1 Homogeneous ice nucleation

The theory for the homogeneous nucleation of ice is similar to that for liquid with some minor differences. First, the thermodynamic driver for a phase change is not the vapor pressure but instead the magnitude of supercooling

\[ \Delta \mu = \mu_i - \mu_l = l_m \Delta T / T_0 \]

where \( \Delta T = T_0 - T \) is the degree of supercooling below the triple point and \( l_m \) is the molecular latent heat of melting. This result can be obtained from a linear first order expansion of the the difference in chemical potential as a function of temperature and pressure relative to the triple point \( T_0 \) and substituting the Clausius-Clapeyron equation and the relationship between chemical potential differences and vapor pressure differences.

\[ \mu_i - \mu_l = \Delta T \left\{ \left( \frac{\partial \mu_v}{\partial e} \right) e^{\text{sat}(T_0)} T_0 - \left( \frac{d e^{\text{sat}}}{d T} \right) T_0 \right\} \]

\[ = \Delta T \left\{ \frac{kT_0}{e} \left( \frac{l_{v, \text{sat}} e}{kT_0^2} - l_v e \right) \right\} \]

Neglecting shape consideration for formation of the ice embryo which we will assume to be quasi-spherical, the total change in free energy required to form an embryo is the combined reduction from the lower potential of ice and the increase due to the surface tension of forming the ice-liquid interface with area \( A_{il} \)

\[ \Delta G = -V_i n_i \Delta \mu + A_{il} \sigma_{il} \]

\[ = -\frac{4}{3} \pi r_i^3 n_i l_m \Delta T / T_0 + 4 \pi r_i^2 \sigma_{il} \]

\( \Delta G \) increases with \( r_i \) for small \( r_i \) and decreases for large \( r_i \). Thus the free energy barrier for spontaneous growth is crossed at the maximum where

\[ \frac{\partial \Delta G}{\partial r_i} = 0 \]

Solving (see assignment) and substituting, we obtain

\[ r^* = \frac{2 \sigma_{il} T_0}{n_i l_m \Delta T} \]

\[ \Delta G^* = \frac{16 \pi \sigma_{il}^3}{3 (n_i l_m \Delta T / T_0)^2} \]

The general formation for the nucleation rate is similar to that discussed previously

\[ J_i (T) = \frac{kT}{h} A_i n_i Z n_i \exp \left( -\frac{\Delta g_{\text{act}}}{kT} - \frac{\Delta G^*}{kT} \right) \]
Figure 1: Figure 7.18 in Lamb and Verlinde. Depiction of the freezing interface.

where $h$ is Planck’s constant, $n_{il} \sim 10^{19}$ m$^{-2}$ is the number density of molecules in the ice surface, $Z$ is the Zeldovich factor ($\sim 0.1$) as before and $n_I = 3.3 \times 10$ molecules/m$^3$ is the number density of liquid molecules.

Note the introduction of a new term, the activation energy that represents an added energy required to restructure the bonds in the liquid phase before they can adopt those lower energy bonds in the ice phase. However, the magnitude of the activation derived from classical theory does not yield results that are in agreement with those measured, suggesting lower activation energies than expected at lower temperatures.

In general nucleation is the conversion of a liquid sphere to solid ice form. In this process a fraction of droplet will be frozen, with concentration $N_f$, and a fraction will be unfrozen, with concentration $-dN_u$

$$\frac{dN_u}{dt} = -\frac{dN_f}{dt}$$

The rate at which the conversion from liquid to solid takes place is given by the nucleation rate $J$.
Figure 2: Temperature at which 99.99% of drops freeze as a function of drop size and cooling rate.

(units number per volume per second) and the droplet volume and the number of unfrozen droplets remaining.

\[ \frac{dN_u}{dt} = -N_u V J_i(T) \]

Thus

\[ dN_u = -N_u V J_i(T) \, dt \]

\[ N_u = N_0 \exp \left( -V J_i(T) t \right) \]  \hspace{1cm} (1)

While the nucleation rate \( J(T) \) itself is a thorny problem, studies by Koop et al. in 2000 have shown that, at equilibrium

\[ \mu_v = \mu_{i}^{\text{sat}} + kT \ln a_v^i \]

So, for a solution, at equilibrium \( \mu_v < \mu_{i}^{\text{sat}} \). Similarly

\[ \mu_i = \mu_{i}^{\text{sat}} + kT \ln a_i^v \]

where \( a_v^i = a_v^w / S_i \), where \( S_i = e_{\text{sat}}(T) / e_{\text{si}}(T) \). Note that the saturation vapor pressure over water is higher than that over ice, so \( S_i \) is greater than 1 except at the triple point. So, if the saturation vapor pressure over liquid is greater than that over ice, then \( S_i > 1 \) and \( a_i^v < a_v^w \) and \( \mu_i < \mu_{i}^{\text{sat}} \) as expected. Koop showed empirically that one only needs to know the difference between the these two activities to obtain the nucleation rate

\[ J = J(\Delta a) = J(a_v^w - a_v^i) \]  \hspace{1cm} (2)

where \( \Delta a \) is about 0.305 Well this is super useful, because at equilibrium, the value of \( a_v^w \) should be the same as the ambient relative humidity. Also, we know the saturation vapor pressure over ice and water so \( a_v^i = e_{\text{si}} a_v^w / e_{\text{sat}} \). Thus, bingo, from the formula Koop provided (Eq. 2) and Eq. 1, we can calculate whether or not a haze aerosol should freeze to form an ice crystal at a given time \( t \). What Koop showed is that the temperature depression required to bring ice in solution into equilibrium for a given degree of solute can be related to the temperature depression required to
Figure 3: Haze droplet cooling and freezing as it rises in the atmosphere. The upper curve gives the melting point of ice in solutions of given water activity. The lower cluster of curves shows how the freezing temperature varies with activity and nucleation rate. From Lamb and Verlinde and Koop et al. (2000)

initiate homogeneous freezing. Any given solution droplet can be made to freeze by diluting it at a given temperature (provided the temperature is sufficiently low to begin with) or by lowering the temperature for a given solution activity, and that these two processes are related.

As stated in the paper “The offset in water activity at any given temperature represents the deviation from solid-liquid equilibrium, in effect the amount of dilution needed for ice to form spontaneously...” and from Baker and Baker “where the liquid-water density becomes locally similar to that of ice, the water molecules can reorient themselves easily into ice embryos”.

At typical atmospheric temperatures, the supersaturation with respect to ice required to freeze droplets is quite surprisingly high, especially for small haze droplets that might be considered the originators of cirrus.
Figure 4: Threshold saturation ratio with respect to ice as a function of temperature for several diameters of liquid aerosol particles. Note that the freezing supersaturation can be very high! From Lamb and Verlinde and Koop et al. (2000)