Heterogeneous Nucleation of Ice

Suspect presence of foreign particle may aid nucleation of ice by allowing ice to form at higher temperatures compared to homogeneous nucleation of freezing – and at lower humidities compared to formation of ice by homogeneous nucleation from the vapor.

Nucleation on a **planar** substrate

From force balance, \[ \sigma_{SV} \cos \varphi + \sigma_{CS} = \sigma_{CV} \]

\[ m = \cos \varphi = \frac{\sigma_{CV} - \sigma_{CS}}{\sigma_{SV}} \]

If \( \sigma_{cs} \) large; contact angle is large

large curvature
Reminder of modes of ice nucleation

Figure 7.27 Depiction of the various modes by which ice nuclei act. Ice nuclei (IN) are shown as solid triangles, and shading represents ice. The black dots in the condensation-freezing mode represent solute, which lowers the melting point.
Both ice and substrate have lattice structure so must examine microscopic properties of the nucleation process.

- **Dislocation** occurs if ice retains its lattice structure right down to the surface of the substrate, or:
  - Ice lattice will deform elastically to coherently join the lattice of the substrate—this results in a strain in the ice lattice.
  - Dislocations normally occur when substrate has a considerably different lattice structure than ice.
  - “Similar” substrates cause a strain in the ice.

<table>
<thead>
<tr>
<th>Dislocation</th>
<th>increases $\sigma_{CS}$</th>
<th>increases contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain</td>
<td>raises $\mu_S$</td>
<td></td>
</tr>
</tbody>
</table>

What is the best nucleating substrate? ("preactivation")
In general a combination of strain and dislocation will exist.

So $\mu_s$ increased due to strain and $\sigma_{cs}$ increased due to dislocations.
Figure 7.28 Schematic of critical ice embryos, showing the effect of the parent phase (vapor or liquid). Based on arguments of Cooper (1974).

Which has the lower barrier to formation of a critical cluster?
Now write $\Delta E$ for nucleation on a substrate, including effects of strain

old term $-n_s kT \ln(p/p_s)$

new term $-n_s kT \ln(p/p_s) + C \varepsilon$  \hspace{1cm} \text{strain term}

$C \varepsilon^2$ represents the increase in $\mu_s$ accounting for strain, resulting from mismatched lattice structures. When the strain term is multiplied by the embryo volume, the contribution to bulk thermodynamic energy is realized.

\[
\therefore \Delta E = V_i \left(-n_s kT \ln(p/p_s) + C \varepsilon^2\right) + \sigma_{SV} A_{SV} + (\sigma_{CS} - \sigma_{CV}) A_{CS}
\]

strain acts to increase bulk term

\hspace{1cm} \text{dislocation increases } \sigma_{cs}
Nucleation on curved substrate

\[ \Delta E^* = \frac{16\pi \sigma_{SV}^3 f(m)}{3[-n_s kT \ln(p/p_s) + C \varepsilon^2]^2} \]

\[ f(m) = \frac{(2 + m)(1 - m)^2}{4} \]

\[ m = \cos \varphi \]

As before, factor accounting for contact angle

So including effects of strain and dislocation, a larger supersaturation with respect to ice is required compared to case where strain and dislocation is not a factor. (Larger energy barrier)

Nucleation on curved substrate

\[ \Delta E^* = \frac{16\pi \sigma_{SV}^3 f(m, x)}{3[-n_s kT \ln(p/p_s) + C \varepsilon^2]^2} \]

\[ x = \frac{r}{r^*} \quad r = \text{radius of curved substrate} \]

As before, factor accounting for contact angle AND size of substrate

\[ f(m, x) \rightarrow 1 \quad \text{for} \quad r_h \rightarrow 0 \quad \text{Homogeneous case} \]

\[ f(m, x) \rightarrow f(m) \quad \text{for} \quad r_h \rightarrow \infty \quad \text{Flat surface} \]
Particles smaller than 0.01 µm radius are probably not effective deposition nuclei.

Dislocation effect seen through \( \varphi \) dependence

Deposition onto ice nucleus at water saturation

Size \( r \) not very important for \( r > 0.1 \mu m \). Particles with largest \( m \) (smallest contact angle) serve as nucleating surface at highest temperatures. As dislocation increases (\( r \) staying constant), \( m \) decreases and nucleation occurs at lower temperatures. Increasing dislocation; increasing \( \varphi \). In general, \( m \) has very large effect on nucleation efficiency of the substrate. When strain is included, \( (C \varepsilon^2) \) the temperature at which nucleation occurs is lowered considerably: \( \Delta T \sim 10^\circ C \) is expected.
IMMERSION FREEZING

We can rely upon previous discussions for nucleation of water on a spherical, insoluble nucleus, and incorporate the effects of lattice strain:

$$\Delta E = f(m, x) \left\{ \frac{4}{3} \pi r^3 \left[ n_s kT \ln \left( \frac{p_L}{p_s} \right) + C \varepsilon^2 \right] + 4\pi r^2 \sigma_{SL} \right\}$$

-Spherical geometry assumed
- Surface properties of nucleus defines $x = \frac{r_n}{r}$
- Radius of nucleus $r_n$ defines $m = \cos \varphi$
Radius of curvature for the critical-sized embryo is found by taking \( \frac{\partial \Delta E}{\partial r} = 0 \)

\[
r^* = \frac{\frac{2\sigma_{LS}}{n_s kT \ln \left( \frac{P_L}{P_S} \right) - C\varepsilon^2}}{2}
\]

Nucleation rate

\[
J_{SL} \approx 2 \times 10^{24} r_n^2 \exp \left( -\frac{\Delta E^*}{kT} \right)
\]

Where \( J_{SL} \) is the number of critically-sized embryos nucleated per unit time per unit area of the nucleus.

Result shown by fig. 4.7 from Young (1993).
For immersion freezing, since $\sigma_{LS}$ (~23 dynes/cm$^2$) is about 4-6 times smaller than $\sigma_{VS}$ (85-122 dynes/cm$^2$), the barrier to nucleation ($\sigma_{xy} \cdot \text{area}$) is considerably lower for immersion freezing compared to deposition (as shown in the schematic on slide 5). As a consequence, a wider variability of substances will serve as freezing nuclei compared to deposition nuclei.
Active sites and the “soccer ball” model

Nucleation sites can be distributed spatially and also have different contact angles.

Fig. 2. Surface of each particle is divided into a number $n_{\text{site}}$ of surface sites. For model calculations $n_{\text{site}} = 1, 10, 100$ is used. Each surface site is associated with a certain energy barrier, represented through contact angle $\theta$. Contact angles are drawn from distribution function $P(\theta)$ (error function) that holds for the ensemble of particles. The contact angle distribution is discretized in 1800 bins between 0 and $\pi$ and through uniformly distributed random numbers $\eta \in [0,1]$ each site is associated with a specific contact angle, shown in the right figure through $\theta_f$.

Niedermeier et al., 2011
In **condensation** freezing, a liquid layer forms by condensation and immediately freezes, as ice embryo becomes supercritical (grows to allow decrease in $\Delta E$). Nuclei for condensation-freezing consists of mixed nuclei, containing soluble and insoluble materials. This process differs from **immersion** freezing in that the ice phase forms rapidly at the temperature at which the condensation process occurs. For immersion freezing, the droplet may freeze when immersed freezing nucleus activates (i.e., after sufficient supercooling occurs).
Contact-freezing (low numbers of IN; takes time)

\[-dN/dt = (K_B(r_p,r_C)+K_T(r_p,r_c))N_pN_C\]

For Brownian and turbulent collection only. Phoretic effects can also be important.

V (Vali): electrostatic precipitation collection
C (Cooper): Drops settled onto particles
D (Deshler): Brownian diffusion collection
Y (Young): wind tunnel (assumed size 1 μm)
Contact freezing: may happen outside-in or inside-out

- Implies that processes (e.g., evaporation) that bring internal particles in contact with the outer drop surface may trigger more ready freezing.

- It is unclear if this process enables a new population of IN in addition to those that act as immersion freezing nuclei.
Stochastic vs. singular models

The **stochastic** hypothesis states that the ability to nucleate ice (its “activity”) per surface area is the same for all IN, either because all IN have identical surface properties or because each aqueous droplet contains a sufficiently large number of IN so that differences in their quality even out. Under these conditions, the nucleation probability can be formulated analogously to the homogeneous case.

In contrast, the **singular** hypothesis assumes that the activity of IN varies and that their total number within water droplets is insufficient to ensure statistical homogeneity among the droplets. According to this hypothesis, the freezing temperature of a droplet is determined by that particle in the droplet whose activity is highest.

To reproduce cloud formation and precipitation, numerical models need to parameterize heterogeneous ice nucleation taking into account the relevant nucleation modes and ice nuclei. **Most models use empirical relations based on the singular hypothesis** to parameterize the IN number concentration as functions of temperature and/or ice saturation.

*Marcolli et al., 2007*
Immersion freezing nucleation: “Singular” nuclei characteristics dominate over stochastic ones

Vali (2008) – lack of dependence of drop freezing on cooling rate for suspended soils in drops means

Fig. 10. Examples of freezing temperatures observed when the rate of cooling was alternated between two values.

Marcolli et al. (2007) freezing of test dust emulsions (reproduced under Creative Commons license of Atmos. Chem. Phys.)
Deactivation was thought to be important in urban and industrial areas where high concentrations of SO₂, NH₃, and NOₓ exist, in addition to high concentrations of Aitken particles. The idea is that surface properties of aerosol are changed due to "coating" (active sites are poisoned or otherwise deactivated).

"Deactivation time"

Deactivation was thought to be important in urban and industrial areas where high concentrations of SO₂, NH₃, and NOₓ exist, in addition to high concentrations of Aitken particles. The idea is that surface properties of aerosol are changed due to "coating" (active sites are poisoned or otherwise deactivated).

Very recent laboratory studies are challenging this concept since not all coatings impede immersion freezing in dilute cloud droplets.
Summary: REQUIREMENTS for “good” IN

• **insoluble**: especially important for freezing and contact nuclei

• **size requirements**: generally larger particles are most effective IN

• **chemical bond requirement**: the particle substrate must have hydrogen bonds available at surface to provide maximum bonding for oncoming water molecules

• **crystallographic requirement**: the geometric structure of molecules in the nucleating substrate must be similar to ice (hexagonal)

• **active site requirement**: surface must have cracks and cleavages which provide good nucleation sites.

Next Questions:

• how many are there?

• What are they exactly??
VARIATION OF IN CONCENTRATIONS WITH TEMPERATURE AND LOCATION.

TYPICALLY, 1 NUCLEI PER LITER ACTIVE AT -20°C.

NO NOTICEABLE VARIATION IN IN CONCENTRATIONS WITH GEOGRAPHICAL LOCATION OR LATITUDE.

FOR TYPICAL CONTINENTAL AIRMASS, 1 IN 10⁶ AEROSOLS SERVE AS ICE NUCLEI

< ICE NUCLEATION PROCESS VERY SELECTIVE!>
More recent data: CSU continuous flow diffusion chamber, many projects, 10 years

![Graph showing ice nuclei concentration versus temperature]
IN dependence on aerosol concentrations reconciles variability in temperature dependence

Berezinski et al. (1986), extrapolated -32°C
Georgii and Kleinjung (1967), -21°C, > 0.6 mm

Small particles aren’t strongly related to [IN]

PACDEX project

$\ln_{IN} @ -32^\circ C$ (std L$^{-1}$)

$\ln_{aer} (scm^{-3})$
Ice formation above -35 °C

Known “ice nuclei”:

• AgI: used in cloud seeding
  – has a crystalline structure similar to ice and a very low solubility in water

• Bacteria: used in snowmaking (Snomax™)

• Dusts: depending on crystallography, T, active sites
Transmission electron microscopy of residuals suggest that IN are ‘large’ carbonaceous particles and dust.

<table>
<thead>
<tr>
<th>Carbonaceous (20-80%)</th>
<th>Metal oxides (20-80%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image of carbonaceous particles" /></td>
<td><img src="image2.png" alt="Image of metal oxides" /></td>
</tr>
</tbody>
</table>

**Carbon**
But what is it?
Bacteria? SOA? Combustion?

**Aluminum**
*Silicon*  
*Calcium*  
*Oxygen*
Carbonaceous residuals have similar morphology to bacterial ice nuclei sampled in the laboratory.

TEM images of carbonaceous IN Amazon field study
TEM of ice nuclei collected in the Pacific Dust Experiment (PacDex), 2007
PARTICLES FORMING ICE AT $T > -35 \, ^\circ C$

For $T < -8 \, ^\circ C$, Snomax readily forms ice below 100% RH

Canary Island dust: only active as warm as $-30 \, ^\circ C$
Some fuels seem to preferentially produce ice nuclei but not all the time.

Duff (3/4)
Oak (2/3)
Fir (9/11)
Chamise (3/7)
Sage (5/7)
Ceanothus (1/2)
Ponderosa Pine (11/16)
Longleaf Pine (4/5)
Wax Myrtle (0/2)
Titi (0/2)
Needlegrass Rush (0/2)
Rice Straw (0/2)
Palmetto (0/4)
Manzanita (0/2)
Hickory (0/3)
Charcoal (0/3)
Common Reed (0/1)
Kudzu (0/2)
Gallberry (0/4)

Detection Limit

Free troposphere (Amazon, ICE-L)

80% no ice nucleation signal above detection limit
FIELD OBSERVATIONS: AMAZONIA

The data at this location could be modeled by a combination of biological particles + Saharan dust transported to Amazonia.
**SUMMARY: PARTICLES INVOLVED IN ATMOSPHERIC ICE FORMATION**

\[ T < -35 \, ^\circ C \]

- All hygroscopic particles – even with small \( \kappa \) – appear to follow the predictions of Koop et al. [2000]
- Some dusts are active at small ice supersaturations of \(~10\%\) (RH \(~70\%\)) in this regime – may influence subsequent homogeneous freezing

\[ T = -35 \, ^\circ C \]

- Have often detected metallic particles, minerals, and carbonaceous particles as immersion IN
- Some smokes
  - Carbonaceous = biological?
- Bacteria are active deposition freezing nuclei
- Some dusts are active at colder end of T range

\[ T > -35 \, ^\circ C \]

- DROPS
  - \( RH_w = 100\% \)

HAZE or DRY PARTICLES

AAAR 2008 Plenary
extras
Aside: Why is $\sigma_{cs}$ increased due to dislocations?

$\text{H}_2\text{O}$ – polar molecule

Interfacial energy $\sigma_{cs}$ is minimized when $\text{H}^+ - \text{O}^-$ dipole aligns with the local $\vec{E}$ field at the surface of the substrate.

$\vec{E}_{local}$ arises due to ionic nature of nucleating material

$\vec{E}$ and $\vec{E}_{local}$ misalignment results in electrical ‘torque’
More on the strain \( C \epsilon^2 \) \( C \) estimated to be \( 1.7 \times 10^{11} \) dynes cm\(^{-2} \) at \( T=0^\circ C \)

Elastic strain \( \hat{\epsilon} \) estimated by, \( \delta = (a_n - a) / a \)

where “a” refers to the length of ice lattice cell.

\( a_n \) represents lattice cell in substrate.

Ice prefers to nucleate with basal face in contact with substrate—so this geometry is appropriate.

• If misfit is small, the number of dislocations is assumed to be small and \( \epsilon = \delta \) (Coherent Nucleation)

• If the misfit is large, it is assumed that the ice lattice does not attempt to accommodate itself to the substrate and \( \epsilon \) is taken to be zero. But \( \sigma_{CS} \) is large! (Incoherent Nucleation)
Summary of ice nucleation regimes

- Condensation/immersion freezing
- Contact-freezing
- Deposition nucleation
- Homogeneous freezing

Ice supersaturation ($S_{\text{ice}} - 1$)

Supercooling (°C)

Slide courtesy Paul DeMott