Chapter 2. Size and Shapes of Nanoparticles

2.1 Size and Shape of Single Particles

(1) Particle shapes and size description

** Particle shapes*

Spherical/cube/angular/cylindrical/acicular/chainlike/fibrous/dendrite etc.

** Primary particles*

Secondary particles:

-Also called agglomerates or aggregates

-Represented by fractal dimension

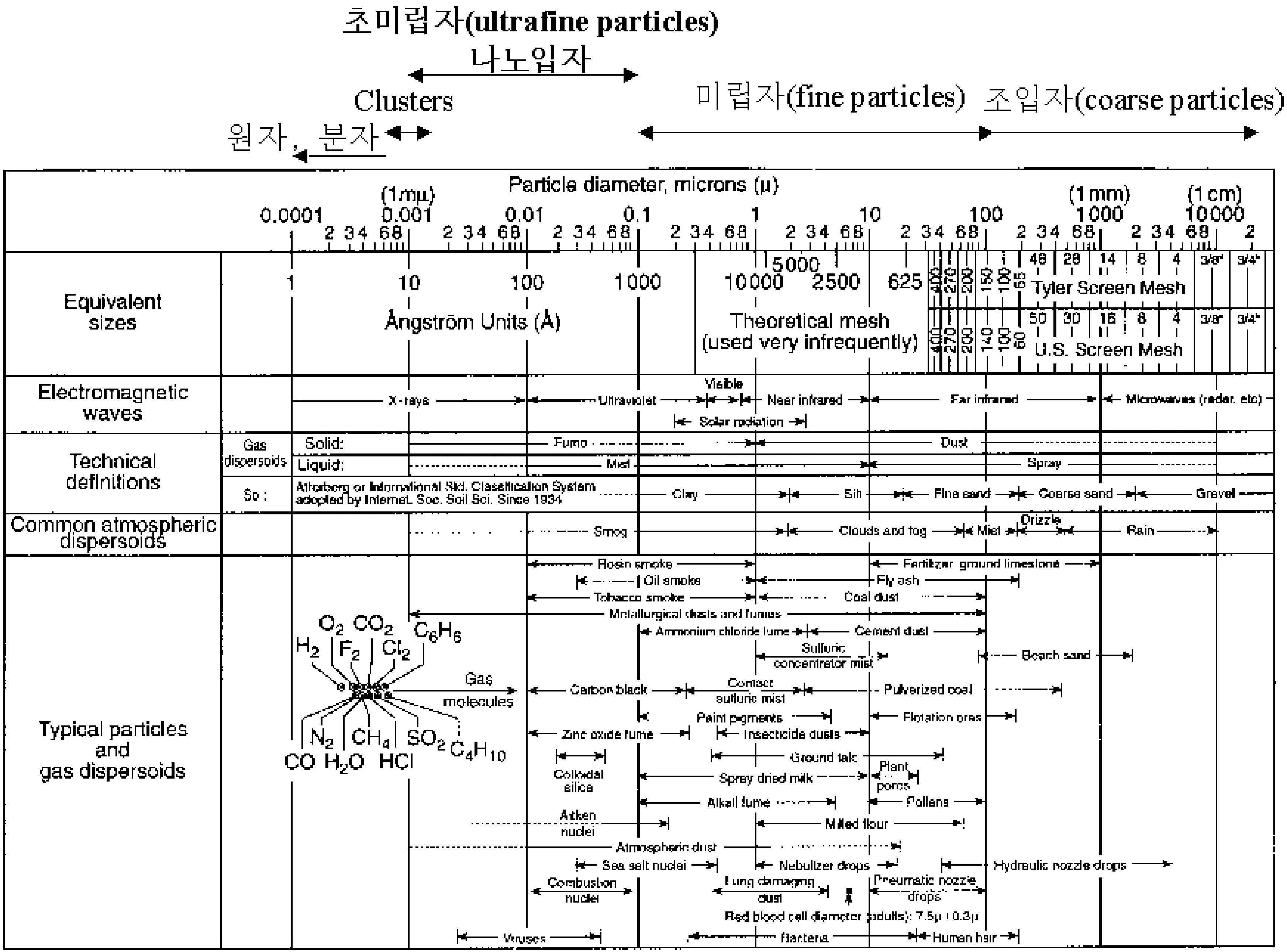
** Particle size*

-Sphere: diameter

-Non-sphere: equivalent diameter

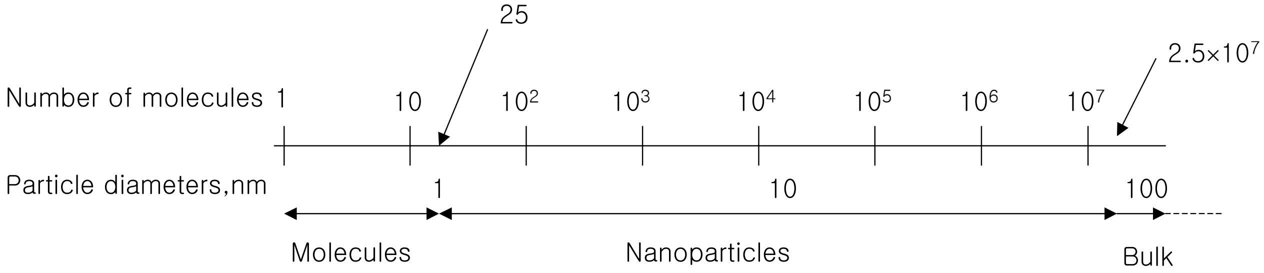
Equivalent diameters	Description	Formula	Remarks
Equivalent volume (sphere) diameter	the diameter of the hypothetical sphere having the same volume as the particle volume	$d_{p,v} = \left(\frac{6V}{\pi} \right)^{1/3}$	
Equivalent surface-volume diameter	the diameter of the hypothetical sphere having the same surface-to-volume ratio as the particle	$d_{p,sv} = \frac{6V}{S}$	
Stokes diameter	the diameter of the hypothetical sphere having the same terminal settling velocity and density as the particle		☞ Later
Aerodynamic diameter	the diameter of the hypothetical unit-density sphere having the same terminal settling velocity as the particle		☞ Later

"Which diameter we use depends on the end use of the information."

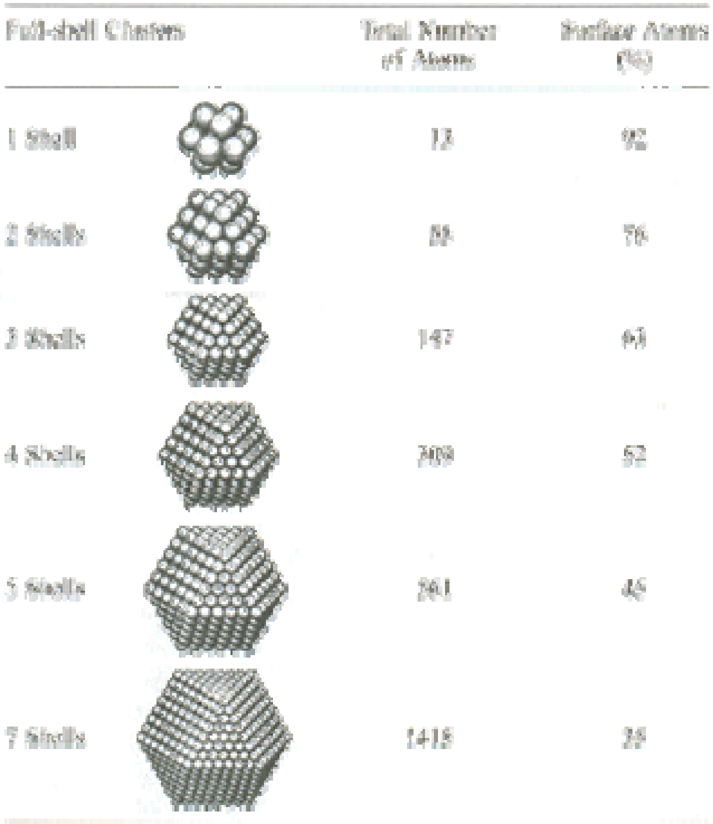


초미립자(ultrafine particles)
나노입자
Clusters
원자, 분자
미립자(fine particles)
조입자(coarse particles)
Particle diameter, microns (μ)
(1 mμ)
(1 mm)
(1 cm)
0.0001
0.001
0.01
0.1
1
10
100
1000
10000
Equivalent sizes
Ångström Units (Å)
Theoretical mesh (used very infrequently)
Tyler Screen Mesh
U.S. Screen Mesh
Electromagnetic waves
X-rays
Ultraviolet
Visible
Near infrared
Far infrared
Microwaves (radar, etc)
Solar radiation
Technical definitions
Gas dispersoids
Solid:
Liquid:
Fume
Dust
Mist
Spray
Soil:
Atterberg or International Std. Classification System adopted by Internat. Soc. Soil Sci. Since 1934
Clay
Silt
Fine sand
Coarse sand
Gravel
Common atmospheric dispersoids
Smog
Clouds and fog
Mist
Drizzle
Rain
Typical particles and gas dispersoids
Rosin smoke
Oil smoke
Tobacco smoke
Metallurgical dusts and fumes
Ammonium chloride fume
Fertilizer, ground limestone
Fly ash
Coal dust
Cement dust
Sulfuric concentrator mist
Beach sand
Carbon black
Contact sulfuric mist
Pulverized coal
Paint pigments
Flotation ores
Zinc oxide fume
Insecticide dusts
Colloidal silica
Ground talc
Spray dried milk
Plant spores
Alkali fume
Pollens
Aitken nuclei
Milled flour
Atmospheric dust
Sea salt nuclei
Nebulizer drops
Hydraulic nozzle drops
Combustion nuclei
Lung damaging dust
Pneumatic nozzle drops
Red blood cell diameter (adults): 7.5μ ± 0.3μ
Viruses
Bacteria
Human hair
Gas molecules
O_2 CO_2 C_6H_6 H_2 F_2 Cl_2
N_2 CH_4 SO_2 C_4H_{10}
CO H_2O HCl

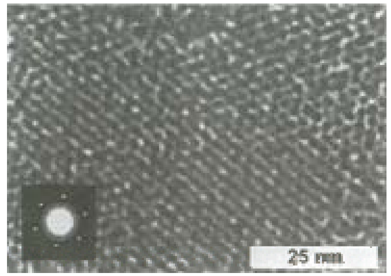
(2) Particle size and constituent atoms (molecules)



* Full shell clusters



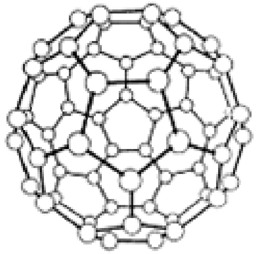
Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35



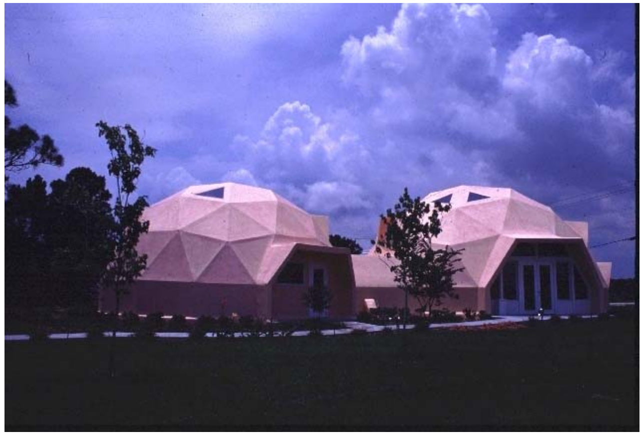
Hexagonal monolayer of Au55 nanoparticles on Poly(vinylpyrrolidone

(3) Size and shape of specific particles

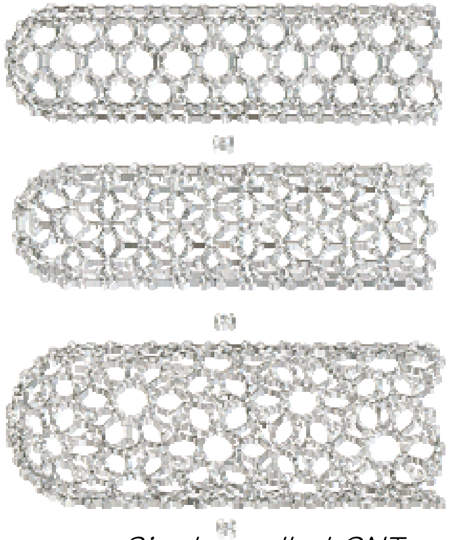
** Fullerene-* *named after the architect, Buckminster Fuller, who designed "Geodesic dome"*



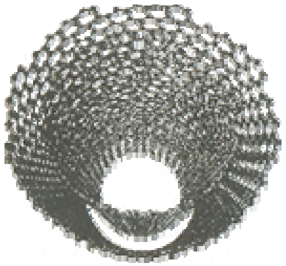
C60- buckminsterfullerene



** Carbon nanotube*



Single-walled CNT
(a) armchair; (b)zigzag; (c)chiral structures



Multi-walled CNT

* *Polymers*

$$V = 0.001661 \frac{M_W}{\rho} \quad nm^3 \quad \text{where } M_w, \rho \text{ in cgs unit}$$

$$\therefore d_v = 0.1469 \left(\frac{M_W}{\rho} \right)^{1/3} \quad nm$$

* *Biological substance*

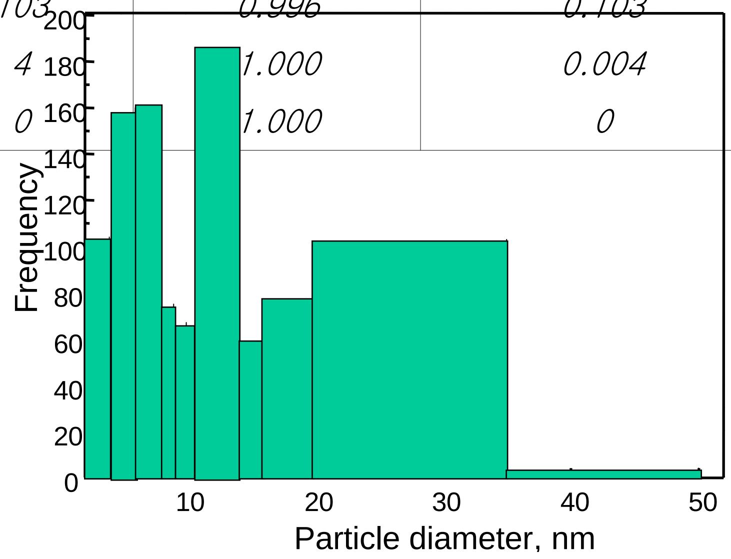
Class	Material	M_w (Da)	Size d (nm)
Amino acids	Glycine (smallest amino acid)	75	0.42
	Tryptophan (largest amino acid)	246	0.67
Nucleotides	Cytosine monophosphate (smallest DNA nucleotide)	309	0.81
	Guanine monophosphate (largest DNA nucleotide)	361	0.86
	Adenosine triphosphate (ATP, energy source)	499	0.95
Other molecules	Steric acid $C_{17}H_{35}CO_2H$	284	0.87
	Chlorophyll, in plants	720	1.1
Proteins	Insulin, polypeptide hormone	6,000	2.2
	Hemoglobin, carries oxygen	68,000	7.0
	Albumin, in white of egg	69,000	9.0
	Elastin, cell-supporting material	72,000	5.0
	Fibrinogen, for blood clotting	400,000	50
	Lipoprotein, carrier of cholesterol (globular shape)	1,300,000	20
	Ribosome (where protein synthesis occurs)		30
	Glycogen granules of liver		150
Viruses	Influenza		60
	Tobacco mosaic, length		120
	Bacteriophage T_2		140

Class	Material	Size d (μm)
Organelles (structures in cells outside nucleus)	Mitochondrion, where aerobic respiration produces ATP molecules	$0.5 \times 0.9 \times 3$
	Chloroplast, site of photosynthesis, length	4
	Lysosome (vesicle with enzymes for digesting macromolecules)	0.7
	Vacuole of amoeba	10
Cells	*Escherichia coli* (*E. coli*) bacterium, length	8
	Human blood platelet	3
	Leukocytes (white blood cells), globular shape	8–15
	Erythrocytes (red blood cells), disk shape	1.5×8
Miscellaneous	Human chromosome	9
	Fascicle in tendon	50–300

2.2 Particle size distribution functions

Data on particle size measurement

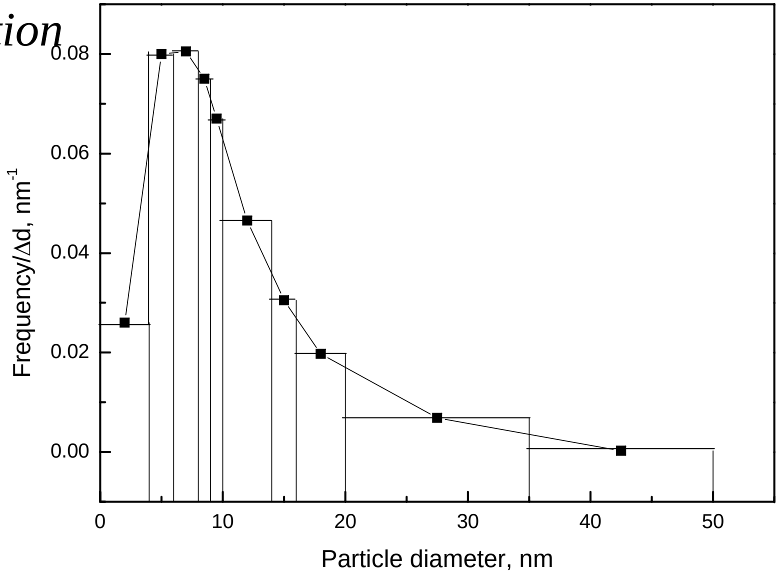
Size Range,nm,, d_{pi}~d_{pi+1}	*Count (Frequency)*	*Cumulative Fraction,* $F_{c,i}$	*Fraction,,* $F_{c,i+1}-F_{c,i}$	$\frac{F_{c,i+1}-F_{c,i}}{d_{p,i+1}-d_{p,i}}$
0-4	104	0.104	0.104	0.026
4-6	160	0.264	0.160	0.080
6-8	161	0.425	0.161	0.0805
8-9	75	0.500	0.075	0.075
9-10	67	0.567	0.067	0.067
10-14	186	0.753	0.186	0.0465
14-16	61	0.814	0.061	0.0305
16-20	79	0.893	0.079	0.0197
20-35	103	0.996	0.103	0.0034
35-50	4	1.000	0.004	0.0001
> 50	0	1.000	0	0.0



(1) Size distribution function

* Count size distribution function

$$\frac{F_{c,i+1} - F_{c,i}}{d_{p,i+1} - d_{p,i}} \quad vs. \quad d_{p,i} \quad \text{Discrete size distribution}$$



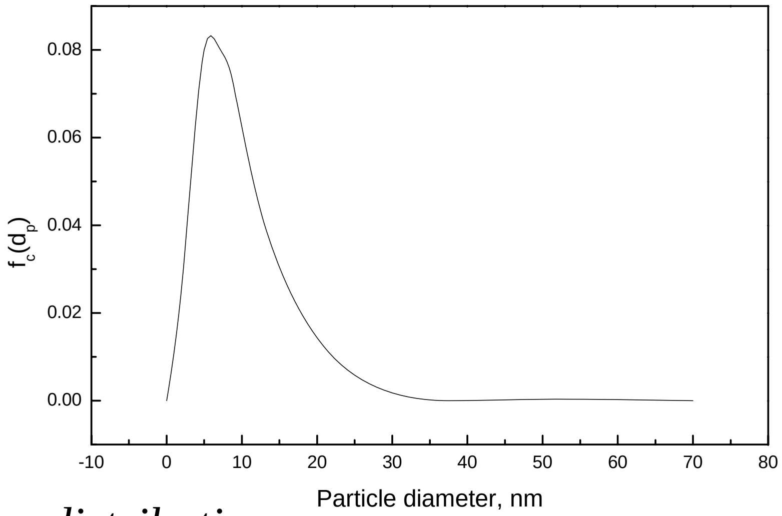
- *Sample data gives size distribution as →*

See the Table on p19 for details

$$\lim_{d_{p,i+1} \to d_{p,i}} \frac{F_{c,i+1} - F_{c,i}}{d_{p,i+1} - d_{p,i}} = \frac{dF_c}{dd_p} = f_c(d_p) \quad vs. \quad d_{p,i} \quad \text{Continuous size distribution}$$

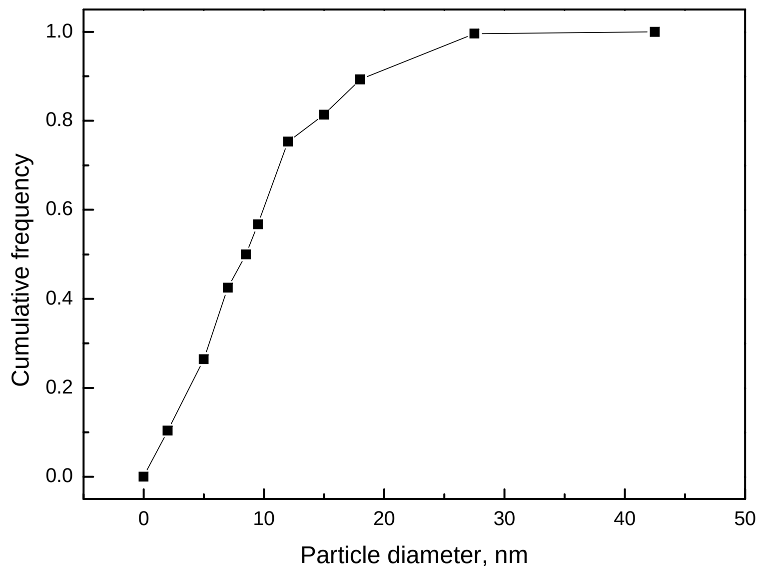
where $f_c(d_p)$ *: count(number) size distribution function*

$f_c(d_p)dd_p$: *fraction of particle counts(numbers) with the diameters between* d_p *and* $d_p + dd_p$



- *Cumulative count size distribution*

$$F_c(d_p) = \int_0^{d_p} f_c(d_p) dd_p$$



- *Sample data gives size distribution as →*

See the Table on p19 for details

** Mass size distribution function* $f_m(d_p)$

$$\lim_{d_{p,i+1}\to d_{p,i}} \frac{F_{m,i+1}-F_{m,i}}{d_{p,i+1}-d_{p,i}} = \frac{dF_m}{dd_p} = f_m(d_p)$$

$f_m(d_p)dd_p$ *: fraction of particle mass with the diameters between* d_p *and* $d_p + dd_p$

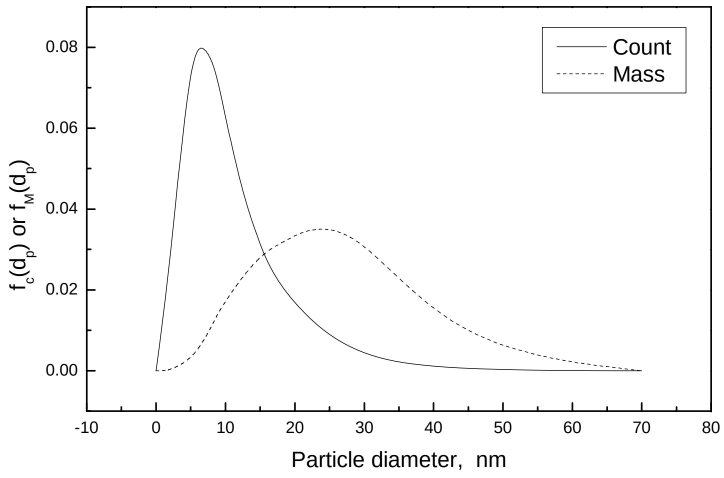
$$f_m(d_p) = \frac{\frac{\pi}{6}\rho_p d_p{}^3 f_c(d_p)}{\int_0^\infty \frac{\pi}{6}\rho_p d_p{}^3 f_c(d_p)dd_p} = \frac{\frac{\pi}{6} d_p{}^3 f_c(d_p)}{\int_0^\infty \frac{\pi}{6} d_p{}^3 f_c(d_p)dd_p} \equiv f_v(d_p)$$

Volume size distribution function

- also called third moment distribution

- Sample data gives mass size distribution as →

See the Table on p19 for details



cf. Second moment distribution function

=surface distribution function

- Cumulative mass size distribution function

(2) Mass distribution functions

$$\lim_{d_{p,i+1}\to d_{p,i}} \frac{F_{M,i+1} - F_{M,i}}{m_{p,i+1} - m_{p,i}} = \frac{dF_M}{dm_p} = f_M(m)$$

$f_M(m)dm$ *: mass fraction of particles having mass between m and m+dm*

$$f_M(m)dm = f_M(m)d\left(\frac{\rho_p \pi d_p^{\,3}}{6}\right) = f_M(m)\frac{\rho_p \pi d_p^{\,2}}{2} dd_p$$

$$\therefore f_m(d_p) = f_M(m)\frac{\rho_p \pi d_p^{\,2}}{2}$$

** surface area distribution functions*

or others: distributions of charge, concentration, shape, price etc.

(3) Averages and Dispersion

Average diameters

For any size distribution function, $f_I(d_p)$*, where I=c, m…*

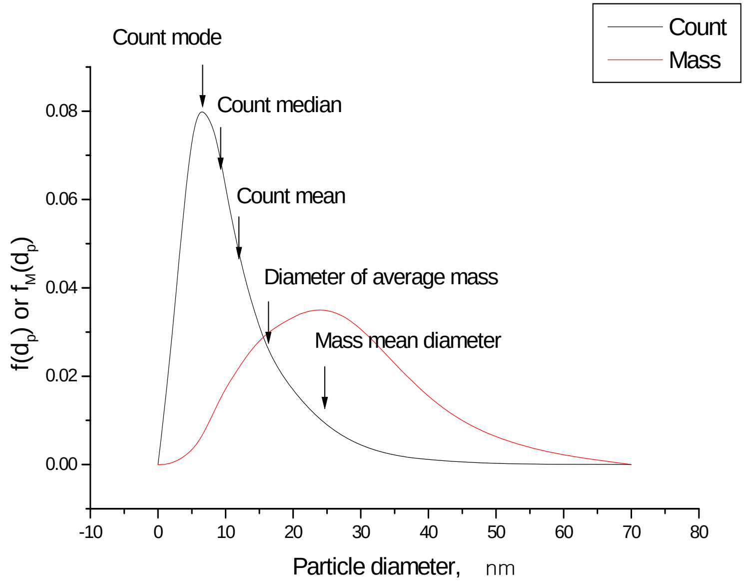
Mean diameter: $$\overline{d_p} = \int_0^\infty d_p f_I(d_p) dd_p$$

e.g. count mean, mass mean…

Medium diameter: d_p *at* $F(d_p)=0.5$

Mode diameter: most frequent size

- *From sample data, count mean diameter = 11.8nm*
  median diameter = 9.0nm
  mode diameter = 6.0nm →



The differences in averages come from skewed distribution with long tail.

** mass (average diameter)>surface (average diameter) >count (average diameter)*

Standard deviation

$$\sigma = \left(\int_0^\infty (\bar{d}_p - d_p)^2 f(d_p) dd_p \right)^{1/2}, \quad nm$$

(4) Diameter of average properties

Diameter of average mass

$$d_{p,\bar{m}} = \left(\frac{6}{\pi \rho_p} \frac{M}{N} \right)^{1/3} = \left(\frac{6}{\pi \rho_p} \frac{\sum m_i}{N} \right)^{1/3} = \left(\frac{6}{\pi \rho_p} \frac{\sum_N \frac{\pi}{6} \rho_p d_p^{\,3}}{N} \right)^{1/3} = \left(\frac{\sum_N d_p^{\,3}}{N} \right)^{1/3}$$

where M: total mass or total mass concentration

N: total number or total number concentration

** In general, for any property* $Q \sim d_p^{\,q}$

Then diameter of average Q

$$d_{p,\bar{Q}} = \left(\frac{\sum_N d_p^{\,q}}{N} \right)^{1/q}$$

(5) Lognormal size distribution function

- Standard form of distribution

** Normal(Gaussian) distribution function*

$$f_G(x)dx = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\bar{x}-x)^2}{2\sigma^2} \right) dx$$

where $\sigma = x_{50\%} - x_{16\%} = x_{84\%} - x_{50\%} = \frac{1}{2}(x_{84\%} - x_{16\%})$

** Lognormal size distribution function*

Replacing x with ln d_p *and* σ *with ln* σ_g

$$f_{LN}(d_p)d(\ln d_p) = \frac{1}{\ln\sigma_g\sqrt{2\pi}} \exp\left(-\frac{(\overline{\ln d_p} - \ln d_p)^2}{2(\ln\sigma_g)^2} \right) d(\ln d_p)$$

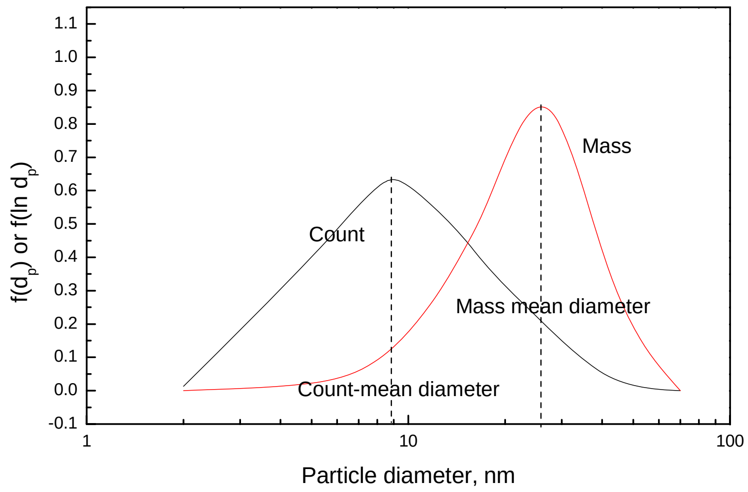
where $\overline{\ln d_p} = \int_0^\infty (\ln d_p) f_{LN}(d_p)d(\ln d_p) = \ln d_{pg}$ d_{pg}*: geometric mean diameter*

$$\overline{\ln\sigma_g} = \left(\int_0^\infty (\overline{\ln d_p} - \ln d_p)^2 f_{LN}(d_p)d(\ln d_p) \right)^{1/2}$$ σ_g*: geometric standard deviation*

$$\textit{where} \qquad \sigma_g = \frac{x_{50\%}}{x_{16\%}} = \frac{x_{84\%}}{x_{50\%}} = \left(\frac{x_{84\%}}{x_{16\%}}\right)^{1/2}$$

- Sample data can be plotted on log scale abscissa ↓

See Table on p19 for details



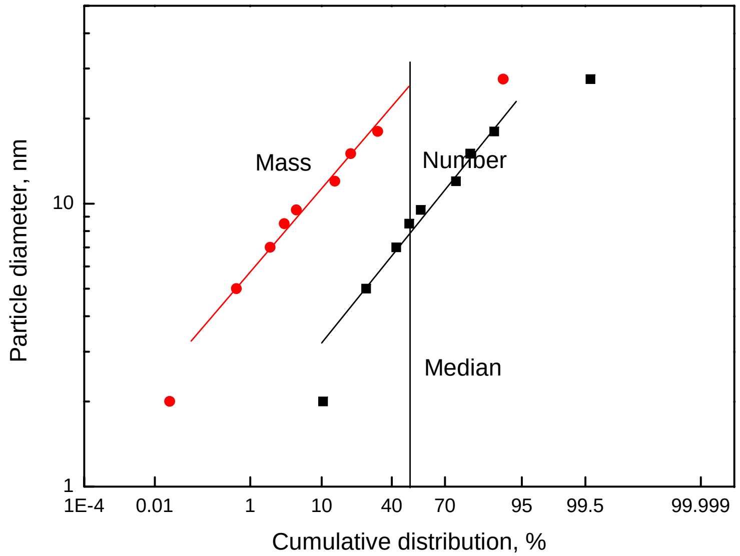
* Log probability diagram

Cumulative lognormal size distribution

$$F_{LN}(d_p) = \int_{-\infty}^{\ln d_p} f_{LN}(d_p)\, d(\ln d_p)$$

- Sample data can be plotted on log-probability coordinates →

See Table on p19 for details



* *Criterion for monodispersity:* σ_g *=1.2~1.4.*

* *Relations of average diameters (Hatch-Choate equation)*

- *From CMD to other average diameter*

$$d_A = CMD \exp(b \ln^2 \sigma_g)$$

where b $\rightarrow$

- *From CMD to diameter of average*

$$d_{\bar{q}} = CMD \exp\left(\frac{p}{2} \ln^2 \sigma_g\right)$$

where p=1 for length, 2 for surface, 3 for volume or mass

To convert from CMD to	*For the value of b*
Mode	*-1*
Count mean diameter	*0.5*
Diameter of average mass	*1.5*
Mass median diameter	*3*
Mass mean diameter	*3.5*

Table. Calculation of various distribution functions

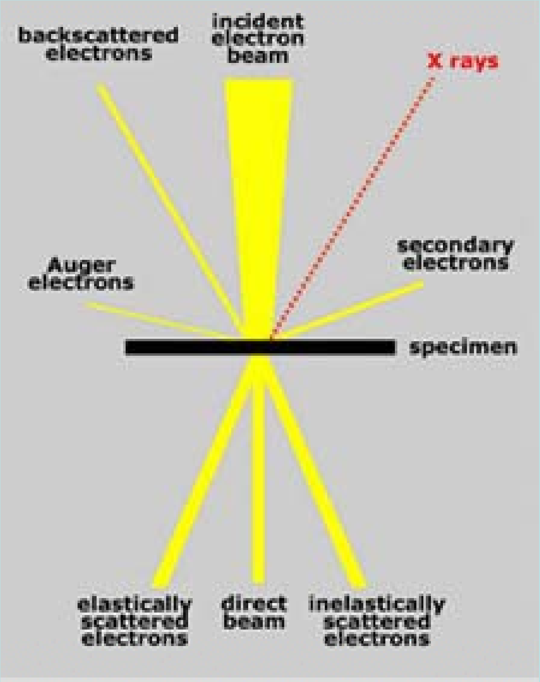
avg dia	frequency	cum frac	fraction/ln d	volume	vol*freq	vol fraction	v fr/del d	largest d	v cum frac	v fr/ln d
0	0	0	0	0	0	0	0	0	0	0
2	104	0.104	0.012539	4.188787	435.6338	0.00023	5.75E-05	4	0.00023	2.77359E-05
5	160	0.264	0.394609	65.44979	10471.97	0.00553	0.002765	6	0.00576	0.013638381
7	161	0.425	0.559646	179.5942	28914.67	0.015269	0.007634	8	0.021029	0.053075427
8.5	75	0.5	0.636764	321.5548	24116.61	0.012735	0.012735	9	0.033764	0.108123873
9.5	67	0.567	0.635912	448.9201	30077.65	0.015883	0.015883	10	0.049647	0.150748857
12	186	0.753	0.552794	904.7779	168288.7	0.088868	0.022217	14	0.138514	0.264115413
15	61	0.814	0.456821	1767.144	107795.8	0.056923	0.028462	16	0.195438	0.426291361
18	79	0.893	0.354032	3053.625	241236.4	0.127389	0.031847	20	0.322826	0.570882282
27.5	103	0.996	0.184055	10889.21	1121589	0.592273	0.039485	35	0.915099	1.058355682
42.5	4	1	0.011215	40194.35	160777.4	0.084901	0.00566	50	1	0.238034813
70	0	1	0	179594.2	0	0	0	70	1	0
					1893703	1				

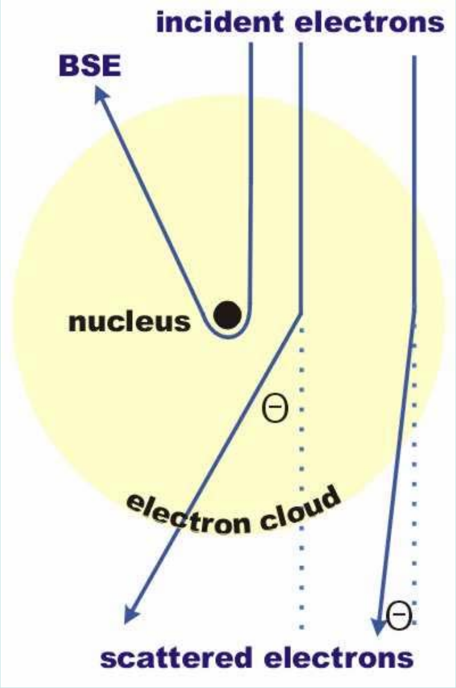
2.3 Observation and size measurment of particles

(1) Electron Microscopy

http://davinci.ethz.ch/solid/_research/elmi/methods.htm

** Electron-matter interaction*



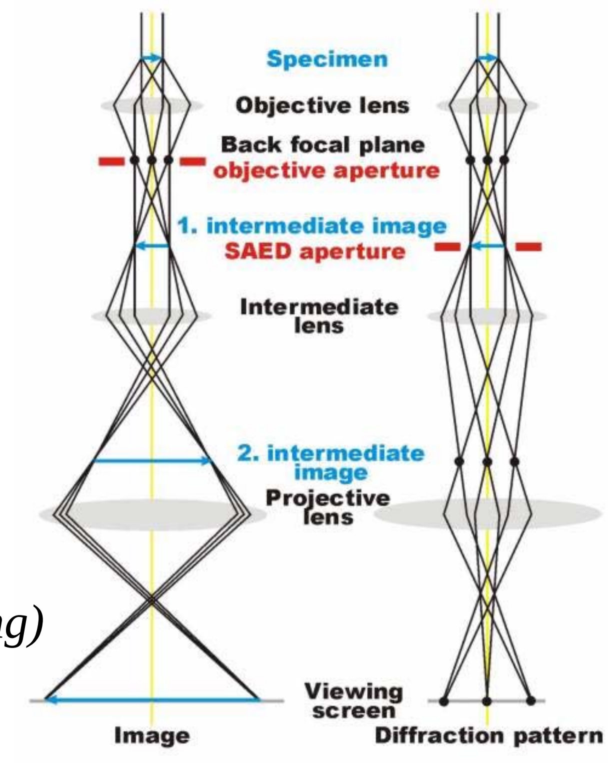


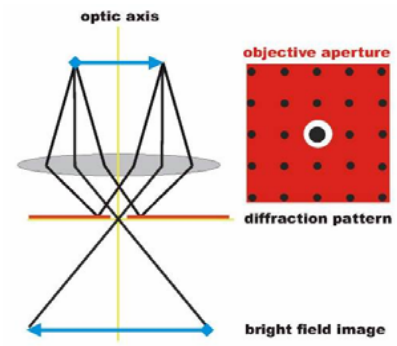
* *Transmission electron microscope*

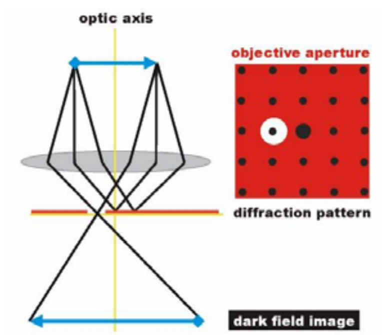
- *Energy: 100KeV ~ 1MeV*
- *Requires thin specimen(<200nm)*
  - *-Increases with the electron energy*
- *High magnification:~ 10^6*

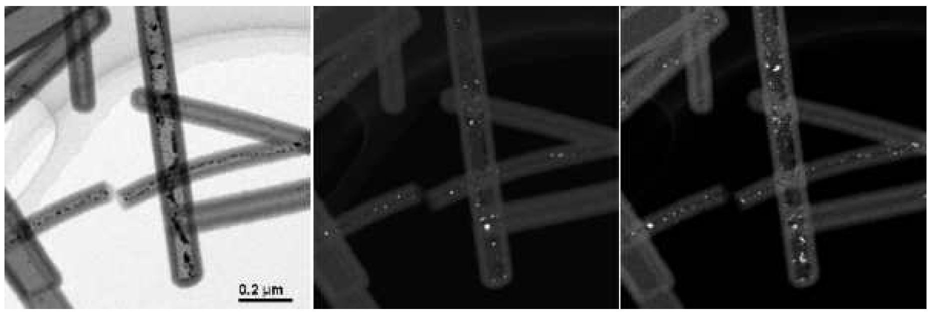
Resolution ~ $\lambda^{3/4}$ where $\lambda = \dfrac{h}{\sqrt{2mqV}}$

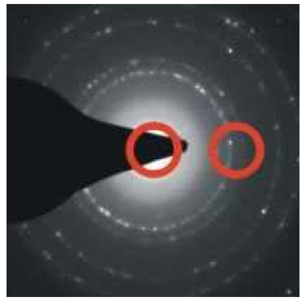
- *Gives images and diffraction patterns(elastic scattering)*











BF, DF and conical DF image of Pt particles inside of SiO_2-NTs

** Scanning electron microscope*

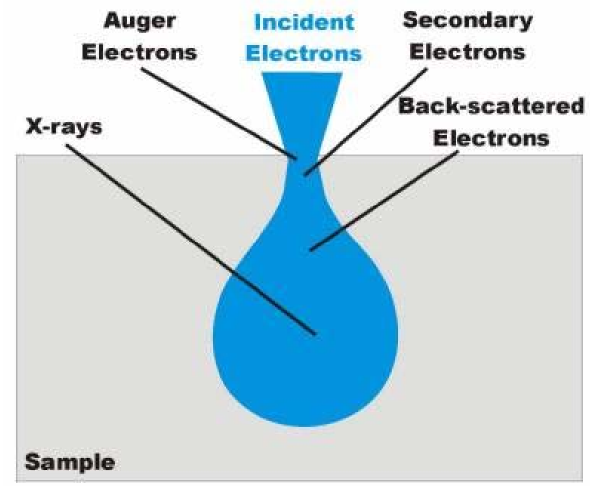
- Imaging from secondary electron(<50eV) imaging (SE)

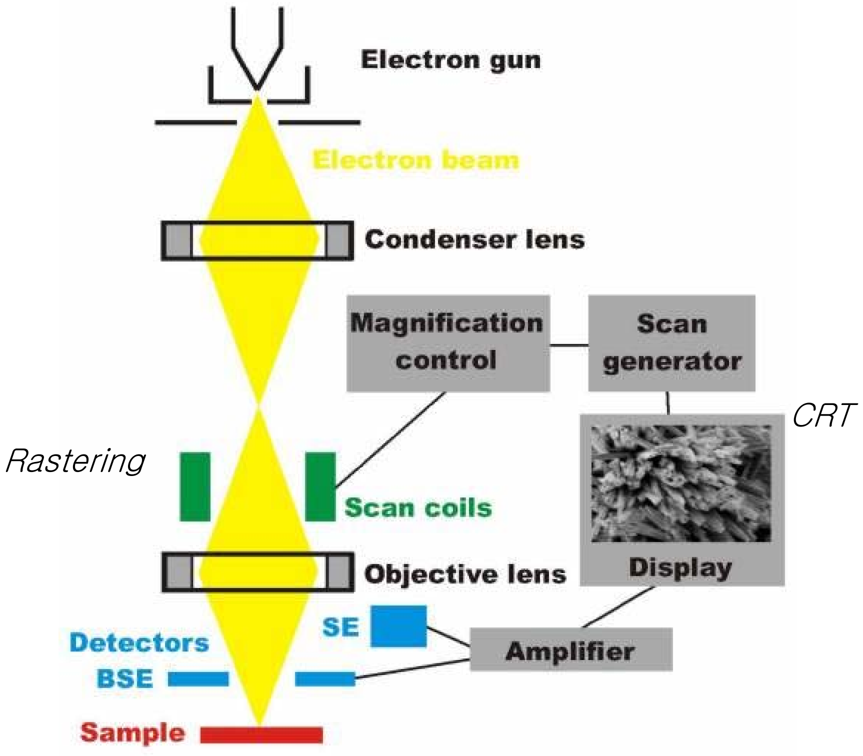
back-scattered electron imaging (BSE)

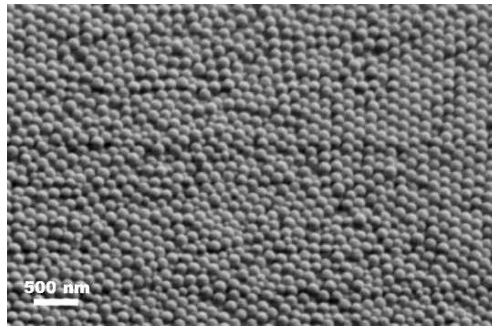
- - Resolution: 2-3nm; magnification: 10~>30,000

- Spot size : 5nm; energy: 2~200eV to 50KeV

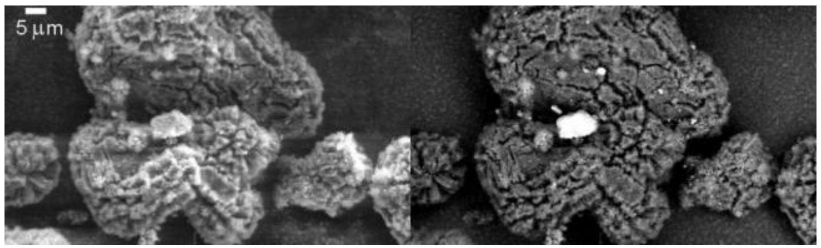
- - Information on chemical composition as well as topography







Latex balls, image from secondary electrons



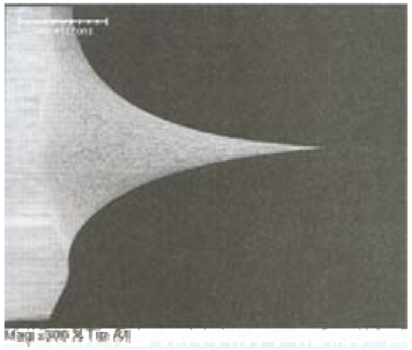
Fe particles in carbon, left: from secondary electrons; Right: from back scattered

** Scanning probe microscopy*

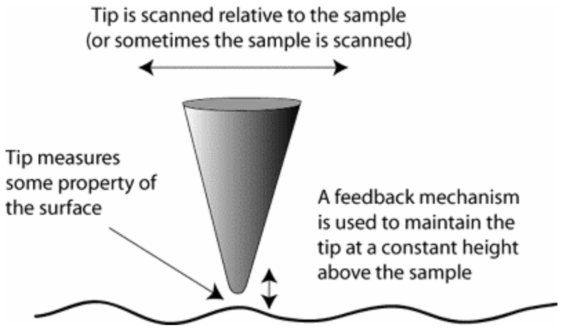
-Used to obtain surface property of the nanostructured materials e.g. films.

-3-D real space imaging and localized measurement of structure and properties

-Obtain topographical data of surface by measuring interaction between tip and surface



STM tip made of tungsten



-From atoms to >250μm$\times$250 μm;

-Vertical ranges of ~15 μm

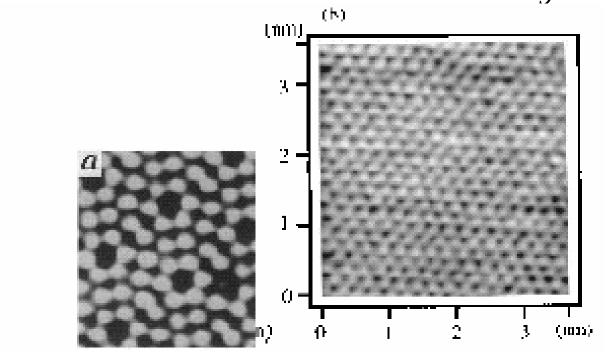
http://www.iap.tuwien.ac.at/www/surface/STM_Gallery/stm_animated.gif

<u>*Scanning tunneling microscope*</u>

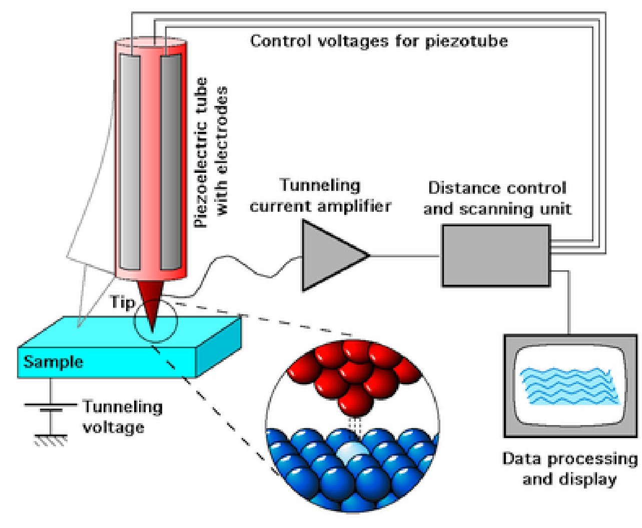
- Constant current mode

- Constant height mode

- STM: restricted to electrically conductive sample surface



a.) STM of silicon [Si (111) 7x7 reconstruction; 2x2 nm]; b.) AFM of graphite

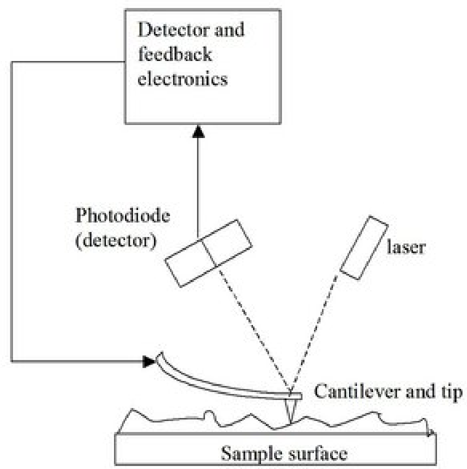


<u>*Atomic force microscope*</u>

-Constant force mode

-Electrostatic interaction, current-induced,

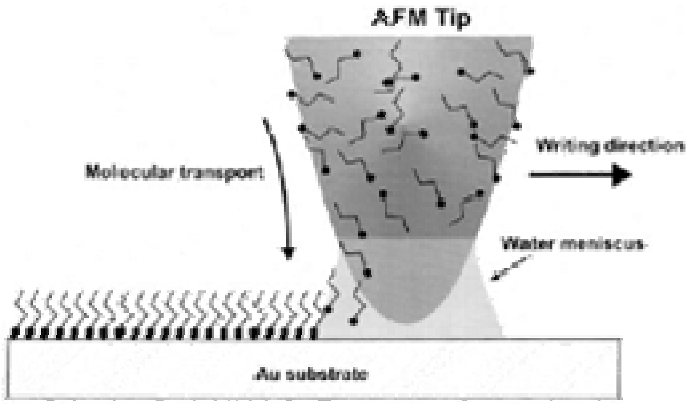
static magnetic interaction, capillary forces

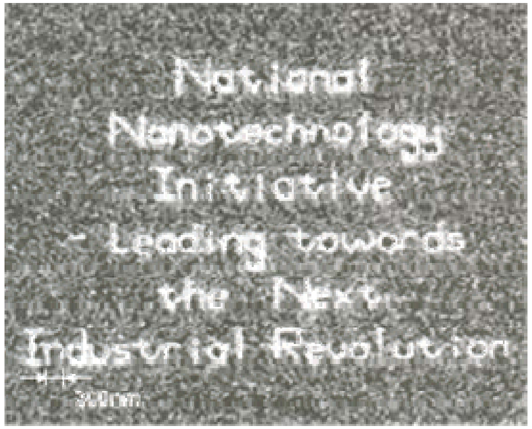


-SPM using other probe and sample-surface interactions

- *Magnetic force microscope*
- *Electrostatic force spectroscopy*
- *Scanning voltage microscope*
- *Kelvin probe microscope*
- *Scanning thermal microscope*
- *Near-field scanning optical microscopy*
- *Scanning capacitance microscope*
- *Force modulation microscope*

- Also used for nanomanipulation, nanolithogrphy and nanodevice (sensor)





Use of “nano-pen”

(2) Light scattering: laser particle sizer

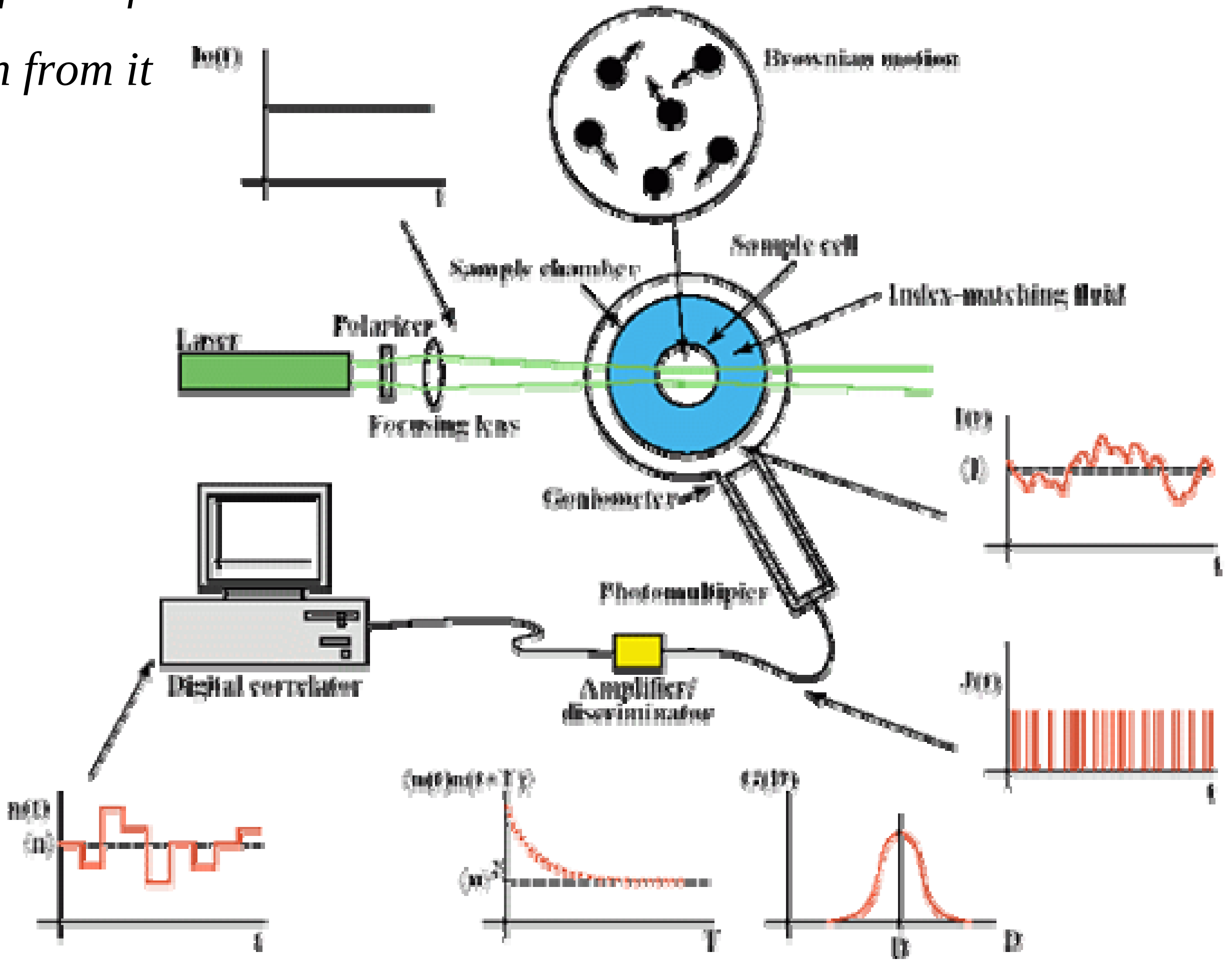
** Dynamic light scattering*

http://www.bic.com/90oper.htm
http://www.ap-lab.com/light_scattering.htm#Dynamic_Light_Scattering

- Data on scattered light intensity vs. time

- Quantifying Brownian diffusion from them

- Deducing size distribution from it



(3) Electrical migration

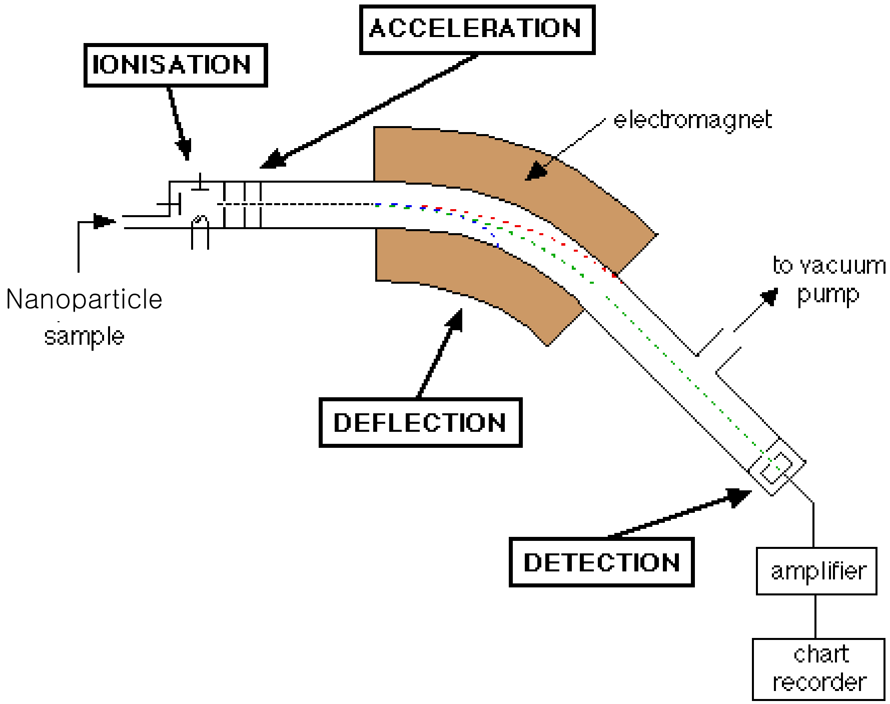
** Mass spectrometry*

- Movement of charged particles in magnetic field

$$\frac{m}{q} = \frac{B^2 r^2}{2V}$$

where m: mass of particle; q: charge; B: field strength; r: bending radius of the duct; V: applied voltage

- Size data from m



* *Differential mobility analyzer*

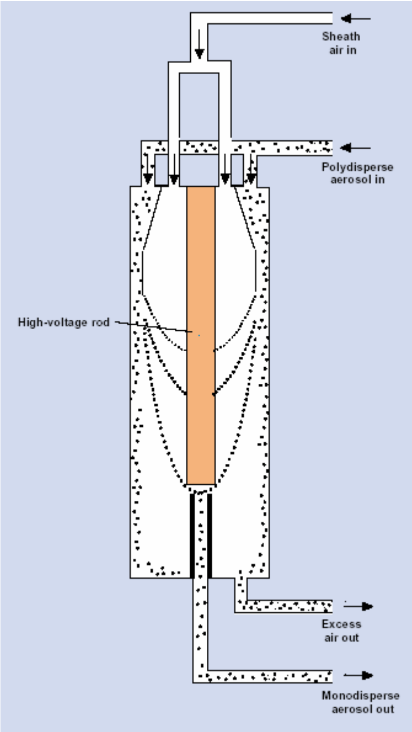
$$Z = \frac{U_e}{E} = \frac{eC}{3\pi\mu d_p}$$ *for singly charged particles*

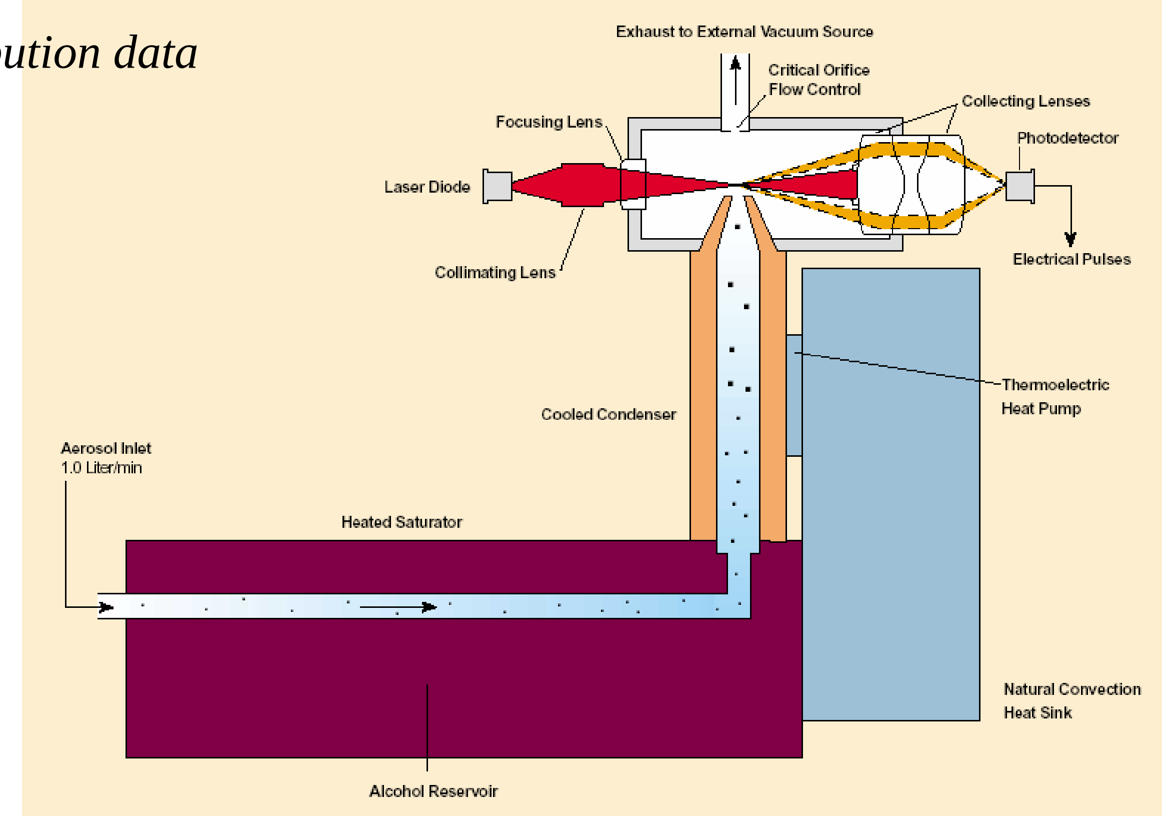
- *Small particles deposit on the central rod*

- *Only particles in very narrow size range can pass through the exit tube*

- *Number concentration measured in condensation nuclei counter*

- *Change E gives size distribution data*





Condensation nuclei(particle) counter