Figure 2.3: Some morphologies grown in lab

2.4.2 Structure of ice and morphology

For this course we just need to consider that, by far, the most common form of water ice in earth's atmosphere is hexagonal ice. This leads to a variety of different crystal morphologies that depend on temperature and supersaturation. The reasons we get these are not well understood, but are due to differences in latent heat release with temperature (and therefore heat flux from the surface of the crystals) and due to rarefaction in the vapour field at different points on the surface of the crystals.

2.4.3 Types of ice nucleation ice nuclei

The general requirement for an IN is that they be in-soluble, perhaps have a similar crystal structure to ice and be quite large so that they have a large surface area for nucleation of a new phase (ice) to occur on. Known ice nuclei are:

- Most mineral particles and desert dust are known to nucleate ice, in appreciable quantities, at temperatures of about -20°C (e.g. Connolly et al., 2009)
- Some (but not all) biological particles are known to nucleate ice at warm temperatures, just below 0°C, but it is difficult for them to be carried up from the ground into clouds.
- Black carbon is a relatively poor ice nucleus of low efficiency, but there can be quite a lot of it in the atmosphere and so even though the efficiency is low it can be a significant source of ice.
- Fluff! Yes washing machine fluff has been shown to nucleate ice, probably due to its biological content.

This is a generalisation, to cover all known ice nuclei is out of the scope of this course. Importantly the number of heterogeneous IN in the atmosphere is about 1×10^5 less that the number of CCN.

2.4.4   Ice nucleation modes

Homogeneous nucleation is the name given to the process where ice forms within a drop that contains no ice nuclei. This occurs due to statistical fluctuations in the bulk of the liquid and can be derived from statistical mechanics—but the derivation is outside of the scope of this course. However, the result is that we can define a nucleation rate, J ($m^{-3}s^{-1}$) which is the number of ice 'germs' (or nuclei) forming in the bulk of the supercooled liquid per unit volume every second. An ice germ is when water molecules arrange themselves statistically to have a structure similar to hexagonal ice. This depends on temperature because when it is warm the molecules have too much thermal energy to stay in the hexagonal structure for long enough and it becomes more favourable at colder temperatures if there are too few molecules in the cluster though they will tend to fall apart, an ice germ is the critical size above which addition of another molecule will result in crystalisation of ice in the drop. This can be parameterised as:

$$\log_{10}(J) = -237.4 - 14.75T_c - 0.307T_c^2 - 0.00287T_c^3 - 0.0000102T_c^4 \qquad (2.41)$$

which is valid for $-65 \leq T_c \leq -30$. Here, T_c is the temperature in degrees celcius. As this is a *stochastic process*, the *ice crystal formation rate* is then calculated using an equation similar to radioactive decay:

$$\frac{dN_{ice}}{dt} = N_{drops}V_{drop}J(T) \qquad (2.42)$$

Heterogeneous ice nucleation occurs when a nucleus acts as a catalyst reducing the temperature needed for ice formation. There are several different modes by which heterogeneous ice nucleation can occur (see Figure 2.4.4):

- Deposition nucleation occurs when water vapour is deposited directly onto a nucleus; it requires supersaturation with respect to ice and temperature below the melting point.
- Condensation-freezing occurs when drops form on ice nuclei and then the ice nucleus becomes active at some temperature.
- Contact nucleation occurs when an ice nucleus comes in contact with a drop at temperatures below the melting point of water.
- Immersion-freezing is pretty much the same as condensation-freezing! It is when particles are immersed in water (for example during a laboratory experiment) and the water is observed to freeze.

Note that contact nucleation is not very effective within growing clouds and recent data suggest that *condensation-freezing* is the dominant mode of ice nucleation in the atmosphere. Also note that the number of condensation freezing nuclei is often observed to depend strongly of temperature (e.g. $N_{IN} = \alpha \exp(\beta T_c)$; and the number of deposition nuclei is observed to depend strongly on ice supersaturation (e.g. $N_{IN} = A \exp(BS_i)$). We will not cover this in detail in this course though.
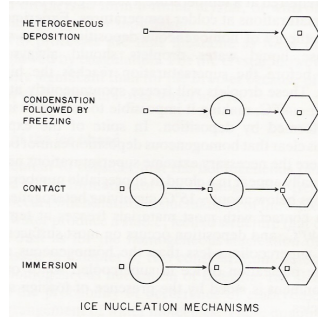
Figure 2.4: Heterogeneous nucleation is thought to occur only different pathways.

2.4.5   Ice-Active Surface-site Density concept

This concept is used to describe heterogeneous ice nucleation in the condensation-freezing / immersion freezing mode. It assumes that at any given temperature the heterogeneous ice nucleating particles contains a specific number of ice-active sites per unit area on their surface. This is quantified by a function referred to as $n_s(T)$.

The number of ice crystals nucleated, N_{ice}, by particles of of area, A_p, of number concentration, N_p,at a given temperature is thus given by:

$$N_{ice} = N_p \left(1 - \exp\left(n_s(T) A_p \right) \right) \tag{2.43}$$

where A_p is the surface area of the particles. This can by integrated over all particle sizes / number concentrations to get the total number of ice crystals.

Also note that, when the ratio $\frac{N_{ice}}{N_p}$ is small, we may apply the usual approximation $\exp x \cong 1 + x$ and assume:

$$n_s \cong \frac{N_{ice}}{N_p \times A_p} \tag{2.44}$$