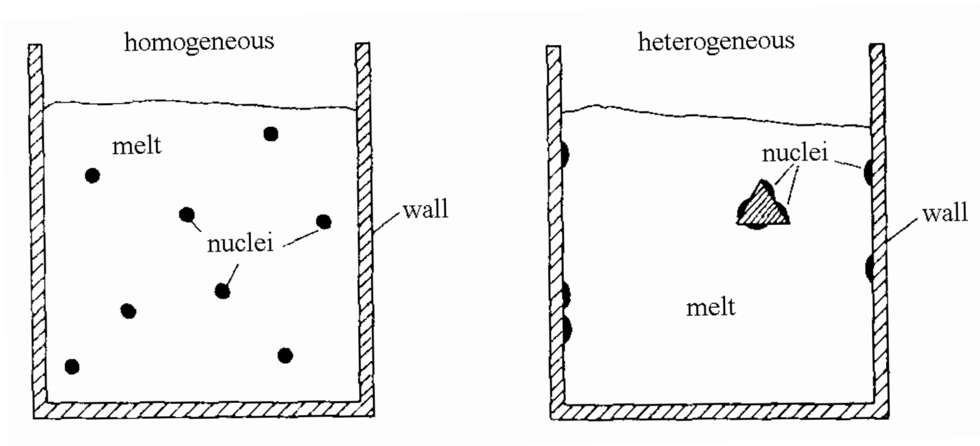
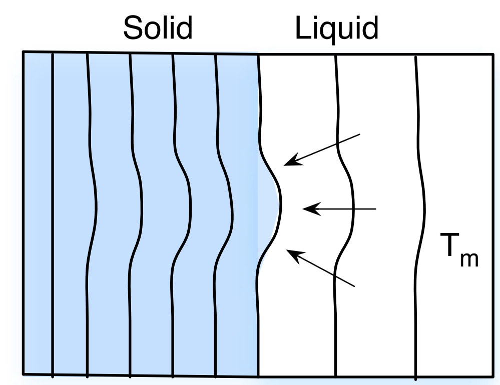




Nucleation and Growth

Topic 4

M.S Darwish

MECH 636: Solidification Modelling

American University of Beirut
الجامعة الأميركية في بيروت

Objectives

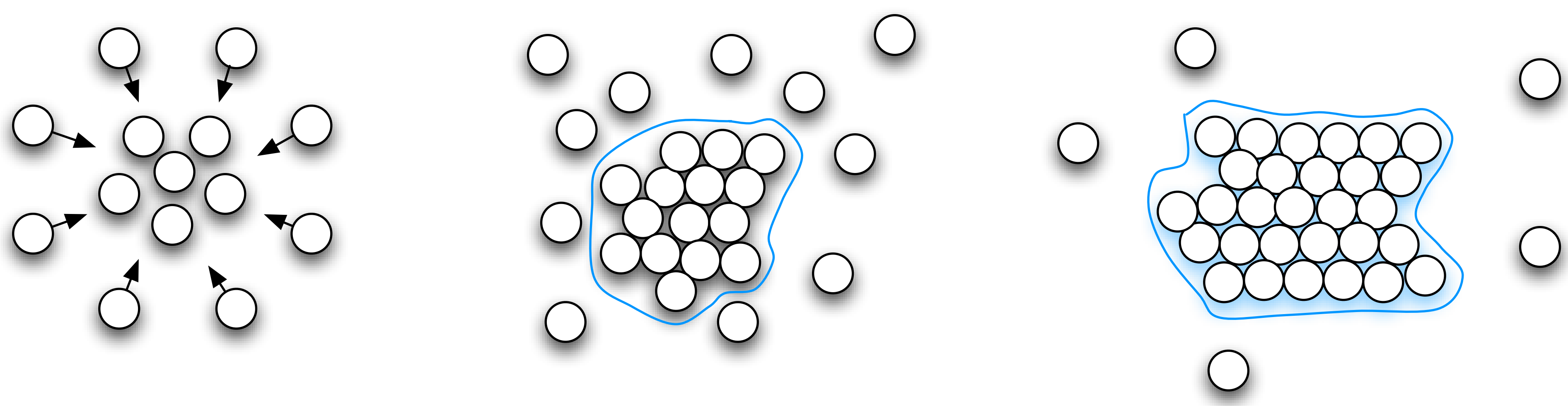
By the end of this lecture you should be able to:

- Explain the term homogeneous as applied to nucleation events
- Understand the concept of critical size and critical free energy
- Differentiate between unstable cluster (embryos) and stable nuclei
- Derive expressions for (r^*,N, ...) in terms of ΔG_v & ΔT.
- List typical heterogeneous nucleation sites for solidification
- Understand the term wetting or contact angle, θ
- Explain why the wetting angle is a measure of the efficiency of a particular nucleation site
- Write an expression relating critical volumes of heterogeneous and homogeneous nuclei.

Introduction

During Solidification the atomic arrangement changes from a random or short-range order to a long range order or crystal structure.

Nucleation occurs when a small nucleus begins to form in the liquid, the nuclei then grows as atoms from the liquid are attached to it.



The crucial point is to understand it as a balance between the free energy available from the driving force, and the energy consumed in forming new interface. Once the rate of change of free energy becomes negative, then an embryo can grow.

Energy Of Fusion

$$\Delta G_V = G_L - G_S = \Delta H_V - T\Delta S$$

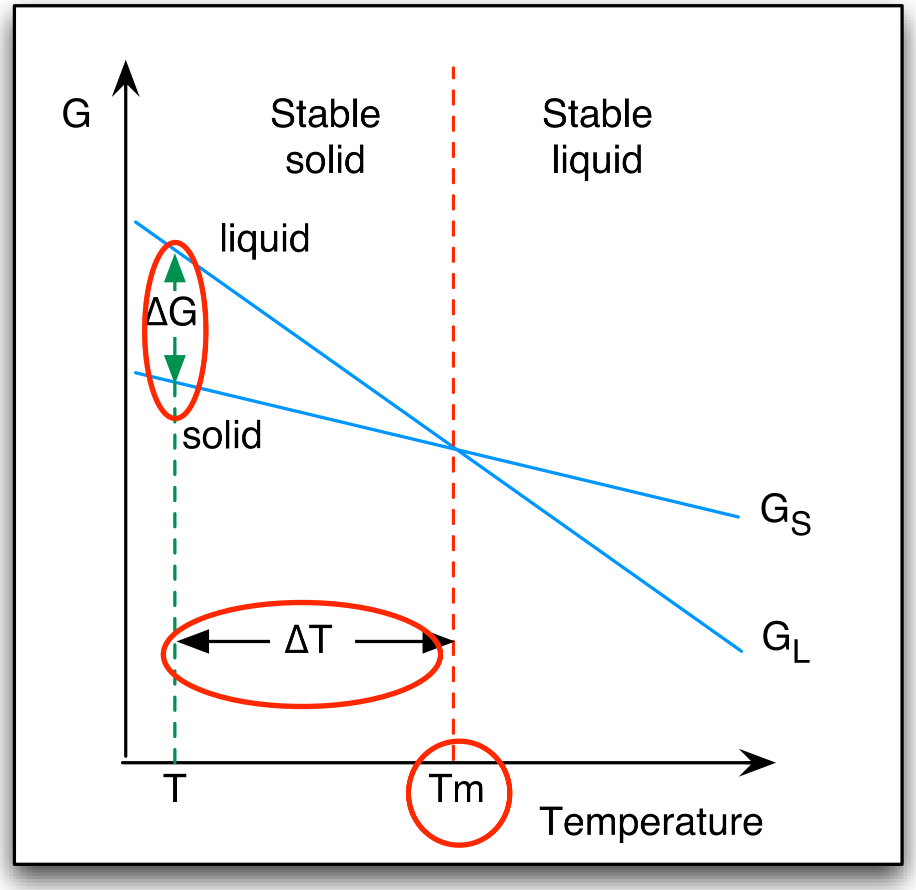
$$\Delta H_V = L_V \quad = \left(\frac{V}{\rho_s}\right) h_m$$

$$T_m = \frac{\Delta H_V}{\Delta S} = \frac{h_m V}{\rho_s \Delta S} \qquad \Delta S = \frac{h_m V}{\rho_s T_m}$$

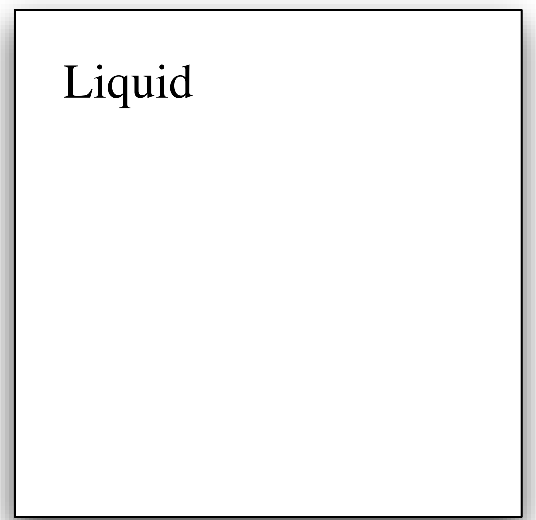
$$\Delta G_V = h_m \frac{V}{\rho_s} - T\frac{h_m V}{\rho_s T_m}$$

$$= \frac{h_m V}{\rho_s}\left(1 - \frac{T}{T_m}\right) = \left(\frac{V}{\rho_s}\right) h_m \frac{\Delta T}{T_m}$$

$$= \frac{L_V \Delta T}{T_m}$$

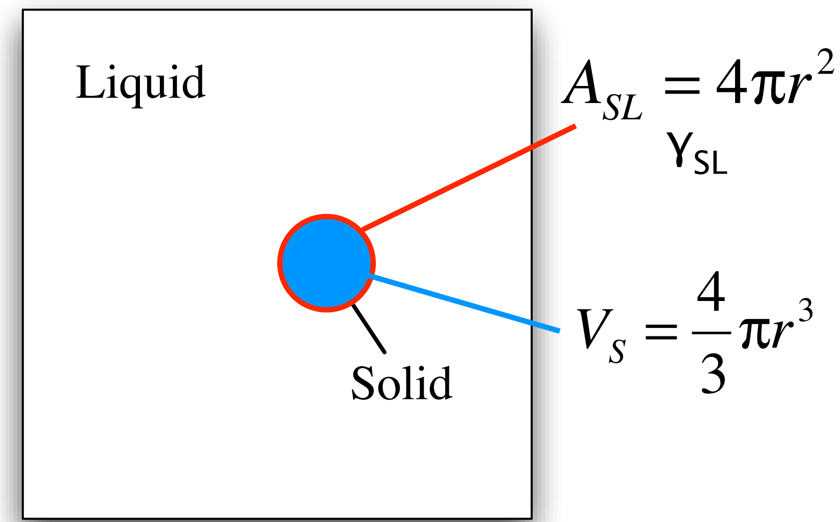


Homogeneous Nucleation



G_1

$$G_1 = (V_S + V_L)G_V^L$$



$G_2 = G_1 + \Delta G$

$$G_2 = V_S G_V^S + V_L G_V^L + A_{SL}\gamma_{SL}$$

$$\Delta G_V = \frac{L_V \Delta T}{T_m}$$

$$\Delta G = G_2 - G_1$$

$$= V_S\left(G_V^S - G_V^L\right) + A_{SL}\gamma_{SL}$$

$$= -V_S \Delta G_V + A_{SL}\gamma_{SL}$$

-ve +ve

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

1. When r is smaller than some r* an increase in r leads to an increase of ΔG -> unstable
2. When r is larger than some r* an increase in r leads to a decrease of ΔG -> stable

Critical radius

Not at $\Delta G=0$!!!

Differentiate to find the stationary point (at which the rate of change of free energy turns negative).

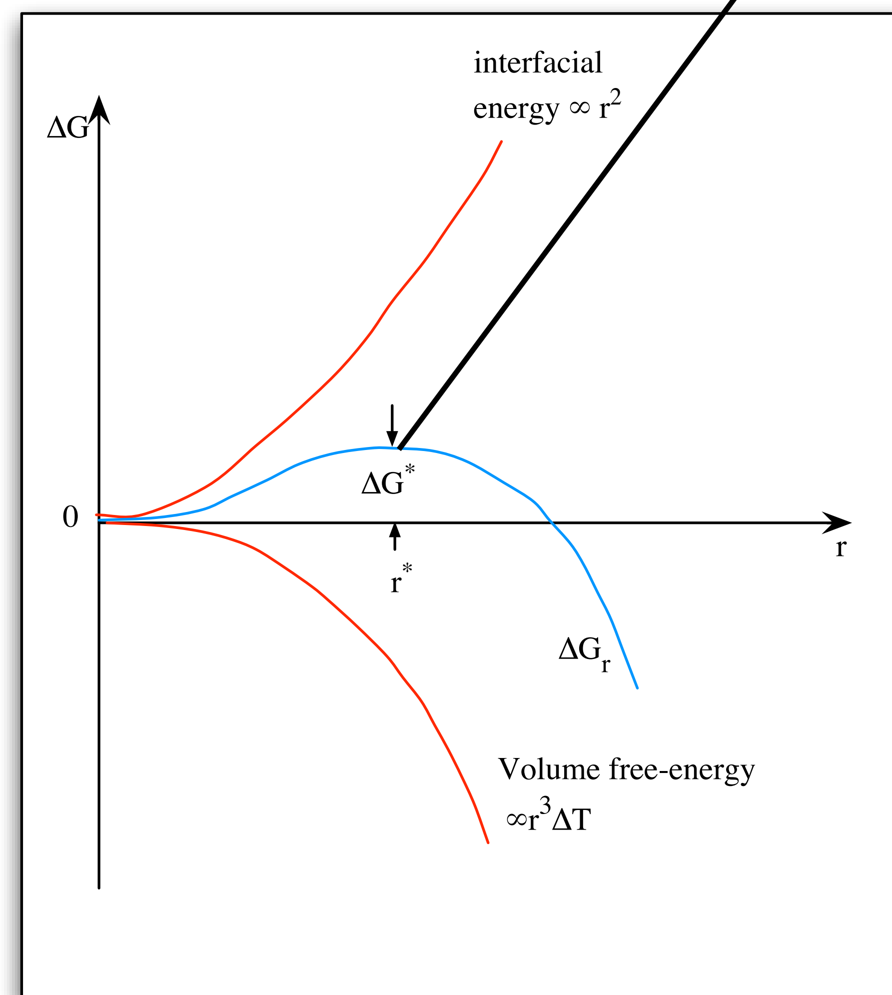
$$\frac{d(\Delta G)}{dr}=0$$

$$-4\pi\left(r^*\right)^2\Delta G_V+8\pi r^*\gamma=0$$

From this we find the critical radius and critical free energy.

$$r^*=\frac{2\gamma_{SL}}{\Delta G_V}=\left(\frac{2\gamma_{SL}T_m}{L_V}\right)\frac{1}{\Delta T}$$

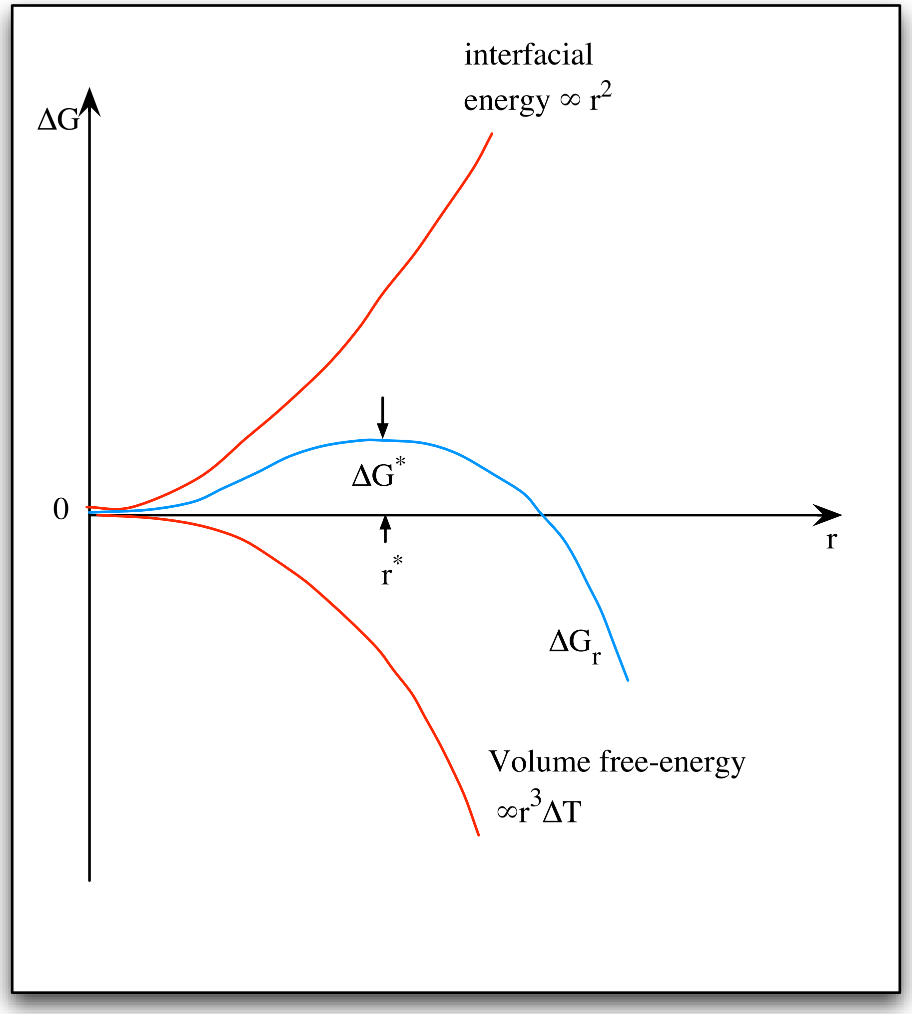
$$\Delta G^*=\frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}=\left(\frac{16\pi\gamma_{SL}^3T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$



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

Cluster and Nuclei

- if $r<r^*$ the system can lower its free energy by dissolution of the solid
- Unstable solid particles with $r<r^*$ are known as clusters or embryos
- if $r>r^*$ the free energy of the system decreases if the solid grows
- Stable solid particles with $r>r^*$ are referred to as nuclei
- Since $\Delta G = 0$ when $r = r^*$ the critical nuclei is effectively in (unstable) equilibrium with the surrounding liquid

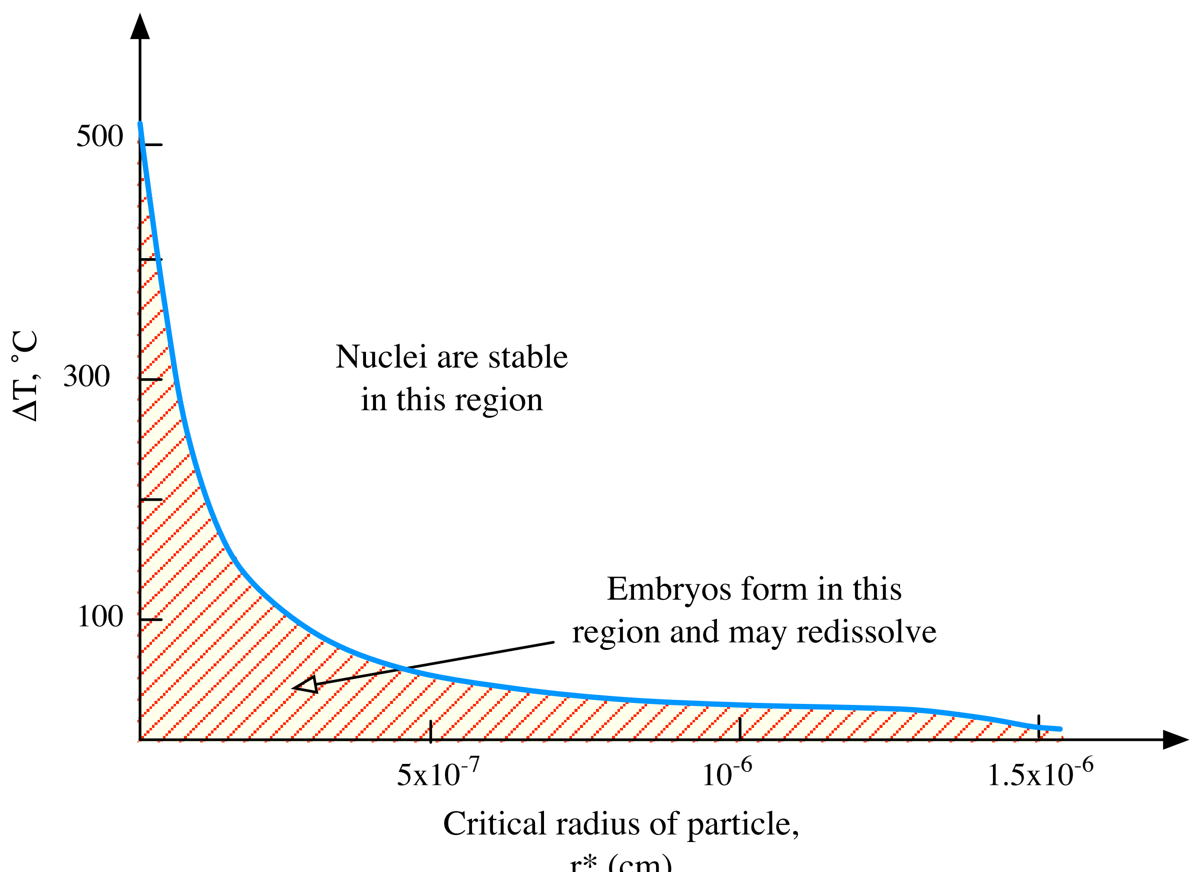


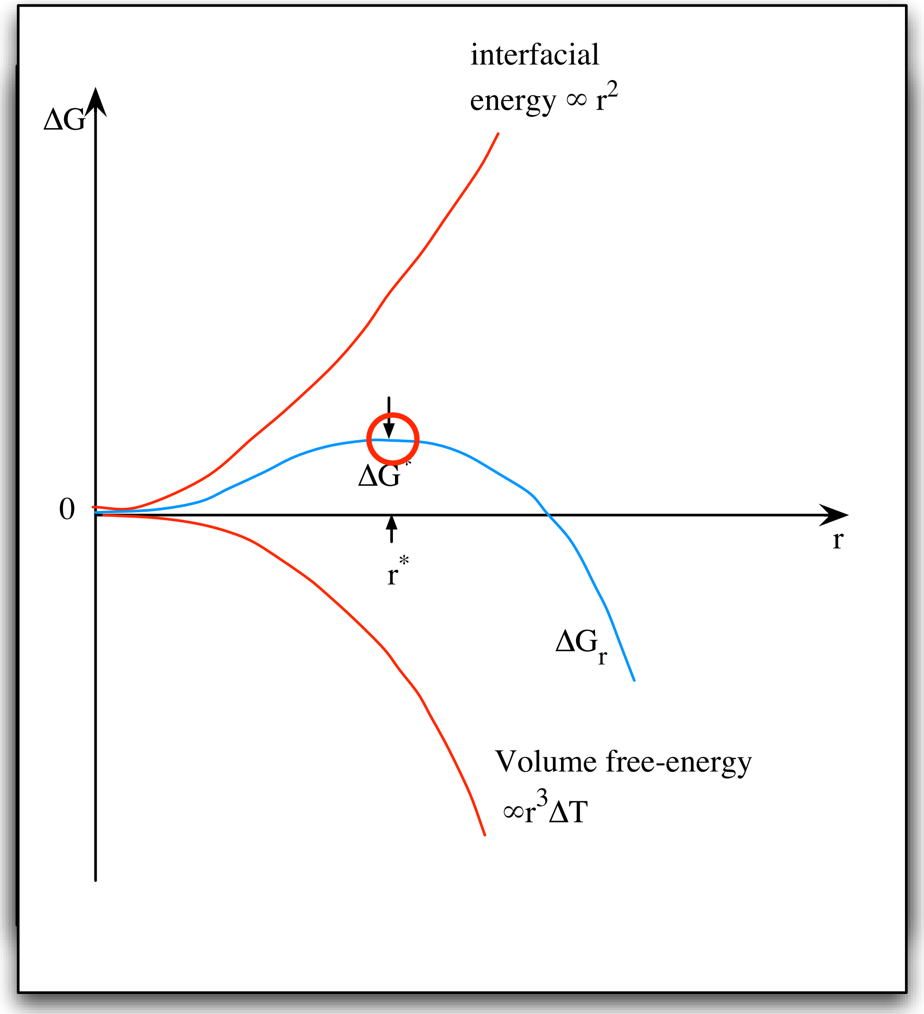
Effect of Undercooling

At r* the solid sphere is at equilibrium with its surrounding thus the solid sphere and the liquid have the same free energy

$$\Delta G_V = \frac{2\gamma_{SL}}{r^*}$$

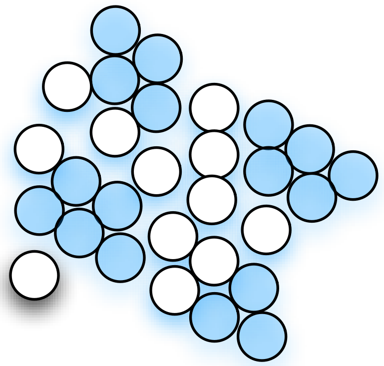
How r^* and ΔG^* decrease with undercooling ΔT





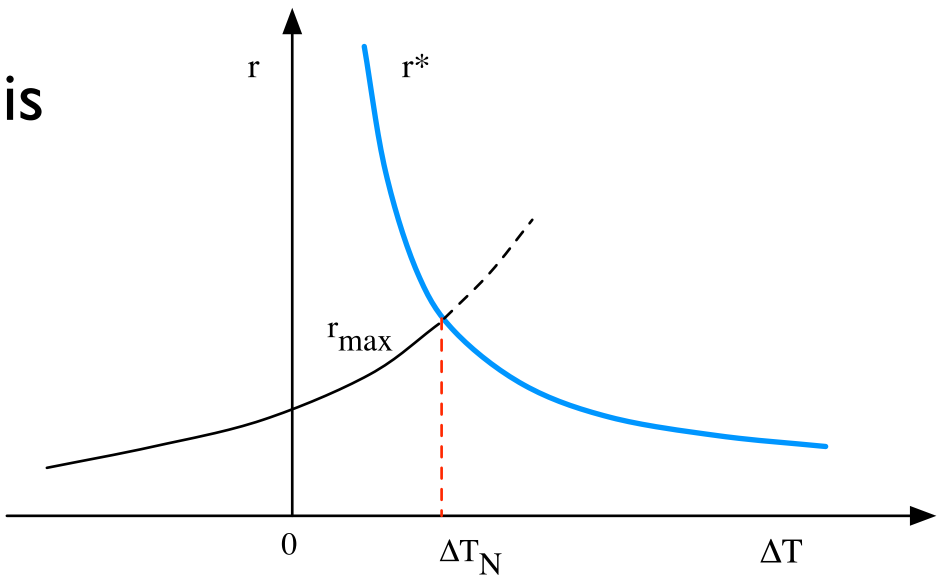
$$-4\pi\left(r^*\right)^2 \Delta G_V + 8\pi r^* \gamma = 0$$

Variation of r* and r_{max} with ΔT



- Although we now know the critical values for an embryo to become a nucleus, we do not know the rate at which nuclei will appear in a real system.
- To estimate the nucleation rate we need to know the population density of embryos of the critical size and the rate at which such embryos are formed.
- The population (concentration) of critical embryos is given by

$$n_r = n_o e^{-\frac{\Delta G_r}{kT}}$$



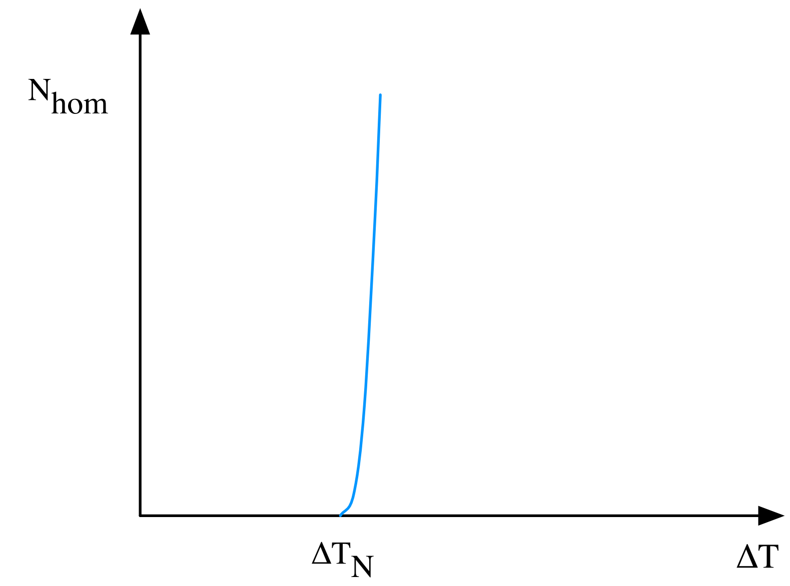
k is the Boltzmann factor, n_o is the total number of atoms in the system

ΔG_r is the excess of free energy associated with the cluster

Homogeneous Nucleation Rate

taking a ΔG equal to ΔG*, then the concentration of clusters to reach the critical size can be written as:

$$C^* = C_o e^{-\frac{\Delta G^*_{\text{hom}}}{kT}} \quad clusters/m^3$$

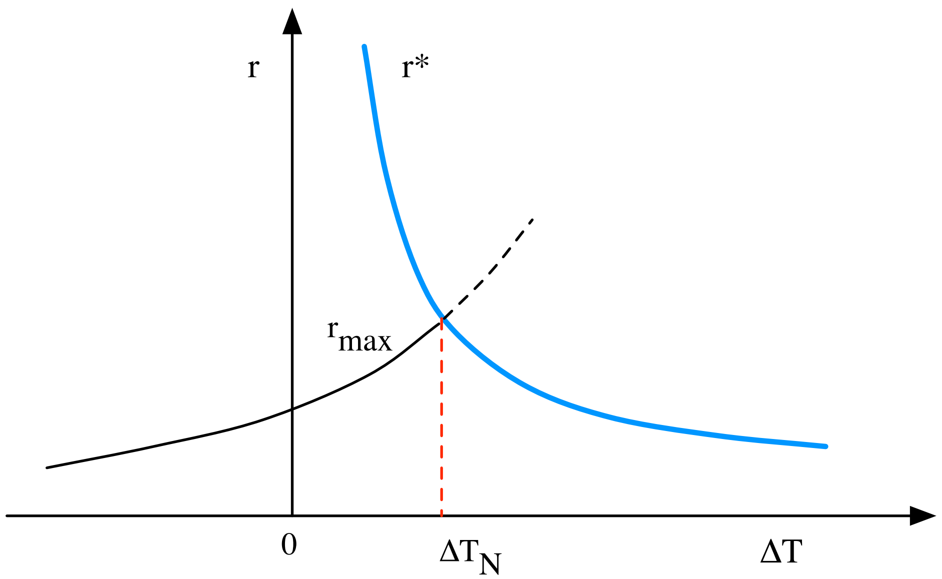


The addition of one more atom to each of these clusters would convert them into stable nuclei

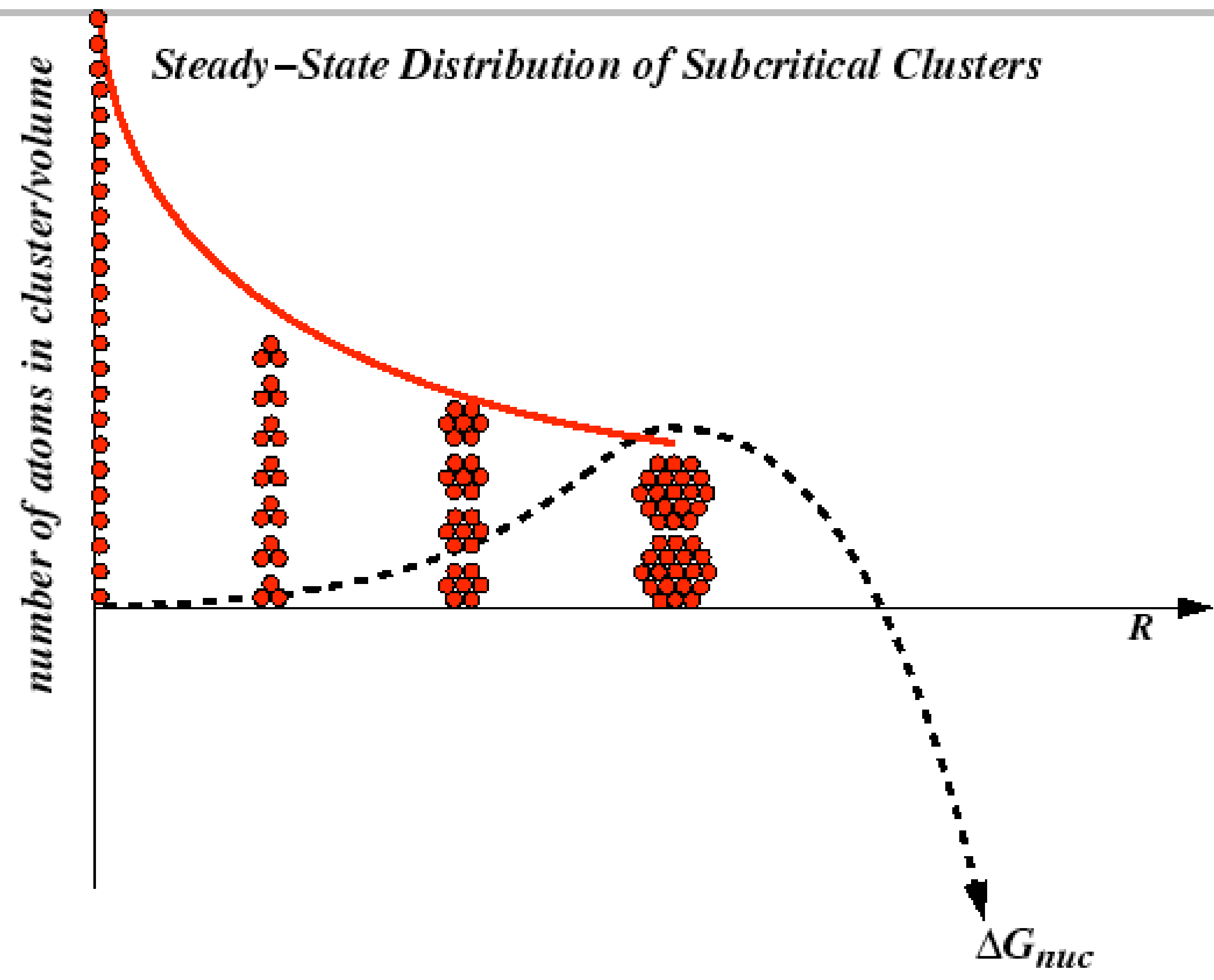
If this happens with a frequency fo,

$$N_{\text{hom}} = f_o C_o e^{-\frac{\Delta G^*_{\text{hom}}}{kT}} \quad nuclei/m^3$$

$$N_{\text{hom}} = f_o C_o e^{-\frac{A}{(\Delta T)^2}} \quad nuclei/m^3 \qquad A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2 kT}$$



The effect of undercooling on the nucleation rate is drastic, because of the non-linear relation between the two quantities as is shown in the plot

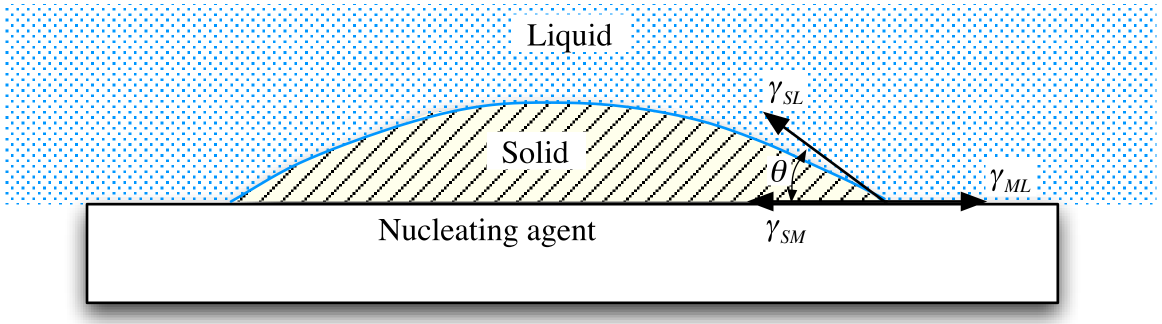


Steady–State Distribution of Subcritical Clusters
number of atoms in cluster/volume
R
ΔG_nuc

Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

it is clear that for nucleation to be facilitated the interfacial energy term should be reduced



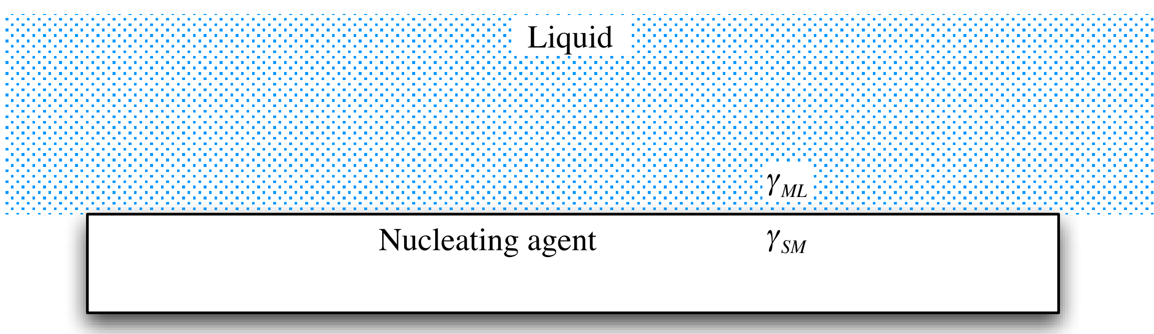
$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL}\cos\theta$$

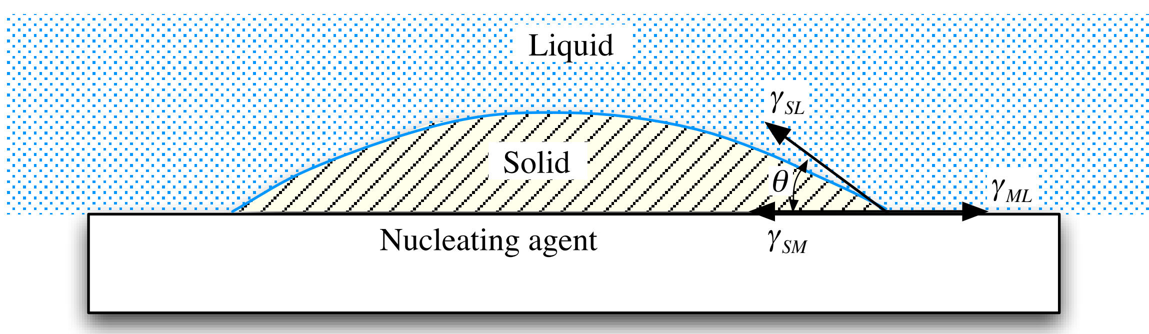
$$\cos\theta = \frac{(\gamma_{ML} - \gamma_{SM})}{\gamma_{SL}}$$

Heterogeneous Nucleation

$$G_1 = (V_S + V_L)G_V^L + (A'_{ML} + A_{ML})\gamma_{ML}$$

$$G_2 = V_S G_V^S + V_L G_V^L + A'_{ML}\gamma_{ML} + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM}$$





$$\Delta G = G_2 - G_1 = -V_S \Delta G_V + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{ML}\gamma_{ML}$$

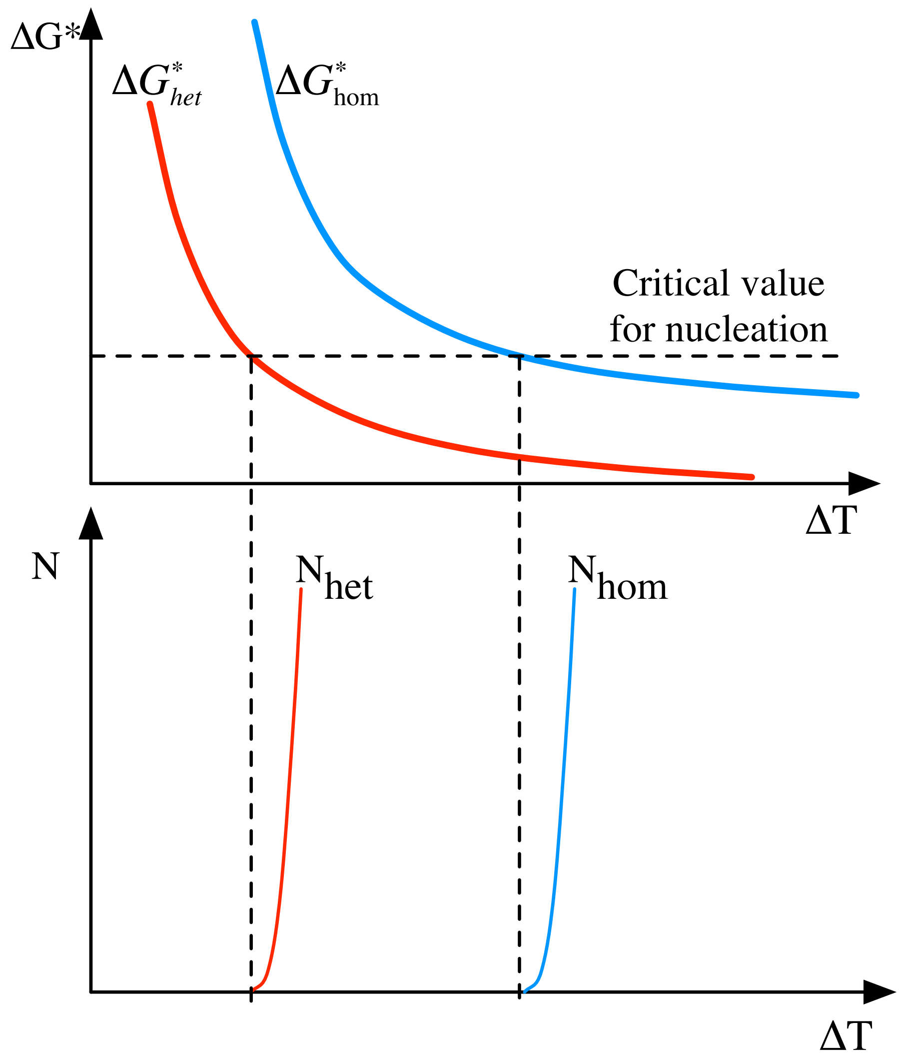
$$\Delta G_{het} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi\gamma_{SL} \right\} S(\theta)$$

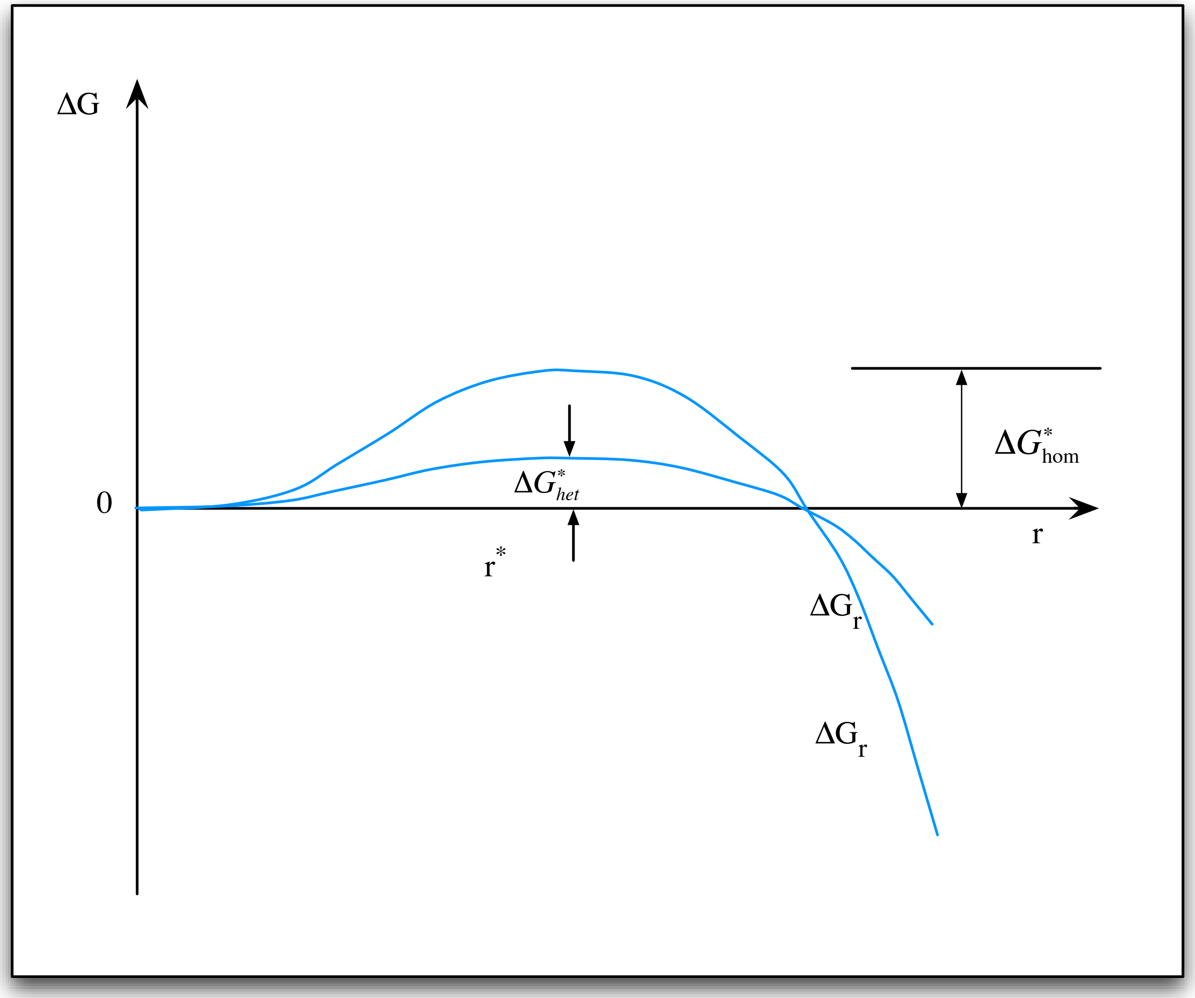
ΔG_{hom}

$$S(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4} \quad <1$$

Critical r and ΔG

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \qquad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} S(\theta)$$





$$\theta = 10^\circ \rightarrow S(\theta) = 10^{-4}$$

$$\theta = 30^\circ \rightarrow S(\theta) = 0.02$$

model does not work for $\theta = 0^\circ$

Heterogeneous Nucleation Rate

$$n^* = n_1 e^{-\frac{\Delta G^*_{het}}{kT}}$$

number of atoms in contact with nucleating agent surface

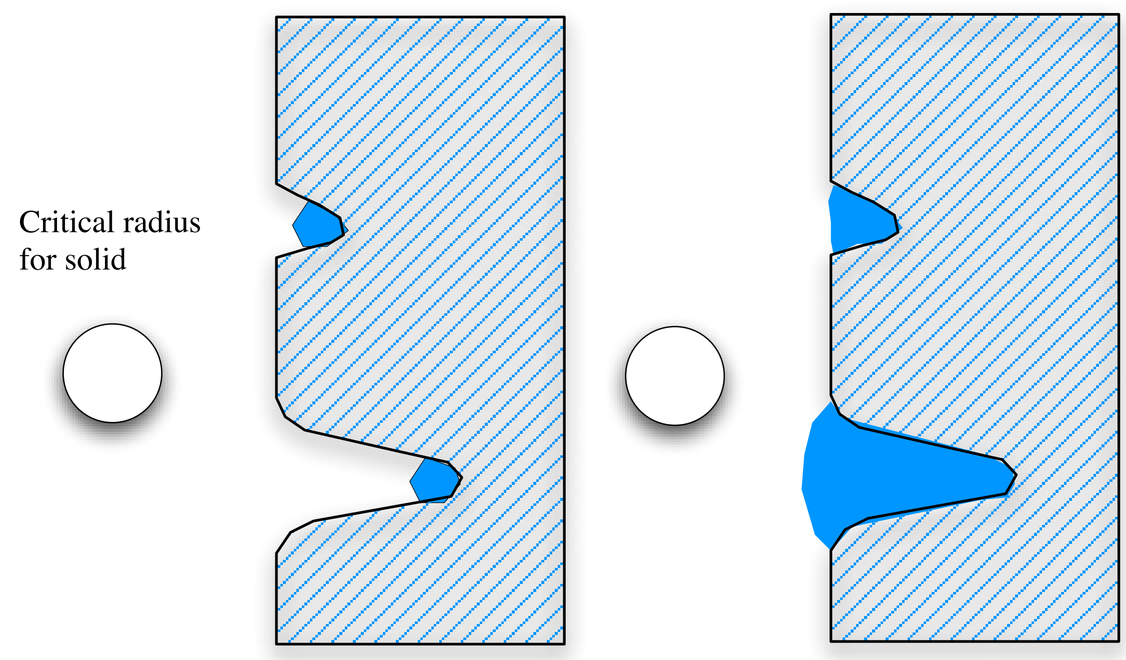
$$N_{het} = f_1 C_1 e^{-\frac{\Delta G^*_{het}}{kT}} \quad nuclei/m^3$$

number of atoms in contact with nucleating agent surface per unit volume

Exercise show that

$$\Delta G^* = \frac{1}{2} V^* \Delta G_v$$

Mould walls not flat



Nucleation in cracks occur with very little undercooling

for cracks to be effective the crack opening should be large enough to allow the solid to grow out without the radius of the solid/liquid interface decreasing below r*

Nucleation of Melting

While nucleation during solidification requires some undercooling, melting invariably occurs at the equilibrium temperature even at relatively high rates of heating.
this is due to the relative free energies of the solid/vapour, solid/liquid and liquid/vapour interfaces.

It is always found that

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

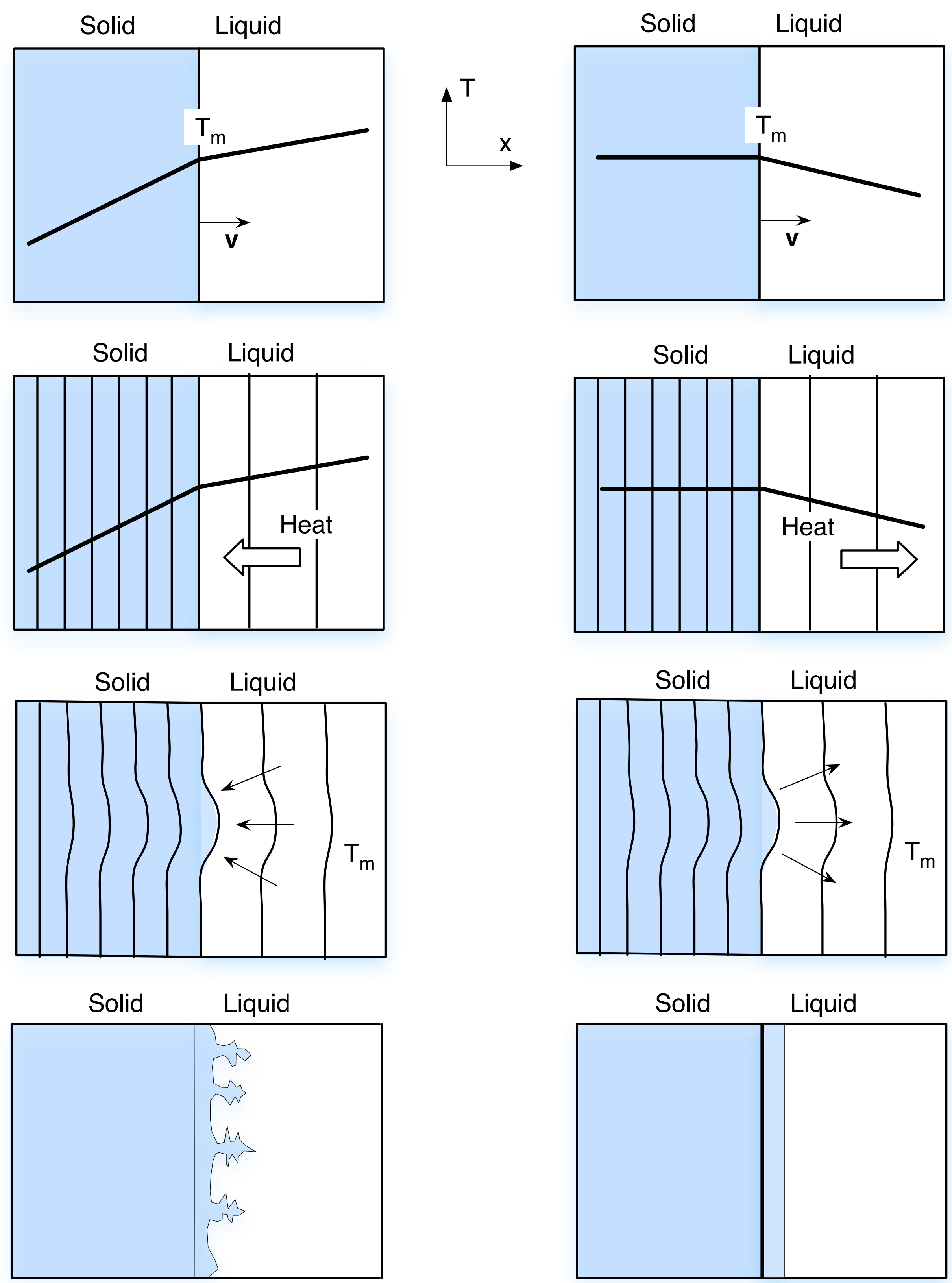
Therefore the wetting angle $\theta = 0$

and no superheating is required for nucleation of the liquid

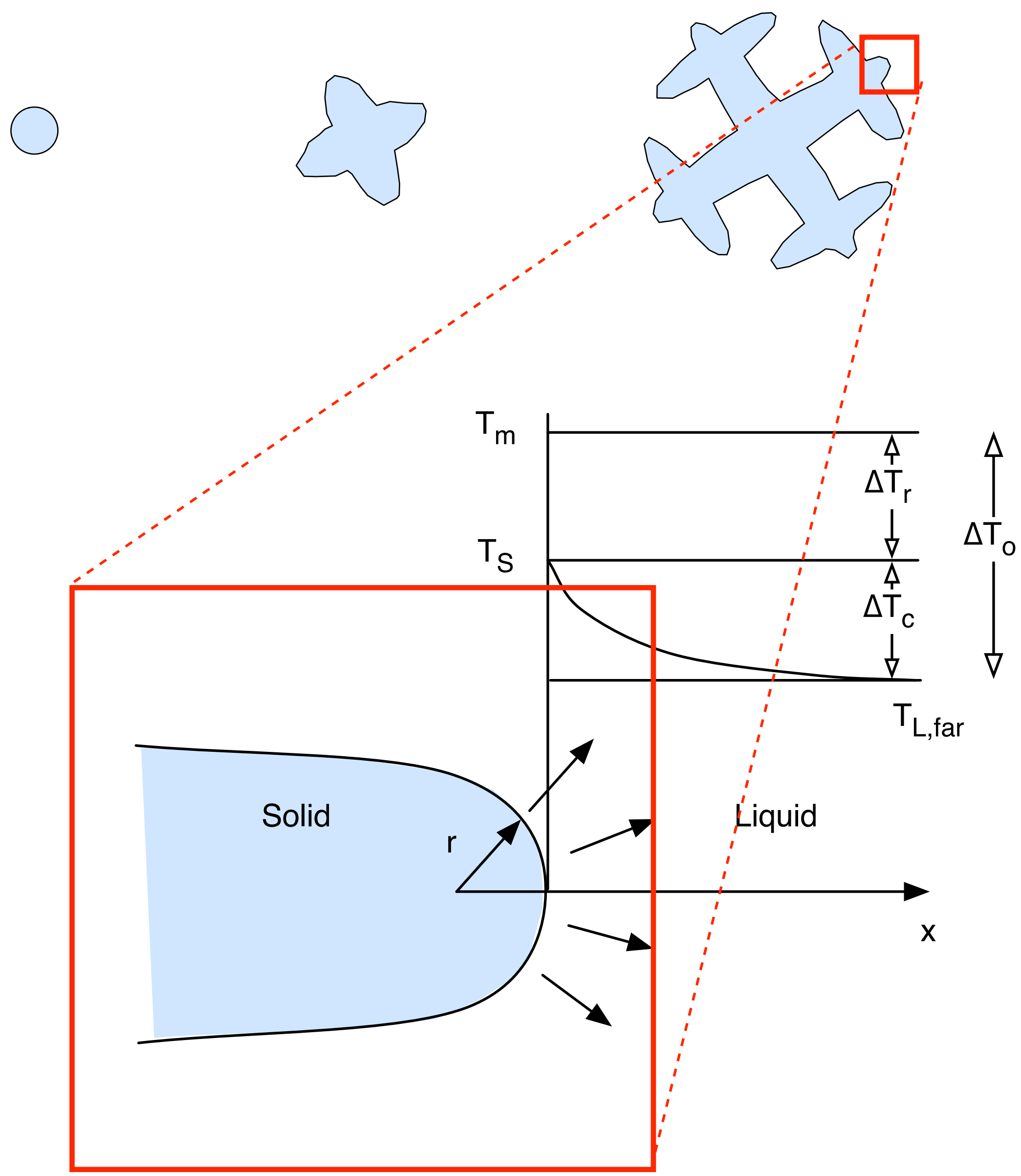
Growth of a Pure Solid

In a pure metal solidification is controlled by the rate at which the latent heat of solidification can be conducted away from the solid/liquid interface.

$$k_S \frac{dT_S}{dx} = k_L \frac{dT_L}{dx} + vL_V$$



Development of Thermal Dendrites



$$k_S \frac{dT_S}{dx} = k_L \frac{dT_L}{dx} + vL_V$$

$$\frac{dT_S}{dx} \approx 0 \qquad \frac{dT_L}{dx} \approx \frac{\Delta T_c}{r}$$

$$v \approx -k_L \frac{dT_L}{dx} \frac{1}{L_V} \approx -\frac{k_L}{L_V} \frac{\Delta T_c}{r}$$

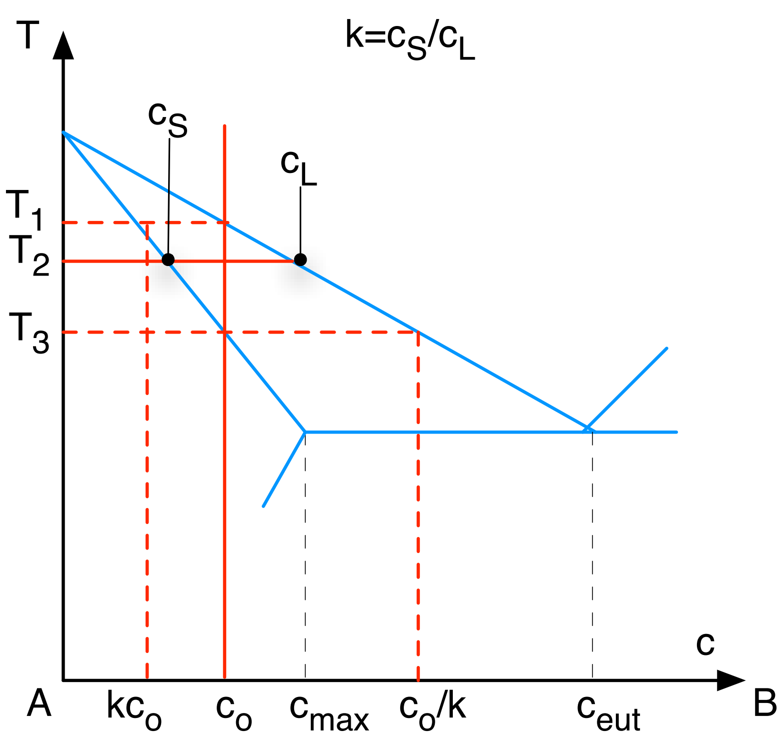
$$\Delta T_r = \frac{2\gamma T_m}{L_V r} \Rightarrow r^* = \frac{2\gamma T_m}{L_V \Delta T_r}$$

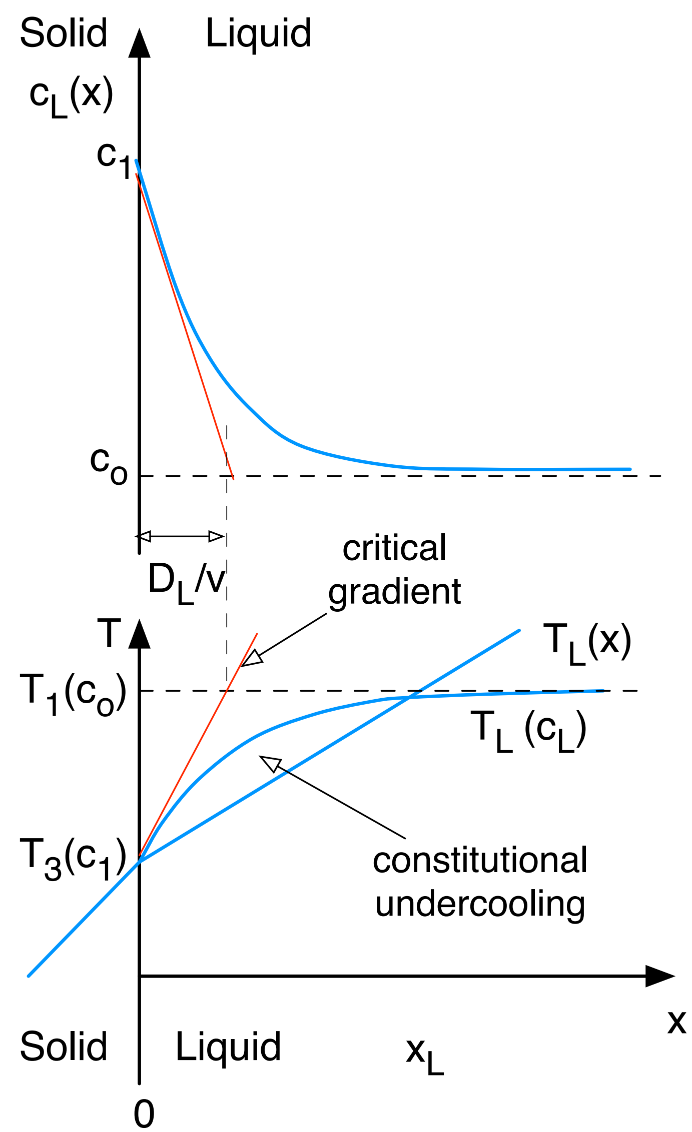
$$v \approx \frac{k_L}{L_V} \frac{1}{r}\left(1 - \frac{r^*}{r}\right)$$

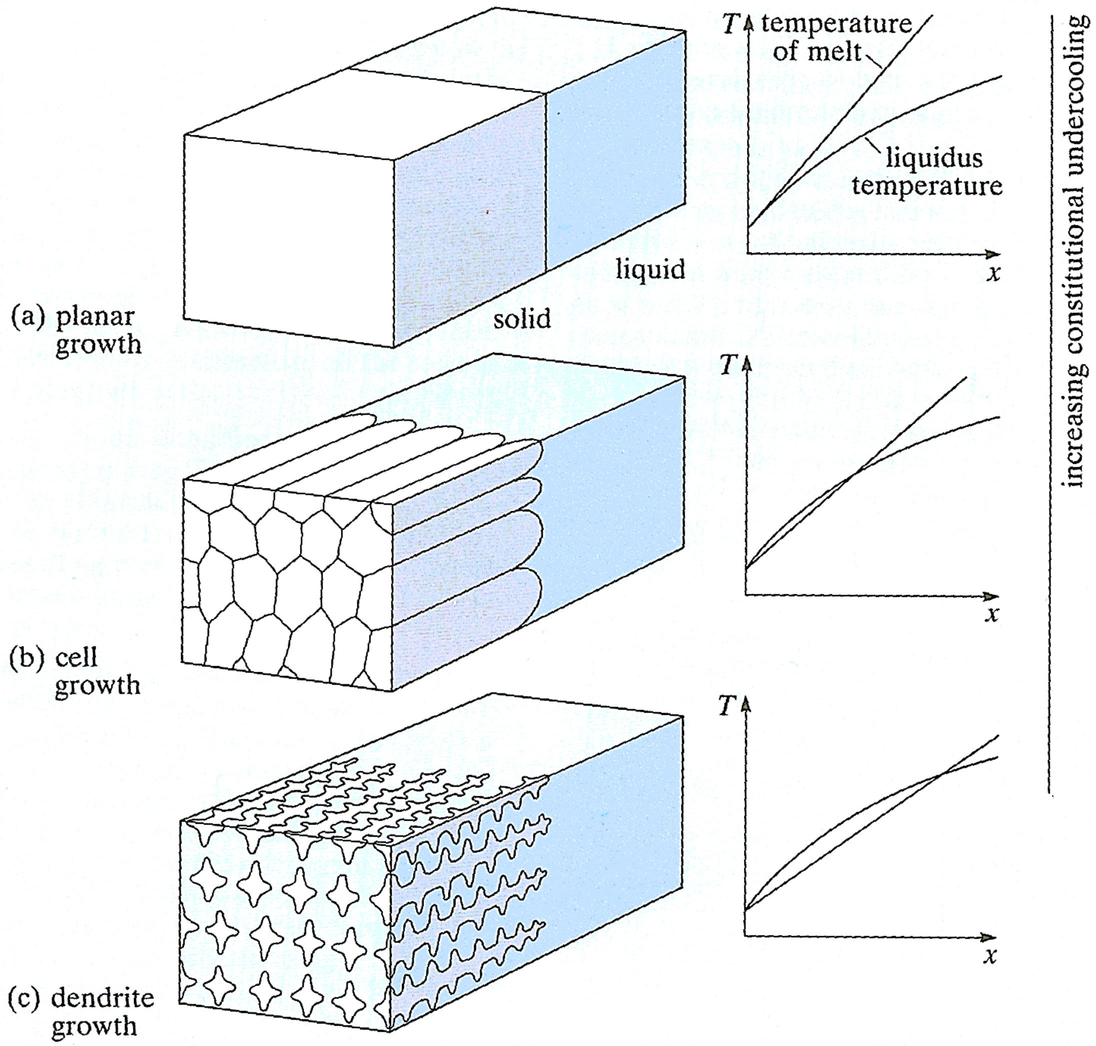
$$r = 2r^*$$

Alloy Solidification

Limited Diffusion in Solid and Liquid







Planar growth → cell growth → dendrite growth

⇑ no undercooling

⇑ moderate undercooling

⇑ strong undercooling

Summary

- By considering the balance between the release of free energy by transformation and the cost of creating new interface, the critical free energy for nucleation and the critical size of the nucleus can be derived.
- The exponential dependence of nucleation rate on undercooling means that, in effect, no nucleation will be observed until a minimum undercooling is achieved.
- The undercooling required for nucleation is increased by volume changes on transformation, but decreased by the availability of heterogeneous nucleation sites.

Units

- Consider the units of the various quantities that we have examined.
  - For driving force, the units are either Joules/mole (ΔGm) or Joules/m3 (ΔGv); dimensions = energy/mole, energy/volume.
  - For interfacial energy, the units are Joules/m2; dimensions = energy/area.
  - For critical radius, the units are m (or nm, to choose a more practical unit); dimensions = length.
  - For nucleation rate, the units are number/m3/s; dimensions are number/volume/ time.
  - For critical free energy, the units are Joules; dimensions are energy. What is less obvious is how to scale the energy against thermal energy. When one calculates a value for ΔG^*, the values turn out to be of the order of 10-19J, or 1eV. This is reasonable because we are calculating the energy associated with an individual cluster or embryonic nucleus, I.e. energies at the scale of atoms. Therefore the appropriate thermal energy is kT (not RT).
  - For the activation energy (enthalpy) of diffusion, in the equation for nucleation rate, the units depend on the source of the information. If the activation energy for diffusion is specified in Joules/mole, then the appropriate thermal energy is RT, for example.

Metal	Freezing Temp. (°C)	Latent Heat of fusion (J/cm3)	Surface enrgy (J/cm2)	Typical undercooling for Hv
Ga	30	488	56 10-7	76
Bi	271	543	54 10-7	90
Pb	327	237	33 10-7	80
Ag	962	965	126 10-7	250
Cu	1085	1628	177 10-7	236
Ni	1453	2756	255 10-7	480
Fe	1538	1737	204 10-7	420
N2O	0			40