



Session 2: Size and surface related phenomena

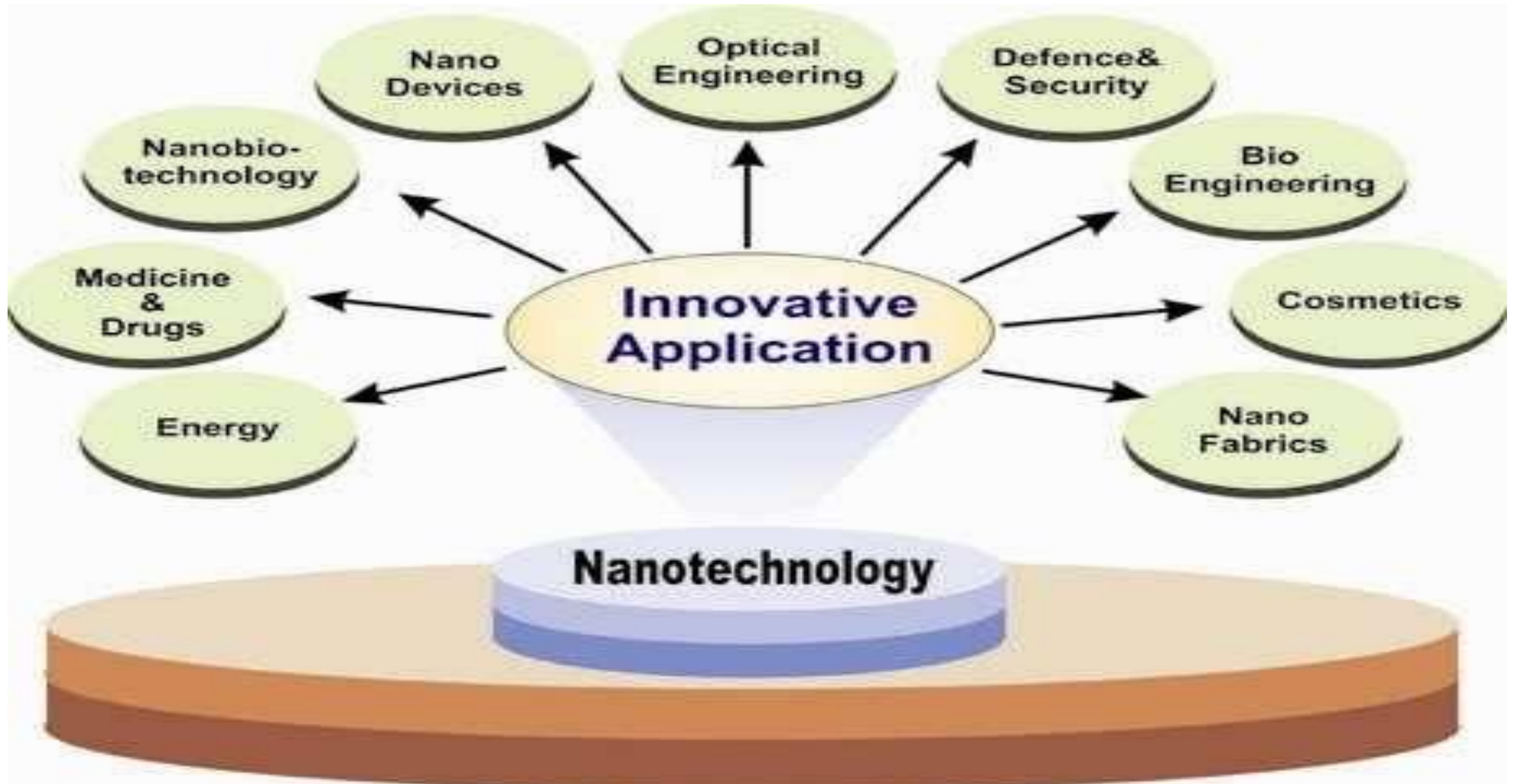
February 7, 2020

Session Objectives

1. Recap:
 - a) Scale of things
 - b) Words associated to Nano
2. List of Fabrication Methods
3. General properties
4. Surface phenomena



Applications of Nanotechnology



The Scale of Things – Nanometers and More

Things Natural

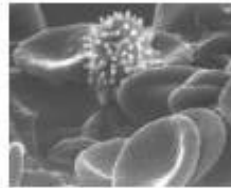


Dust mite
200 μm

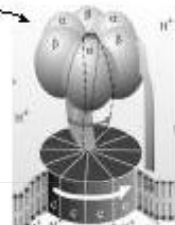


Human hair
 $\sim 60\text{--}120\ \mu\text{m}$ wide

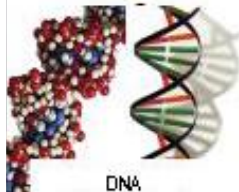
Red blood cells
with white cell
 $\sim 2\text{--}5\ \mu\text{m}$



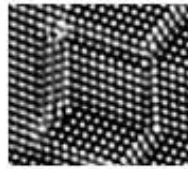
$\sim 10\ \text{nm}$ diameter



ATP synthase



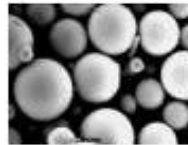
DNA
 $\sim 2\text{--}12\ \text{nm}$ diameter



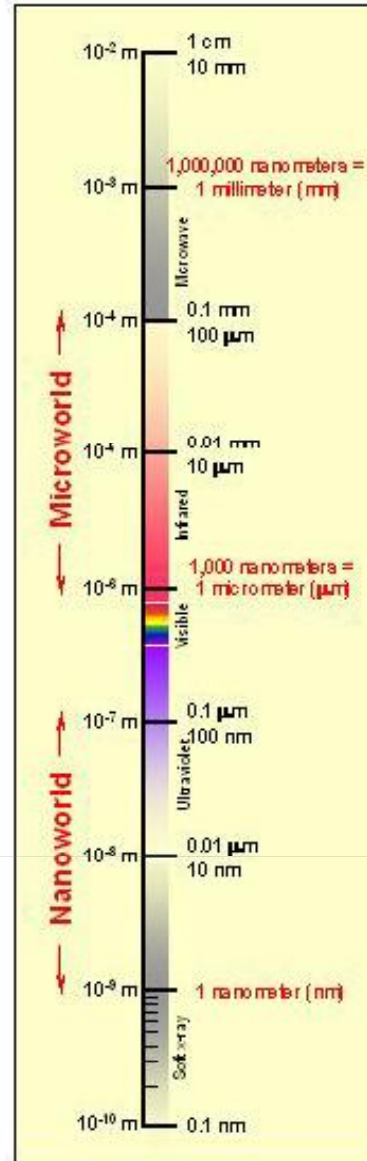
Atoms of silicon
spacing \sim tenths of nm



Ant
 $\sim 5\ \text{mm}$



Fly ash
 $\sim 10\text{--}20\ \mu\text{m}$



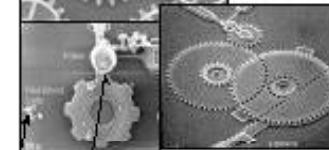
Things Manmade



Head of a pin
1-2 mm

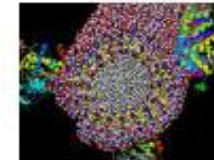
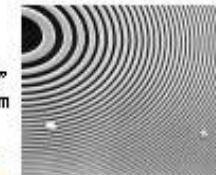


Micro Electro Mechanical (MEMS) devices
10 - 100 μm wide

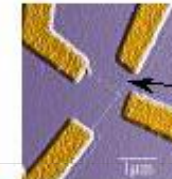


Pollen grain
Red blood cells

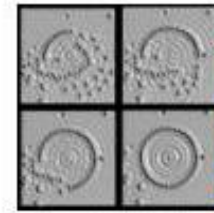
Zone plate x-ray "lens"
Outer ring spacing $\sim 35\ \text{nm}$



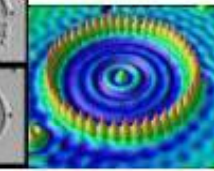
Self-assembled,
Nature-inspired structure
Many 10s of nm



Nanotube electrode

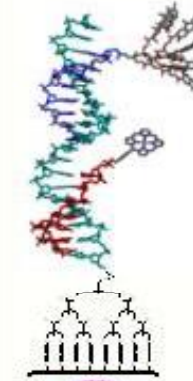


Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14 nm

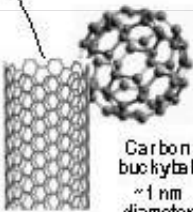


Carbon nanotube
 $\sim 1.3\ \text{nm}$ diameter

The Challenge

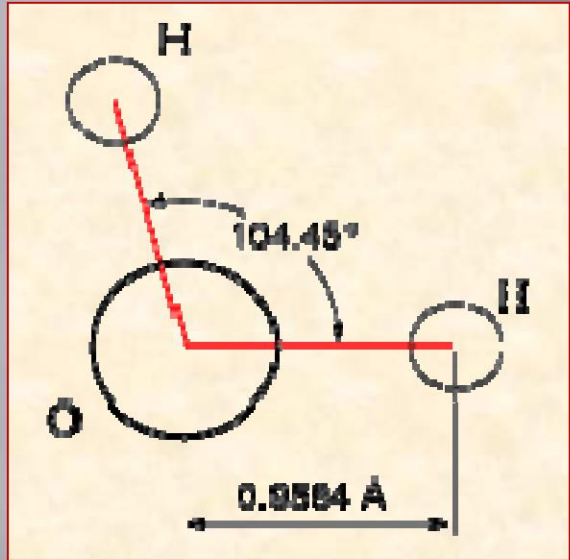


*Fabricate and combine
nanoscale building
blocks to make useful
devices, e.g., a
photosynthetic reaction
center with integral
semiconductor storage.*



Office of Science and Technology
Office of Nanoscience and Nanotechnology
National Science Foundation

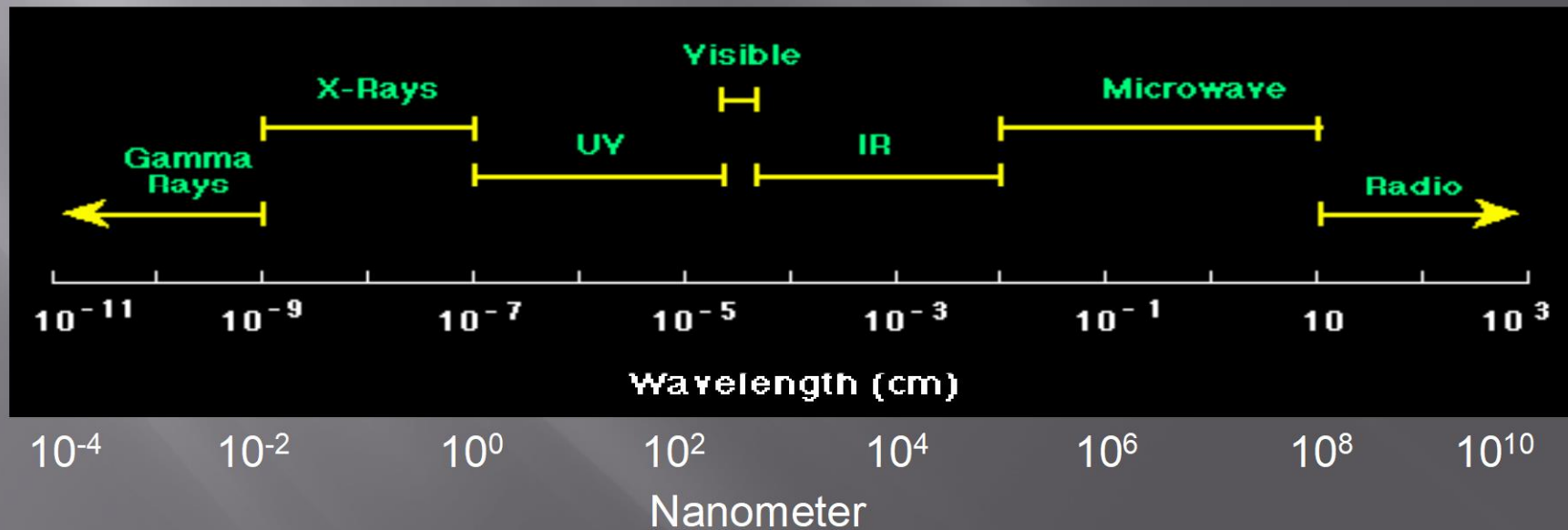
Scale of things



C-C bond – 1.5 angstroms

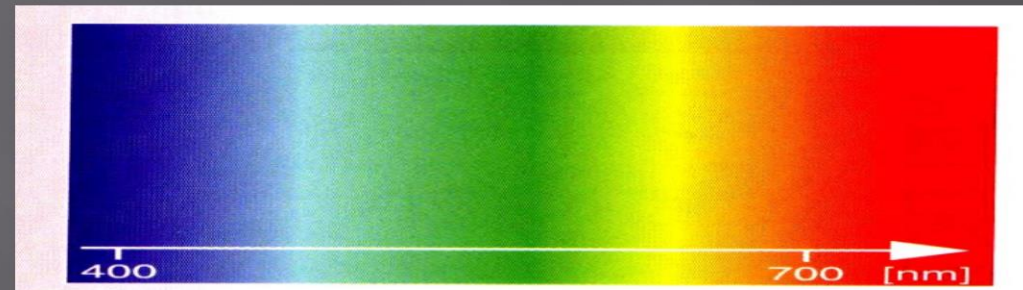
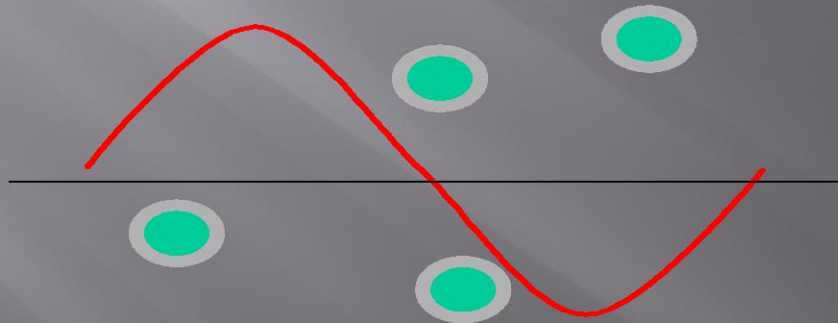
C-H bond – 1.1 angstroms

Ethanol: CH₃-CH₂OH



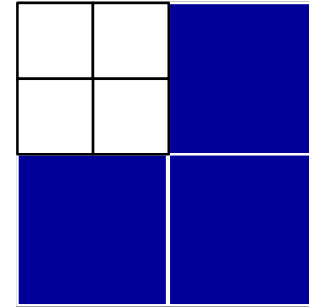
Nanocomposites: Optical Clarity

- ▣ **Size** and **refractive index** of particles are important
- ▣ Nanoparticles are smaller than the wavelength of visible light; reduces chance of light scattering



Calculate

1. Calculate the total surface when you divide a cube with an 1 cm edge:
 - 8 smaller cubes.
 - 16 smaller cubes.
 - 32 smaller cubes.
 - 64 smaller cubes.
 - 128 smaller cubes.
 - 256 smaller cubes.
 - 512 smaller cubes.
2. How important is this?



Calculate

1. How many iron atoms can be inside a cube with a 30 nm, 10 and 3nm edge?
2. How many iron atoms are on the surface of each cube?

Nano-Scale & Conventional Polymeric Size

Type	Size
Polymer latex size	50-500 nm
Hiding grade TiO_2	200-250 nm
Polyurethane dispersion particle size	50-100 nm
Polymer molecular size in solution	2-100 nm

Surface Area

$$\text{Volume} = \frac{4}{3} \pi r^3$$

$$\text{Surface area} = 4 \pi r^2$$

If the density of TiO₂
is 4 grs/cm³, and


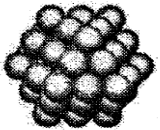
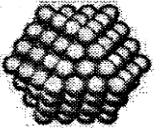
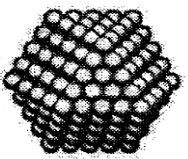
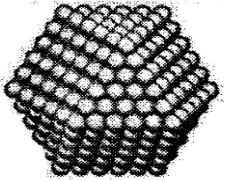
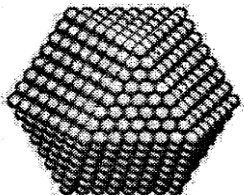
What is the

What is the

What is the

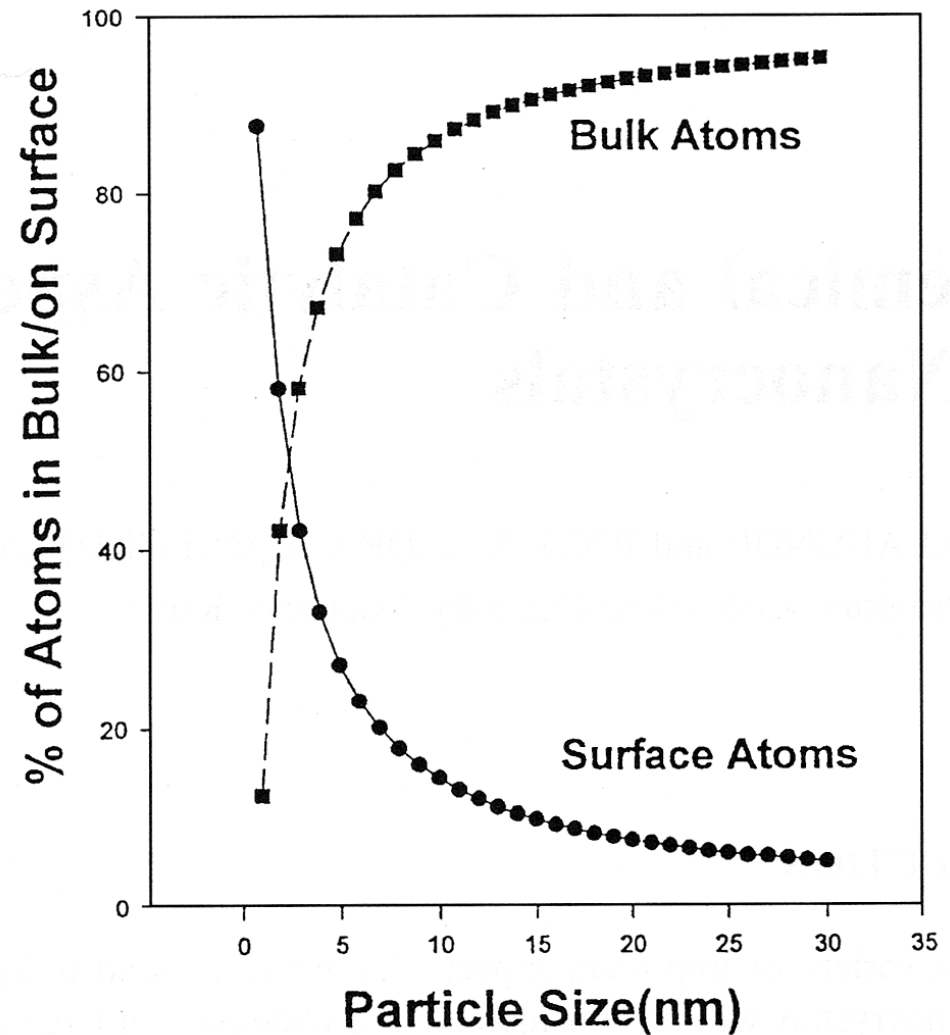
If the particle diameter is:	# particles per gram?	Surface area per gram?	Surface area per volume?
200			
20			
2			

Percentage of Surface Atoms

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1. Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

Surface to Bulk Atoms Ratio

- Spherical iron nanocrystals
- J. Phys. Chem. 1996, Vol. 100, p. 12142

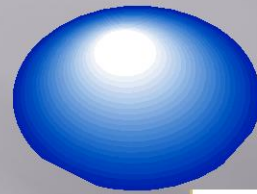


Surface Area Dependence on Size



59,1 km²

The surface area of spherical nanoparticles of 150 nm in 1m³ is approximately equivalent to

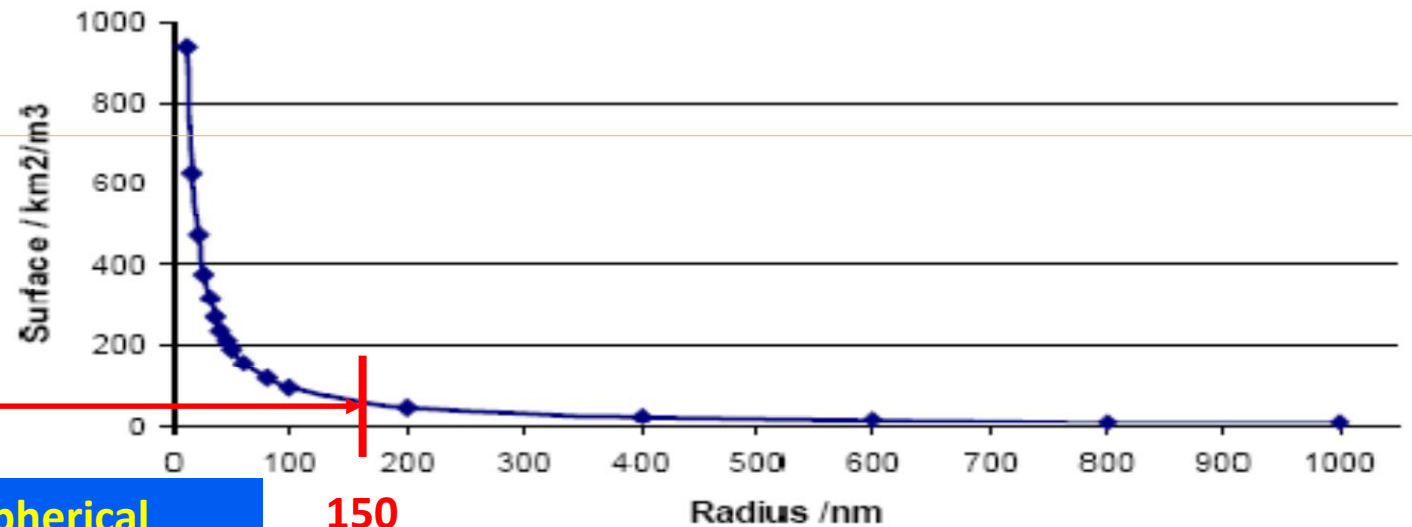


$$A = 4\pi r^2$$

Nanomaterials:
Dependence on Size

By the way... the surface area of our lungs is approximately 70-100m²

Specific Surface Area of Nanoparticles



150

Surface Material Content

A particle of 10 nm diameter has 20% of its atoms on the surface

A particle of 2 nm diameter has 80% of its atoms on the surface

A particle of 1 nm diameter has 80% of its atoms on the surface

Interfacial Material Content

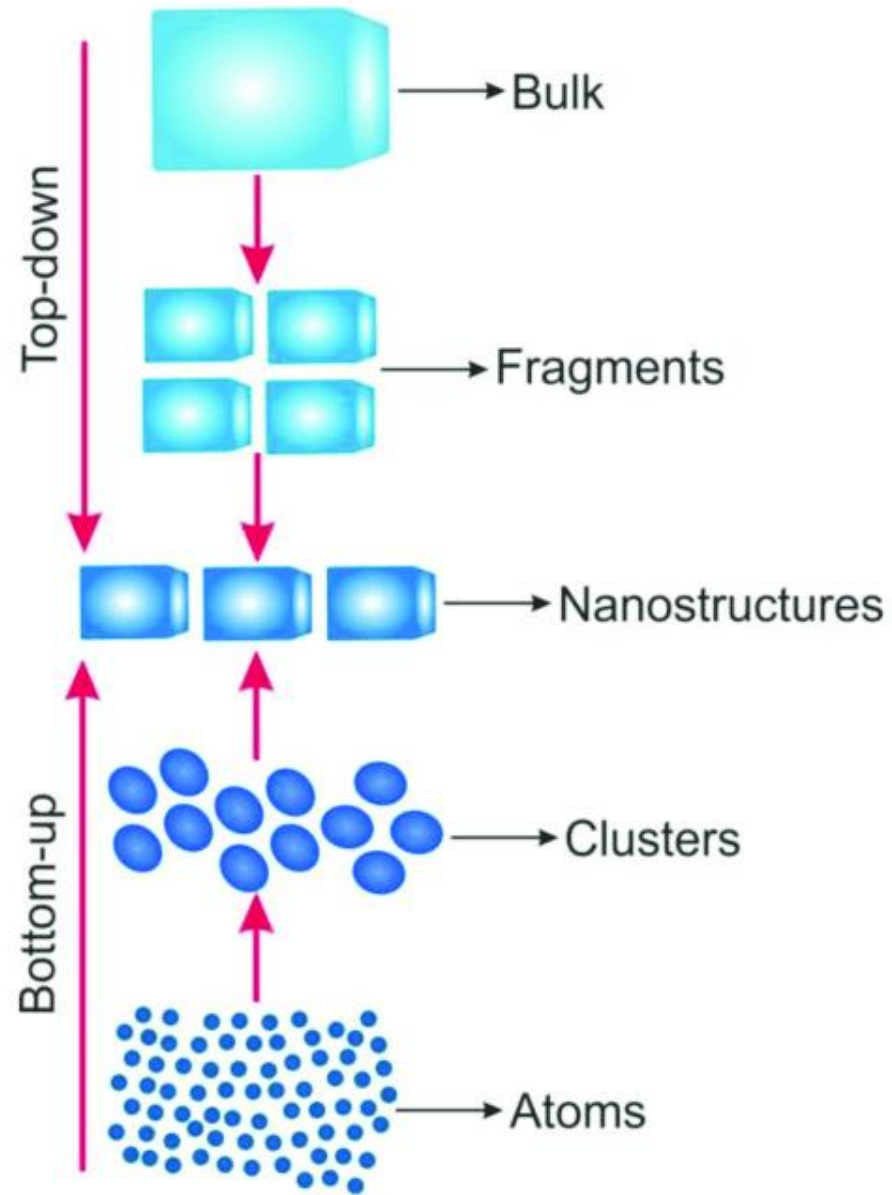
Particle Diameter (nm)	300	250	200	150	100	50
Interfacial Volume Fraction	0.03	0.04	0.05	0.06	0.10	0.22



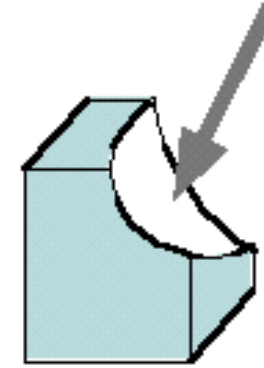
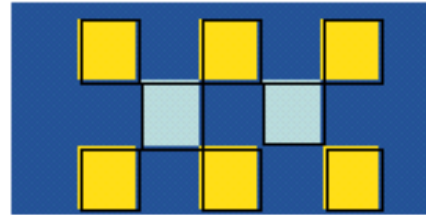
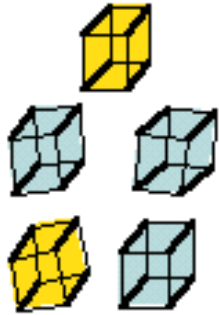
10 nm Interfacial Layer

Dispersed particle volume fraction is 0.3 in all cases

Fabrication Methods



Nanostructured Material



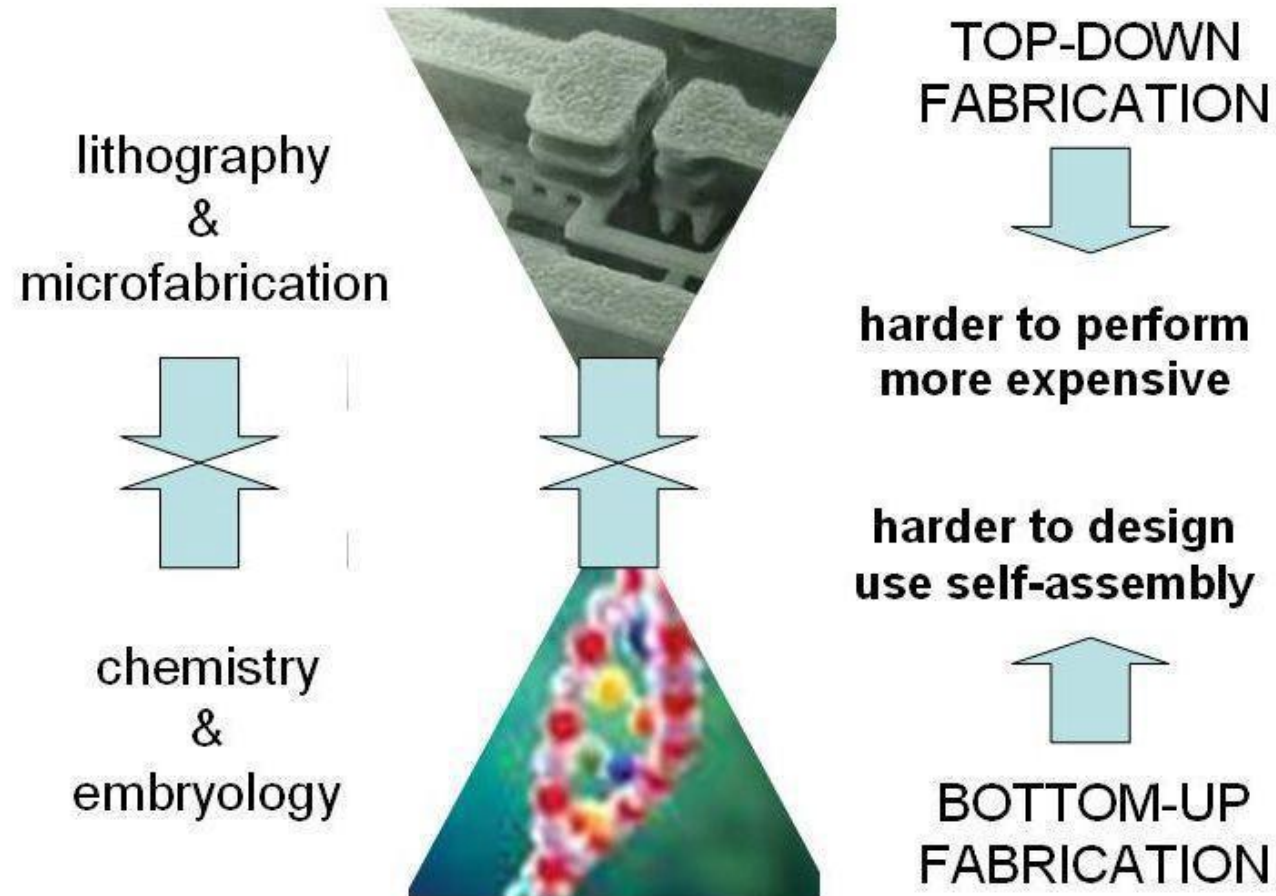
Assemble from
Nano- building Blocks



'Sculpt' from Bulk



Top Down vs. Bottom Up




Fabrication

Microfabrication techniques:

- Photolithography
- Soft lithography
- Film deposition
- Etching
- Bonding

Nanofabrication techniques

- Molecular self assembly 
- Colloid monolayer lithography
- Electron beam lithography
- Focused ion beam lithography
- Electrically induced nanopatterning
- X-ray lithography
- Ion projection lithography
- Rapid prototyping
 - direct deposition,
 - three-dimensional printing,
 - selective laser sintering,
 - laser stereolithography,
 - evaporation-induced self assembly,
 - pen lithography,
 - ink-jet printing and
 - dip-coating techniques

Nano Particles Dimensions

- Zero Dimension: Nano particles, nano dots
- One Dimension: Nano wire
- Two Dimension: Nano films

Some Fabrication Process for Nanomaterials

- **Nanoparticles (0D):**
 - colloidal processing,
 - flame combustion,
 - phase segregation.
- **Nanorods or nanowires (1D):**
 - template-based electroplating,
 - vapor-liquid-solid growth (VLS),
 - spontaneous anisotropic growth.
- **Thin films (2D):**
 - molecular beam epitaxy (MBE)
 - atomic layer deposition (ALD)
- **Nanostructured bulk materials :**
 - self-assembly of nano sized particles for photonic band gap crystals.

Nanofabrication techniques

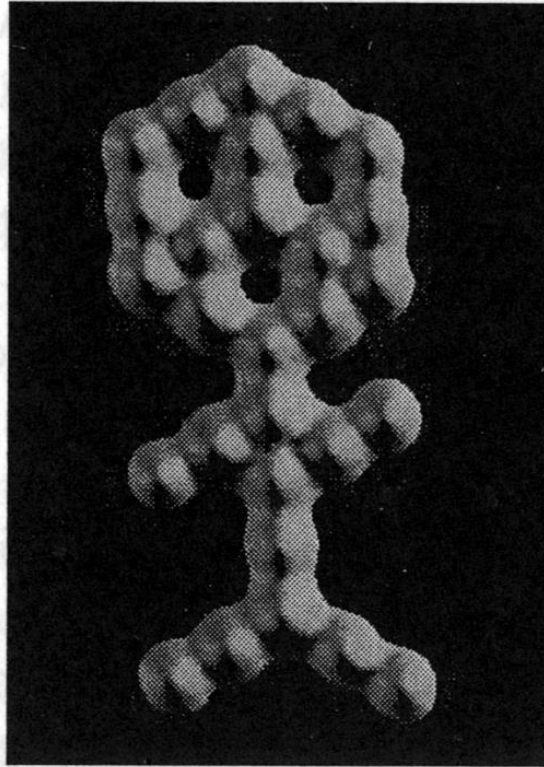


Fig. 1.6. A molecular person consisting of 14 carbon monoxide molecules arranged on a metal surface fabricated and imaged by scanning tunneling microscopy. [P. Zeppenfeld & D.M. Eigler, *New Scientist* **129**, 20 (23 February 1991), and <http://www.almaden.ibm.com/vis/stm/atomo.html>]

Properties

Mechanical

Electrical

Physical

Optical

Thermal

Chemical

Quantum

Some physical properties affected by size

Nanomaterials exhibit remarkable different characteristics from their bulk form:

- Melting point decreases as size of Au nanoparticles reduce.
- Energy gap of Si nanoparticles is larger than that of bulk Si (1.12 eV).

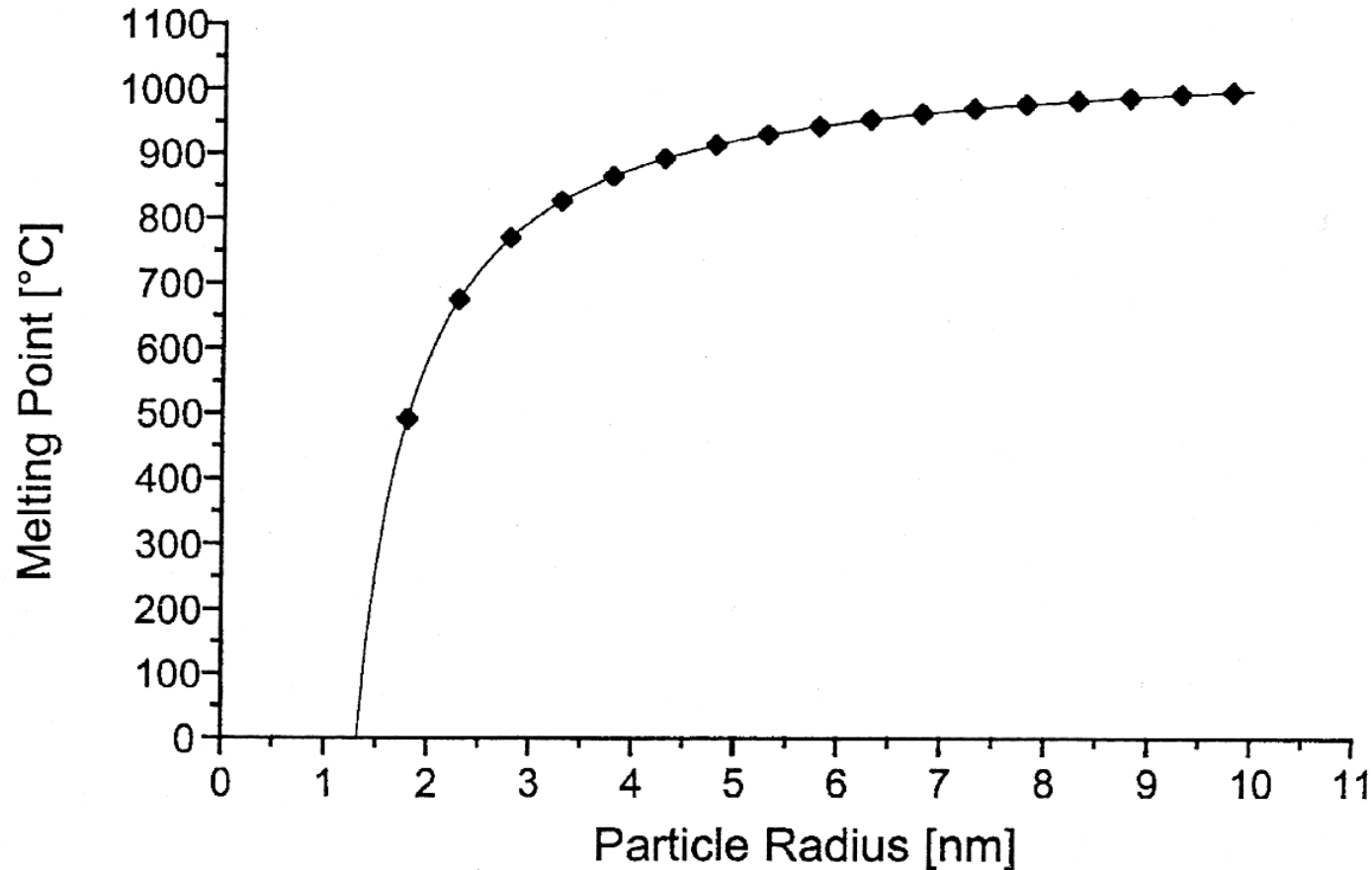
Melting point of Au nanoparticles

diameter	T _m
bulk	1,064°C
20 nm	~ 990°C
5 nm	~ 850°C
4 nm	~ 750°C
2 nm	~ 330°C

Eg of Si materials

diameter	E _g
bulk	1.12 eV
10 nm	~ 1.20 eV
7 nm	~ 1.29 eV
5 nm	~ 1.62 eV
3 nm	~ 2.60 eV

Thermal: melting point



- Why ?

- Phenomenon?

The melting point decreases dramatically
as the particle size gets below 5 nm

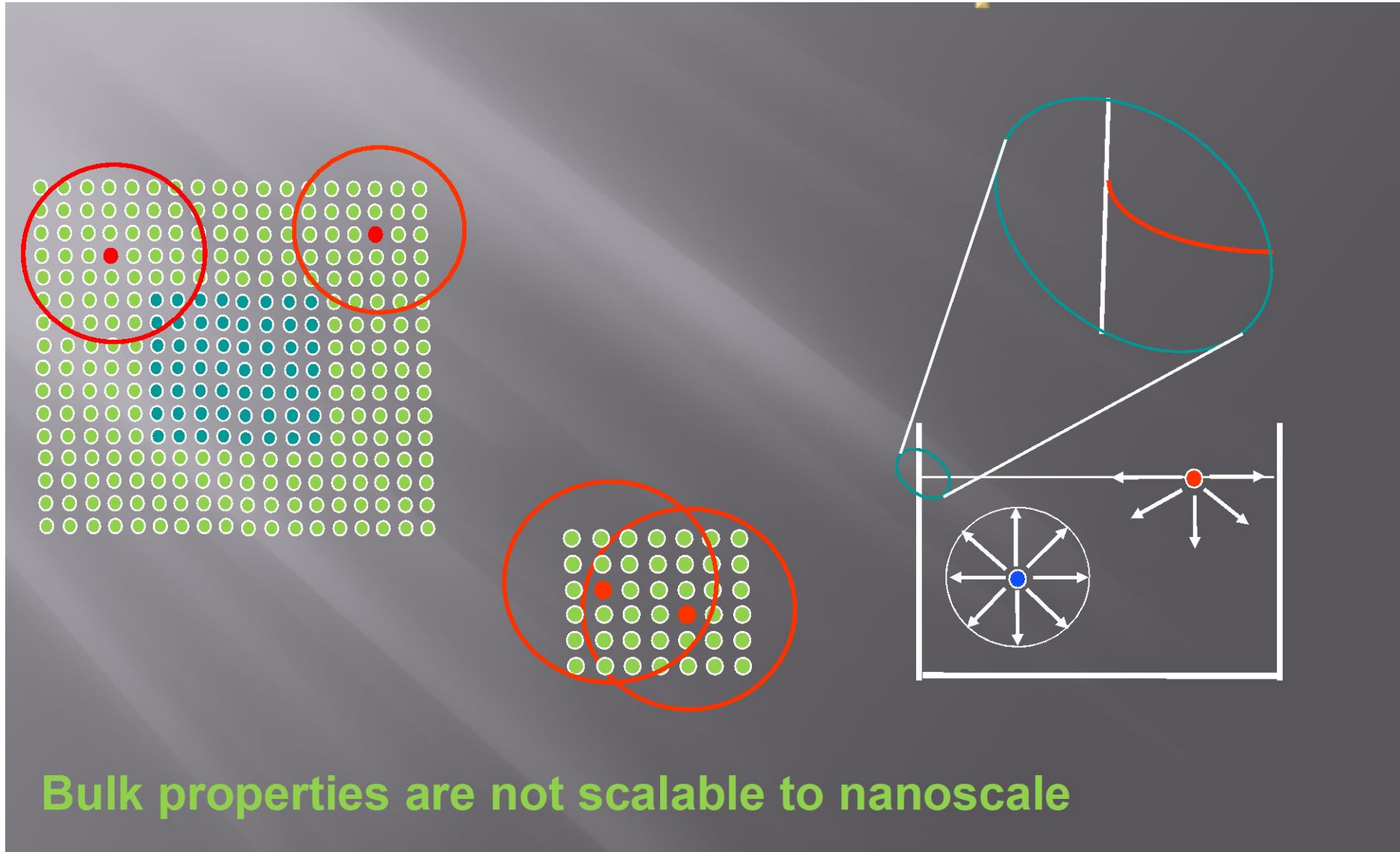
Melting Point Dependence on Particle Size

- Lowering of the melting point is proportional to $1/r$
- ΔT can be as large as couple of hundred degrees when the particle size gets below 10 nm
- Most of the time, the surface tension coefficient (σ) is unknown; by measuring the melting point as a function of radius, σ can be estimated.

Note:

For nanoparticles embedded in a matrix, melting point may be lower or higher, depending on the strength of the interaction between the particle and matrix.

Bulk vs. Surface Properties

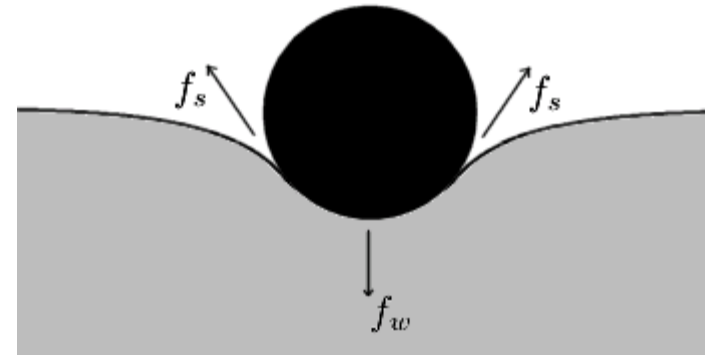
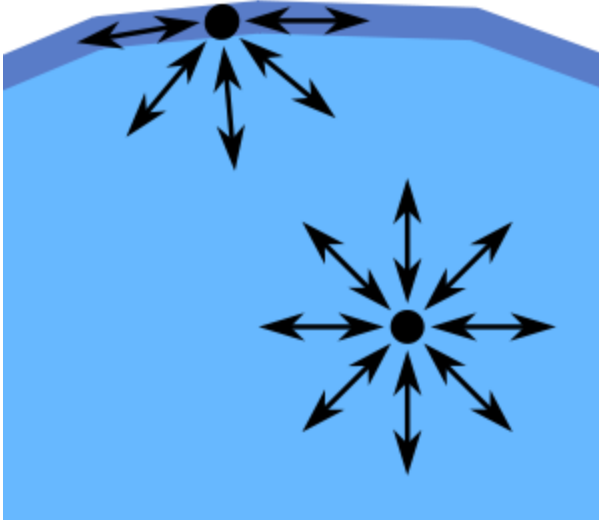


Challenges in Nanotechnology

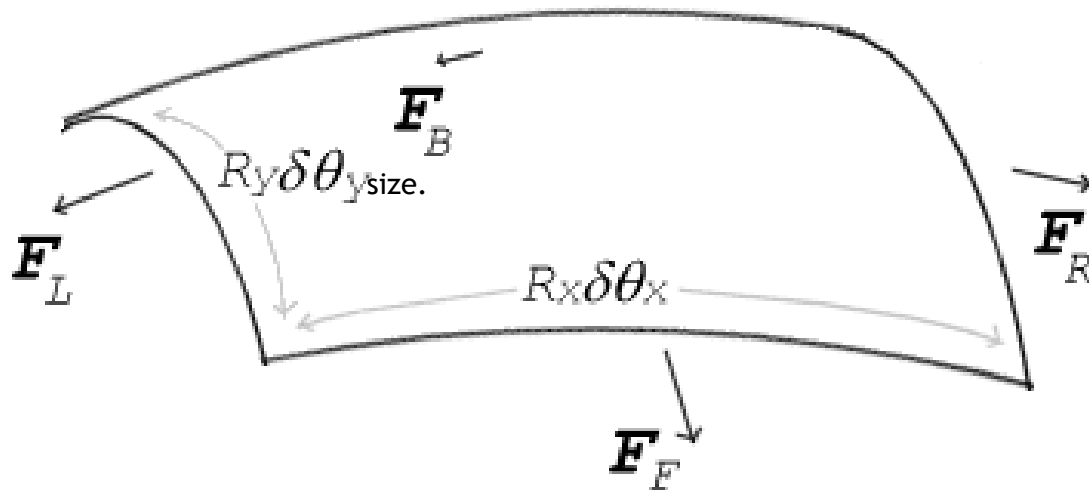
- Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio.
- Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure, that all together result in desired physical properties.
- Prevent nanomaterials and nanostructures from coarsening through either Ostwald ripening or agglomeration as time evolves.

Recess

Surface Tension



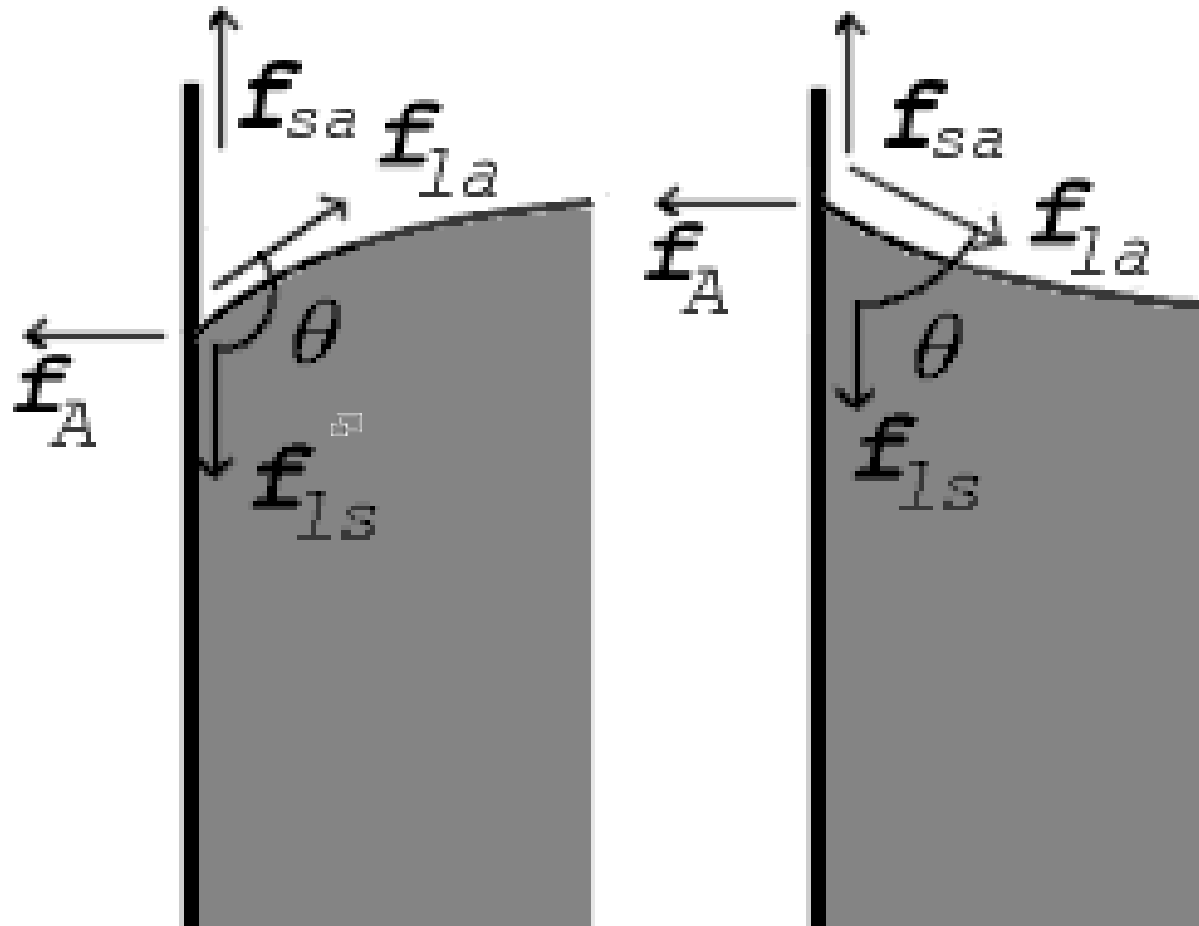
Young-Laplace equation



$$\Delta p = \gamma \left(\frac{1}{R_x} + \frac{1}{R_y} \right)$$

Δp for water drops of different radii at <u>STP</u>				
Droplet radius	1 <u>mm</u>	0.1 mm	1 <u>μm</u>	10 <u>nm</u>
Δp (<u>atm</u>)	0.0014	0.0144	1.436	143.6

Solid Wall-Liquid Interactions



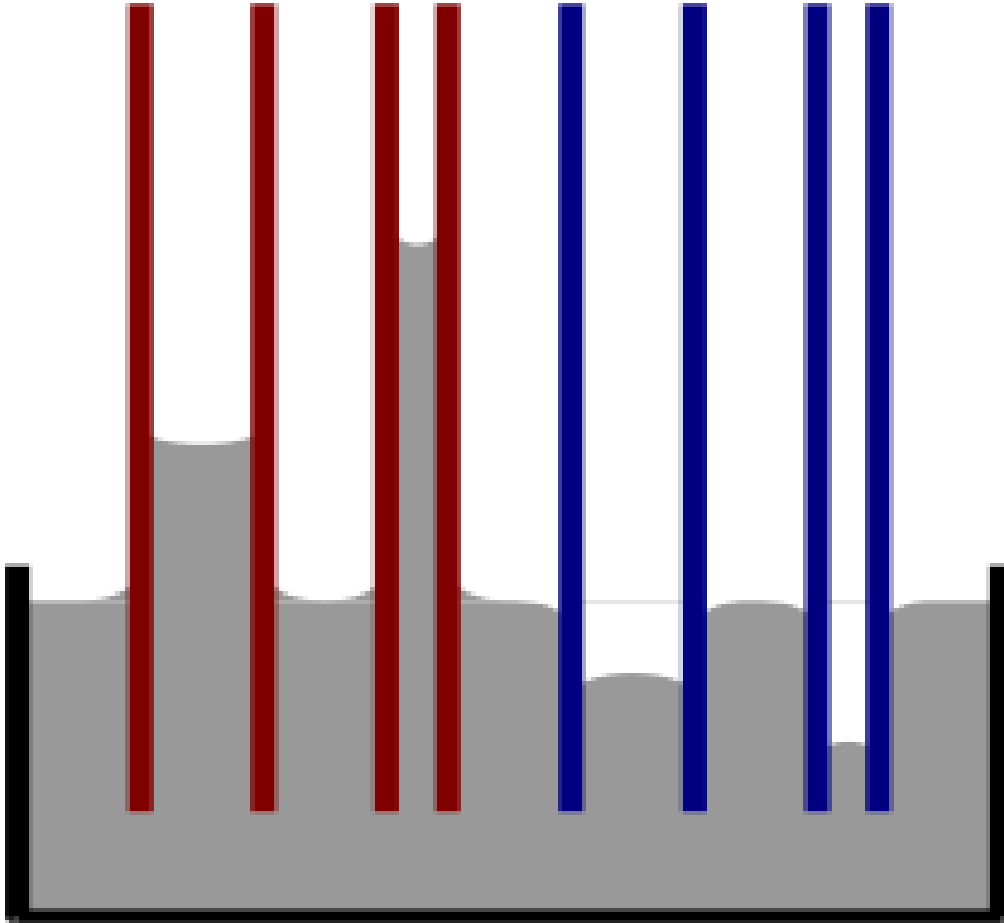
Forces at contact point shown for contact angle greater than 90° (left) and less than 90° (right)

Typically:

$$\gamma_{la} > \gamma_{ls} - \gamma_{sa} > 0$$

Liquid	Solid	Contact angle
<u>water</u>	soda-lime glass lead glass fused quartz	0°
<u>ethanol</u>		
<u>diethyl ether</u>		
<u>carbon tetrachloride</u>		
<u>glycerol</u>		
<u>acetic acid</u>		
<u>water</u>	paraffin wax	107°
	silver	90°
<u>methyl iodide</u>	soda-lime glass	29°
	lead glass	30°
	fused quartz	33°
<u>mercury</u>	soda-lime glass	140°
Some liquid-solid contact angles ^[5]		

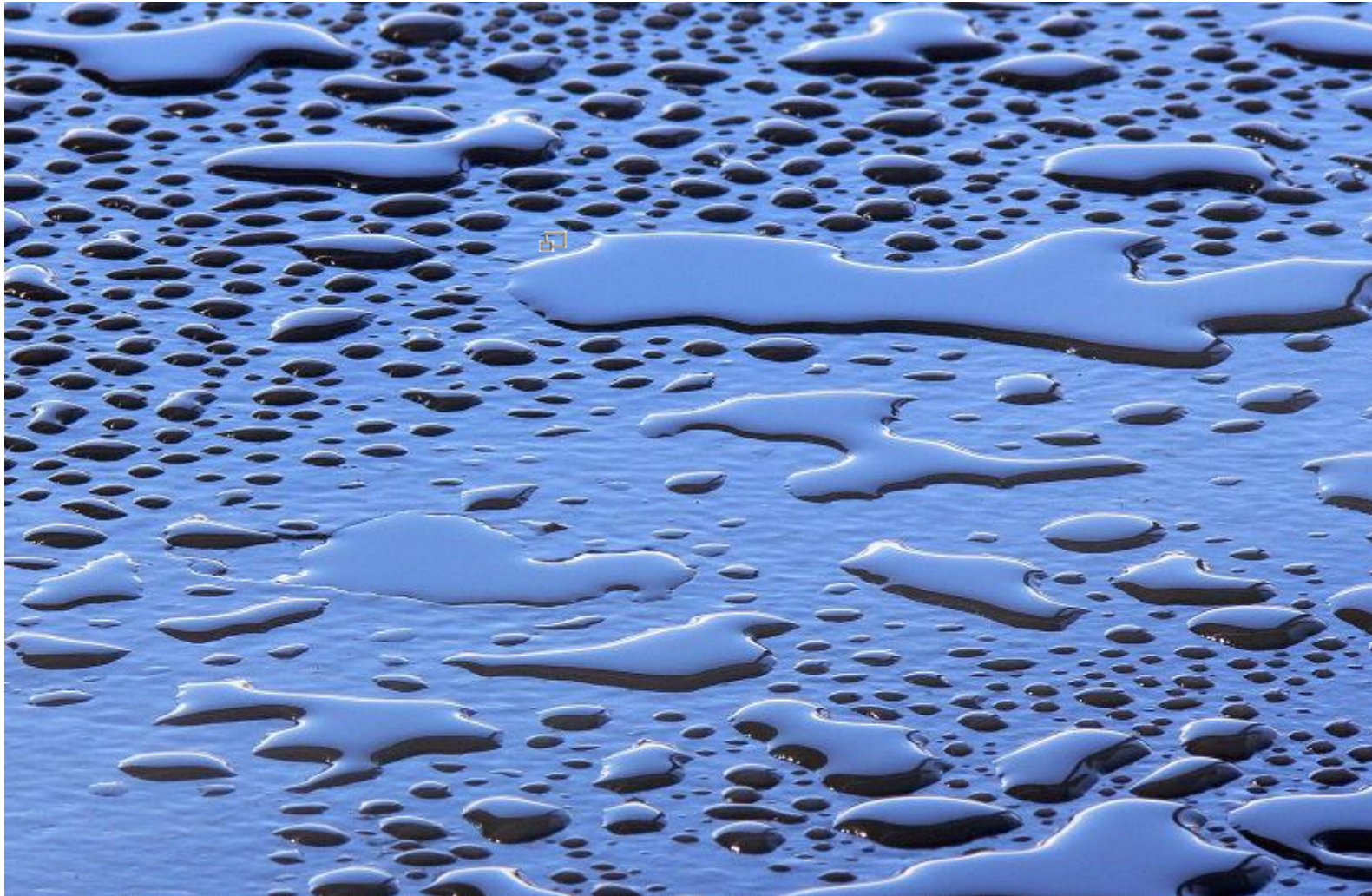
Measuring surface tension



$$h = (2 \gamma_{la} \cos \theta) / (\rho g r)$$

Illustration of capillary rise and fall.
Red: contact angle less than 90° ;
Blue=contact angle greater than 90°

What is the height of a “puddle”?



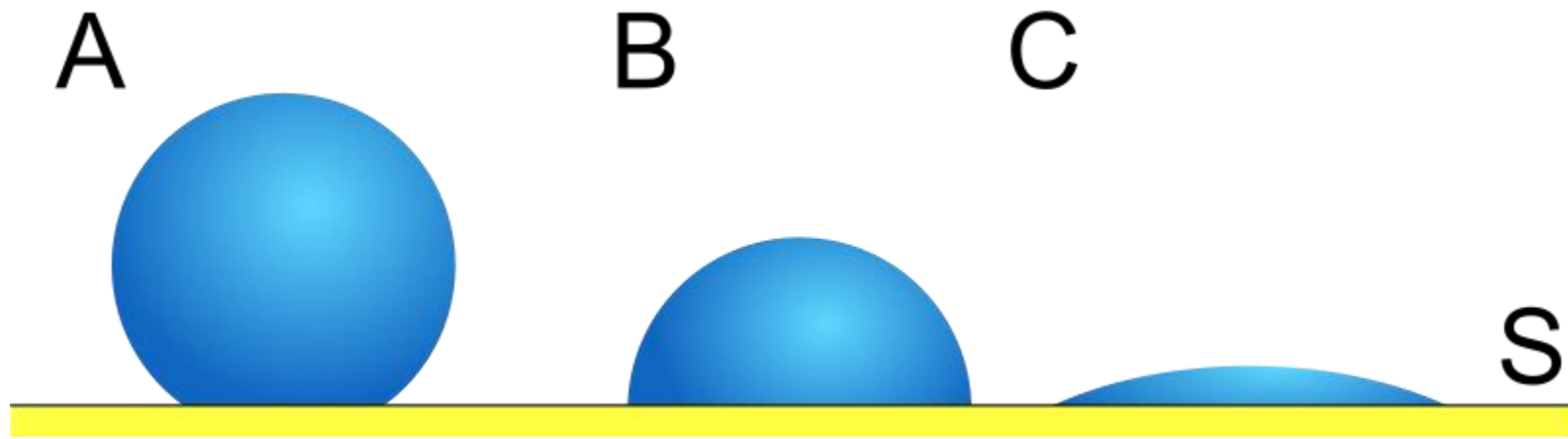


Illustration of how lower contact angle leads to reduction of puddle depth

$$h = 2\sqrt{\frac{\gamma}{g\rho}}$$

$$h = \sqrt{\frac{2\gamma_{la}(1 - \cos\theta)}{g\rho}}$$

For water on paraffin at 25°C $\theta=107^\circ$ $\gamma_{H_2O} = 72 \frac{\text{dyn}}{\text{cm}}$ $\rho_{H_2O} = 1.0 \frac{\text{g}}{\text{cm}^3}$ $h_{H_2O} = 0.44 \text{ cm}$
 For mercury on glass: $\theta=140^\circ$ $\gamma_{Hg} = 487 \frac{\text{dyn}}{\text{cm}}$ $\rho_{Hg} = 13.5 \frac{\text{g}}{\text{cm}^3}$ $h_{Hg} = 0.36 \text{ cm}$

What is the pressure inside a bubble?



The pressure inside a soap bubble can be derived from thermodynamic free energy considerations. At constant temperature and particle number, $dT = dN = 0$, the differential Helmholtz free energy is given by

$$dF = -PdV + \gamma dA$$

where P is the difference in pressure inside and outside of the bubble, and γ is the surface tension. In equilibrium, $dF = 0$, and so,

$$PdV = \gamma dA$$

For a spherical bubble, the volume and surface area are given simply by

$$V = \frac{4}{3}\pi R^3 \rightarrow dV = 4\pi R^2 dR$$

and $A = 4\pi R^2 \rightarrow dA = 8\pi R dR$

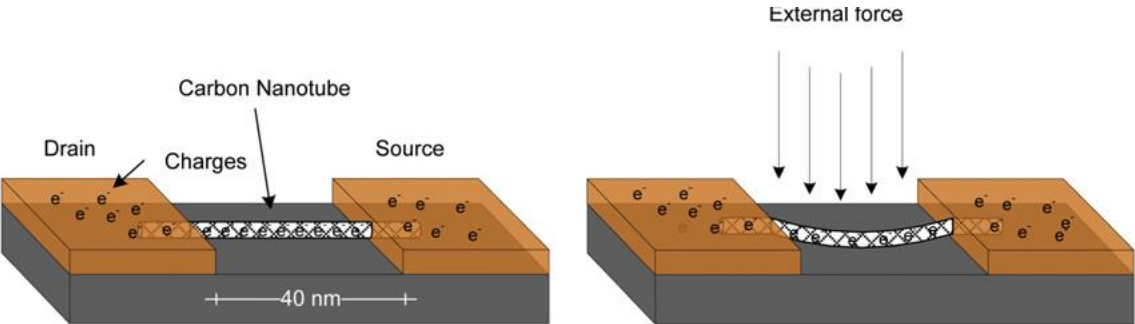
Substituting these relations into the previous expression, we find $P = \frac{2}{R}\gamma$

which is equivalent to the Young-Laplace equation when $R_x = R_y$.

Surface tension of various liquids in dyn/cm against air.
Mixture %'s are by weight; dyne/cm is also called mN/m in S.I. units

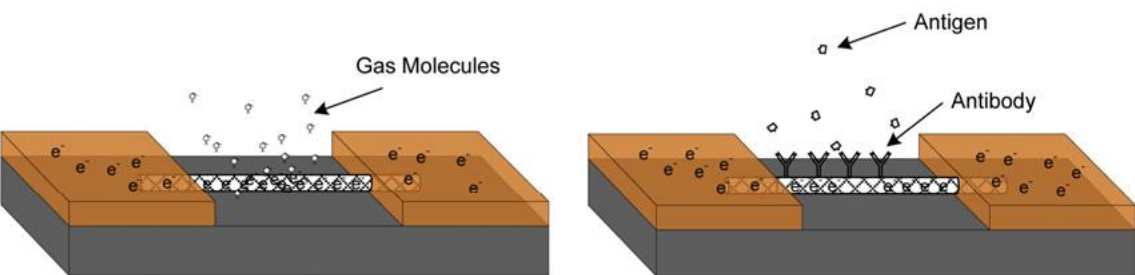
Liquid	Temperature ° C	Surface tension, γ
Acetic acid	20	27.6
Acetic acid (40.1%) + Water	30	40.68
Acetic acid (10.0%) + Water	30	54.56
Acetone	20	23.7
Diethyl ether	20	17
Ethanol	20	22.27
Ethanol (40%) + Water	25	29.63
Ethanol (11.1%) + Water	25	46.03
Glycerol	20	63
n-Hexane	20	18.4
Hydrochloric acid 17.7M aqueous solution	20	65.95
Isopropanol	20	21.7
Mercury	15	487
Methanol	20	22.6
n-Octane	20	21.8
Sodium chloride 6.0M aqueous solution	20	82.55
Sucrose (55%) + water	20	76.45
Water	0	75.64
Water	25	71.97
Water	50	67.91
Water	100	58.85

Video



(a) CNT-based FET transistor.

(b) Physical nanosensor.



(c) Chemical nanosensor.

(d) Biological nanosensor.

