A 30-minute flight segment and a 3-day lab experiment asking questions about ice formation in the atmosphere, and about the stochastic versus singular character of heterogeneous ice nucleation.

Gabor Vali
Talk given at the ICIS-07 Third International Workshop on Ice Nucleation
Karlsruhe, September 26, 2007
Zones of ice and liquid clouds by temperature.
Frequency distributions of ice mass observed at different temperatures.

Source: Field et al., 2005
(Quart. J. Roy. Meteor. Soc.)
Ice particle concentrations from aircraft measurements (2D-C probe) in various projects

Source: Gultepe et al., 2001 (Int'l J. Climat.)
cloud radar

in situ probes

University of Wyoming King Air aircraft
wyice97 feb19+1 00:21:37 - 00:23:48
downwind leg starting at 5950 m altitude
<table>
<thead>
<tr>
<th>Cloud</th>
<th>Time</th>
<th>Echo top</th>
<th>Penetration altitude</th>
<th>Est. min. temperature (°C)</th>
<th>LWC (g m(^{-3}))</th>
<th>2D ice conc. (L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>00:21</td>
<td>6400 m</td>
<td>5800 m</td>
<td>−26</td>
<td>~ 0.05</td>
<td>50</td>
</tr>
<tr>
<td>A</td>
<td>00:27</td>
<td>(horizontal beam)</td>
<td>5930 m</td>
<td>−26</td>
<td>~ 0.05</td>
<td>35</td>
</tr>
<tr>
<td>A</td>
<td>00:32</td>
<td>6200 m</td>
<td>6060 m</td>
<td>−25</td>
<td>0.10</td>
<td>5</td>
</tr>
<tr>
<td>A</td>
<td>00:34</td>
<td>6200 m</td>
<td>6060 m</td>
<td>−25</td>
<td>0.12</td>
<td>2</td>
</tr>
</tbody>
</table>

Change in composition accompany the lowering of the height of cloud top.
- shorter growth time, hence poorer detection
- real change in aerosol (ice nucleus) content
B and D

wyice97 feb19+1, 00:42:35 - 00:44:25
eastbound leg at 5230 m altitude
<table>
<thead>
<tr>
<th>Cloud</th>
<th>Time</th>
<th>Echo top</th>
<th>Penetration altitude</th>
<th>Est. min. temperature (°C)</th>
<th>LWC (g m⁻³)</th>
<th>2D ice conc. (L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>00:21</td>
<td>6400 m</td>
<td>5800 m</td>
<td>−26</td>
<td>~ 0.05</td>
<td>50</td>
</tr>
<tr>
<td>A</td>
<td>00:27</td>
<td>(horizontal beam)</td>
<td>5930 m</td>
<td>−26</td>
<td>~ 0.05</td>
<td>35</td>
</tr>
<tr>
<td>A</td>
<td>00:32</td>
<td>6200 m</td>
<td>6060 m</td>
<td>−25</td>
<td>0.10</td>
<td>5</td>
</tr>
<tr>
<td>A</td>
<td>00:34</td>
<td>6200 m</td>
<td>6060 m</td>
<td>−25</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>B</td>
<td>00:37</td>
<td>6900 m</td>
<td>6120 m</td>
<td>−28</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>D</td>
<td>00:39</td>
<td>6400 m</td>
<td>6120 m</td>
<td>−26</td>
<td>0.12</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>00:42</td>
<td>6400 m</td>
<td>5200</td>
<td>−16</td>
<td>(6) in evap. trail</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>00:44</td>
<td>5700 m (conv.)</td>
<td>5230</td>
<td>−21</td>
<td>0.4</td>
<td>2</td>
</tr>
</tbody>
</table>

Rough indication of temperature trend, as expected.

Given the complexities of clouds and the limitation of measurement techniques, cloud structure need to be considered, and data scrutiny is essential.
One Cb over the Asir Mountains, Saudi Arabia
Summary of ice concentrations by cloud types - Duero Basin, Spain
Cooper, 1986

for cases where ice concentration can be attributed to nucleation
Size distribution of germs: \[ N(n) = N_0 e^{-\Delta G(n)/kT} \]

Nucleation rate: \[ J = A e^{-\Delta G^*/kT} \] \([L^{-3} T^{-1}]\)

Deposition: \[ J = A \exp \left[-B \frac{\sigma^3}{T^3} \frac{1}{(\ln S)^2}\right] \]

Freezing: \[ J = A_f \sigma_{i/w}^{1/2} \exp \left[-B_f \frac{\sigma_{i/w}^3}{kT} \frac{1}{\ln(T_0/T)^2}\right] \] Jominy and Austin (1987)
How to determine $J$ experimentally??

Approach A: Bring to $S$ or $T$ a large number of identical volumes with the same probability of containing an identical nucleus.

Approach B: Repeated exposure of the same sample to the same $S$ or $T$, assuming that the nucleus remains unaltered.

Both approaches have to accept that $S$ or $T$ has to be reached at some finite rate from the stable state of the parent substance, i.e. $S=0$ or $T=0$
Koop 2004 (Z. Phys. Chem):

Differential scanning calorimetry of emulsion of water in oil

Fig. 14. The homogeneous volume nucleation rate coefficient of ice in water, $J(T)$, as a function of temperature (black line [95]). The data points indicate the median freezing temperatures of water droplets for various conditions; squares: for droplets of different size at a cooling rate of $1\, \text{K min}^{-1}$, circles: for different cooling rates and a droplet with a radius of $1\, \mu\text{m}$. 
Benz et al. 2005 (J. Photochem. Photobiol.)

Cloud chamber observation of rate of ice formation

Fig. 8. Filled symbols: nucleation rates $J(T)$, this work, including corrections for all known systematic uncertainties, error bars shown for one experiment only. Thick solid line: parameterisation of the nucleation rate by Pruppacher [10] and adopted by Koop et al. [35] in their parameterisation of $J(T,a)$, as explained in text; thin solid line: parameterisation proposed by Jeffery and Austin [13]; dash-dotted line: parameterisation based on measurements in clouds by Heymsfield and Miloshevich (H & M) [26]; large open circles: cloud chamber study by DeMott and Rogers [19]; dashed line with error range (thin dashed lines): levitated droplet measurements by Stöckel et al. [36]; open star: levitated droplet measurement by Duft and Leisner [18]. Short dashed line in lower left corner: emulsified droplet measurements of Taborek [37].
Repeated freezing of a single drop with long chain alcohol monolayer during cycles of steady cooling.

Rate = number freezing within interval / number not frozen at that temperature

**FIG. 1.** The nucleation temperature as a function of iteration number for a 10 μL water sample containing $2.5 \times 10^{-10}$ mol of (○) pentacosanol (C$_{25}$H$_{52}$O), (●) hexacosanol (C$_{26}$H$_{54}$O), (□) heptacosanol (C$_{27}$H$_{56}$O), and (■) octacosanol (C$_{28}$H$_{58}$O).

**FIG. 2.** The freezing rate as a function of temperature for a 10 μL water sample containing $2.5 \times 10^{-10}$ mol of (○) pentacosanol (C$_{25}$H$_{52}$O), (●) hexacosanol (C$_{26}$H$_{54}$O), (□) heptacosanol (C$_{27}$H$_{56}$O), and (■) octacosanol (C$_{28}$H$_{58}$O). As described in the text the solid lines represent the best-fit curves of Eq. (5) to the experimental data.
**Figure 1.** Measured freezing points for seven droplets exposed to cooling/heating cycles with 10 K min$^{-1}$ as a function of iteration number. Six droplets are coated with 1-nonadecanol, one remained uncoated. Coated droplets: (circles and squares) $r = 1100 \, \mu m$; (diamonds and downward-pointed triangles) $r = 370$ and 320 $\mu m$, respectively; and (stars and right-pointed triangles) $r = 31$ and 48 $\mu m$, respectively. Uncoated droplet: (crosses) $r = 1100 \, \mu m$.

**Figure 3.** Measured heterogeneous ice nucleation rate coefficients for six single water droplets coated with nonadecanol as a function of temperature. The symbols are the same as in Figure 1. The horizontal and vertical thin lines are the errors in temperature and the uncertainties due to the Poisson statistics on the 95% level, respectively. Additionally, an isothermal measurement of $j_{\text{het}}$ (left-pointed triangle) at 266.15 K is shown.$^{23}$ (Dashed line) Best fit of the CNT with a constant $\alpha$ of 52.4$^{\circ}$. (Solid line) Best fit of the CNT with $\alpha$ as a linear function of temperature (see Figure 4). (Dashed dotted line) Best fit with the approach of Seeley and Scidler.$^{8}$

**Figure 4.** (Circles) Calculated $\alpha$ values for water droplets coated with nonadecanol as a function of temperature (see Table 1). (Solid line) Linear fit of the circles: $\alpha(T) = 571.50 - 2.015T$, where $T$ is given in Kelvin. $\alpha$ is given in degree and the function is valid for 248 K $\leq T \leq 268$ K.
Gabor Vali
Karslruhe, September 2007

Frozen drops (filled circles) at -9 and -13°C in two consecutive runs
distilled water control drops in bottom row (gray circles)
aug22-24/67 experiment with soil suspension
Repeated freezing of drops with soil suspension - 110 drops, 57 cycles

Mean freezing temperature decreases 0.05°C per cycle.

Rank correlation between first and last run significant to 0.01%
Random variation with $\sigma = 0.28^\circ\text{C}$ accounts for 78% of observations. The remainder is roughly described by normal pdf with $= \sigma 1.8^\circ\text{C}$.
for normal distribution:
\[ \sigma(x_i - x_j) \approx 1.4 \times \sigma(x_i - \langle x \rangle) \]
The contribution of *stochastic* fluctuations in embryo growth to the determination of freezing temperatures is ± 0.2°C, on top of a temperature determined by the *singular* properties of the nucleus. This can be seen in terms of a nucleation rate $J$ rising sharply within that narrow temperature interval, with the characteristic temperature fixing the base temperature.

![Diagram](image)
**Positives:**
- alcohol monolayer, soil, silver iodide, *Ps. syr.* results are very similar
- by separating the effect of molecular fluctuations from alterations of the nuclei with time, the nucleation rate $J$ is found to be a steeper function of temperature than in previous work

**Unresolved:**
- better definition of the form of the rate function
- reconcile with dependence on cooling rate
- temperature dependence of the rate function
Consequences

• The rate function is not a unique property of the substance, but has to be formulated/adjusted specifically to every nucleus/site (singularity). As an approximation this may be an additive term to temperature.

• Fitting a rate function to observations from repeated freezing of single drops that assumes that the nucleus remains unaltered during the process can lead to erroneous results.