Glassy aerosols and their role in cloud formation

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Aerosol properties affect climate
The response of particles to changing RH and temperature is key

This is important for an aerosol’s:
• ability to scatter light
• role in cloud formation
Hygroscopic properties of a model system: Ammonium sulphate

Adapted from Tang and Munkelwitz, JGR, 1994
Ammonium sulphate: cirrus ice formation

Mohler et al., APC 2003
Atmospheric aerosol are not made of ammonium sulphate!

A ‘typical’ PALMS single particle mass spec of UT aerosol

Murphy et al., Science, 1998
What is the impact of ‘typical’ large molecules on aerosol properties?
Large molecules slow diffusion and increase viscosity

How viscous can liquid become?
Viscosity of some common ‘liquids’

- **Water**
- **Peanut butter**
- **A glass**
- **Bitumen (pitch)**
- **Honey**
The pitch drop experiment

- Set up in 1927
- Bitumen is a highly viscous liquid ($10^{11}$ cP).
- 8 drops so far and the next one is overdue
Demonstration of glass formation
An example of ultra-viscous or glassy aerosol particles: iodic acid (HIO$_3$)
Raman microscope coupled to a RH and temperature controlled cell
Using Raman microscopy to probe droplets

Deliquescence point from Kumar et al. ACP (2010)
HIO$_3$ behaves like a solid at low RH
On increasing RH – becomes liquid

0 % RH

20 % RH

25 % RH

25 % RH
Many secondary organic aerosol may be in amorphous solid state

Virtanen et al., Nature 2010
Cirrus clouds in the tropical tropopause layer
Clouds serve as a cold trap – dehydrating air entering the stratosphere.

15-18 km, 180-200 K

Subvisible cirrus

Troposphere

Stratosphere
Deceasing temperature
Increasing relative humidity

Ice particle
<-36°C

Supercooled solution droplet

Soluble particle, e.g. NaCl

solid particle, e.g. dust

Homogeneous

Heterogeneous

Textbook cirrus formation
Glass formation in citric acid solutions

![Graph showing glass formation in citric acid solutions with temperature (K) on the y-axis and composition (wt% Citric acid) on the x-axis. The graph includes data points and a trend line. A molecular structure of citric acid is also shown on the right.]
Glass formation in citric acid solutions

Glass formation in citric acid solutions

![Graph showing the relationship between temperature, composition, water activity, and relative humidity for glass formation in citric acid solutions. The graph illustrates the temperature range, composition range, and the effect of water activity and relative humidity on the glass formation process.]
Ice doesn’t crystallise in glassy solutions: diffraction patterns of citric acid droplets

Murray, ERL, 2008; Murray, ACP, 2008
What is the impact of glassy particles on TTL cirrus?

Murray, ACP, 2008: Glassy droplets take up water slowly.
Inhibition of Crystallisation Experiments
AIDA cloud simulation chamber, Karlsruhe, Germany
The AIDA chamber, Karlsruhe Institute of Technology
Expansion experiments with citric acid
• Above 212 K: classic liquid droplet behaviour
• Below 212 K: ice nucleates heterogeneously

Murray et al., Nature Geoscience, 3, 233-237, 2010
Heterogeneous nucleation is a general property of glassy solutions.

- **Raffinose/M5AS**
  - Temperature vs. (%RH)
  - Data points and lines indicating glass transition, ice nucleation onset, and experimental trajectory.

- **Levoglucosan**
  - Temperature vs. (%RH)
  - Similar data points and lines as Raffinose/M5AS.

- **Raffinose**
  - Temperature vs. (%RH)
  - Data points and lines indicating glass transition and ice nucleation onset.

- **HMMA**
  - Temperature vs. (%RH)
  - Data points and lines indicating glass transition and ice nucleation onset.
What affect do glassy aerosol particles have on tropical cirrus?

Advanced Particle Simulation Code (APSCm-1D)

Steven Dobbie (Leeds)
Bernd Kärcher (Oberpfaffenhofen)
Heterogeneous nucleation on glassy aerosol results in low number densities and high in-cloud RH

- Small number of ice crystals nucleate in het case.
- RH stays high in het case.
Similar results for a wide range of cooling rates

Murray et al., Nature Geoscience, 3, 233-237, 2010
Summary

• Atmospheric aerosol may exist in a glassy state at low RH or at low temperature.
• Glassy aerosol nucleate ice heterogeneously at low supersaturation – this strongly impacts cirrus cloud properties.