Lectures 19-20: Dynamics of Aerosol Populations - Coagulation

Quick review: Dynamics of single aerosol particles (Lectures 6-7)

Gas molecules

$$\bar{c}_B = \left(\frac{8RT}{\pi M_B}\right)^{1/2}$$

$$\lambda = 2\frac{D}{\bar{c}}$$

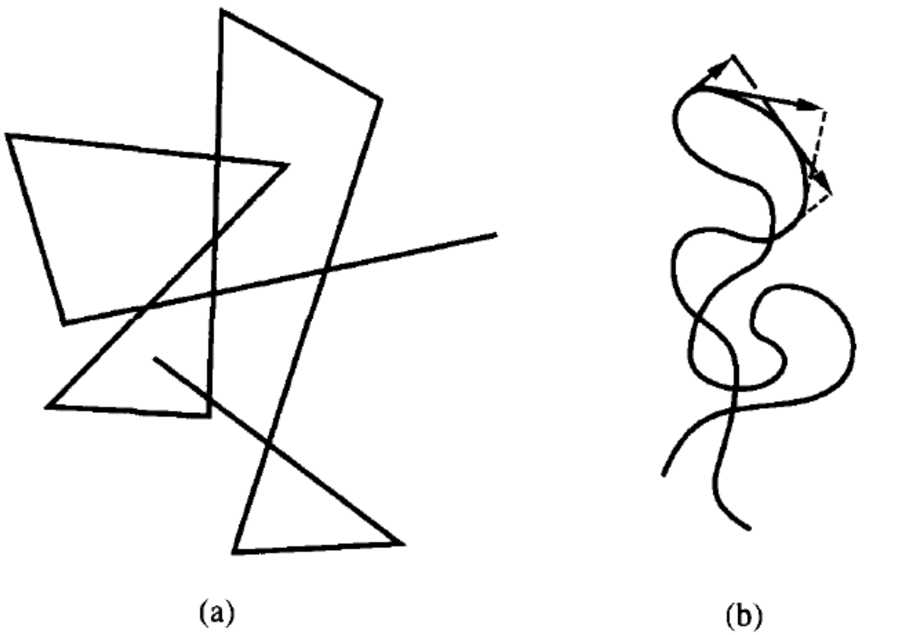


FIGURE 9.11 A two-dimensional projection of the path of (a) an air molecule and (b) the center of a 1-μm particle. Also shown is the apparent mean free path of the particle.

Particles

$$\bar{c}_p = \left(\frac{8kT}{\pi m_p}\right)^{1/2}$$

$$D = \frac{1}{2}\bar{c}_p \lambda_p$$

$$D = \frac{kTC_c}{3\pi\mu D_p}$$

$$\lambda_p = \frac{C_c}{6\mu}\sqrt{\frac{\rho k T D_p}{3}}$$

C_c: *slip correction factor* (noncontinuum effects)

Motion of particle in gas medium

$$m_p \frac{d\mathbf{v}}{dt} = \sum_i \mathbf{F}_i$$

Motion of particle in gas medium

GRAVITATIONAL SETTLING OF AN AEROSOL PARTICLE

in a fluid with velocity **u**

$$m_p \frac{d\mathbf{v}}{dt} = m_p\mathbf{g} + \frac{3\pi\mu D_p}{C_c}(\mathbf{u} - \mathbf{v})$$

for $Re < 0.1$

TABLE 9.4 Characteristic Time Required for Reaching Terminal Settling Velocity

D_p, μm	τ, s
0.05	4×10^{-8}
0.1	9.2×10^{-8}
0.5	1×10^{-6}
1.0	3.6×10^{-6}
5.0	7.9×10^{-5}
10.0	3.14×10^{-4}
50.0	7.7×10^{-3}

$$\tau \frac{d\mathbf{v}}{dt} = \tau\mathbf{g} + \mathbf{u} - \mathbf{v}$$

$$\tau = \frac{m_p C_c}{3\pi\mu D_p}$$

is the characteristic *relaxation time* of the particle.

Motion of a Charged Particle in an Electric Field

$$m_p \frac{d\mathbf{v}}{dt} = \frac{3\pi \mu D_p}{C_c}(\mathbf{u} - \mathbf{v}) + q\mathbf{E}$$

At steady state in the absence of a background fluid velocity, the particle velocity is such that the electrical force is balanced by the drag force and

$$\mathbf{v}_e = \frac{q C_c}{3\pi \mu D_p}\mathbf{E}$$

where $\mathbf{v}_e$ is termed the *electrical migration velocity*.

Defining the electrical mobility of a charged particle B_e as $B_e = \frac{q C_c}{3\pi \mu D_p}$

$$\mathbf{v}_e = B_e \mathbf{E}$$

BROWNIAN MOTION OF AEROSOL PARTICLES

Langevin equation

$$m_p \frac{d\mathbf{v}}{dt} = -\frac{3\pi\mu D_p}{C_c}\mathbf{v} + m_p\mathbf{a}$$

The random acceleration **a** is a discontinuous term, since it represents the random force exerted by the suspending fluid molecules that imparts an irregular, jerky motion to the particle.

$$\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau}\mathbf{v} + \mathbf{a}$$

dot product

$$\mathbf{r}\cdot\frac{d\mathbf{v}}{dt} = -\frac{1}{\tau}\mathbf{r}\cdot\mathbf{v} + \mathbf{r}\cdot\mathbf{a}$$

ensemble averaging

$$<\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + <\mathbf{r}\cdot\mathbf{a}> \quad = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}>$$

$$\frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> = <\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> + <\frac{d\mathbf{r}}{dt}\cdot\mathbf{v}>$$

$$<\mathbf{r}\cdot\frac{d\mathbf{v}}{dt}> = \frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> - <v^2>$$

$$\frac{d}{dt}<\mathbf{r}\cdot\mathbf{v}> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + <v^2> = -\frac{1}{\tau}<\mathbf{r}\cdot\mathbf{v}> + \frac{3kT}{m_p}$$

$$< \mathbf{r} \cdot \mathbf{v} > = \frac{3kT\tau}{m_p} + c\exp(-t/\tau)$$

$$< \mathbf{r} \cdot \mathbf{v} > = < \mathbf{r} \cdot \frac{d\mathbf{r}}{dt} > = \frac{1}{2}\frac{d}{dt} < r^2 >$$

$$\frac{1}{2}\frac{d}{dt} < r^2 > = \frac{3kT\tau}{m_p} + c\exp(-t/\tau)$$

for $t \gg \tau$,

$$\frac{1}{2}\frac{d}{dt} < r^2 > = \frac{3kT\tau}{m_p}$$

$$< r^2 > = \frac{6kT\tau}{m_p} t = \frac{2kTC_c t}{\pi \mu D_p}$$

$$< x^2 > = < y^2 > = < z^2 > = \tfrac{1}{3} < r^2 >.$$

$$< x^2 > = < y^2 > = < z^2 > = \frac{2kTC_c}{3\pi \mu D_p} t$$

This result, first derived by Einstein by a different route, has been confirmed experimentally.

Quick review: Mass transport to or from atmospheric particles : Condensation and Evaporation (Lecture 12)

Knudsen number:

$$Kn = \frac{2\lambda}{D_p} = \frac{\lambda}{R_p}$$

$$J_c = 4\pi R_p D_g (c_\infty - c_s)$$

$$J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$$

$$J = f(K_n, \alpha)\, J_c$$

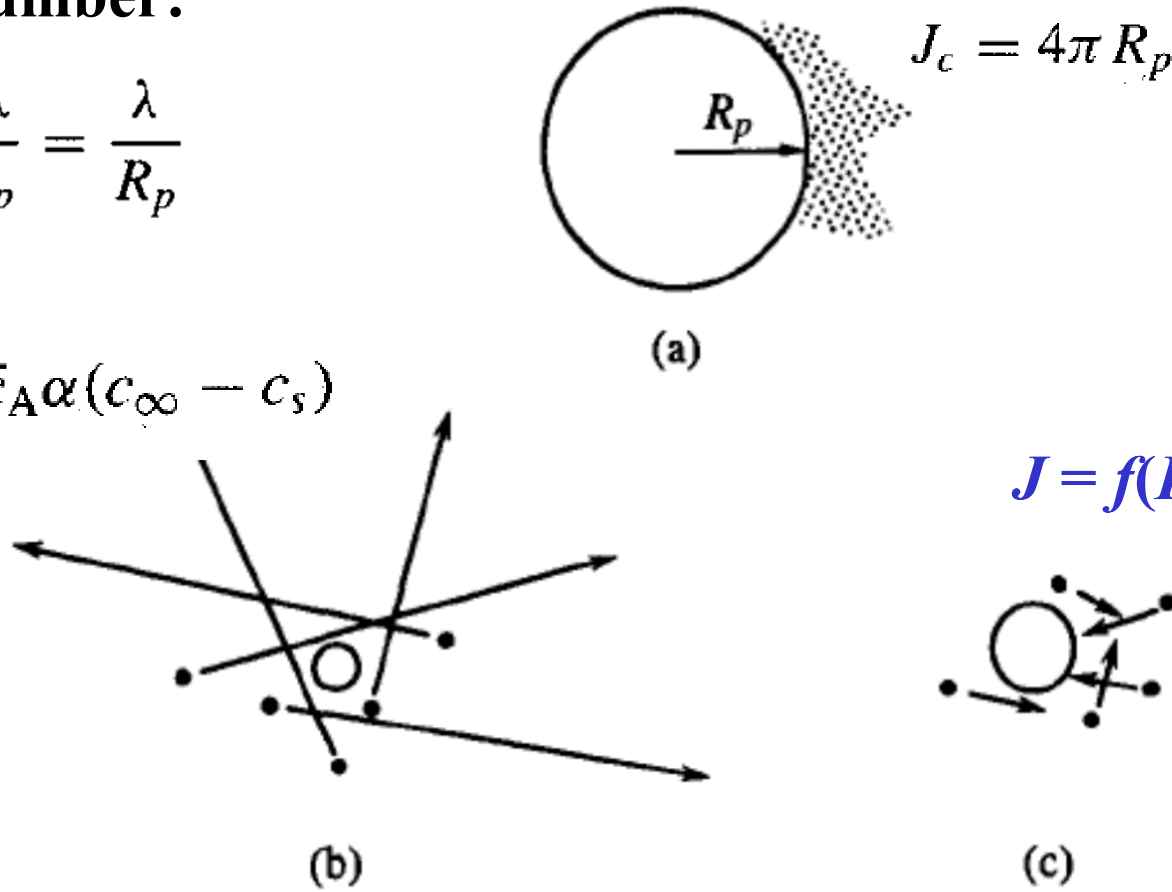


FIGURE 9.1 Schematic of the three regimes of suspending fluid–particle interactions: (a) continuum regime ($Kn \rightarrow 0$), (b) free molecule (kinetic) regime ($Kn \rightarrow \infty$), and (c) transition regime ($Kn \sim 1$).

A mass balance on the growing or evaporating particle is

$$\frac{\rho_p}{M_A}\frac{d}{dt}\left(\frac{4}{3}\pi R_p^3\right) = J_c$$

$$\frac{dR_p}{dt} = \frac{D_g M_A}{\rho_p R_p}(c_\infty - c_s) \qquad R_p^2 = R_{p0}^2 + \frac{2D_g M_A}{\rho_p}(c_\infty - c_s)\,t$$

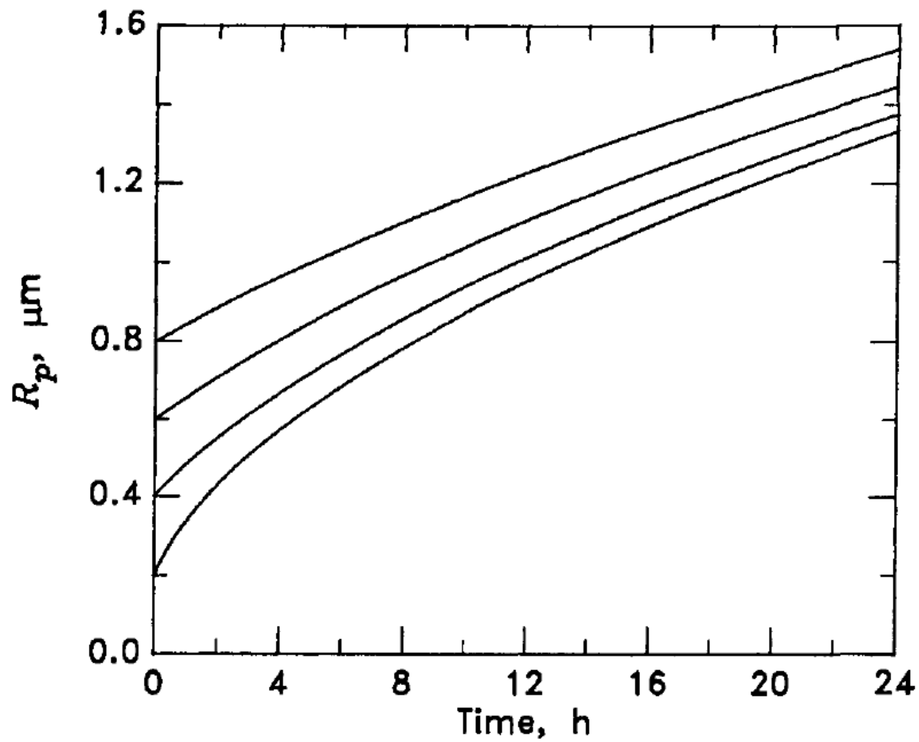


FIGURE 12.1 Growth of aerosol particles of different initial radii as a function of time for a constant concentration gradient of 1 μg m^{-3} between the aerosol and gas phases ($D_g = 0.1$ cm^2 s^{-1}, $\rho_p = 1$ g cm^{-3}).

Coagulation: Particle-particle interaction

Aerosol particles suspended in a fluid may come into contact because of their Brownian motion or as a result of their motion produced by hydrodynamic, electrical, gravitational, or other forces. Brownian coagulation is often referred to as thermal coagulation.

Continuum Regime

the steady-state coagulation rate ($cm^{-3}\ s^{-1}$) between #1 and #2 particles is

$$J_{12} = 2\pi(D_{p1} + D_{p2})(D_1 + D_2)N_1 N_2$$

$$J_{12} = K_{12} N_1 N_2$$

$$K_{12} = 2\pi(D_{p1} + D_{p2})(D_1 + D_2)$$

$$D_i = \frac{kT}{3\pi\mu D_{pi}}$$

$$K_{12} = \frac{2kT}{3\mu}\frac{(D_{p1} + D_{p2})^2}{D_{p1} D_{p2}}$$

Transition and Free Molecular Regime

Diffusion equations cannot describe the motion of particles inside a layer of thickness λ_p adjacent to an absorbing wall:

$$K_{12} = 2\pi(D_{p1} + D_{p2})(D_1 + D_2)\beta$$

Fuchs:

$$\beta = \left(\frac{D_{p1} + D_{p2}}{D_{p1} + D_{p2} + 2(g_1^2 + g_2^2)^{1/2}} + \frac{8(D_1 + D_2)}{(\bar{c}_1^2 + \bar{c}_2^2)^{1/2}(D_{p1} + D_{p2})} \right)^{-1}$$

$$Kn_i = \frac{2\lambda_{\text{air}}}{D_{pi}}$$

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

$$\ell_i = \frac{8D_i}{\pi \bar{c}_i}$$

$$g_i = \frac{1}{3D_{pi}\ell_i} \left[(D_{pi} + \ell_i)^3 - (D_{pi}^2 + \ell_i^2)^{3/2} \right] - D_{pi}$$

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

Dahneke:

$$\beta_D = \frac{1 + Kn_D}{1 + 2\,Kn_D(1 + Kn_D)}$$

$$Kn_D = \frac{2(D_1 + D_2)}{\bar{c}_{12} R_p}$$

$$R_p = R_{p1} + R_{p2} \text{ and } \bar{c}_{12} = (c_1^2 + c_2^2)^{1/2}$$

Difference between β derived by Fuchs and Dahneke is less than 4%.

$$Kn \to 0,\ \beta = 1$$

$$Kn \to \infty \qquad K_{12} = \pi(R_{p1} + R_{p2})^2(\bar{c}_1^2 + \bar{c}_2^2)^{1/2}$$

TABLE 13.2 Coagulation Coefficients of Monodisperse Aerosols in Air[c]

$\beta = 1$

D_p, μm	K_0, $cm^3\ s^{-1}$[a]	K, $cm^3\ s^{-1}$[b]
0.002	690×10^{-10}	8.9×10^{-10}
0.004	340×10^{-10}	13×10^{-10}
0.01	140×10^{-10}	19×10^{-10}
0.02	72×10^{-10}	24×10^{-10}
0.04	38×10^{-10}	23×10^{-10}
0.1	18×10^{-10}	15×10^{-10}
0.2	11×10^{-10}	11×10^{-10}
0.4	8.6×10^{-10}	8.2×10^{-10}
1.0	7.0×10^{-10}	6.9×10^{-10}
2.0	6.5×10^{-10}	6.4×10^{-10}
4.0	6.3×10^{-10}	6.2×10^{-10}

[a]Coagulation coefficient neglecting kinetic effects.
[b]Coagulation coefficient including the kinetic correction.
[c]Parameter values given in Figure 13.5.

TABLE 13.3 Coagulation Coefficients ($cm^3 s^{-1}$) of Atmospheric Particles[a]

	D_{p1} (μm)					
D_{p2} μm	0.002	0.01	0.1	1.0	10	20
0.002	8.9×10^{-10}	5.7×10^{-9}	3.4×10^{-7}	7.8×10^{-6}	8.5×10^{-5}	17×10^{-5}
0.01	5.7×10^{-9}	19×10^{-10}	2.5×10^{-8}	3.4×10^{-7}	3.5×10^{-6}	7.0×10^{-6}
0.1	3.4×10^{-7}	2.5×10^{-8}	15×10^{-10}	5.0×10^{-9}	4.5×10^{-8}	9.0×10^{-8}
1	7.8×10^{-6}	3.4×10^{-7}	5.0×10^{-9}	6.9×10^{-10}	2.1×10^{-9}	3.9×10^{-9}
10	8.5×10^{-5}	3.5×10^{-6}	4.5×10^{-8}	2.1×10^{-9}	6.1×10^{-10}	6.8×10^{-10}
20	17×10^{-5}	7.0×10^{-6}	9.0×10^{-8}	3.9×10^{-9}	6.8×10^{-10}	6.0×10^{-10}

[a] Parameter values given in Figure 13.5.

Questions:

Lifetime of particles due to coagulation for particles of different concentrations and sizes?

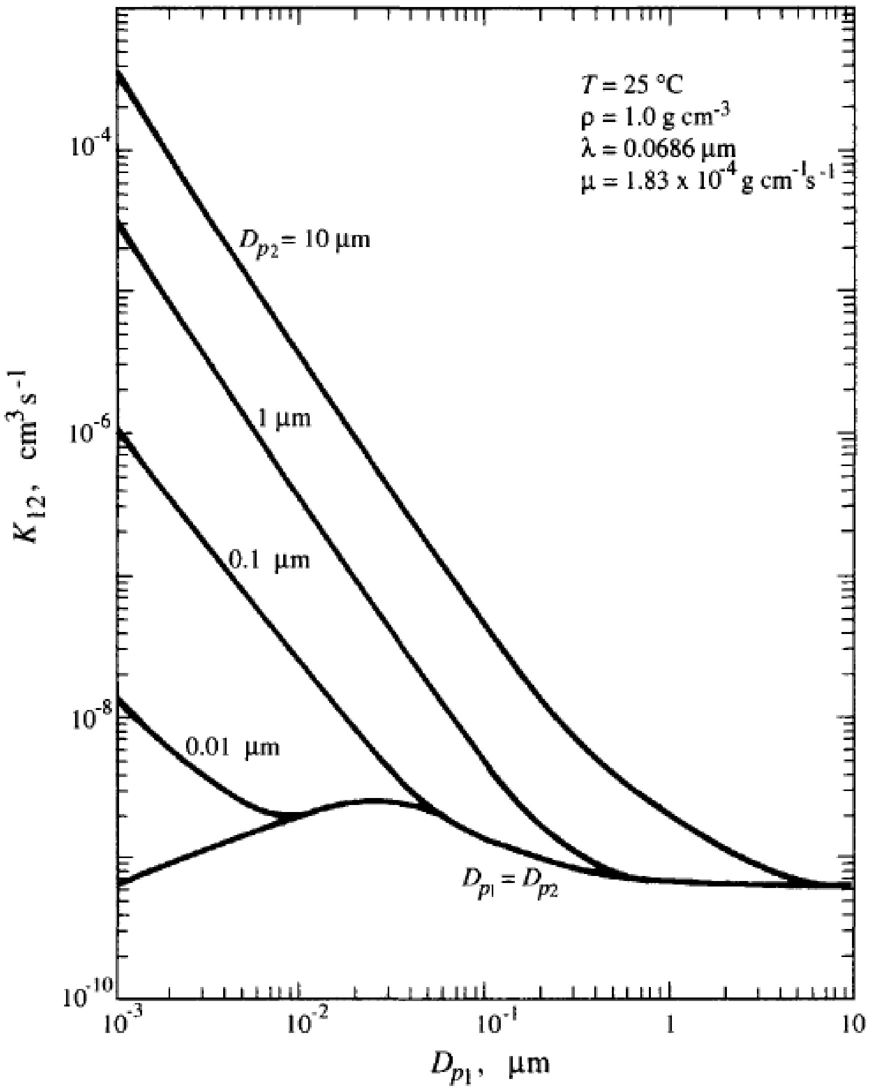


FIGURE 13.5 Brownian coagulation coefficient K_{12} for coagulation in air at 25°C of particles of diameters D_{p1} and D_{p2}. The curves were calculated using the correlation of Fuchs in Table 13.1. To use this figure, find the *smaller* of the two particles as the abscissa and then locate the line corresponding to the larger particle.

continuum regime

$$K_{11} = \frac{8kT}{3\mu}$$

free molecular regime

$$K_{11} = 4\left(\frac{6kT}{\rho_p}\right)^{1/2} D_{p1}^{1/2}$$

In the continuum regime if $D_{p2} \gg D_{p1}$,

$$\lim_{D_{p2} \gg D_{p1}} K_{12} = \frac{2kT}{3\mu}\frac{D_{p2}}{D_{p1}}$$

In the free molecular regime if $D_{p2} \gg D_{p1}$,

$$\lim_{D_{p2} \gg D_{p1}} K_{12} = \left(\frac{3kT}{\rho_p}\right)^{1/2} \frac{D_{p2}^2}{D_{p1}^{3/2}}$$

What's the collision coefficient of H2SO4 molecules?

Coagulation in Laminar Shear Flow $\Gamma = du/dy$

$$J_{\text{coag}} = K_{12}^{LS} N_1 N_2 = \frac{\Gamma}{6}(D_{p1} + D_{p2})^3 N_1 N_2$$

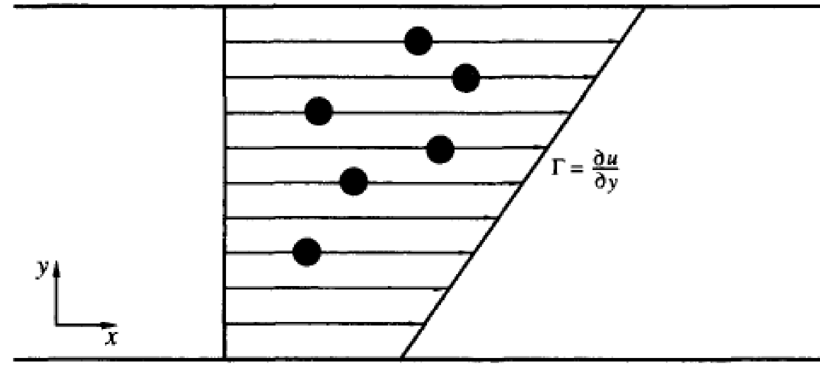


FIGURE 13.A.1 Schematic illustrating collisions of particles in shear flow.

Coagulation in Turbulent Flow

$$K_{12}^{TS} = \left(\frac{\pi \varepsilon_k}{120\nu}\right)^{1/2} (D_{p1} + D_{p2})^3$$

Coagulation from Gravitational Settling

$$K_{12}^{GS} = \frac{\pi D_{p1}^2}{4}(v_{t1} - v_{t2})E(D_{p1}, D_{p2}), \qquad D_{p1} \gg D_{p2}$$

E is the collision efficiency.

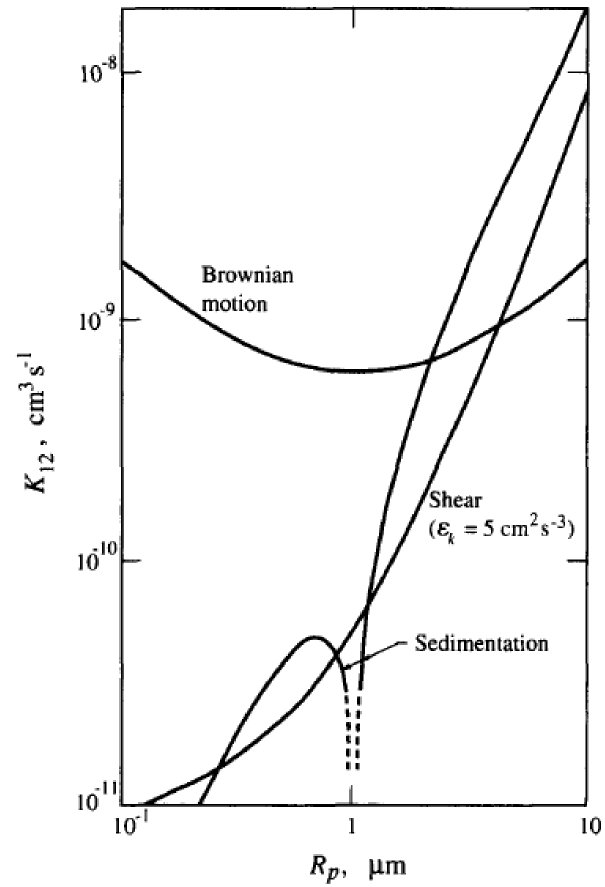


FIGURE 13.A.2 Comparison between coagulation mechanisms for a particle of 1 μm radius as a function of the particle radius of the second interacting particle.

Dynamics of Aerosol Populations

Discrete Distribution

$N_k(t)$ as the number concentration (cm^{-3}) of particles containing k monomers.

Continuous Distribution

continuous size distribution function $n(v, t)(\mu m^{-3}\ cm^{-3})$:

number of particles per cubic centimeter having volumes in the range from v to $v + dv$.

$$N(t) = \int_0^\infty n(v, t)\, dv$$

The mass of a particle, m, or the diameter, D_p, can also be used as the independent variable for the mathematical description of the aerosol distribution.

concentration of particles dN in the size range R_p to $R_p + dR_p$ is given by

$$dN = n_R(R_p, t)\, dR_p$$

Coagulation

Discrete coagulation equation

$$\frac{dN_k(t)}{dt} = \frac{1}{2}\sum_{j=1}^{k-1} K_{j,k-j}N_jN_{k-j} - N_k\sum_{j=1}^{\infty} K_{k,j}N_j, \quad k \geq 2$$

Continuous coagulation equation

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_{v_0}^{v-v_0} K(v-q,q)n(v-q,t)n(q,t)dq$$

$$-n(v,t)\int_{v_0}^{\infty} K(q,v)n(q,t)\,dq$$

Solution of the coagulation equation -- discrete

Assuming $K_{k,j} = K$

$$\frac{dN_k(t)}{dt} = \frac{1}{2}K \sum_{j=1}^{k-1} N_j(t)N_{k-j}(t) - KN_k(t) \sum_{j=1}^{\infty} N_j(t)$$

$$= \frac{1}{2}K \sum_{j=1}^{k-1} N_j(t)N_{k-j}(t) - KN_k(t)N(t)$$

$$\frac{dN(t)}{dt} = \frac{1}{2}K \sum_{k=1}^{\infty}\sum_{j=1}^{k-1} N_{k-j}(t)N_j(t) - KN^2(t)$$

$$= -\frac{1}{2}KN^2(t)$$

If $N(0) = N_0$,

$$N(t) = \frac{N_0}{1 + (t/\tau_c)} \qquad \tau_c = \frac{2}{K N_0}$$

τ_c is the characteristic time for coagulation

At $t = \tau_c$, $N(\tau_c) = \frac{1}{2} N_0$. Thus, τ_c is the time necessary for reduction of the initial number concentration to half its original value. The timescale shortens as the initial number concentration increases. Consider an initial population of particles of about 0.2 μm diameter, for which $K = 10 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$. The coagulation timescales for $N_0 = 10^4\ \mathrm{cm^{-3}}$ and $10^6\ \mathrm{cm^{-3}}$ are

$$N_0 = 10^4\ \mathrm{cm^{-3}} \qquad \tau_c \cong 55\ \mathrm{h}$$

$$N_0 = 10^6\ \mathrm{cm^{-3}} \qquad \tau_c \cong 33\ \mathrm{min}$$

Need to know how to estimate typical values of τ under different K and N0

assuming that $N_1(0) = N_0$

that is, at $t = 0$ all particles are of size $k = 1$

$$N(t) = \frac{N_0}{1 + (t/\tau_c)}$$

$$\frac{dN_1}{dt} = -KN_1N \quad \Rightarrow \quad N_1(t) = \frac{N_0}{[1 + (t/\tau_c)]^2}$$

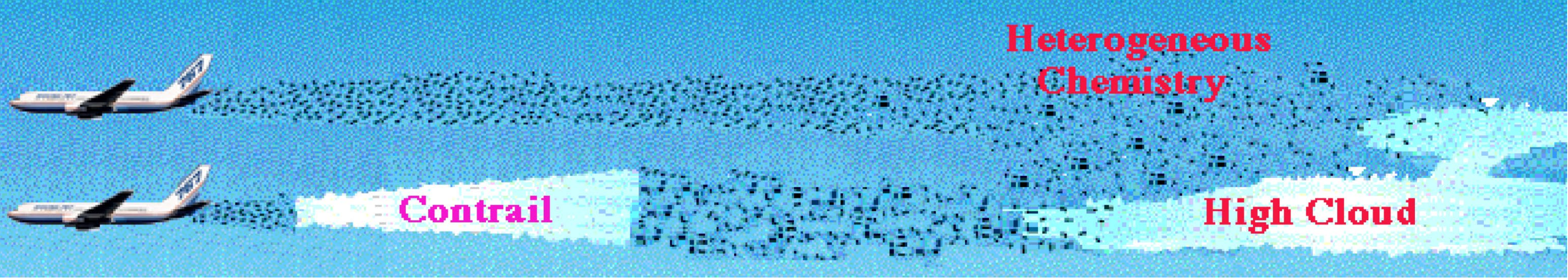
$$\frac{dN_2}{dt} = \tfrac{1}{2}KN_1^2 - KN_2N \quad \Rightarrow \quad N_2(t) = \frac{N_0(t/\tau_c)}{[1 + (t/\tau_c)]^3}$$

$$N_k(t) = \frac{N_0(t/\tau_c)^{k-1}}{[1 + (t/\tau_c)]^{k+1}}, \qquad k = 1, 2, \ldots$$

$$t/\tau_c \gg 1 \qquad N(t) \simeq \frac{N_0}{t/\tau_c} = \frac{2}{Kt}$$

$$N_k(t) \simeq N_0 \left(\frac{\tau_c}{t}\right)^2$$

$$t/\tau_c \ll 1 \qquad N_k(t) \simeq N_0 \left(\frac{t}{\tau_c}\right)^{k-1}$$



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Aerosol invariance in expanding coagulating plumes

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$$\frac{dn_p}{dt} = -\frac{n_p}{V}\frac{dV}{dt} - \frac{1}{2}K_c n_p^2$$

$$N_p \equiv n_p V$$

$$\frac{dN_p}{dt} = -\frac{1}{2}\frac{K_c}{V}N_p^2$$

$$N_p(t) = \frac{N_{po}}{\left(1 + \frac{1}{2}N_{po}\int_o^t K_c / V\, dt\right)}$$

Table 1. Asymptotic Coagulation/Dispersion Solutions for a Constant Coagulation Kernel

$V(t)$		N_T (asymptote)	t_c (coag)
$V_o = const$		$\frac{2V_o}{K_c t}$	$\frac{2V_o}{N_{po} K_c} \equiv t_{co}$
$V_o + vt$ $t_o \equiv V_o / v$		$\frac{2V_o}{K_c t_o ln\left(t / t_o \right)}$	$\approx t_{co};\ t_{co} << t_o$ $t_o exp(t_{co}/t_o);\ t_o << t_{co}$
$V_o \left(\frac{t}{t_i} \right)^{\alpha}$	$\alpha > 1$	$\frac{2V_o(\alpha - 1)}{K_c t_i}$	$\approx t_i \quad t_i >> (\alpha - 1) t_{co}$
$t \geq t_i$	$\alpha = 1$	$\frac{2V_o}{K_c t_i ln(t / t_i)}$	$t_i exp\left(t_{co} / t_i \right)$
$\alpha \geq 0$	$\alpha < 1$	$\frac{2V_o(1 - \alpha)}{K_c t_i} \left(\frac{t_i}{t} \right)^{1-\alpha}$	$\approx t_i \quad t_i >> (1 - \alpha) t_{co}$

Solution of the coagulation equation -- continuous

assuming a constant coagulation coefficient $K(q, v) = K$:

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}K\int_0^v n(v-q,t)n(q,t)\,dq - Kn(v,t)N(t)$$

$$N(t) = \frac{N_0}{1+(t/\tau_c)}$$

$$\frac{\partial n(v,t)}{\partial t} + \frac{KN_0}{1+t/\tau_c}n(v,t) = \frac{1}{2}K\int_0^v n(v-q,t)n(q,t)\,dq$$

assuming that initially

$$n(v,0) = A\exp(-Bv)$$

$$= \frac{N_0}{V_0}\exp\left(\frac{-v}{V_0}\right)$$

$$N_0 = \int_0^\infty n(v,0)\,dv = \frac{A}{B}$$

$$V_0 = \int_0^\infty vn(v,0)\,dv = \frac{1}{B}$$

$$n(v,t) = \frac{N_0}{V_0(1+t/\tau_c)^2} \exp\left(-\frac{v}{V_0(1+t/\tau_c)}\right)$$

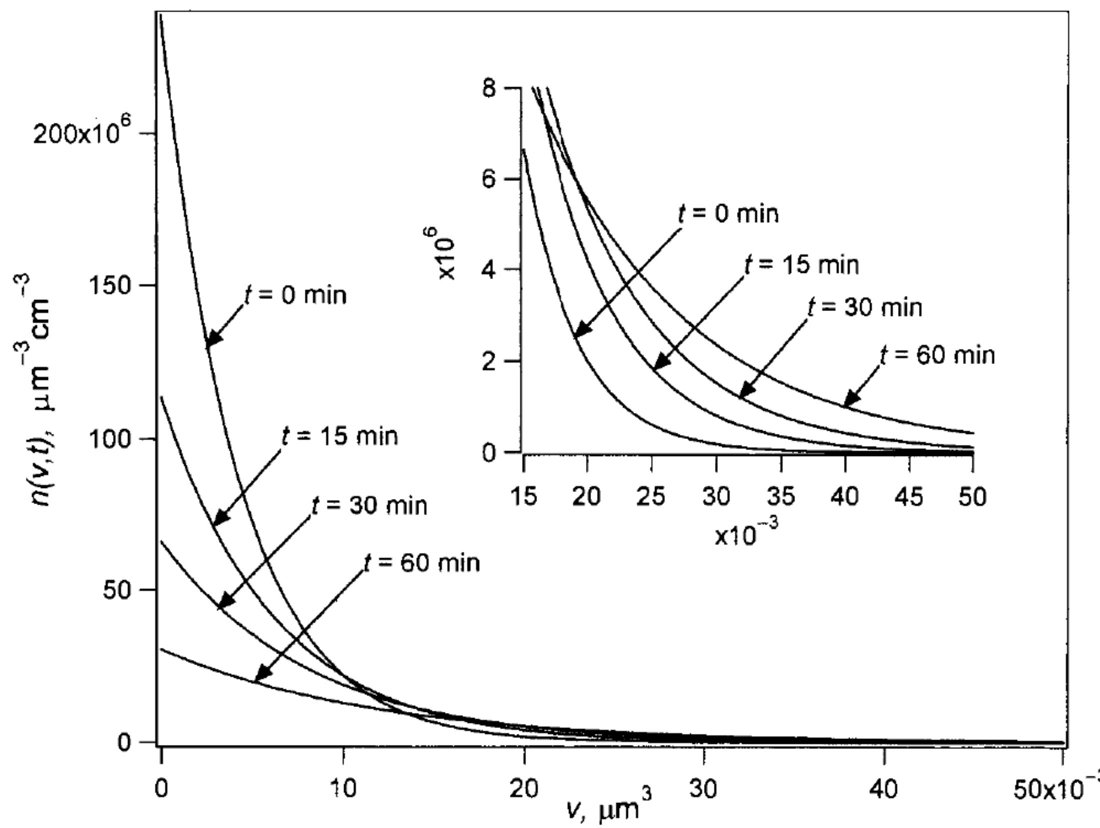
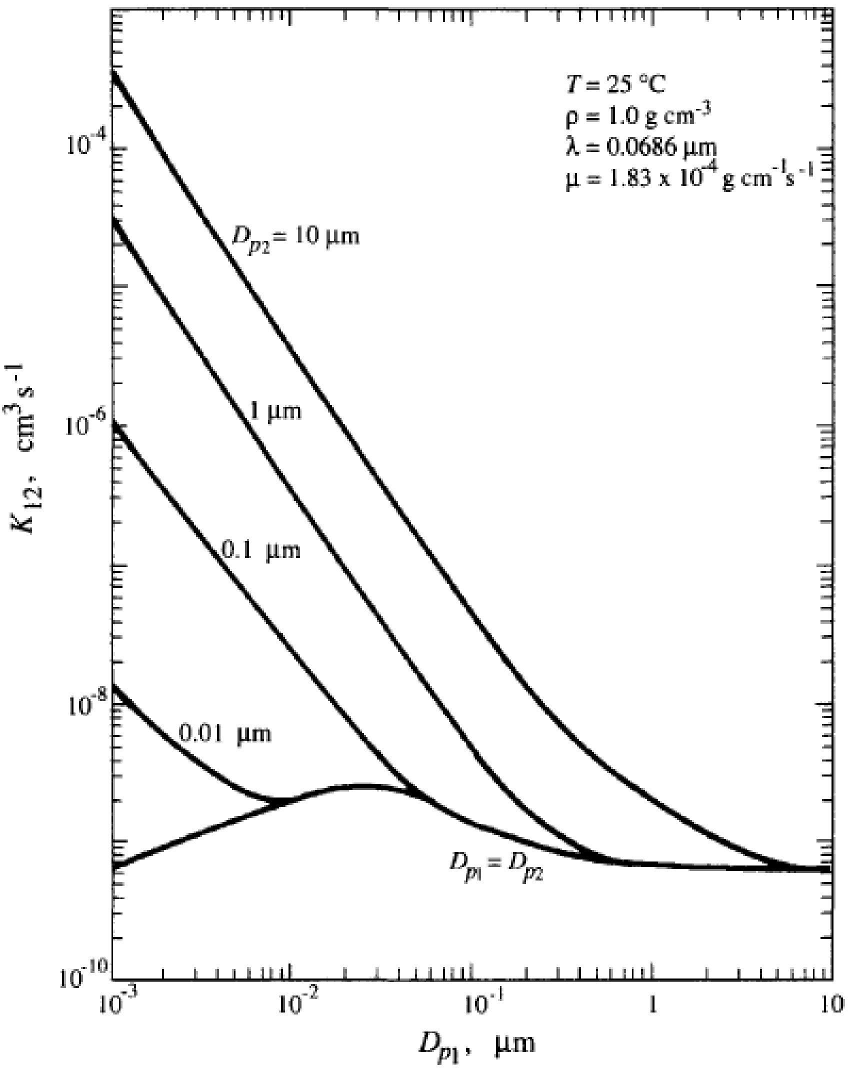
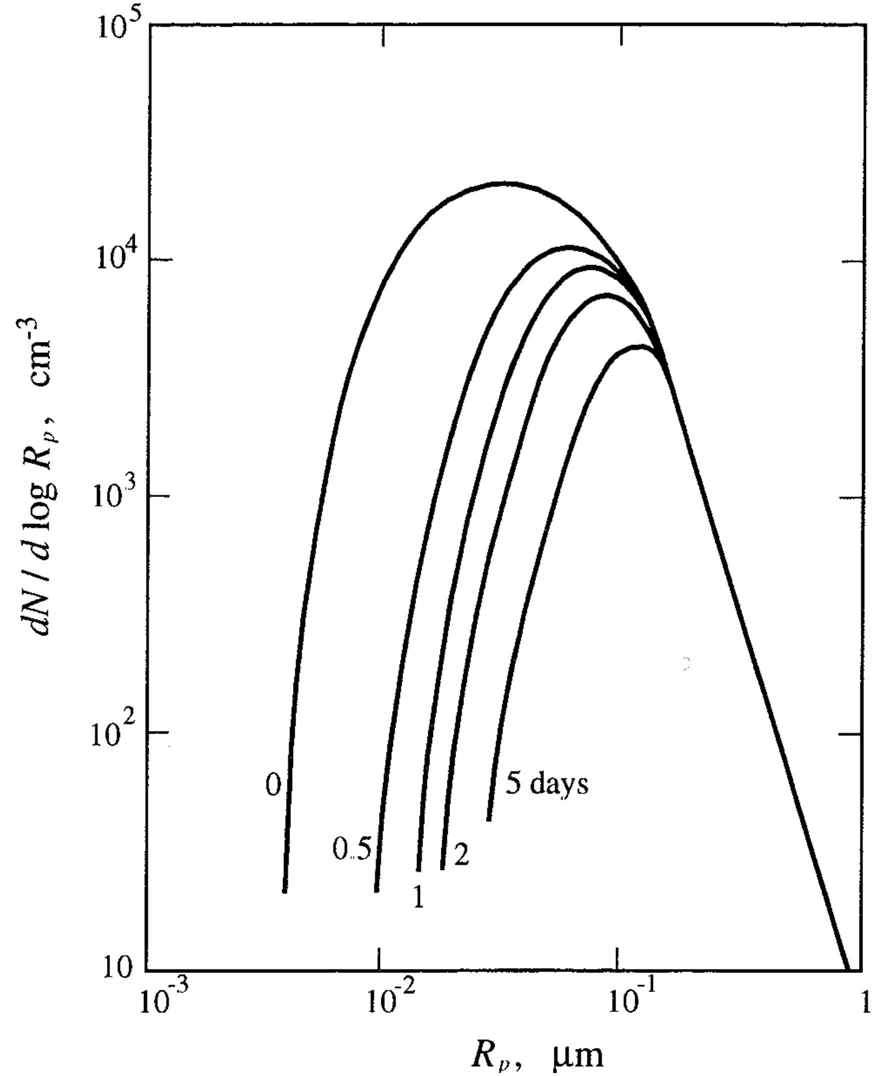


FIGURE 13.6 Solution of the continuous coagulation equation for an exponential initial distribution given by (13.78). The following parameters are used: $N_0 = 10^6\ \mathrm{cm}^{-3}, V_0 = 4189\ \mu\mathrm{m}^3\ \mathrm{cm}^{-3}$, and $\tau_c = 2000\ \mathrm{s}$.

In reality, coagulation coefficients depend on sizes of colliding particles





Evolution of a coagulating particle population size distribution during a period of 5 days (Butcher and Charlson, 1972)