

- Ability to synthesize nanoscale building blocks with control on size, composition etc.
- further assembling into larger structures with designed properties will revolutionize materials manufacturing
- Manufacturing metals, ceramics, polymers, etc. at exact shapes without machining
- Lighter, stronger and programmable materials
- Lower failure rates and reduced life-cycle costs

Top-Down versus Bottom-Up Manufacturing

- **Top-down** manufacturing starts with bulk materials which are then whittled down, until the features that are left are nanoscale.

Example

crystalline drugs may be milled until the individual particle sizes are 100 nm, or smaller. At this size, the particles have a much larger surface area in relation to volume than would more conventional microscale particles. This allows them to dissolve much faster – which is critical for certain drugs that are not very soluble in water

Bottom-Up Manufacturing

- **Bottom-up** manufacturing involves creating objects or materials from individual atoms or molecules and then joining them together in a specific fashion.

Think about how a table is built. A plank of wood is connected to three or four posts, through the use of screws and wood-glue. The posts may also be made of wood. Simple enough.

To build materials by bottom-up approach, the first requirement is to have clusters of the material consisting of a few (3-10⁷) molecules. One such system of clusters of particles is the colloidal system.

Surface in nanoparticles

The surface/ volume ratio in nano scale:

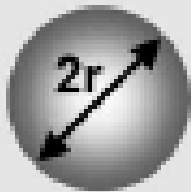
$$R = \frac{A}{V} = \frac{6}{D}$$

The ratio is inversely proportional to the particle size

The same is valid for the surface per mole, which is of great importance in thermodynamic considerations

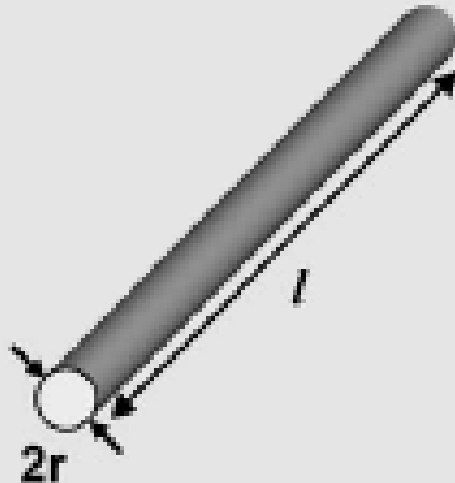
Surface/ volume ratio for different shapes

Particulate Materials



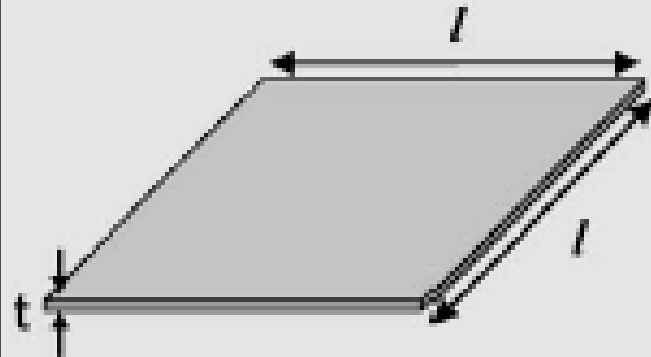
$$\frac{3}{r}$$

Fibrous Materials



$$\frac{2}{r} + \frac{2}{l}$$

Layered Materials

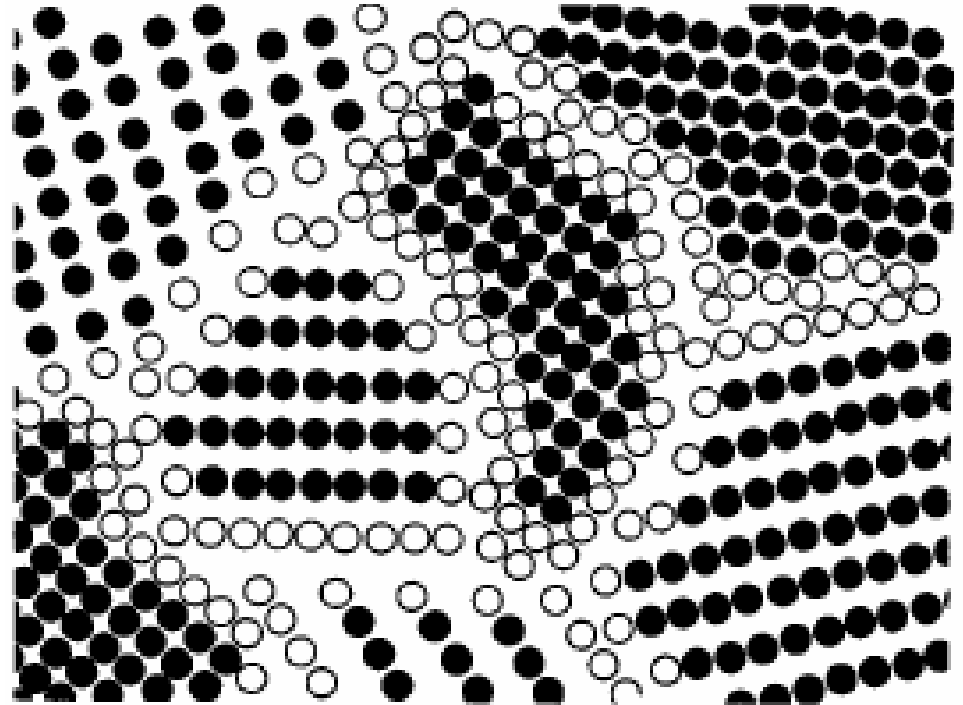


$$\frac{2}{t} + \frac{4}{l}$$

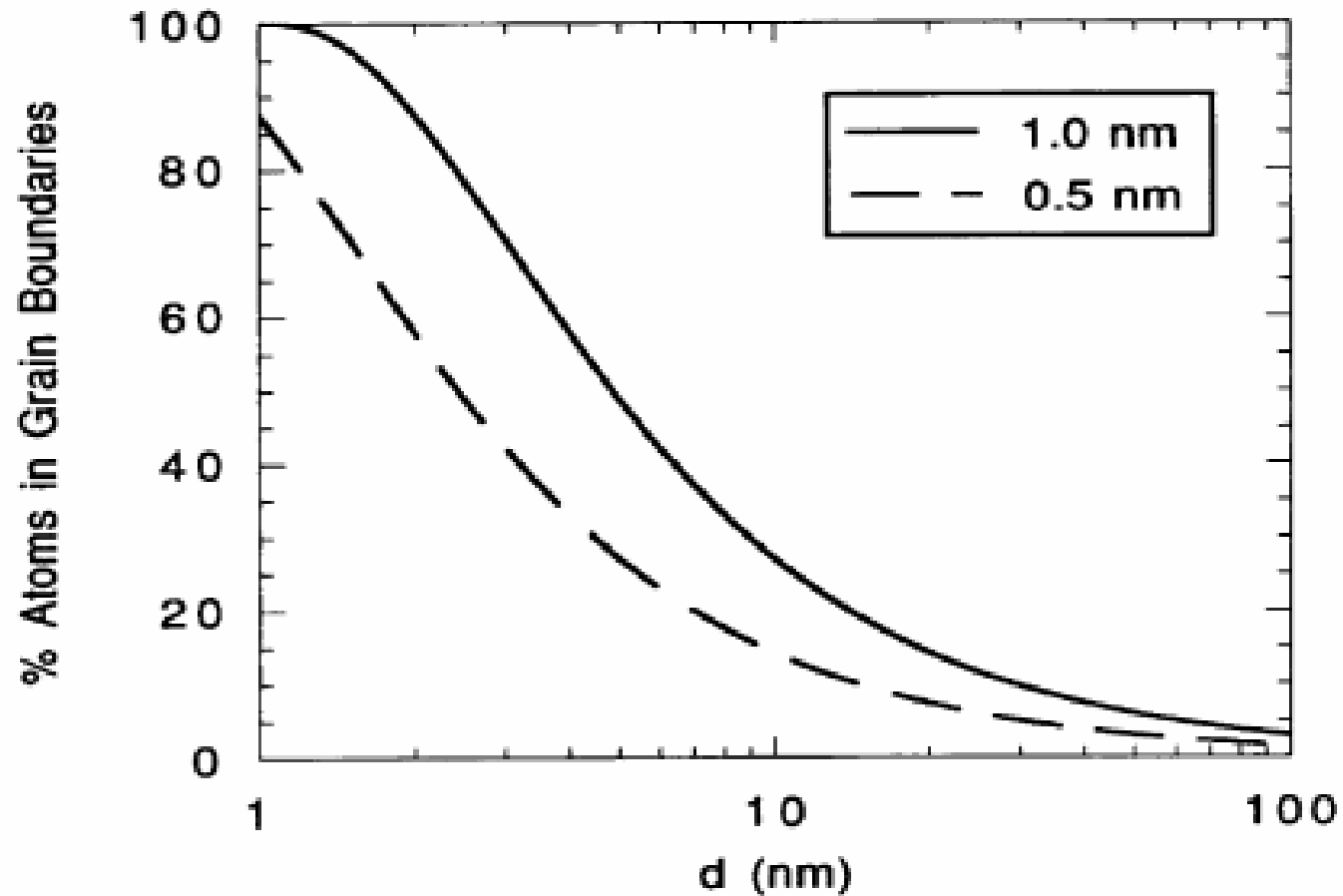
In nanomaterials the surface forms a sharp interface between a particle and its surrounding. This is free surface in the case of particulate materials, or grain boundaries in bulk material.

Grain boundaries in nanocrystalline materials

A large portion of material is placed in the surface (the grain boundaries)



Distribution of atoms in grain boundaries (thickness of boundaries 0.5-1 nm)



Surface energy

Particles are produced by breaking a large solid piece of material into smaller parts.

Therefore the bonds between the neighboring atoms need to be cut. The energy of bonding between each two atoms in the lattice, u , is active and to separate a bond energy u is required.

For each new surface energy $u/2$ is required. So:

$$\gamma_0 = Nu/2$$

N = the number of broken bonds per unit area

Homework

It is claimed that the surface energy increases with $1/D$ (considering D as grain or particle diameter), obtain a relation between molar surface energy (U_{surface}), and D by assuming:

U_{surface} : surface energy of a particle

γ : specific surface energy

M : molar weight

ρ : density of the material

consequences of surface energy

Clausius-Clapeyron law:

$$p = p_{\infty} \exp(4\gamma V_m / DRT)$$

p_{∞} = Vapor pressure over a flat surface

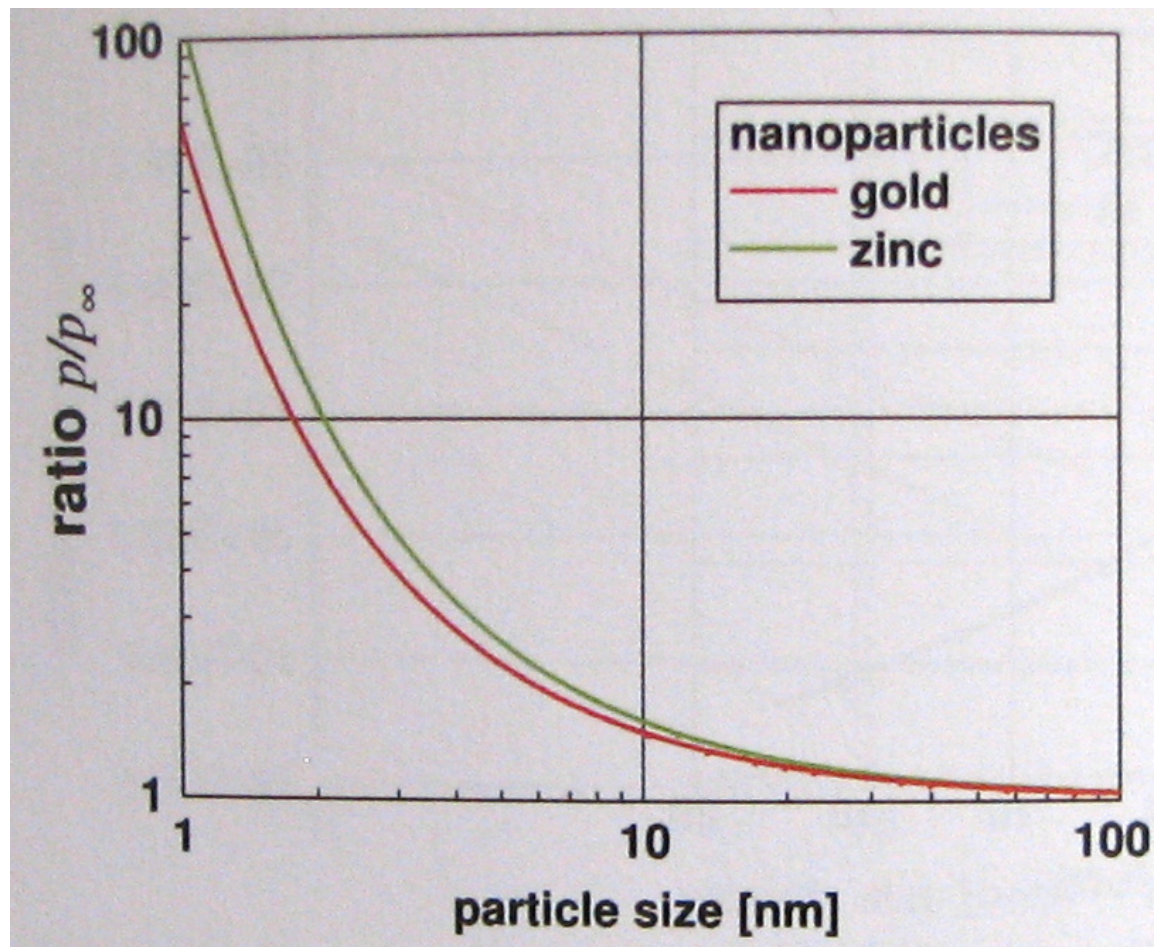
V_m : molar volume

R : gas constant

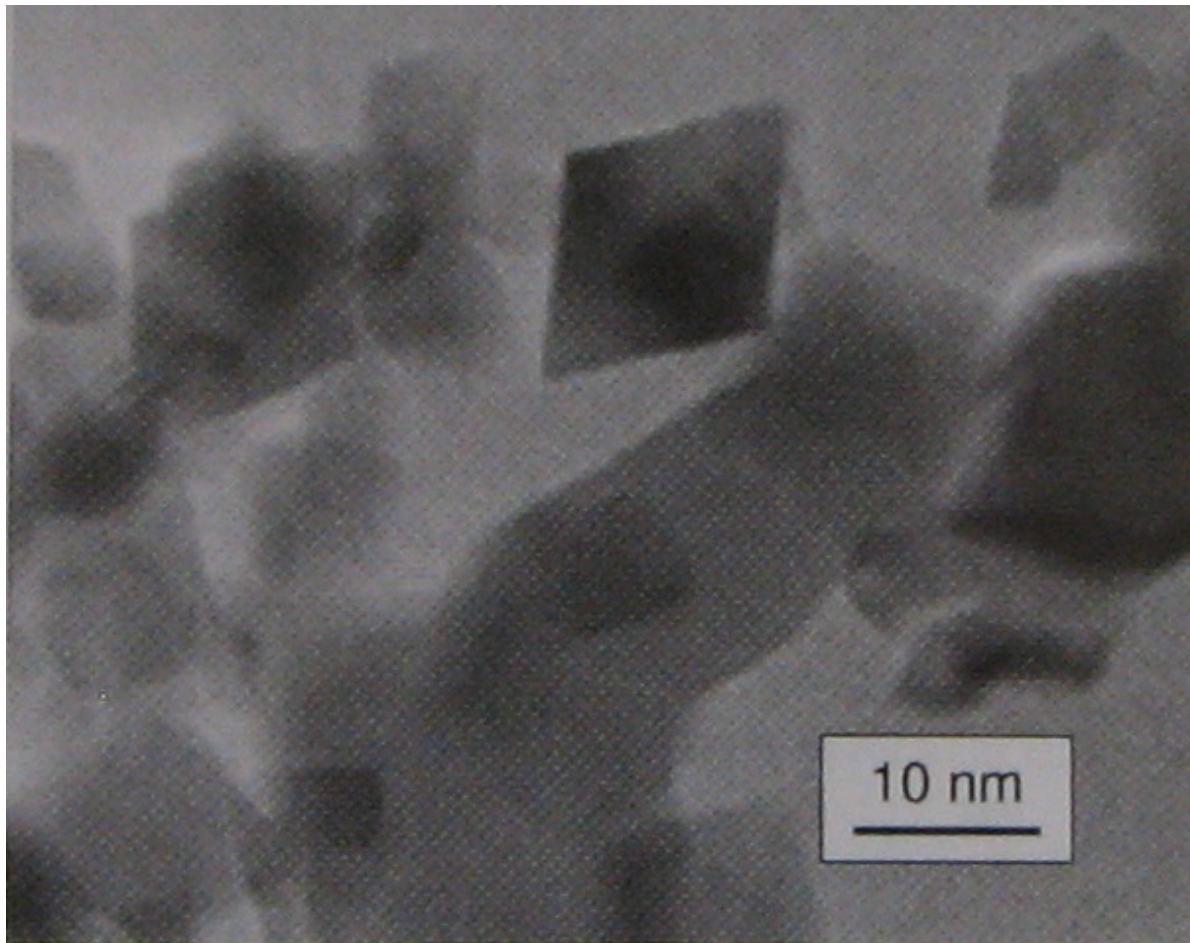
D : particle diameter

Assuming constant temperature, over a curved surface:

$$P \propto \exp(1/D)$$



**Faceted ceria (CeO_2) nanoparticles:
Particles of materials with an extremely low vapor pressure may be faceted, even when produced by high temperature processes**



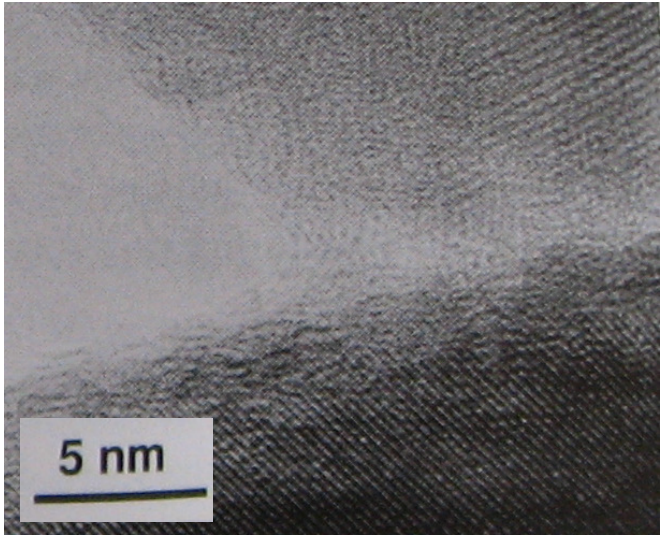
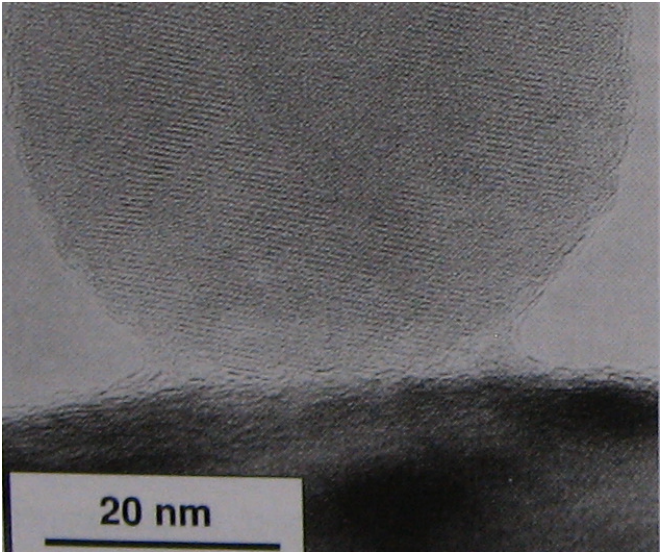
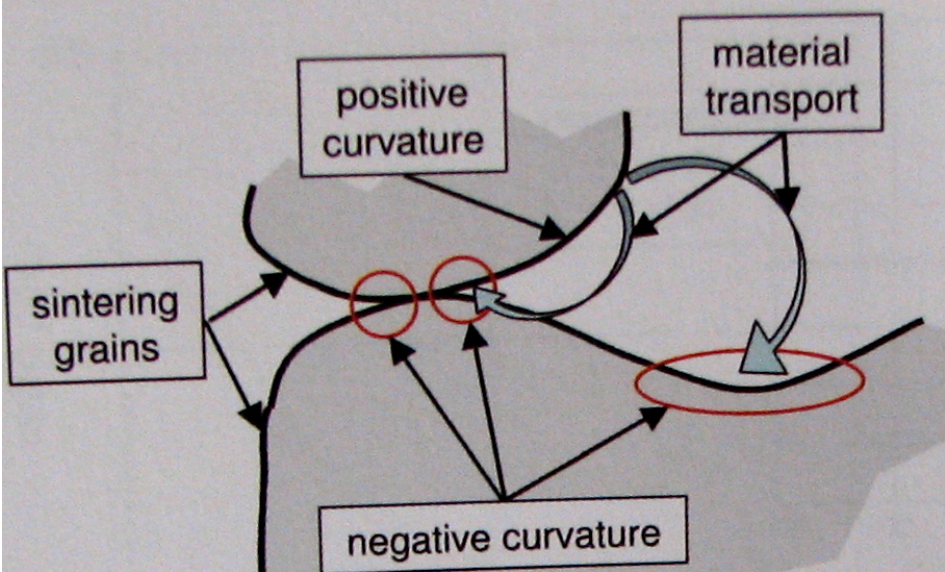
Nanoparticle production

- It is easier to produce small particles of materials with a low vapor pressure in gas-phase reactions.

Sintering

- In sintering, in necks negative curvatures decrease the vapor pressure and sintering starts from this points

Sintering



Some recommended topics:

- Carbon nano-tubes
- ZnO nano-particles and nano-rods
- Ferrofluids
- Copper- carbon nanotube composite
- Nanocomposite coatings
- Metal matrix nano-composites
- Nanocrystalline intermetallics
- Intermetallic matrix composites
- ODS alloys
- Processing of structural nanocrystalline materials