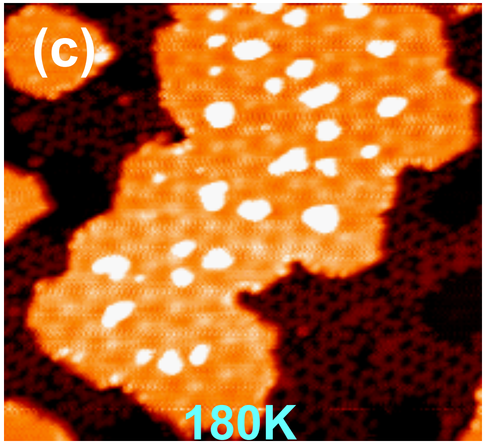


$N \propto E_d/[(i+2)kT]$, i : number of atoms in critical nucleus

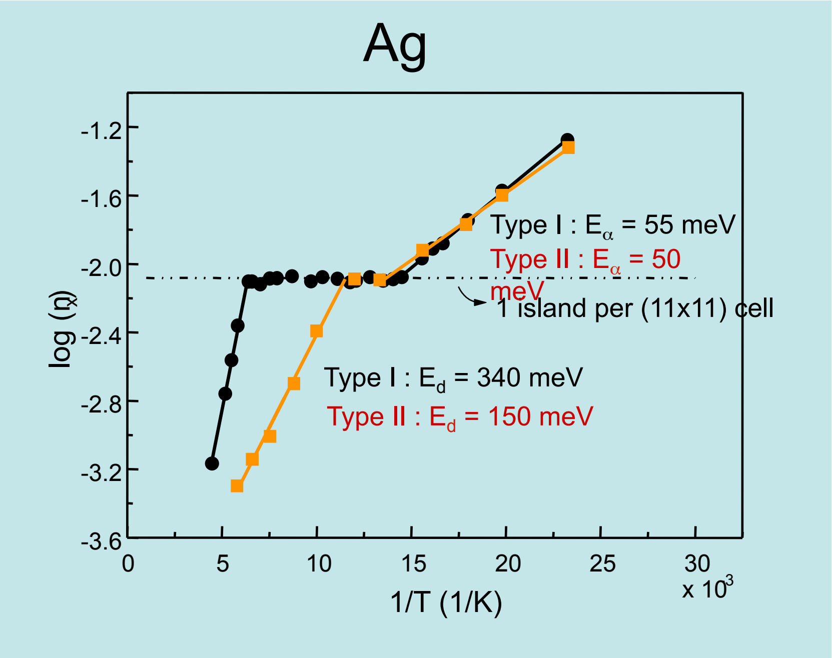
Diffusion barriers for Ag and Pb nanopucks



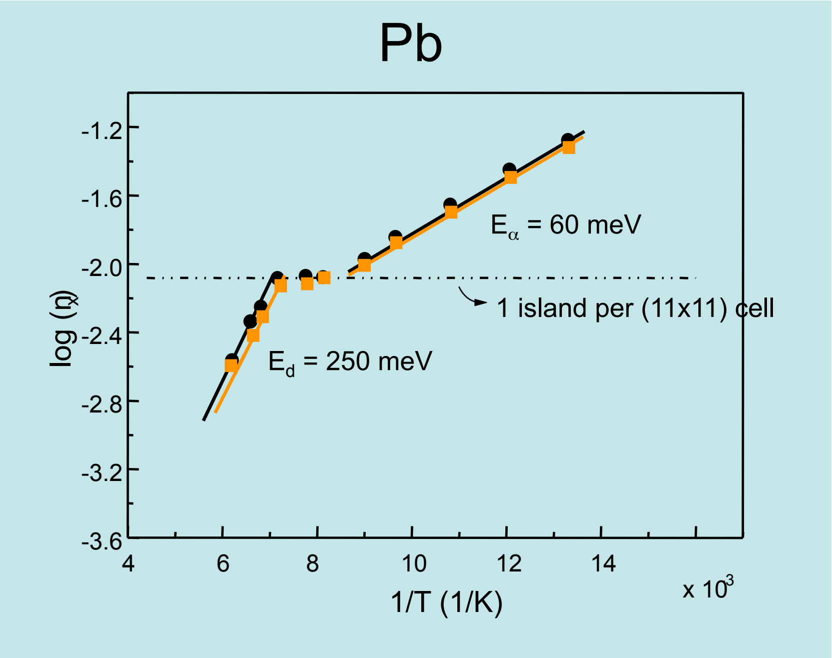




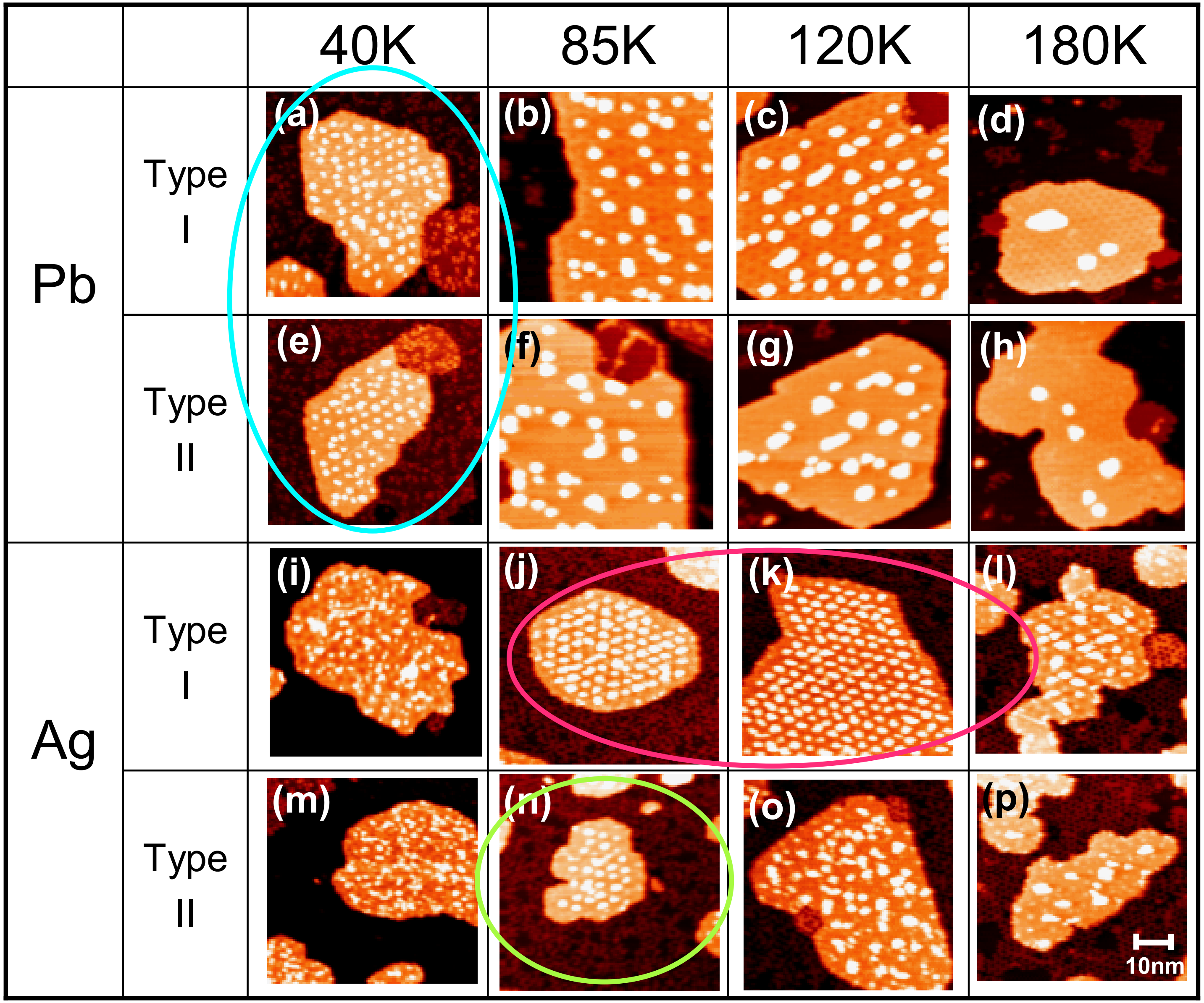
Ag



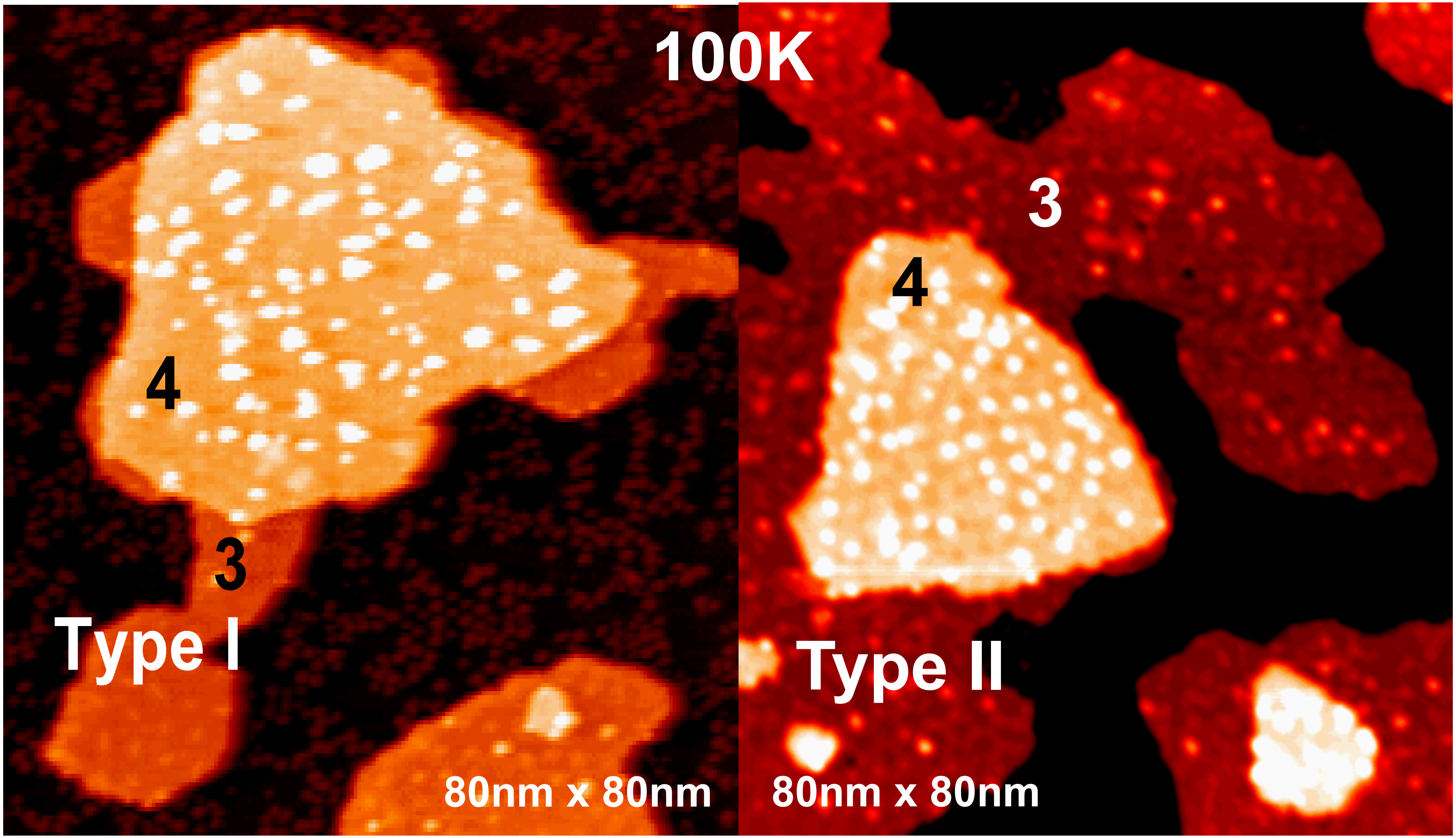
Pb



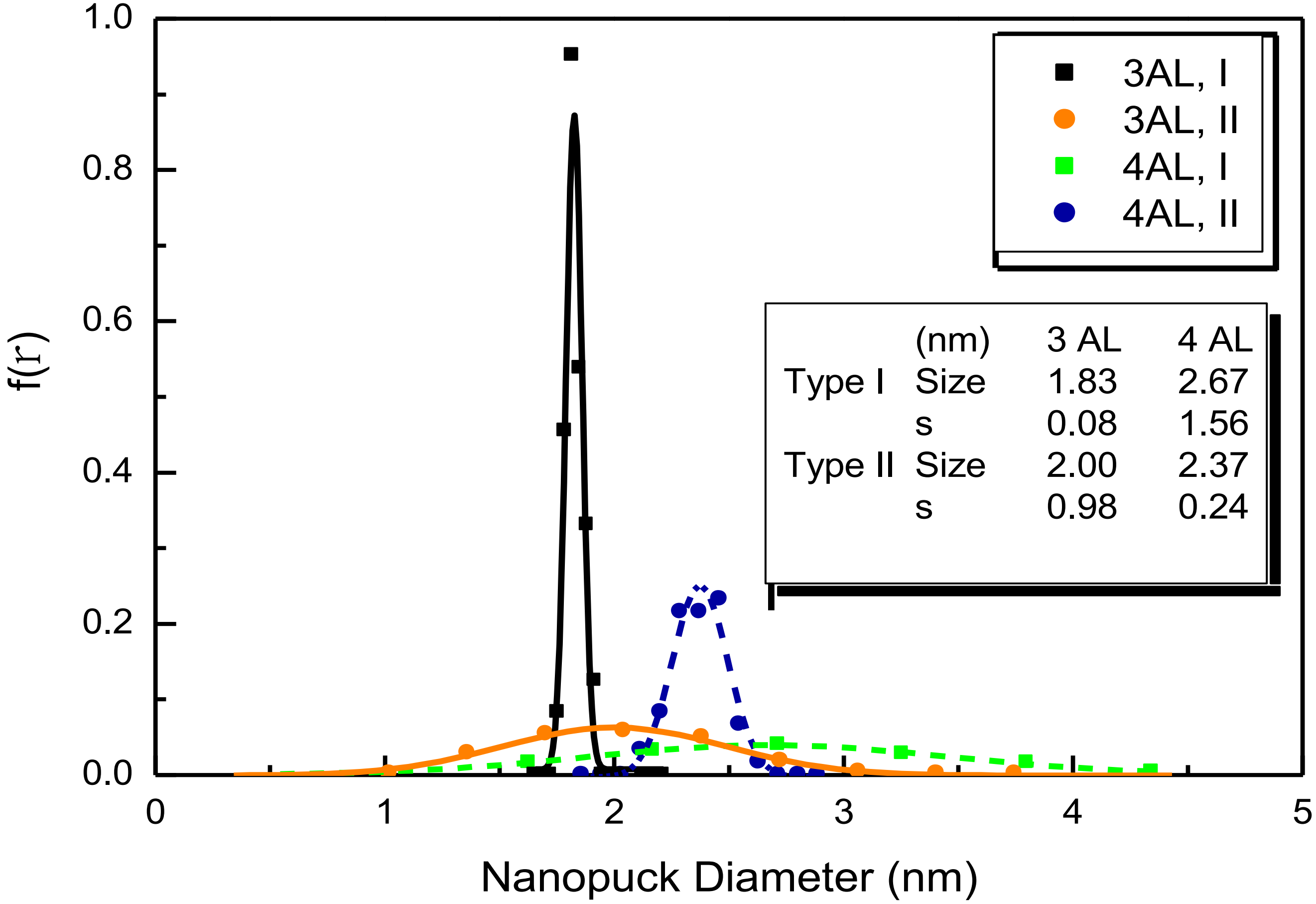
Formation of Pb and Ag nanopucks



Ag nanopucks on Pb islands of 4-layer thickness



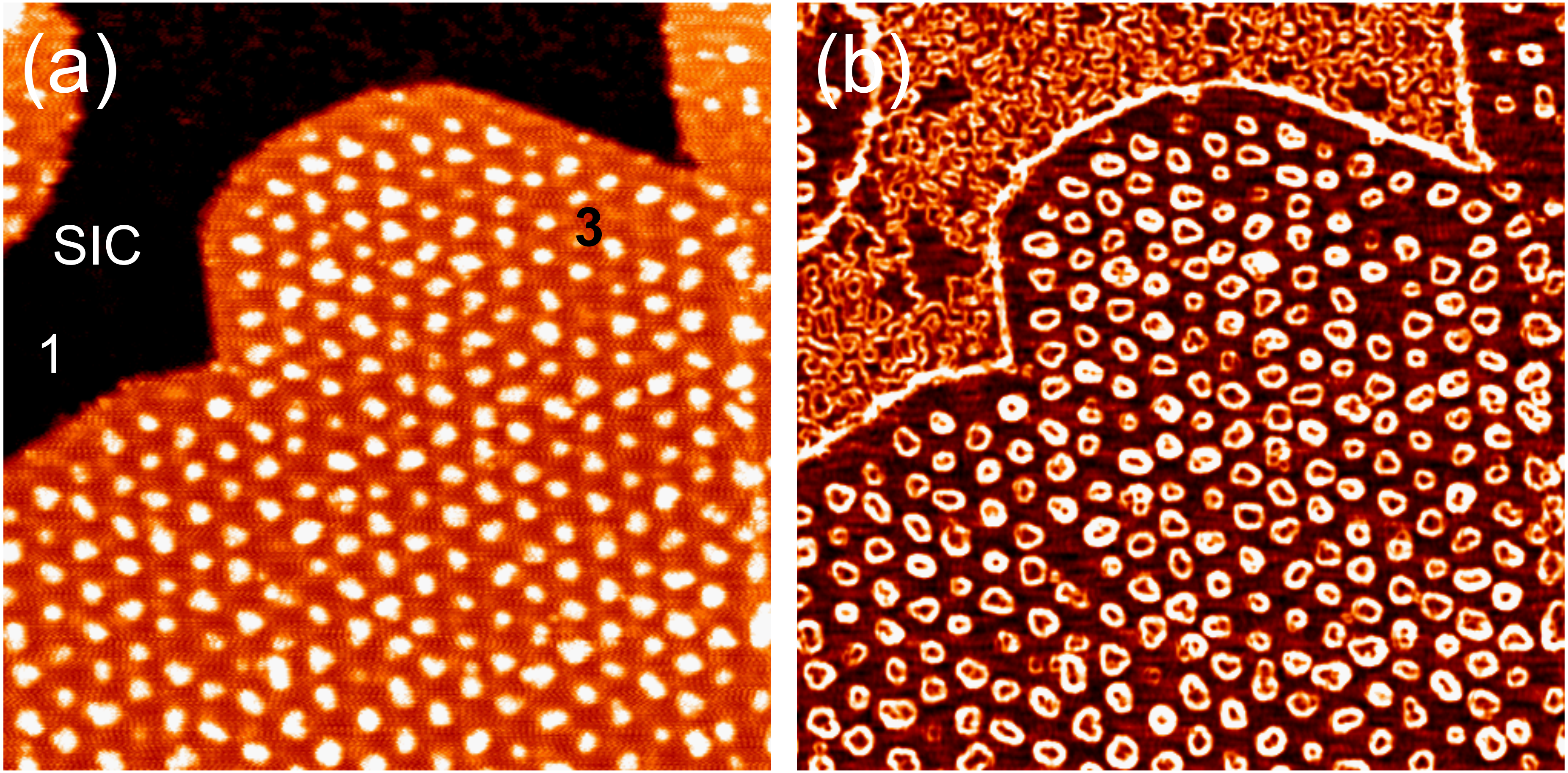
Size distribution of nanopucks



	(nm)	3 AL	4 AL
Type I	Size	1.83	2.67
	s	0.08	1.56
Type II	Size	2.00	2.37
	s	0.98	0.24

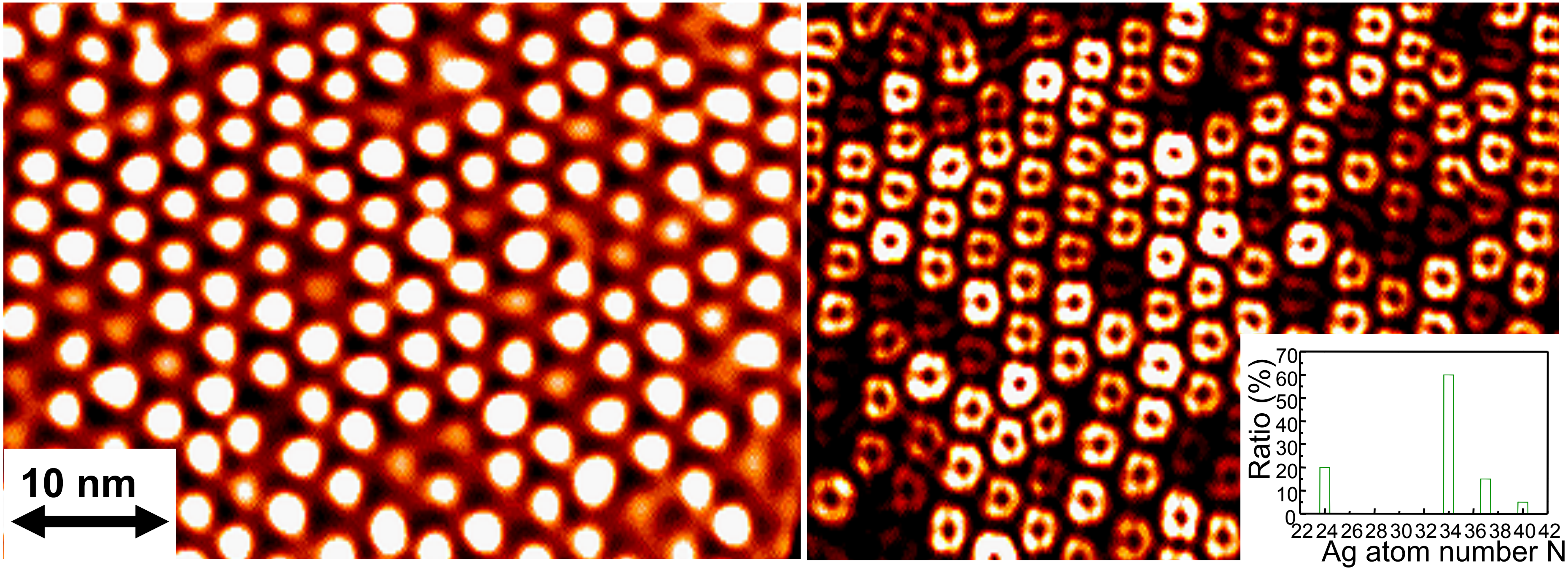
Spatial orderliness : **I (3AL) > II (4AL)** > II (3AL) > I (4AL)

Sizes and shapes of nanopucks



Ag 0.2 ML T = 120 K

Size-, site- & shape-controlled self-organized growth



Definition of a composite

A material having two or more distinct constituents or phases, and have to satisfy the following criteria:

1. Both constituents have to present in reasonable proportions, say greater than 5%;
2. The constituents phases have different properties, and hence the composite properties are noticeably different from the properties of the constituents;
3. A man-made composite is usually produced by intimately mixing and combining the constituents by various means.

Nanocomposites: Composites contain two or more nano-sized fillers.
(Nano-structural composites)

Hierarchical nanocomposites

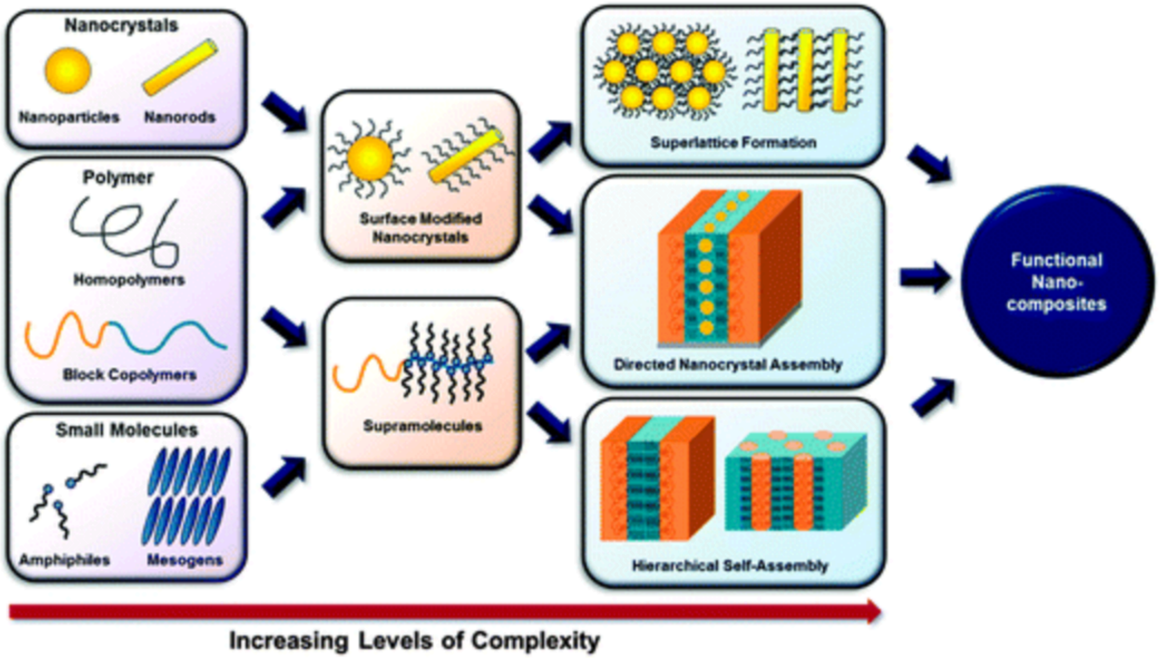
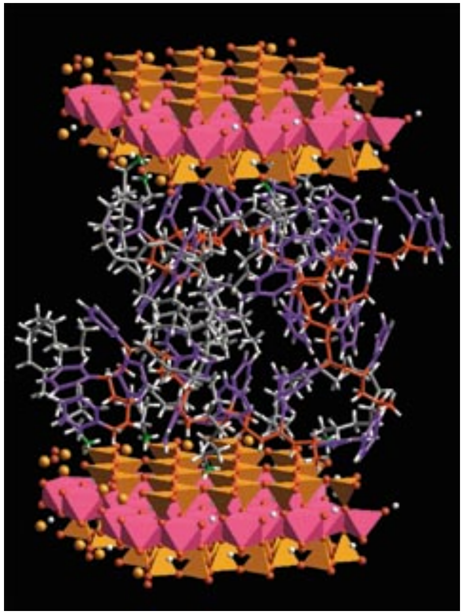


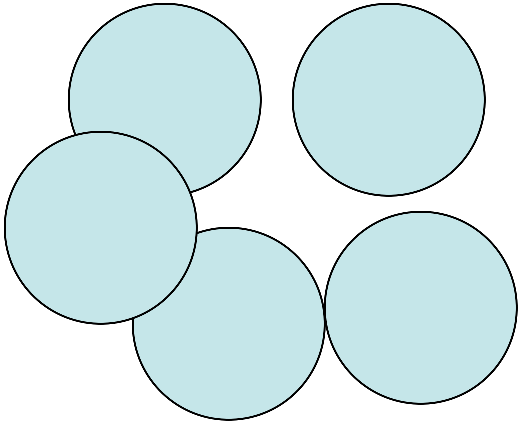
Fig. 1 Hierarchical co-assemblies of nanocrystals, polymers, and small molecules toward functional nanocomposites.

Why Nanocomposites?

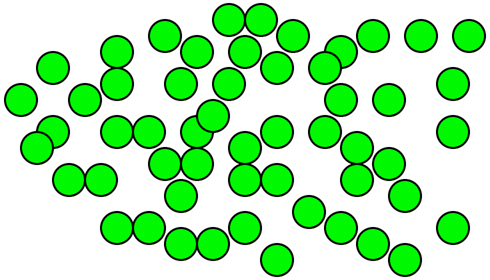
Size does matter

Increased surface area on nanoparticles





Microparticles

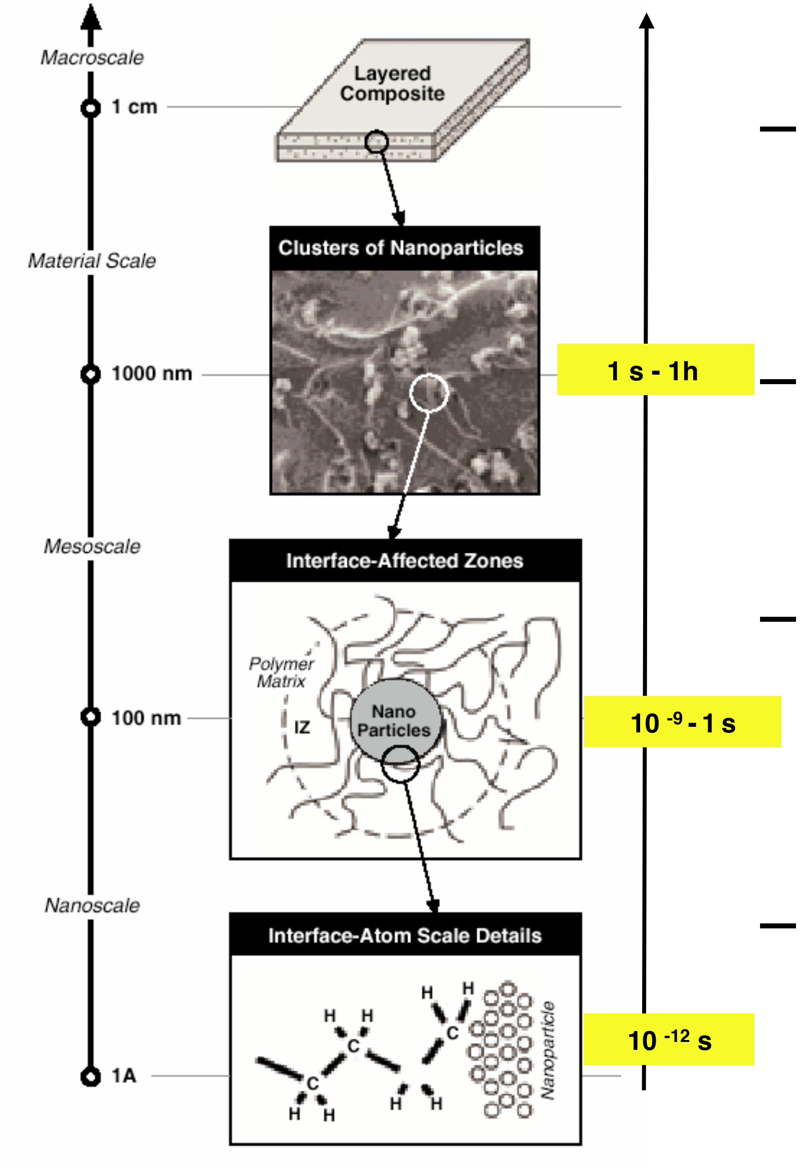


Nanoparticles

Why nanocomposites? → Multi-functionality

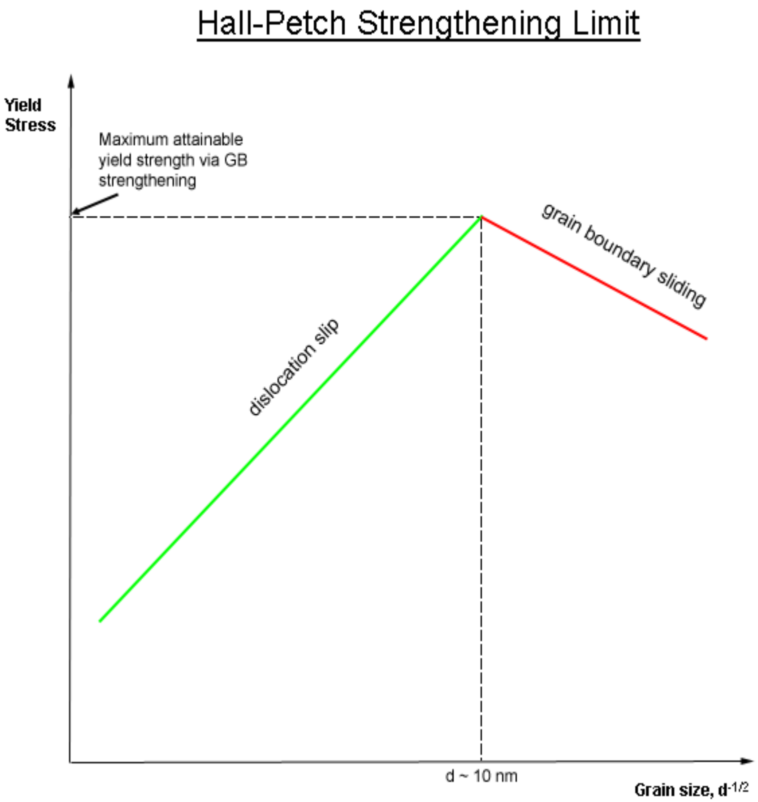
- Small filler size:
  - High surface to volume ratio
    - Small distance between fillers → bulk interfacial material
  - Mechanical Properties
    - Increased ductility with no decrease of strength,
    - Scratching resistance
  - Optical properties
    - Light transmission characteristics particle size dependent

Nanocomposite as a Multiscale System



- Macroscale composite structures
- Clustering of nanoparticles - micron scale
- Interface - affected zones - several to tens of nanometers - gradient of properties
- Polymer chain immobilization at particle surface is controlled by electronic and atomic level structure

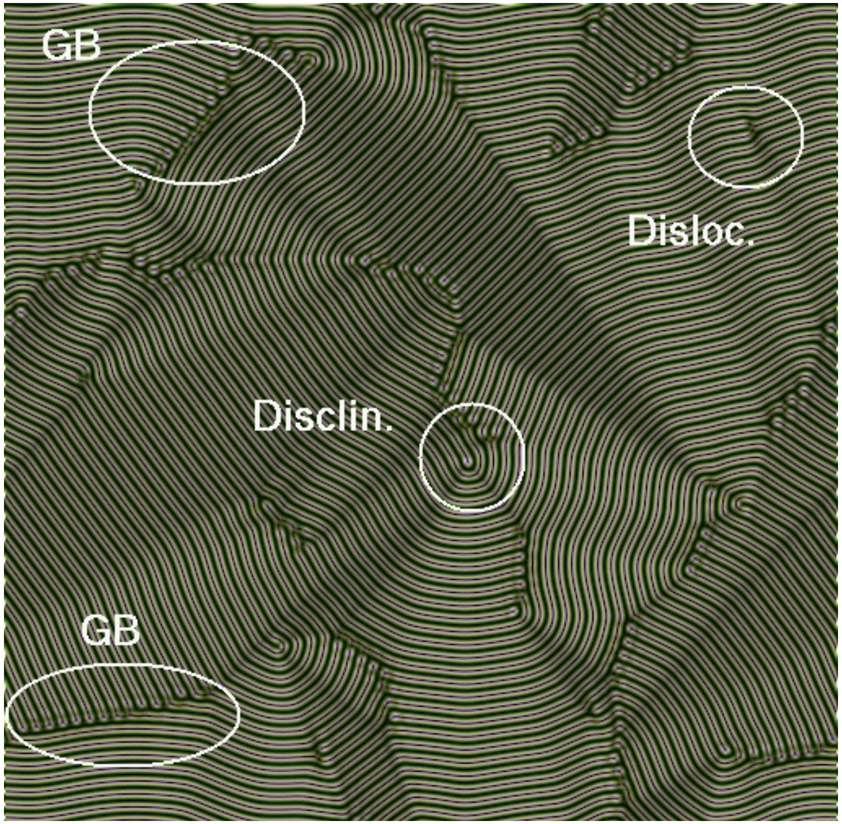
Hall–Petch equation



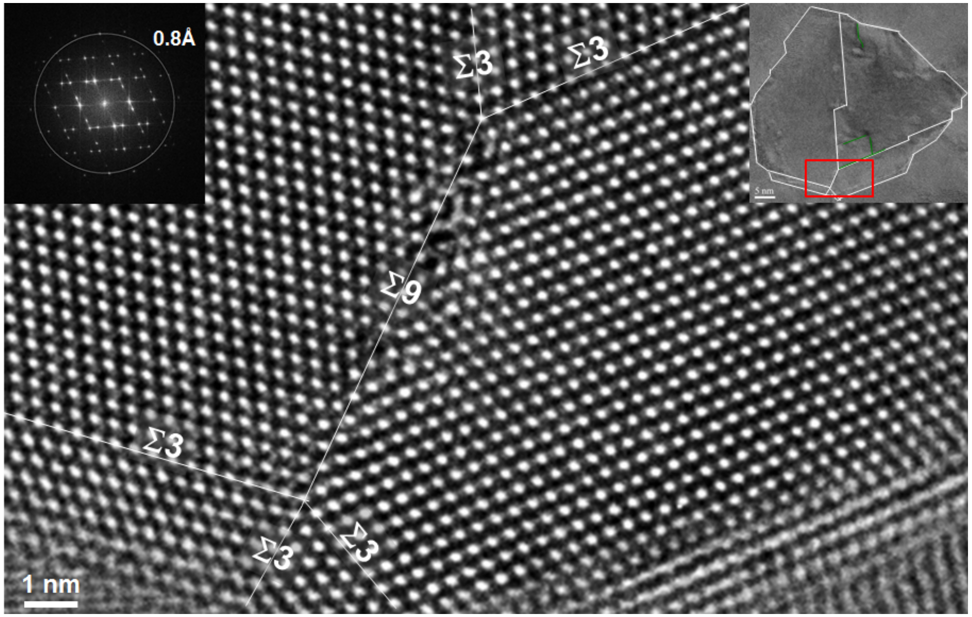
The relation between yield stress and grain size is described mathematically by the :

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

In grain-boundary strengthening, the grain boundaries act as pinning points impeding further dislocation propagation. Since the lattice structure of adjacent grains differs in orientation, it requires more energy for a dislocation to change directions and move into the adjacent grain.



Grain boundary



Triple line boundary