Kinetics of Phase Transitions

Last time

Heat capacity and calorimetry

Today

Kinetics of phase transitions

Next time

Glasses and metastable states

Kinetics of phase transitions

So far, we've considered the thermodynamics of phase changes.

But often, phase transitions are kinetically controlled.

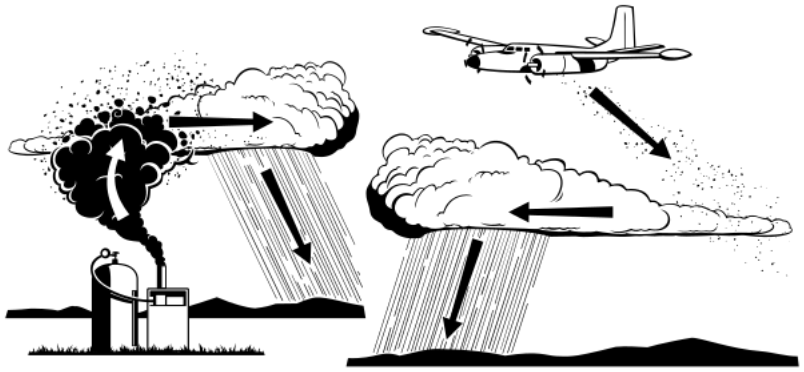
Mentimeter

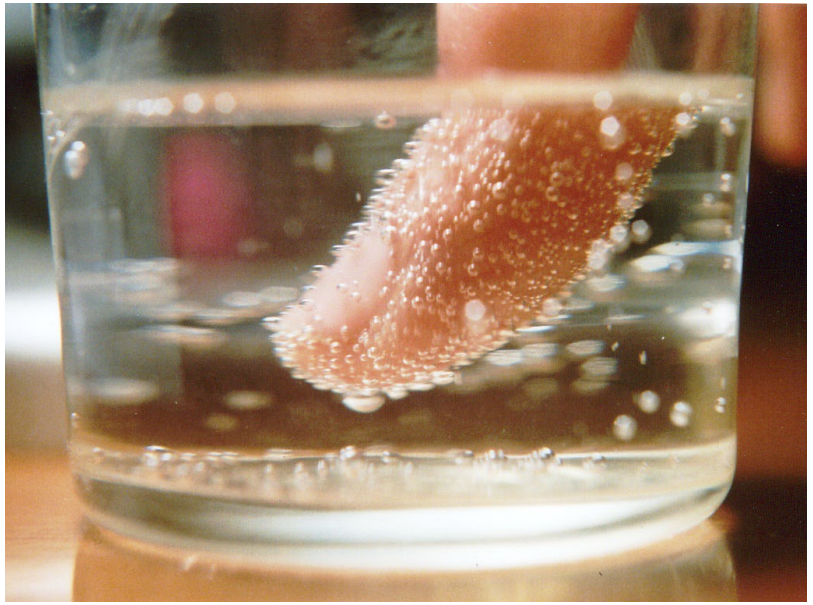
Nucleation and growth









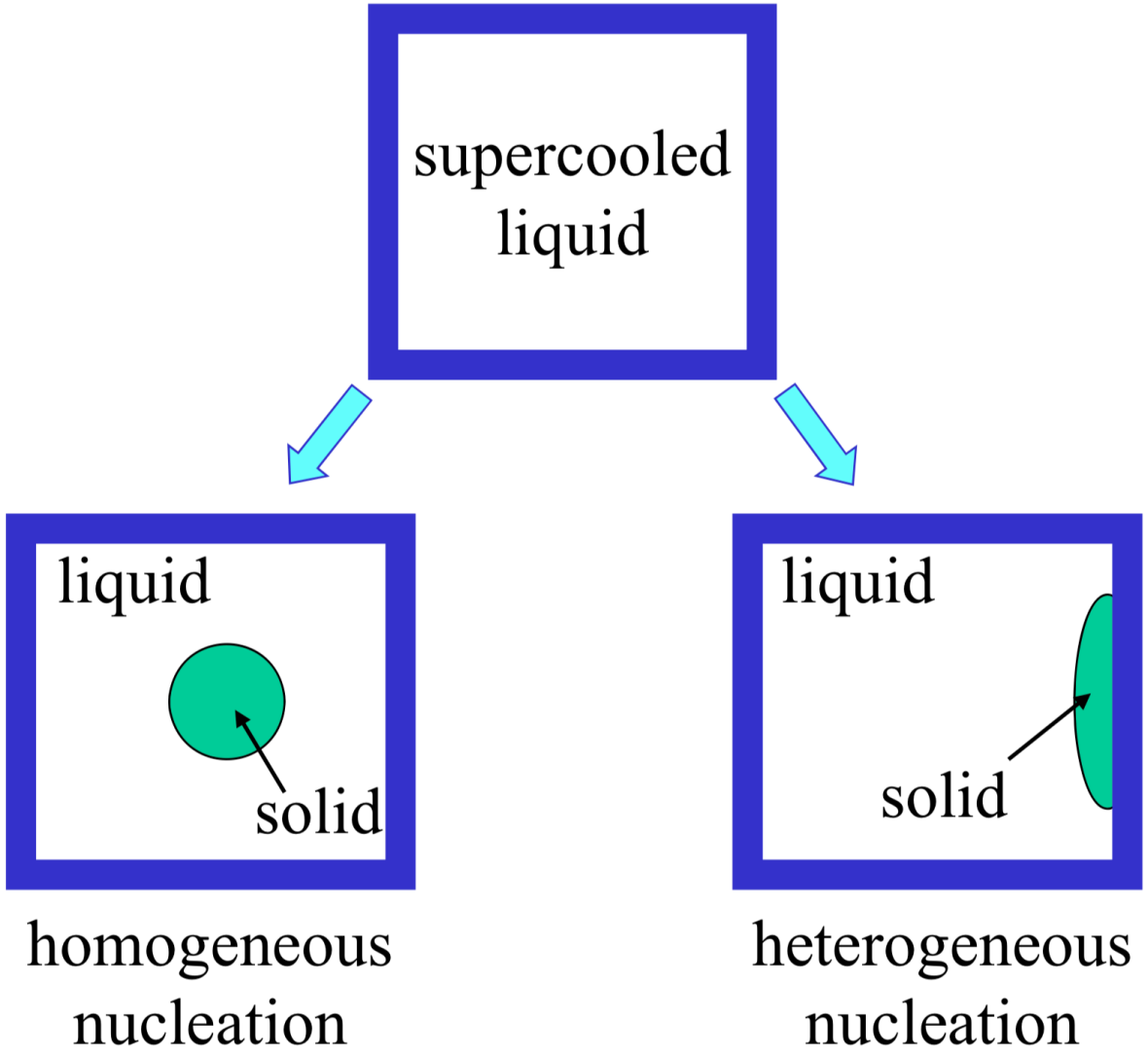


Nucleation and growth

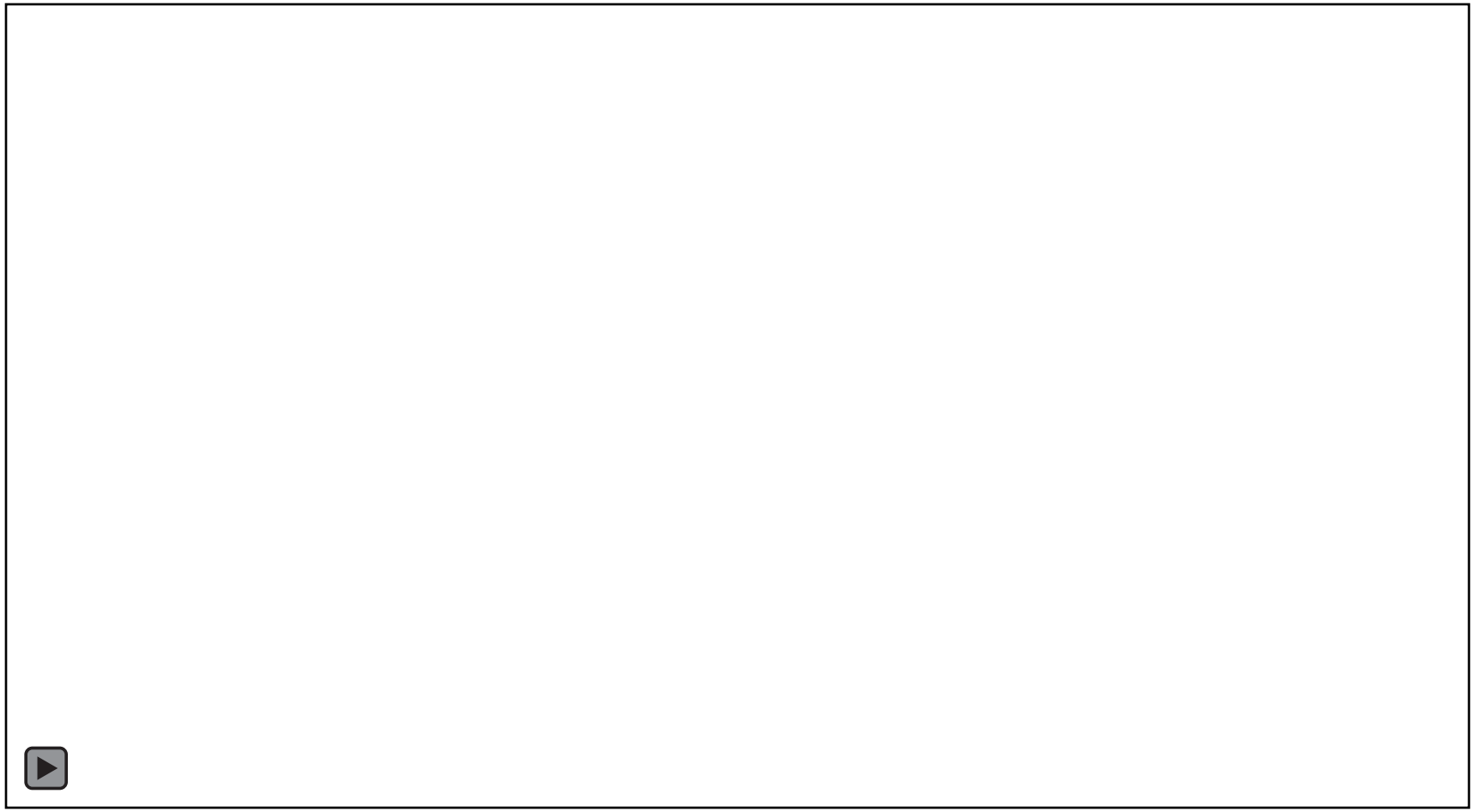
Nucleation and growth is the main mechanism of phase transformation in materials

Heterogeneous: new phase appears on walls of container, impurity particles, etc.

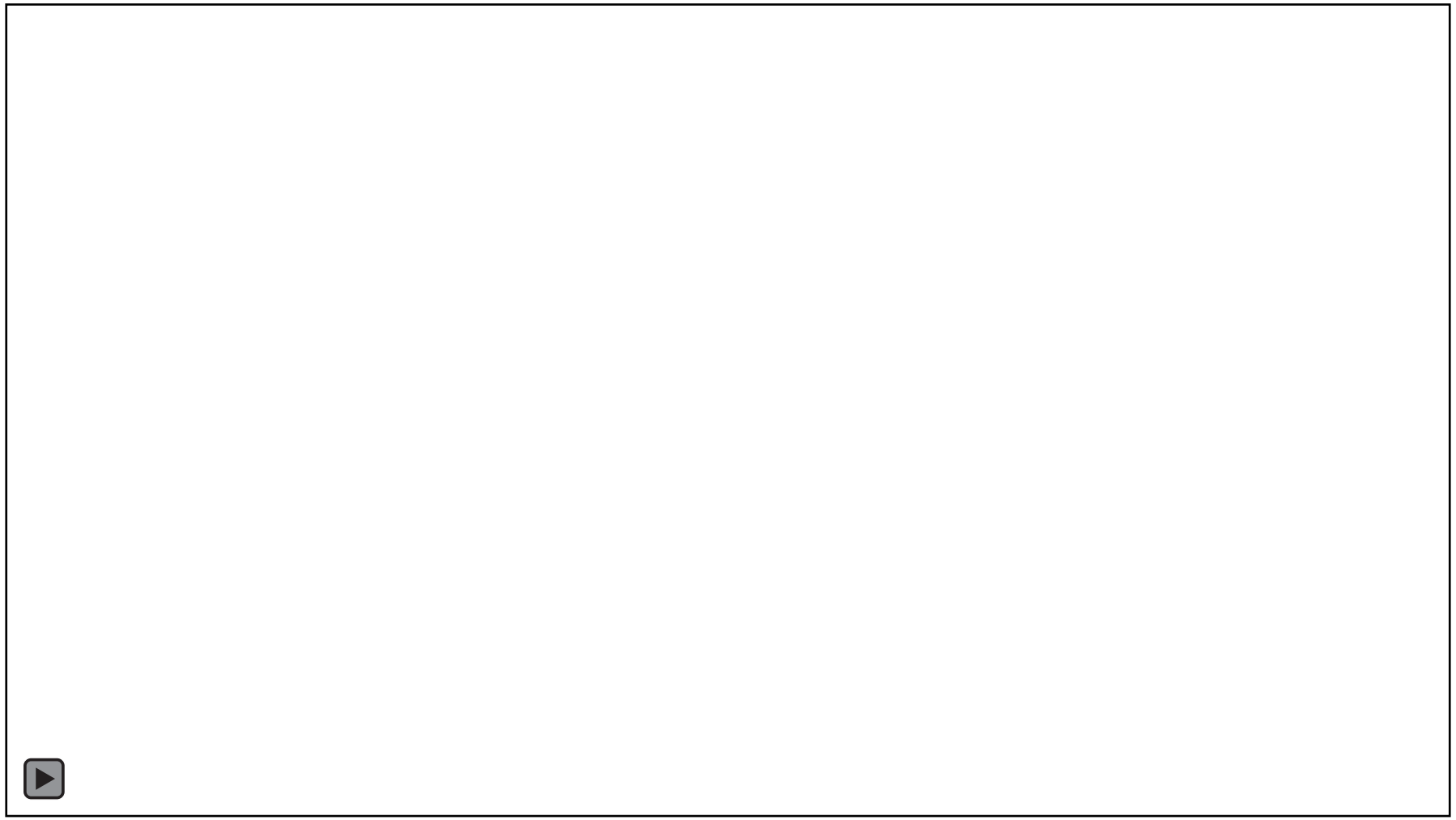
Homogeneous: solid nuclei appear spontaneously



Nucleation and growth

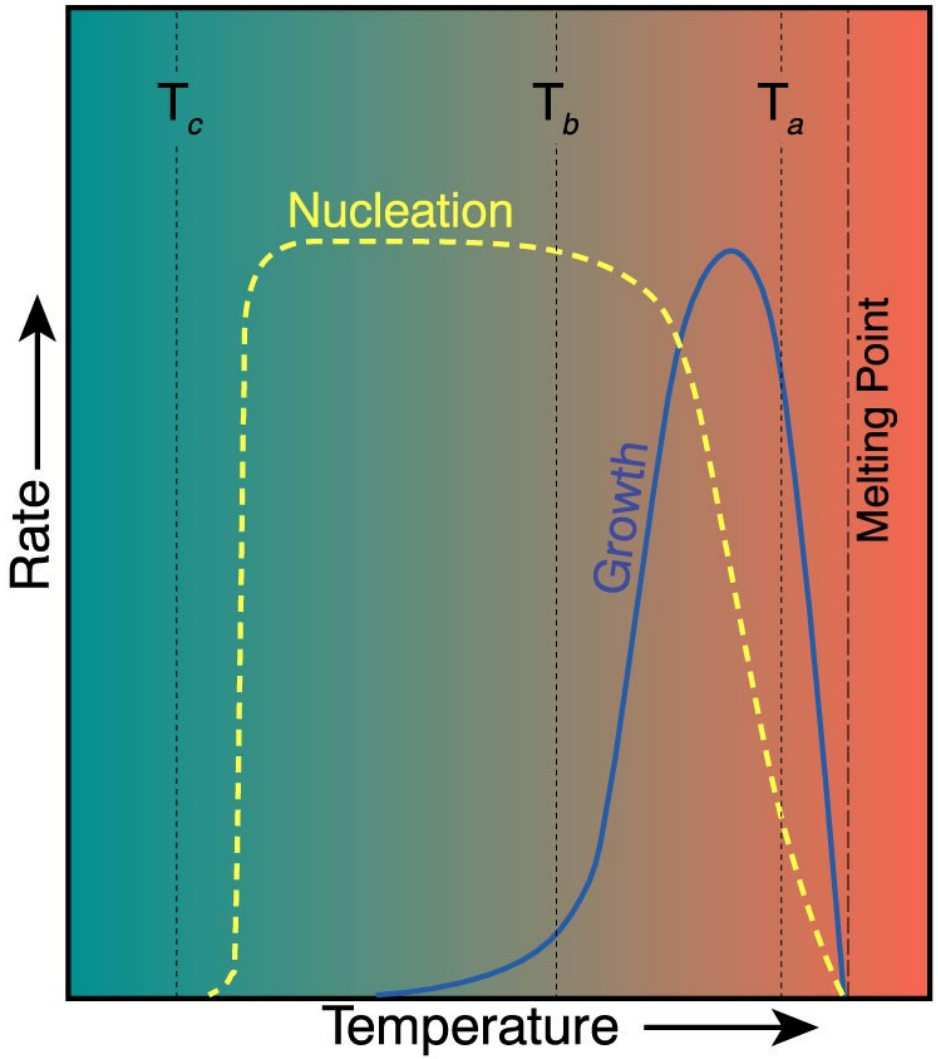


Nucleation and growth



Nucleation and growth: Overview

Slow cooling results in minor undercooling (T_a), so rapid growth and slow nucleation produce fewer coarse-grained crystals. Rapid cooling permits more undercooling (T_b), so that slower growth and rapid nucleation produce many fine-grained crystals. Very rapid cooling involves little if any nucleation or growth (T_c), producing a glass.



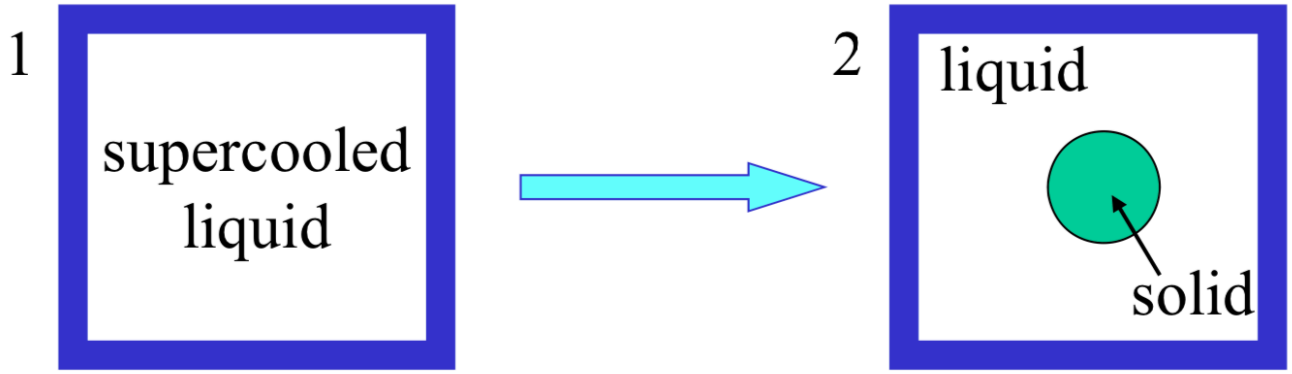
Nucleation and growth



Virgin coconut oil melts around 24 °C

Because room temperature is just below the melting point, nucleation can be very slow and large grains can form

Is homogeneous nucleation spontaneous?

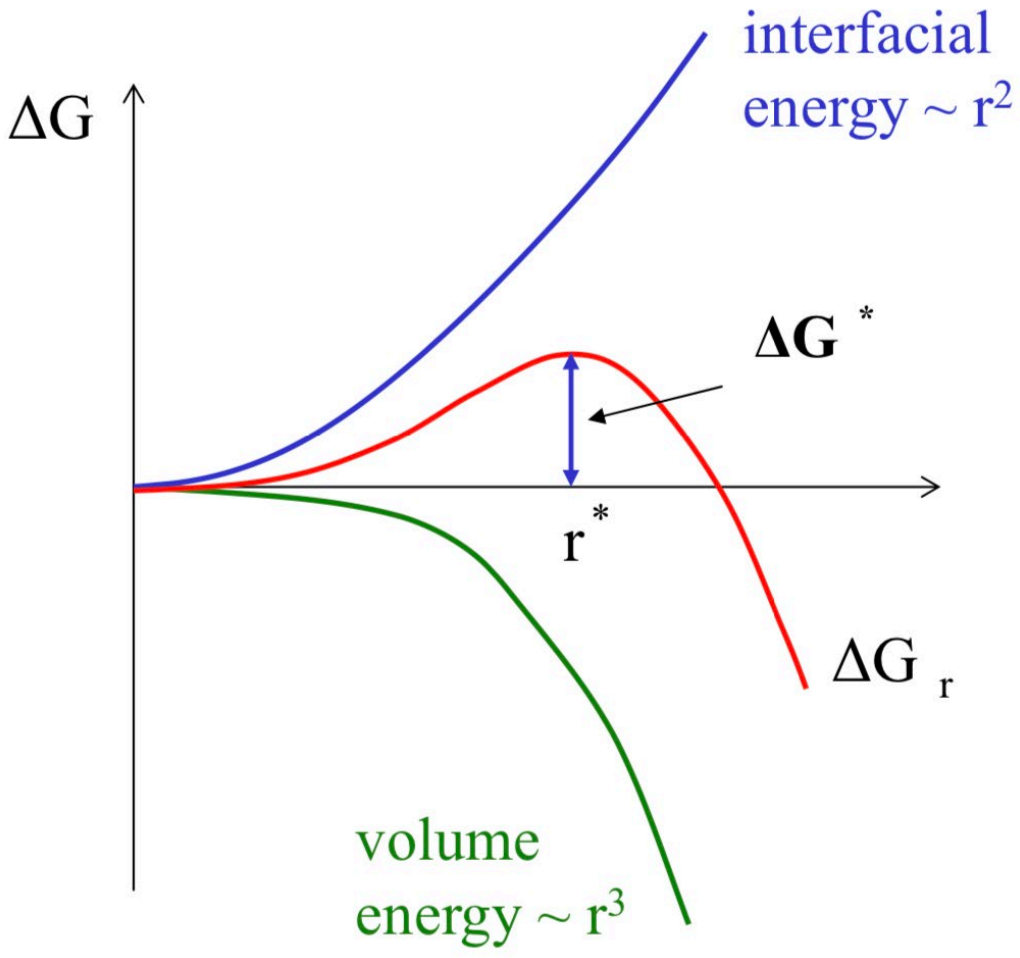


$$\Delta G = G_f - G_i = -V\left(G_V^L - G_V^S\right) + A\gamma$$

$$= \underbrace{-V\Delta G_V}_{\text{Negative below } T_m} + \underbrace{A\gamma}_{\text{Interfacial energy, always positive}}$$



Barrier to nucleation



$$\Delta G = -V\Delta G_V + A\gamma$$

For a spherical nucleus of radius *r*:

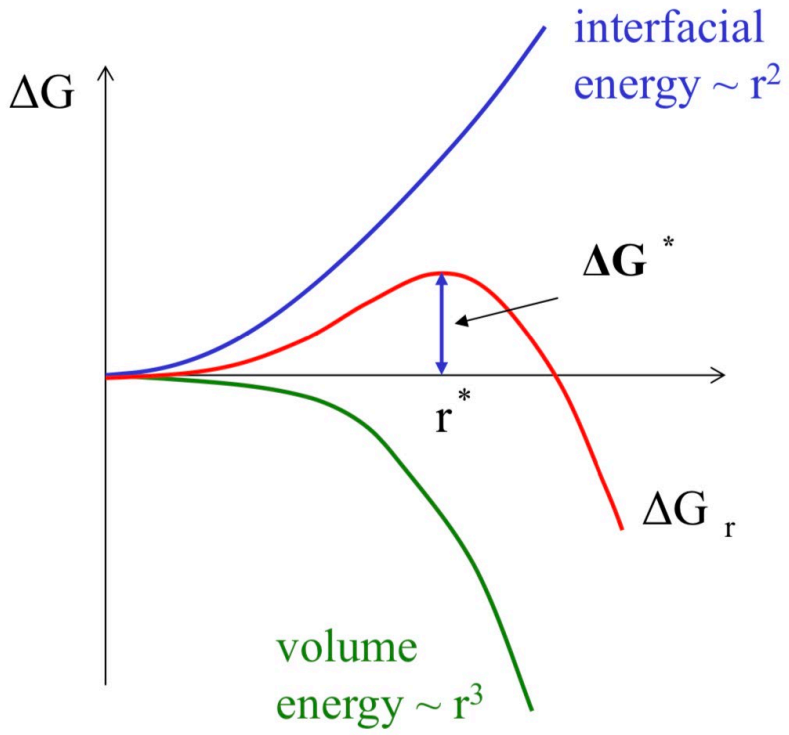
$$V = \frac{4}{3}\pi r^3 \qquad A = 4\pi r^2$$

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

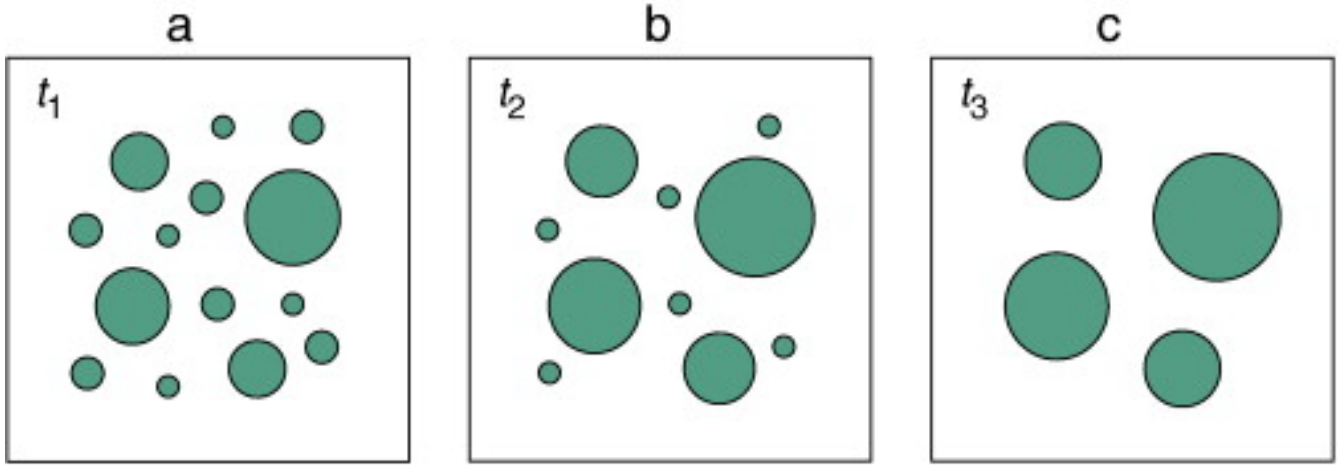
At r^*, $dG/dr = 0$, giving:

$$r^* = \frac{2\gamma}{\Delta G_V} \qquad \Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_V^2}$$

Ostwald ripening / coarsening



Nuclei smaller than r^* will shrink, while those larger than r^* will grow



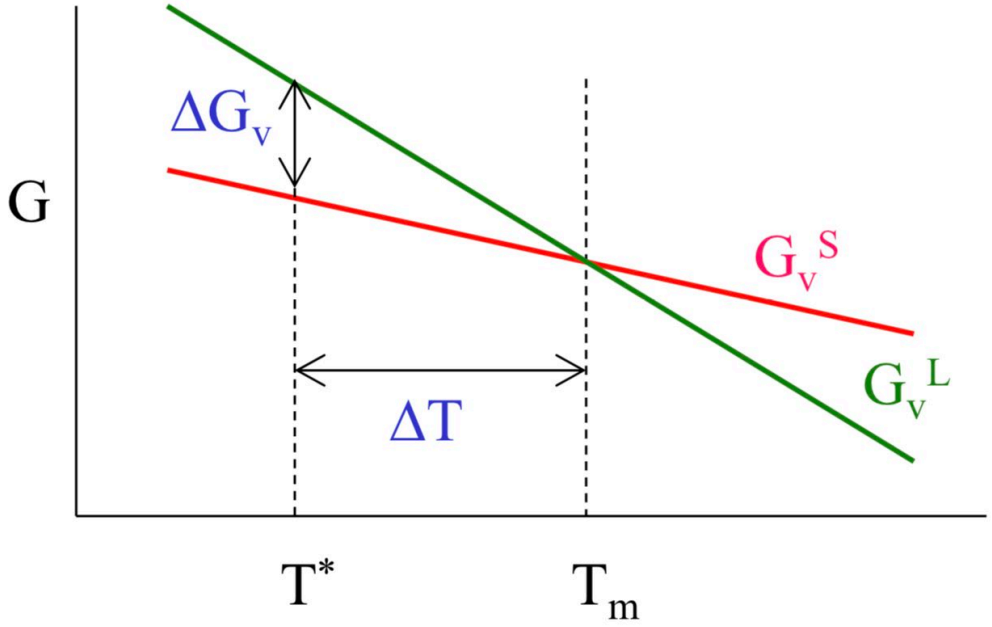
Barrier to nucleation

We can say more about the driving force for nucleation, $\Delta G_V = G_V^L - G_V^S$

At T_m:

$$\Delta G_V = \Delta H_V^m - T_m \Delta S_V^m = 0$$

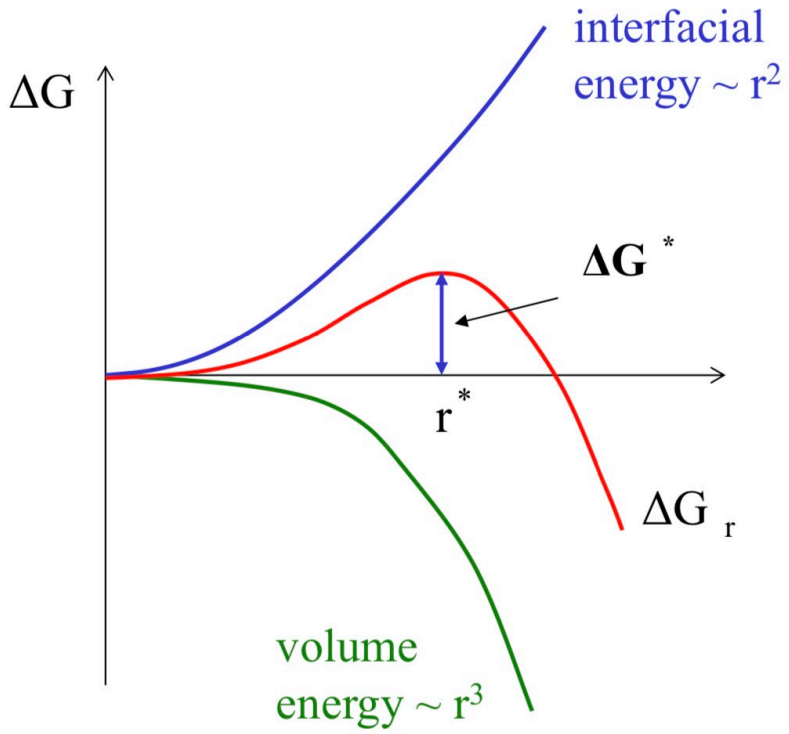
$$\Delta S_V^m = \Delta H_V^m / T_m$$



At T^* (assuming H and S are T-independent for small undercooling ΔT):

$$\Delta G_V \approx \Delta H_V^m - T^* \frac{\Delta H_V^m}{T_m} = \frac{\Delta H_V^m \Delta T}{T_m}$$

Barrier to nucleation



$$r^* = \frac{2\gamma}{\Delta G_V} \qquad \Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_V^2}$$

$$r^* = \frac{2\gamma T_m}{\Delta H_V^m}\frac{1}{\Delta T} \qquad \Delta G^* = \frac{16\pi\gamma^3 T_m^2}{3(\Delta H_V^m)^2}\frac{1}{\Delta T^2}$$

Both the nucleation radius and the barrier to nucleation decrease with increasing undercooling

Kinetics of nucleation

The rate of fluctuations of size ΔG^* is given by the Arrhenius equation:

$$\dot{N} \sim v_d \exp\left(-\frac{\Delta G^*}{k_B T}\right) \sim \exp\left(-\frac{Q_d}{k_B T}\right) \exp\left(-\frac{A}{\Delta T^2}\right)$$

Attempt frequency of crossing barrier

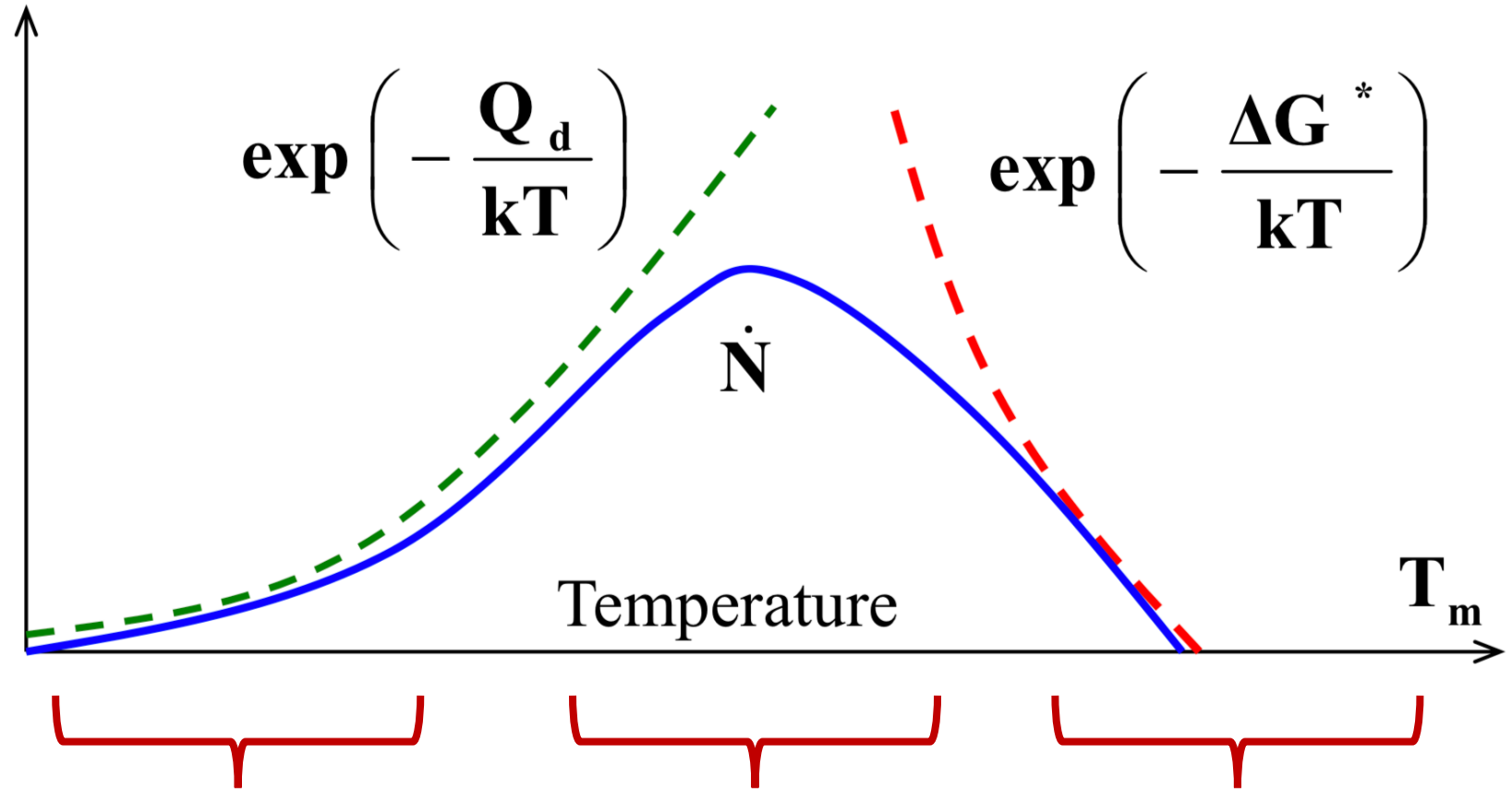
Probability of successfully overcoming barrier

Assumed to have same kinetics as diffusion

ΔG^* copied over from last slide

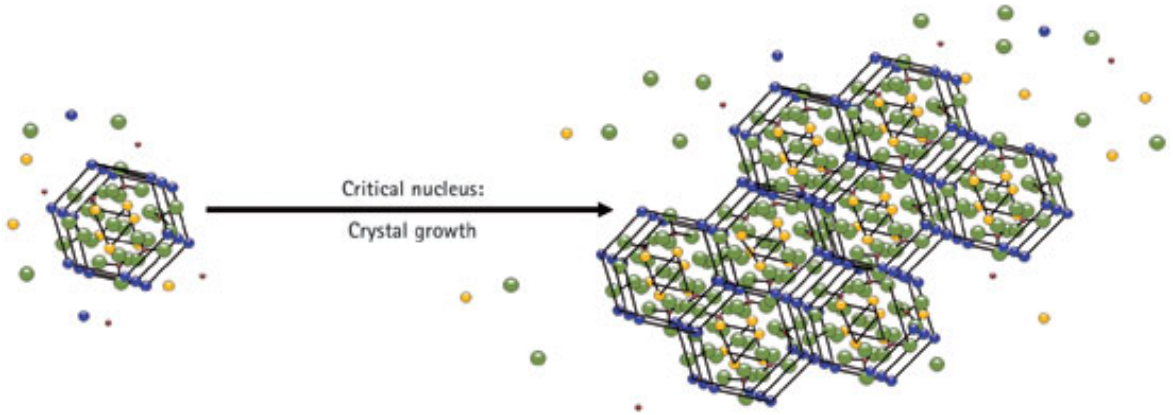
Mentimeter

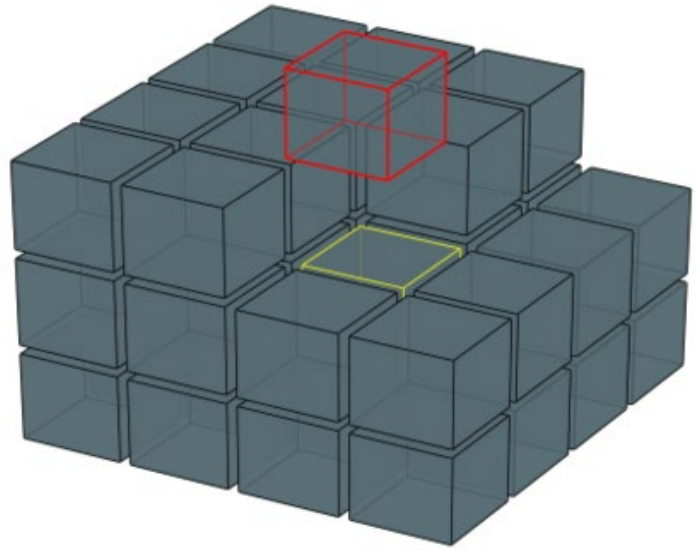
Kinetics of nucleation

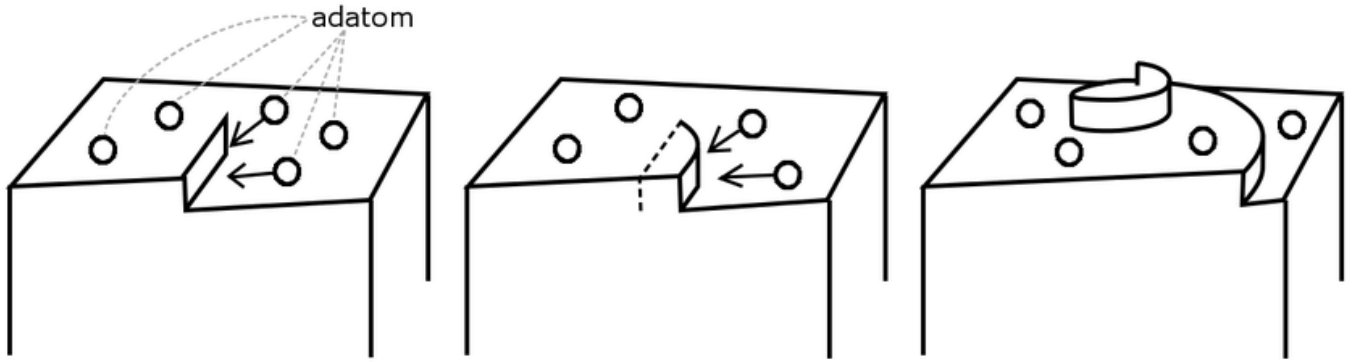


Growth

After nucleation comes growth.







Kinetics of growth

Growth is generally diffusion controlled because it requires long-range atomic rearrangement.

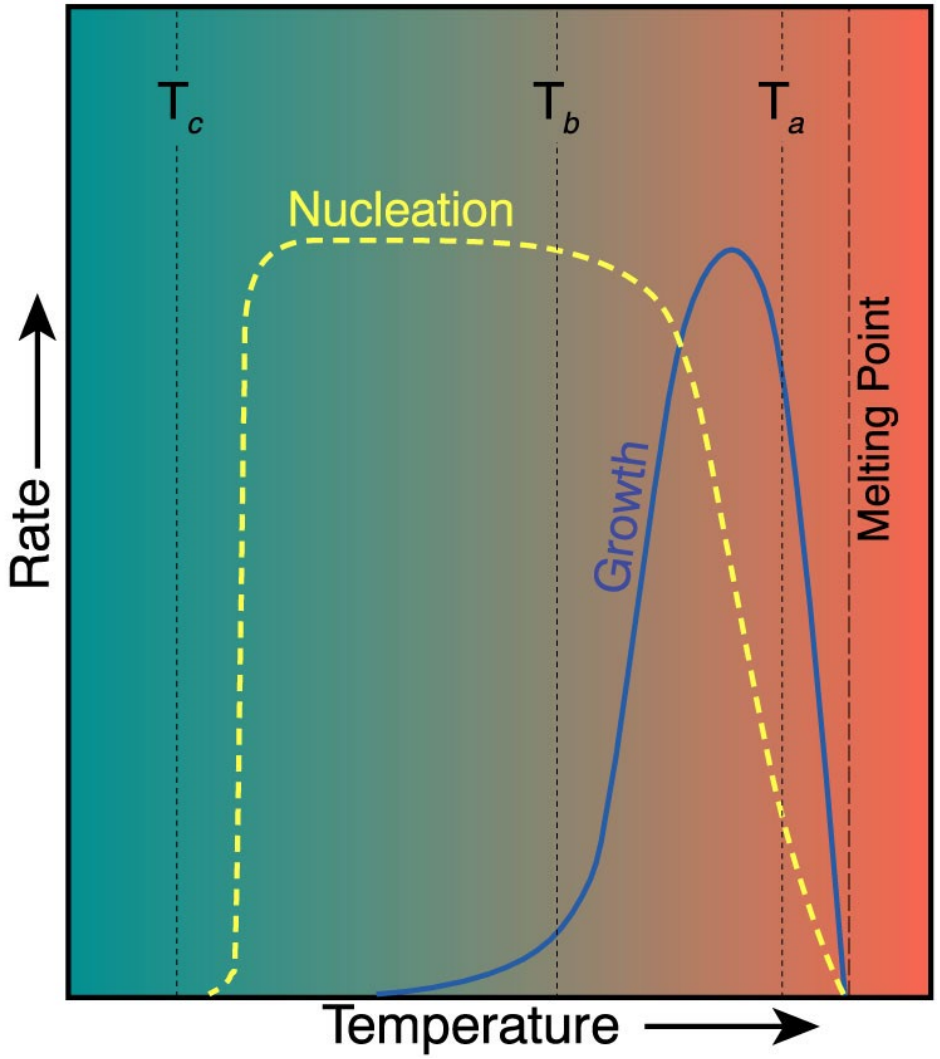
Therefore, it slows down with decreasing temperature.

Diffusion-controlled growth often leads to dendrites, because supersaturation is highest at the tips of the extremities.





Nucleation and growth: Overview



Mentimeter

Igneous rocks

Igneous rocks can be classified by texture (crystal size), which is governed by how fast magma cools.

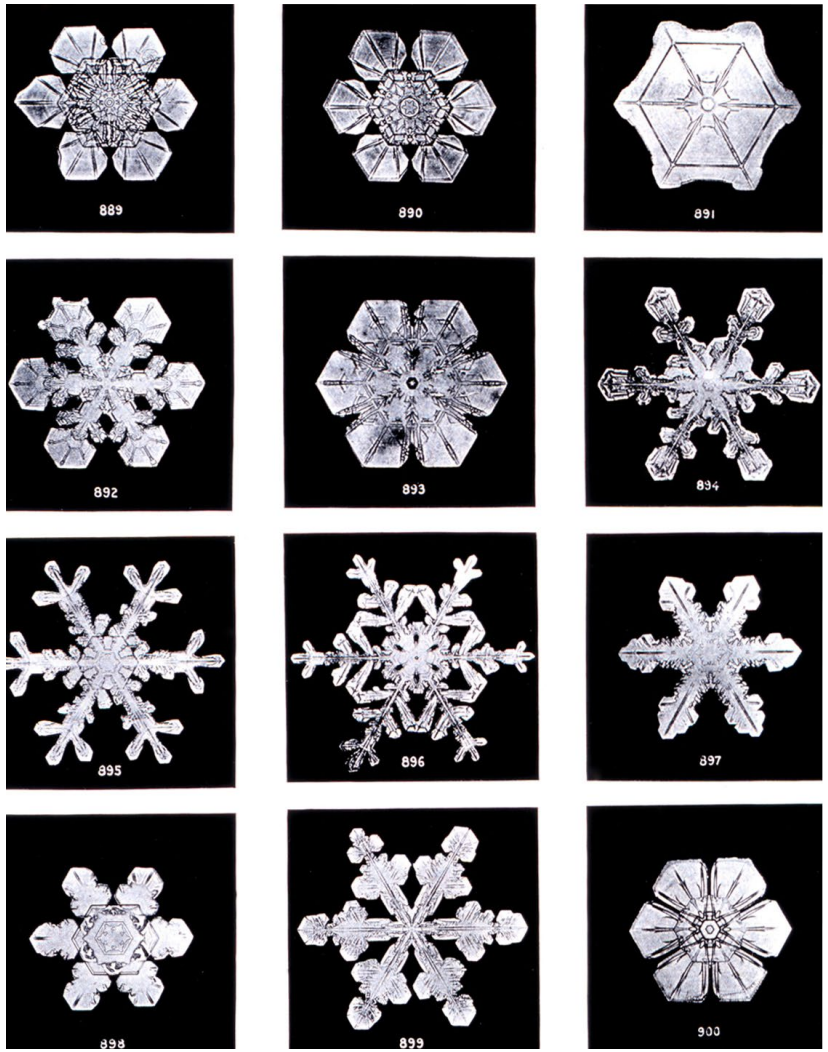
The same magma can give different rocks if it cools at different rates.

Fine-grained rocks are formed in volcanic eruptions (strong undercooling), while coarse-grained rocks form if magma cools slowly underground.



Snowflakes

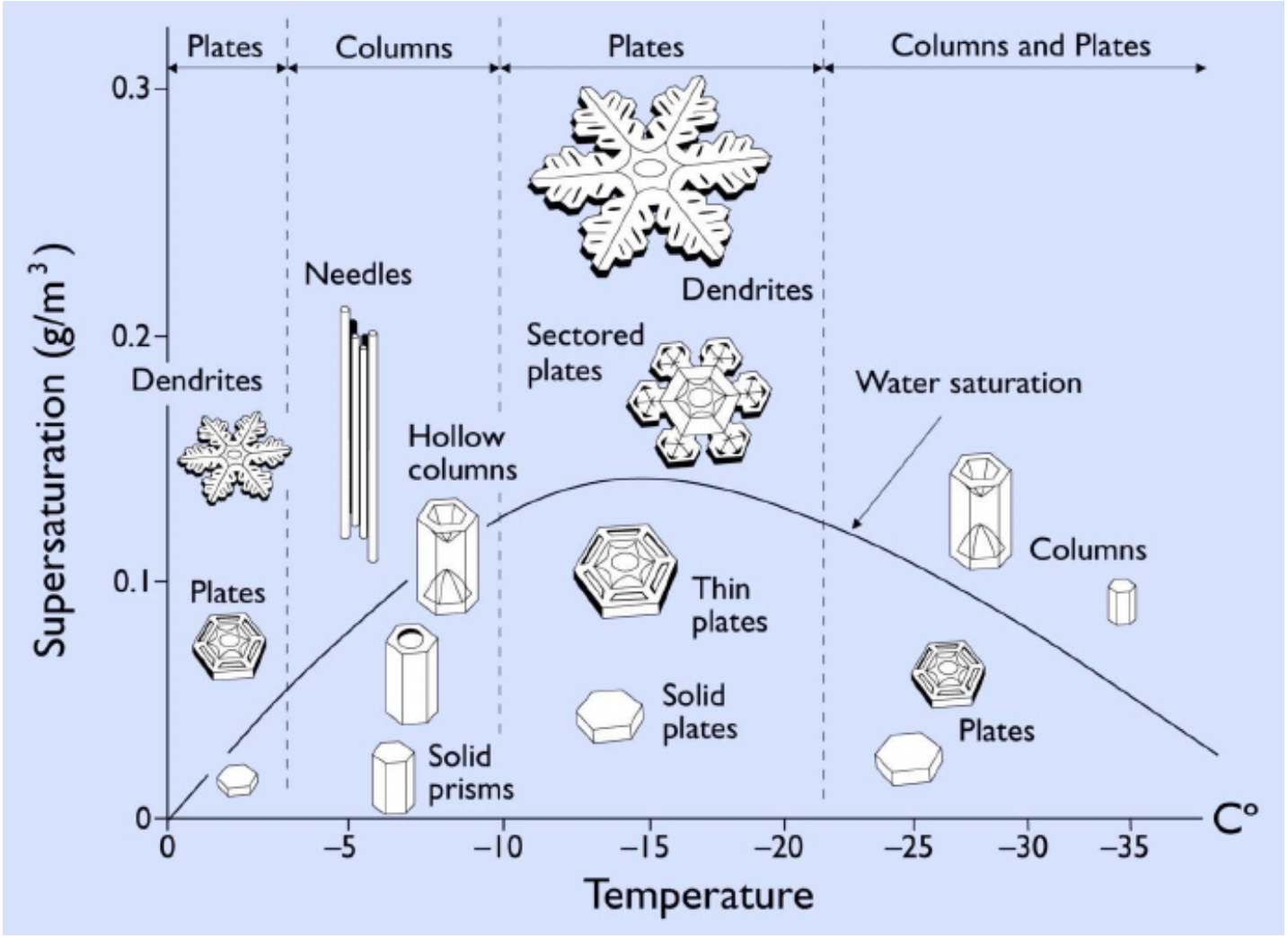
Subtle difference in crystal growth rates can significantly affect the resulting crystals



Snowflakes

Nakaya diagram (Ukichiro Nakaya, 1930s)

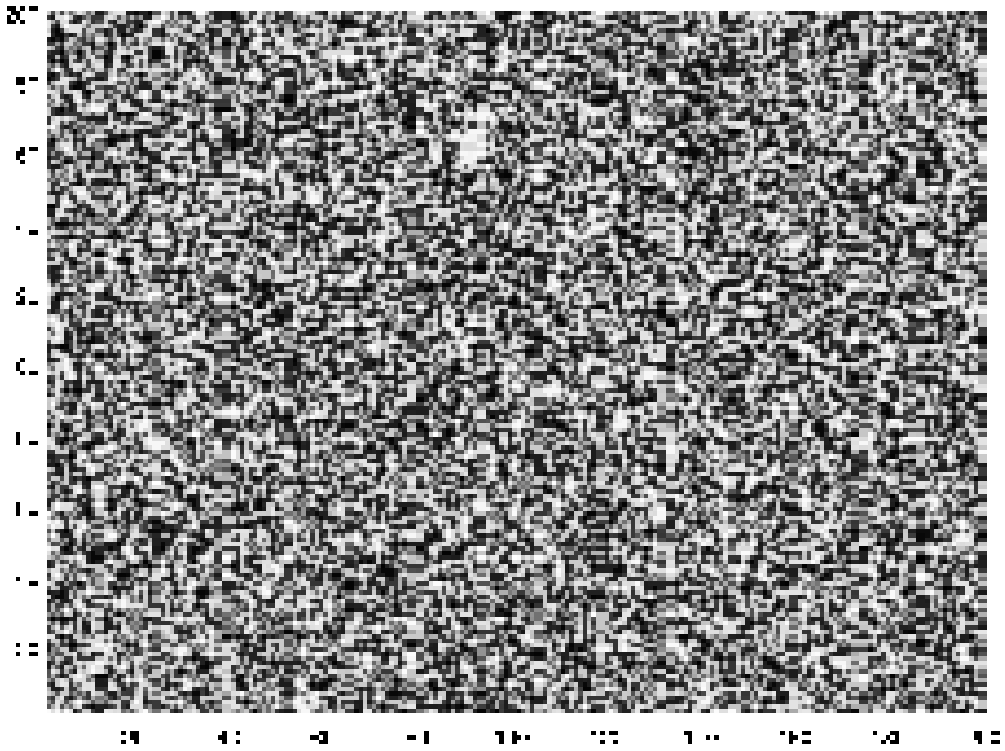




Spinodal decomposition

Spinodal decomposition is another mechanism of phase transition. It can occur in mixtures where there is no barrier to nucleation. Its dynamics is driven solely by diffusion.

Example: at high *T*, a water-oil mixture forms a single phase. If suddenly cooled to a temperature where oil-rich and water-rich phases coexist, the oil and water molecules will begin to cluster. The clusters will grow and coalesce into large phases.



Summary

Key points:

- Nucleation and growth is the most common mechanism of phase transition
- There is a barrier to nucleation, caused by surface tension, which decreases with supercooling (or superheating)
- The extent of supercooling governs the size of resulting crystals

Next time

Next time, we'll apply what we've learned in past few lectures to the formation and properties of glasses.