Structure of Water and Ice

- Water molecules are bent at an angle of 104.5° (see Fig. 1).

- Due to the different electron affinities of hydrogen and oxygen, water molecules have a permanent electric dipole.
  
  - The oxygen side of the molecule is negatively charged, while the hydrogen side is positively charged.

![Figure 1: Structure of a water molecule.](image)

- Because of this structure, the intermolecular (Van Der Waals) forces are important, and leads to the interesting behavior of water compared to other substances.

- The density of water does not monotonically increase as temperature decreases. Instead, it reaches a maximum at about 4°C (see Fig. 2).
  
  - Unlike most other substances the solid phase of water is actually less dense than the liquid phase.

- Ice crystals have different shapes, or habits, depending on the temperature and saturation ratios under which they form.
  
  - The most common shapes are hexagonal plates, hexagonal columns, and dendrites.
Formation of Ice Crystals

- Ice crystals can form either by the freezing of super-cooled water droplets, or via deposition.

- Just as condensation requires a nucleus to provide a surface for the embryonic water droplet to form around, so too does deposition.

- Ice crystals must form around some nuclei.
  - The exception is perhaps some cirrus clouds, which form at temperatures cold enough that homogeneous nucleation of ice crystals may occur.

- The nuclei for deposition are called ice nuclei.

- Ice nuclei are rare. Only one out of 10 million aerosols is an effective ice nuclei.

- Little is known about ice nuclei, but it appears that the primary ice nuclei in the atmosphere is the mineral kaolinite, which is found in many soils.

- Certain bacteria may also be ice nuclei.

- Because ice nuclei are so rare, it is common to find clouds consisting of super-cooled liquid water droplets at temperatures as cold as $-15^\circ\text{C}$, and super-cooled liquid clouds have even been found at temperatures as low as $-40^\circ\text{C}$.
These super-cooled water droplet will freeze instantly upon impact with objects, and are a primary concern when aircraft fly through such clouds since they form ice on the wings, propellers, and engine intakes.

The smaller the drop, the more likely it is to be super-cooled at very low temperatures.

- Once an ice crystal forms it can grow by diffusion, accretion, or aggregation.
- The saturation vapor pressure over liquid water, $e_s$, is greater than that over ice, $e_i$. This is shown in Fig. 3 for temperatures ranging from 0 to $-40^\circ C$.

![Figure 3: Saturation vapor pressure over ice versus over liquid water as a function of temperature. Left axis shows the ratio of $e_s/e_i$. Right axis shows level of supersaturation over ice for saturation over liquid.](image)

- The saturation vapor pressure over ice is lower than that for liquid water because it is more difficult for water molecules to escape from the ice phase. This is because they are more tightly bound together in the ice phase.

**Diffusional Growth of Ice Crystals**

- Diffusional growth of ice crystals is more rapid than that of liquid water droplets because the saturation vapor pressure over ice is less than that over water.
• The diffusional growth equation for ice crystals is very similar to that for water droplets, and is
\[
\frac{dm}{dt} = 4\pi CD(\rho_{v_b} - \rho_{vR}),
\]
where \(\rho_{v_b}\) is the absolute humidity away from the crystal, and \(\rho_{vR}\) is the absolute humidity at the crystal surface.

• The only thing really different from (1) compared to the similar equation we used for the diffusional growth of water droplets is the inclusion of the shape factor, \(C\).
  – The shape factor depends on the shape (habit) of the crystal.
  – The approximate shape factors for various habits are shown in Table 1.

<table>
<thead>
<tr>
<th>Shape</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>(2R/\pi)</td>
</tr>
<tr>
<td>Prolate spheroid (used for ice needles)</td>
<td>(\frac{\sqrt{a^2 + b^2}}{\ln (a + \sqrt{a^2 + b^2}/b)})</td>
</tr>
<tr>
<td>Oblate Spheroid</td>
<td>(\frac{a\sqrt{1-b^2}}{\arcsin \sqrt{1-b^2/a}})</td>
</tr>
</tbody>
</table>

Table 1: Shape factors for various crystal habits. The factors \(a\) and \(b\) refer to the semi-major and semi-minor axes. For the plate, \(R\) refers to the nominal radius of the equivalent disk.

• As with water droplets, an equation for the balance of latent heat of sublimation added to the crystal, and that diffused away from the crystal, must also be used when discussing diffusional growth. This equation is
\[
\rho_{v_b} - \rho_{vR} T_R - T_b = KL_s D,
\]
where \(L_s\) is the latent heat of sublimation.

• A form of the Clausius-Clapyron equation is used to determine the saturation absolute humidity over ice at the surface of the crystal.

• Equations (1) and (2), along with the Clausius-Clapeyron equation are a system of three equations in three unknowns \((m, \rho_{vR},\) and \(T_R)\), and can therefore be solved for the mass growth rate, \(dm/dt\).

• As with the growth rate equation for liquid droplets from Lesson 6, the growth rate equation for ice crystals does not have an analytic solution, and must be solved numerically. A simplified growth rate equation is
\[
\frac{dm}{dt} = \frac{4\pi C(S_i - 1)}{F_k + F_d},
\]

4
where

\[ F_k = \left( \frac{L_a}{R_v T} - 1 \right) \frac{L_v}{K T} \quad (4) \]
\[ F_d = \frac{R_v T}{e_i D}. \quad (5) \]

- In (3) thru (5) it is the latent heat of sublimation that must be used. The subscript \( i \) indicates that we need the saturation ratio and saturation vapor pressure over ice, and not liquid water.

- The growth rate of an ice crystal is highly dependent on temperature. Figure 1 shows a plot of normalized growth rate versus temperature.\(^1\)
  - The growth rate of ice crystals increases until about \(-15^\circ C\), and then decreases as temperatures continue to get colder.
  - Although the supersaturation ratio continues to increase at colder temperatures, there is very little actual water vapor in the air at these very cold temperatures. This is why the crystal growth rate slows down at very cold temperatures.

- Equation (3) is only an approximation, and may over-predict or under-predict the growth rate. This is because it does not include:
  - **Ventilation:** The air immediately surrounding the crystal is replaced as the crystal falls, whereas the derivation of (3) assumes the crystal is in equilibrium with the surrounding air, and that the vapor field is axisymmetric.
  - **Kinetic effects:** In order to join the ice crystals lattice structure a water vapor molecule must join in a particular orientation. Just because a water vapor molecule contacts the crystal does not mean it will adhere and add mass to the crystal.

- Equation (3) likely over-predicts growth for small crystals, and it more accurate for larger crystals.

### Branching versus Faceting

- Ice crystals grow through the competing processes of **branching** and **faceting**.

  **Faceting:** In low humidity environments (not much supersaturation) the water vapor diffuses fairly uniformly onto the crystal and builds up the facets or faces. Such crystals will be hexagonal plates or columns.

  **Branching:** Branching occurs in environments with a high supersaturation ratio. In these environments the water vapor diffuses preferentially toward the vertexes of the crystal. This forms arms and tendrils.

\(^1\)The normalized growth rate is simply the growth rate divided by the maximum growth rate.
Figure 4: Normalized growth rate from (3) versus temperature, for 100% relative humidity. The symbol $\dot{m}$ is shorthand for $dm/dt$. Maximum growth rate occurs near $-15^\circ C$.

Aggregation and Accretion

- In supercooled clouds the ice crystals grow at the expense of the liquid water droplets. This is known as the cold-cloud or Bergeron process.

- Diffusional growth of ice crystals is faster than diffusional growth of water droplets.

- Unlike diffusional growth of water droplets, diffusional growth of ice crystals can explain how very small precipitation consisting of single crystals (the frozen equivalent of drizzle) can form.

- In order to get larger precipitation such as snow flakes or graupel, additional processes such as aggregation or accretion are still required.

**Aggregation:** This is the frozen equivalent of collision-coalescence. Larger crystals fall and overtake smaller crystal, which then stick to the larger crystal. This can be described by an equation similar to that which we derived for collision-coalescence, and is

$$\frac{dm}{dt} = EM_{ice}\pi R^2(u_L - u_s),$$  \(6\)
where \( u_L \) is the fall speed of the large crystal, and \( u_s \) is the fall speed of the small crystal, \( R \) is the effective radius of the larger crystal, and \( \bar{E} \) is the average collection efficiency. The term \( M_{\text{ice}} \) is the mass of ice contained in the small crystals.

**Accretion:** Accretion describes the collection of supercooled liquid droplets by a falling ice crystal. The supercooled liquid droplets freeze on contact with the crystal. This is how graupel and hail are formed. The equation for growth by accretion is also very similar to that for collision-coalescence and aggregation, and for completeness is written here,

\[
\frac{dm}{dt} = \bar{E} M_{\text{liq}} \pi R^2 u(R),
\]

where we ignore the fall speed of the smaller droplets.

**Collision-coalescence versus Bergeron**

- In warm clouds (those whose tops are not appreciably colder than freezing), the collision-coalescence process is the only process that can explain the initiation and growth of precipitation.

- In cold clouds, either or both processes may be at work to explain initiation of precipitation.

- The relative importance of either process depends on the type of cloud. The Bergeron process is likely more important in stratiform clouds, whereas collision-coalescence is more important in convective clouds.

- In stratiform clouds, ice crystals from the very cold upper levels fall into the cold lower levels where they grow rapidly. As they fall further, they continue to grow by accretion and aggregation. So, the precipitation is initiated in the upper levels, but grows in the lower levels.