Overhead Slides for

Chapter 16

of

Fundamentals of Atmospheric Modeling

by

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Coagulation

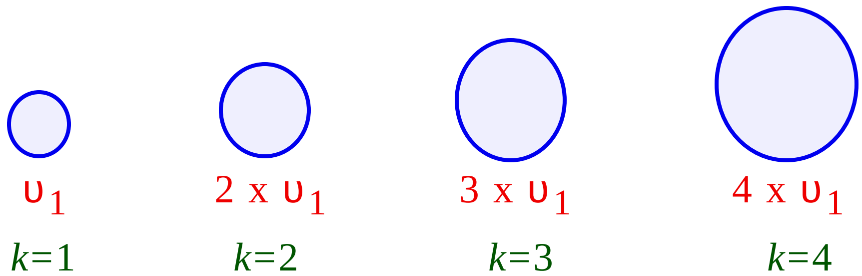
Process by which particles collide and stick together

Integro-differential coagulation equation

$$\frac{\partial n_\upsilon}{\partial t} = \frac{1}{2}\int_0^{\upsilon} \beta_{\upsilon-\bar{\upsilon},\bar{\upsilon}}\, n_{\upsilon-\bar{\upsilon}}\, n_{\bar{\upsilon}}\, \mathrm{d}\bar{\upsilon} - n_\upsilon \int_0^{\infty} \beta_{\upsilon,\bar{\upsilon}}\, n_{\bar{\upsilon}}\, \mathrm{d}\bar{\upsilon} \qquad (16.1)$$

Coagulation Over Monomer Size Structure

Fig. 16.1. Monomer size structure.



Coagulation equation over monomer size structure

$$\frac{\partial n_k}{\partial t} = \frac{1}{2}\sum_{j=1}^{k-1} \beta_{k-j,j} n_{k-j} n_j - n_k \sum_{j=1}^{\infty} \beta_{k,j} n_j \qquad (16.2)$$

Rewrite in fully implicit finite difference form

$$\frac{n_{k,t} - n_{k,t-h}}{h} = \frac{1}{2}\sum_{j=1}^{k-1} P_{k,j} - \sum_{j=1}^{\infty} L_{k,j} \qquad (16.3)$$

Production rate

$$P_{k,j} = \beta_{k-j,j} n_{k-j,t} n_{j,t} \qquad (16.4)$$

Loss rate

$L_{k,j} = \beta_{k,j} n_{k,t} n_{j,t}$ --> $P_{k,j} = L_{k-j,j}$

Rewrite (16.3) (16.5)

$$n_{k,t} = n_{k,t-h} + \frac{1}{2} h \sum_{j=1}^{k-1} \beta_{k-j,j} n_{k-j,t} n_{j,t} - h \sum_{j=1}^{\infty} \beta_{k,j} n_{k,t} n_{j,t}$$

Semi-Implicit Coagulation Over Monomer Structure

Write loss rate in semi-implicit form

$$L_{k,j} = \beta_{k,j} n_{k,t} n_{j,t-h} \qquad (16.6)$$

Substitute (16.6) into (16.3)

$$n_{k,t} = n_{k,t-h} + \frac{1}{2} h \sum_{j=1}^{k-1} \beta_{k-j,j} n_{k-j,t} n_{j,t-h} - h \sum_{j=1}^{\infty} \beta_{k,j} n_{k,t} n_{j,t-h} \qquad (16.7)$$

Rearrange --> number (but not volume) conserving equation

$$n_{k,t} = \frac{n_{k,t-h} + \frac{1}{2} h \sum_{j=1}^{k-1} \beta_{k-j,j} n_{k-j,t} n_{j,t-h}}{1 + h \sum_{j=1}^{\infty} \beta_{k,j} n_{j,t-h}} \qquad (16.8)$$

Volume (but not number) conserving equation

$$v_{k,t} = \frac{v_{k,t-h} + h \sum_{j=1}^{k-1} \beta_{k-j,j} v_{k-j,t} n_{j,t-h}}{1 + h \sum_{j=1}^{\infty} \beta_{k,j} n_{j,t-h}} \qquad (16.9)$$

where $v_{k,t} = \upsilon_k n_{k,t}$

Semi-Implicit Coagulation Over Arbitrary Structure

Volume of intermediate particle

$$V_{i,j} = \upsilon_i + \upsilon_j \qquad (16.10)$$

Volume fraction of $V_{i,j}$ partitioned to each model bin k

$$f_{i,j,k} = \begin{cases} \left(\dfrac{\upsilon_{k+1} - V_{i,j}}{\upsilon_{k+1} - \upsilon_k}\right)\dfrac{\upsilon_k}{V_{i,j}} & \upsilon_k \le V_{i,j} < \upsilon_{k+1} \quad k < N_B \\ 1 - f_{i,j,k-1} & \upsilon_{k-1} < V_{i,j} < \upsilon_k \quad k > 1 \\ 1 & V_{i,j} \ge \upsilon_k \quad k = N_B \\ 0 & \text{all other cases} \end{cases}$$

(16.11)

Substitute fractions into (16.9)

$$v_{k,t} = \frac{v_{k,t-h} + h\sum_{j=1}^{k}\left(\sum_{i=1}^{k-1} f_{i,j,k}\beta_{i,j} v_{i,t} n_{j,t-h}\right)}{1 + h\sum_{j=1}^{N_B}\left(1 - f_{k,j,k}\right)\beta_{k,j} n_{j,t-h}} \qquad (16.12)$$

Semi-Implicit Coagulation Over Arbitrary Structure

Substitute $v = n\upsilon$ --> Another volume conserving solution

$$n_{k,t} = \frac{n_{k,t-h} + \dfrac{h}{\upsilon_k} \sum_{j=1}^{k} \left(\sum_{i=1}^{k-1} f_{i,j,k} \upsilon_i \beta_{i,j} n_{i,t} n_{j,t-h} \right)}{1 + h \sum_{j=1}^{N_B} \left(1 - f_{k,j,k}\right) \beta_{k,j,t-h} n_{j,t-h}} \qquad (16.13)$$

Volume concentration solution when multiple components

$$v_{q,k,t} = \frac{v_{q,k,t-h} + h \sum_{j=1}^{k} \left(\sum_{i=1}^{k-1} f_{i,j,k} \beta_{i,j} v_{q,i,t} n_{j,t-h} \right)}{1 + h \sum_{j=1}^{N_B} \left[\left(1 - f_{k,j,k}\right) \beta_{k,j} n_{j,t-h} \right]} \qquad (16.14)$$

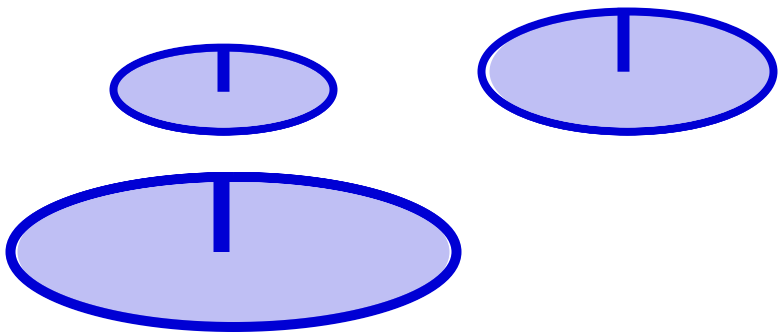
Coagulation Over Multiple Structures

Internally-mixed structure (I)
    Contains particles with all components

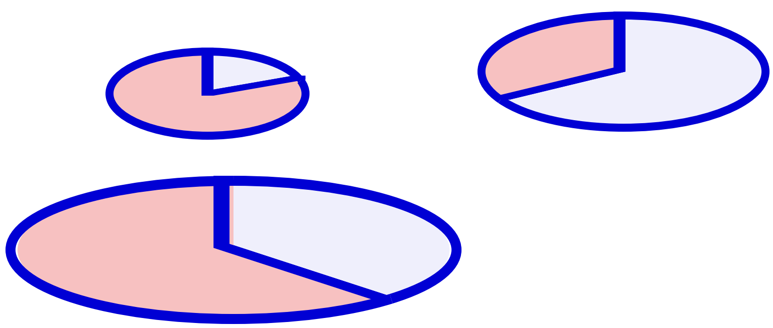
Externally-mixed structure (E)
    Contains particles with at least one component

Fig. 16.1. Externally- and internally-mixed size structures

E_1



E_2



I

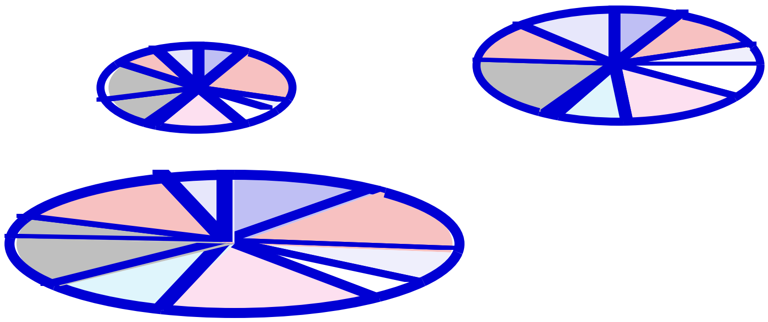


Table 16.1. Changes in number and volume when coagulation occurs among externally- and internally-mixed particles.

		Number				Volume		
Coagulating Pairs		E_1	E_2	I		E_1	E_2	I
E_1 w/ E_1		(-)	---	---		(0)	---	---
E_1 w/ E_2		(-)	(-)	(+)		(-)	(-)	(+)
E_1 w/ I		(-)	---	(0)		(-)	---	(+)
I w/ I		---	---	(-)		---	---	(0)

Coagulation Over Multiple Structures

Volume concentration of component q in size bin k of the N^{th} externally-mixed particle

$$v_{q,Nk,t} = \frac{v_{q,Nk,t-h} + h \sum_{j=1}^{k} \left(\sum_{i=1}^{k-1} f_{i,j,k} \beta_{Ni,Nj} v_{q,Ni,t} n_{Nj,t-h} \right)}{1 + h \sum_{j=1}^{N_B} \left[\left(1 - f_{k,j,k}\right) \beta_{Nk,Nj} n_{Nj,t-h} + \sum_{\substack{M=1 \\ M \neq N}}^{N_T} \beta_{Nk,Mj} n_{Mj,t-h} \right]}$$

(16.15)

N_T = number of particle types (external plus internal)
N, M = denote separate particle distributions
N_B = number of size bins
N_E = number of externally-mixed types
N_V = number of volume components

solved for each $k = 1, N_B$, $N = 1, N_E$, and $q = 1, N_V$.

Number concentration of externally-mixed particles in bin k

$$n_{Nk,t} = \frac{n_{Nk,t-h} + \frac{h}{\upsilon_k} \sum_{j=1}^{k} \left(\sum_{i=1}^{k-1} f_{i,j,k} \beta_{Ni,Nj} \upsilon_i n_{Ni,t} n_{Nj,t-h} \right)}{1 + h \sum_{j=1}^{N_B} \left[\left(1 - f_{k,j,k}\right) \beta_{Nk,Nj} n_{Nj,t-h} + \sum_{\substack{M=1 \\ M \neq N}}^{N_T} \beta_{Nk,Mj} n_{Mj,t-h} \right]}$$

(16.16)

Coagulation Over Multiple Structures

Volume concentration of component q and size k of the internally-mixed particle, denoted with index number N

$$v_{q,Nk,t} = \frac{v_{q,Nk,t-h} + h\sum_{M=1}^{N_T}\left[\sum_{j=1}^{k} n_{Mj,t-h}\left(\sum_{i=1}^{k-1} f_{i,j,k}\beta_{Ni,Mj}v_{q,Ni,t} + \sum_{\substack{I=1\\ I\neq M}}^{N_X}\sum_{i=1}^{k} f_{i,j,k}\beta_{Ii,Mj}v_{q,Ii,t}\right)\right]}{1 + h\sum_{\substack{M=1\\ k\neq N_B}}^{N_T}\left[\sum_{j=1}^{N_B}\left(1 - f_{k,j,k}\right)\beta_{Nk,Mj}n_{Mj,t-h}\right]} \tag{16.17}$$

Number concentration in size bin k of internally-mixed type

$$n_{Nk,t} = \frac{v_{q,Nk,t-h} + h\sum_{M=1}^{N_T}\left[\sum_{j=1}^{k} n_{Mj,t-h}\left(\sum_{i=1}^{k-1} f_{i,j,k}\beta_{Ni,Mj}v_{q,Ni,t} + \sum_{\substack{I=1\\ I\neq M}}^{N_X}\sum_{i=1}^{k} f_{i,j,k}\beta_{Ii,Mj}v_{q,Ii,t}\right)\right]}{1 + h\sum_{\substack{M=1\\ k\neq N_B}}^{N_T}\left[\sum_{j=1}^{N_B}\left(1 - f_{k,j,k}\right)\beta_{Nk,Mj}n_{Mj,t-h}\right]} \tag{16.18}$$

Coagulation Kernel

Coagulation kernel (rate coefficient)

- Brownian diffusion
- Convective Brownian diffusion enhancement
- Gravitational collection
- Turbulent inertial motion
- Turbulent shear

Brownian diffusion

- Particles diffuse randomly, collide, and coalesce

Knudsen number

$$\mathrm{Kn}_{a,i} = \frac{\lambda_a}{r_i} \qquad (16.19)$$

Mean free path of an air molecule

$$\lambda_a = \frac{2\eta_a}{\rho_a \bar{v}_a} = \frac{2\nu_a}{\bar{v}_a} \qquad (16.20)$$

Thermal velocity of an air molecule

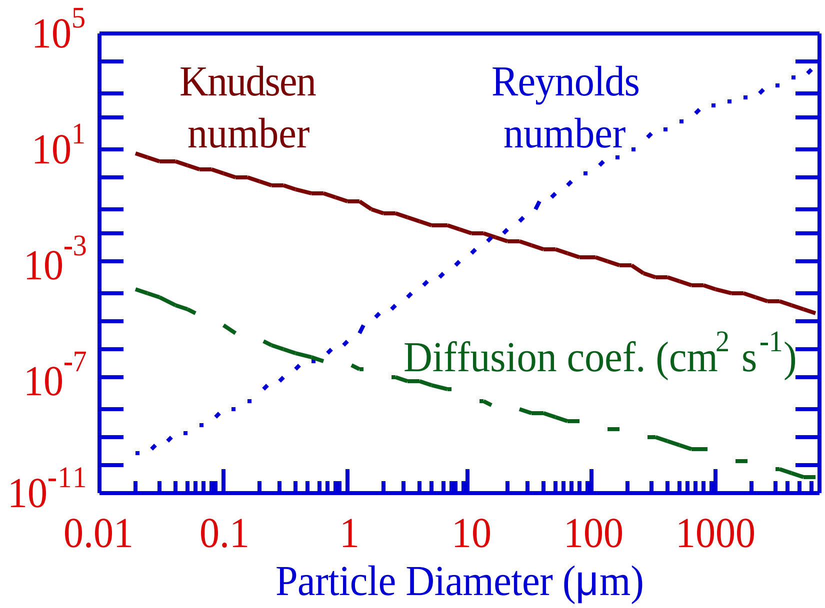
$$\bar{v}_a = \left(\frac{8 k_B T}{\pi \bar{M}}\right)^{1/2} \qquad (16.21)$$

Particle Reynolds number

$$\mathrm{Re}_i = 2 r_i V_{f,i} / \nu_a \qquad (16.22)$$

Particle Properties

Fig. 16.3. Knudsen number for air, Reynolds number, and diffusion coefficient of falling particles as a function of diameter when T = 292 K, p_a = 999 mb, and ρ_p = 1.0 g cm^{-3}.



Brownian Diffusion Kernel

Continuum regime

$\mathrm{Kn}_{a,i} \ll 1 \rightarrow r_i \gg \lambda_a$ and particle resistance to motion is due to viscosity of the air.

Free molecular regime

$\mathrm{Kn}_{a,i} \gg 10 \rightarrow r_i \ll \lambda_a$ and particle resistance to motion is due to inertia of air molecules hit by particles.

Example 16.1.

	T	= 288 K
	p_a	= 1013 mb
	r_i	= 0.1 μm.
--->	$\bar{v}_a$	= 4.59 x 10^4 cm s^{-1}
--->	η_a	= 1.79 x 10^{-4} g cm^{-1} s^{-1}
--->	ρ_a	= 0.00123 g cm^{-3}
--->	λ_a	= 6.34 x 10^{-6} cm
--->	$\mathrm{Kn}_{a,i}$	= 0.63

Continuum regime Brownian coag. rate (cm^3 partic. s^{-1})

$$\beta^B_{i,j} = 4\pi\left(r_i + r_j\right)\left(D_{p,i} + D_{p,j}\right) \qquad (16.23)$$

Particle diffusion coefficient

$$D_{p,i} = \frac{k_B T}{6\pi r_i \eta_a} G_i \qquad (16.24)$$

Cunningham slip-flow correction to particle resistance to motion

$$G_i = 1 + \mathrm{Kn}_{a,i}\left[A' + B' \exp\left(-C'/\mathrm{Kn}_{a,i}\right)\right] \qquad (16.25)$$

Brownian Diffusion Kernel

Free molecular regime Brownian coag. rate (cm^3 partic. s^{-1})

$$\beta_{i,j}^{B} = \pi\left(r_i + r_j\right)^2\left(\bar{v}_{p,i}^2 + \bar{v}_{p,j}^2\right)^{1/2} \qquad (16.26)$$

Particle thermal velocity

$$\bar{v}_{p,i} = \left(\frac{8k_B T}{\pi \bar{M}_{p,i}}\right)^{1/2} \qquad (16.27)$$

Interpolate between continuum and free molecular regimes

$$\beta_{i,j}^{B} = \frac{4\pi\left(r_i + r_j\right)\left(D_{p,i} + D_{p,j}\right)}{\dfrac{r_i + r_j}{r_i + r_j + \left(\delta_i^2 + \delta_j^2\right)^{1/2}} + \dfrac{4\left(D_{p,i} + D_{p,j}\right)}{\left(\bar{v}_{p,i}^2 + \bar{v}_{p,j}^2\right)^{1/2}\left(r_i + r_j\right)}} \qquad (16.28)$$

Mean distance from center of a sphere reached by particles leaving the sphere's surface and traveling a distance $\lambda_{p,i}$

$$\delta_i = \frac{\left(2r_i + \lambda_{p,i}\right)^3 - \left(4r_i^2 + \lambda_{p,i}^2\right)^{3/2}}{6r_i\lambda_{p,i}} - 2r_i \qquad (16.29)$$

Particle mean free path (cm)

$$\lambda_{p,i} = \frac{2D_{p,i}}{\pi\bar{v}_{p,i}} \qquad (16.29)$$

Brownian Diffusion Enhancement

Eddies created in the wake of a large, falling particle enhance diffusion to the particle surface

Brownian diffusion enhancement coagulation kernel

$$\beta_{i,j}^{DE} = \begin{cases} \beta_{i,j}^{B} 0.45\mathrm{Re}_j^{1/3}\,\mathrm{Sc}_{p,i}^{1/3} & \mathrm{Re}_j \le 1;\ \ r_j \ge r_i \\ \beta_{i,j}^{B} 0.45\mathrm{Re}_j^{1/2}\,\mathrm{Sc}_{p,i}^{1/3} & \mathrm{Re}_j > 1;\ \ r_j \ge r_i \end{cases} \qquad (16.30)$$

Particle Schmidt number

$$\mathrm{Sc}_{p,i} = \nu_a / D_{p,i} \qquad (16.31)$$

Differential Fall Velocities

Collision and coalescence when one particle falls faster than and catches up with another

Differential fall velocity coagulation kernel

$$\beta_{i,j}^{GC} = E_{i,j}\pi\left(r_i + r_j\right)^2 \left|V_{f,i} - V_{f,j}\right| \qquad (16.32)$$

Collection (coalescence) efficiency

$$E_{i,j} = \frac{60 E_{V,i,j} + E_{A,i,j}\,\mathrm{Re}_j}{60 + \mathrm{Re}_j} \qquad r_j \ge r_i \qquad (16.33)$$

$E_{i,j}$ simplifies to

$E_{Vi,j}$ when $\mathrm{Re}_j \ll 1$ (viscous flows)

$E_{Ai,j}$ when $\mathrm{Re}_j \gg 1$ (potential flows)

$$E_{V,i,j} = \begin{cases} \left[1 + \dfrac{0.75\ln\left(2\mathrm{K}_{i,j}\right)}{\mathrm{K}_{i,j} - 1.214}\right]^{-2} & \mathrm{K}_{i,j} > 1.214 \\ 0 & \mathrm{K}_{i,j} \le 1.214 \end{cases} \qquad (16.34)$$

$$E_{A,i,j} = \frac{\mathrm{K}_{i,j}^2}{\left(\mathrm{K}_{i,j} + 0.5\right)^2}$$

Stokes number

$$\mathrm{K}_{i,j} = V_{f,i}\left|V_{f,j} - V_{f,i}\right| / r_j g \qquad r_j \ge r$$

Turbulent Inertia and Shear

Coagulation kernel due to turbulent inertial motion

Collision between drops moving relative to air

$$\beta_{i,j}^{TI} = \frac{\pi \varepsilon_k^{3/4}}{g \nu_a^{1/4}} \left(r_i + r_j \right)^2 \left| V_{f,i} - V_{f,j} \right| \qquad (16.35)$$

Coagulation kernel due to turbulent shear

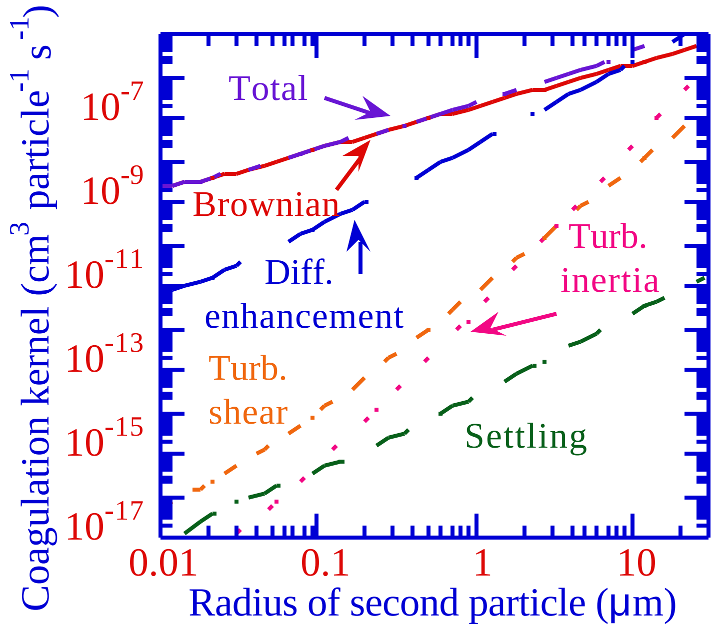
Collisions due to spatial variations in turbulent velocities of drops moving with air

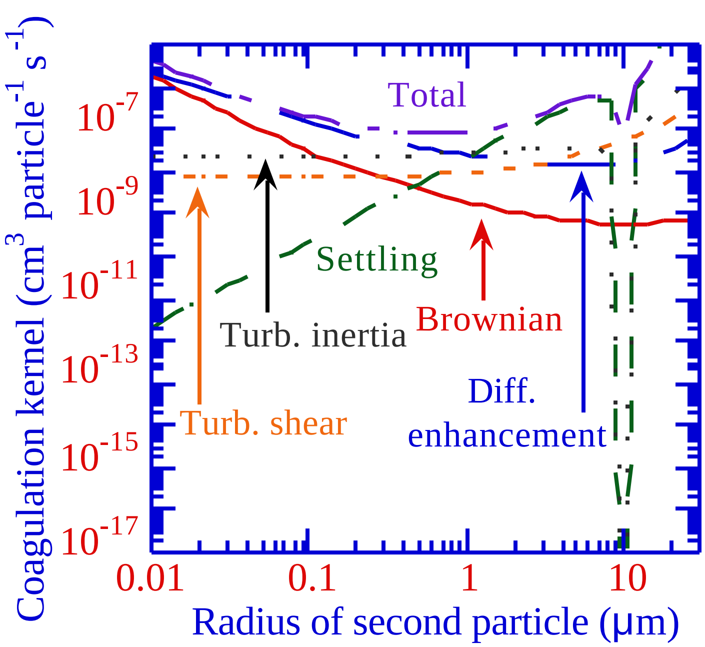
$$\beta_{i,j}^{TS} = \left(\frac{8 \pi \varepsilon_k}{15 \nu_a} \right)^{1/2} \left(r_i + r_j \right)^3 \qquad (16.36)$$

ε_k = dissipation rate of turbulent energy per gram of medium (cm^2 s^{-3})

Comparisons of Coagulation Kernels

Figs. 16.4 a and b. Coagulation kernels when particle of (a) 0.01 μm and (b) 10 μm in radius coagulate at 298 K.





Smoluchowski's (1918) Solution

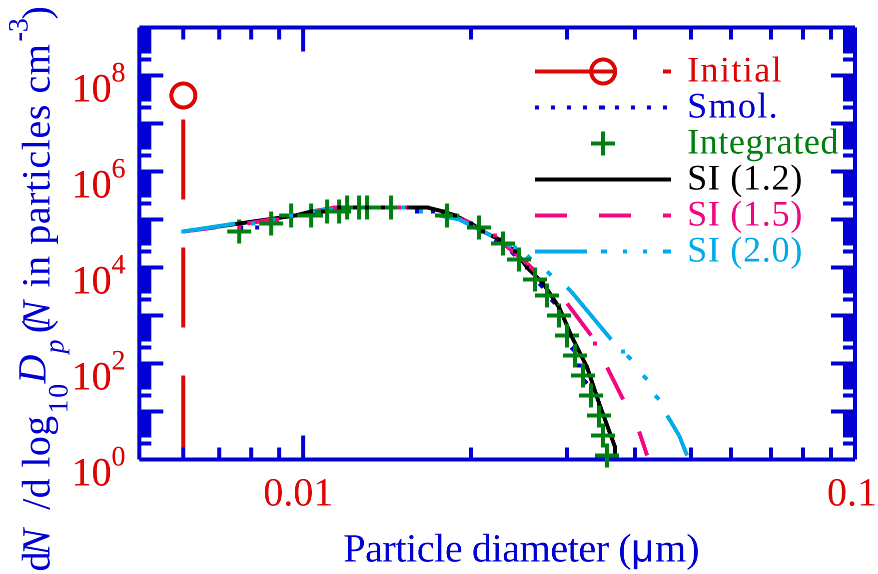
Assume monomer size distribution, constant rate, and initial monodisperse distribution

$$n_{k,t} = \frac{n_{T,t-h}\left(0.5h\beta n_{T,t-h}\right)^{k-1}}{\left(1 + 0.5h\beta n_{T,t-h}\right)^{k+1}} \qquad (16.37)$$

Coagulation kernel

$$\beta = \frac{8k_BT}{3\eta_a} \qquad (16.38)$$

Fig. 16.5. Comparison of Smoluchowski's solution, an integrated solution, and three semi-implicit solutions.



Self-Preserving Solution

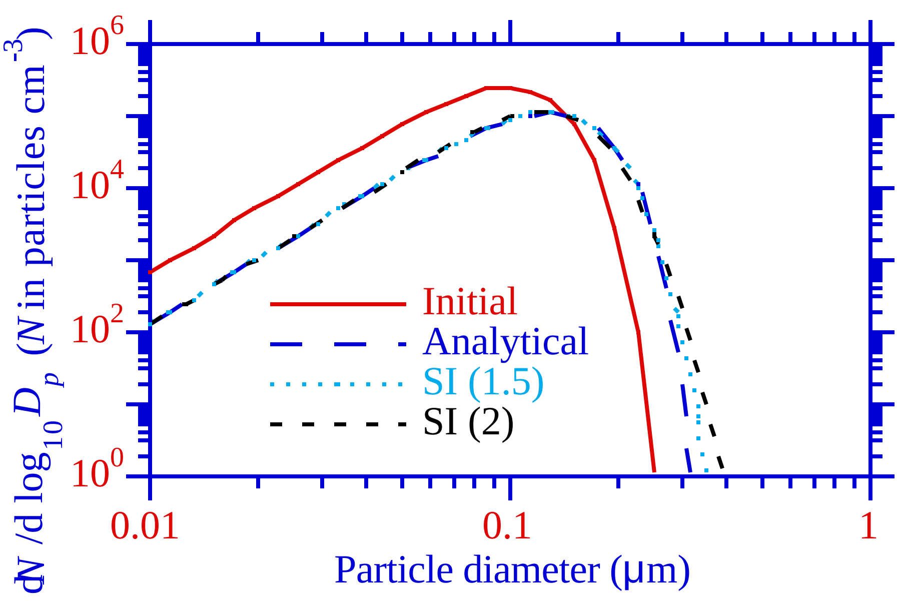
Self-preserving size distribution

$$n_{i,t-h} = \frac{n_{T,t-h}\Delta\upsilon_i}{\upsilon_p}\exp\left(\frac{\upsilon_i}{\upsilon_p}\right) \qquad (16.39)$$

Solution to coagulation over self-preserving distribution

$$n_{i,t} = \frac{n_{T,t-h}\Delta\upsilon_i/\upsilon_p}{\left(1+0.5h\beta n_{T,t-h}\right)^2}\exp\left(-\frac{\upsilon_i/\upsilon_p}{1+0.5h\beta n_{T,t-h}}\right) \qquad (16.40)$$

Fig. 16.6. Self-preserving versus semi-implicit solutions



Effect of Coagulation

Coagulation affects the number concentration of particles smaller than 0.2 μm in size

Fig. 16.7. Estimated change in size-distributed aerosol number and volume at Claremont over a 24-hour period when coagulation, alone, was considered.