Collision and Coagulation of Particles

- Important especially for the case of high concentration
- Particle collision leads to a reduction in total number and an increase in the average size
- Influence the determination of particle growth & morphology
- Why does collision occur ?

: difference in particle velocity (in vector)

(Brownian motion, Shear flow, turbulent motion, Differential sedimentation, External force(electrically, acoustically))

Collision and Coagulation of Particles

- Fast coalescence limit : can assume spherical particle (competition between collision and coalescence)

  N_{ij} : number of collisions per unit time per unit volume between particles of volumes (v_i, v_j) : (unit #/cm^3 sec)

$$N_{ij} = \beta(v_i, v_j) n_i n_j$$

β : collision frequency function or coagulation coefficient : cm^3/sec

Rate of formation of particles of size v_k

$v_i + v_j = v_k \qquad \frac{1}{2}\sum_{i+j=k} N_{ij}$

For the case of i=j, $\frac{1}{2}\beta(v_{i,}\ v_j)n_i n_j.$

$\leftarrow$ due to the indistinguishability of two equal sized particles.)

half particle: red : half particle: blue

$$\beta(v_{i,} v_j)\frac{n_i}{2}\frac{n_i}{2} = \frac{1}{4}\beta n_i^{\ 2} \qquad \beta(v_{i,} v_j)(\frac{n_i}{4}\frac{n_i}{4} + \frac{n_i}{4}\frac{n_i}{4}) = \frac{1}{8}\beta n_i^{\ 2}$$

$$\beta(v_{i,} v_i)(\frac{n_i}{8}\frac{n_i}{8} + \frac{n_i}{8}\frac{n_i}{8} + \frac{n_i}{8}\frac{n_i}{8} + \frac{n_i}{8}\frac{n_i}{8}) = \frac{1}{16}\beta n_i^{\ 2}$$

$$\therefore \beta n_i^{\ 2}(\frac{1}{4} + \frac{1}{8} + \frac{1}{16} + \cdots),\ \sin ce \sum_{n=2}^{\infty} 2^{-n} = \frac{1}{2}$$

$= \frac{1}{2}\beta n_i^{\ 2}$ as a result of indistinguishability of coagulating particles

Rate of loss of particles of v_k

$$\text{loss} = \sum_{i=1}^{\infty} N_{ik}$$

$$\therefore \frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} N_{ij} - \sum_{i=1}^{\infty} N_{ij}$$

$$= \frac{1}{2} \sum_{i+j=k} \beta(v_{i,} v_j) n_i n_j - n_k \sum_{i=1}^{\infty} \beta(v_{i,} v_j) n_i$$

Particle dynamics equation for discrete size when coagulation alone is considered.

Coagulation mechanisms

- **Brownian Coagulation**
- **Laminar Shear**
- **Turbulent Shear**
- **Differential Sedimentation**

Brownian coagulation : important for d_p << 1㎛

$\lambda_g < d_p < 1\mu m \rightarrow$ continuum approach

: thermal motion of gas molecules and its associated random motion of small particles

1. equal-sized particles of radius r_p at concentration n_0

: imagine one particle to be stationary

: point particle deposition on the fixed particle

$$\frac{\partial n}{\partial t} = D\left(\frac{\partial^2 n}{\partial r^2} + \frac{2}{r}\frac{\partial n}{\partial r}\right) \quad n(r,\, 0) = n_0 \quad n(\infty,\, t) = n_0 \quad n(2r_p,\, t) = 0$$

Sol. $n(r,t) = n_0\left(1 - \frac{2r_p}{r}\, erfc\left(\frac{r - 2r_p}{2\sqrt{Dt}}\right)\right)$

The rate at which particles arrive at the surface $r=2r_p$

$$J = 16\pi r_p^{\,2} D \left.\frac{\partial n}{\partial r}\right)_{r=2r_p} = 8\pi r_p D n_0 \left(1 + \frac{2r_p}{\sqrt{\pi D t}}\right)$$

initially very rapid collision, but

$$2r_p \big/ \sqrt{\pi D t} << 1,$$

collision rate approaches the steady state

$$\rightarrow 8\pi r_p D n_0$$

When r_{p1} and r_{p2} have Brownian motion simultaneously,

$$D_{ij} = \frac{\overline{\left|\vec{x}_i - \vec{x}_j\right|^2}}{2t} = \frac{\overline{\left|\vec{x}_i\right|^2}}{2t} + \frac{\overline{\left|\vec{x}_j\right|^2}}{2t} - 2\frac{\overline{(\vec{x}_i \cdot \vec{x}_j)}}{2t}$$

$$\langle x^2 \rangle = 2Dt$$

r_{p1} : fixed $\rightarrow$ same problem

$D \rightarrow D_{12} \quad r \rightarrow r_{p1} + r_{p2}$

$$n_2 = n_{20}\left(1 - \frac{r_{p1} + r_{p2}}{r}\, erfc\left(\frac{r-(r_{p1}+r_{p2})}{2\sqrt{D_{12}t}}\right)\right)$$

$J = 4\pi(r_{p1} + r_{p1})D_{12}n_{20}(1+\cdots) \leftarrow$ steady solution per a single #1 particle

When there are more than one #1 particle, total collision rate between #1 and #2 particles per unit volume

$$J = 4\pi(r_{p1} + r_{p1})D_{12}n_{20}n_{10} \leftarrow \text{\#/cm3 sec}$$

$$= N_{ij} = \beta(v_{i,} v_j)n_i n_j$$

$$\beta(v_{i,} v_j) = 4\pi(D_1 + D_2)(r_{p1} + r_{p2})$$

$$= 2\pi(D_1 + D_2)(d_{p1} + d_{p2})$$

$$= \frac{2kT}{3\mu}\left(\frac{1}{v_1^{1/3}} + \frac{1}{v_2^{1/3}}\right)\left(v_1^{1/3} + v_2^{1/3}\right)$$

$$D_1 = \frac{kT}{3\pi\mu d_{p1}} \qquad D_2 = \frac{kT}{3\pi\mu d_{p2}}$$

free-molecular regime, i.e., $d_p \ll \lambda_g$ →kinetic theory

$f(v)d^3v$: mean number of particles per unit volume with center of mass velocity in the range between v and $v + dv$

$$f(v) = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-mv^2 / 2kT\right)$$

: Maxwell-Boltzmann distribution

$$\bar{v} = \frac{1}{n}\int v f(v) d^3 v$$

$$d^3 v = dv_x dv_y dv_z$$

in spherical coordinate

$$d^3 v = v^2 dv \sin\theta \, d\theta \, d\vartheta$$

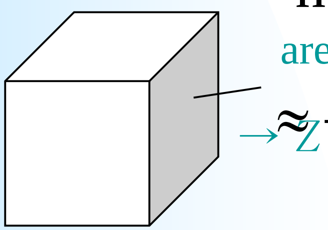
$$\therefore \bar{v} = \frac{1}{n}\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} v^2 dv \sin\theta \, d\theta \, d\vartheta \, f(v) v$$

$$= \frac{4\pi}{n}\int_0^{\infty} f(v) v^3 dv = \left(\frac{8kT}{\pi m}\right)^{1/2} : \text{mean speed}$$

Collision rate per unit area

#/m^{2}sec : number of collisions per unit area per unit time

i) crude calculation



number of particle having Z-direction velocity

$\approx \frac{n}{6}$ per unit volume

particle with $\bar{v}$ moves $\bar{v}dt$ in dt, which makes volume $\bar{v}dtA$

$\therefore$ total number of particles which strike

per unit area per unit time $\approx \frac{1}{6}n\bar{v} \approx n\bar{v}$

ii) Exact calculation : consider the distribution of particle velocity

consider particles with velocity v to v+dv its

direction θ to $\theta + d\theta$ and ϑ to $\vartheta + d\vartheta$

$f(v)d^3v \quad vdt \quad dA\cos\theta$: number of particles of this type that strike the area dA in time dt

total number of particles that strike a unit area of the wall per unit time

$$\Phi_0 = \int f(v) v \cos\theta d^3v$$

$$0 < v < \infty \qquad 0 < \vartheta < 2\pi \qquad 0 < \theta < \frac{\pi}{2} \qquad \frac{\pi}{2} < \theta < \pi$$

: particles leaving from the wall

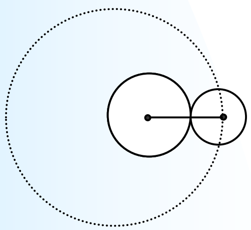
$$d^3v = v^2 dv \sin\theta \, d\theta \, d\vartheta$$

$$\therefore \Phi_0 = \int_0^\infty f(v) v^3 dv \int_0^{\frac{\pi}{2}} \sin\theta \, \cos\theta \, d\theta \times \int_0^{2\pi} d\vartheta = \pi \int_0^\infty f(v) v^3 dv$$

$$\bar{v} = \frac{4\pi}{n} \int_0^\infty f(v) v^3 dv \qquad \therefore \Phi_0 = \frac{1}{4} n\bar{v} \quad \text{Effusion flux}$$

Fix d_{p_1} particle

$$\overline{v_{12}} = \left(\overline{v_1}^2 + \overline{v_2}^2\right)^{1/2}$$: mean speed



$$\therefore \pi\left(d_{p1} + d_{p2}\right)^2 \frac{1}{4} n_2 \overline{v_{12}}$$

collision rate per single particle of 1

$\therefore$ total collision rate between 1 and 2 particles per unit volume

$$N_{12} = \pi\left(d_{p1} + d_{p2}\right)^2 \frac{1}{4} n_2 \overline{v_{12}} n_1$$

$$\therefore \beta = \frac{\pi}{4}\left(d_{p1} + d_{p2}\right)^2 \overline{v_{12}}$$

$$\overline{v_{12}} = \sqrt{\overline{v_1}^2 + \overline{v_2}^2} = \frac{4(3kT)^{1/2}}{\pi \rho_p^{1/2}} \left(\frac{1}{d_{p1}^3} + \frac{1}{d_{p2}^3} \right)^{1/2}$$

$$\therefore \beta = \left(\frac{3kT}{\rho_p} \right)^{1/2} \left(d_{p1} + d_{p2} \right)^2 \left(\frac{1}{d_{p1}^3} + \frac{1}{d_{p2}^3} \right)^{1/2}$$

$$v_1 = \frac{1}{6} \pi d_{p1}^3 \qquad v_2 = \frac{1}{6} \pi d_{p2}^3$$

$$\left(\frac{6v_1}{\pi} \right)^{1/3} = d_{p1}^3 \qquad \left(\frac{6v_2}{\pi} \right)^{1/3} = d_{p2}^3$$

$$\beta = \left(\frac{3}{4\pi} \right)^{1/6} \left(\frac{6kT}{\rho_p} \right)^{1/2} \left(\frac{1}{v_i} + \frac{1}{v_j} \right)^{1/2} \times \left(v_i^{1/3} + v_j^{1/3} \right)^2 \quad \text{Eq. (7-17)}$$

Transition regime? Fuchs formula

TABLE 10.1 Fuchs Form of the Brownian Coagulation Coefficient K12

$$K_{12} = 2\pi(D_1 + D_2)(D_{p1} + D_{p2})\left[\frac{D_{p1} + D_{p2}}{D_{p1} + D_{p2} + 2g_{12}} + \frac{8(D_{p1} + D_{p2})}{\bar{c}_{12}(D_{p1} + D_{p2})}\right]^{-1}$$

$$D_i = \frac{kT}{3\pi\mu D_{pi}}\left[\frac{5 + 4Kn_i + 6Kn_i^2 + 18kn_i^3}{5 - Kn_i + (8+\pi)Kn_i^2}\right] \text{Phillips(1975)}$$

$$g_{12} = \left(g_1^2 + g_2^2\right)^{1/2} \qquad g_1 = \left(\frac{1}{(3D_{pi}l_i)}\right)\left[\left(D_{pi} + l_i\right)^3 - \left(D_{pi}^2 l_i^2\right)^{3/2}\right] - D_{pi}$$

$$l_i = \frac{8D_i}{\pi \bar{c}_i} \qquad \bar{c}_i = \left(\frac{8kT}{\pi m_1}\right)^{1/2} \qquad Kn_i = \frac{2\lambda_{air}}{D_{pi}}$$

$$\bar{c}_{12} = \left(\bar{c}_1^2 + \bar{c}_2^2\right)^{1/2}$$

TABLE 10.1. Fuchs Form of the Brownian Coagulation Coefficient K_{12}

$$K_{12} = 2\pi(D_1 + D_2)(D_{p1} + D_{p2})\left[\frac{D_{p1} + D_{p2}}{D_{p1} + D_{p2} + 2g_{12}} + \frac{8(D_1 + D_2)}{\bar{c}_{12}(D_{p1} + D_{p2})}\right]^{-1}$$

$$D_i = \frac{kT}{3\pi\mu D_{pi}}\left[\frac{5 + 4\mathrm{Kn}_i + 6\mathrm{Kn}_i^2 + 18\mathrm{Kn}_i^3}{5 - \mathrm{Kn}_i + (8 + \pi)\mathrm{Kn}_i^2}\right] \quad \text{Phillips (1975)}$$

$$g_{12} = (g_1^2 + g_2^2)^{1/2}$$

$$g_i = (1/(3D_{pi}l_i))[(D_{pi} + l_i)^3 - (D_{pi}^2 + l_i^2)^{3/2}] - D_{pi}$$

$$l_i = 8D_i/\pi\bar{c}_i$$

$$\bar{c}_i = (8kT/\pi m_i)^{1/2}$$

$$\mathrm{Kn}_i = 2\lambda_{\mathrm{air}}/D_{pi}$$

$$\bar{c}_{12} = (\bar{c}_1^2 + \bar{c}_2^2)^{1/2}$$

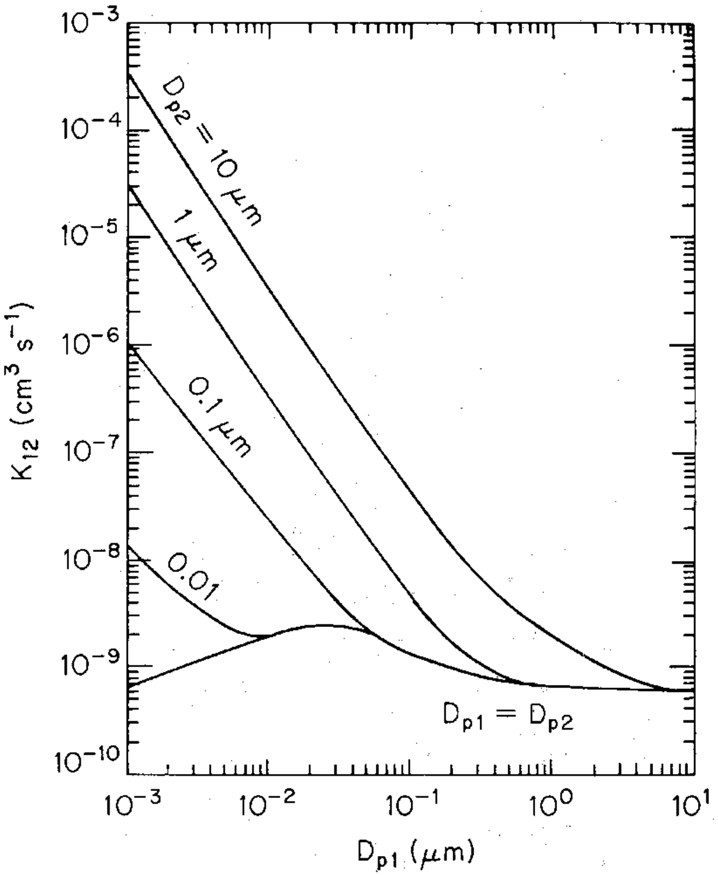


Fig.13 Brownian coagulation coefficient $K(D_{pi}, D_{pj})$ for particles of density ρ_p = 1 g cm^{-3} in air at 298K, 1atm

- continuum regime $d_{p1} = d_{p2}$

$$\rightarrow \beta = \frac{8kT}{3\mu}$$; independent of particle size

free molecular $\rightarrow \beta = 4\left(\frac{6kT}{\rho_p}\right)^{1/2} d_p^{1/2}$

The maximum occurs near $0.02\mu m$ $(\rho_p = 1\ g/cc)$

The reason is that large particle has low diffusivity and small particle has small cross-section area $\rightarrow$

The maximum near $0.02\mu m$

- For given d_{p1}, if d_{p2} becomes larger,

  target area increases proportionally to $d_p{}^2$

  but, diffusivity decreases with $\dfrac{1}{d_p}$

$$\lim \beta = \frac{2kT}{3\mu}\frac{d_{p2}}{d_{p1}} \qquad \therefore d_{p2}{}^2 \times \frac{1}{d_{p2}} = d_{p2}$$

for free molecular regime, $\displaystyle \lim_{d_{p2}>>d_{p1}} \beta = \left(\frac{3kT}{\rho_p}\right)^{1/2} \frac{d_{p2}{}^2}{d_{p1}{}^{3/2}}$

Coagulation coefficient increases more rapidly with dp2 for free molecular regime than for continuum regime