ESCI 340 – Cloud Physics and Precipitation Processes

Chapter 5 – Cloud Droplet Formation

<u>Effects of Ambient Pressure on $\boldsymbol{e_s}$</u>

- Recall from Chapter 2 that the atmosphere can't hold an unlimited amount of water vapor. Temperature sets a limit on how much moisture can exist in the air at saturation. The vapor pressure at saturation is called the ***saturation vapor pressure***, $\boldsymbol{e_s}$.

- The saturation vapor pressure, e_s over a **<u>flat surface</u>** of **<u>pure liquid water</u>** is given by the ***Clausius-Clapeyron equation***:

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

Where e_0 is the vapor pressure at temperature, T_0, and L_v is the latent heat of vaporization. We set $T_0 = 273.15K$, $e_0 = 611\ Pa$ and $L_v = 2.5 \times 10^6 J - kg^{-1}$.

  - The asterisk on e_s^* indicates that this is the saturation vapor pressure for **<u>pure</u>** liquid water.

  - The (∞) tells us that the surface is flat, where the radius of curvature is infinite. In other words, lines drawn perpendicular to the surface would not converge.

  - Thus, $e_s^*(\infty)$ is read as the *"saturation vapor pressure over a flat surface of pure liquid water."*

- The *Clausius-Clapeyron equation*, as expressed in the form above, assumes that the pressure in a volume of liquid is equal to the vapor pressure above the liquid. Therefore, this also means that the rates of evaporation and condensation are equal.

  - This can only be true if the air above is ***pure water vapor*** with no impurities.

  - If there is a mixture of dry air and vapor above the liquid, then the liquid is put under more pressure, so $p = p_d + e$. Because the liquid is under higher pressure, more water molecules evaporate which increases the vapor pressure, and nullifies the equation above.

- To see if we can really use the *Clausius-Clapeyron equation*, as expressed above for a mixture of dry air and water vapor, such as in the real atmosphere, we need to look at the ***Poynting equation***, which relates the change in saturation vapor pressure, e_s to the change in total pressure, p:

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

Where α_l is the specific volume of the liquid and α_v is the specific volume of the vapor

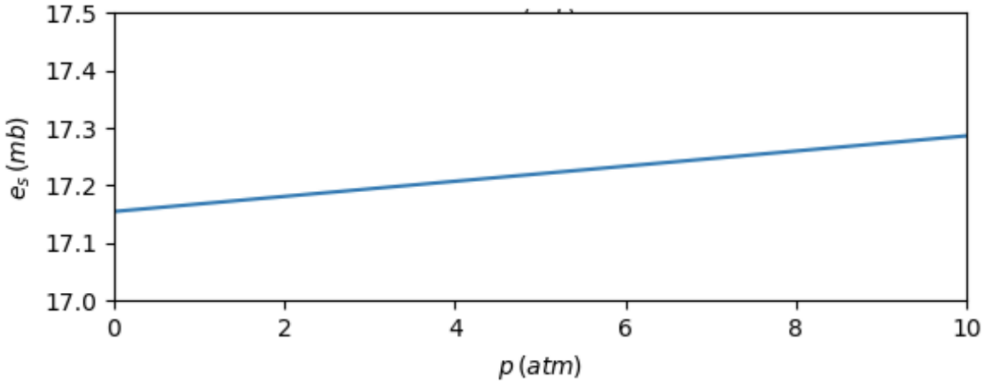
  - This relation states that as long as temperature is held constant, the derivative of saturation vapor pressure with respect to total pressure is given by the ratio of the specific volume of liquid water to the specific volume of water vapor.

- The *Poynting equation* can then be integrated to show how the saturation vapor pressure, e_s depends on the total pressure, p. The equation below tells us that increasing total pressure p will increase the saturation vapor pressure e_s, which means that the vapor pressure e calculated using the *Clausius-Clapeyron equation* will be too low if we have a mixture of both dry air and water vapor.

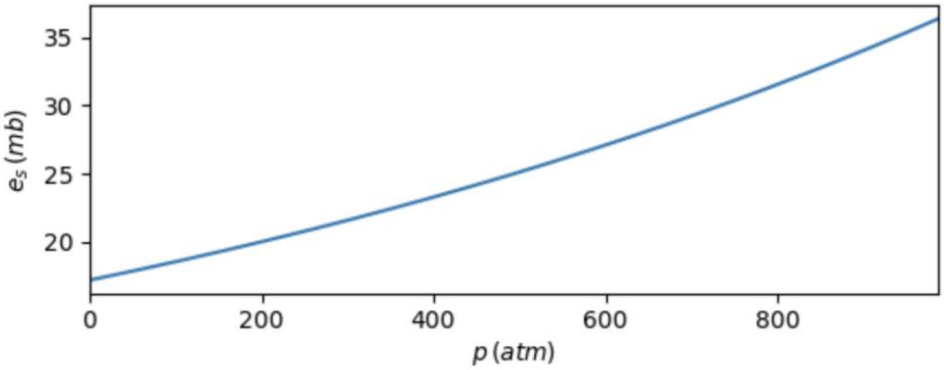
$$e_s(p) = e_{s0} \exp\left[\frac{\alpha_l}{R_v T}(p - e_{s0})\right]$$

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

  - The plot below illustrates the effect of total pressure, p on saturation vapor pressure, e_s is very small at pressures up to 10 atm (~1,000 hPa). Therefore, under most conditions, the increase in e_s due to an increase in ambient p is ignored.



- However, the effect of total pressure in the liquid on saturation vapor pressure cannot be ignored when discussing cloud droplet formation.
    - Water droplets are held together by surface tension. On the surface of a water droplet, water molecules possess unique characteristics that allow them to bond forming a “skin” around the droplet. It is the tension on the skin squeezes the droplet together.
    - Pressure on the inside of a cloud droplet is greater than the pressure on the outside. The smaller the droplet, the greater the pressure is on the inside due to its smaller radius of curvature. This is important because when cloud droplets form, they’re very tiny, are tightly curved, and the pressure on the inside is tremendous.
    - The plot below conveys the same data as in the plot above, but the x-axis has been extended to show ambient pressures, p of 0-1,000 atm. Notice that once ambient pressures are on the order of several hundred atmospheres, it greatly affects the saturation vapor pressure, e_s. This is precisely why a curvature effect must be applied to the ***Clausius-Clapeyron equation***.



- 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 greater distances.

      Note!! *Attractive and repulsive forces do exist between water molecules in liquid form. Only when water is in the vapor form do we treat it as an ideal gas where no attractive or repulsive forces exist.*

      This can be thought of as if two molecules are pushed close together, there will be repulsion, but as they move apart, there is more attraction.

- These molecular attractions and repulsions can be modeled by the ***Lennard-Jones potential***, which is the potential energy between two molecules based on the distance they are apart:

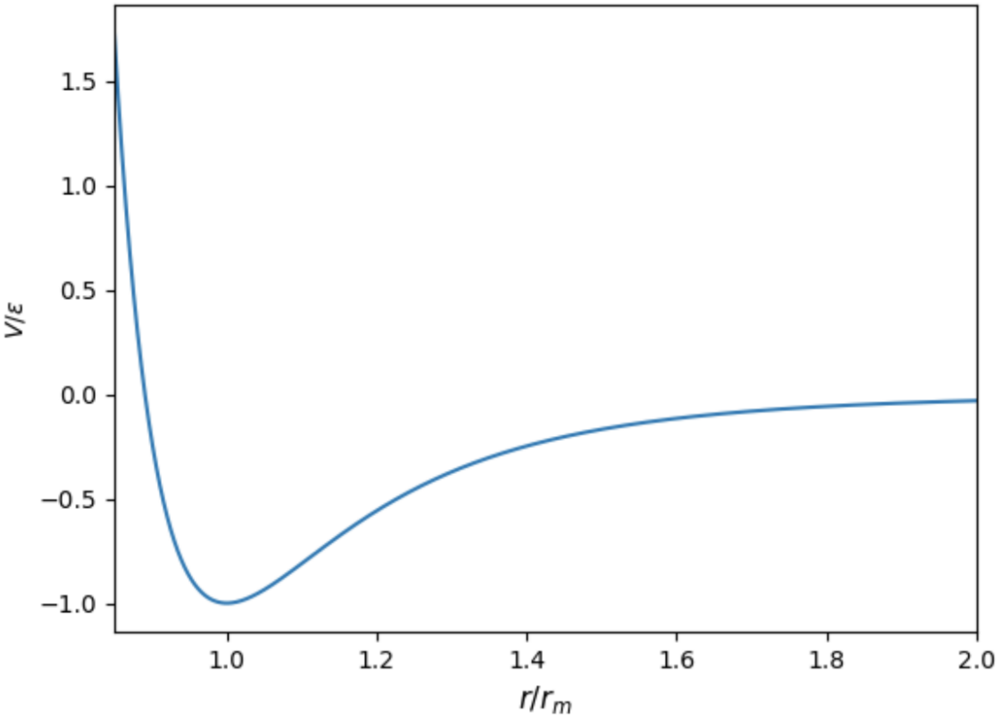
$$\boldsymbol{V = \varepsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right]}$$

Where ε is the depth of the potential well, r is the distance between molecules, r_m is the minimum distance.

  - The term raised to the 12th power represents short-range repulsive forces that push the molecules apart.

  - The term raised to the 6th power represents longer-range attractive forces which try to bring the molecules closer.

  - When $r = r_m$, the potential is minimized, and the molecules are content.



- The thought is that as pressure squeezes the molecules closer together, it enhances their repulsive forces allowing molecules near the surface of the fluid to escape more readily into the vapor outside the fluid. This in turn raises the saturation vapor pressure, e_s.

The Curvature Effect

- Recall that 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 pressure of the surrounding air. The pressure inside a droplet of radius r is given by:

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

Where p_0 is the ambient pressure and η is the surface tension of the drop, which has a value of $0.075\ N\ m^{-1}$.

  - When the radius gets smaller, the correction factor becomes larger.

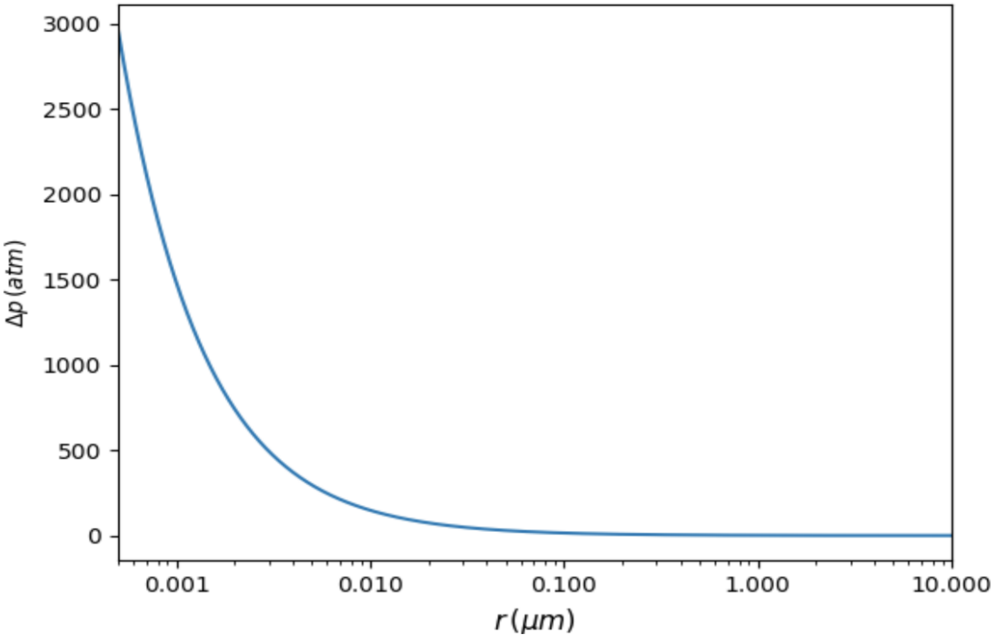
- Rearranging the equation above gives us the pressure differential across a droplet interface as a function of radius:

$$\boldsymbol{\frac{2\eta}{\underbrace{r}} = p(r) - p_0} \quad \text{or} \quad \boldsymbol{\underbrace{\Delta p} = p(r) - p_0}$$

- The relationship between water drop radius r (µm) and the pressure differential Δp is plotted below.

  - Notice that Δp is ~0 for all radiuses ≥ 0.1 µm, which means the correction factor can be ignored for fully developed cloud droplets ($r = 0.1 - 0.25\ \mu m$).

  - However, when cloud droplets first form, their radii are very small and have high pressures. Thus, for droplets < 0.1 µm, the curvature effect cannot be ignored.



- To find the saturation vapor pressure, e_s over a droplet of radius r, we can use the chain rule of partial derivatives to write:

$$\left(\frac{\partial e_s}{\partial r}\right)_T = \underbrace{\left(\frac{\partial e_s}{\partial p}\right)_T}\left(\frac{\partial p}{\partial r}\right)_T$$

$\partial e_s/\partial r$ comes straight from the *Poynting equation*,
and $\partial p/\partial r$ is found by differentiating $p(r)$.

  - Recalling that $\underbrace{\partial e_s/\partial p} = \alpha_l/\alpha_v$, by substitution, the equation above becomes:

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

  - From the ***ideal gas law*** of pure water vapor ($e = \rho_v R_v T$), we can assume $e = e_s$ and substitute $1/\alpha_v$ in for ρ_v, then rearrange to get:

$$e = \frac{R_v T}{\alpha_v} \quad \rightarrow \quad \alpha_v = \frac{R_v T}{e_s}$$

  - This can then be substituted in for α_v, then rearranged:

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

  - Rearranging once again to get all e_s on the left-hand side of the equation yields:

$$\frac{1}{e_s}\left(\frac{\partial e_s}{dr}\right)_T = -\frac{2\alpha_l \eta}{R_v T r^2} \quad \rightarrow \quad \left(\frac{\partial \ln e_s}{\partial r}\right)_T = -\frac{2\alpha_l \eta}{R_v T r^2}$$

  - The equation above can then be integrated with respect to r between radius r and a radius of ∞:

$$\int_r^\infty \left(\frac{\partial \ln e_s}{\partial r}\right)_T \partial r = -\int_r^\infty \frac{2\alpha_l \eta}{R_v T r^2}\partial r$$

$$\ln e_s(r)\Big|_r^\infty = -\frac{2\alpha_l \eta}{R_v T}\int_r^\infty \frac{\partial r}{r^2} \quad \rightarrow \quad \ln e_s(r)\Big|_r^\infty = -\frac{2\alpha_l \eta}{R_v T}\left(-\frac{1}{r}\right)\Big|_r^\infty$$

$$\ln e_s(\infty) - \ln e_s(r) = \frac{2\alpha_l \eta}{R_v T}\left(\frac{1}{\infty} - \frac{1}{r}\right)$$

- Using our rules of natural logarithms for the left-hand side of the equation above, and simplifying the right-hand side gives us:

$$\ln \frac{e_s(\infty)}{e_s(r)} = -\frac{2\alpha_l \eta}{R_v T r}$$

- Exponentiating both sides will cancel out the natural logarithm:

$$exp\left(\ln \frac{e_s(\infty)}{e_s(r)}\right) = exp\left(-\frac{2\alpha_l \eta}{R_v T r}\right) \rightarrow \frac{e_s(\infty)}{e_s(r)} = exp\left(-\frac{2\alpha_l \eta}{R_v T r}\right)$$

- To isolate $e_s(r)$, just algebraically rearrange the equation above:

$$e_s(r) = \frac{e_s(\infty)}{exp\left(-\frac{2\alpha_l \eta}{R_v T r}\right)} \rightarrow e_s(r) = e_s(\infty) exp\left(\frac{2\alpha_l \eta}{R_v T r}\right)$$

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

Where $a = {}^{2\alpha_l \eta}/_{R_v T}$

- Thus, the equation above in **red** states that the saturation vapor pressure over a droplet of radius r is larger than that over a flat surface with an infinite radius of curvature. This, by definition, is called the ***curvature effect***.

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

  - Notice that as r gets larger, $\exp\left(\frac{a}{r}\right)$ approaches one, which reaffirms the idea that this correction factor can be ignored for cloud droplets with large radii.

- The ***equilibrium saturation ratio***, S_{eq} is defined as the saturation ratio needed for the droplet to be in equilibrium. It is given by the equation:

$$S_{eq} = {}^{e_s(r)}/_{e_s^*(\infty)}$$

  - For very small droplets with radii < 0.1 μm, the equilibrium saturation ratio, S_{eq} is upwards of four, or a relative humidity of 400%. Droplets with radii ≥ 0.1 μm, S_{eq} is around one, or 100% relative humidity.

  - This is why ***homogenous nucleation***, which is the condensation of pure water vapor, doesn't occur at 100% relative humidity.

The Solute Effect

- The addition of an impurity, or ***solute***, to liquid water lowers the saturation vapor pressure, although the physical reason for why this occurs not yet known. This effect is quantified by ***Raoult's Law***:

$$\boldsymbol{e_s = \chi_w e_s^*}$$

Where χ_ω is the ***mole fraction of water***.

  - The mole fraction of water is defined as the number of moles of water, n_w per total number of moles of water plus the number of moles of solute, n_s:

$$\boldsymbol{\chi_\omega = \frac{n_w}{n_w + n_s}}$$

  - For dilute solutions, the mole fraction of water can be approximated by:

$$\boldsymbol{\chi_w \cong 1 - \frac{n_s}{n_w}}$$

  This results from the fact that $\frac{1}{1+x} \cong 1 - x$ for $x \ll 1$, where the $\ll$1 means *much, much* less than 1 by a factor of 10.

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

$$\boldsymbol{n_w = \frac{m_w}{M_w}}$$

Where m_w is the mass of the droplet and M_w is the molar mass of water.

  - The mass of the spherical droplet, m_w can be found by:

$$\boldsymbol{m_w = \rho_l V}$$

Where $\rho_l = 997 kg/m^3$ is the density of liquid water
and V can be substituted with $\frac{4}{3}\pi r^3$.

  - The equation above can then be substituted into the equation that calculates the number of moles of water in a droplet, n_w:

$$\boldsymbol{n_w = \frac{4\pi\rho_l r^3}{3M_w}}$$

- The number of moles of solute, n_s can be found by:

$$\boldsymbol{n_s = i\frac{m_s}{M_s}}$$

Where m_s is the mass of the solute added, M_s is the molar mass of the solute and 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.

- By putting the two equations above in **red** into the equation above in **blue**, we get:

$$\boldsymbol{\chi_w \cong 1 - \frac{i\frac{m_s}{M_s}}{\frac{4\pi\rho_l r^3}{3M_w}} \quad \rightarrow \quad \chi_w = 1 - i\frac{m_s}{M_s}\frac{3M_w}{4\pi\rho_l r^3}}$$

$$\boldsymbol{\chi_w = 1 - \frac{3im_s}{4\pi\rho_l}\frac{M_w}{M_s}\frac{1}{r^3}}$$

  - The equation above in **green** can then be rewritten as:

$$\boldsymbol{\chi_w = 1 - \frac{b}{r^3}}$$

Where $b = \frac{3im_s}{4\pi\rho_l}\frac{M_w}{M_s}$

- From Raoult's Law, $e_s = \chi_w e_s^*$, the ratio of e_s/e_s^* for a droplet is:

$$\boldsymbol{\frac{e_s}{e_s^*} = 1 - \frac{b}{r^3}}$$

Combined Curvature and Solute Effects

- The curvature effect makes it more difficult to form cloud droplets by raising the saturation vapor pressure, while the solute effect makes it easier by having the opposite effect. In the real world, both effects are present and must be accounted for.

- To find the saturation vapor pressure over an impure droplet with radius r, the equations for ***curvature effect*** and ***solute effect*** can be combined to give:

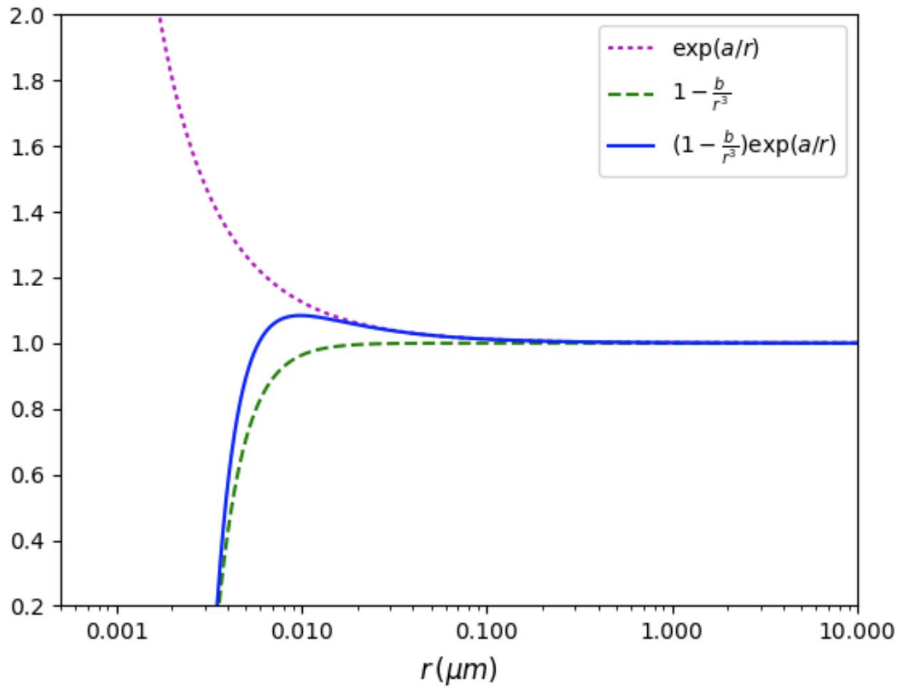
$$\boldsymbol{e_s(r) = e_s^*(\infty)\left(1-\frac{b}{r^3}\right)exp\left(\frac{a}{r}\right)}$$

Where $e_s^*(\infty)$ can be substituted with the *Clausius-Clapeyron equation*.

- Dividing both sides by $e_s^*(\infty)$ gives us an equation in terms of $e_s(r)/e_s^*(\infty)$, which is the equilibrium saturation ratio, S_{eq}:

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

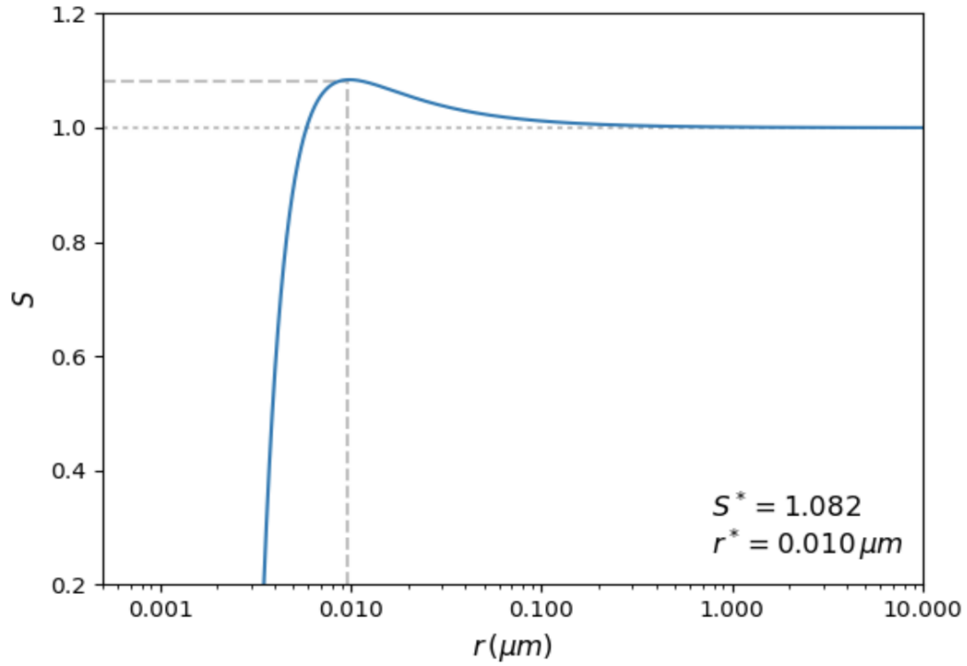
- The plot below shows the **curvature** and **solute** effects separately, and also their combined effects in **blue**. This graph of S_{eq} combining both the *curvature* and *solute* effects is called a ***Kohler curve***:



  - Note that neither effect is important once droplets are >1.0 µm in radius. It is only very small droplets for which the curvature and solute effects must be considered.

Stability of Droplets

- We're now going to take a closer look at ***Kohler curves*** using the one below as an example. The one below is for a droplet containing 0.25 attograms (10^{-18} grams) of NaCl at a temperature of 275K. Dashed lines show the locations of radius r and equilibrium saturation ratio, S_{eq}.



  - Notice that the equilibrium saturation ratio, S_{eq} asymptotically approaches a value of one (relative humidity of 100%) as the droplet's radius increases.

  - The Kohler curve becomes a maximum at the ***critical radius*** denoted by r^*. The value of the critical radius is 0.1 μm.

  - The value of the equilibrium saturation ratio, S_{eq} at the critical radius is called the ***critical saturation ratio***, and is denoted by S^*.

- The location of the critical radius, r^* is found by utilizing the equation for equilibrium saturation ratio, $S_{eq} = (1 - b/r^3)\exp{(a/r)}$ and setting $\partial S_{eq}/\partial r = 0$ and solving for r. Because of the form of the equation above, finding r^* is not straightforward. Instead, we must use the Maclaurin series expansion of:

$$\boldsymbol{e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots}$$

Which for small values of x can be truncated to $e^x \cong 1 + x$.

  - Applying this approximation to the curvature term in the equation for S_{eq} results in $\exp(a/r) = 1 + a/r$. This equation then becomes:

$$S_{eq} \cong \left(1 - \frac{b}{r^3}\right)\left(1 + \frac{a}{r}\right)$$

$$\cong 1 + \frac{a}{r} - \frac{b}{r^3} - \frac{ab}{r^4}$$

  - The last term in the equation above is much smaller than all the other terms, and so it can be ignored. Thus, an alternative expression for the Kohler curve is:

$$S_{eq} \cong 1 + \frac{a}{r} - \frac{b}{r^3}$$

  - Taking the $\partial/\partial r$ of the equation above in **purple**, setting the result equal to zero, and then solving for r yields an expression for the critical radius, r^*:

Step 1: Take the derivative

$$\frac{\partial}{\partial r}\left[1 + \frac{a}{r} - \frac{b}{r^3}\right] = \frac{\partial}{\partial r}\left[1 + ar^{-1} - br^{-3}\right]$$

$$= -ar^{-2} + 3br^{-4} = -\frac{a}{r^2} + \frac{3b}{r^4}$$

Step 2: Set the result equal to zero and solve for r

$$r^4 \times 0 = \left(-\frac{a}{r^2} + \frac{3b}{\cancel{r^4}}\right) \times r^4 \rightarrow 0 = -ar^2 + 3b$$

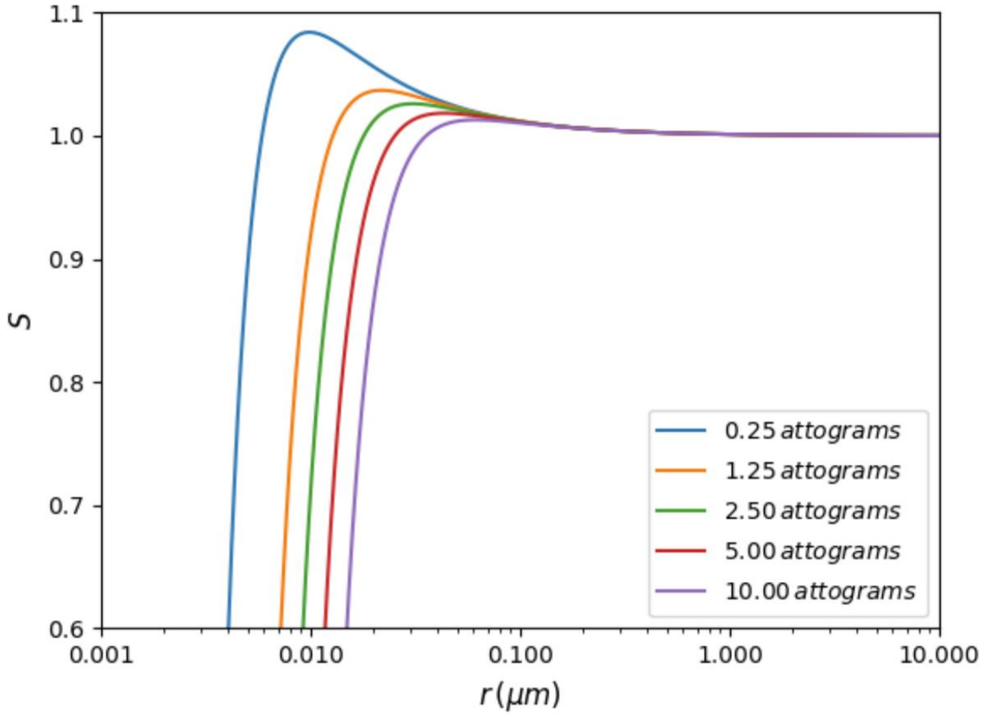
$$\frac{\cancel{a}r^2}{\cancel{a}} = \frac{3b}{a} \rightarrow \sqrt{r^2} = \sqrt{\frac{3b}{a}} \rightarrow r^* = \sqrt{\frac{3b}{a}}$$

  - Plugging this back into the equation above in **purple** yields the expression for the critical saturation ratio, S^*:

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

- The significance of the critical radius, r^* is that it marks the transition from a stable equilibrium to an unstable equilibrium of the droplets. But what does this mean?

- At radii below the critical radius ($r < r^*$), the droplets are in ***stable equilibrium***.
    - If a droplet increases in radius, its equilibrium saturation ratio is *greater* than the environment ($S_{eq} > S_{env}$). So, the droplet requires more humidity than the environment can provide, so it shrinks back down to its original radius.
    - If a droplet decreases in radius, its equilibrium saturation ratio is *less* than the environment ($S_{eq} < S_{env}$). So, the droplet requires less humidity than the environment is providing, so it grows back up to its original radius.
    - Droplets at radii below the critical radius r^* are called ***haze particles***.
- At radii greater than the critical radius ($r > r^*$), the droplets are in ***unstable equilibrium***.
    - If the environmental saturation ratio is equal to the critical saturation ratio ($S_{env} = S^*$), then droplets with radii larger than the critical radius ($r > r^*$) will grow spontaneously as they need less humidity than the environment is providing. When this occurs, the droplets are said to be ***activated***. This is because to the right of r^*, the equilibrium saturation ratio, S_{eq} decreases with increasing radius.
- Adding more impurity to a droplet decreases its critical saturation ratio, S^* and increases the critical radius, r^*. So, on a ***Kohler curve***, the line shifts down and to the right as shown in the figure below:



Atmospheric Aerosols

- Aerosols are fine solid particles or liquid droplets suspended in the air, which include dust, dirt, pollen, sea spray, smoke and volcanic ash. They can be broken down into three different groups based on their size:

  - ***Aitkin nuclei*** – particle with $r < 0.1\ \mu m$

  - ***Large particles*** – $0.1\ \mu m \leq r < 1.0\ \mu m$

  - ***Giant particles*** – particle with $r \geq 1.0\ \mu m$

- 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, aerosol size distributions are modeled by the ***Junge distribution*** shown below:

$$\boldsymbol{n_d(D) = cD^{-\beta}}$$

- They are formed either directly by disintegration of liquids or solids (known as ***primary sources***), or indirectly by condensation of gases in a process called ***gas-to-particle conversion***. Indirect sources are also known as secondary sources.

  - Examples of ***primary sources*** include:

    - Wind-generated dust
    - Sea spray
    - Forest fires
    - Combustion

  - The main **gases** responsible for ***gas-to-particle conversion*** are:

    - Sulfur dioxide (SO_2)
    - Nitrogen dioxide (NO_2)
    - Ammonia (NH_4)
    - many hydrocarbons

- Aerosols are important to have in the atmosphere because without them, there'd be no cloud condensation nuclei. To get clouds, a relative humidity upwards of 400% would be required for any condensation to occur. Condensation nuclei provide the impurity for the solute effect and lower the saturation vapor pressure.

Cloud Condensation Nuclei (CCN)

- Homogenous nucleation does not occur in the atmosphere since the environmental saturation ratio rarely exceeds 1.02 (relative humidity of 102%). Hence why the solute effect is extremely important. Certain aerosols provide the impurity for the solute effect which lowers saturation vapor pressure making it easier for condensation.

- Not all aerosols or nuclei can be considered cloud condensation nuclei, abbreviated as CCN. In fact, there are two types of aerosols:

    - ***Hygroscopic nuclei*** – These are the nuclei that are attractive to water vapor molecules and act as collection sites for condensation.

    - ***Hydrophobic nuclei*** – These are the nuclei that are repellent to water and therefore cannot act as sites for condensation.

- It should be noted that **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.