

Cloud Physics Lab

LAB 4: Formation of Cloud Droplets

Homogeneous and Heterogeneous Nucleation

Introduction:

The reason why cloud droplets are observed to form in the atmosphere when ascending air just reaches equilibrium saturation is that the atmosphere contains significant concentrations of particles of micron and sub-micron size, which have an affinity for water. A droplet will be stable if its size exceeds a certain critical value. What determines the critical value is the balance between the opposing rates of growth and decay. The decay process depends strongly upon the temperature of the droplet and its surface tension.

In this Lab, you will be required to investigate the curvature effect and solution effect on the formation of cloud droplet.

Objective:

- Plot and study the curvature effect (Kelvin's equation) as a function of cloud droplet radius.
- Plot and study the solute effect (Raoult's law) as a function of cloud droplet radius.

Theory:

Homogeneous nucleation (The curvature effect)

Homogeneous nucleation is the simplest means of forming cloud is through homogeneous nucleation where in pure vapor condenses to form droplets. Survival of the droplet is determined by a balance between condensation and evaporation.

The saturation vapor pressure over a curved surface is higher than that over a flat surface and is given by:

$$e_s(r, T) = e_s(r = \infty, T) \exp\left(\frac{2\sigma}{rR_v\rho_L T}\right) \quad (1)$$

where $e_s(r = \infty, T)$ is the saturation vapor pressure over a flat surface, where $e_s(r, T)$ is the saturation vapor pressure over a curved surface, r is the radius of the droplet, σ is the surface tension (in force per unit length) and liquid water density, ρ_L , at temperature, T , and R_v is the gas constant for water vapor. The surface tension of water is approximately 7.5×10^{-2} N/m for typical conditions.

For a cloud to grow, the vapor pressure must be greater than the e_s . We can determine the critical radius for a droplet to grow given a supersaturation, S , defined as:

$$S = \frac{e}{e_s(r = \infty, T)} \quad (2)$$

Setting $e = e_s(r, T)$ which gives the threshold for neutral conditions above which the droplet will grow and combining (1) and (2) yields:

$$\ln \left[\frac{e_s(r_c, T)}{e_s(r = \infty, T)} \right] = \ln \left[\frac{e}{e_s(r = \infty, T)} \right] = \ln[S] = \left(\frac{2\sigma}{r_c R_v \rho_L T} \right)$$

Therefore, the critical radius, r_c , is:

$$r_c = \left(\frac{2\sigma}{R_v \rho_L T \ln[S]} \right) \quad (3)$$

Given a supersaturation, S , for a droplet to be stable, it must grow to at least a radius of r_c . Note that the larger S is, the smaller r_c . So very small droplets indeed require higher supersaturations to grow. For $S = 1.01$, or a supersaturation of 100%, r_c is 0.121 microns. Droplets larger than this will grow. Droplets smaller than this will evaporate.

Heterogeneous nucleation (Solute effect)

Water condenses onto existing particles of atmospheric aerosol termed cloud condensation nuclei CCN. These particles support condensation at supersaturation values well below those required for homogeneous nucleation - primarily because of their size. Hygroscopic particles, like sodium chloride and ammonium sulfate are even more effective. In the presence of moisture NaCl and $(\text{NH}_4)_2\text{SO}_4$ absorb vapor and readily dissolve. The resulting solution has a saturation vapor pressure below that of pure water - because e_s is proportional to the absolute concentration of water molecules on the surface of the droplet. Consequently, a droplet containing dissolved salt favors condensation more than would a pure water droplet of the same size.

Aerosols are categorized as hydrophobic, neutral and hygroscopic depending on how they interact with water. Water condenses onto condensation or hygroscopic nuclei. The effect is that when some of the solute is added to the water liquid the solute molecules replace some of the liquid water molecules in the surface layer. This reduces the number of water vapor molecules at the surface and these molecules bind water more tightly to water than water does to itself. The net effect is to reduce the saturation vapor pressure required to create equilibrium where the number of water molecules leaving the surface is equal to the number of gas phase molecules striking and sticking to the surface.

For a plane surface, according to Raoult's law:

$$\frac{e'}{e_s(r = \infty, T)} = \frac{n_0}{n + n_0} \quad (4)$$

where e' is the equilibrium vapor pressure over a solution consisting of n_0 molecules of water and n molecules of the solute. When $n \ll n_0$, we can further write:

$$\frac{e'}{e_s(r = \infty, T)} = 1 - \frac{n}{n_0} \quad (5)$$

For solutions in which the dissolved molecules are dissociated, (5) must be modified by multiplying n by the factor, i , which is the degree of ionic dissociation. For sodium

chloride and ammonium sulfate which are important CCNs, $i \sim 2$ and can be used in the absence of more detailed information about i . The number of effective ions, n , in a solute of mass, m_s , is given by:

$$n = iN_a \frac{m_s}{M_s} \quad (6)$$

where N_a is Avagadro's number, m_s is the molecular mass of the solute. Likewise, the number of water molecules in a mass, m , of water is:

$$n_0 = N_a \frac{m}{M_w} \quad (7)$$

Therefore

$$\frac{e'}{e_s(r = \infty, T)} = 1 - \frac{iN_a \frac{m_s}{M_s}}{N_a \frac{m}{M_w}} = 1 - \frac{iM_w m_s}{M_s m} = 1 - \frac{3iM_w m_s}{4M_s \pi r^3 \rho_L} = 1 - \frac{b}{r^3} \quad (8)$$

where $b = \frac{3iM_w m_s}{4M_s \pi \rho_L}$ and ρ_L is the mass density of liquid water. Equation (8) is called Raoult's law.

Kohler Curve

Plugging (8) into (1) yields:

$$\frac{e'_s(r, T)}{e_s(r = \infty, T)} = \left[1 - \frac{b}{r^3} \right] \exp\left(\frac{2\sigma}{rR_v \rho_L T} \right) = \left[1 - \frac{b}{r^3} \right] \exp\left(\frac{a}{r} \right) \quad (9)$$

When r is not too small, this may be approximated as:

$$\frac{e'_s(r, T)}{e_s(r = \infty, T)} = \left[1 + \frac{a}{r} - \frac{b}{r^3} \right] \quad (10)$$

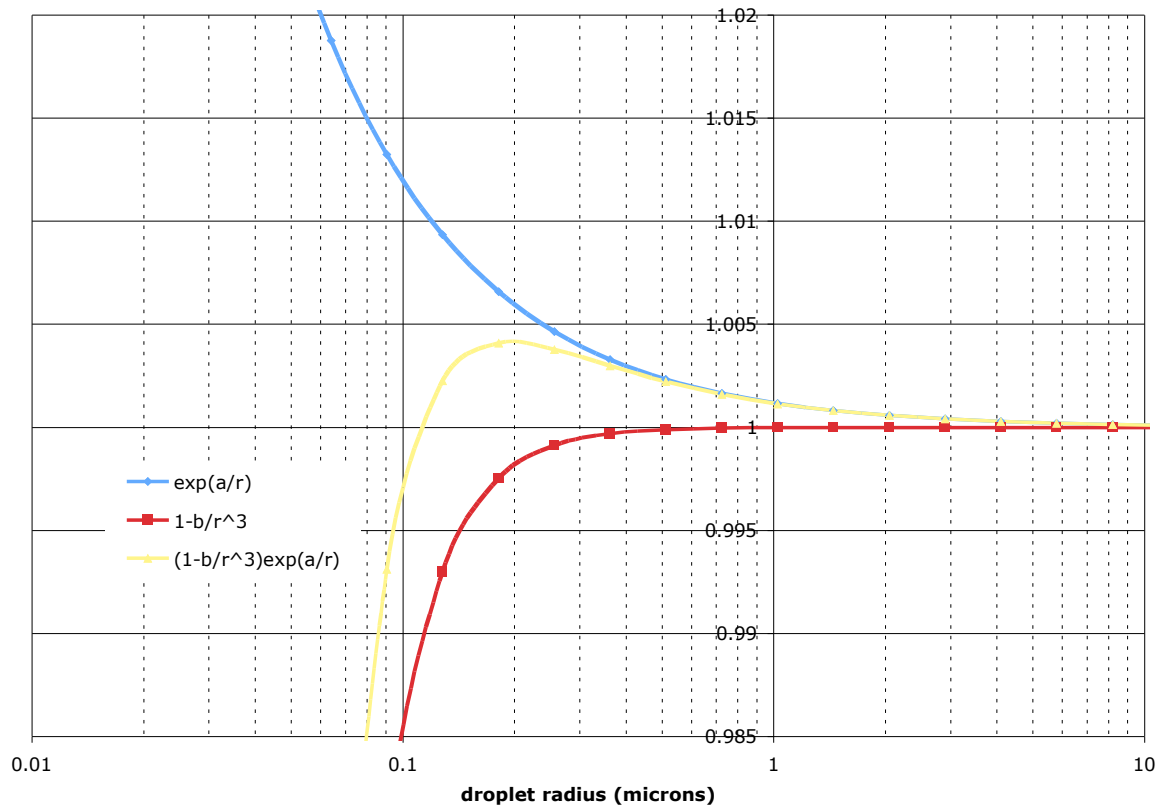
The a/r term is a *curvature* term representing the increase in the saturation vapor pressure due to the curvature of the surface and the b/r^3 term is the *solution* term. $a \sim 3.3 \times 10^{-7}/T$ (in m) and $b \sim 4.3 \times 10^{-6} im_s/M_s$ (in m^3).

The figure below shows these curves for a cloud condensation nucleus, M , of 10^{-19} kg of NaCl (table salt) and a temperature of 273 K.

Finding the point where the slope is zero yields the peak super saturation, S^* , for (9) and corresponding radius, r^* , given by:

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

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



Materials and Procedures:

1. Run the Matlab script **Lab4a.m** to plot Kelvin's equation for different temperatures.
2. Run Matlab script **Lab4b.m** to plot Raoult's law for different solute mass.

Analysis and Conclusions:

1. Discuss the behavior of the saturation ratio with cloud droplet radius of the curvature effect plot.
2. Discuss the behavior of the saturation ratio with cloud droplet radius of the solute effect plot.

Questions:

1. What did you learn about curvature and solute effects by completing the activity?
2. How does the temperature affect the curvature effect?
3. How dose solute mass affect the saturation ratio?