The Kelvin Equation: Why does a droplet form?

The basic question is what makes the existence of a droplet thermodynamically preferable to the existence only of water vapor. We have already derived an expression for the saturation vapor pressure over water. But what is the vapor pressure over a solution droplet? Atmospheric liquid clouds nucleate on tiny aerosol particles with dry diameters less than 1 \( \mu \text{m} \) diameter. These aerosol particles are the “seeds” of clouds. Without them, clouds could not exist in anything like the form we observe.

Below we discuss some of the physics that is relevant to cloud formation

**Step 1**

Gas molecules must collide and stick, to form a nucleus of a few molecules that is thermodynamically stable. It turns out that the stability of such a nucleus is favored by low temperatures (low particle energies). Thirteen molecules seems to be the magic number required to get things going. The physics of nucleation formation is beyond the level of this course.

**Step 2**

Once, a nucleus is formed, a certain supersaturation is required to maintain the droplet in equilibrium with its environment, and a higher supersaturation to enable it to grow. We have shown that that \( \Delta \mu = \mu_v - \mu_l = 0 \) if \( e = e^{sat}(T) \). This is strictly true only over a flat surface of water. Over a curved surface, it turns out that \( e > e^{sat}(T) \) for equilibrium. Qualitatively, the reason is that the total energy of the liquid surface includes not just the energy of water molecules themselves, but also the energy required to stretch the surface of the water into a curve. Consider that if the droplet were to burst, the surface tension would provide available energy to do dynamic work on the droplet.

We have shown that over a plane surface of water, the potential energy difference is related to the pressure through

\[
\mu_v - \mu_l = kT \ln e/e^{sat}
\]

Lets imagine a box of fixed volume \( V \) with nothing but water vapor in it, and out of this box a droplet forms. What we want to ask is what is the change in pressure associated with such a transformation, and under what conditions would a spontaneous drop in pressure result in formation of a droplet (i.e. we would have a spontaneous process that requires no external work). If we can answer this question and show these conditions regularly occur in the atmosphere, then we’ve successfully explained why cloud droplets form from thin air.

For the empty box, the total energy that is available for vapor flows is just the initial potential energy of the water vapor

\[
G_i = N_v \mu_v
\]

where, \( N_v \) is the initial number of vapor molecules.

For a box of fixed volume, a reduction in the number of water vapor molecules corresponds to an increase in the number of liquid molecules making up a droplet. So, with the droplet in it, the total energy of the system is the sum of the potential energy of the droplet, the energy of the
remaining vapor, and the surface tension energy associated with the curvature of the droplet

\[ G_f = N_l \mu_l + (N_v - N_l) \mu_v + \sigma A \]

where, \( N_l \) is the number density of water molecules in the box, \( \mu_l \) is the potential energy of liquid water molecules, \( A \) is the surface area of the droplet, and \( \sigma \) is the surface tension of the droplet, which is about

\[ \sigma = 7.5 \times 10^{-2} \text{N m}^{-1} = 7.5 \times 10^{-2} \text{J m}^{-2} \]

Therefore, the change in energy associated with droplet formation is

\[ \Delta G = G_f - G_i = A\sigma - N_l (\mu_v - \mu_l) \]

which is kind of intuitive if you think about it. It takes positive energy to form surface tension; whatever energy change is associated with going from vapor to liquid is a pressure drop provided \( \mu_v > \mu_l \)

But we can go further. Remembering that at constant temperature

\[ \mu_v - \mu_l = kT \ln \frac{e}{e_{sat}} \]

we can substitute to get

\[ \Delta G = A\sigma - N_l kT \ln \left( \frac{e}{e_{sat}} \right) \]

which we can show is equivalent to

\[ \Delta G = A\sigma - mR_v T \ln \left( \frac{e}{e_{sat}} \right) \]

where \( m \) is the mass of the droplet, or, since \( m = 4\rho_l \pi r^3 / 3 \)

\[ \Delta G = 4\pi r^2 \sigma - 4 \frac{\pi \rho_l r^3}{3} R_v T \ln \left( \frac{e}{e_{sat}} \right) \]

where \( r \) is the radius. Our requirement for a spontaneous process is that potential energy declines with time.

\[ \Delta G < 0 \]

So

\[ \Delta G = 4\pi r^2 \sigma - 4 \frac{\pi \rho_l r^3}{3} R_v T \ln \left( \frac{e}{e_{sat}} \right) < 0 \]

To analyze this equation, we examine two conditions

**Condition I:** \( e < e_{sat} \)

In this case, both terms are positive, and \( \Delta G \) increases exponentially with increasing \( r \). Since we require \( \Delta G < 0 \) for an irreversible transformation, the droplet cannot form without external work, for example by lifting the parcel so that it expands and cools.
**Condition II:** \( e > e^{\text{sat}} \)

Now the second term is negative, and if it dominates, then \( \Delta G < 0 \). Plotting the equation, we would see that initially \( \Delta p \) increases with \( r \), it reaches a maximum, and then decreases with \( r \). The question is what is the critical radius \( r^* \) required for just a tiny increase extra to send the droplet on its way to spontaneous irreversible growth?

To calculate, \( r^* \), we simply take the differential of \( \Delta G \) with respect to \( r \) and equate to zero.

\[
\frac{d\Delta G}{dr} = 8\pi r^2 \sigma - 4\pi \rho_r r^2 R_v T \ln \left( \frac{e}{e^{\text{sat}}} \right) = 0
\]

\[
r^* = \frac{2\sigma}{\rho_r R_v T \ln \left( \frac{e}{e^{\text{sat}}} \right)}
\]

Solving we get the saturation vapor pressure over a pure droplet, taking into account its surface tension.

\[
e^{\text{sat}}(r) = e^{\text{sat}} \exp \left( \frac{2\sigma}{\rho_r R_v T r} \right)
\]

This is known as the Kelvin equation.

A couple of things to notice about this equation. First as \( r \) approaches infinity, the curvature effect on the saturation vapor pressure becomes insignificant. In other words, even if the droplet is a sphere, from a thermodynamic standpoint, it can basically be considered to be a flat surface. For atmospheric applications, the Kelvin effect can be neglected, and we can consider droplets to be essentially flat if they are larger than about 1 \( \mu m \). Second, at the other extreme, for extremely small droplets, huge supersaturations are required for the droplet to be in equilibrium with its environment. For recently nucleated particles, say 0.1 \( \mu m \) across, the supersaturation at equilibrium is in excess of 100\% (i.e. 200\% relative humidity). We *never* get relative humidities this high in the atmosphere, and since any pure droplet forming from vapor must start from an embryo of a few molecules, clearly pure water droplets cannot form in the atmosphere.

There is actually a slightly more direct way to get at the Kelvin equation that I present here for the sake of interest. To see how, we could also right the Kelvin Equation in the form

\[
e^{\text{sat}}(r) = e^{\text{sat}} \exp \left( \frac{2\sigma}{\rho_n r kT} \right) = e^{\text{sat}} \exp \left( \frac{2\sigma}{\rho_r R_v T} \right)
\]

Notice the similarity to the hypsometric equation

\[
p(z) = p_0 \exp \left( -gz/R_d T \right) = p_0 \exp \left( -(\rho gz) / (\rho R_d T) \right)
\]

Remember that we argued that \( \Delta \mu = -\Delta w \), the amount of work per molecule it takes to do something. Here, \( \Delta w \) could refer to the amount of work per molecule required to stretch molecules into a curved surface with radius \( r \), in which case

\[
\Delta w = \sigma \frac{dA}{\rho_n dV} = \frac{2\sigma}{\rho_n r}
\]

where \( \rho_n \) is the number density of molecules. For comparison, with the hypsometric equation \( \Delta w = -\rho gz \). The denominator in the exponent is just \( \rho RT \) in one form or another.
Figure 1: Dependence of the supersaturation of water vapor at equilibrium over a pure water droplet. The size of a 13 molecule nucleus is shown for reference.