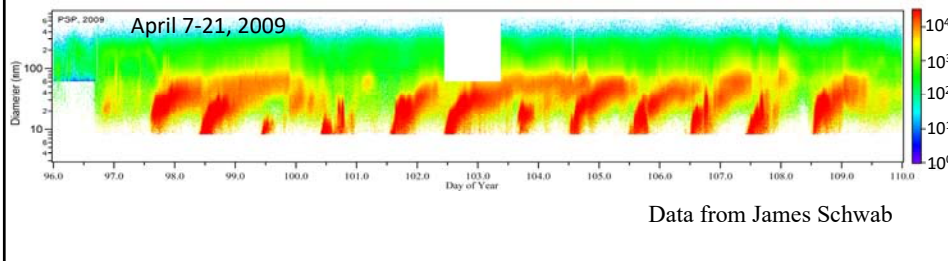


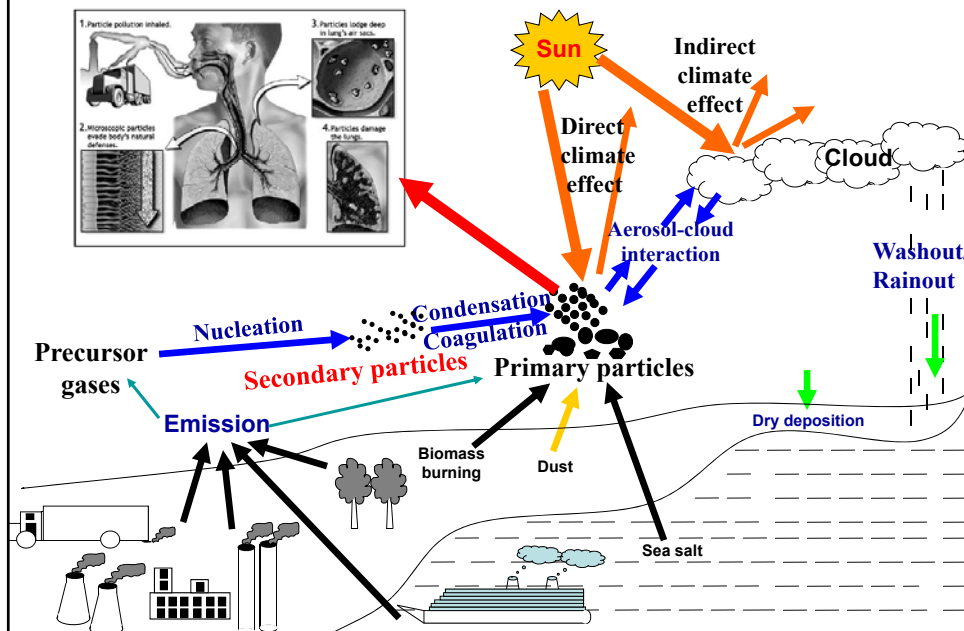
MODULE 3: Atmospheric Aerosols

Lecture 4: Aerosol Microphysical Processes: Growth, Coagulation, and Deposition

Evolution of particle size distributions in the atmosphere



Physical processes controlling aerosol properties

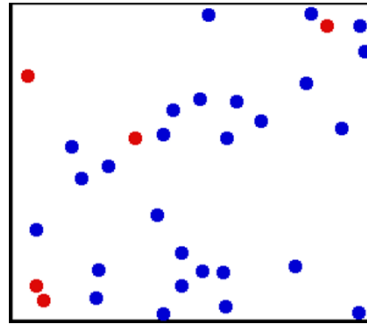


Properties of Gaseous Medium

Under room T (20 °C) and P (1 atm):

1. Number of molecules in per cm³ air:
 $2.5 \times 10^{19} \text{ cm}^{-3}$
2. Mean diameter of air molecules:
0.35 nm
3. Mean distance between air molecules:
3.5 nm
4. Mean velocity of air molecules:
500 m/s
5. Mean free path of air molecules:
65 nm

Gaseous medium



Knudsen Number and three regimes of gas-particle interactions

Knudsen number (K_n):

ratio of the molecular mean free path length to particle radius (R_p)

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

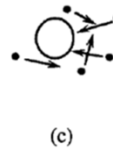
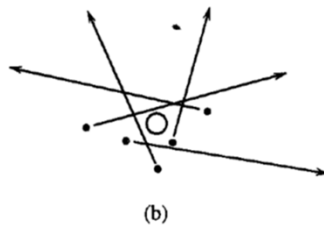
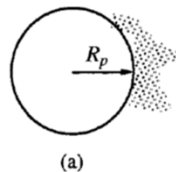
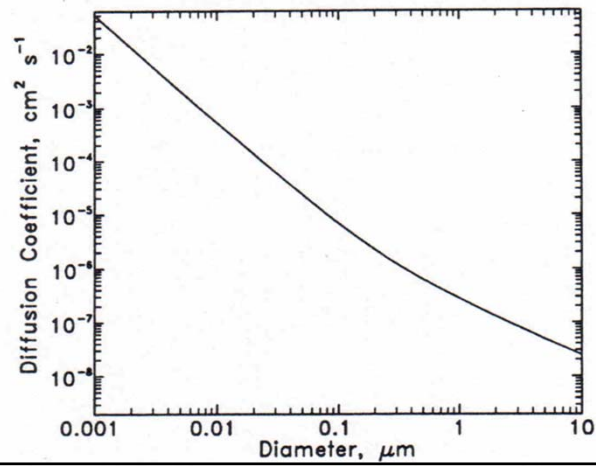


FIGURE 8.1 Schematic of the three regimes of suspending fluid-particle interactions: (a) continuum regime ($Kn \rightarrow 0$), (b) free molecule (kinetic) regime ($Kn \rightarrow \infty$), and (c) transition regime ($Kn \sim 1$).

Particle Diffusivity

Mean square displacement in 1-D, by diffusion: $\langle x^2 \rangle = 2Dt$

Where $D = k_B T C_c / (3\pi\mu D_p)$ is the particle diffusion coefficient. μ is the gas viscosity, C_c is the slip (or non-continuous) correction factor.



Mass transfer: Diffusion flux

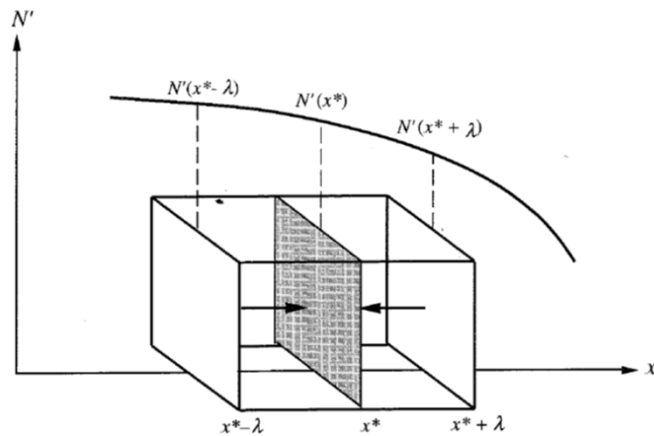


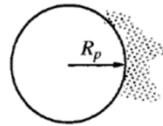
FIGURE 8.4 Control surfaces for molecular diffusion as envisioned in the elementary kinetic theory of gases.

$$J = -D(\partial N' / \partial x)$$

Condensation/Evaporation: Gas-particle interaction

$$c(\infty, t) = c_\infty$$

$$c(R_p, t) = c_s$$



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

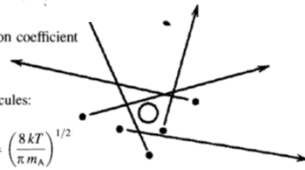
$$J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$$

α is the molecular accommodation coefficient

\bar{c}_A is the mean speed of the molecules:

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

k is the Boltzmann's constant while m_A is the mass of one A molecule



(b)

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

$$\frac{J}{J_c} = 0.75\alpha \frac{1 + Kn \Delta/\lambda_{AB}}{0.75\alpha + Kn + (\Delta/\lambda_{AB})Kn^2}$$



(c)

FIGURE 8.1 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 ($Kn \sim 1$).

Condensation/Evaporation of particles in the continuum regime

A mass balance on the growing or evaporating particle is

$$\frac{\rho_p}{M_A} \frac{d}{dt} \left(\frac{4}{3} \pi R_p^3 \right) = J_c \quad M_A \text{ (g/mol) is the molecular weight of A}$$

$$\frac{dR_p}{dt} = \frac{D_g M_A}{\rho_p R_p} (c_\infty - c_s)$$

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

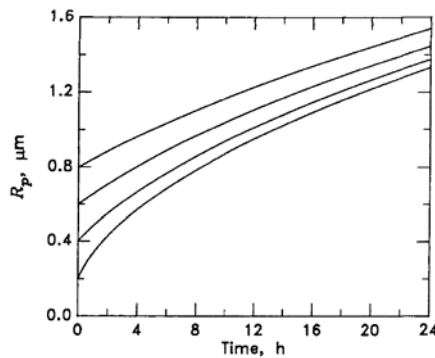
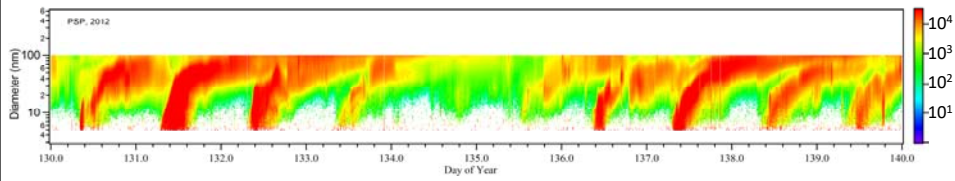


FIGURE 12.1 Growth of aerosol particles of different initial radii as a function of time for a constant concentration gradient of $1 \mu\text{g m}^{-3}$ between the aerosol and gas phases ($D_g = 0.1 \text{ cm}^2 \text{ s}^{-1}$, $\rho_p = 1 \text{ g cm}^{-3}$).

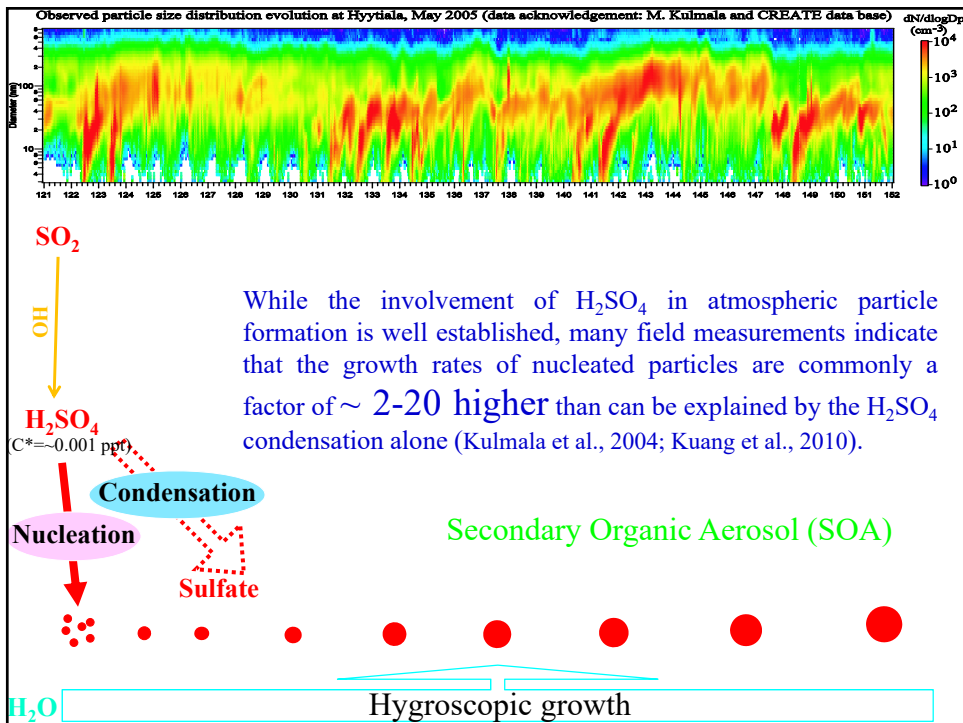
Growth rates of ultrafine particles in the kinetic regime



$$\frac{\rho_p}{M_A} \frac{d}{dt} \left(\frac{4}{3} \pi R_p^3 \right) = J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s)$$

$$\frac{dD_p}{dt} = 2 \frac{dR_p}{dt} = ?$$

Q: If the observed growth rate (diameter) of 5-10 nm particles is 3 nm/hr and H₂SO₄ is assumed to be the only condensing gas, what is the concentration of H₂SO₄ gas ?



Coagulation: Particle-particle interaction

Aerosol particles suspended in the air may come into contact because of their Brownian motion or as a result of their motion produced by gravitational, electrical, or other forces.

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

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

N_1 and N_2 are number concentrations ($\# \text{ cm}^{-3}$) of #1 and #2 particles, K_{12} is the coagulation coefficient.

Kinetic or free molecule Regime

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

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

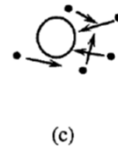
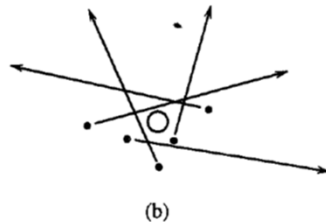
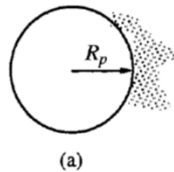


FIGURE 8.1 Schematic of the three regimes of suspending fluid-particle interactions: (a) continuum regime ($Kn \rightarrow 0$), (b) free molecule (kinetic) regime ($Kn \rightarrow \infty$), and (c) transition regime ($Kn \sim 1$).

Continuum Regime

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

$$J_{12} = 2\pi(D_{p1} + D_{p2})(D_1 + D_2)N_1N_2$$

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

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

$$D_i = \frac{kT}{3\pi\mu D_{pi}} \quad \text{is the particle diffusion coefficient}$$

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

Transition 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:

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

$$K_{ni} = \frac{2\lambda_{in}}{D_{pi}}$$

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

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

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

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

Coagulation

Discrete coagulation equation

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

Continuous coagulation equation

$$\begin{aligned} \frac{\partial n(v, t)}{\partial t} &= \frac{1}{2} \int_{v_0}^{v-v_0} K(v-q, q) n(v-q, t) n(q, t) dq \\ &\quad - n(v, t) \int_{v_0}^{\infty} K(q, v) n(q, t) dq \end{aligned}$$

Solution of the coagulation equation -- discrete

Assuming $K_{k,j} = K$

$$\begin{aligned} \frac{dN_k(t)}{dt} &= \frac{1}{2} K \sum_{j=1}^{k-1} N_j(t) N_{k-j}(t) - K N_k(t) \sum_{j=1}^{\infty} N_j(t) \\ &= \frac{1}{2} K \sum_{j=1}^{k-1} N_j(t) N_{k-j}(t) - K N_k(t) N(t) \end{aligned}$$

$$\begin{aligned} \frac{dN(t)}{dt} &= \frac{1}{2} K \sum_{k=1}^{\infty} \sum_{j=1}^{k-1} N_{k-j}(t) N_j(t) - K N^2(t) \\ &= -\frac{1}{2} K N^2(t) \end{aligned}$$

If $N(0) = N_0$,

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

$$\tau_c = \frac{2}{KN_0}$$

τ_c is the characteristic time for coagulation

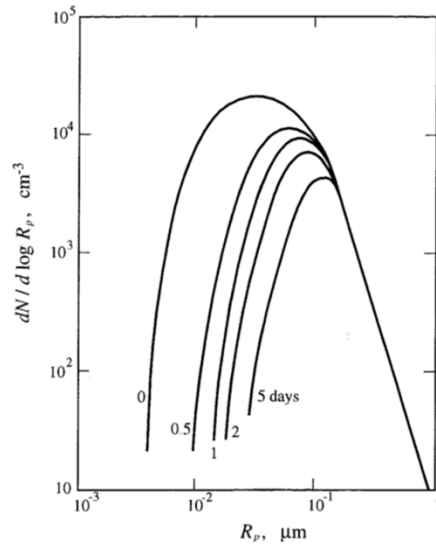
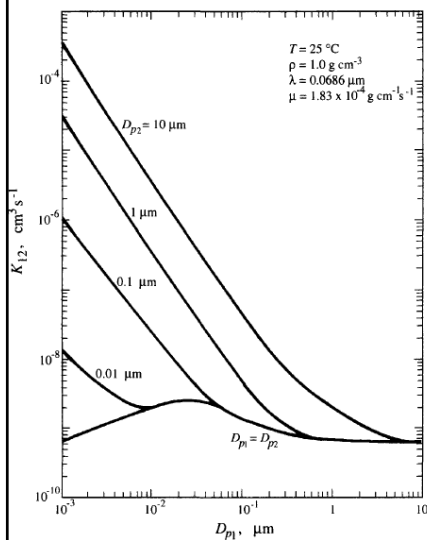
At $t = \tau_c$, $N(\tau_c) = \frac{1}{2}N_0$. Thus, τ_c is the time necessary for reduction of the initial number concentration to half its original value. The timescale shortens as the initial number concentration increases. Consider an initial population of particles of about $0.2 \mu\text{m}$ diameter,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

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

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

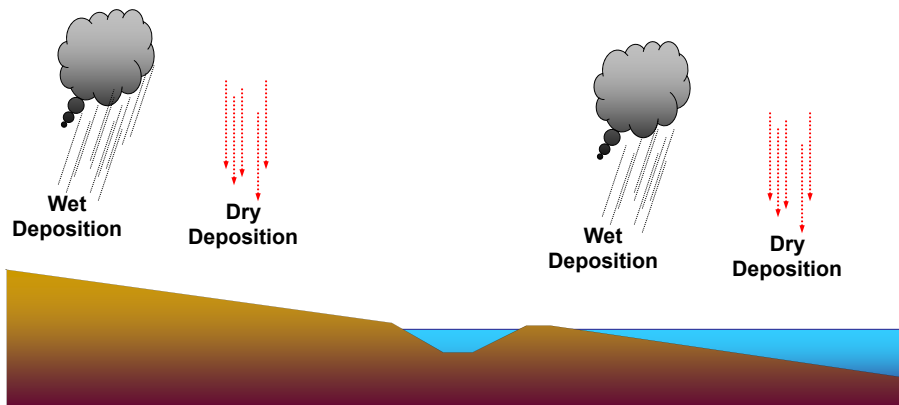
Need to know how to estimate typical values of τ under different K and N_0

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)

Dry and Wet Deposition



19

Dry and Wet Deposition

- Dry deposition – removal of gases and particles by a direct transfer from the atmosphere to the surface.
- Wet deposition – removal of gases and particles carried to the surface in water – rain, snow, fog etc.
- Wet deposition of gaseous species requires that they be water soluble. Terms used are rainout, or washout.

20

Dry Deposition

Three separate steps

- (1) Species must be transported close to the surface
- (2) Species must cross to the surface
- (3) Species must be taken up on the surface.

21

Terminal Settling Velocity

The drag force on a particle moving at a speed of v in the air is (Stokes' law)

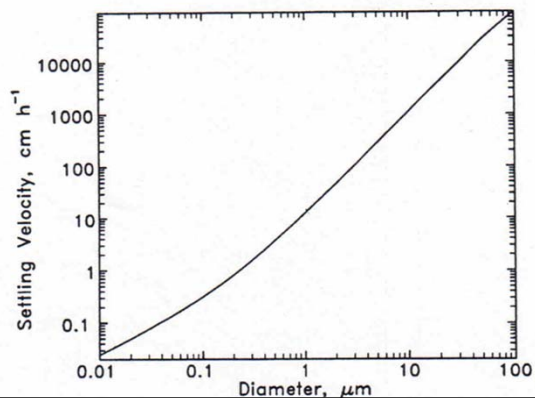
$$F_{\text{drag}} = 3\pi\mu D_p v / C_c$$

When the drag force balances gravity

$$m_p g = 3\pi\mu D_p v / C_c$$

Velocity that results from this balance is the settling (or terminal) velocity

$$v_t = m_p g C_c / (3\pi\mu D_p)$$



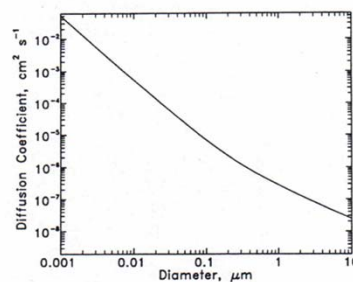
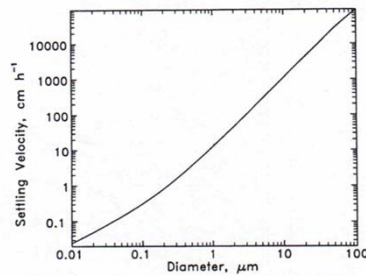
Gravitational Settling vs. Diffusion

In 1 hour, how far does a 10 micron particle move due to gravity? How far does it move by diffusion?

What about for a 0.01 micron particle?

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

What do you conclude about the relative importance of gravitation settling for big and small particles?



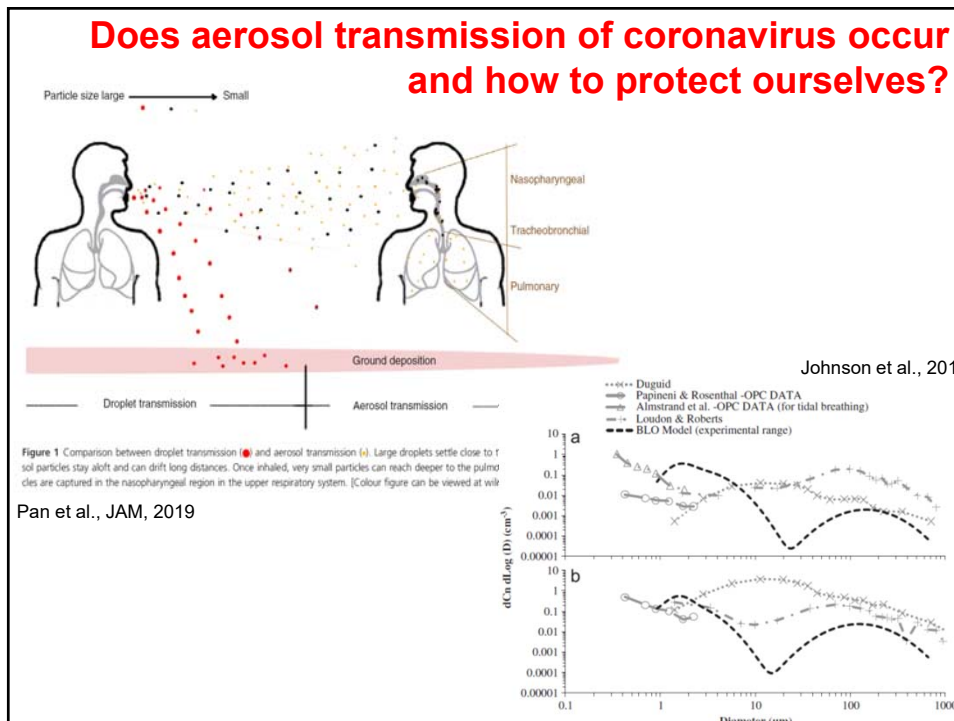
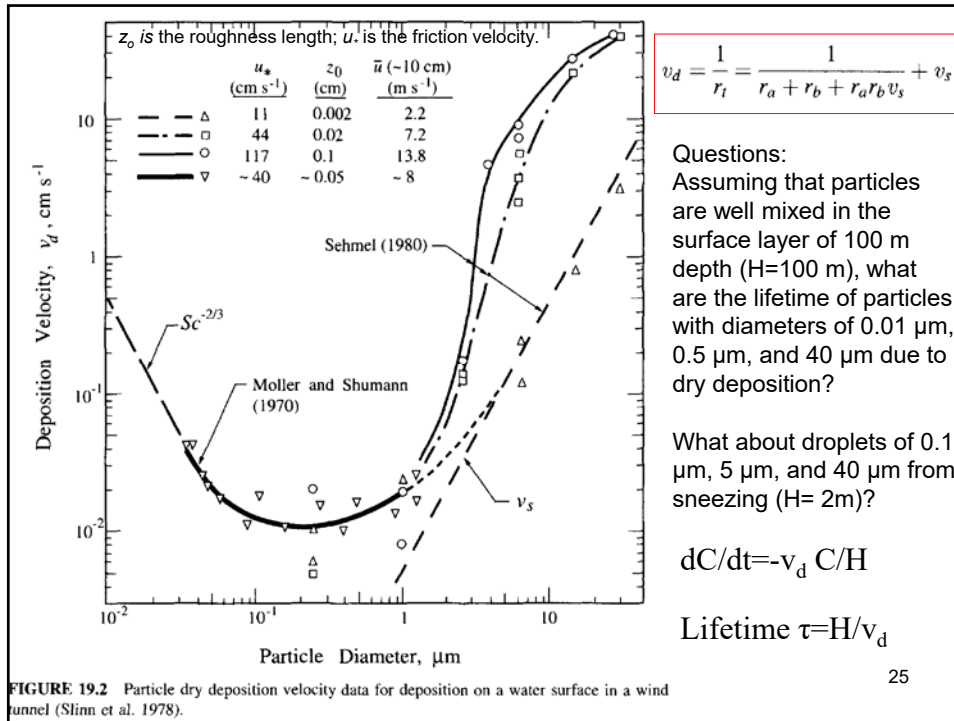
Dry deposition flux is directly proportional to the local concentration C of the depositing species, at some reference height above the surface (e.g., 10m or less)

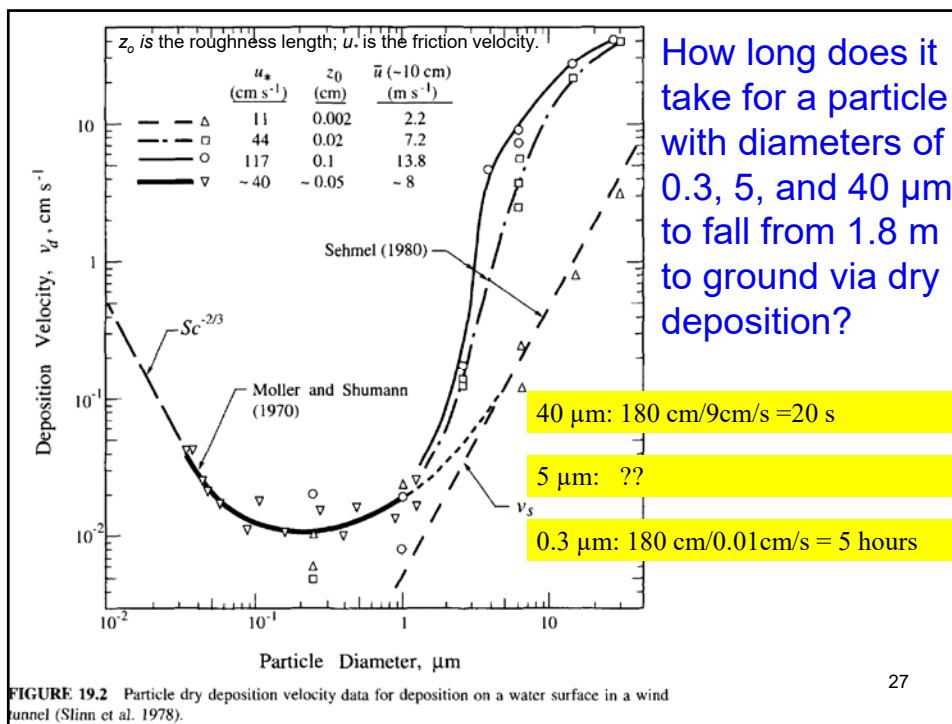
$$F = -v_d C$$

The process of dry deposition of gases and particles is generally represented as consisting of three steps:

- (1) aerodynamic transport down through the atmospheric surface layer to a very thin layer of stagnant air just adjacent to the surface;
- (2) molecular (for gases) or Brownian (for particles) transport across this thin stagnant layer of air, called the *quasi-laminar sublayer*, to the surface itself;
- (3) uptake at the surface.

Each of these steps contributes to the value of the deposition velocity v_d .



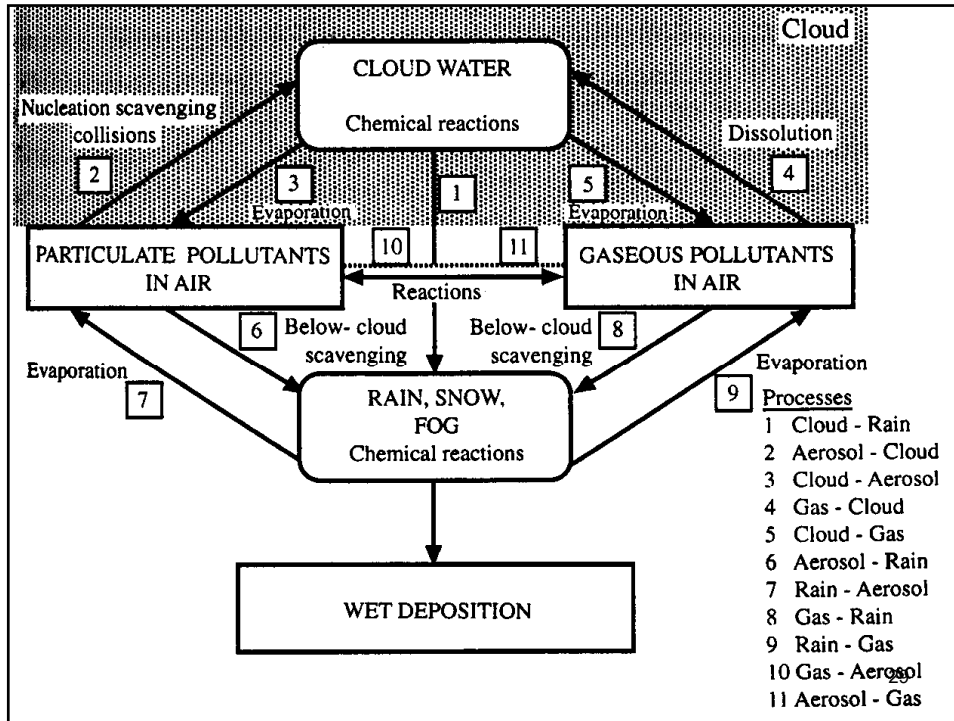


Wet Deposition

Wet deposition refers to the natural processes by which material is scavenged by atmospheric hydrometeors (cloud and fog drops, rain, snow) and is consequently delivered to the Earth's surface. A number of different terms are used: precipitation scavenging, wet removal, washout, and rainout. *Rainout* usually refers to in-cloud scavenging and *washout*, to below-cloud scavenging by falling rain, snow, and so on.

1. Precipitation scavenging, that is, the removal of species by a raining cloud
2. Cloud interception, the impaction of cloud droplets on the terrain usually at the top of tall mountains
3. Fog deposition, that is, the removal of material by settling fog droplets
4. Snow deposition, removal of material during a snowstorm

In all of these processes three steps are necessary for wet removal of a material. Specifically, the species (gas or aerosol) must first be brought into the presence of condensed water. Then, the species must be scavenged by the hydrometeors, and finally it needs to be delivered to the Earth's surface. Furthermore, the compound may undergo chemical transformations during each one of the above steps.



PRECIPITATION SCAVENGING OF PARTICLES

The below-cloud scavenging (washout) rate of aerosol particles of diameter d_p can be written as

$$\frac{dn_M(d_p)}{dt} = -\Lambda(d_p)n_M(d_p)$$

where the scavenging coefficient $\Lambda(d_p)$ is given by

$$\Lambda(d_p) = \int_0^{\infty} \frac{\pi}{4} D_p^2 U_i(D_p) E(D_p, d_p) N(D_p) dD_p$$

Calculation therefore of the aerosol scavenging rate, for a given aerosol diameter d_p , requires knowledge of the droplet size distribution $N(D_p)$ and the scavenging efficiency $E(D_p, d_p)$.

The collision efficiency $E(D_p, d_p)$ is by definition equal to the ratio of the total number of collisions occurring between droplets and particles to the total number of particles in an area equal to the droplet's effective cross-sectional area. A value of $E = 1$ implies that all particles in the geometric volume swept out by a falling drop will be collected.

Slinn (1983) proposed the following correlation for E that fits experimental data:

$$E = \frac{4}{\text{Re Sc}} [1 + 0.4 \text{Re}^{1/2} \text{Sc}^{1/3} + 0.16 \text{Re}^{1/2} \text{Sc}^{1/2}] + 4\phi[\omega^{-1} + (1 + 2 \text{Re}^{1/2})\phi] + \left(\frac{\text{St} - S^*}{\text{St} - S^* + \frac{2}{3}} \right)^{3/2}$$

$$S^* = \frac{1.2 + \frac{1}{12} \ln(1 + \text{Re})}{1 + \ln(1 + \text{Re})}$$

$\text{Re} = D_p U_i \rho_a / 2\mu_a$ (Reynolds number of raindrop based on its radius)

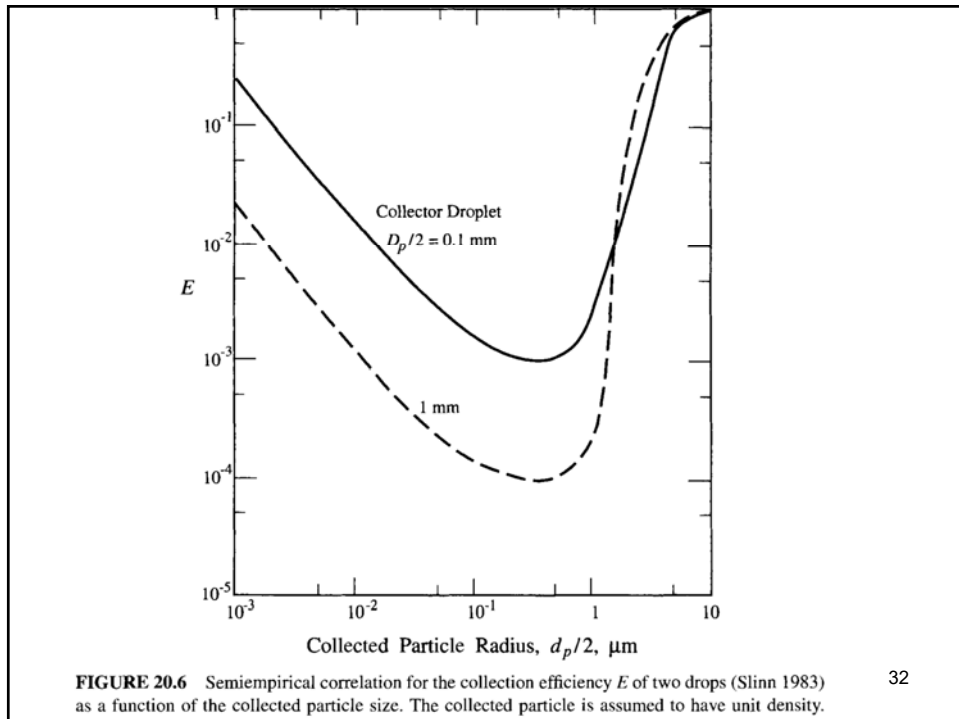
$\text{Sc} = \mu_a / \rho_a D$ (Schmidt number of collected particle)

$\text{St} = 2\tau(U_i - u_i) / D_p$ (Stokes number of collected particle, where τ is its characteristic relaxation time)

$\phi = d_p / D_p$ (ratio of diameters)

$\omega = \mu_w / \mu_a$ (viscosity ratio)

31



32

For monodisperse aerosols and raindrops, the scavenging coefficient can be calculated as

$$\Lambda(d_p) = \frac{3 E(D_p, d_p) p_0}{2 D_p}$$

Where $p_0 = \frac{\pi}{6} D_p^3 U_r(D_p) N_D$ is the rainfall intensity (mm/hr)

33

$$\frac{dn_M(d_p)}{dt} = -\Lambda(d_p)n_M(d_p)$$

$$n = n_0 \exp(-t/\tau)$$

$\tau = 1/\Lambda$ is the lifetime of particles due to rain washout

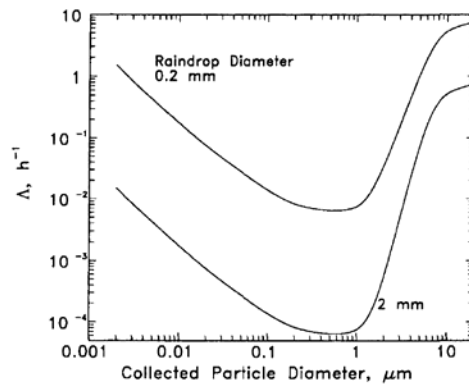


FIGURE 20.7 Scavenging coefficient for monodisperse particles as a function of their diameter collected by monodisperse raindrops with diameters 0.2 and 2 mm assuming a rainfall intensity of 1 mm h^{-1} .

What is the lifetime of particles of 0.01, 0.5, and 10 μm due to washout for the two raindrop diameters and assumed rainfall intensity in the figure?

34

Key knowledge points of Lecture 4:

1. Condensation is a key process to grow freshly nucleated particles of a few nanometers to sizes that can act as cloud condensation nuclei or cause adverse health impacts. The growth rate depends on the concentration of condensing gaseous.
2. Coagulation is an important process to reduce or limit the particle number concentration but increase the particle sizes. Based on typical coagulation rates and particle number concentration, one can calculate the lifetime of particles due to coagulation.
3. Dry and wet deposition process is the main sink of particles in the atmosphere. The deposition rates depend strongly on particle sizes.