Session 2: Size and surface related phenomena

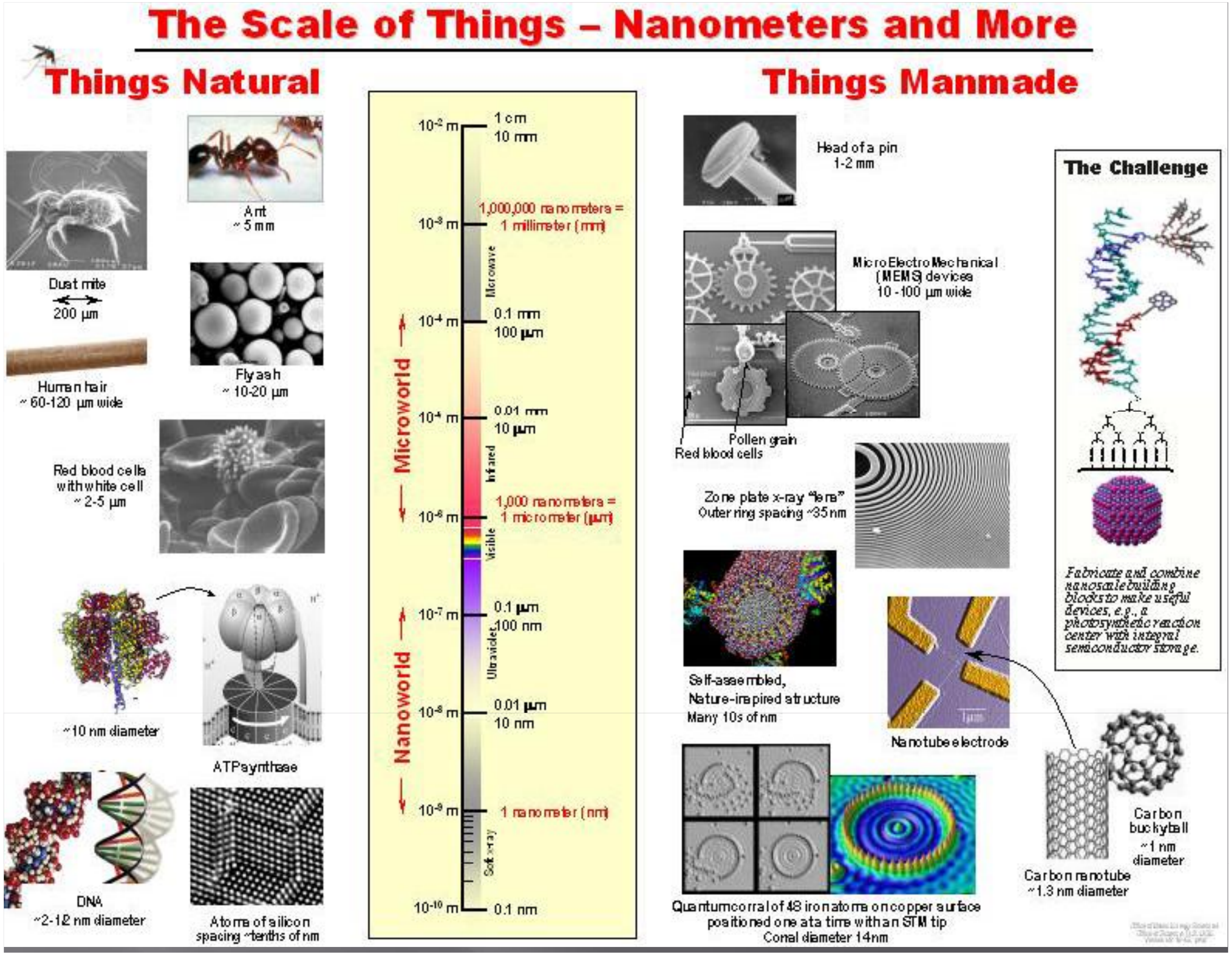
February 7, 2020

Session Objectives

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

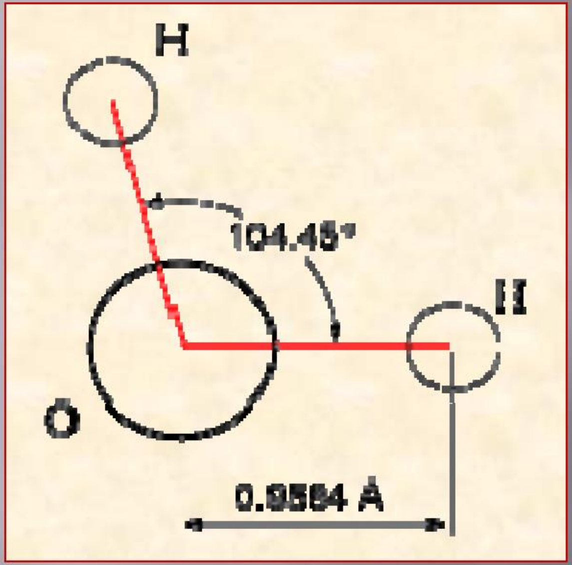

Nanotechnology
Nanomaterials
new
molecular
many
study
devices
developing
nanoparticles
dimensions
technology
scale
materials
nanoscale
nanotech
applications
cells
debate
various
used
whether
solar
concerns
see
size
physics
based
structures
introduction
well
display
sometimes
conventional
Nanomedicine
nanorods
generation
implications
advocacy
lighting
hand
including
science
made
develop
controlling
electronics
medical
much
traditional
special
combats
includes
colloid
Progress
within
nanometers
regulation
least
directly
among
products
impact
global
one
vast
biological
approaches
raises
next
unique
commercial
future
economics
bulk
rise
deals
also
properties
fullerenes
effects
arising
Development
speculation
self-assembly
led
issues
carbon
ing
present
imagj
cost
Generally
diverse
incorporating
semiconductor
flavor
environmental
dimension
dots
Interface
toxicity
doomsday
completely
production
nanotubes
medicine
scenarios
create
groups
control
range
may
extensions
using
warranted
useful
quantum
smaller
investigating
energy
matter
shortened
given
governments
Silicon
involves
atomic
potential
subfields
ranging
device

Applications of Nanotechnology



http://www.nano.gov/html/facts/The_scale_of_things.html

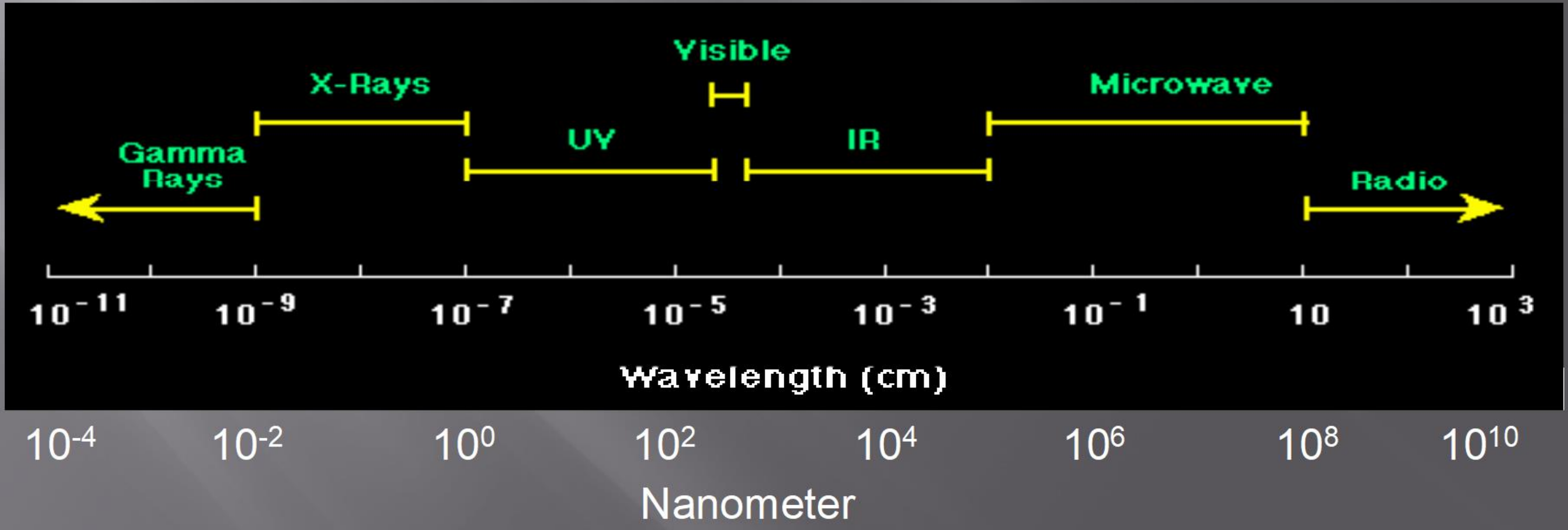
Scale of things



C-C bond – 1.5 angstroms

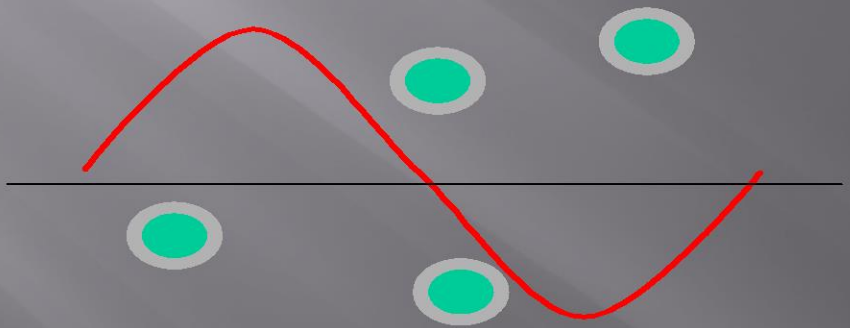
C-H bond – 1.1 angstroms

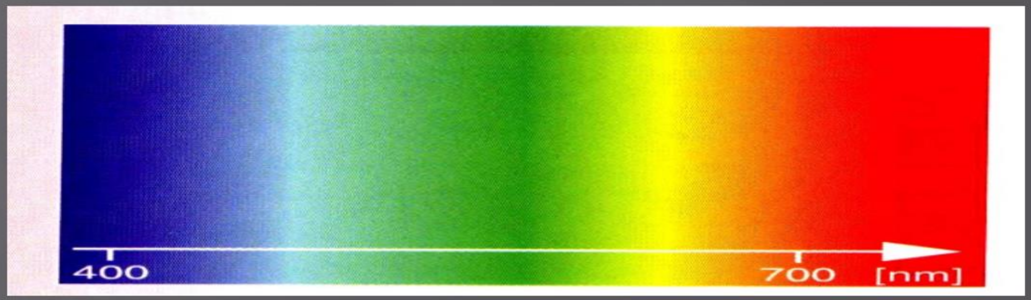
Ethanol: CH_3-CH_2OH



Nanocomposites: Optical Clarity

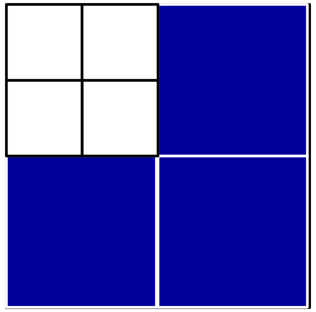
- Size and refractive index of particles are important
- Nanoparticles are smaller than the wavelength of visible light; reduces chance of light scattering





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

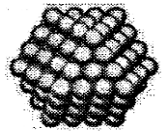
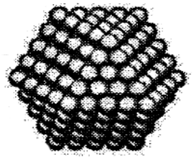
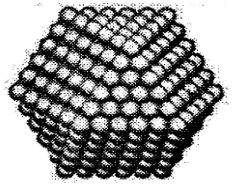
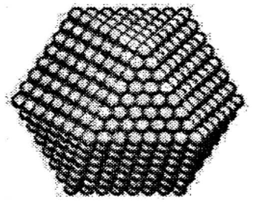
Surface Area

Volume= $4/3\ \pi\ r^3$

Surface area= $4\ \pi\ r^2$

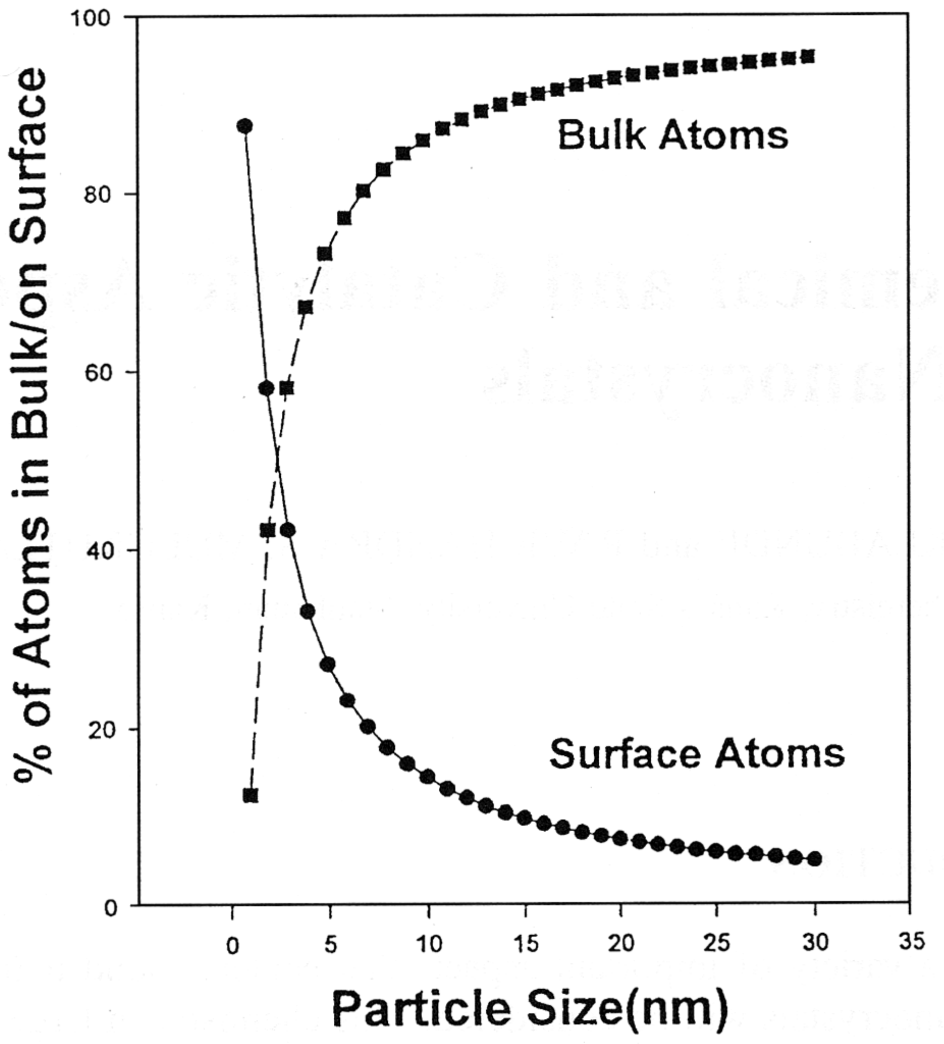
If the density of TiO_2 is 4 grs/cm^3, and	What is the	What is the	What is the
If the particle diameter is:	**# particles per gram?**	**Surface area per gram?**	**Surface area per volume?**
200			
20			
2			

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

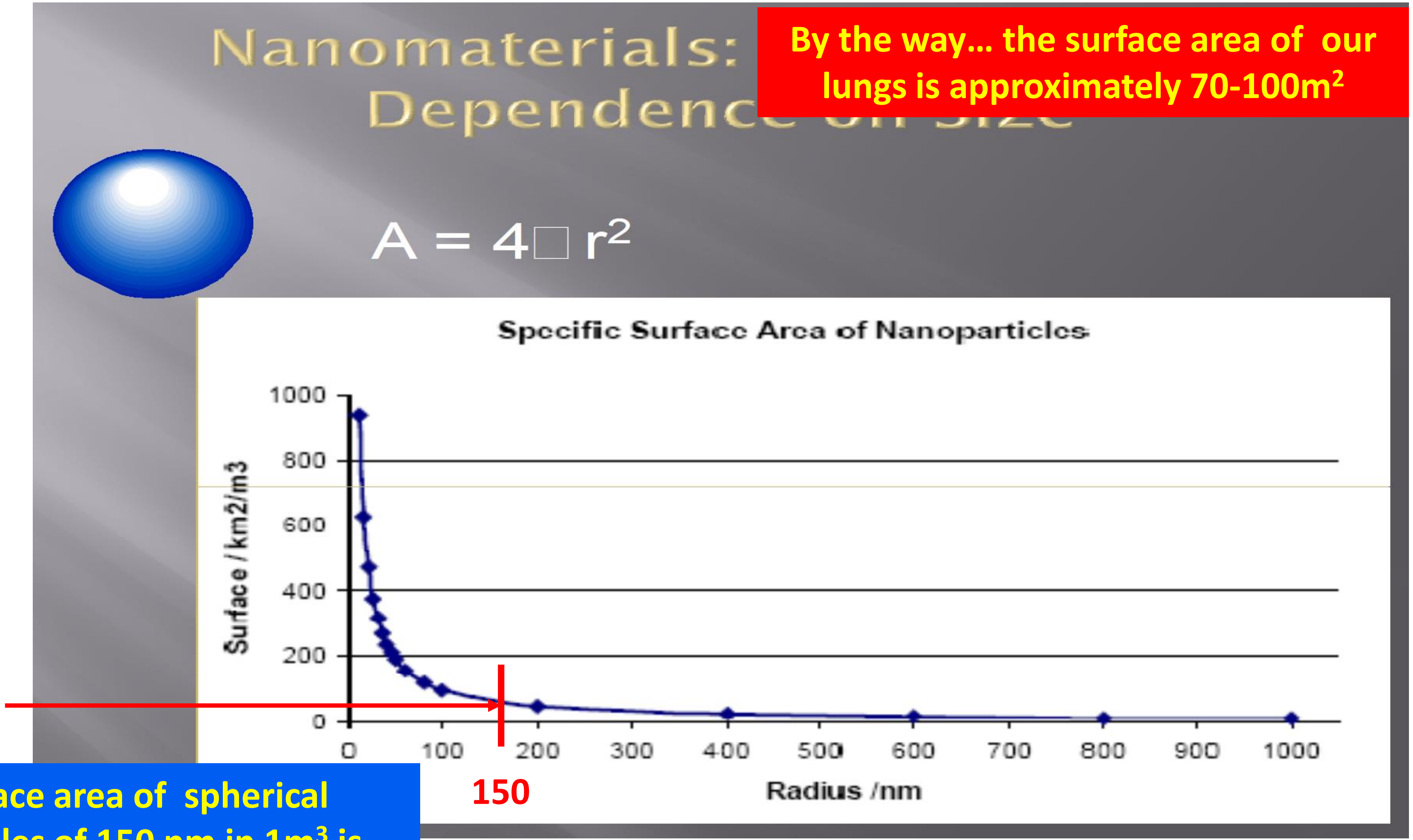
Surface to Bulk Atoms Ratio

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



Surface Area Dependence on Size

59,1 km²



By the way... the surface area of our lungs is approximately 70-100m^2

The surface area of spherical nanoparticles of 150 nm in 1m^3 is approximately equivalent to

Surface Material Content

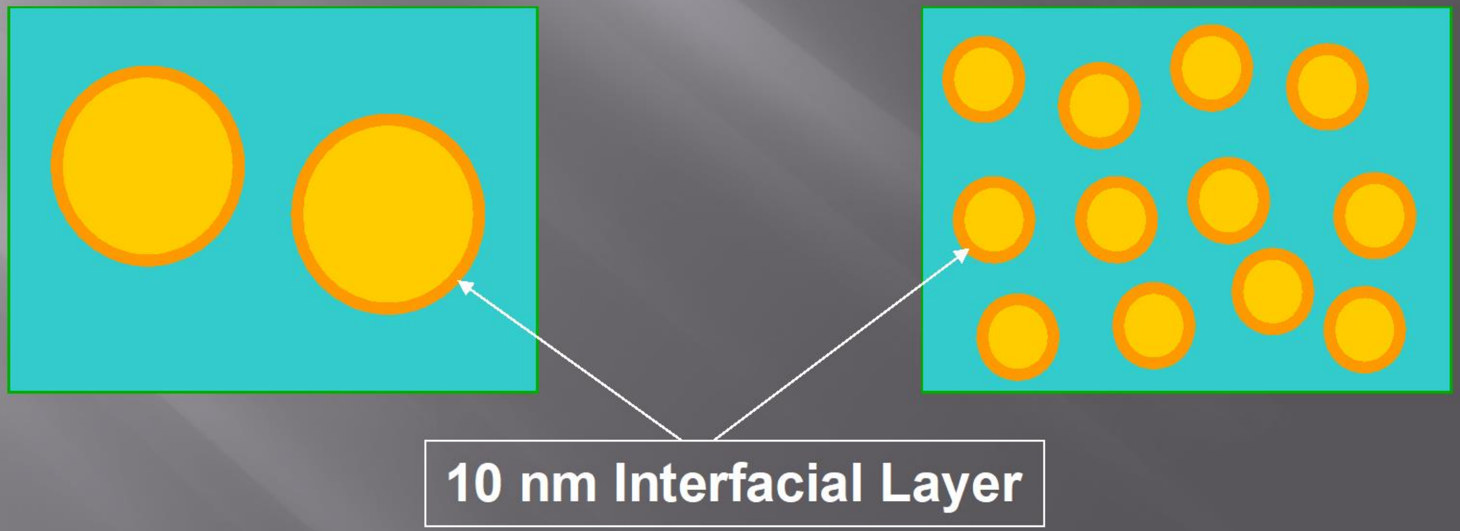
A particle of 10 nm diameter has 20% of its atoms on the surface

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

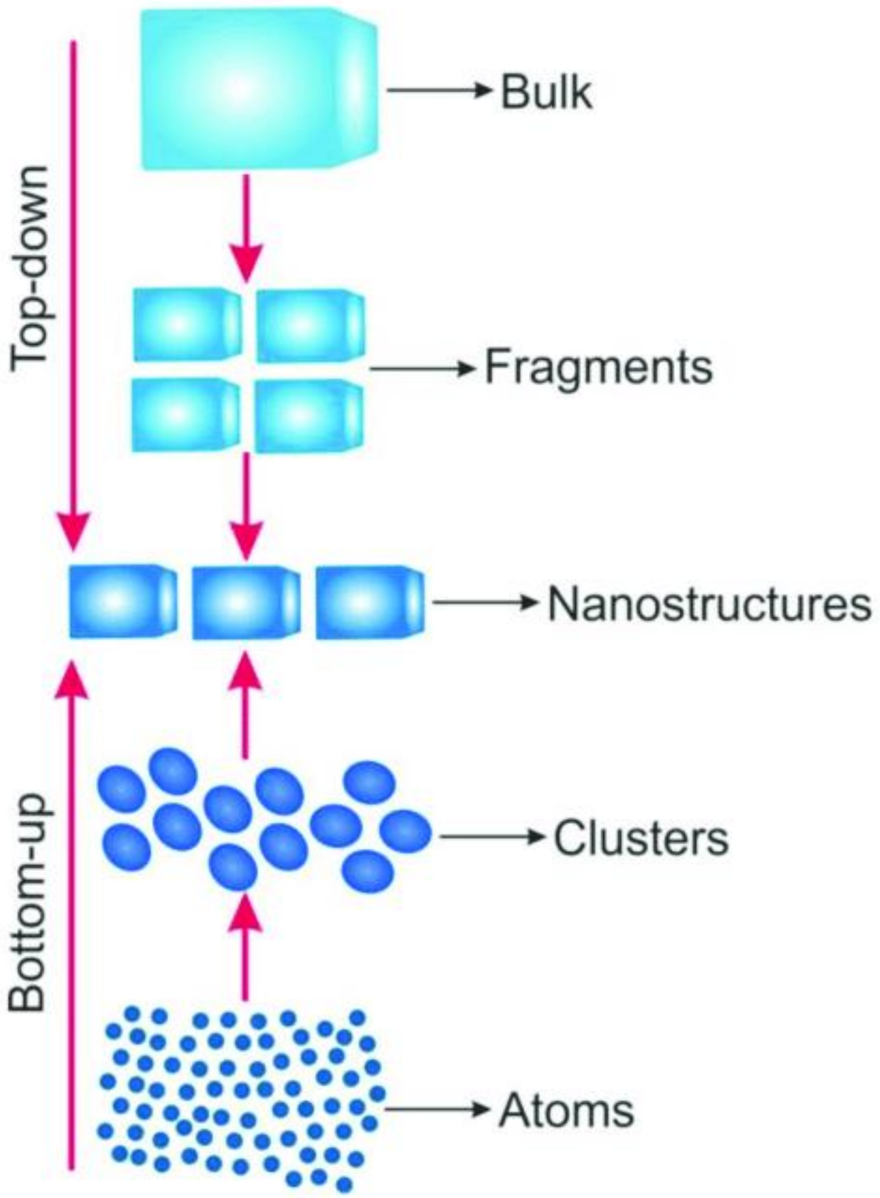
Interfacial Material Content

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



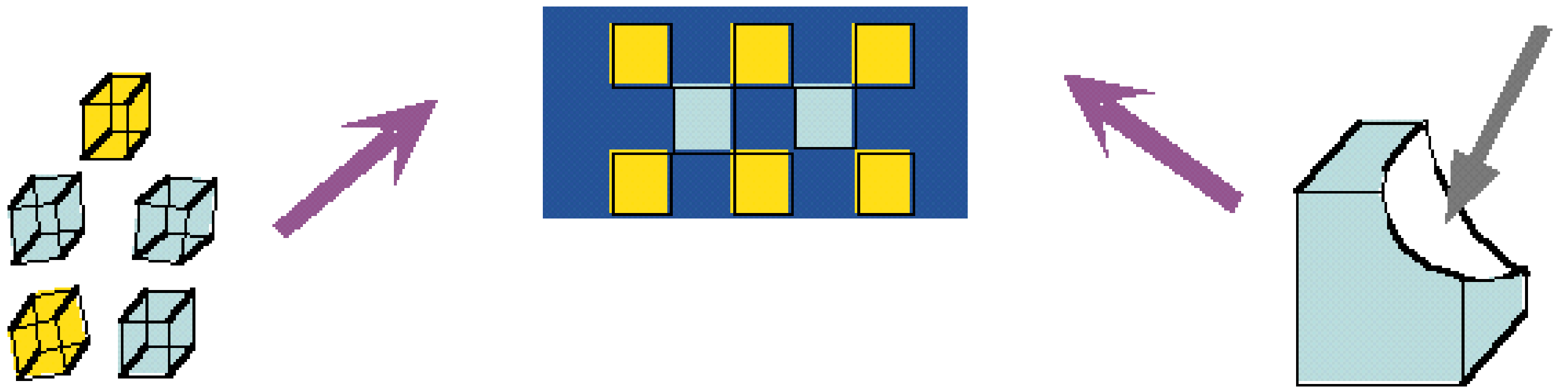
Dispersed particle volume fraction is 0.3 in all cases

Fabrication Methods



Galstyan, Vardan & Bhandari, Manohar & Sberveglieri, Veronica & Sberveglieri, Giorgio & Comini, Elisabetta. (2018). Metal Oxide Nanostructures in Food Applications: Quality Control and Packaging. Chemosensors. 6. 16. 10.3390/chemosensors6020016.

Nanostructured Material

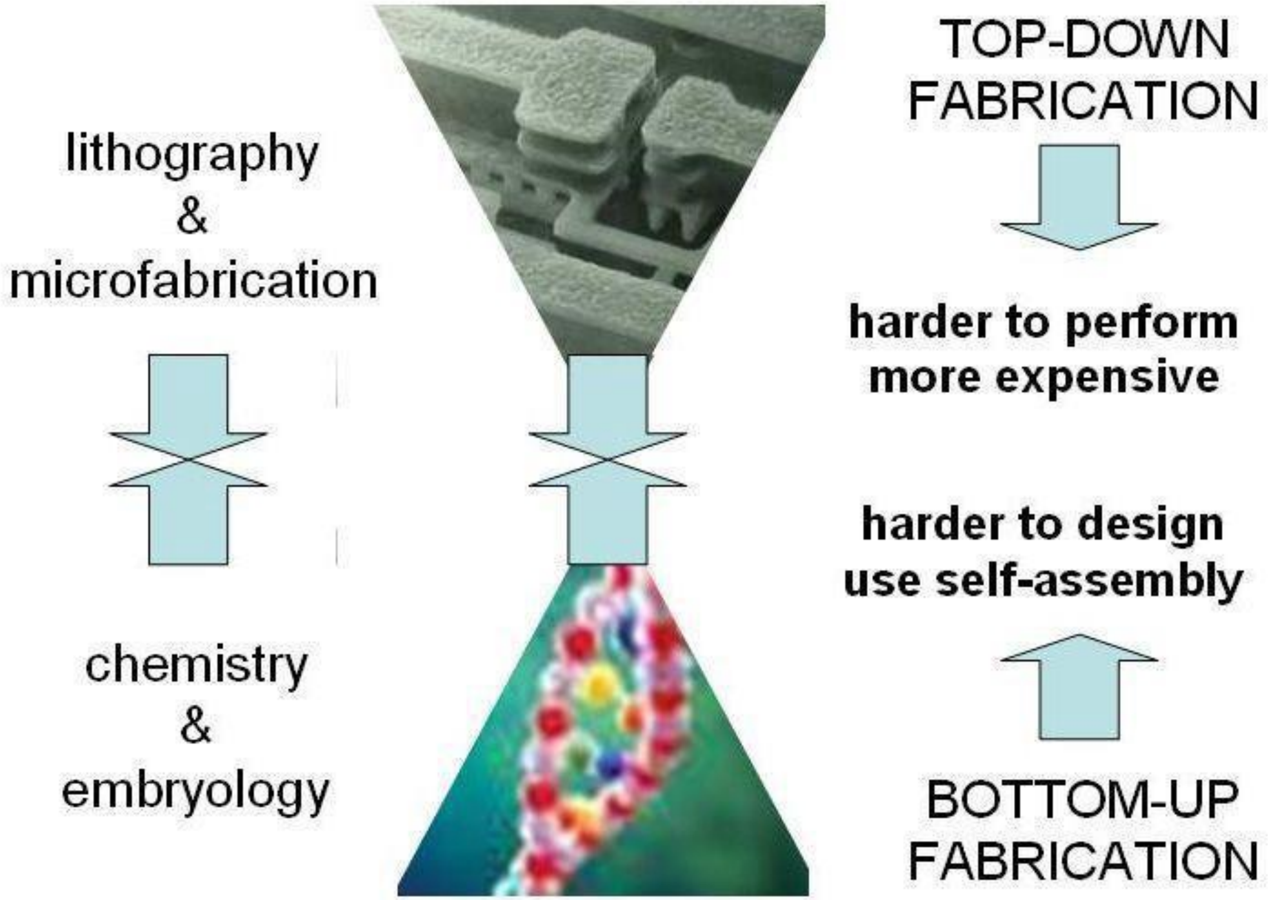


Assemble from
Nano- building Blocks

'Sculpt' from Bulk

CHAPTER 2: SYNTHESIS and ASSEMBLY Evelyn L. Hu (*University of California, Santa Barbara*); David T. Shaw (*State University of New York, Buffalo*) http://www.wtec.org/loyola/nano/fh02_01.gif

Top Down vs. Bottom Up



***Nano sensors and Nano fabrication* —** A World so Small, Made Big;
https://medium.com/@Farah_36879/nano-sensors-and-nano-fabrication-a-world-so-small-made-big-9a44c32321c0

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 partricles, 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

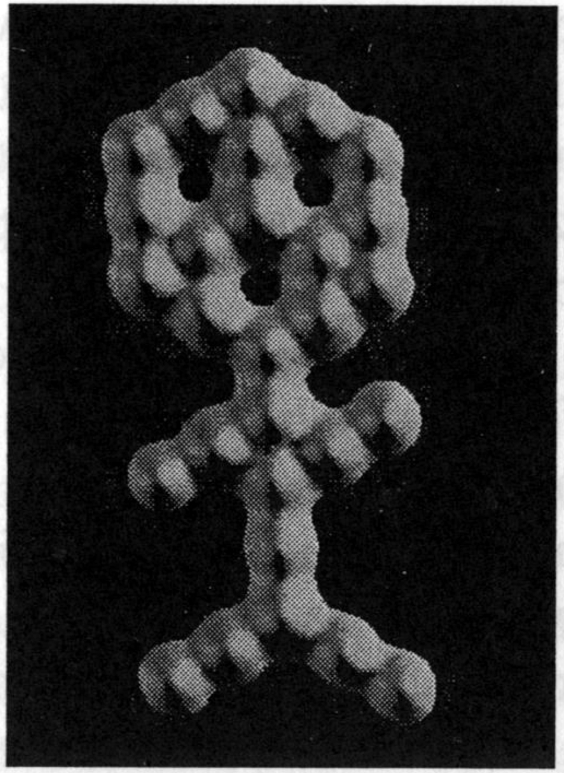


Fig. 1.6. A molecular person consisting of 14 carbon monoxide molecules arranged on a metal surface fabricated and imaged by scanning tunneling microscopy. [P. Zeppenfeld & D.M. Eigler, *New Scientist* **129,** 20 (23 February 1991), and http://www.almaden.ibm.com/vis/stm/atomo.html]

Properties

Mechanical

Electrical

Physical

Optical

Thermal

Chemical

Quantum

Some physical properties affected by size

Nanomaterials exhibits 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).

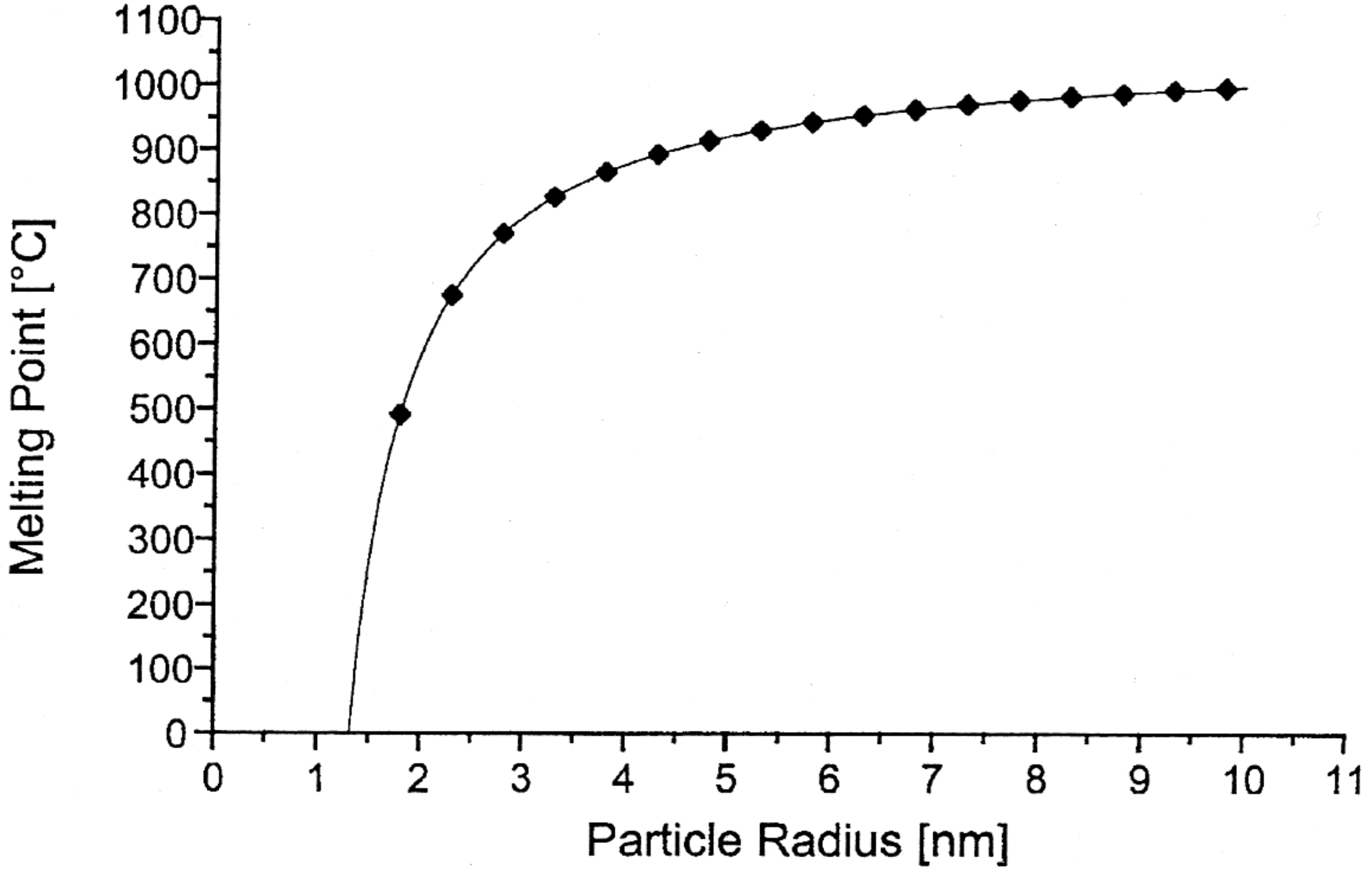
Melting point of Au nanoparticles

diameter	Tm
bulk	1,064℃
20 nm	~ 990℃
5 nm	~ 850℃
4 nm	~ 750℃
2 nm	~ 330℃

Eg of Si materials

diameter	Eg
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



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

Source: Nanoscale Materials in Chemistry, Wiley, 2001

- Why ?
- Penomenon?

Melting Point Dependence on Particle Size

- Lowering of the melting point is proportional to 1/r

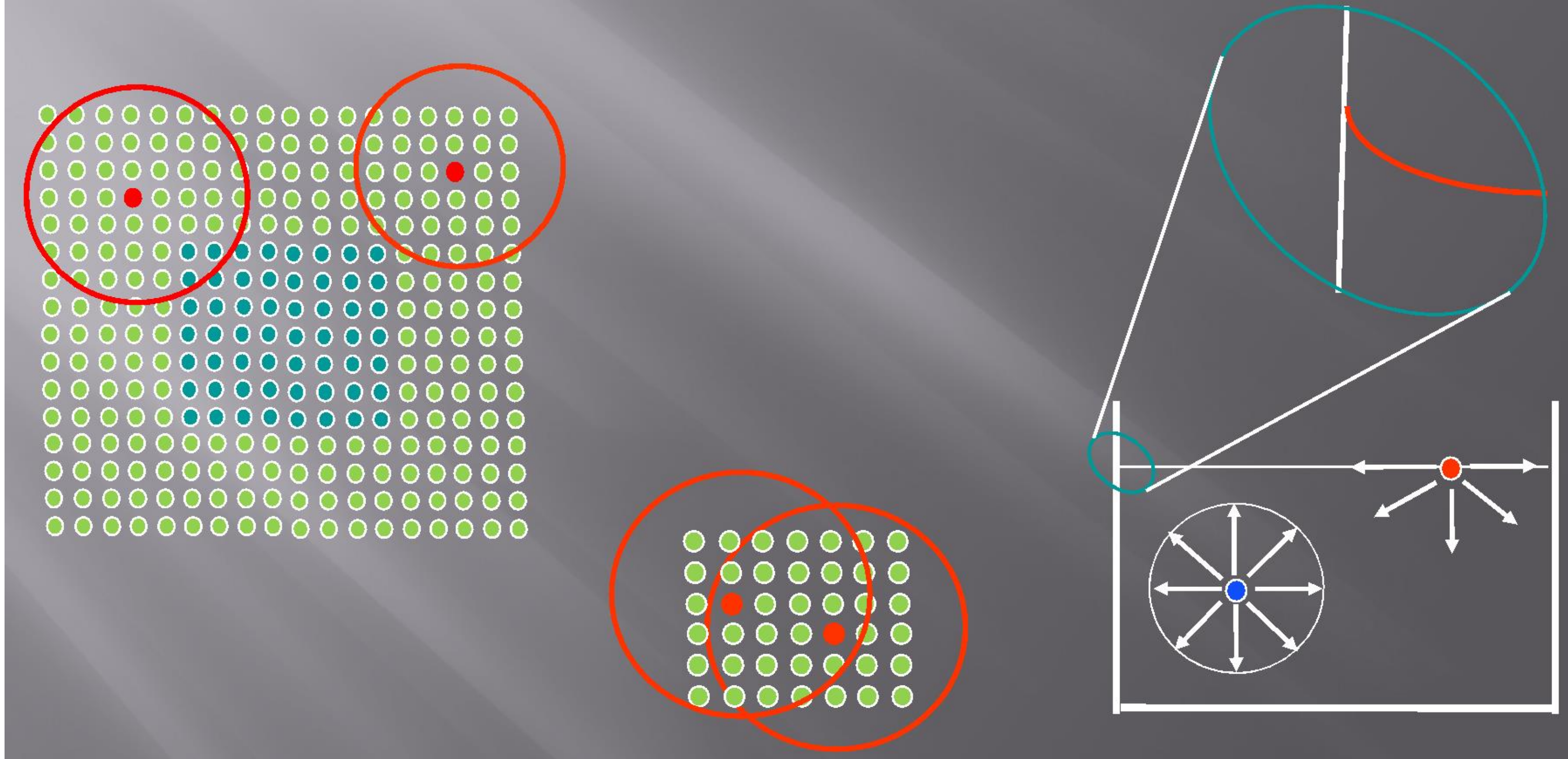
- ΔT can be as large as couple of hundred degrees when the particle size gets below 10 nm

- 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



Bulk properties are not scalable to nanoscale

Challenges in Nanotechnology

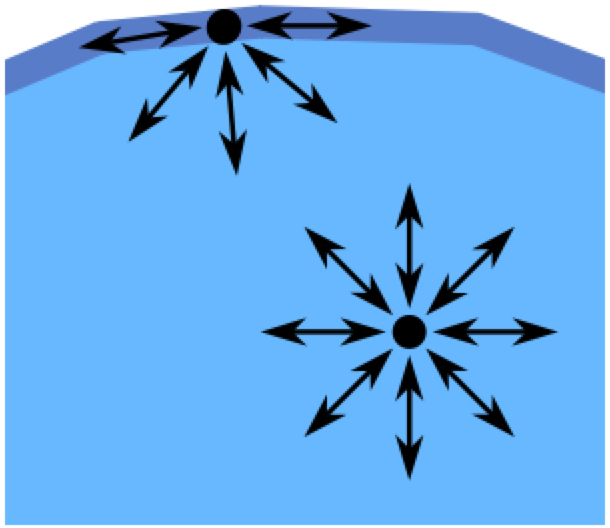
- Overcome the huge surface energy, a result of enormous surface area or large surface to volume ratio.

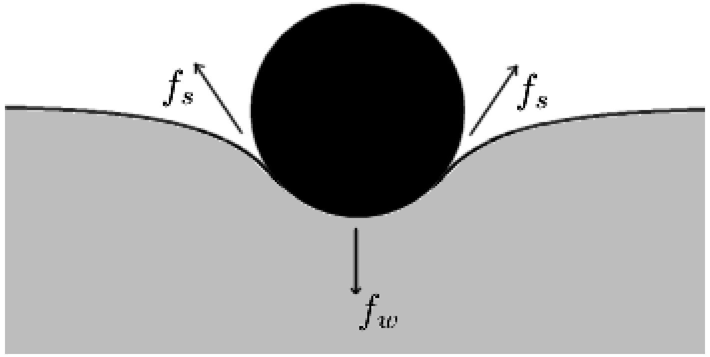
- Ensure all nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure, that all together result in desired physical properties.

- Prevent nanomaterials and nanostructures from coarsening through either Ostwald ripening or agglomeration as time evolutes.

Recess

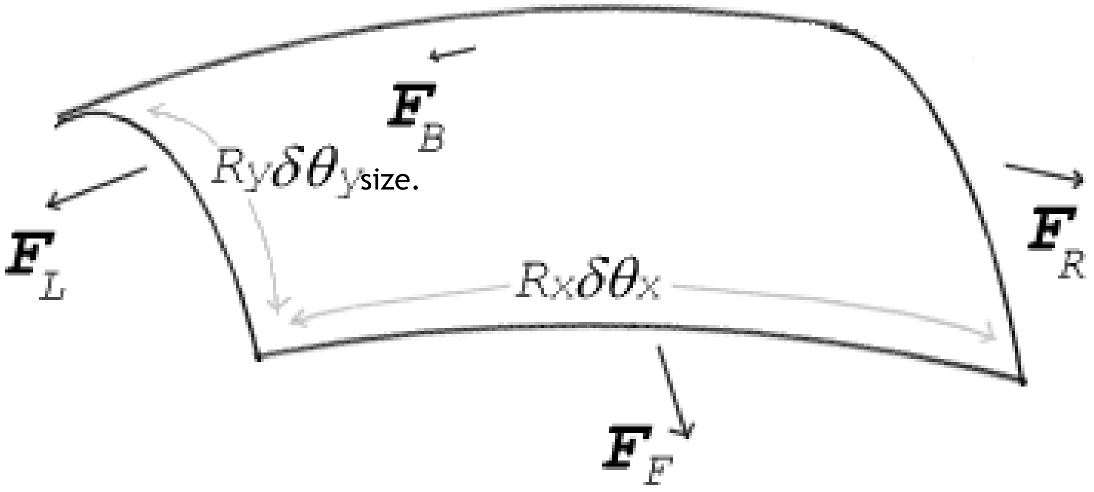
Surface Tension





http://en.wikipedia.org/wiki/Surface_tension

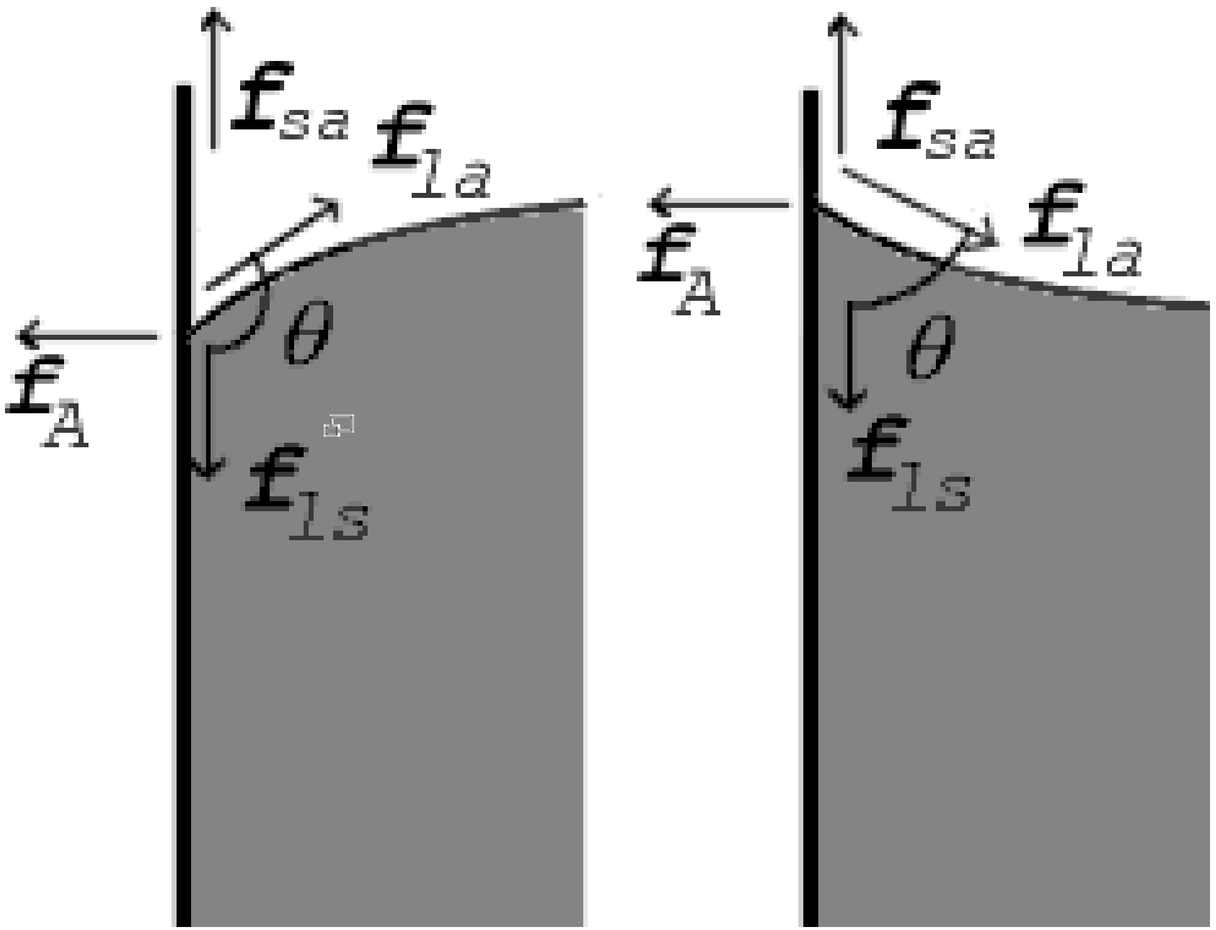
Young-Laplace equation



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

Δp for water drops of different radii at STP				
Droplet radius	1 mm	0.1 mm	1 μm	10 nm
Δp (atm)	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)

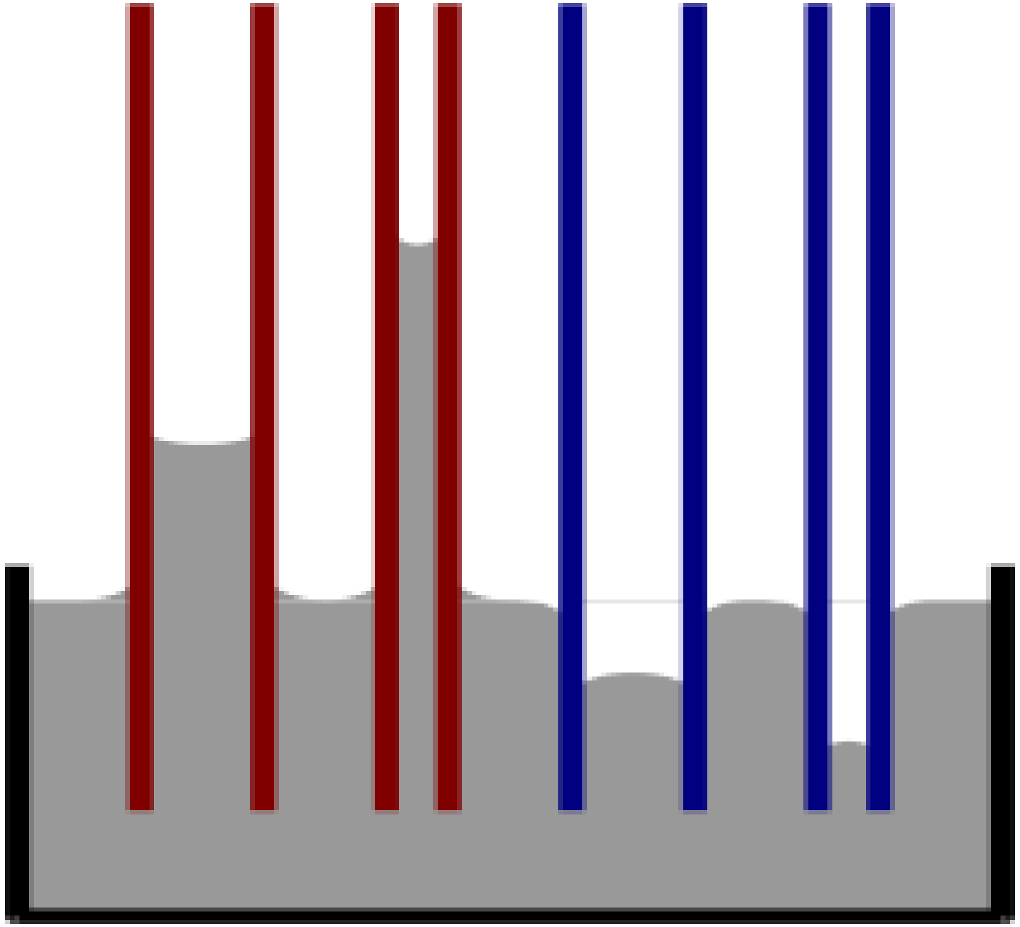
Typically:

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

Liquid	Solid	Contact angle
water	soda-lime glass	0°
ethanol	lead glass	
diethyl ether	fused quartz	
carbon tetrachloride		
glycerol		
acetic acid		
water	paraffin wax	107°
	silver	90°
methyl iodide	soda-lime glass	29°
	lead glass	30°
	fused quartz	33°
mercury	soda-lime glass	140°

Some liquid-solid contact angles[5]

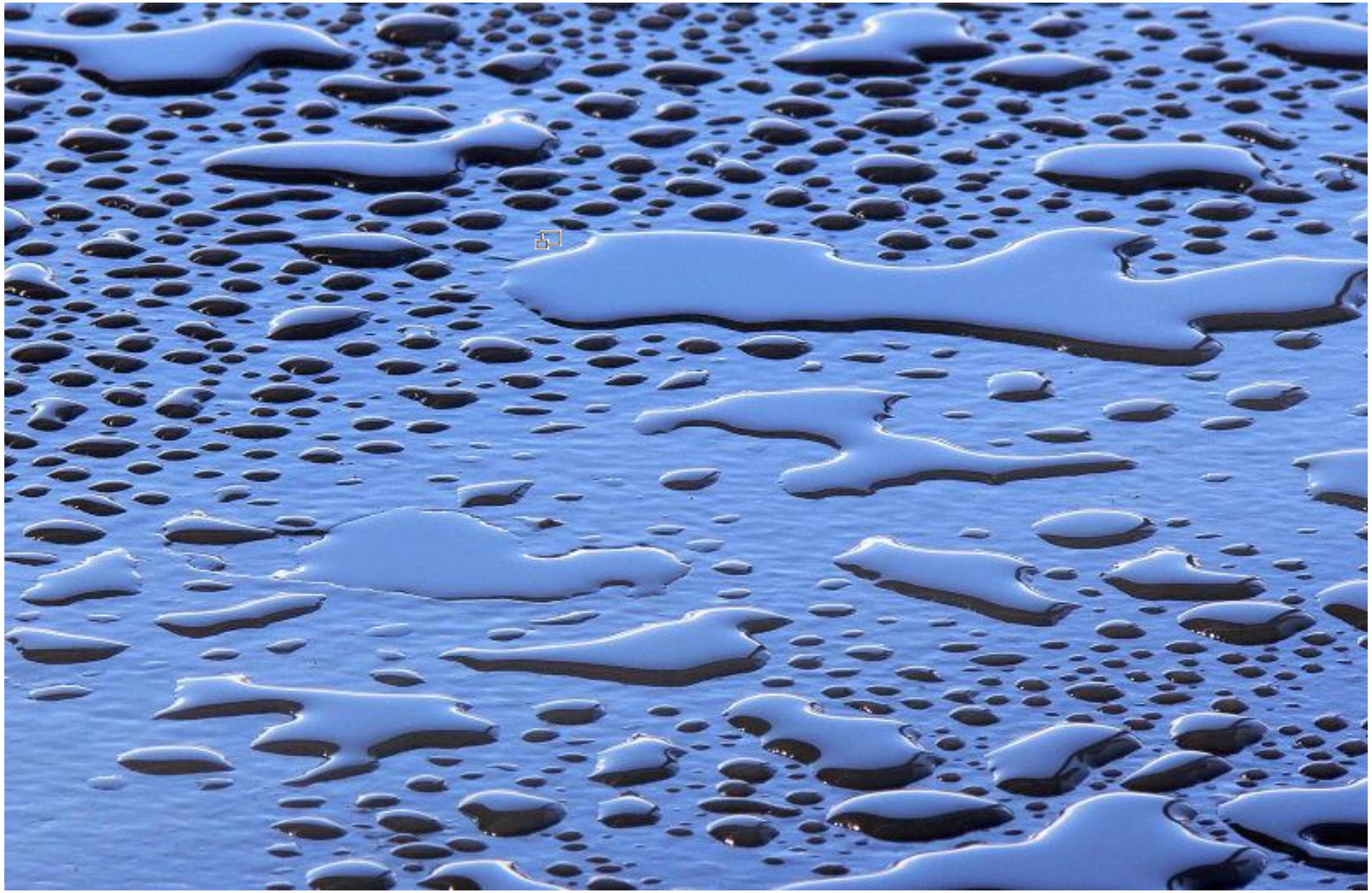
Measuring surface tension



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

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”?



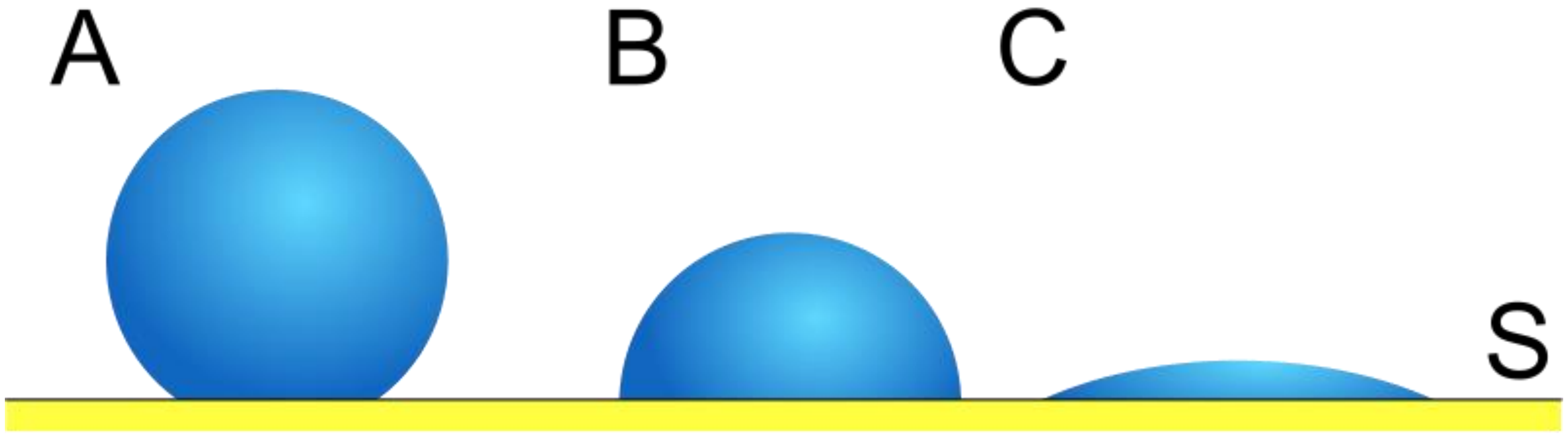


Illustration of how lower contact angle leads to reduction of puddle depth

$$h = 2\sqrt{\frac{\gamma}{g\rho}} \qquad\qquad h = \sqrt{\frac{2\gamma_{\mathrm{la}}\left(1-\cos\theta\right)}{g\rho}}.$$

For water on paraffin at 25^{o}C $\theta = 107°$ $\gamma_{\mathrm{H_2O}} = 72\ \frac{\mathrm{dyn}}{\mathrm{cm}}$ $\rho_{\mathrm{H_2O}} = 1.0\ \frac{\mathrm{g}}{\mathrm{cm}^3}$ $h_{\mathrm{H_2O}} = 0.44\ \mathrm{cm}$

For mercury on glass: $\theta = 140°$ $\gamma_{\mathrm{Hg}} = 487\ \frac{\mathrm{dyn}}{\mathrm{cm}}$ $\rho_{\mathrm{Hg}} = 13.5\ \frac{\mathrm{g}}{\mathrm{cm}^3}$ $h_{\mathrm{Hg}} = 0.36\ \mathrm{cm}$

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 equilbrium, $dF = 0$, 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

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

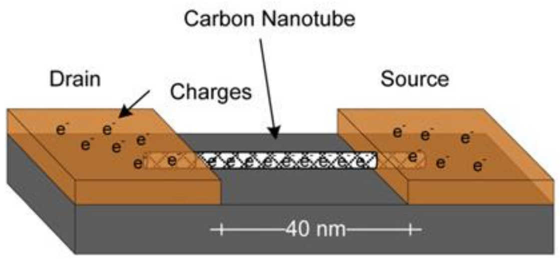
Substituting these relations into the previous expression, we find $P = \frac{2}{R}\gamma$

which is equivalent to the Young-Laplace equation when Rx = Ry.

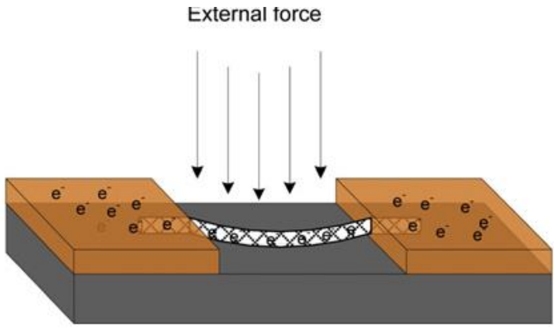
Surface tension of various liquids in dyn/cm against air.
Mixture %'s are by weight; dyne/cm is also called mN/m in S.I. units

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

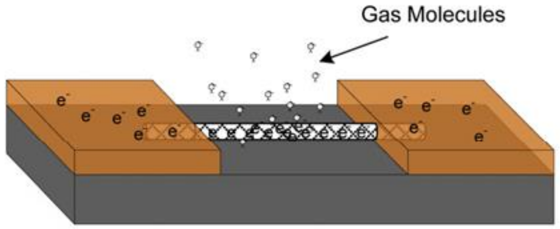
Video



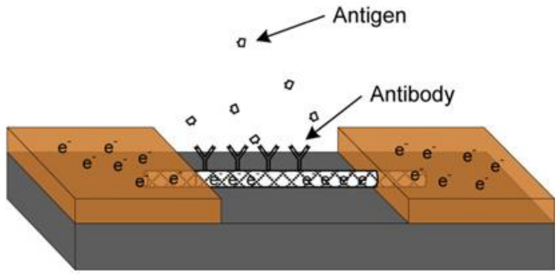
(a) CNT-based FET transistor.



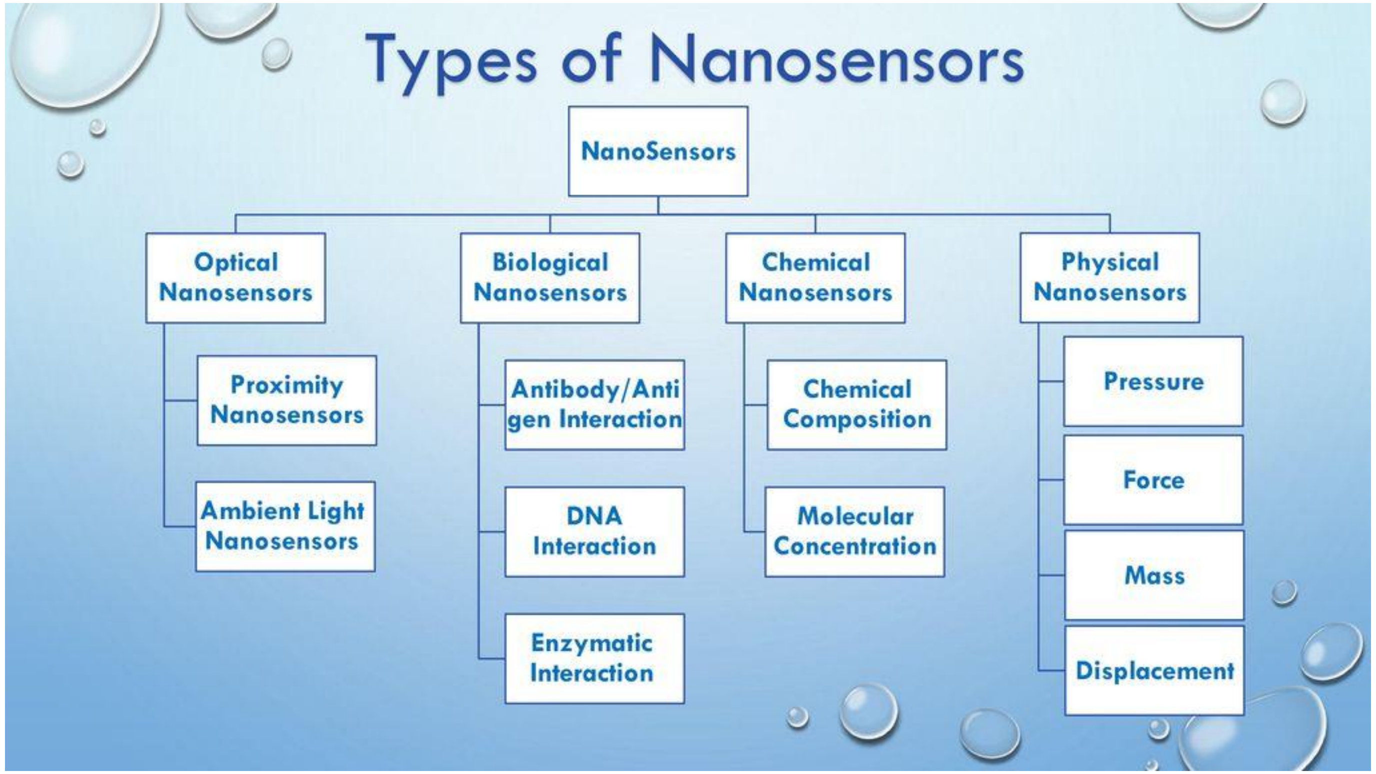
(b) Physical nanosensor.



(c) Chemical nanosensor.



(d) Biological nanosensor.



Nano sensors and Nano fabrication — A World so Small, Made Big; https://medium.com/@Farah_36879/nano-sensors-and-nano-fabrication-a-world-so-small-made-big-9a44c32321c0