Chapter 1. Particle Size Analysis

1.1 Introduction

Particle size/particle size distribution: a key role in determining the bulk properties of the powder...

Size ranges of particles (x)

μ - Coarse particles : >10 m

μ - Fine particles : ~1 m

μ - Ultrafine(nano) particles : <0.1 m (100nm)

1.2 Describing the Size of a Single Particle

Description of regular-shaped particles: Table 3.1

Figure 3.1

Geometric diameters

- Martin's diameter
- Feret diameter
- Shear diameter

Equivalent (sphere) diameters Figure 3.2

- Equivalent volume (sphere) diameters:

the diameter of the hypothetical sphere having the same volume

π $$x_v = \left(\frac{6V}{\ } \right)^{1/3}$$

- Equivalent surface diameter:

the diameter of the hypothetical sphere having the same surface area

π $$x_s = \left(\frac{S}{\ } \right)^{1/2}$$

- *Surface-volume diameter:*

    the diameter of the hypothetical sphere having the same surface-to-volume ratio

$$x_{sv} = \frac{6V}{S}$$

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

Worked Example 3.1

Worked Example 3.6

1.3 Description of Population of Particles

Particle size ~ *diameter,* x *(μm)*

Figure 3.3

Frequency distribution $f_N(x)$, *[fraction]*

$f_N(x)dx$:

fraction of particle counts (numbers) with diameters between x *and* $x+dx$

Cumulative distribution : $F_N(a) = \int_0^a f_N(x)dx$, *[fraction]*

$$f_N(x) = \frac{dF_N(x)}{dx}$$

Mass(or volume) distribution $f_M(x)$, *(mass fraction/μm)*

$f_M(x)dx$:

fraction of particle mass with diameters between x *and* $x+dx$

$$f_M(x)dx = \frac{\frac{\pi\rho}{6}x^3 f_N(x)dx}{\int_0^\infty \frac{\pi\rho}{6}x^3 f_N(x)dx} = \frac{x^3 f_N(x)dx}{\int_0^\infty x^3 f_N(x)dx} = f_V(x)$$

π

π

Surface-area size distribution function

$$f_S(x)\,dx = \frac{x^2 f(x)\,dx}{\int_0^\infty x^2 f(x)\,dx} = \frac{x^2 f(x)\,dx}{\int_0^\infty x^2 f(x)\,dx}$$

Figure 3.4

Table 3.3

1.4 Conversion Between Distributions

From above

$$f_M(x) = f_V(x) = \frac{x^3 f_N(x)}{\int_0^\infty x^3 f_N(x)\,dx} = k_V x^3 f_N$$

$$\text{where} \quad k_V = \frac{1}{\int_0^\infty x^3 f_N(x)\,dx}$$

$$f_S(x) = \frac{x^2 f_N(x)}{\int_0^\infty x^2 f_N(x)\,dx} = k_S x^2 f_N$$

$$\text{where} \quad k_S = \frac{1}{\int_0^\infty x^2 f_N(x)\,dx}$$

$$f_M(x) = f_V(x) = k_V x^3 f_N = k_V x^3 \frac{f_S(x)}{k_S x^2} = \frac{k_V}{k_S} x f_S(x)$$

$$\text{where} \quad k_V = \frac{1}{\int_0^\infty x^3 f_N(x)\,dx}$$

Worked Example 3.2

Worked Example 3.3

Worked Example 3.4

1.5 Describing the Population by a Single Number

1) Averages

Mode: most-frequent size

Median: x *at* $F(x) = 0.5$

Mean: Table 3.4

$$\text{In general, } g(\bar{x}) = \int_0^\infty g(x) f(x)\,dx = \int_0^1 g(x)\,dF(x)$$

- *Arithmetic mean:* $g(x) = x$

$$\bar{x} = \int_0^\infty x f(x)\,dx = \int_0^1 x\,dF(x)$$

$$\text{where } F(x) \text{ can be } F_N(x),\ F_S(x) \text{ and } F_V(x)$$

* *Also called first moment average*

If $F(x) = F_N(x)$, $\bar{x}_{aN} = \int_0^1 x\,dF_N$

Arithmetic mean diameter of number distribution

If $F(x) = F_S(x)$,

$$\bar{x}_{aS} = \int_0^1 x\,dF_S = \frac{\int_0^1 x\,dF_S}{\int_0^1 dF_S} = \frac{\int_0^1 x^3\,dF_N}{\int_0^1 x^2\,dF_N} = \bar{x}_{SV}$$

Arithmetic mean diameter of surface area distribution *Surface-volume mean diameter (Sauter mean diameter)*

- *Geometric mean (* $g(x) = \ln x$ *)*

$$\log x_g = \overline{\log x} = \left[\int_0^1 \log x\,dF\right]$$

- *Harmonic mean (* $g(x) = \frac{1}{x}$ *)*

$$\frac{1}{\bar{x}_h} = \left[\int_0^1 \frac{1}{x}\,dF\right]$$

Figure 3.6

Worked example 3.5

2) Standard deviation

$$\sigma = \left[\int_0^{\infty} (x - \bar{x})^2 dF(x) \right]^{1/2} = \left[\int_0^{\infty} (x - \bar{x})^2 f(x) dx \right]^{1/2}$$

Degree of dispersion

1.7 Common Methods of Displaying Size Distribution

1) Arithmetic Normal(Gaussian) distribution: Figure 3.7

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

and

$$\sigma = x_{84\%} - x_{50\%} = x_{50\%} - x_{16\%} = 0.5(x_{84\%} - x_{16\%})$$

- *Hardly applicable to particle size distribution Figure 3.8*

∵ *Particles : no negative diameter/distribution with long tail*

2) Lognormal distribution :

위의 정규분포함수에서 x를 $\ln x$로 σ를 $\ln \sigma_g$로 바꾸면 얻어진다.

$$f(\ln x) d\ln x = \frac{1}{(\ln \sigma_g)\sqrt{2}} \exp\left[- \frac{(\ln x - \overline{\ln x})^2}{2(\ln \sigma_g)^2} \right] d\ln x$$

where $\overline{\ln x} = \int_0^1 \ln x dF(x) = \int_0^1 \ln x dF(\ln x) = \int_{-\infty}^{\infty} \ln x f(\ln x) d\ln x = \ln x_g$

x_g*: geometric mean(median) diameter*

$$\ln \sigma_g = \left[\int_0^{\infty} (x - \bar{x})^2 dF(x) \right]^{1/2} = \left[\int_{-\infty}^{\infty} (\ln x - \ln x_g)^2 f(\ln x) d\ln x \right]^{1/2}$$

σ_g *: geometric standard deviation*

Figure 3.9

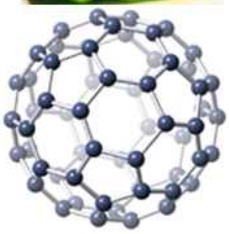
$$\sigma_g = \frac{x_{84\%}}{x_{50\%}} = \frac{x_{50\%}}{x_{16\%}} = \left[\frac{x_{84\%}}{x_{16\%}} \right]^{\frac{1}{2}}$$

* *Dispersity criterion*

- *Monodisperse* : $\sigma = 0$ *or* $\sigma_g = 1$, *in actual* $\sigma_g < 1.2$
- *Polydisperse:* $\sigma_g > 1.4$ (or 1.2)

1.S1 Understanding Size of Nanoparticles

Comparison with bulk



Buckminster fullerene

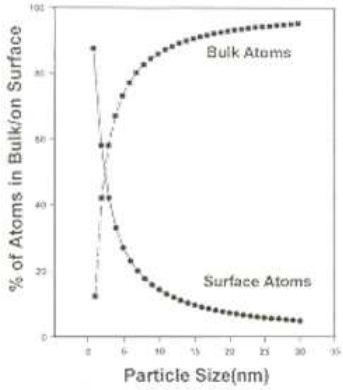
Football

Planet earth

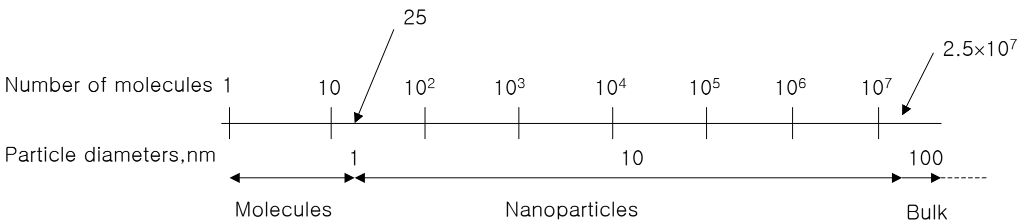
if a buckyball (60 carbon atoms arranged into a sphere with a diameter of approximately 1nm) were expanded to the size of a football, the football would correspondingly be expanded so that it was much bigger than the size of Earth (becoming approximately the size of Neptune or Uranus – about 50,000km in diameter).

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

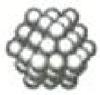
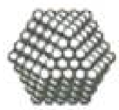
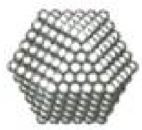
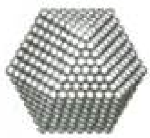
Atoms(molecules) in nanoparticles



Calculated values form spherical iron nanoparticles



Extremely small nanoparticles!

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

Full-shell clusters

* *Polymers-Nanoparticles?*

$$V = 0.001661 \frac{M_w}{\rho}, \ in \ \ nm^3$$

where M_w*(molecular weight) and* ρ*(density) in cgs units*

Example.

분자량이 100,000이고 밀도가 1g/cm^3*인 고분자 물질의 부피와, 구라고 가정하고 지름을 구해 보아라.*

$$0.001661 \cdot \frac{100000}{1} = 166.1 \qquad V := 166.1\,nm^3$$

$$166.1 = \frac{\pi}{6} x^3 \text{ solve}, x \rightarrow \begin{bmatrix} (-3.4100468132921324412) - 5.9063743368103145235 \cdot i \\ (-3.4100468132921324412) + 5.9063743368103145235 \cdot i \\ 6.8200936265842648825 \end{bmatrix}$$

$$x := 6.82\,nm$$

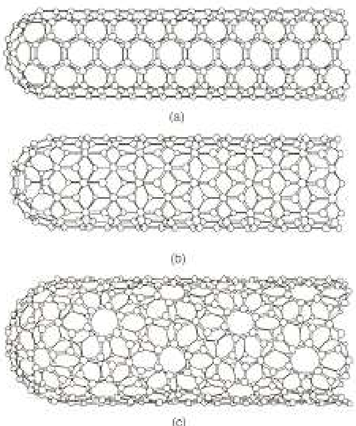
* *Biological substance-Nanoparticles?*

$$d_v = 0.1469 \left(\frac{M_w}{\rho} \right)^{1/3}, \ in \ \ nm$$

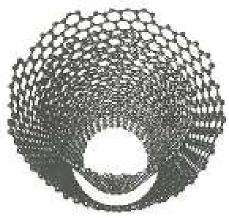
Class	Material	M_w (Da)	Size d (nm)
Amino acids	Glycine (smallest amino acid)	75	0.42
	Tryptophan (largest amino acid)	246	0.67
Nucleotides	Cytosine monophosphate (smallest DNA nucleotide)	309	0.81
	Guanine monophosphate (largest DNA nucleotide)	361	0.86
	Adenosine triphosphate (ATP, energy source)	499	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

* *Special nanoparticles(nanomaterials)-carbon nanotubes*



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



Multi-walled CNT

1.S2 Size-Related Properties of Nanoparticles

* *Finite size effect - small number of atoms and electrons*

* *Surface/interface effect - large fraction of active surface atoms*

Example.

Consider a sphere with a diameter with a diameter of 1um. If this mass of sphere is converted (through a size reduction process) to spheres with a diameter of 1nm, calculate the increase in surface area of the smaller sized spheres.

Surface area of 1um-sphere

$$\pi\left(1\cdot10^{-6}m\right)^2 = 3.142\times10^{-12}m^2$$

Number of 1nm-spheres from 1um spheres

$$\frac{\left(1.0\cdot10^{-6}\right)^3}{\left(1.0\cdot10^{-9}\right)^3} = 1\times10^9$$

Total surface area of 1-nm spheres

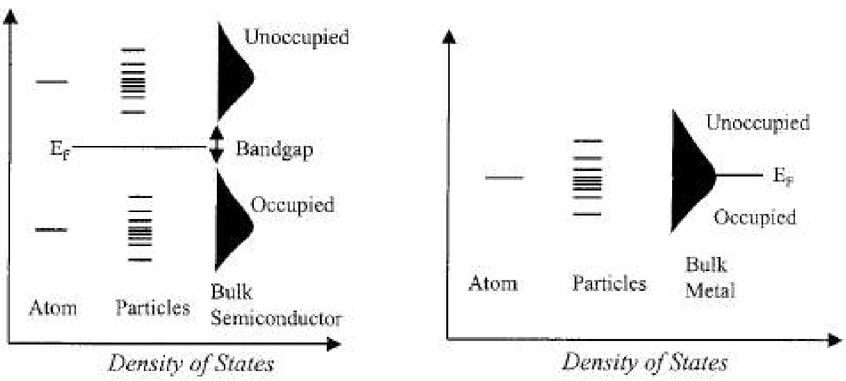
$$1\cdot10^9\pi\,(1nm)^2 = 3.142\times10^{-9}m^2$$

$$\frac{3.142\cdot10^{-9}m^2}{3.142\cdot10^{-12}m^2} = 1\times10^3$$ times increase...

+

(1) Quantum size (confinement) effects

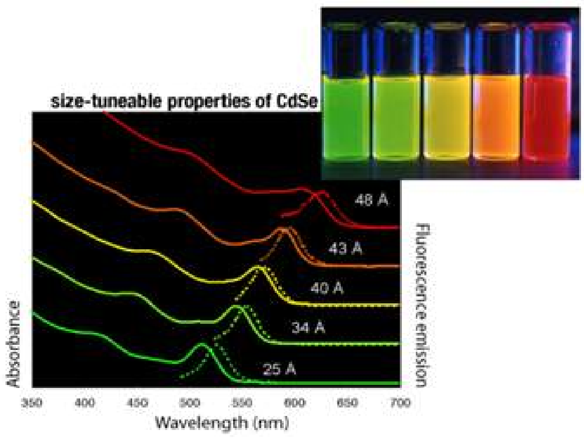
- *Small number of atoms and electron as size decreases(<de Broglie wavelength*)*



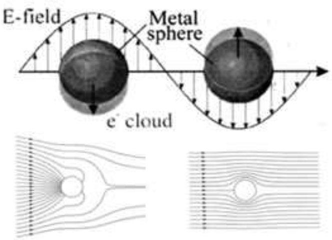
Energy Levels in Semiconductor and Metal Particles

<u>Optical properties of semiconductors</u>

- *Rapidly increase in band gap with a decreasing size*
- *Blue shift*



(2) Surface plasmon resonance of metal nanoparticles



- Coherent excitation of all the free electrons by light, leading to an in-phase oscillation for particles ($x < \lambda_{light}$)

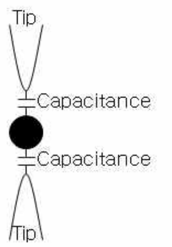
- Intense SP absorption bands at a certain wavelength

(3) Coulomb Blockade

Ohm's law, $I = \frac{V}{R}$,

I is linear with respect to V

A single electron can be added



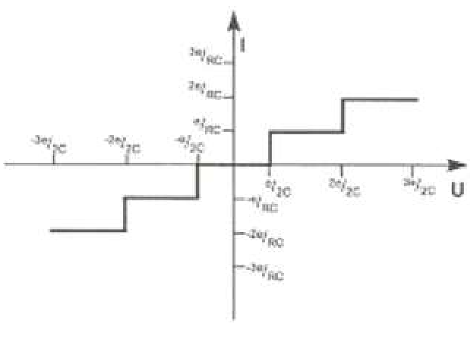
when $E > \frac{e^2}{2C}$ *or* $V = \frac{dE}{de} > \frac{e}{C}$

where $C(x) = 2\pi x \varepsilon_0 \varepsilon_r$

For bulk materials $(x \to \infty)$, $C(\infty) = \infty$ *and* $V \to 0$

For nanoparticles $(x \downarrow)$, $C(x) \downarrow$ *and* $V \to finite$

When $E \gg kT$ *and* $R \gg \frac{h}{e^2}$



Coulomb blockade

** Single electron transistor*

(3) Magnetic properties of ferromagnetic particles

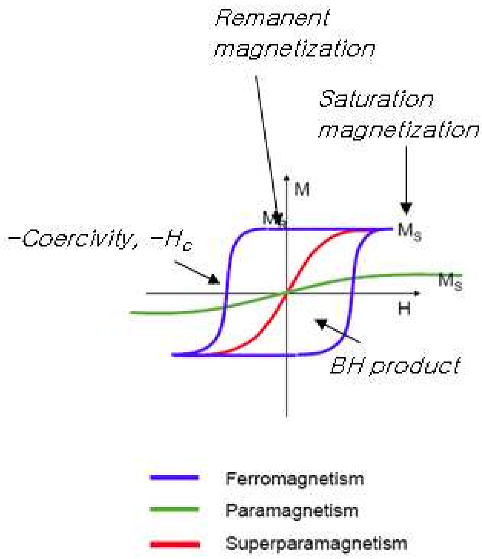
- Ferromagnetic materials

Atoms: unpaired electrons → domain formation

Bulk: multidomain

cf. diamagnetism, paramagnetism

- Behavior of ferromagnetic materials under magnetic field: BH diagram



- For small particles($x: 10 \sim 100nm$), single domain is in the lowest energy state →

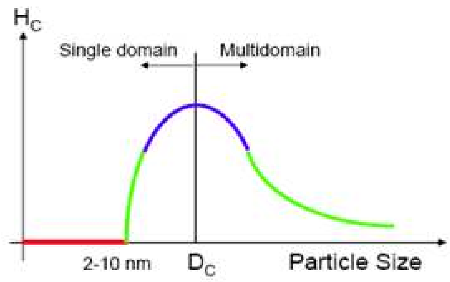
"Single- domain particles"

· Used for magnetic recording media

- For smaller particles($x < 15nm$)

· Thermal fluctuation > magnetic alignment as the size decreases →

"Superparamagnetism"



· No hysteresis loop and high M_s

· *Used in biomedical application, ferrofluids, sensors*

1.9 Methods of Particle Size Measurement

1) Sieving

2) Microscopy

Electron microscopy

3) Sedimentation

4) Permeametry

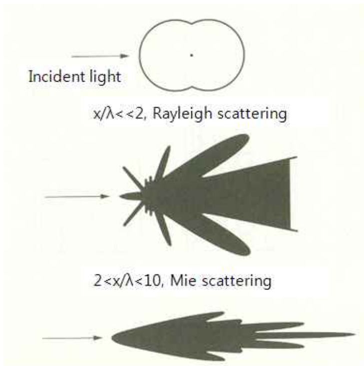
5) Electrical methods

· *Electrical mobility*

· *Electrozone sensing*

6) Laser Diffraction

· *Optical particle counter*



10<x/λ, Fraunhoffer scattering

· *Photon correlation spectroscopy (dynamic light scattering)*