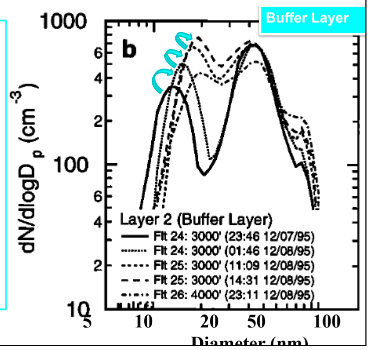
What is the dynamic (i.e. time-dependent) signature of condensation in an aerosol size distribution?

Observed Particle Growth in Buffer Layer

- Growth from 10 to 30 nm observed in buffer layer
  - 2-D equivalent to "banana" pattern.
  - Observed over 36 hr (3 flights).
  - Slow growth rate (0.5 nm/hr) [*cf.* 3-10 nm/hr].



Russell et al. 1998

Apply Mass Transfer to Size Distribution

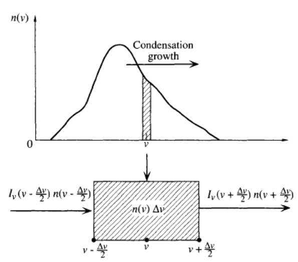


FIGURE 13.1 Schematic of differential mass balance for the derivation of growth equation for a particle population.

Small Particles "Catch up" to Big Particles

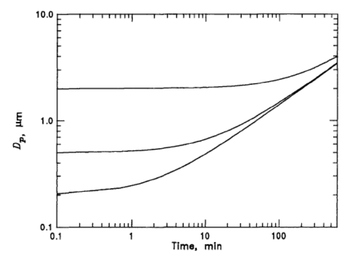


FIGURE 13.2 Growth of particles of initial diameters 0.2, 0.5, and 2 μm assuming $D_i = 0.1\ cm^2\ s^{-1}$, $M_i = 100\ g\ mol^{-1}$, $(p_i - p_{eq,i}) = 10^{-9}$ atm (1 ppb), $T = 298$ K, and $\rho_p = 1\ g\ cm^{-3}$.

Growth of Single Mode

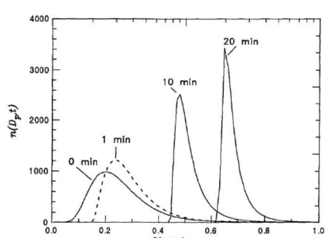
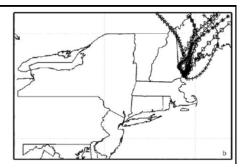
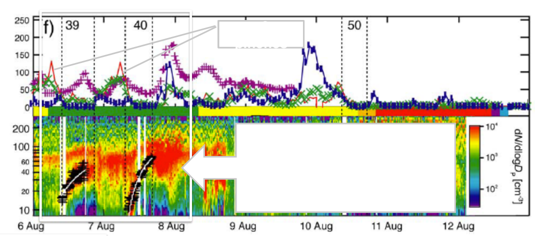


FIGURE 13.3 Evolution of a lognormal distribution (initially $\overline{D}_p = 0.2\ \mu m$, $\sigma_g = 1.5$) assuming $D_i = 0.1\ cm^2\ s^{-1}$, $M_i = 100\ g\ mol^{-1}$, $(p_i - p_{eq,i}) = 10^{-9}$ atm (1 ppb), $T = 298$ K, and $\rho_p = 1\ g\ cm^{-3}$.

Coastal Marine Boundary Layer (MBL)



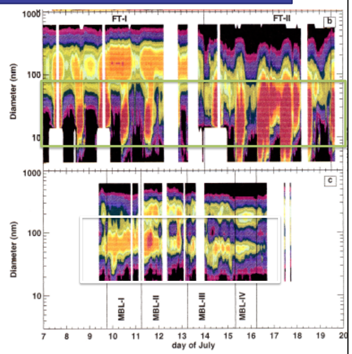
- Appledore Island (ICARTT 2004)



Russell et al. 1998

Polluted Free Troposphere (FT)

- Tenerife (ACE 2 1997)
  - Sub-100 nm particles in FT attributed to transported pollution.
  - No growth observed in coastal MBL.
  - Mixing of dry FT into humid MBL could have induced nucleation
    - No observations of MBL nucleation.

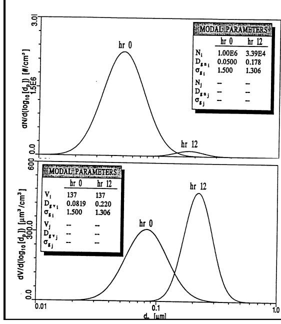


Raes et al. 1997

Aerosol Processes

- Deposition
- Condensation
- Coagulation
- Nucleation
- "Cloud Processing" (Activation+Growth+ Evaporation)

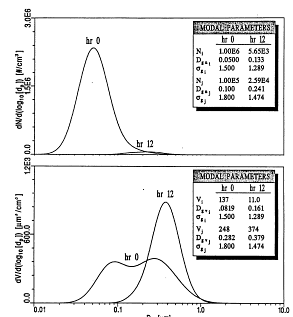
Single-Mode Aerosol Dynamics



Consider:
Did number change?
Did mass/volume change?
Did size change?

Whitby et al. 1982 Fig. 5.2a,b

Two-Mode Aerosol Dynamics



Consider:
Did number change?
Did mass/volume change?
Did size change?

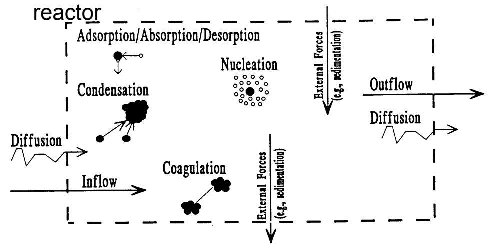
Whitby et al. 1982 Fig. 5.8a,b

Aerosol Dynamics

- Aerosol Populations (multiple particles)
  - Accounting for mass transfer simultaneously for a series of parallel events
  - What is the signature for condensation in a population?
- Coagulation (multiple processes)
  - When does coagulation occur?
  - When is coagulation unlikely?
  - What is the signature for coagulation?

Aerosol "Dynamics": Multiple Processes

- Imagine an air parcel as a wall-less chemical reactor



Whitby et al. 1982

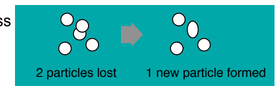
TABLE 1: Aerosol Processing Time Scales

process	time scale formula[a]	urban	remote marine	free troposphere	nonurban continental
transport	L/V or H^2/K_z	2−5 days	1−2 weeks	3 days−2 weeks	1−2 weeks
condensation	$[4\pi D_i \int n(R_p) R_p F \, dR_p]^{-1}$ (eq 5)	0.01−1 hour	1−10 hours	2−20 hours	0.5−20 hours
coagulation (3 nm)	$[4\pi D_s \int n_l(R_{pl}) R_{pl} \beta \, dR_{pl}]^{-1}$ (eq 7)	0.1−1 hour	5−15 hours	~1 day	1−3 hours
coagulation (30 nm)	same	0.1−2 days	10−30 days	~50 days	1−5 days
sulfate production (aerosol)	$M_{S(VI)}/[W_L(k_{H_2O_2} p_{H_2O_2} + k_{O_3} p_{O_3}) p_{SO_2}]$	1 week	0.1−1 day	3 weeks	1−3 weeks
sulfate production (fog)	same	0.1−1 hour	0.01−3 hours	N/A	1 hour
sulfate production (cloud)	same	0.5−5 hours	0.01−3 hours	N/A	1 hour
sulfate production (vapor)	$M_{S(VI)}/[k p_{OH} p_{SO_2}]$	0.1−5 days	1−3 weeks	1−3 weeks	1−3 weeks
deposition (~0.3 μm)	H/v_d	~1 month	~1 month	N/A	~1 month
deposition (<0.03 or >3 μm)	H/v_d	0.5−10 days	0.5−10 days	N/A	0.5−10 days

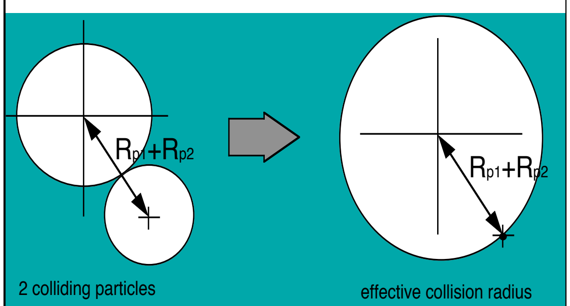
[a] L = characteristic horizontal extent of region; V = characteristic horizontal velocity; H = mixing layer depth; K_z = characteristic vertical eddy diffusivity; v_d = deposition velocity; $M_{S(VI)}$ = typical aerosol sulfate concentration; W_L = liquid water content; $p_{H_2O_2}$, p_{OH}, p_{SO_2}, and p_{O_3} = ambient partial pressures; k = SO_2 + OH gas-phase reaction rate constant; $k_{H_2O_2}$ = S(IV) + H_2O_2 pH-dependent rate constant (includes solubility of gases); k_{O_3} = S(IV) + O_3 pH-dependent rate constant (includes solubility of gases).

Pandis et al., 1995

- **Coagulation** is growth by collision of particles
  - decreases particle number
  - increases particle size
  - no net change in particle mass



- the process of coagulation is almost entirely controlled by the physical properties of a particle, namely the particle ambient **diameter**



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[a] L = characteristic horizontal extent of region; V = characteristic horizontal velocity; H = mixing layer depth; K_z = characteristic vertical eddy diffusivity; v_d = deposition velocity; $M_{S(VI)}$ = typical aerosol sulfate concentration; W_L = liquid water content; $p_{H_2O_2}$, p_{OH}, p_{SO_2}, and p_{O_3} = ambient partial pressures; k = SO_2 + OH gas-phase reaction rate constant; $k_{H_2O_2}$ = S(IV) + H_2O_2 pH-dependent rate constant (includes solubility of gases); k_{O_3} = S(IV) + O_3 pH-dependent rate constant (includes solubility of gases).

Pandis et al., 1995

- Example: assume continuum mechanics apply and that both particles have equal radii, then the distribution of particles satisfies $\dfrac{\partial N}{\partial t} = D\left(\dfrac{\partial^2 N}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial N}{\partial r}\right)$
- with the boundary conditions
$$N(r,0) = N_0$$
$$N(r,t) = N_0 \; @ \; r \to \infty$$
$$N(2R_p, t) = 0$$
- which is solved by:
$$N(r,t) = N_0\left[1 - \frac{2R_p}{r}\,\mathrm{erfc}\left(\frac{r - 2R_p}{2\sqrt{Dt}}\right)\right]$$
- and the rate at which particles arrive at the surface of a single particle is
$$J = 16\pi R_p^2 D\left(\frac{\partial N}{\partial r}\right)_{r=2R_p} = 8\pi R_p D N_0\left(1 + \frac{2R_p}{\sqrt{\pi D t}}\right)$$
- At steady state, this gives simply $J = 8\pi R_p D N_0$

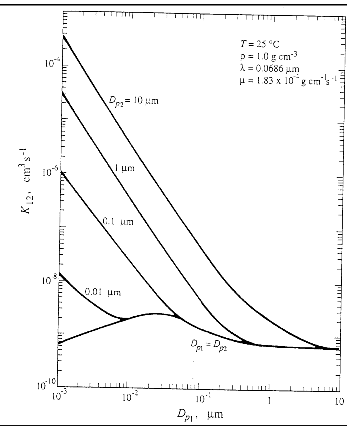
- Example: In order to evaluate the relative diffusivity of the particles, we need to consider the mean of the velocity of particle 1 to particle 2 $\langle |dr_1 - dr_2|^2 \rangle = \langle dr_1^2 \rangle + \langle dr_2^2 \rangle - 2\langle dr_1 \bullet dr_2 \rangle$
- if the motions of both particles are independent of each other, then the covariance term is zero $\langle dr_1 \bullet dr_2 \rangle = 0$ so that the mean relative velocity become $\langle |dr_1 - dr_2|^2 \rangle = \langle dr_1^2 \rangle + \langle dr_2^2 \rangle$
- But we also know that the Brownian diffusion coefficients are defined by
$$\langle |dr_1 - dr_2|^2 \rangle = 6D_{12}t$$
$$\langle dr_1^2 \rangle = 6D_1 t$$
$$\langle dr_2^2 \rangle = 6D_2 t$$
- From these relationships we deduce that the diffusivity of particle 1 relative to particle 2 is simply the sum of the diffusivities of both particles $D_{12} = D_1 + D_2$
- We can now generalize the previous expression for the rate of collision of two particles of the same size to two particles of any size; the change in particle number is then described by
$$N_2(r,t) = N_{20}\left(1 - \frac{(R_{p_1} + R_{p_2})}{r}\,\mathrm{erfc}\frac{r - (R_{p_1} + R_{p_2})}{2\sqrt{D_{12}t}}\right)$$
- implying a collision rate of
$$J = 4\pi(R_{p_1} + R_{p_2}) D_{12} N_{20}\left(1 + \frac{(R_{p_1} + R_{p_2})}{\sqrt{\pi D_{12} t}}\right)$$
- which at steady state is simply
$$J = 4\pi(R_{p_1} + R_{p_2}) D_{12} N_{20}$$

- For non-continuum regime, the correction factor β can be included to correct the collision rate so that we get the following expressions for the coagulation rate

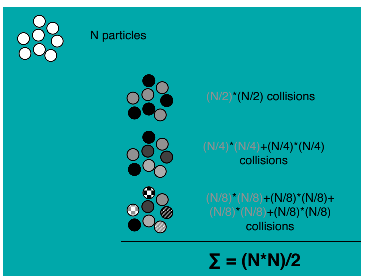
$$J_{12} = 4\pi\left(R_{p_1} + R_{p_2}\right)\left(D_1 + D_2\right)\beta N_1 N_2$$

- where in this case the applicable Knudsen number is defined by the relative particle diffusivity

$$Kn_D = \frac{2D_{12}}{\bar{c}_{12} R_p}$$



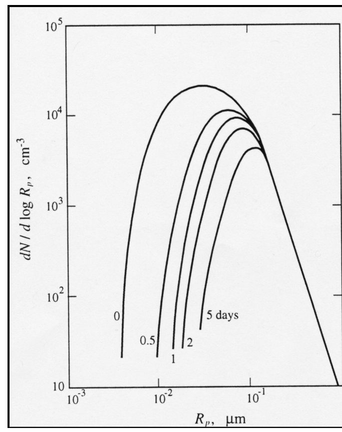
Seinfeld and Pandis, 1998



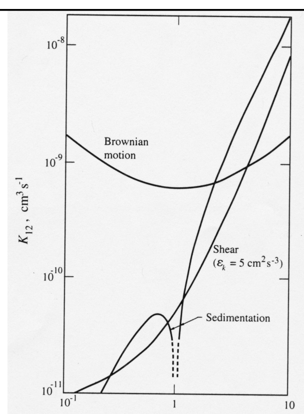
$$J_{12} = 4\pi\left(R_{p_1} + R_{p_2}\right)D_{12}N_{10}N_{20}$$

$$J_{12} = K_{12}N_1N_2$$

$$K_{12} = 4\pi\left(R_{p_1} + R_{p_2}\right)\left(D_1 + D_2\right)$$



Seinfeld and Pandis, 1998



Seinfeld and Pandis, 1998

- Tobacco smoke that enters the lungs by inhalation has about 2 s of potential evolution time before it reaches the alveoli in the lungs. Assume that the inhaled concentration is 10^{10} cm^{-3} and that the initial aerosol diameter is 20 nm. By what factor does the average particle size of the tobacco smoke particles increase as a result of coagulation only during the time that it takes for the smoke to travel from the cigarette to the smoker's lungs?

- Consider the rate at which new particles are grown by coagulation. Assume that the number of 20 nm particles is effectively constant during this process (N_1), then we find that

$$\frac{dN}{dt} = \frac{1}{2}K_{11}N_1^2$$