Box 3 - Crystal growth

Crystallisation from saturated solutions or from melts shows that randomly distributed seeds generally form in a first experiment. They can grow further to give large size crystals (with luck or work !) suitable for physical studies.

Random nucleation occurs in a first step. It is thought to be related to the competing influence of the negative free energy of crystallisation ΔG_v and positive interfacial free energy γ, which prevents the growth of small and relatively unstable initial nuclei. The free energy of formation for a spherical particle is approximated by :

$$\Delta G_f = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

A critical radius r_c is defined ; particles with $r < r_c$ statistically disappear, and particles with $r > r_c$ grow :

$$\left(\frac{\partial \Delta G_f}{\partial r}\right)_{r=r_c} = 0 = 4\pi r_c^2 \Delta G_v + 8\pi r_c \gamma \qquad\qquad r_c = -2\frac{\gamma}{\Delta G_v} \Rightarrow \Delta G_f^c = \frac{16}{3}\pi\frac{\gamma^3}{(\Delta G_v^c)^2}$$

The nucleation rate is proportional to $K = \exp(-\frac{\Delta G_f^c}{RT})$. A small activation energy ΔG_f^c gives a large nucleation rate.

Crystal growth, in the second step, implies a flow of matter, together with heat and momentum transfer. Crystallisation is exothermic and heat must be evolved from the system. External forces (gravity, stirring, electric or magnetic field...) are or can be applied. Therefore, modelisation of crystal growth is complex and generally impossible without drastic approximations.