Chapter Four
Growth of Cloud Droplets by Diffusion

Flux

- A flux is the amount of something passing through a unit of area in a unit of time.
- The units of flux are the units of whatever is being transported, divided by area and time. Examples are:

  Mass flux: kg m^{-2} s^{-1}

  Energy flux: J m^{-2} s^{-1}
  Particle flux: m^{-2} s^{-1}

- The flux is actually a vector that points in the direction of the transport.
- In component form in Cartesian coordinates the flux vector is:

$$\vec{F} = F_x \hat{i} + F_y \hat{j} + F_z \hat{k} \qquad (4.1)$$

Growth Rate of Droplet by Diffusion

- Once a cloud droplet forms it continues to grow by diffusion of water vapor onto its surface (condensation).
- Figure 1 illustrates a droplet of radius R with radial vapor fluxes at the surface of the droplet denoted by $\vec{F}_R$

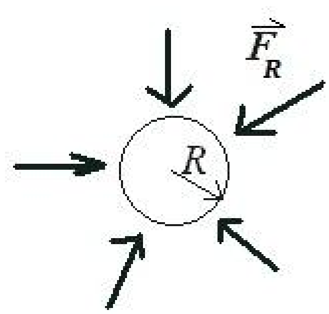

Figure 1: Convergence of radial vapor fluxes $\vec{F}_R$ at the surface of the droplet results in droplet growth.

- For simplicity we will assume that the fluxes are *axisymmetric*, meaning that the fluxes only change with distance from the droplet, not with the angle. Another way of saying this is that the fluxes are *isotropic*.

- If we multiply the flux at the surface of the droplet by the surface area of the droplet we obtain the rate of change of molecules of the droplet,

$$\frac{dn}{dt} = -4\pi R^2 F_R \tag{4.2}$$

  - Note that F_R itself is negative, since it is pointing inward toward the droplet. That is why there is a negative in front of (4.2), so that dn/dt will be positive.

- The flux F_R at the surface of the droplet is given by Fick's first law of diffusion $\vec{F} = -D\nabla N$ where D is the *diffusivity*, and is $F_R = -\hat{k}\cdot D(\nabla N)_R = -D(\partial N/\partial r)_R$. Therefore (4.2) becomes:

$$\frac{dn}{dt} = 4\pi D R^2 \left(\frac{\partial N}{\partial r}\right)_R \tag{4.3}$$

  - Keep in mind that n is the number of water molecules in the droplet itself, whereas N is the number density of water vapor molecules in the air.

- We find $(\partial N/\partial r)_R$ as follows:

  - We assume that N does not change with time, so that from Fick's second law of diffusion $\frac{\partial N}{\partial t} = D\nabla^2 N$ we have:

$$\nabla^2 N = 0 \tag{4.4}$$

  - In spherical coordinates with the droplet at the origin, and since the vapor concentration is axisymmetric, (4.4) becomes

$$\frac{\partial}{\partial r}\left(r^2 \frac{\partial N}{\partial r}\right) = 0 \tag{4.5}$$

  - Integrating (4.5) twice with respect to r results in

$$N(r) = -\frac{c_1}{r} + c_2 \tag{4.6}$$

    where c_1 and c_2 are the constants of integration. We find them by applying the boundary conditions

$$\begin{aligned} N(r \gg R) &= N_b \\ N(R) &= N_R \end{aligned} \tag{4.7}$$

where N_b is the background vapor concentration well away from the droplet.

- Applying the boundary conditions (4.7) to (4.6) results in

$$c_1 = (N_b - N_R)R$$
$$c_2 = N_b$$

- Putting these constants back into (4.6) results in

$$N(r) = -\frac{(N_b - N_R)R}{r} + N_b \tag{4.8}$$

- And finally, by taking $\partial/\partial r$ of (4.8) and evaluating the result at $r = R$, we get

$$\left.\frac{\partial N}{\partial r}\right|_R = \frac{N_b - N_R}{R} \tag{4.9}$$

- Putting (4.9) into (4.3) gives us our growth-rate equation for the droplet,

$$\frac{dn}{dt} = 4\pi DR(N_b - N_R) \tag{4.10}$$

  - If the background vapor concentration is larger than that at the droplet surface, $N_b > N_R$, the droplet will grow due to condensation.

  - If the background vapor concentration is smaller than that at the droplet surface, $N_b < N_R$, the droplet will shrink due to evaporation.

Growth Rate in Terms of Droplet Mass and Radius

- Equation (4.10) can be converted to an equation for the mass growth rate, *dm/dt*, as follows:

  - Multiply both sides of (4.10) by the molar mass of water, M_w, and divide by Avogadro's number, N_A,

$$\frac{M_w}{N_A}\frac{dn}{dt} = \frac{M_w}{N_A}4\pi DR(N_b - N_R) \tag{4.11}$$

  - Since mass is

$$\frac{M_w}{N_A}n = m$$

and absolute humidity is

$$\frac{M_w}{N_A}N = \rho_v$$

(4.11) becomes

$$\frac{dm}{dt} = 4\pi DR(\rho_{vb} - \rho_{vR}) \qquad (4.12)$$

- What would be most convenient is to have an equation for the growth-rate in terms of the radius of the droplet. We can construct this using the chain rule for derivatives,

$$\frac{dR}{dt} = \frac{dR}{dm}\frac{dm}{dt} \qquad (4.13)$$

  - The mass of a droplet is

$$m = \frac{4}{3}\pi\rho_l R^3$$

  so

$$\frac{dR}{dm} = \frac{1}{4\pi\rho_l R^2} \qquad (4.14)$$

- From (4.12), (4.13) and (4.14) we get

$$R\frac{dR}{dt} = \frac{D}{\rho_l}(\rho_{vb} - \rho_{vR}) \qquad (4.15)$$

Other Equations Needed to Solve for Growth Rate

- Equation (4.15) gives us the ability to integrate forward in time to find an expression for ***R(t)***, the radius of the droplet at any future time ***t***.
  - We do not know what value of ρ_{vR} to use, since this depends on the temperature of the surface of the droplet.
  - However, we can assume that at the surface of the droplet the air is saturated, so that $\rho_{vR} = \rho_{vs}$, where ρ_{vs} is the *saturation absolute humidity*.
  - From the ideal gas law for water vapor

$$\rho_{vR} = \rho_{vs} = \frac{e_s}{R_v T_R} \qquad (4.16)$$

    where T_R is the temperature at the surface of the droplet.

    * Note that T_R is not necessarily the same as the air temperature. The droplet warms or cools depending on whether there is condensation or evaporation at the droplet's surface.
  - e_s is the saturation vapor pressure over a curved, impure droplet which we know to be

$$e_s = e_o \left(1 + \frac{a}{R} - \frac{b}{R^3}\right) \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T_R}\right)\right] \tag{4.17}$$

so that

$$\rho_{vR} = \frac{e_o}{R_v T_R}\left(1 + \frac{a}{R} - \frac{b}{R^3}\right) \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T_R}\right)\right] \tag{4.18}$$

- Equations (4.15) and (4.18) are two equations, but we have three unknown quantities: R, ρ_{vR}, and T_R. therefore we still need one more equation in order to have a closed set that we can solve.

- The third equation comes from balancing the gain of latent heat due to condensation with the loss of sensible heat due to thermal diffusivity.

  - The gain of latent heat due to condensation is given by

$$J_{latent} = L_v \frac{dm}{dt} = 4\pi R L_v D(\rho_{vb} - \rho_{vR}) \tag{4.19}$$

  - The sensible lost to the air by diffusion is

$$J_{sensible} = -4\pi R K(T_R - T_b) \tag{4.20}$$

  where K is the thermal diffusivity of air and T_b is the temperature of the air.

  - Balancing the sensible and latent heats by setting (4.19) equal to (4.20) results in

$$\rho_{vb} - \rho_{vR} = \frac{K}{L_v D}(T_R - T_b) \tag{4.21}$$

Calculations of Growth Rates

- Equations (4.15), (4.18) and (4.21) are three equations for three unknown quantities, R, ρ_{vR}, and T_R. The equations are rewritten here,

$$R\frac{dR}{dt} = \frac{D}{\rho_l}(\rho_{vb} - \rho_{vR})$$

$$\rho_{vR} = \frac{e_o}{R_v T_R}\left(1 + \frac{a}{R} - \frac{b}{R^3}\right) \exp\left[\frac{L_v}{R_v}\left(\frac{1}{T_o} - \frac{1}{T_R}\right)\right]$$

$$\rho_{vb} - \rho_{vR} = \frac{K}{L_v D}(T_R - T_o)$$

- We can solve these three equations to find the growth rate and radius of a droplet at any future time, *t*.

- However, the equations are quite complex and cannot be solved analytically. They need to be solved numerically.

- A somewhat simplified, though not as accurate, set of growth equations is

$$R\frac{dR}{dt} X \frac{S \; Z1 \, Z \frac{a}{R} \, \Gamma \frac{b}{R^3}}{F_k \; \Gamma F_d} \tag{4.22}$$

$$F_k \; X \; \frac{L_v}{R_v T_b} Z1 \; \frac{L_v \partial_l}{K T_b} \tag{4.23}$$

$$F_d \; X \frac{\partial_l R_v T_b}{D e_{s|}^*} \tag{4.24}$$

where the saturation vapor pressure used in calculating F_d is that for a flat surface of pure water

- These equations still need to be integrated numerically. The result for a droplet starting at radius r_o = 0.75 µm is shown in Figure 2.

- Note that after 20 hours the droplet is still only has a radius slightly larger 60 µm.

- Figure 3 shows the effect of doubling the mass of solute. Although the droplet initially grows faster with more solute, the growth rates quickly become the same.

Final Comments on Diffusional Growth

- In order to be large enough to fall fast enough to reach the ground without evaporating, a droplet has to reach a size of at least 0.1 mm in diameter (0.05 mm or 50 µm in radius).

- A typical raindrop has a diameter of 2 mm (radius of 1 mm, or 1000 µm).

- Clouds can form and rain start to fall in a matter of 30 minutes or so.

- Diffusional growth explains how very tiny, brand-new cloud droplets grow to typical cloud droplet sizes, but is too slow to explain how precipitation forms.

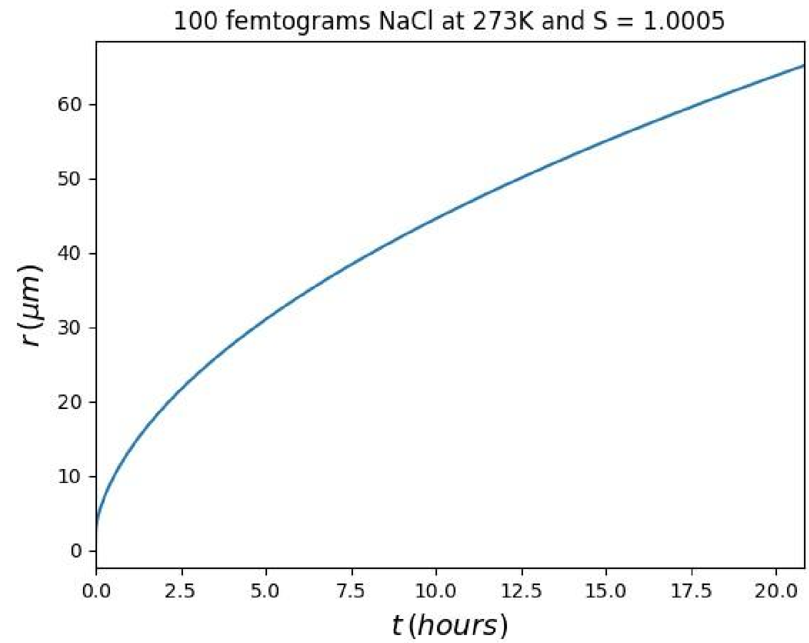

Figure 4: Growth of droplet initially of radius 0.75 μm for a solute of 100 femtograms of NaCl.

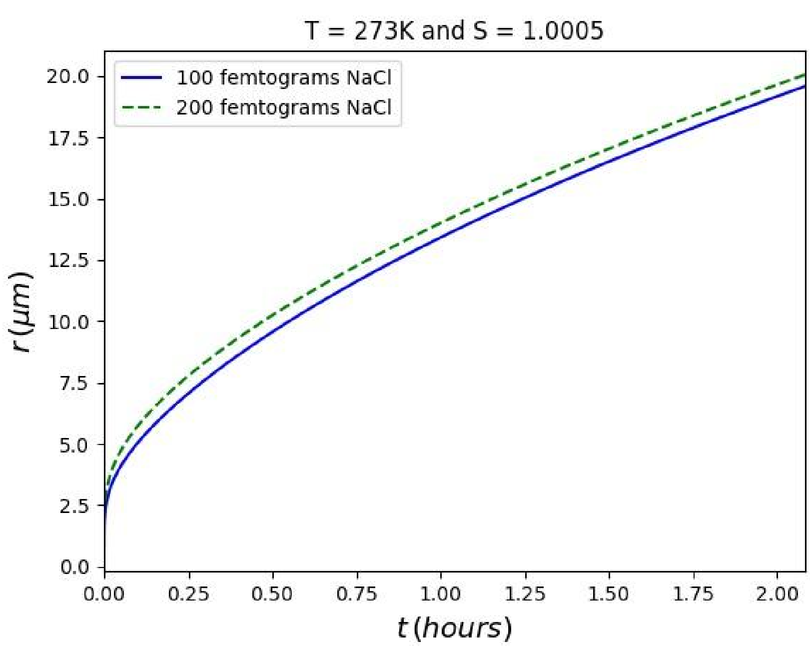

Figure 5: Growth of droplet initially of radius 0.75 μm for two different solute masses.