

ESCI 340 - Cloud Physics and Precipitation Processes  
Lesson 5 - Cloud Droplet Formation  
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## References:

*A Short Course in Cloud Physics, 3rd ed.*, Rogers and Yau, Ch. 6

## Effects of Ambient Pressure on $e_s$

- The saturation vapor pressure over a flat surface of pure water is given by the Clausius-Clapeyron equation,

$$e_s^*(\infty) = e_0 \exp \left[ \frac{L_v}{R_v} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (1)$$

- We have placed an asterisk on  $e_s^*$  to indicate that this is the saturation vapor pressure for *pure* water.
- The  $(\infty)$  tells us that the surface is flat (radius of curvature is infinite).
- Thus,  $e_s^*(\infty)$  is read as ‘the saturation vapor pressure over a flat surface of pure water’.
- Equation (1) assumes that the pressures in the liquid is equal vapor pressure above the liquid.
  - This is only true if there is pure water vapor above the liquid.
  - If there is a mixture of dry air and vapor above the liquid, then the pressure in the liquid will be the combined pressure of the dry air and vapor,  $p = p_d + e$ , and so (1) is now suspect.
- To see if we can really use (1) for a mixture of dry air and vapor, such as in the real atmosphere, we need to look to the **Poynting equation**, which relates the saturation vapor pressure to the total pressure.

- We won’t derive the Poynting equation. We will just state it as<sup>1</sup>

$$\left( \frac{\partial e_s}{\partial p} \right)_T = \frac{\alpha_l}{\alpha_v}, \quad (2)$$

where  $\alpha_l$  is the specific volume of the liquid, and  $\alpha_v$  is the specific volume of the vapor.

- Equation (2) can be integrated to obtain (see Exercises)

$$e_s(p) = e_{s0} \exp \left[ \frac{\alpha_l}{R_v T} (p - e_{s0}) \right], \quad (3)$$

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<sup>1</sup>A derivation of the Poynting equation can be found in my thermodynamics lesson notes for phase changes at [http://www.atmos.millersville.edu/~adecaria/ESCI341/esci341\\_lesson13\\_phasechanges.pdf](http://www.atmos.millersville.edu/~adecaria/ESCI341/esci341_lesson13_phasechanges.pdf)

where  $e_{s0}$  is the saturation vapor pressure without any external pressure (meaning that that the total pressure is the same as the saturation vapor pressure,  $p = e_{s0}$ ).

- Equation (3) tells us that increasing total pressure  $p$  will increase the saturation vapor pressure. Therefore, the vapor pressure we get from the Clausius-Clapeyron equation will be too low if we have a mixture of dry air and water vapor.
- As Fig. 1 illustrates, the effect of total pressure on saturation vapor pressure is very small, even at total pressures of up to 10 atmospheres.
- The increase in saturation vapor pressure due to ambient pressure is therefore usually ignored.

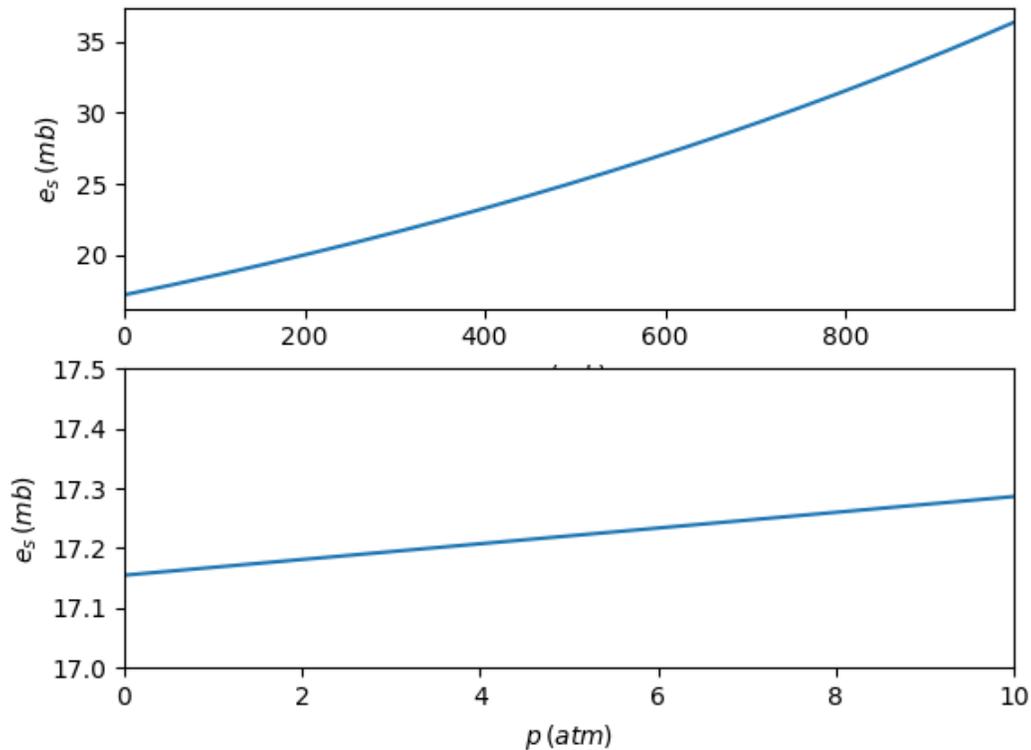


Figure 1: Saturation vapor pressure as a function of total pressure.

- The physical explanation for the increase in saturation vapor pressure with total pressure is not entirely known.
  - It likely has to do with the fact that repulsive forces between molecules dominate at short distances, while attractive forces dominate at larger distance.
  - Molecular attractions and repulsions are often modeled by the **Lennard-Jones potential**, which is

$$V = \varepsilon \left[ \left( \frac{r_m}{r} \right)^{12} - 2 \left( \frac{r_m}{r} \right)^6 \right], \quad (4)$$

where  $\varepsilon$  is the depth of the potential well. A plot of (4) is shown in Fig. 2.

- The term raised to the twelfth power represents short-range repulsive forces that push the molecules apart.
- The term raised to the sixth power represents longer-range attractive forces which try to bring the molecules together.
- When  $r = r_m$  the potential is a minimum.
- The thought is that pressure squeezes the molecules closer to each other, enhancing their repulsive forces and allowing molecules on the surface of the fluid to escape more readily into the vapor outside of the liquid.

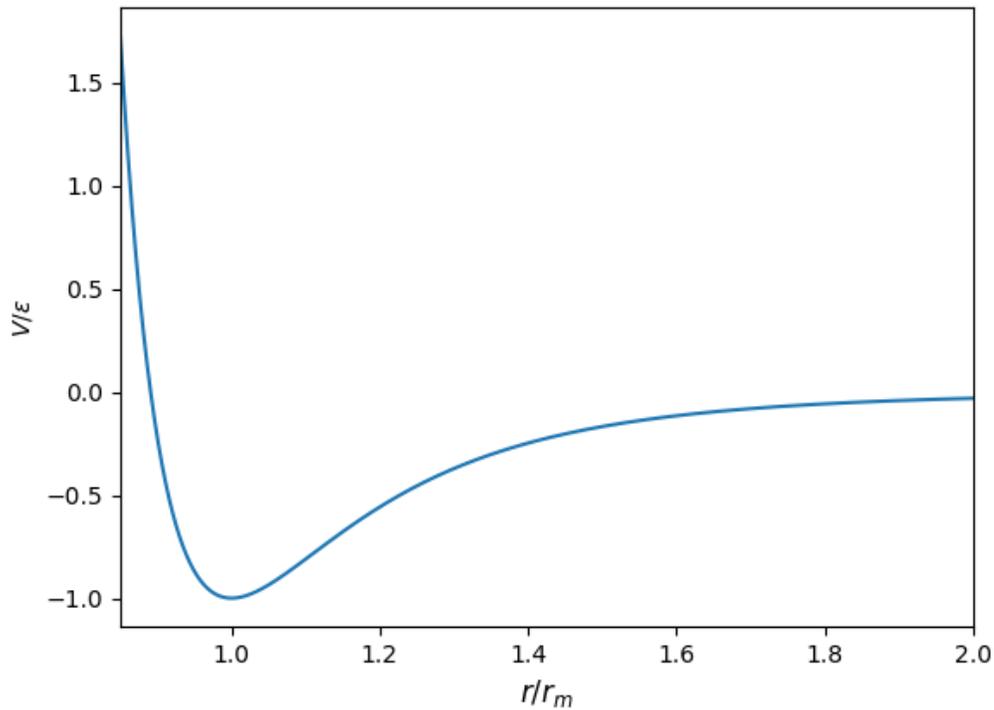


Figure 2: Lennard-Jones potential. The distance between molecules is  $r$ . The potential is a minimum at  $r = r_m$ .

## Curvature Effect

- Water droplets are held together by surface tension.
- Due to the squeezing of the droplet by the surface tension, the pressure inside of a water droplet is higher than the surrounding air. The pressure inside a droplet of radius  $r$  is given by the formula

$$p(r) = p_0 + \frac{2\eta}{r} \quad (5)$$

where  $p_0$  is the pressure outside of the droplet and  $\eta$  is the surface tension.<sup>2</sup>

- A plot of the pressure difference across the droplet interface as a function of radius is shown in Fig. 3.
  - Note that very small droplets have tremendous internal pressures.
  - A 1 nm droplet has an internal pressure of about 1500 atmospheres.

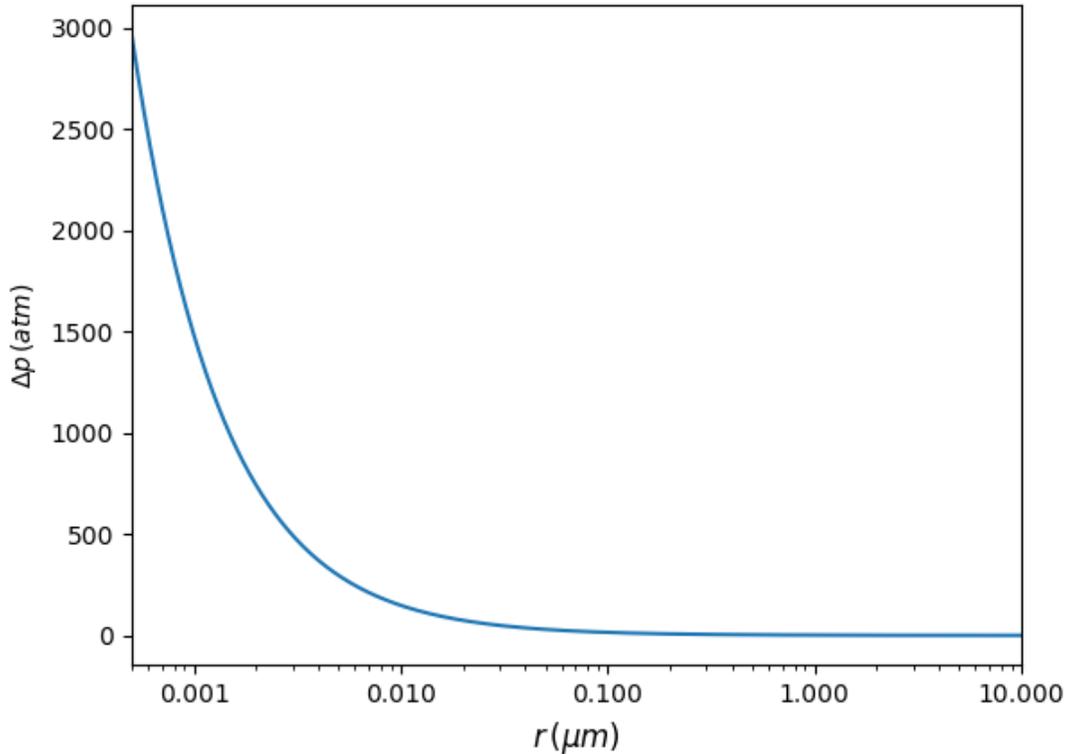


Figure 3: Pressure difference across droplet interface,  $\Delta p = p(r) - p_0$ , as a function of radius.

- Because newly formed water droplets are so small, and therefore have tremendous internal pressures, we can not ignore the effects of pressure on saturation vapor pressure when dealing with the formation of cloud droplets.
- To find the saturation vapor pressure over a droplet we use the chain rule to write

$$\left(\frac{\partial e_s}{\partial r}\right)_T = \left(\frac{\partial e_s}{\partial p}\right)_T \left(\frac{\partial p}{\partial r}\right)_T. \quad (6)$$

$\partial e_s/\partial r$  comes straight from the Poynting equation, (2), and  $\partial p/\partial r$  is found by differentiating (5). Equation (6) then becomes

$$\left(\frac{\partial e_s}{\partial r}\right)_T = -\frac{\alpha_l}{\alpha_v} \frac{2\eta}{r^2}. \quad (7)$$

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<sup>2</sup> $\eta$  has a value of approximately  $0.075 \text{ N m}^{-1}$ .

– From the ideal gas law for pure water vapor we have

$$\alpha_v = \frac{R_v T}{e_s},$$

and substituting this into (7) and rearranging yields

$$\left( \frac{\partial \ln e_s}{\partial r} \right)_T = \frac{2\alpha_l \eta}{R_v T r^2}. \quad (8)$$

– Integrating (8) with respect to  $r$  from  $\infty$  to  $r$  results in<sup>3</sup>

$$e_s(r) = e_s(\infty) \exp\left(\frac{a}{r}\right), \quad (9)$$

where

$$a = \frac{2\alpha_l \eta}{R_v T}. \quad (10)$$

- Equation (9) states that the saturation vapor pressure over a droplet of radius  $r$  is larger than that over a flat surface. This is called the **curvature effect**.
- The **equilibrium saturation ratio**  $S_{eq}$  is defined as the saturation ratio needed for the droplet to be in equilibrium. It is given by  $S_{eq} = e_s(r)/e_s^*(\infty)$ .
  - Figure 4 shows a plot of equilibrium saturation ratio,  $e_s^*(r)/e_s^*(\infty)$ , as a function of droplet radius for a pure water droplet.
  - For very small droplets the equilibrium saturation ratio is upwards of 4, or a relative humidity of 400%!
  - This is why **homogeneous nucleation**, which is the condensation of pure water vapor, doesn't occur at 100% relative humidity.

## Solute Effect

- The addition of an impurity, or **solute**, to liquid water lowers the saturation vapor pressure. This effect is quantified by **Raoult's Law**,

$$e_s = \chi_w e_s^* \quad (11)$$

where  $\chi_w$  is the **mole fraction of water**. The mole fraction of water is defined as the number of moles of water per total number of moles of water plus solute,

$$\chi_w = \frac{n_w}{n_w + n_s}. \quad (12)$$

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<sup>3</sup>If we are dealing with pure water we could put asterisks on both  $e_s(r)$  and  $e_s(\infty)$  in (9).

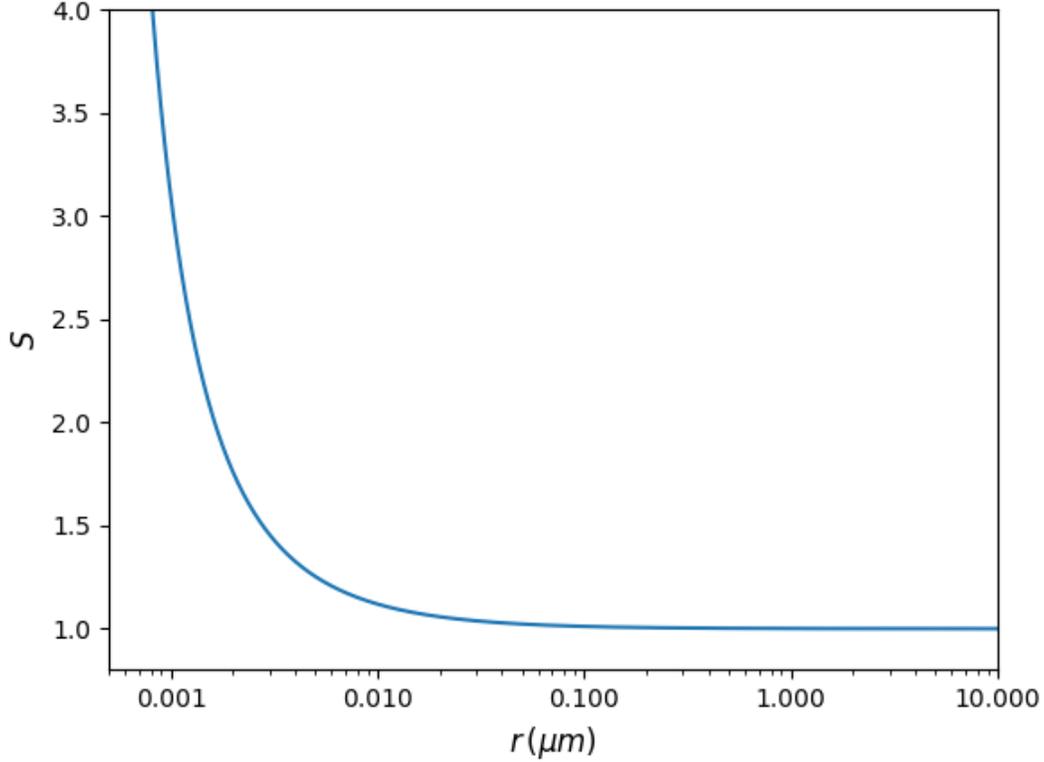


Figure 4: Equilibrium saturation ratio versus droplet radius for pure water.

- For dilute solutions the mole fraction of water can be approximated by<sup>4</sup>

$$\chi_w \cong 1 - \frac{n_s}{n_w}. \quad (13)$$

- To apply Raoult's Law to a spherical droplet of radius  $r$  we need to find the number of moles of water in the droplet. This is given by

$$n_w = \frac{m_w}{M_w} \quad (14)$$

where  $m_w$  is the mass of the droplet, and  $M_w$  is the molar mass of water.

- The mass of a spherical droplet is

$$m_w = \frac{4}{3}\pi\rho_l r^3, \quad (15)$$

where  $\rho_l$  is the density of liquid water.

- From (14) we have

$$n_w = \frac{4\pi\rho_l r^3}{3M_w}. \quad (16)$$

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<sup>4</sup>This results from the fact that  $\frac{1}{1+x} \cong 1 - x$  for  $x \ll 1$ .

- The number of moles of solute is

$$n_s = i \frac{m_s}{M_s} \quad (17)$$

where  $i$  is the **ion factor**. The ion factor is an integer that is equal to the number of ions that the solute dissociates into when dissolved.

- The mole fraction of water in a spherical droplet is given by putting (16) and (17) into (13) to get

$$\chi_w = 1 - \frac{b}{r^3} \quad (18)$$

where

$$b = \frac{3im_s M_w}{4\pi\rho_l M_s}. \quad (19)$$

- From Raoult's Law, (11), the ratio of  $e_s/e_s^*$  for a droplet is

$$\frac{e_s}{e_s^*} = 1 - \frac{b}{r^3}. \quad (20)$$

- The decrease of saturation vapor pressure due to dissolved impurities is known as the **solute effect**.

## Combined Curvature and Solute Effects

- The curvature effects makes it more difficult to form cloud droplets, while the solute effect makes it easier.
- In real droplets both effects are present, and so we need to combine them to find the saturation vapor pressure over an impure droplet, which is given by

$$e_s(r) = e_s^*(\infty) \left(1 - \frac{b}{r^3}\right) \exp\left(\frac{a}{r}\right). \quad (21)$$

- The equilibrium saturation ratio,  $S_{eq}$ , for the droplet is defined as  $S_{eq} = e_s(r)/e_s^*(\infty)$ , and so is

$$S_{eq} = \left(1 - \frac{b}{r^3}\right) \exp\left(\frac{a}{r}\right). \quad (22)$$

- Figure 5 shows plots of the curvature and solute effects separately, and also their combined effects.
- Note that neither effect is important once droplets are larger than 1  $\mu\text{m}$  in radius. It is only very small droplets for which the curvature and solute effects must be considered.
- A plot of  $S_{eq}$  combining both the curvature and solute effects is called a **Kohler curve**. The solid line in Fig. 5 is an example of a Kohler curve.

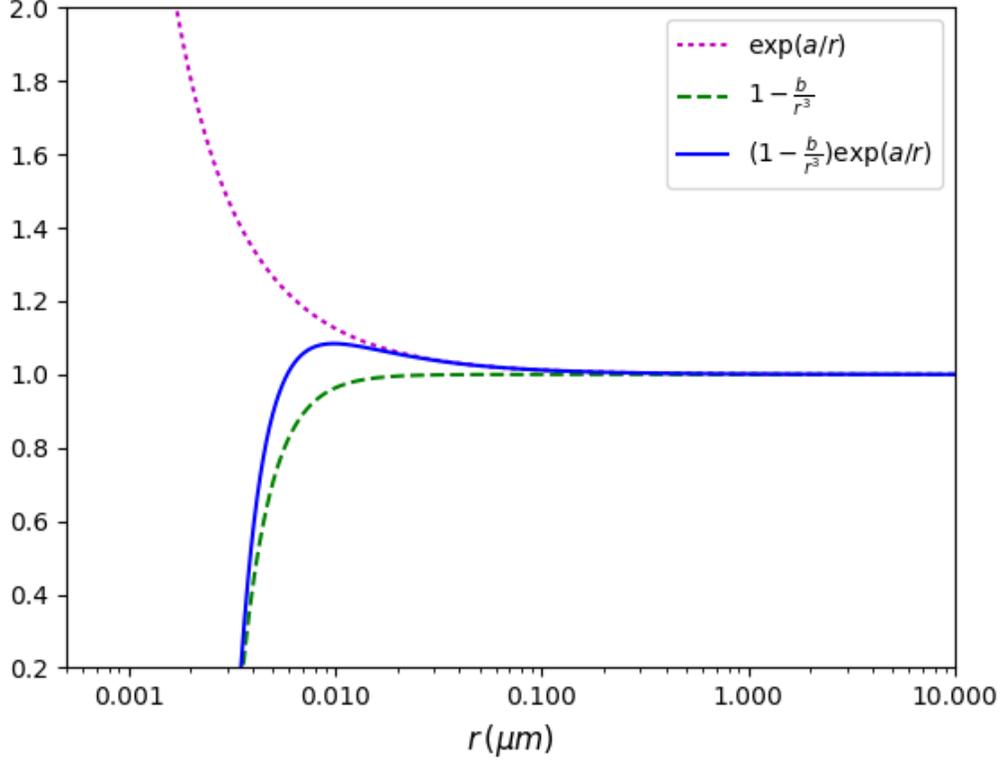


Figure 5: Plots of curvature and solute effects separately, and also combined. The plots are for a droplet containing 0.25 attograms of NaCl at a temperature of 275K.

## Stability of Droplets

- We now take a more detailed look at a Kohler curve, using the one shown in Fig. 6 as an example.
  - The Kohler curve becomes a maximum at the **critical radius** denoted by  $r^*$ .
  - The value of equilibrium saturation ratio at the critical radius is called the **critical saturation ratio**, and is denoted as  $S^*$ .
  - as radius gets larger the equilibrium saturation ratio goes asymptotically to unity (relative humidity of 100%), represented by the dotted line in Fig. 6.
- The location of the critical radius,  $r^*$ , is found by setting  $\partial S_{eq}/\partial r = 0$  and solving for  $r$ .
  - Because of the form of (22), finding the location of  $r^*$  is not straight-forward.
  - Instead, we have to use the McLaren series expansion of  $e^x = 1 + x + x^2/2! + x^3/3! + \dots$ , which for small values of  $x$  can be truncated to  $e^x \cong 1 + x$ .
  - Applying this approximation to the curvature term in (22) results in  $\exp(a/r) = 1 + a/r$ . Equation (22) then becomes

$$S_{eq} \cong 1 + \frac{a}{r} - \frac{b}{r^3} - \frac{ab}{r^4}. \quad (23)$$

- The last term in (23) is much smaller than all the other terms, and so can be ignored. Thus, an alternative expression for the Kohler-curve is

$$S_{eq} \cong 1 + \frac{a}{r} - \frac{b}{r^3}. \quad (24)$$

- Taking  $\partial/\partial r$  of (24), setting the result equal to 0, and then solving for  $r$  yields the expression for the critical radius

$$r^* = \sqrt{\frac{3b}{a}}. \quad (25)$$

- Putting (25) back into (24) yields the expression for the critical saturation ratio,

$$S^* = 1 + \sqrt{\frac{4a^3}{27b}}. \quad (26)$$

- The significance of the critical radius is that it marks the transition from a stable equilibrium to an unstable equilibrium of the droplets.
- At radii below the critical radius ( $r < r^*$ ) the droplets are in stable equilibrium.
  - If a droplet increases in radius it would require an equilibrium saturation ratio that is larger than the environment ( $S_{eq} > S_{env}$ ). The droplet will evaporate and shrink back down to its original radius.
  - If a droplet decreases in radius it would require an equilibrium saturation ratio that is less than the environment ( $S_{eq} < S_{env}$ ). The droplet will then grow back up to its original radius.
  - Droplets at radii below the critical radius are called ***haze particles***.
- At radii greater than the critical radius ( $r > r^*$ ), the droplets are in unstable equilibrium.
  - If a droplet grows larger it immediately finds itself in a supersaturated environment, because to the right of  $r^*$  the equilibrium saturation ratio decreases with radius. Thus, the droplet will continue to grow, and as it grows larger it requires even less of a saturation ratio.
  - Droplets whose size exceeds  $r^*$  will thus grow spontaneously.
  - Droplets whose size exceeds  $r^*$  are said to be ***activated***
- Adding more impurity to a droplet decreases  $S^*$ , and increases  $r^*$ . This is shown in Fig. 7.

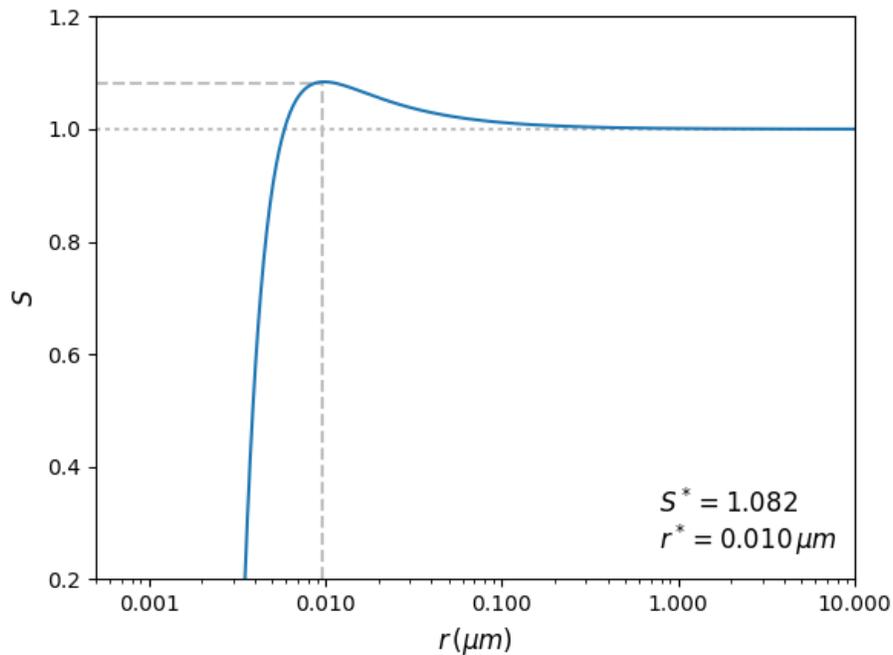


Figure 6: Kohler curve for a droplet containing 0.25 attograms of NaCl at a temperature of 275K. Dashed lines show locations of  $r^*$  and  $S^*$ . The equilibrium saturation ratio asymptotically approaches a value of one as radius increases.

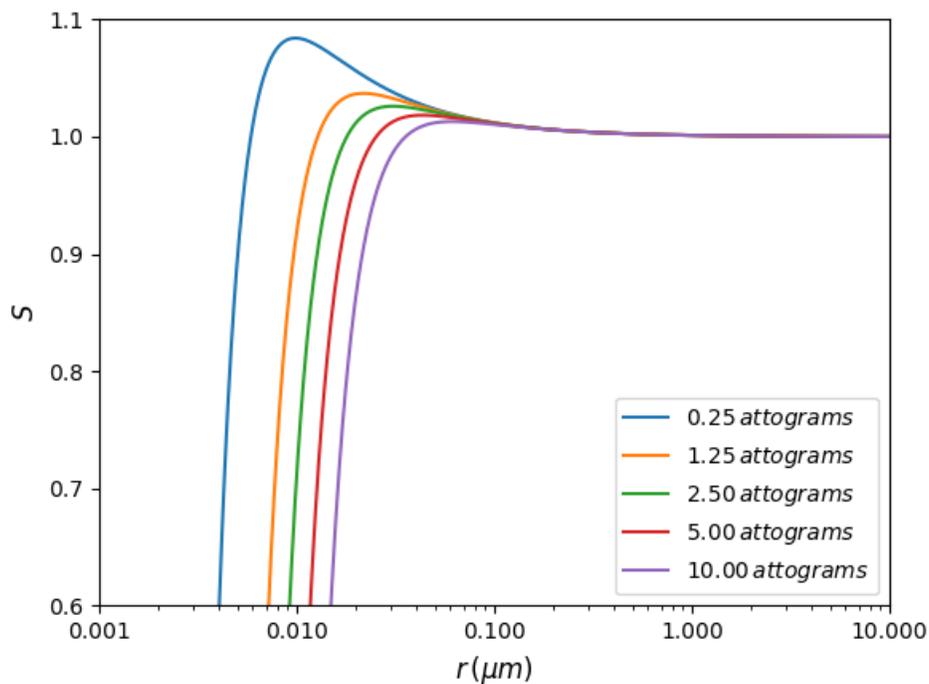


Figure 7: Kohler curves for varying masses of NaCl at a temperature of 275K. Note that as the mass of the solute increases the critical radius also increases, while the critical saturation ratio decreases.

# Atmospheric Aerosols

- Aerosols are formed either directly by disintegration of liquids or solids (known as **primary sources**), or indirectly by condensation of gases in a process known as **gas-to-particle conversion**. Indirect sources are also known as **secondary sources**.
- Examples of primary sources are
  - wind-generated dust
  - sea spray
  - forest fires
  - combustion
- The main gases responsible for gas-to-particle conversion are
  - Sulfur dioxide (SO<sub>2</sub>)
  - Nitrogen dioxide (NO<sub>2</sub>)
  - Ammonia (NH<sub>3</sub>)
  - many hydrocarbons
- Aerosols are broken into three different groups based on size. These groups are
  - Aitkin nuclei particle with  $r < 0.1\mu\text{m}$ .
  - Large particles  $0.1\mu\text{m} \leq r < 1.0\mu\text{m}$ .
  - Giant particles  $r \geq 1.0\mu\text{m}$
- The size distribution of aerosol populations can be specified by a distribution function  $n_d(D)$ , where  $D$  is the **equivalent diameter** (the diameter of a spherical particle with the same volume as the actual particle).
- In many instances the aerosol size distribution is given by the **Junge distribution**,

$$n_d(D) = cD^{-\beta}. \quad (27)$$

## Cloud Condensation Nuclei

- Homogeneous nucleation does not occur in the atmosphere, since saturation ratio rarely exceeds 1.02. Therefore, the solute effect is extremely important!
- The solute for the solute effect comes from aerosol particles in the air.
- There are two types of aerosols:

**Hygroscopic nuclei:** These are nuclei that are attractive to water vapor molecules, and act as collection sites for condensation

**Hydrophobic nuclei:** These are nuclei that are repellent to water and therefore cannot act as sites for condensation

- Not all hygroscopic nuclei are important for cloud droplet formation. Since saturation ratio rarely exceeds 1.01, only those nuclei that activate at  $S < 1.02$  are available for forming cloud droplets. It is these nuclei that are known as **cloud condensation nuclei**, or **CCN**.

## Exercises

1. In (2) substitute for  $\alpha_v$  from the ideal gas law for water vapor, and then integrate over pressure to obtain (3). To find the value of the constant of integration, use the boundary value  $e_s = e_{s0}$  when  $p = e_{s0}$ .

2. Show that

$$r^* = \sqrt{\frac{3b}{a}}$$

and

$$S^* = 1 + \sqrt{\frac{4a^3}{27b}}.$$

3. For the Junge distribution, (27):

- (a) Show that the total area of particles having diameters between  $D_1$  and  $D_2$  is

$$A_{D_1:D_2} = \frac{\pi c}{3 - \beta} (D_2^{3-\beta} - D_1^{3-\beta}).$$

- (b) The total mass of particles having diameters between  $D_1$  and  $D_2$  is

$$M_{D_1:D_2} = \frac{\pi c \rho}{6(4 - \beta)} (D_2^{4-\beta} - D_1^{4-\beta}),$$

where  $\rho$  is the density of the particles.