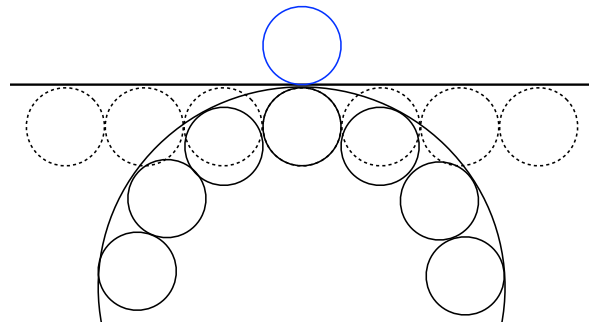


9. Surface-Curvature Effects on Saturation

Until now, when we mentioned saturation vapor pressure, we always meant saturation over a *flat* surface. Does it matter if the surface is flat or curved, as, for example, curved surface of water droplets? The answer is: it depends. More precisely, it depends on how much it is curved.

Let's consider a tiny cloud droplet in equilibrium with the vapor around it. As in the case of flat surface, the equilibrium implies that the flux of molecules evaporating from the surface equals the flux of molecules condensing on the same surface. The question is which surface, flat or curved, is easier for the water molecules to leave?



Qualitatively, it is clear that a molecule just above the surface would feel less attraction from a tiny droplet than over a flat surface as illustrated by the figure above. One can see that the distance from the departing molecule (shown in blue color) and the rows of molecules away from the departing molecule increases faster in the case of the curved surface. As the attractive forces become weaker with increasing distance, we would expect that it is easier for water molecules to leave a droplet than a flat surface. As the result, the evaporation flux over the droplet is expected to be larger than the evaporation flux over the flat surface, all other things being equal. Thus, in equilibrium, the condensation flux over droplets should also be larger than the flux over flat surface. This implies, that the number of water molecules, or, equivalently, saturation vapor pressure, above the droplet with radius r should also be larger:

$$e_s(r) > e_s(\infty)$$

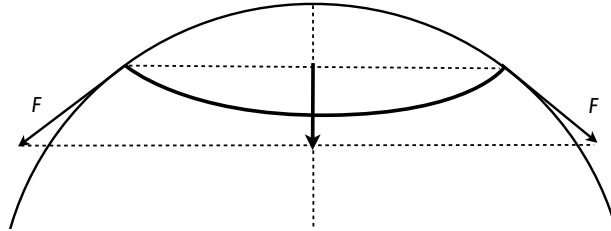
Above, the flat surface has infinite radius.

Let's now derive quantitative expression for the dependence of the saturation vapor pressure on droplet radius. The attractive forces that hold the surface together can be quantified by the concept of the *surface tension*. If we draw an imaginary line of length l on the surface of liquid, then the force that is required to hold the surface together along that line is proportional to l

$$F = \sigma l$$

with the coefficient of proportionality σ called a *surface-tension coefficient*. For water, its value is $7.5 \times 10^{-2} \text{ N/m}$. If we multiply and simultaneously divide the units of σ by units of length, m , we get Nm/m^2 , or, remembering that Nm are units of work or energy, that is *Joules*, J , we have the units of surface tension coefficient are J/m^2 . Thus, another interpretation of the surface tension coefficient is that it is the amount of the surface energy it takes to create one unit area of the surface.

In the case of a droplet, the surface tension creates additional pressure inside that droplet. It is easy to see why in the figure below. The surface forces that keep a part of the droplet surface 'attached' to the rest of the droplet have the component normal to the surface towards the droplet center. Taken per unit area, that force constitutes the additional pressure entirely due to surface tension. It is also easy to see that without curvature, the surface-tension force would not have a component perpendicular to the surface, and, hence, no additional pressure.



It is pretty straightforward to compute the magnitude of surface-tension pressure p_t . Let's consider a droplet of radius r . Let's try to increase droplet's radius by a small amount dr . It will take some work against the tension pressure $p_t dV$, which will go into the energy σdA needed to create the new droplet surface area dA :

$$p_t dV = \sigma dA$$

The droplet's volume is $V = (4/3)\pi r^3$, while surface area is $A = 4\pi r^2$. Therefore, $dV = \frac{dV}{dr} dr = 4\pi r^2 dr$ and $dA = \frac{dA}{dr} dr = 8\pi r dr$. Substituting those expressions in the above equation, we obtain a so-called Laplace formula for the surface-tension pressure:

$$p_t = \frac{2\sigma}{r} \tag{9.1}$$

One can see that in the case of flat surface, that is when $r \rightarrow \infty$, $p_t = 0$. It is easy to estimate that additional pressure inside a droplet with $1 \mu\text{m}$ radius is 1.5 higher than normal atmospheric pressure!

Let's now assume that we have a droplet with radius r is thermodynamic equilibrium with the vapor around. Let's perturb the radius of the droplet slightly, while leaving temperature strictly constant. Then, obviously, the saturation vapor pressure should also change to keep the droplet-vapor system in equilibrium, that is

$$de_s = dp_t = 2\sigma d\left(\frac{1}{r}\right) \quad (9.2)$$

Using the ideal gas law for the vapor $e_s v_v = R_v T$, and replace the specific volume v_v with $1/\rho_L$, where ρ_L ($=1000 \text{ kg/m}^3$) is the density of liquid water, (9.2) can be rewritten as

$$\frac{de_s}{e_s} = -\frac{2\sigma}{R_v T \rho_L} d\left(\frac{1}{r}\right) \quad (9.3)$$

Integrating from radius r to infinity,

$$\int_{e_s(r)}^{e_s(\infty)} \frac{de_s}{e_s} = -\frac{2\sigma}{R_v T \rho_L} \int_r^{\infty} d\left(\frac{1}{r}\right)$$

we get a so-called Kelvin equation, first derived by William Thomson, also known as Lord Kelvin, in the 19th century:

$$e_s(r) = e_s(\infty) e^{\frac{2\sigma}{R_v T \rho_L r}} \quad (9.4)$$

The Kelvin equation can be also written as

$$e_s(r) = e_s(\infty) e^{ar} \quad (9.5)$$

where

$$a = \frac{2\sigma}{R_v T \rho_L} \quad (9.6)$$

is some characteristic droplet radius, which, for normal atmospheric conditions, $a \approx 0.001 \text{ } \mu\text{m}$. Thus, the saturation vapor pressure increases with decreasing droplet size. The equilibrium or critical radius of a droplet with a given environmental relative humidity R_h is given by

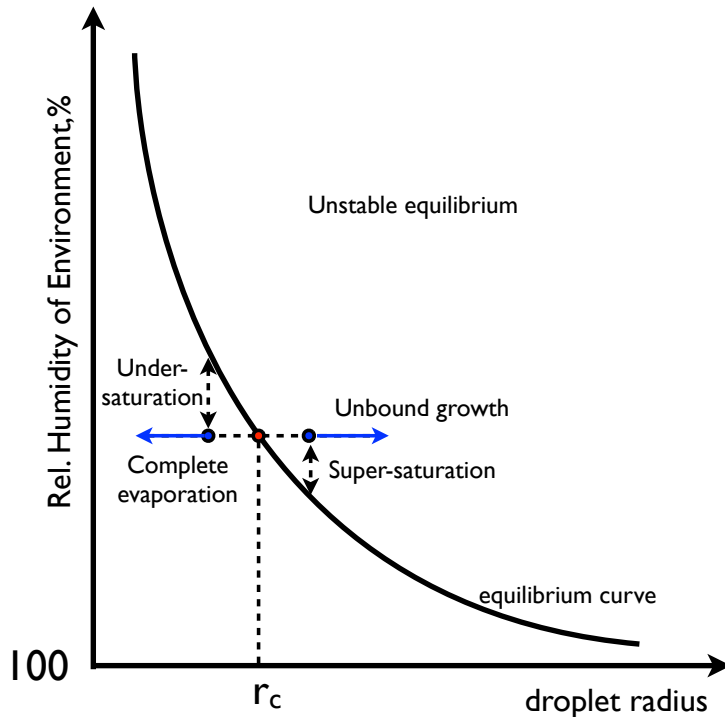
$$r_c = \frac{2\sigma}{R_v T \rho_L \ln(R_h)} \quad (9.8)$$

Here is the table showing the dependence of critical droplet radius on the environmental relative humidity.

Equil. Rel. Humidity, %	Critical radius, μm	Number of molecules
1000	0.00005	20
300	0.001	200
150	0.003	3,000
110	0.01	30,000
100.1	1	a lot

One can see that the curvature effect is important only for very tiny droplets, generally smaller than the characteristic size a , which is much smaller than the typical cloud-droplet size larger than $1 \mu\text{m}$. Notice that the equilibrium relative humidity for droplets of any size is always higher than 100%. This means that given enough time, droplets of pure water of any size will evaporate when relative humidity is exactly 100%.

Let's assume that we have super-saturated environment (relative humidity $> 100\%$) that has the vapor pressure to keep in equilibrium a tiny droplet with some radius r_c . Is the equilibrium stable? Let take a look at the following qualitative diagram.



The position of the droplet in equilibrium is shown by the red dot. What would happen if we add several molecules to that droplet, thus, increasing its size just slightly? The size of the droplet would increase as shown by a blue dot to the right from the red dot. It is easy to see that the equilibrium relative humidity for that larger

droplet is now lower than the environmental; therefore, the droplet would experience super-saturated conditions and, hence, would continue to grow, which, in turn, would create even more super-saturated conditions. Let's consider opposite situation, that is, the droplet is made slightly smaller than the equilibrium size. One can then see that for a smaller droplet, the required equilibrium relative humidity is now higher than the environmental. Therefore, the droplet would experience under-saturated conditions, and continue to evaporate. Evaporation would further decrease the radius and create even more under-saturated conditions. Eventually, the droplet would evaporate completely. Thus, we conclude that the equilibrium of a droplet of pure water with the radius equal to the critical is unstable. Similar conclusion can be reached if instead of changing droplet's radius, we change the environmental relative humidity, just slightly. That is, the droplet in equilibrium with relative humidity would grow unbound if the relative humidity is slightly increased, or completely evaporate if relative humidity is slightly decreased.