Notes on Ice Formation in the Atmosphere – 7 October 2019

Formation of snow crystals in the atmosphere occurs mainly via the freezing of water droplets. The general process can be summarized with three very simple steps:

1) Formation of water droplets from the vapor
2) Freezing of water droplets into ice crystals
3) Growth of ice crystals

So first we will consider how water droplets form and then how they freeze.

In the absence of other particles, clouds from when the air is supersaturated, or when relative humidity is above 100%. Relative humidity is defined as the ratio of vapor pressure to equilibrium vapor pressure (when both (usually, if not at a triple point) phases are stable and equal numbers of molecules are entering and leaving the phases. Mathematically, this is defined as

\[ e \equiv \text{vapor pressure} \]
\[ e_s \equiv \text{equilibrium vapor pressure (also called saturation vapor pressure)} \]

Then relative humidity is:

\[ RH \equiv \frac{\text{vapor pressure}}{\text{saturation vapor pressure}} = \frac{e}{e_s(T)} \]

This varies from 0 to 1 (or 0 to 100% as more commonly quoted in weather reports). A relative humidity of 100% represents the lines of the phase diagram (see below), as the vapor pressure for gas and liquid phases is equivalent to the saturation vapor pressure.

For clouds to form (air with water droplets or ice crystals), with no nucleation particles the relative humidity would generally be 100%. Thus, clouds are more likely to form when saturation vapor pressure are lower (easier to get to 100% relative humidity). Since equilibrium vapor pressure is lower when temperature is lower, cooling a parcel of air will lower the saturation vapor pressure.
and increase the relative humidity. The usual way to cool air is through rising air which cools air via expansion.

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**Aside: Why air cools in the atmosphere**

Rising air generally occurs via four processes:

1) Synoptic storms – rising air in regions of low pressure
2) Convection – cumulus clouds and super pop-up thunderstorms
3) Orographic lifting – air rises over an obstruction (a mountain range or ice sheet)
4) Frontal lifting – warm air rises over cold air

Rising air is why precipitation is greater in the mountains than in the surrounding plains and why precipitation is greater on the windward slope of mountains than the leeward slope.

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**Other considerations for making water droplets in the atmosphere:**

**Curvature**

Furthermore, considering phase transitions of pure water is not really appropriate because to form a water droplet from the vapor requires constructing a geometry shape of high curvature. Equilibrium vapor pressure is defined as relative to a flat surface, so forming a water droplet requires a higher saturation vapor pressure than for flat surfaces. Saturation vapor pressures for convex surface (such as small spheres of water) are greater than saturation vapor pressures for flat surfaces which are greater than saturation vapor pressures for concave surfaces.

This is due to the hydrogen bonds that must be broken to take water from liquid to vapor or ice to vapor. Flat surfaces have to break more bonds that convex surfaces, so it is harder for evaporation to occur, so the saturation vapor pressure of flat surfaces is lower. Or, more succinctly, it is easier to evaporate from corners.

The change in the phase diagram for concave and convex surfaces relative to flat surfaces is shown to the left.

**Due to curvature effects, it is necessary to have a relative humidity of greater than 100% to form water from pure water vapor because the water droplet must be a convex surface.**
Cloud condensation nuclei/atmospheric aerosols

In the atmosphere, there are often soluble particles that facilitate condensation. These particles are sometimes termed atmospheric aerosols or for our purposes, cloud condensation nuclei. There are so many of these particles that essentially all water droplets in all clouds worldwide (besides in very cold environments) form by condensation of water vapor onto these cloud condensation nuclei (CCN).

What are these particles made of?

- Sea salt
- Soluble organic molecules from vegetation
- Sulfate, resulting from oxidation of sulfur gases emitted by
  - Volcanoes
  - Algae
  - Fossil fuel burning (mainly coal and oil)

Nucleation on aerosol particles is favored because:

1. No need to form a small convex surface because the particle already serves that purpose.

2. Saturation vapor pressure over the solution (the water droplet) is less than that over pure water because salt dissolves in liquid water but not in the solid or vapor (under normal conditions). So, if salt is present, liquid is favored and the liquid range as a function of temperature is expanded due to the presence of salt (see phase diagram at right). The result is what would be a small supersaturation over pure water can be a large liquid saturation over a salt solution. Salt can attract water and form water droplets for relative humidity less than 100%.

As the droplet grows the curvature decreases and the dilution of salt increases. However, if enough salt is initially present than the droplet will grow until the curvature effect on vapor pressure is very small, and the droplet will continue to grow as essentially pure water. This means that typically relative humidity in clouds is higher than 100% but only slightly so (100.1-100.5% is common). If fewer cloud nuclei (CCN) are present, then the relative humidity must be higher before condensation occurs.

Typically, CCN concentrations are:

<table>
<thead>
<tr>
<th>Locale</th>
<th>Particle concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Remote ocean</td>
<td>~100 per cm³</td>
</tr>
<tr>
<td>Rural land</td>
<td>~1,000 per cm³</td>
</tr>
<tr>
<td>Urban land</td>
<td>~10,000 per cm³</td>
</tr>
</tbody>
</table>
If you prefer a drawing of this process, it generally occurs as pictured below:

From water droplets to ice crystals

As you go up in the atmosphere, temperature goes down by ~6 deg/km, so it is common to have below-freezing temperatures in clouds even in the tropics. Ice occurs in clouds that extend above the 0°C level. High clouds (commonly cirrus) consist entirely of ice crystals.

Freezing of water droplets

1. As water droplets of pure water cool, they freeze. This doesn’t happen at 0°C though. You have to cool below freezing, maybe not much below, but maybe a lot below.
2. There are lots of hydrogen bonds in the liquid, but in ice basically all (~100%) are formed. However, water molecules at the ice-water interface make fewer hydrogen bonds because there is nothing to bond with above the surface. Thus, the water molecules on the surface have fewer bonds than water molecules in either the solid or liquid phases. For small crystals, the interface is a large fraction of the total number of water molecules, so the droplet would prefer to stay liquid unless there is already a surface present to attach to via hydrogen bonds.
3. A bucket of water will freeze at very close to 0°C because the wall of the bucket serves as a nucleation surface on which to begin growing ice. It has many sites to start ice crystal growth, but you only need one.
4. Once an ice embryo forms in a droplet then the whole droplet freezes.
5. Pure water will freeze at about -37°C. Freezing happens above -37°C is there is an appropriate solid impurity present, which we call “ice-forming nuclei” or “ice nuclei” (IN).

Particles that can serve as ice nuclei have the following characteristics:

1. Insolubility in water
2. Capable of hydrogen bonding
3. A lattice spacing similar to that in ice
4. Crystal structure with hexagonal symmetry
Common nuclei include:

<table>
<thead>
<tr>
<th>Material</th>
<th>Threshold temperature for ice nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td>0°C</td>
</tr>
<tr>
<td>AgI (silver iodide), artificial</td>
<td>-4°C</td>
</tr>
<tr>
<td>Clay minerals (dust, feldspar best)</td>
<td>-10°C</td>
</tr>
<tr>
<td>Vegetation dust (dried &amp; crumbled leaves, bacteria)</td>
<td>≤-4°C</td>
</tr>
</tbody>
</table>

Clay minerals are commonly found at the center of most ice crystals.

If we contrast the two subsets of atmospheric aerosols that form snow and ice nuclei, we have:

<table>
<thead>
<tr>
<th>Cloud condensation nuclei (CCN)</th>
<th>Ice nuclei (IN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small (radius &lt; 0.1 µm)</td>
<td>Large (radius ~1 µm)</td>
</tr>
<tr>
<td>Soluble (salt)</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Common (~1000/cm³; 10⁶/L)</td>
<td>Rare (10/L)</td>
</tr>
</tbody>
</table>

Thus, although nearly all cloud droplets contain CCN, only a small fraction contain IN. Ice crystal growth on clay would look like:

You can also get a water droplet that initially grows on a salt speck which then freezes when it touches the clay which has a lattice structure conducive to ice growth.

Once an ice crystal is nucleated, it grows via two mechanisms:

1. From the vapor. In mixed cloud, an ice crystal will grow at the expense of water crystals. This is due the difference in saturation vapor pressure between ice and water. It is easier for molecules to leave the liquid than the solid. Thus, a mixed cloud that is saturated with respect to the liquid is supersaturated with respect to the solid phase (ice Ih).
2. Riming (collision of super-cooled water droplets).
   a. Snow crystal forms by freezing of water droplet.
   b. Droplet grows by vapor deposition until it is large enough to fall.
   c. Falls through clouds and freezes when contacts ice.

If you collect snow crystals and view them under the microscope, may will be rimed. To get unrimed snow, you generally have to go to high altitude or a polar ice sheet.
**Ice Crystal Shapes (or “habits”)**

The basic shapes are all hexagonal, but the precise form of the shape depends on temperature and humidity. If low humidity, water molecules pass the outside corners with higher saturation vapor pressure and do to the cozy inside corners and are deposited there (there can even be mass loss from the outside corners to the inside corners). If high humidity, then the water molecules latch onto the first ice promontory, which is generally an outside corner.

In mixed clouds, with very small supersaturation with respect to the solid (near equilibrium), there is slow growth as columns. Both axes (the a-axis and c-axis) tend to grow at the same rate, resulting in a small surface to volume ratio. By contrast, fast growth in a super-saturated environment leads to large surface to volume forms with more intricate (dendritic) forms.

See slides for more information on this.

**Ice Accumulation on Surface**

Ice can also accumulate directly on a surface via three mechanisms:

1. Surface rime (white) – super-cooled water droplets freeze on impact.
2. Glaze (freezing rain, generally clear) – raindrop at 0°C falls on a cold surface (< 0°C) and then freezes.
3. Frost – vapor deposition of ice directly on a surface.