

ESCI 341 – Atmospheric Thermodynamics
Lesson 14 – Curved Droplets and Solutions
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References: *Thermodynamics and an Introduction to Thermostatistics*, Callen
Physical Chemistry, Levine
A short Course in Cloud Physics, Rogers and Yau
Thermodynamics of Clouds, Dufour and Defay

SURFACE TENSION

- **At the surface between a liquid and a vapor, there is a thin layer known as the *surface layer*.**
- **The surface layer is only about 3 molecules thick, but has some important properties.**
- **The specific internal energy of the molecules in the surface layer is greater than that for molecules deeper within the fluid. This is because the molecules in the surface layer don't have intermolecular forces pulling on them from all sides.**
- **If you want to increase the surface area of the fluid, you have to bring molecules from the interior of the fluid to the surface. This requires work (because you are increasing their energy).**

- **If you increase the surface area by an amount, dA , then the number of molecules that must be raised to the surface is proportional to dA .**

Therefore, the work required is also proportional to dA

$$dW \propto dA = \eta dA. \quad (1)$$

- **The proportionality constant, η , has units of energy per area, or force per length. It is called the *surface tension*.**
- **For water (at meteorological temperatures) $\eta \approx 0.075$ N/m.**
- **Because of surface tension, a droplet of water has a pressure greater than that of its surroundings.**
- **The difference in pressure across a spherically curved interface is given by**

$$\Delta p = p - p_0 = \frac{2\eta}{r}, \quad (2)$$

where r is the radius of curvature, p is the pressure inside the drop, and p_0 is the pressure outside the drop.¹

- For a droplet with radius of 1.5 μm , this means a pressure difference of 1000 mb (about 1 atm) between the inside and outside of the droplet.

THE CURVATURE EFFECT

- In the last lesson we derived the Poynting Equation,

$$\left(\frac{\partial e_s}{\partial p}\right)_T = \frac{\alpha_l}{\alpha_v}, \quad (3)$$

which shows the effects of pressure on the saturation vapor pressure. An increase in pressure increases the saturation vapor pressure.

- For most applications the increase in saturation vapor pressure due to an increase in pressure is small. That is why we don't usually concern ourselves with modifying the Clausius-Clapeyron equation to account for air pressure.
- However, in a curved droplet the pressure is greatly increased. Thus, we expect that the saturation vapor pressure over a curved drop will be greater than over a flat surface.
- We start by using the chain rule to write

$$\left(\frac{\partial e_s}{\partial r}\right)_T = \left(\frac{\partial e_s}{\partial p}\right)_T \left(\frac{\partial p}{\partial r}\right)_T. \quad (4)$$

- From the Poynting equation we have

$$\left(\frac{\partial e_s}{\partial p'}\right)_T = \frac{\alpha_l}{\alpha_v}, \quad (5)$$

and so (4) becomes

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

- Since the vapor is an ideal gas we can substitute $\alpha_v = R_v T / e_s$ to get

¹ A derivation of this can be found in Dufour and Defay, pp. 3-6

$$\left(\frac{\partial \ln e_s}{\partial r}\right)_T = \frac{\alpha_l}{R_v T} \left(\frac{\partial p}{\partial r}\right)_T. \quad (7)$$

o From (2) we have

$$\left(\frac{\partial p}{\partial r}\right)_T = -\frac{2\eta}{r^2} \quad (8)$$

so that (7) becomes

$$\left(\frac{\partial \ln e_s}{\partial r}\right)_T = -\frac{2\eta\alpha_l}{R_v T} \frac{1}{r^2}. \quad (9)$$

o Integrating (9) yields

$$\ln e_s(r) = \frac{2\eta\alpha_l}{R_v T} \frac{1}{r} + C. \quad (10)$$

o When $r = \infty$ then $C = \ln e_s(\infty)$, so (10) becomes

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

or

$$e_s(r) = e_s(\infty) \exp\left(\frac{2\eta\alpha_l}{R_v T} \frac{1}{r}\right). \quad (11)$$

o Defining

$$a = \frac{2\eta\alpha_l}{R_v T} \quad (12)$$

we get

$$e_s(r) = e_s(\infty) \exp\left(\frac{a}{r}\right). \quad (13)$$

- *A decrease in drop size increases the saturation vapor pressure.*

HOMOGENEOUS NUCLEATION

- Condensation occurring in the absence of condensation nuclei is known as *homogeneous nucleation*.
- In order to get a stable water droplet to form, the ambient vapor pressure must be equal to the saturation vapor pressure of the droplet, $e = e_s(r)$.

- Since $e_s(r) > e_s(\infty)$ (due to the curvature effect), it is impossible to get a stable water droplet to form unless the volume is *supersaturated*, meaning $e > e_s^*(\infty)$, where $e_s^*(\infty)$ is the saturation vapor pressure over a flat surface of pure water.

- The amount of supersaturation is given by the saturation ratio,

$$S = e/e_s^*(\infty). \quad \text{Saturation Ratio} \quad (14)$$

- A saturation ratio of unity means the relative humidity is 100%.
- A saturation ratio greater than unity implies supersaturation.
- An embryonic water droplet forms due to chance collisions of water vapor molecules.
 - Since embryonic water droplets are so small (a droplet consisting of 20 water molecules would have a radius of about 0.00052 μm), they are unstable unless saturation ratios exceed 10.
 - Even if a droplet should grow by chance collisions to a size of near 100 water molecules, it would still require a saturation ratio of nearly 4 (relative humidity of 400%) in order to be stable, and not evaporate.
- In the atmosphere, saturation ratios are rarely larger than 1.01 (101% relative humidity). Therefore, homogeneous nucleation cannot be responsible for the formation of cloud droplets.

THE SOLUTE EFFECT

- For an ideal solution (a very dilute solution), the specific Gibbs free energy of liquid water containing a solute is

$$g_l = g_l^* + R_v T \ln \chi_l, \quad (15)$$

where g_l^* is the specific Gibbs free energy of pure water, and χ_l is the mole fraction of water, defined as

$$\chi_l = \frac{n_l}{n_l + n_s}, \quad (16)$$

(n_l is the number of moles of water, and n_s is the number of moles of solute).

- The superscript ‘*’ refers to pure, liquid water.

- Equation (15) shows that dissolving an impurity in water lowers the Gibbs free energy of the solution (the smaller χ_l becomes, the more negative the last term in Eq. (15) becomes, decreasing the specific Gibbs free energy).
- It is not straightforward to understand why adding a solute lowers the Gibbs free energy. A qualitative argument is:
 - The specific Gibbs free energy is

$$g = h - Ts. \quad (17)$$

- Adding a solute will increase the entropy of the system (entropy of mixing), and therefore decrease the specific Gibbs free energy.
 - The solute molecules will also affect the intermolecular forces, and could result in a lowering of the internal energy (and hence, enthalpy) of the system.
- Since at equilibrium

$$g_l = g_v,$$

and since adding an impurity to the water causes g_l to decrease, then g_v must decrease if equilibrium is to be maintained. For the vapor we have

$$dg_v = -s_v dT + \alpha_v de_s. \quad (18)$$

From Eq. (18) we see that in order to decrease g_v the saturation vapor pressure must decrease (at constant temperature).

- *Adding an impurity to water will lower the saturation vapor pressure. This is called the solute effect.*
- To derive quantitatively what effect the impurity has on vapor pressure, we start with

$$dg_l = dg_v. \quad (19)$$

To find an expression for dg_l we differentiate Eq. (15) to get

$$dg_l = dg_l^* + R_v \ln x_l dT + R_v T d(\ln \chi_l). \quad (20)$$

We know that

$$dg_l^* = -s_l^* dT + \alpha_l^* de_s,$$

so Eq. (20) becomes

$$dg_l = -s_l^* dT + \alpha_l^* de_s + R_v \ln x_l dT + R_v T d(\ln \chi_l). \quad (21)$$

Setting Eq. (18) and Eq. (21) equal to each other [as per Eq. (19)] results in

$$-s_l^* dT + \alpha_l^* de_s + R_v \ln \chi_l dT + R_v T d(\ln \chi_l) = -s_v dT + \alpha_v de_s. \quad (22)$$

- Our aim is to find out how e_s varies with χ_l , at constant T . Therefore, we can ignore the dT terms in Eq. (22) and get

$$\alpha_l^* de_s + R_v T d(\ln \chi_l) = \alpha_v de_s,$$

or

$$(\alpha_v - \alpha_l^*) de_s = R_v T d(\ln \chi_l). \quad (23)$$

- Since $a_v \gg a_l^*$ this becomes

$$\alpha_v de_s = R_v T d(\ln \chi_l),$$

and from the ideal gas law, $R_v T = e_s \alpha_v$, so we are left with

$$d(\ln e_s) = d(\ln \chi_l). \quad (24)$$

- Integrating this from $\chi_l = 1$ (pure water) we get

$$\ln \left(\frac{e_s}{e_s^*} \right) = \ln \chi_l,$$

which is also

$$e_s = \chi_l e_s^* \quad \text{Raoult's Law} \quad (25)$$

o This result is known as *Raoult's law*.

- For very dilute solutions we can approximate χ_l as

$$\chi_l \cong 1 - n_s / n_l. \quad (26)$$

- The number of moles of solute and liquid are given by

$$n_{solute} = im_s / M_s$$

$$n_l = m_l / M_l$$

where m is mass, M is molecular weight, and i is the ion factor (the number of ions that one molecule of substance dissociates into).

Therefore, the mole fraction of liquid water is

$$\chi_l = 1 - i \frac{m_s}{m_l} \frac{M_l}{M_s}. \quad (27)$$

- The mass of the liquid in the droplet is

$$m_l = \frac{4}{3} \pi \rho_L r^3$$

so that the Eq. (27) is

$$\chi_l = 1 - \frac{3im_s}{4\pi\rho_L} \frac{M_l}{M_s} \frac{1}{r^3} = 1 - b/r^3. \quad (28)$$

Using Eq. (28) in Raoult's Law [Eq. (25)] results in

$$e_s = \left(1 - b/r^3\right) e_s^* \quad (29)$$

where

$$b = \frac{3im_s}{4\pi\rho_L} \frac{M_l}{M_s}. \quad (30)$$

- In reality, water droplets in the atmosphere are not ideal solutions, because they are not very dilute. However, we often approximate them as though they were ideal, and use Raoult's law, understanding that it is only an approximation.

COMBINING THE CURVATURE AND SOLUTE EFFECTS

- If we have a curved surface of pure water, the curvature effect tells us that

$$e_r^*(r) = e_s^*(\infty) \exp(a/r) \quad (31)$$

- If the droplet is impure, we need to also invoke the solute effect to get

$$e_s = \left(1 - \frac{b}{r^3}\right) \exp(a/r) e_s^*(\infty). \quad (32)$$

- Recall that $e_s^*(\infty)$ is found from the Clausius-Clapeyron equation, we get the full expression for the saturation vapor pressure over an impure, curved droplet,

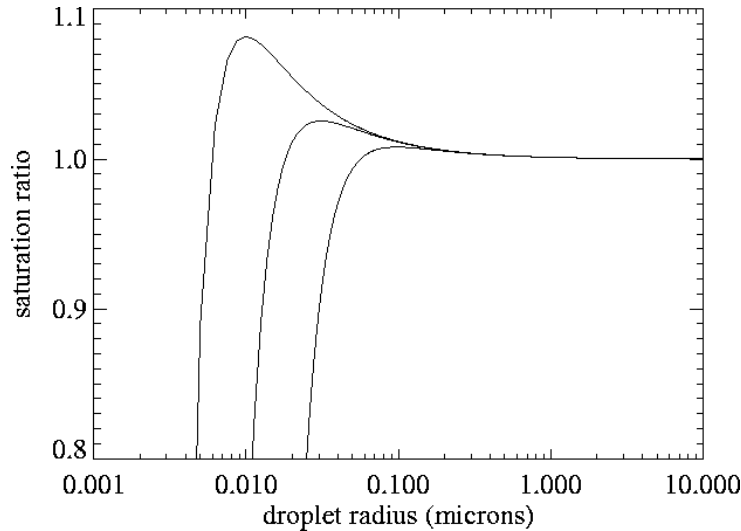
$$e_s = e_0 \left(1 - \frac{b}{r^3}\right) \exp(a/r) \exp\left[\frac{L}{R_v} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right]. \quad (33)$$

STABILITY OF DROPLETS

- In order for a droplet to be stable, the ambient vapor pressure must be equal to the saturation vapor pressure, $e = e_s$. This means the saturation ratio, S , must be [from Eq. (32)]

$$S = e/e_s^*(\infty) = \left(1 - \frac{b}{r^3}\right) \exp(a/r) \quad (34)$$

- A plot of Eq. (34) for a droplet containing three different amounts of solute (each curve differs in solute mass by a factor of 10) is shown below. The tallest curve is for the least amount of solute.



- A plot like that shown above is sometimes referred to as a *Kohler curve*.
- Making use of the approximation that for small x , $e^x \approx 1 + x$, we can write

$$S \cong 1 + \frac{a}{r} - \frac{b}{r^3}. \quad (35)$$

- The radius at which the Kohler curve is a maximum can be found by taking $\partial S / \partial r$ and setting it equal to zero. This radius is called the *critical radius*, r^* , and the saturation ratio at this point is called the *critical saturation ratio*, S^* . They have values of

$$\begin{aligned} r^* &= \sqrt{3b/a} \\ S^* &= 1 + \sqrt{4a^3/27b} \end{aligned} \quad (36)$$

- Note that in (36) the ‘*’ does not refer to pure, liquid water.
- The critical radius is of fundamental importance for cloud droplet growth.
- At radii below the critical radius ($r < r^*$) the droplets are in stable equilibrium. If S increases the droplets will grow to a larger size and then stop. If S decreases the droplets will shrink to a smaller size and then stop.
 - Droplets at radii below the critical radius are called *haze* particles.
- At radii above the critical radius ($r > r^*$) the equilibrium is unstable, and the droplets will spontaneously grow larger, even though S is not increasing.

- Droplets whose radius equals the critical radius ($r = r^*$) are said to be *activated*.
- *Note that stable droplets can form at saturation ratios well below unity.*