Chapter 11 Size Enlargement

11.1 Introduction

Size enlargement - agglomeration of particles

cf. coagulation

Why enlarge the particles?

- To reduce dust hazard
- To reduce cake and lump formation
- To increase flow properties
- To increase bulk density for storage
- To increase nonsegregating mixtures
- To provide defined metered quantity of active ingredients
- To control surface-to-volume ratio

How enlarge the particles?

- Granulation: agglomeration by agitation
- Machine granulation :compaction(tabletting), extrusion
- Sintering ☞ next section
- Spray drying ☞ Chapter 8
- Prilling

11.2 Interparticle Forces

(1) *Van der Waals Forces*

원자에서 일시적으로 형성된 쌍극자가 주변 원자의 쌍극자화를 유도하고, 이 현상이 분자간에, 그리고 나아가 물체간 상호작용(인력)으로 나타난다.

Molecule to molecule

Short-range forces caused by the fluctuation in electron clouds

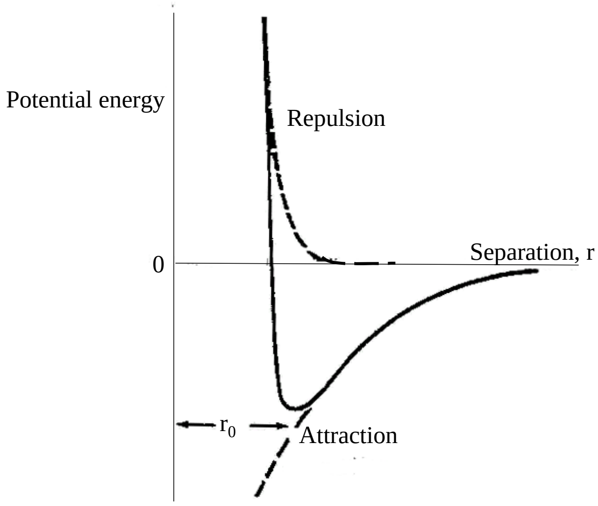
- Also called London dispersion forces

Potential energy between two molecules

$$W(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Repulsion **Attraction**

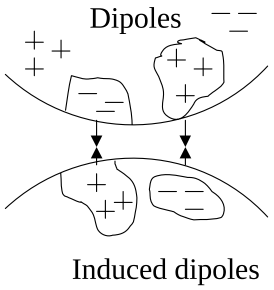
Lennard-Jones(6-12) potential



Intermolecular force

$$F(r) = -\frac{dW(r)}{dr}$$

Particle-to-particle and Particle-to-wall

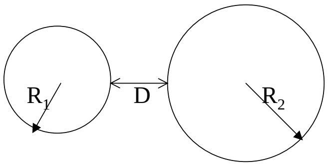


Neglecting the repulsive part of the potenial, $W(r) = \frac{C}{r^6}$

$W_{between\ two\ bodies}$: obtained by integrating the forces between all molecular pairs in two bodies

- *Hamaker* theory
- Lifshiz theory

Between two spheres



$$W = -\frac{A}{6D}\frac{R_1R_2}{R_1+R_2}$$

where A : Hamaker constant

Between sphere and wall

$$W = -\frac{AR}{6D}$$

Between two plates

$$W = \frac{A}{12\pi D^2}$$

Table 1. Hamaker constants

Interacting solids			Hamaker constant, A(10^{-20} J)	
solid	media	solid	Calculated	Measured
Quartz	vacuum(air)	Quartz	6.5	5-6
Mica	vacuum(air)	Mica	10	13.5
Metals	vacuum(air)	Metals	30-50	-
PTFE	vacuum(air)	PTFE	3.8	-
Quartz	Water	Quartz	8.83	-
Mica	Water	Mica	2.0	2.2
PTFE	Water	PTFE	0.33	-
(Air)	Water	(Air)	3.7	-
Quartz	Water	(Air)	-1.0	-

Ex. 10μm 입자와 평면의 van der Waals 부착력을 구하여라. Hamaker 정수 A= $1\times10^{-19}J$, 분리거리는 0.4nm로 계산한다. 또 입자밀도가 1000kg/m^3일 때 입자의 중력은 얼마인가?

Ans. 부착력은 5.2×10^{-7}N, 중력은 5.1×10^{-12}N

*표면의 요철이 있으면 부착력은 계산치보다 매우 작아진다. 분리거리 0.4nm에 표면조도가 0.1nm이면 1/6만으로 감소!

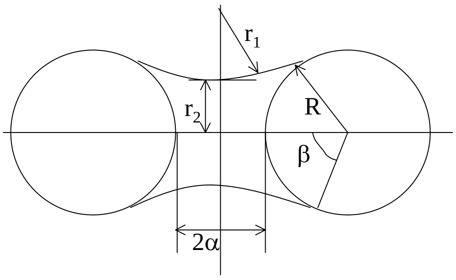
(2) Forces due to Adsorbed Liquid Layers

Overlapping of adsorbed layers

Dependent on area of contact and tensile strength of the adsorbed layers

(3) Forces due to Liquid Bridges

For pendular state



Assuming complete wetting

$$F = \pi r_2^2 P_L + 2\pi\gamma r_2$$

where P_L : negative pressure of the liquid bridge due to its negative curvature

여기서 부압(negative pressure)이란 오목한(concave) 형태의 물체 안에서의 압력이 가지는 특징이다.

Since $P_L = \gamma\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$,

$$F = 2\pi r_2\gamma + \pi r_2^2\gamma\left[\frac{1}{r_1} - \frac{1}{r_2}\right]$$

By geometric consideration

$$F = \frac{2\pi R\gamma}{1 + \tan(\beta/2)}$$

* As the size of the liquid bridge(β) ↓, F ↑

즉 가교 액량이 줄어들면 액가교력은 커진다. 그러나 액가교량이 완전히 없어질 때까지 이론이 연장되는 것은 아니다.

If $r_1 << r_2$,

즉 두개의 같은 크기의 입자(x)가 붙었을 때

By geometrical manipulation

$$F = \pi \gamma x$$

* Strong granules in which the quantity of liquid is not critical...

Example : For water at 25°C, $\gamma = 0.072 N/m$

For $x = 10 \mu m$, $F_L = \pi \cdot 0.072 \cdot 10 \times 10^{-6} = 2.26 \times 10^{-6} N$

cf. For equal-sized particles,

$$W = -\frac{A}{6D} \frac{R_1 R_2}{R_1 + R_2} = -\frac{Ax}{6D}$$

Assuming $A = 1 \times 10^{-19} J$ and $D = 0.4 nm$,

$$F_{vW} = -\frac{dW}{dD} = -\frac{Ax}{6D^2} = \frac{1 \times 10^{-19} \cdot 10 \times 10^{-6}}{6 \cdot (1 \times 10^{-9})^2} = 1.67 \times 10^{-7} N$$

액 가교 힘의 크기가 van der Waals 힘보다 10배 더 크다..

* Granule strength continuously decreases in funicular, capillary and droplet states.

(4) Electrostatic Forces

Friction caused by interparticle collision

Transfer of electrons between bodies

- Coulombic Force : charged(q_1) particle-to-charged(q_2) particle

$$F = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r^2}$$

where ε_0 : dielectric constant of vacuum

r : the distance between the centers of two particles

Electrical field strength by charge q_1

$$E = \frac{1}{4\pi\varepsilon_0 r^2} q_1$$

$$\therefore F = q_2 E$$

Also applicable to space charge forces in a cloud of charged particles(e.g., ESP)

Adhesive Force = Force at contact

Since $q = \pi x^2 \sigma$ and $r_c = (x_1 + x_2)/2$

where σ : surface charge density (C/m^2)

$$\therefore F = \frac{\pi\sigma_1\sigma_2}{\varepsilon}\left(\frac{x_1 \cdot x_2}{x_1 + x_2}\right)^2$$

Example : $\sigma = 26.5\times10^{-6} C/m^2$, $x = 10\mu m$ and $\rho_p = 1000 kg/m^3$

$$F_{Coulomb} = \frac{\pi}{4\varepsilon_0}\sigma^2 x^2 = \frac{\pi}{4\cdot 8.85\times10^{-12}} \cdot (26.5\times10^{-6})^2 \cdot (10^{-5})^2$$

$$= 6.23\times10^{-9} N$$

cf. $F_g = 5.13\times10^{-12} N$

(5) Solid bridges

Crystalline bridges

Liquid binder bridges

Solid binder bridges

(6) Comparison and Interaction between Forces

Humidity vs. van der Waals forces, interparticle friction, liquid bridges and electrostatic forces

Figure 11.2 Tensile strength for various bonding mechanisms

11.3 Granulation

(1) Introduction

Agitation: distribute liquid binder and impart energy to particles and granules

(2) Granulation Rate Process

Wetting

Rate of penetration of liquid

$$\frac{dz}{dt} = \frac{R_p \gamma \cos\theta}{4\mu z}$$

Washburn equation

where R_p: average pore radius, depending on particle size and packing density ☞ packing..

θ : dynamic contact angle

μ : viscosity of liquid, depending on the binder concentration

Growth Figure 11.3

nucleation - shatter

coalescence -breakage

layering - attrition

abrasive transfer

Ennis and Litster(1997)

Define $Stk \equiv \frac{\rho_{gr} V_{app} x}{16\mu}$ ☞Box on p274

$$Stk^* = \left(1 + \frac{1}{e}\right) \ln\left(\frac{h}{h_a}\right)$$

where e: coefficient of restitution

h_a: surface roughness of granules

i) noninertial regime: $Stk < Stk^*$

- all collisions effective for coalescence
- rate of wetting controls
- independent of viscosity, ingredient size and kinetic

energy

ii) inertial regime: Stk begins to increase Stk^*

- the proportion of successful collision decreases
- dependent on viscosity, ingredient size and kinetic energy

iii) coating regime: average Stk exceeds Stk^*

- granule growth is balanced by breakage
- growth continues by coating of primary particles onto existing granules

※ ordered mixture

Granule consolidation

- increase in granule density by closer packing density
- squeeze out liquid

cf. granule breakage

Granule breakage

- Shattering, fragmentation and wear

(3) Simulation of Granule Growth

$$\underbrace{\text{Rate of increase of number of granules in size interval v to v+dv}}_{(11.7)} = \underbrace{\text{Rate of inflow of granules in size interval v to v+dv} - \text{Rate of outflow of granules in size interval v to v+dv}}_{(11.8)} + \underbrace{\text{Rate at which granules enter size range v to v+dv by growth} - \text{Rate at which granules leave size range v to v+dv by breakage}}_{(11.9)\ +(11.10)+(11.11)}$$

(4) Granulation Equipments Table 11.1

Tumbling granulator Figure 11.4

- tumbling inclined drum and pan

- operate in continuous mode

Mixer graunulator

- rotating agitator
- from 50 rpm(horizontal pug mixer-fertilizer)
  to 3000 rpm(vertical Schugi high shear continuous granulator
  -detergent, agricultural chemicals)

Fluidized bed granulators

- bubbling or spouted bed Figure 11.5
- operate in batch or continuous mode
- good heat and mass transfer
- mechanical simplicity
- combine drying stage with granulation
- produce small granules
- running cost and attrition rates : higher