Karlsruhe Institute of Technology

Institute for Applied Materials

Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
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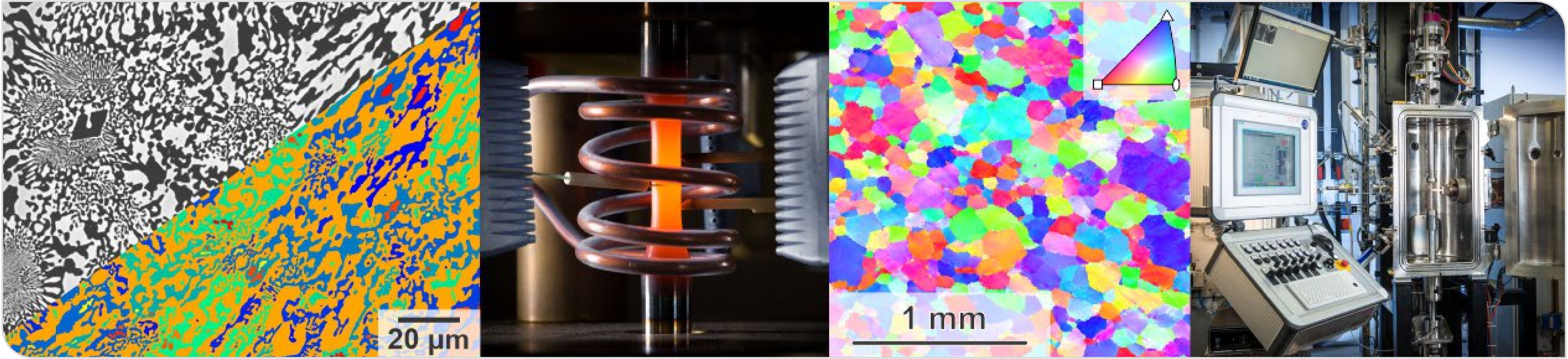


Topics

- Single-Component Systems
  - Solidification and Allotropic Transformations (Discontinuous)
    - Probability for Critical Nuclei
    - Temperature-Time Evolution
    - Nucleation & Growth as a Function of Time
    - Complications:
      - Anisotropic Surface/Interface Energies
      - Anisotropic Growth Rates
      - Heat Dissipation

Nucleation

- A nucleation rate η might be considered that describes the number of newly activated nuclei in a certain time and within a certain volume, e.g. with $[\eta] = \frac{1}{\mathrm{m}^3\ \mathrm{s}}$.
- Since the nucleation process is determined by fluctuations, an Arrhenius type probability might be assumed (similar to what we have done for diffusion in Ch. 1b):

$$\eta \propto \exp - \frac{\Delta G^{\mathrm{c}}}{k_{\mathrm{B}}\, T}$$

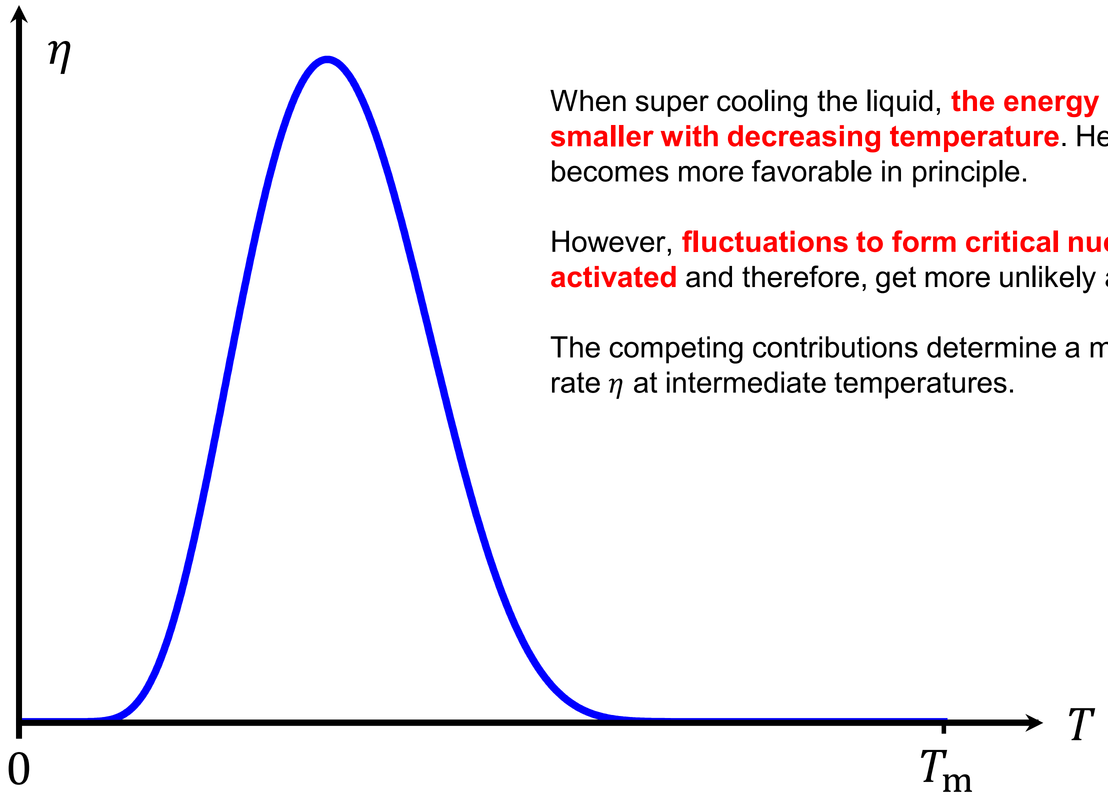
- In contrast to other thermally activated processes, the activation barrier changes strongly with temperature in case of solidification since:

$$\Delta G^{\mathrm{c}} \propto \frac{T_{\mathrm{m}}}{\Delta T^2}$$

- Hence, we obtain:

$$\eta \propto \exp - \frac{T_{\mathrm{m}}}{\Delta T^2\, T} = \exp - \frac{T_{\mathrm{m}}}{(T_{\mathrm{m}} - T)^2\, T}$$

Nucleation

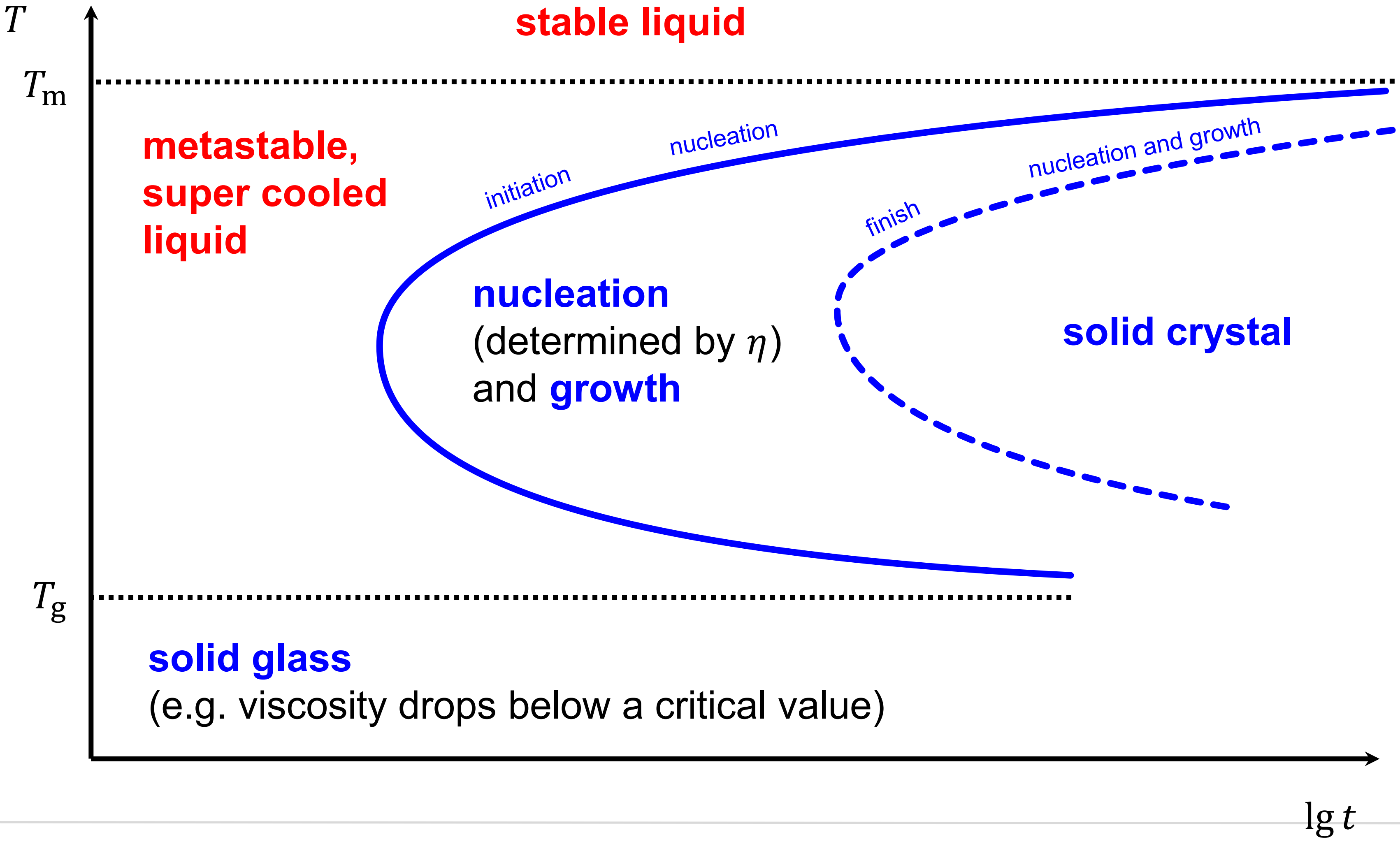


When super cooling the liquid, **the energy barrier ΔG^c gets smaller with decreasing temperature**. Hence, nucleation becomes more favorable in principle.

However, **fluctuations to form critical nuclei are thermally activated** and therefore, get more unlikely at low temperatures.

The competing contributions determine a maximum nucleation rate η at intermediate temperatures.

Time-Temperature-Transformation



Nucleation & Growth

- Simplified conditions of linear isothermal growth might be assumed in the following.
- **The growth occurs homogenous and isotropic at linear growth rate v** with $[v] = \mathrm{m/s}$.
- **A nucleation rate η is considered constant.**
- In a short period of time $\mathrm{d}\tau$:
  - The number of newly formed nuclei is $N = V\,\eta\,\mathrm{d}\tau$.
  - The existing nuclei grow by $\mathrm{d}R = v\,\mathrm{d}\tau$ to a radius of $R = v\,(t-\tau)$ when nucleation took place at time τ.
  - The total volume is then:

$$V^{\mathrm{S}} = \int_0^t \mathrm{d}V^{\mathrm{S}} = \int_0^t \frac{4}{3}\pi\,v^3\,(t-\tau)^3\,V\,\eta\,\mathrm{d}\tau = \frac{4}{3}\pi\,v^3\,V\,\eta \int_0^t (t-\tau)^3\,\mathrm{d}\tau = \frac{4}{3}\pi\,v^3\,V\,\eta\left[-\frac{1}{4}(t-\tau)^4\right]_0^t = \frac{\pi}{3}\,v^3\,V\,\eta\,t^4$$

  - Since the growth of the solid occurs free in the liquid, the volume fraction during isothermal solidification can thus be approximated by:

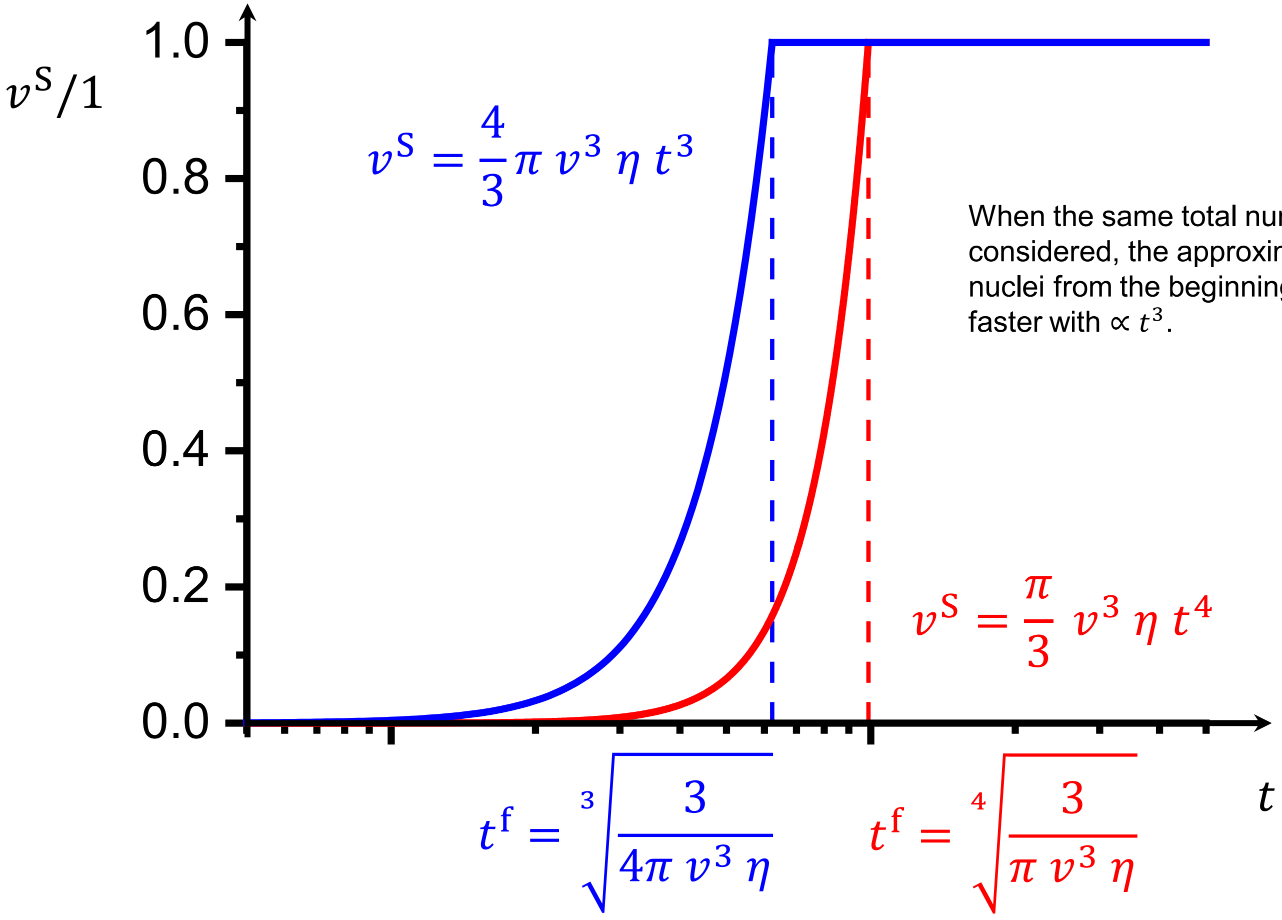
$$v^{\mathrm{S}} = \frac{V^{\mathrm{S}}}{V} = \frac{\pi}{3}\,v^3\,\eta\,t^4$$
$$v^{\mathrm{L}} = 1 - v^{\mathrm{S}}$$

Nucleation & Growth

- When all nucleation sites are activated from the beginning:
  - $N = V\,\eta = \text{const.}$ (note that $[\eta] = \frac{1}{\text{m}^3}$) and $R = v\,t$
  - The volume fraction of the solid is:

$$v^{\text{S}} = \frac{V^{\text{S}}}{V} = \frac{4}{3}\pi\,v^3\,\eta\,t^3$$
$$v^{\text{L}} = 1 - v^{\text{S}}$$

Nucleation & Growth



$$v^{\mathrm{S}} = \frac{4}{3}\pi\, v^3\, \eta\, t^3$$

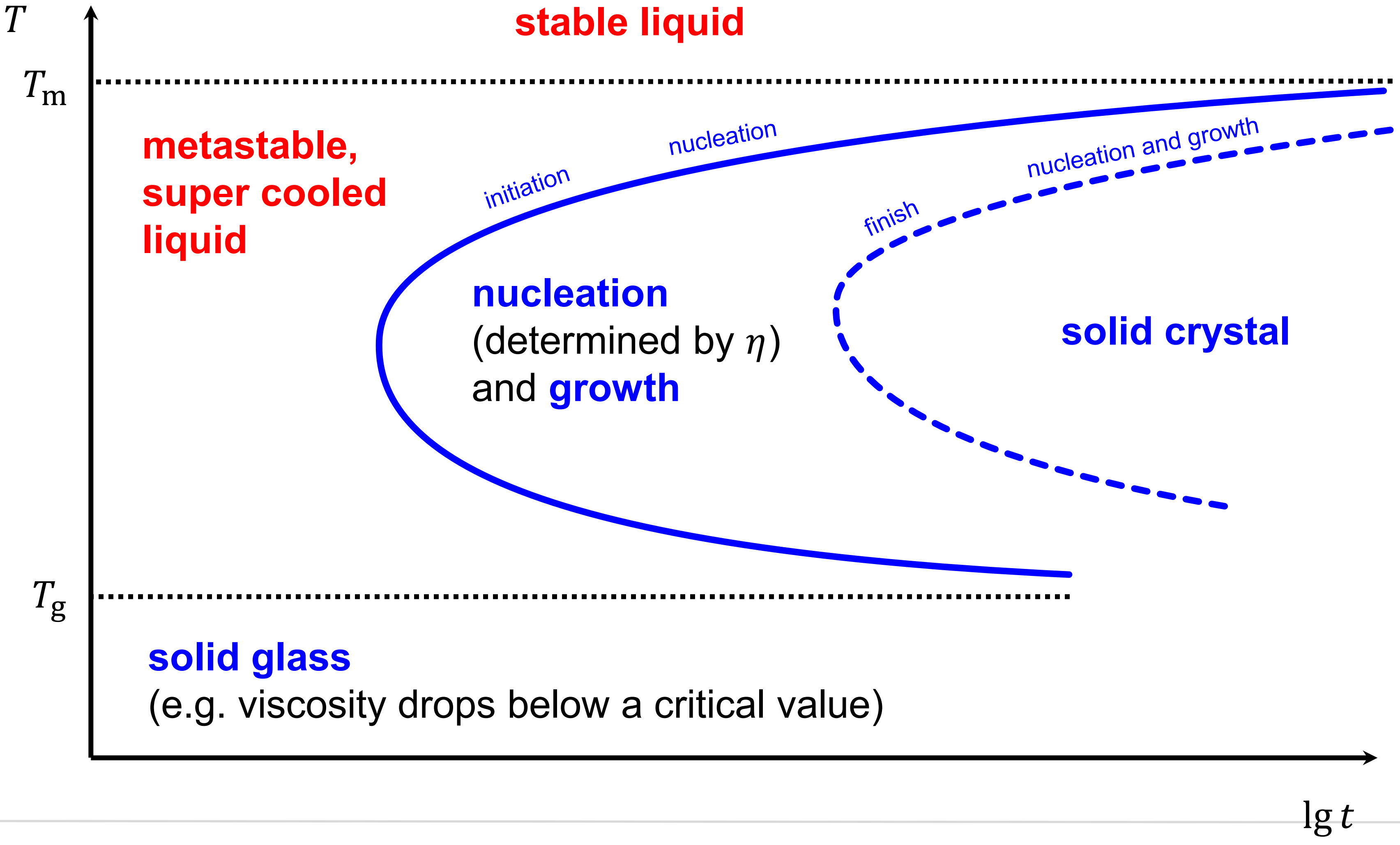
$$v^{\mathrm{S}} = \frac{\pi}{3}\, v^3\, \eta\, t^4$$

$$t^{\mathrm{f}} = \sqrt[3]{\frac{3}{4\pi\, v^3\, \eta}}$$

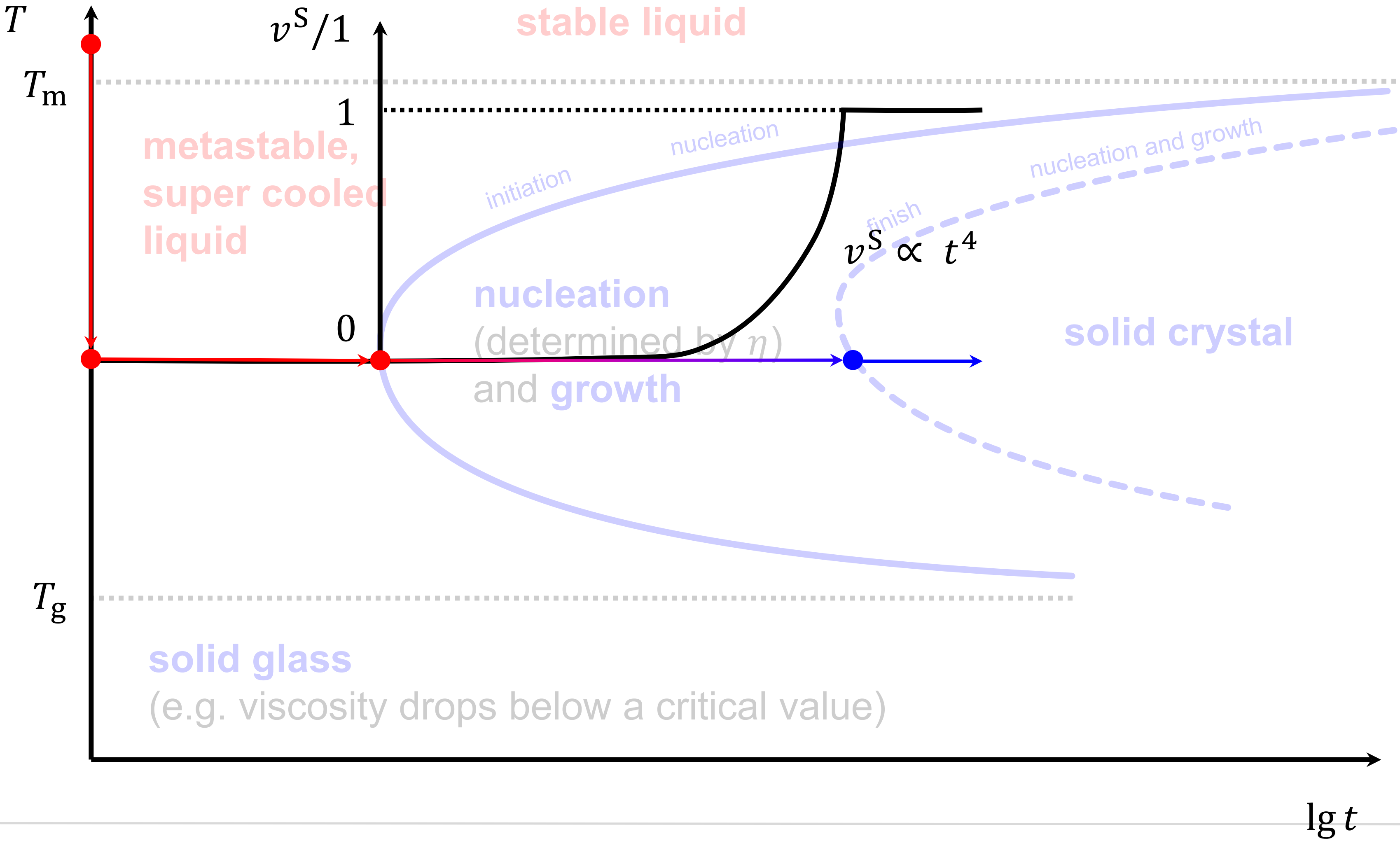
$$t^{\mathrm{f}} = \sqrt[4]{\frac{3}{\pi\, v^3\, \eta}}$$

When the same total number of nuclei is considered, the approximation with active nuclei from the beginning proceeds of course faster with $\propto t^3$.

Time-Temperature-Transformation



Time-Temperature-Transformation

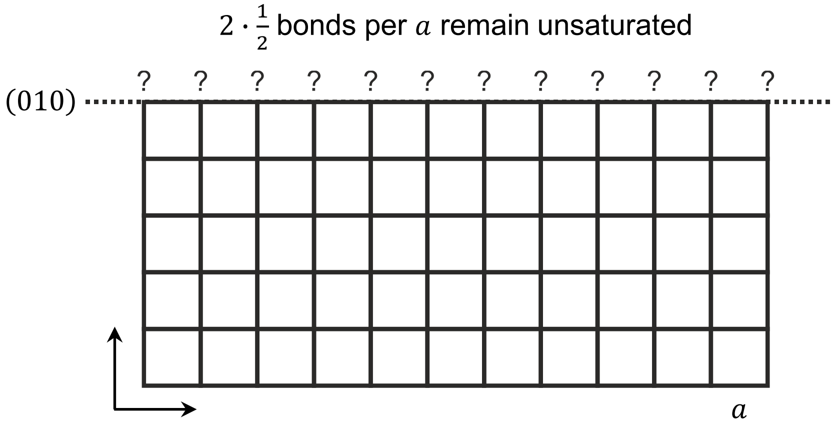


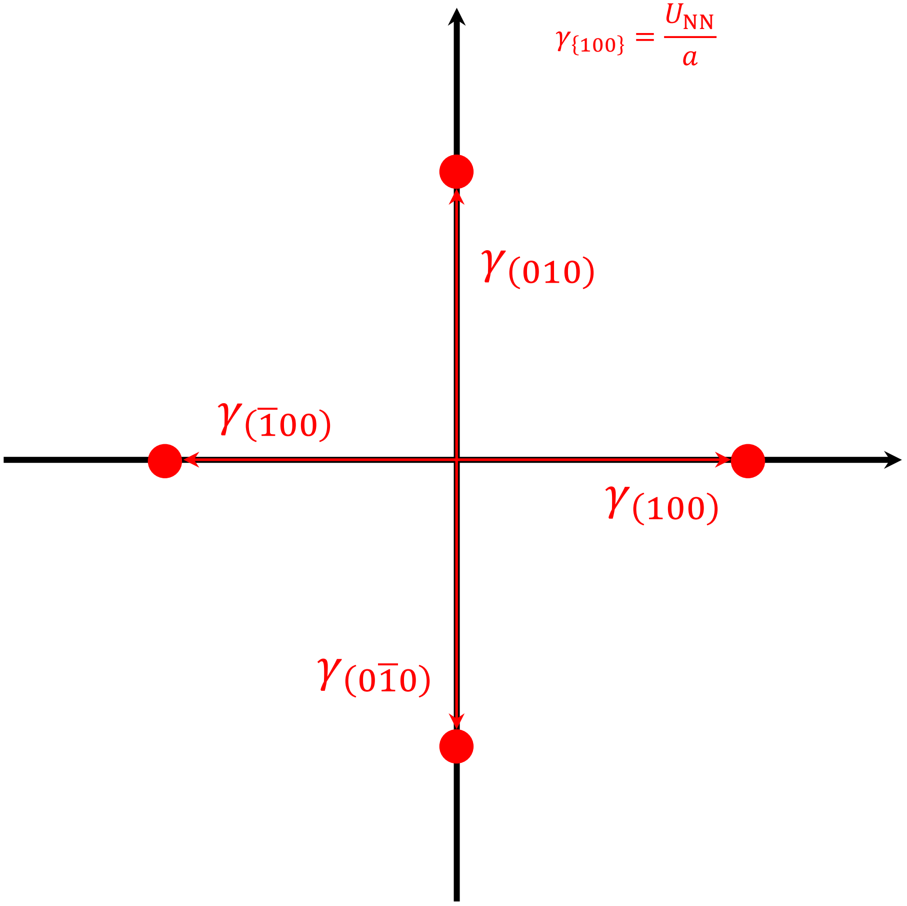
Intricacies

- In reality, several intricacies occur leading to deviations from the simple considerations shown on the slides before:
  - (facet energy) In general, surface/interface energies of crystals are anisotropic. The magnitude of γ varies depending on the surface/interface facet under consideration.
  - (facet growth) The growth of these facets during solidification also occurs anisotropic. Hence, a competition between differently fast growing facets is to be considered.
  - (heat transfer) Finally, solidification (and other transformations) releases heat. Hence, in order to maintain the melting/freezing temperature at the solidification front, the heat dissipation needs to be considered as important factor for the growth of the solid.

Anisotropic Surface/Interface Energy

- The surface energies of crystals are dominated by unsaturated bonds.
- If we assume a simple 2D cubic crystal where only NN interactions of the binding energy U_{NN} are considered (Kossel crystal), the surface energies are:

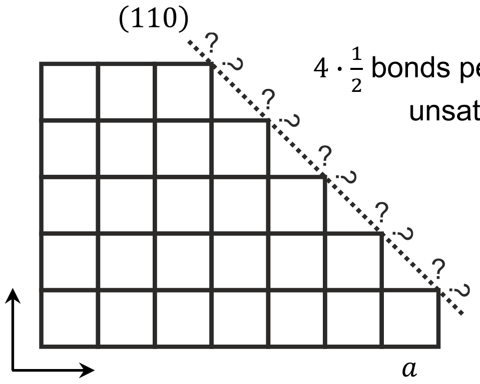




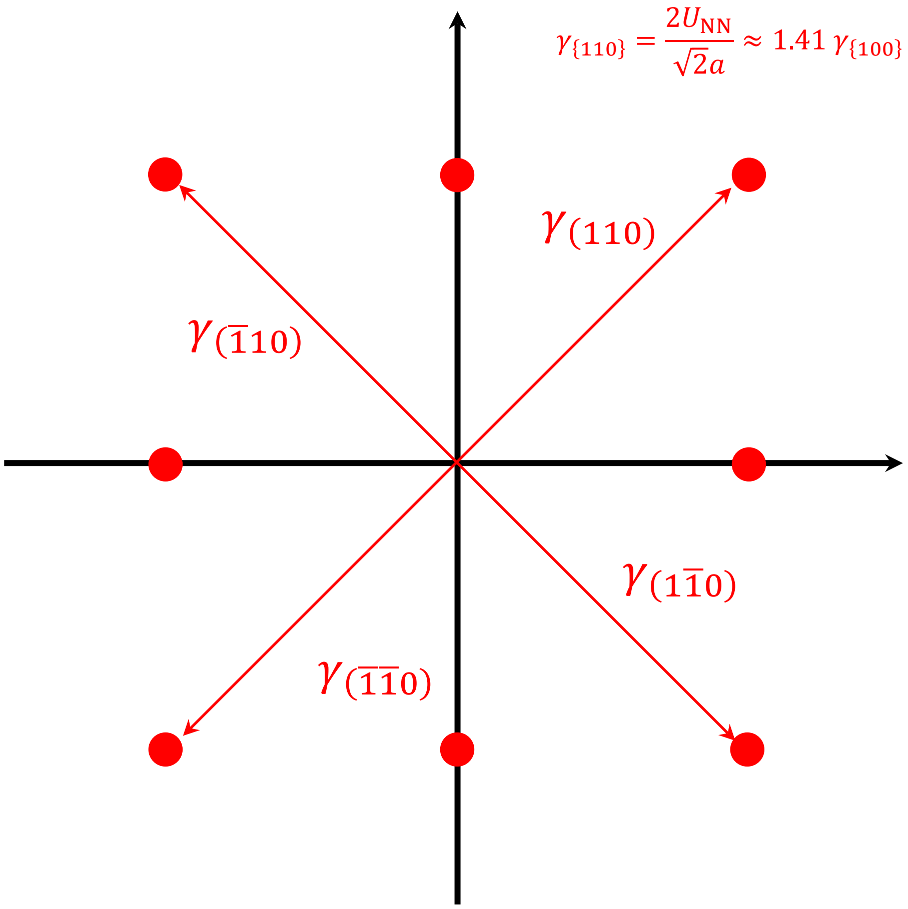
lowest surface energy (smallest number of unsaturated bonds per unit length surface)

Anisotropic Surface/Interface Energy

- The surface energies of crystals are dominated by unsaturated bonds.
- If we assume a simple 2D cubic crystal where only NN interactions of the binding energy U_{NN} are considered (Kossel crystal), the surface energies are:



$4 \cdot \frac{1}{2}$ bonds per $\sqrt{2}a$ remain unsaturated



$$\gamma_{\{110\}} = \frac{2U_{\mathrm{NN}}}{\sqrt{2}a} \approx 1.41\,\gamma_{\{100\}}$$

maximum surface energy (largest number of unsaturated bonds per unit length surface)

Anisotropic Surface/Interface Energy

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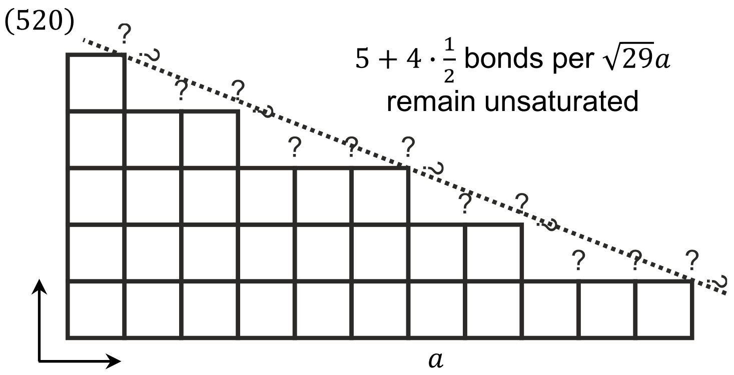
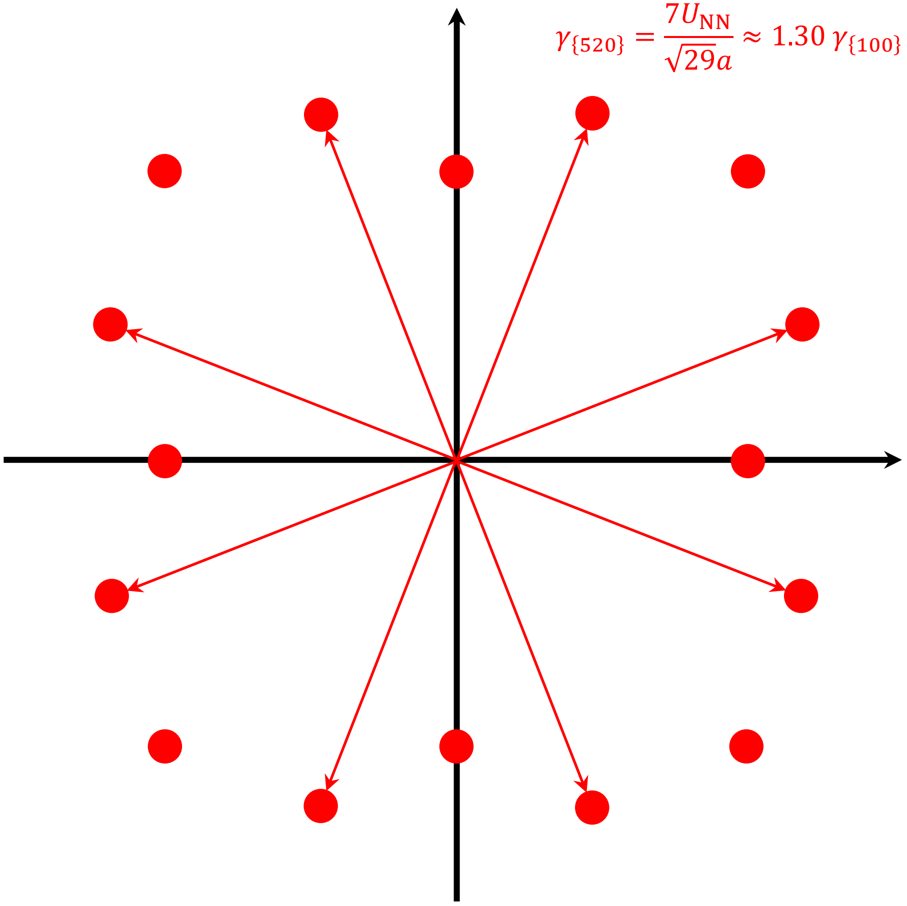


$5 + 4 \cdot \frac{1}{2}$ bonds per $\sqrt{29}a$
remain unsaturated

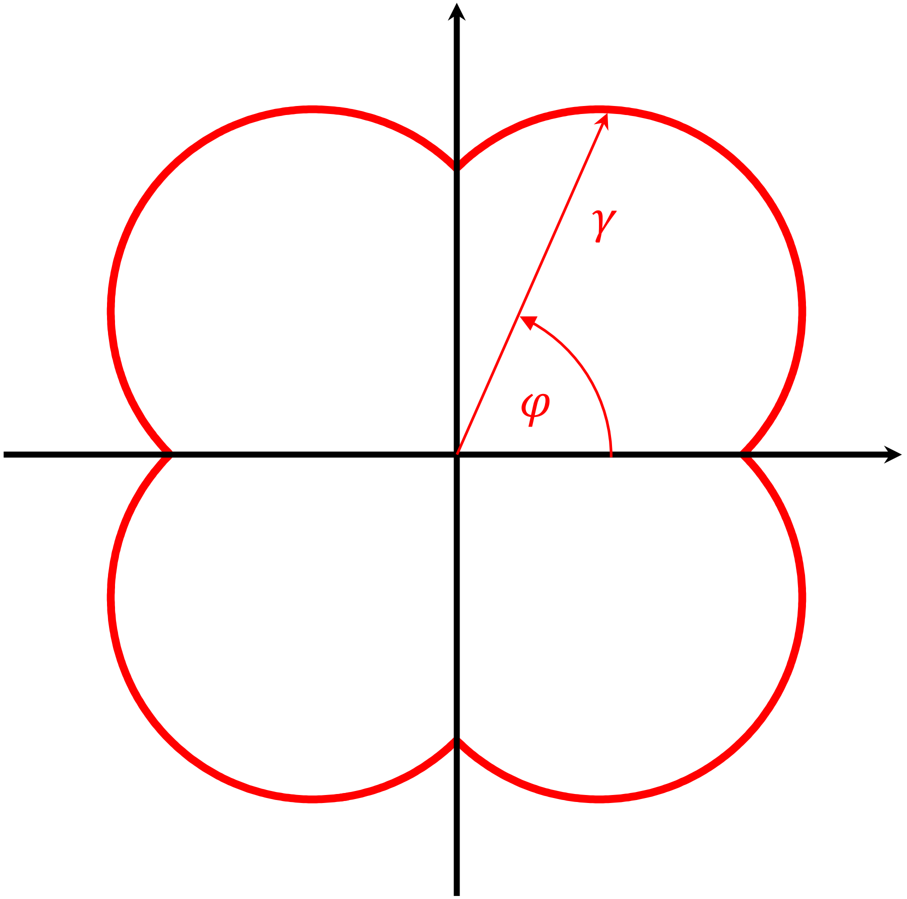


$$\gamma_{\{520\}} = \frac{7U_{\mathrm{NN}}}{\sqrt{29}a} \approx 1.30\,\gamma_{\{100\}}$$

intermediate surface energy

Anisotropic Surface/Interface Energy

- The surface energies of crystals are dominated by unsaturated bonds.
- If we assume a simple 2D cubic crystal where only NN interactions of the binding energy U_{NN} are considered (Kossel crystal), the surface energies are:



$$\gamma = \frac{U_{\mathrm{NN}}}{a}\left(|\sin\varphi| + |\cos\varphi|\right)$$

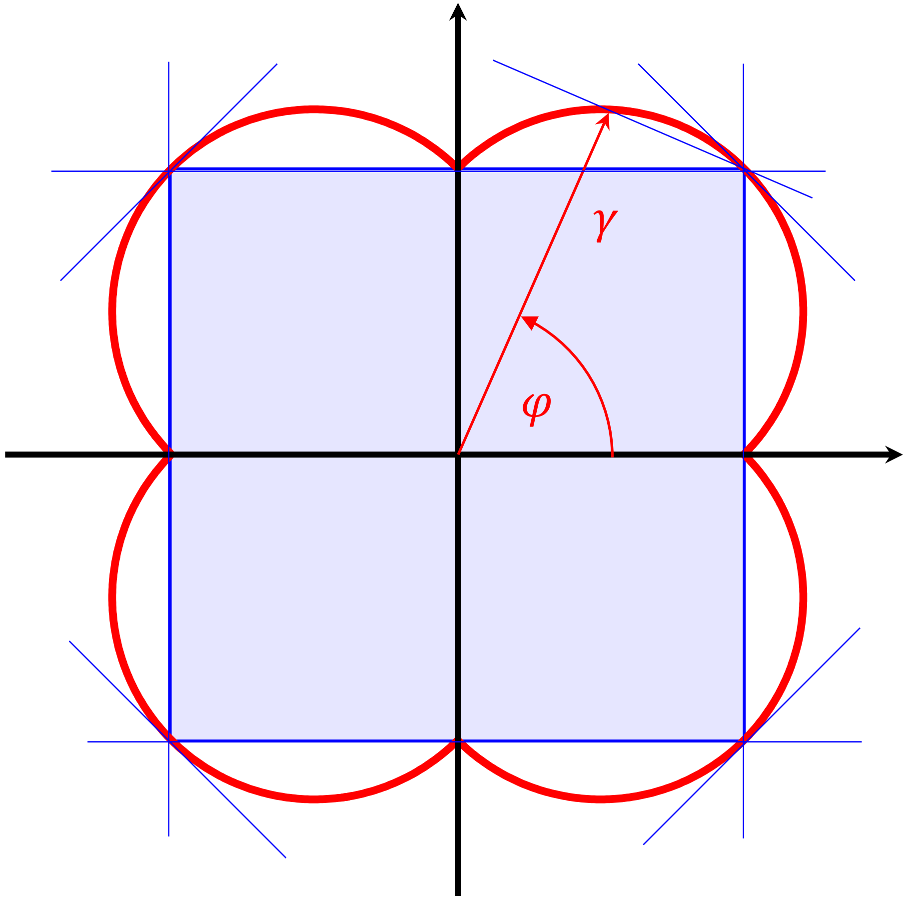
Wulff's Construction

- The equilibrium shape of a crystal is given by a minimum excess Gibbs free energy ΔG:

$$\Delta G = \sum_f \gamma_f \, A_f$$

- f are the different facets of the crystal, γ_f the surface/interface energies of the facets, and A_f the areas of these facets.
- The geometry with minimum excess energy is found by performing Wulff's construction:
    - Determine all perpendicular planes for each connection line of the origin to the $\gamma(\varphi)$ function.
    - The inner envelope of these planes are the equilibrium shape.

$$\gamma = \frac{U_{\mathrm{NN}}}{a}\left(|\sin\varphi| + |\cos\varphi|\right)$$



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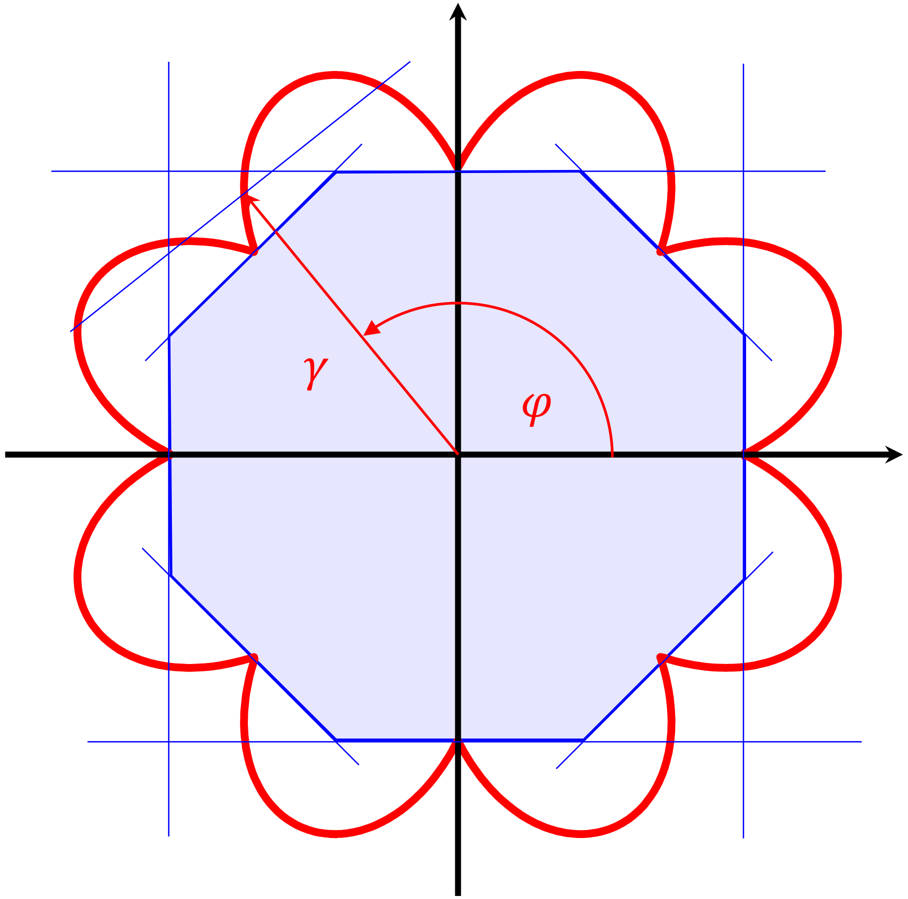
  - The inner envelope of these planes are the equilibrium shape.

$$\gamma = \frac{U_{\mathrm{NN}}}{a}(|\sin 2\varphi| + |\cos 2\varphi|)$$



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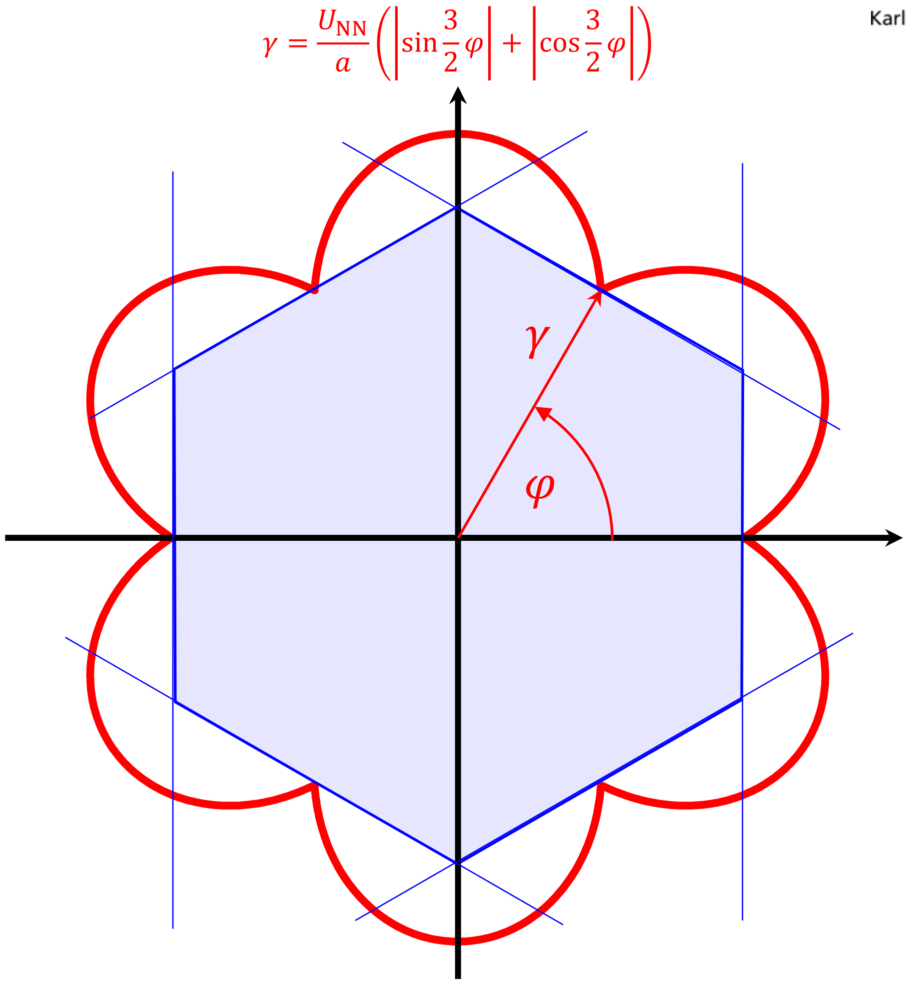
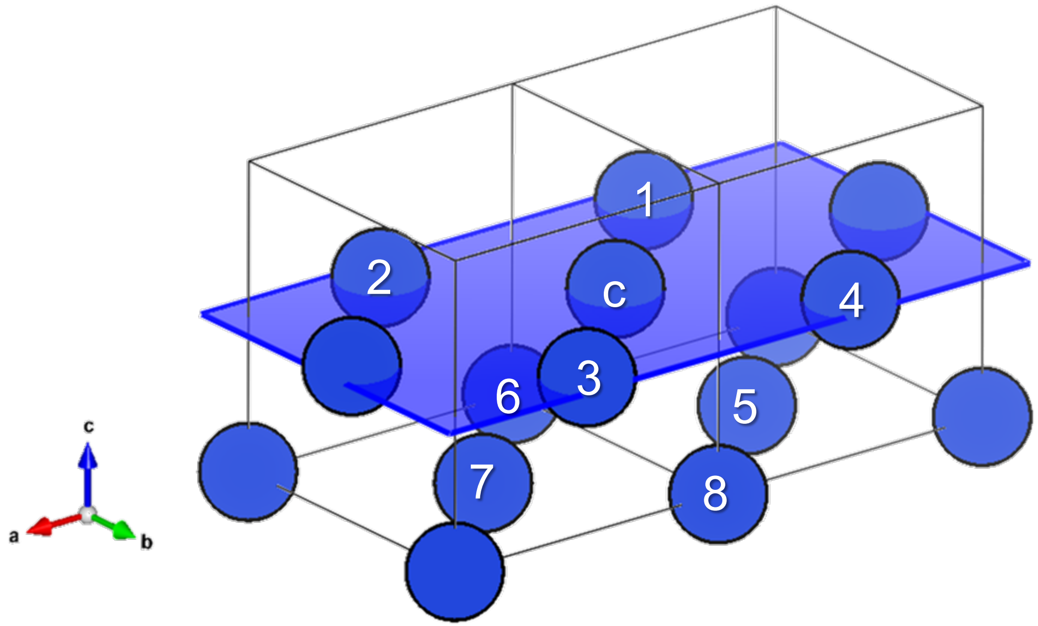


Wulff's Construction

- Cu prototype structure (fcc, A2)

- Area: $A_{\{100\}} = a^2$
- No. of atoms: $N_{\{100\}} = 1 + 2 \cdot \frac{1}{2} = 2$
- Energy of broken NN bonds:

$$U_{\text{broken}} = (12 - 8)U_{\text{NN}}$$

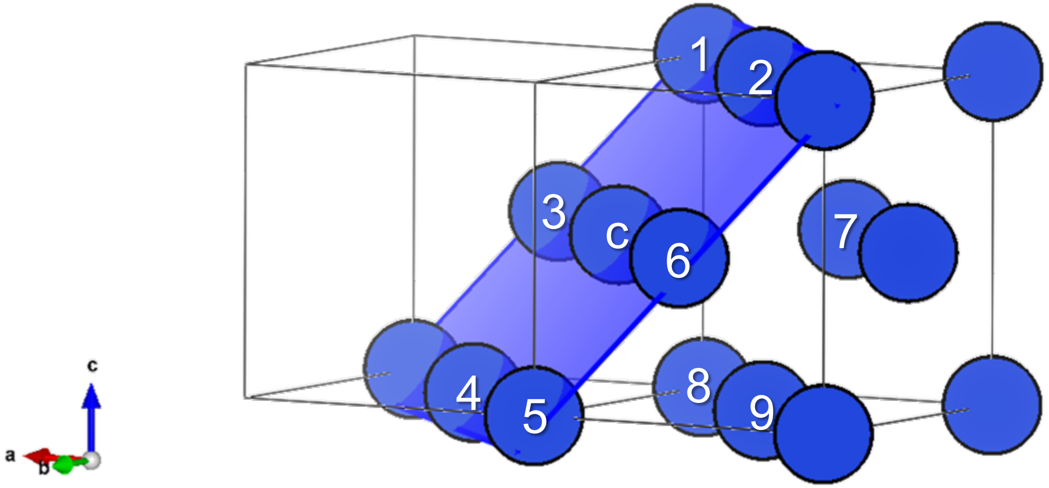


$$\gamma_{\{100\}} = \frac{N_{\{100\}}\, U_{\text{broken}}}{A_{\{100\}}} = 8\,\frac{U_{\text{NN}}}{a^2}$$

Wulff’s Construction

- Cu prototype structure (fcc, A2)

- Area: $A_{\{111\}} = \sqrt{\frac{3}{2}}a \cdot \frac{\sqrt{2}}{2}a = \frac{\sqrt{3}}{2}a^2$
- No. of atoms: $N_{\{111\}} = 3 \cdot \frac{1}{2} + 3 \cdot \frac{1}{6} = 2$
- Energy of broken NN bonds:
  $$(12 - 9)U_{\mathrm{NN}}$$



$$\gamma_{\{111\}} = \frac{12}{\sqrt{3}}\frac{U_{\mathrm{NN}}}{a^2} \approx 6.93\frac{U_{\mathrm{NN}}}{a^2}$$

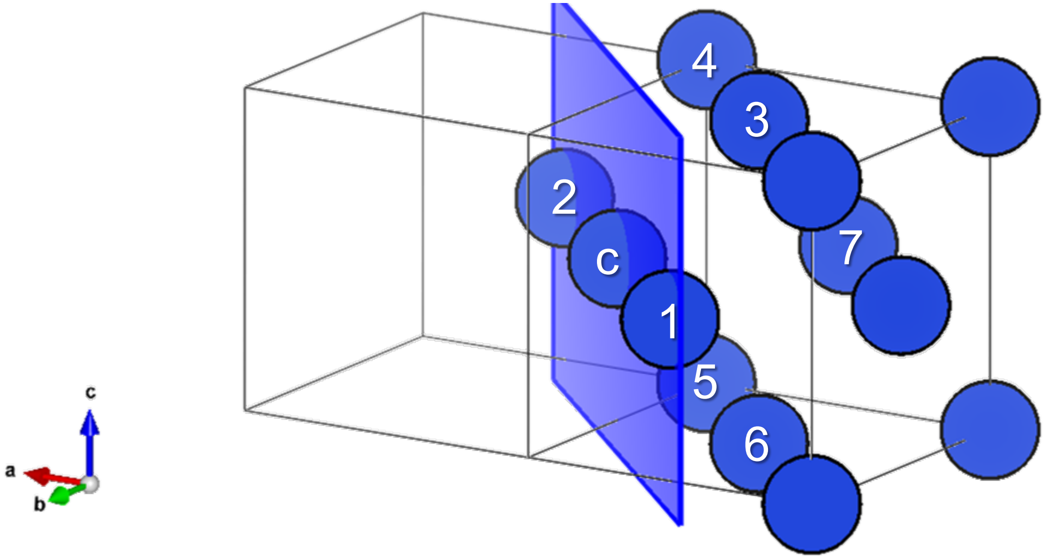
Wulff's Construction

- Cu prototype structure (fcc, A2)

- Area: $A_{\{110\}} = \sqrt{2}a \cdot a = \sqrt{2}a^2$
- No. of atoms: $N_{\{111\}} = 2 \cdot \frac{1}{2} + 4 \cdot \frac{1}{4} = 2$
- Energy of broken NN bonds:

$$(12 - 7)U_{\mathrm{NN}} + 1U_{\mathrm{NN}}$$

$$\gamma_{\{110\}} = \frac{12}{\sqrt{2}} \frac{U_{\mathrm{NN}}}{a^2} \approx 8.49 \frac{U_{\mathrm{NN}}}{a^2}$$



Wulff's Construction

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- Area: $A_{\{110\}} = \sqrt{2}a \cdot a = \sqrt{2}a^2$
- No. of atoms: $N_{\{111\}} = 2 \cdot \frac{1}{2} + 4 \cdot \frac{1}{4} = 2$
- Energy of broken NN bonds:

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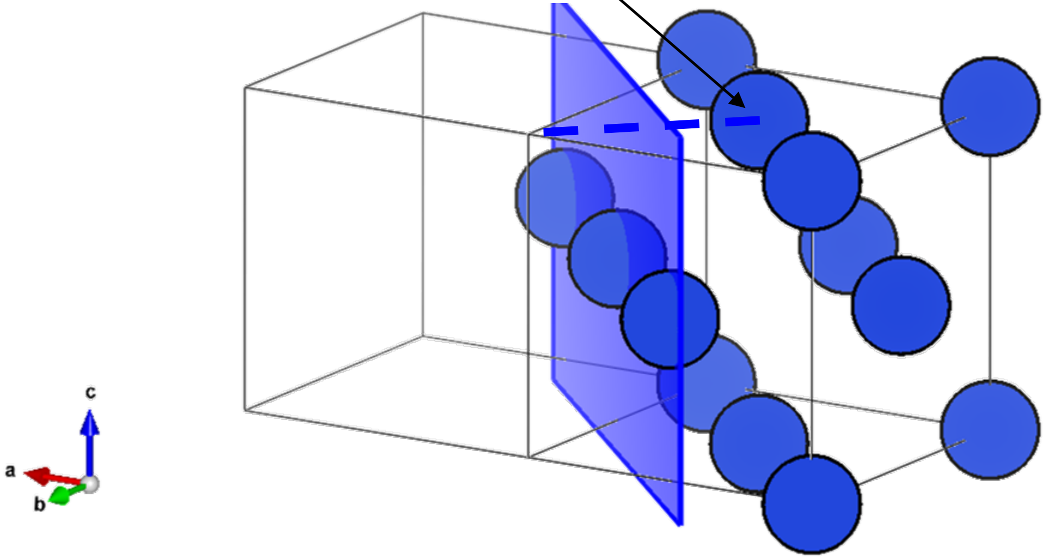
$$\gamma_{\{110\}} = \frac{12}{\sqrt{2}}\frac{U_{\mathrm{NN}}}{a^2} \approx 8.49\frac{U_{\mathrm{NN}}}{a^2}$$

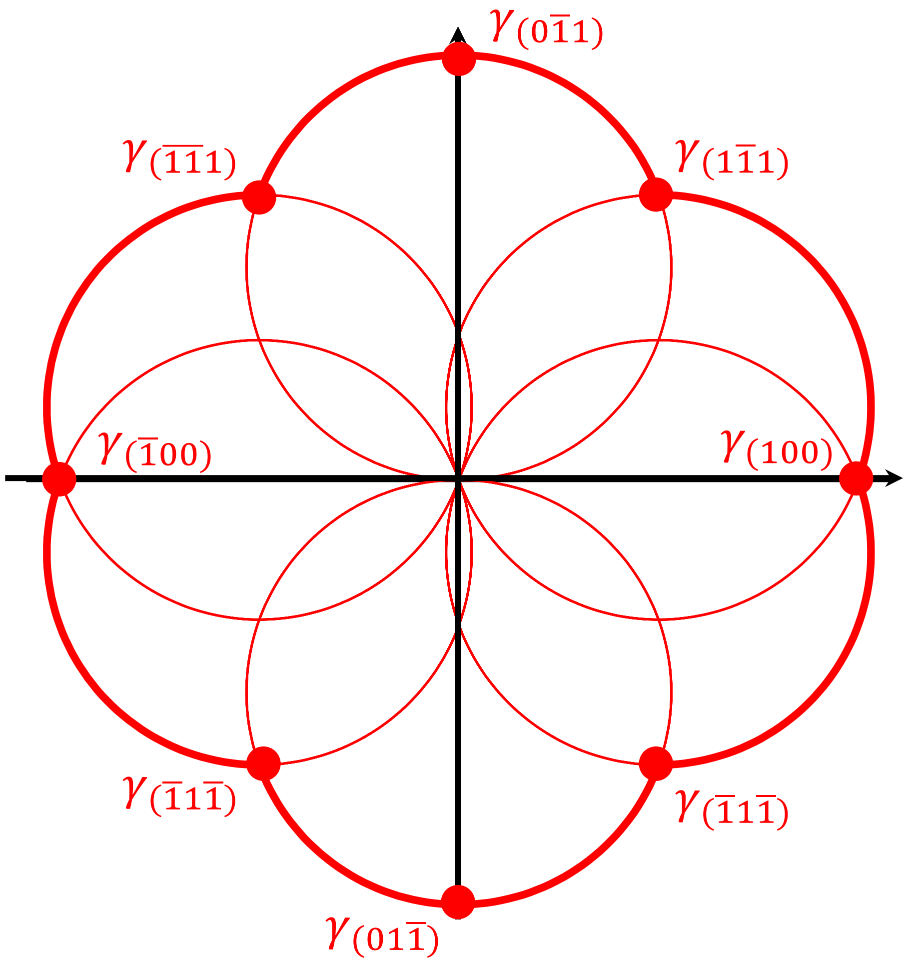


Note that these sub-surface atoms also contribute with 1 broken NN bond per unit cell of the surface facet!

Wulff’s Construction

- Cu prototype structure (fcc, A2)

$$\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$$

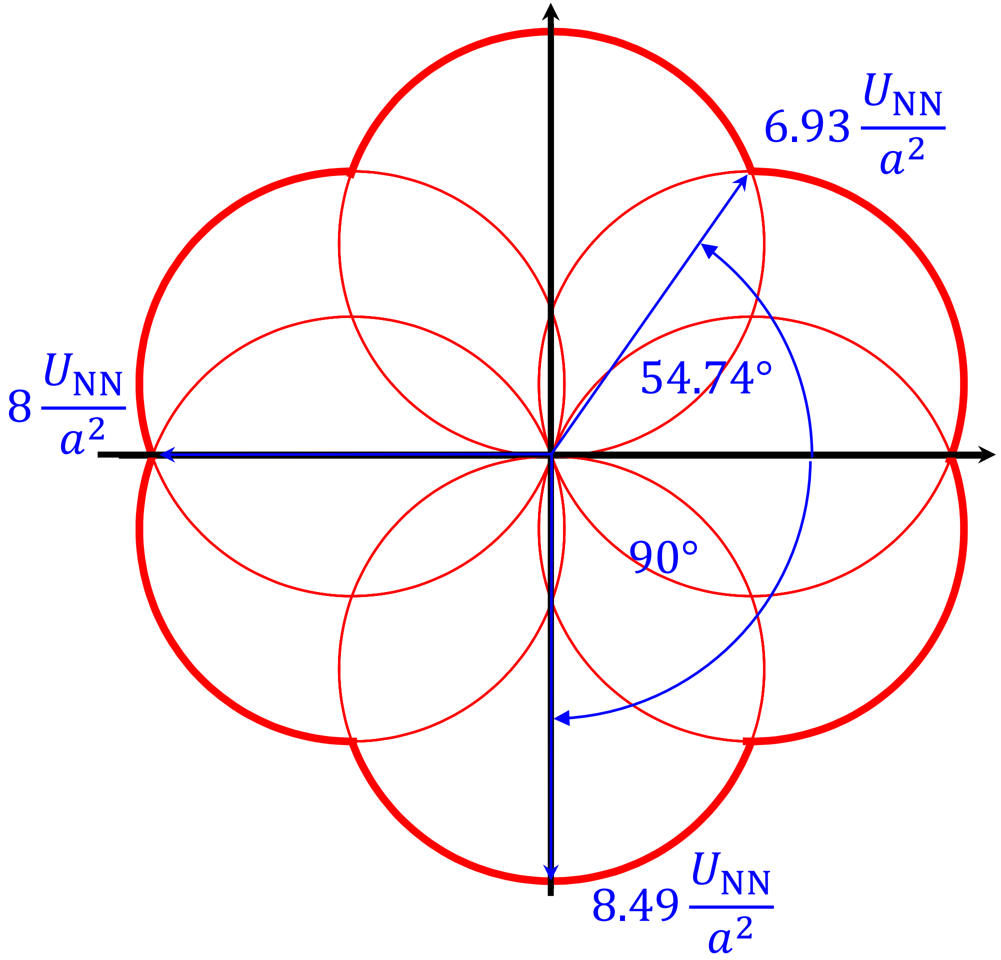


intersection along (011)

Wulff’s Construction

- Cu prototype structure (fcc, A2)

$\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$

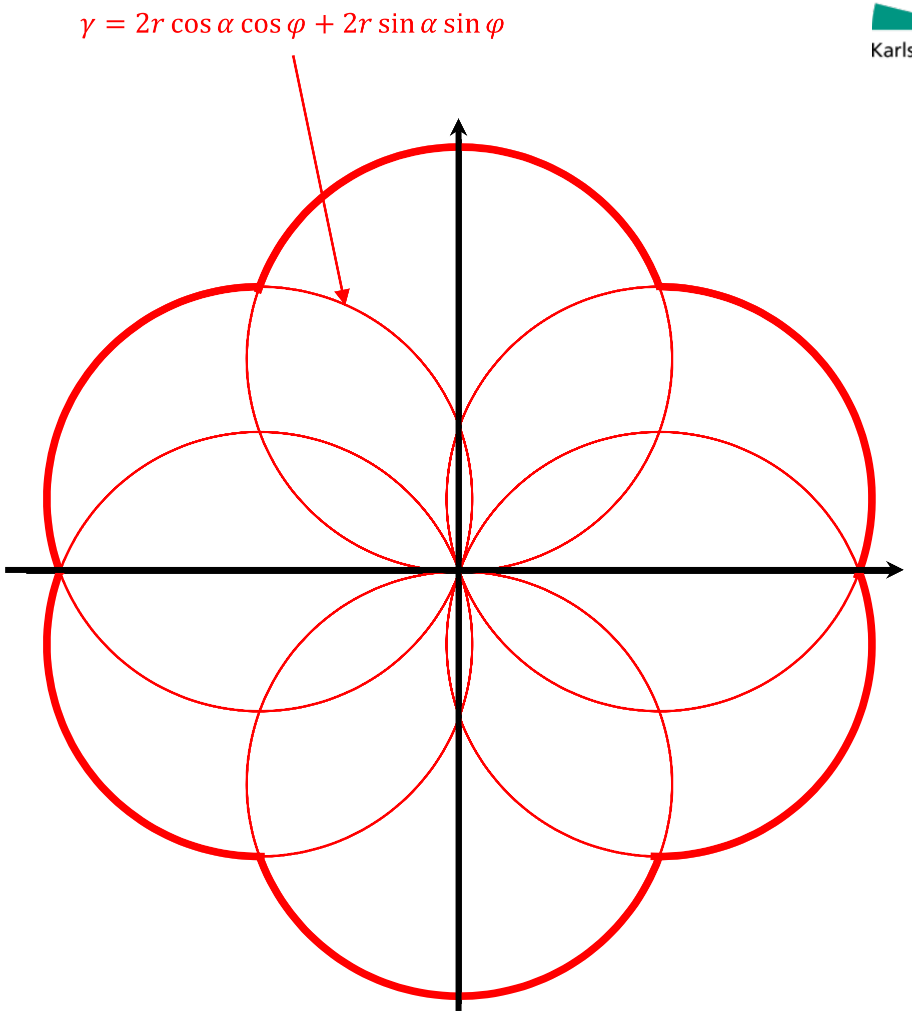


intersection along (011)

Wulff's Construction

- Cu prototype structure (fcc, A2)

$$\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$$



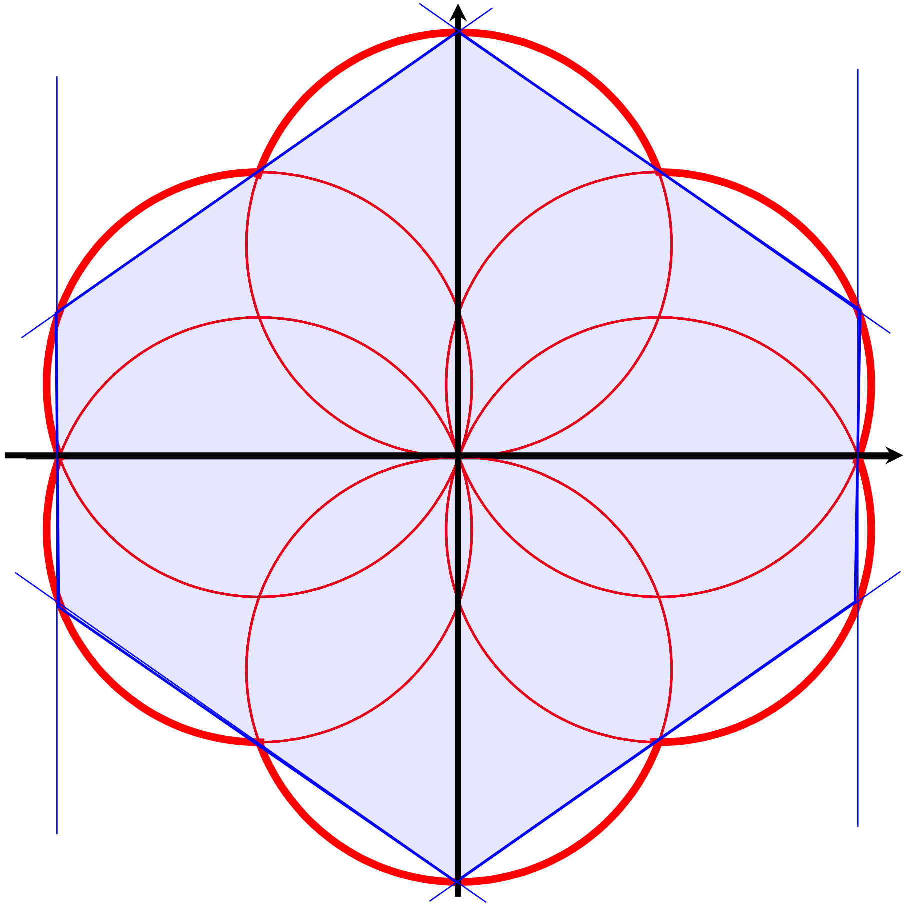
intersection along (011)

Wulff’s Construction

- Cu prototype structure (fcc, A2)

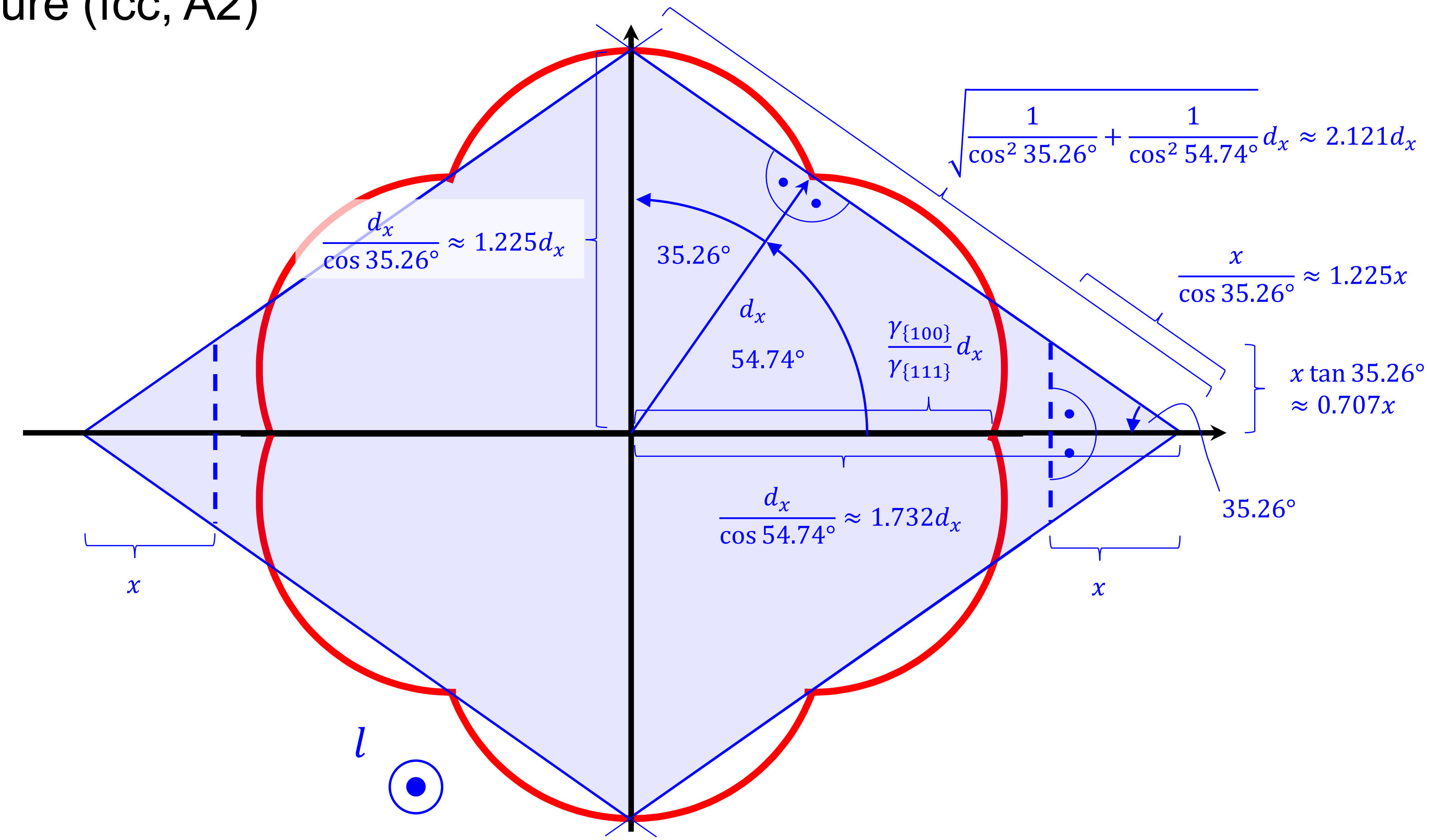
$\gamma_{\{110\}} > \gamma_{\{100\}} > \gamma_{\{111\}}$

only {111} and {100} facets



Wulff’s Construction

- Cu prototype structure (fcc, A2)



Wulff’s Construction

- Cu prototype structure (fcc, A2)
- Total interface/surface energy:

$$\Delta G = \sum\nolimits_f \gamma_f\, A_f \approx 4l\left(\gamma_{\{111\}}(2.121 d_x - 1.225x) + \gamma_{\{100\}}\, 0.707x\right)$$

$$= 4\,\gamma_{\{111\}}\, l\left(2.121 d_x + \left(1.225\ - 0.707\frac{\gamma_{\{100\}}}{\gamma_{\{111\}}}\right)x\right)$$

$$= 4\,\gamma_{\{111\}}\, l\, d_0\left(2.121\sqrt{1 + 0.333\left(\frac{x}{d_0}\right)^2} + \left(1.225\ - 0.707\frac{\gamma_{\{100\}}}{\gamma_{\{111\}}}\right)\frac{x}{d_0}\right)$$

- Constant volume $V_0 = V_x$:

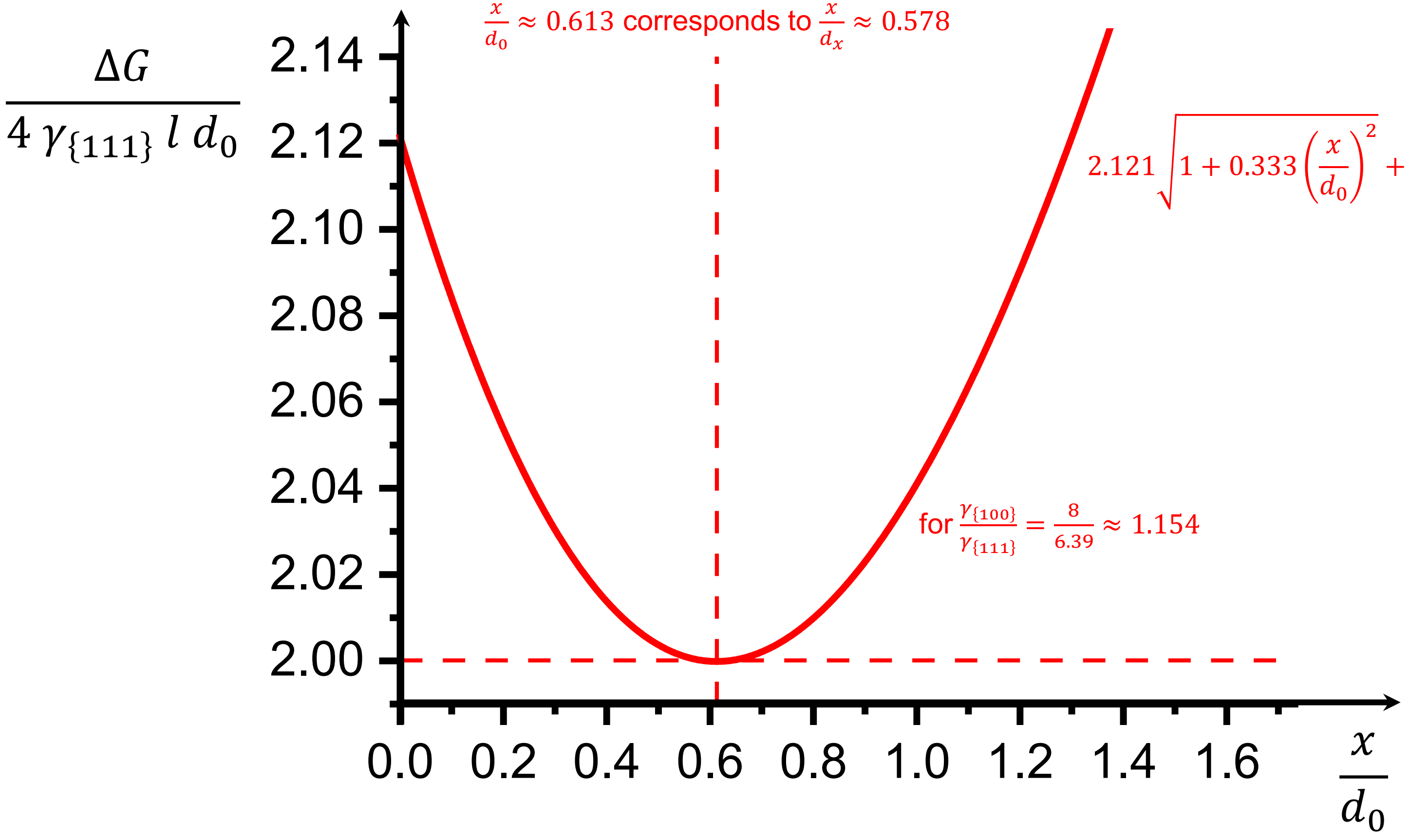
$$V_0 \approx 4l\left(\frac{1}{2}1.732 d_0 \cdot 1.225 d_0\right) = 4l \cdot 1.061 d_0$$

$$V_x \approx 4l\, d_x^2\left(1.061 - 0.353\left(\frac{x}{d_x}\right)^2\right)$$

$$d_x = d_0\sqrt{1 + 0.333\left(\frac{x}{d_0}\right)^2}$$

Wulff’s Construction

- Cu prototype structure (fcc, A2)



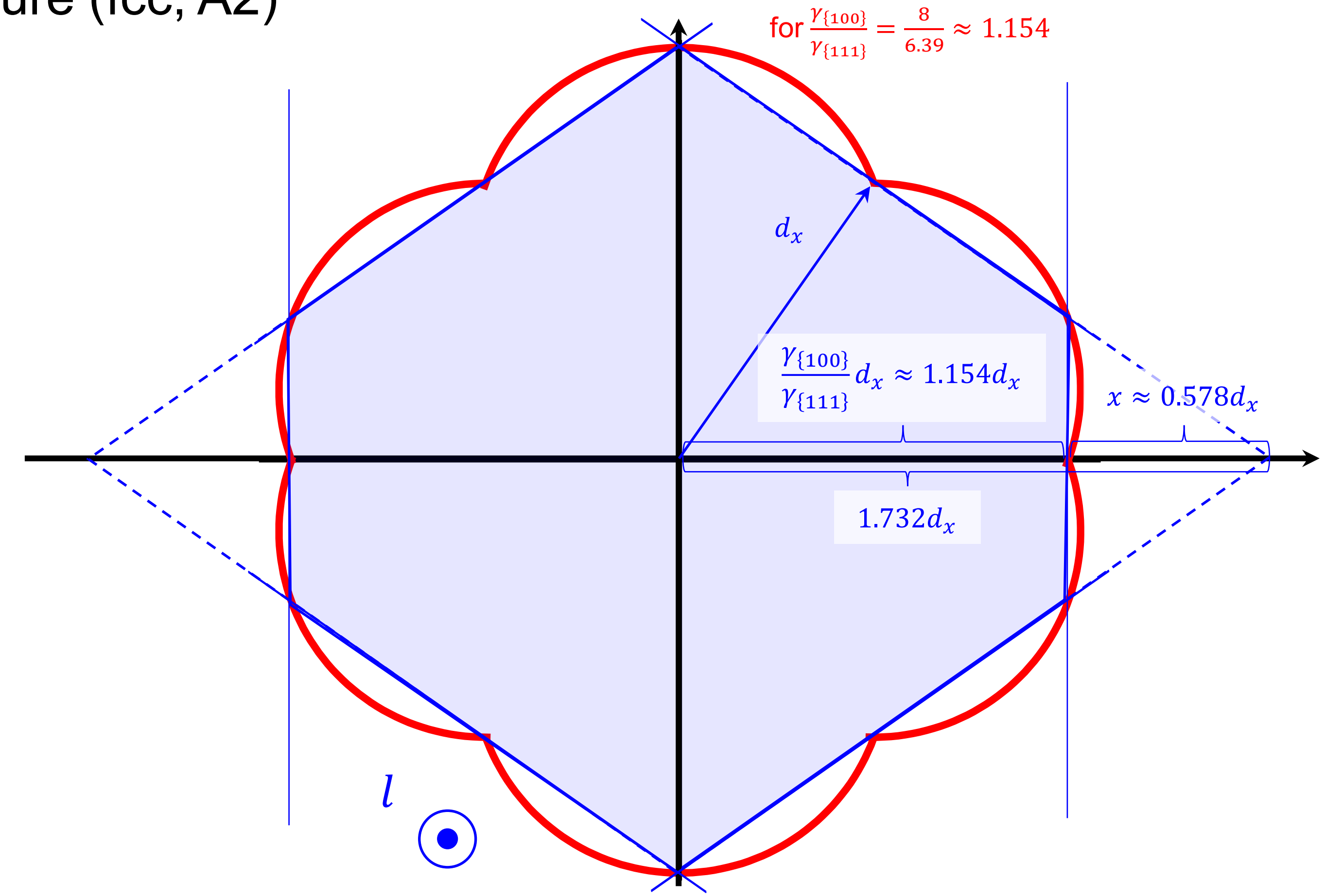
Minimum total surface/interface energy is observed at $\frac{x}{d_0} \approx 0.613$ corresponds to $\frac{x}{d_x} \approx 0.578$

$$2.121\sqrt{1+0.333\left(\frac{x}{d_0}\right)^2}+\left(1.225-0.707\frac{\gamma_{\{100\}}}{\gamma_{\{111\}}}\right)\frac{x}{d_0}$$

for $\frac{\gamma_{\{100\}}}{\gamma_{\{111\}}} = \frac{8}{6.39} \approx 1.154$

Wulff’s Construction

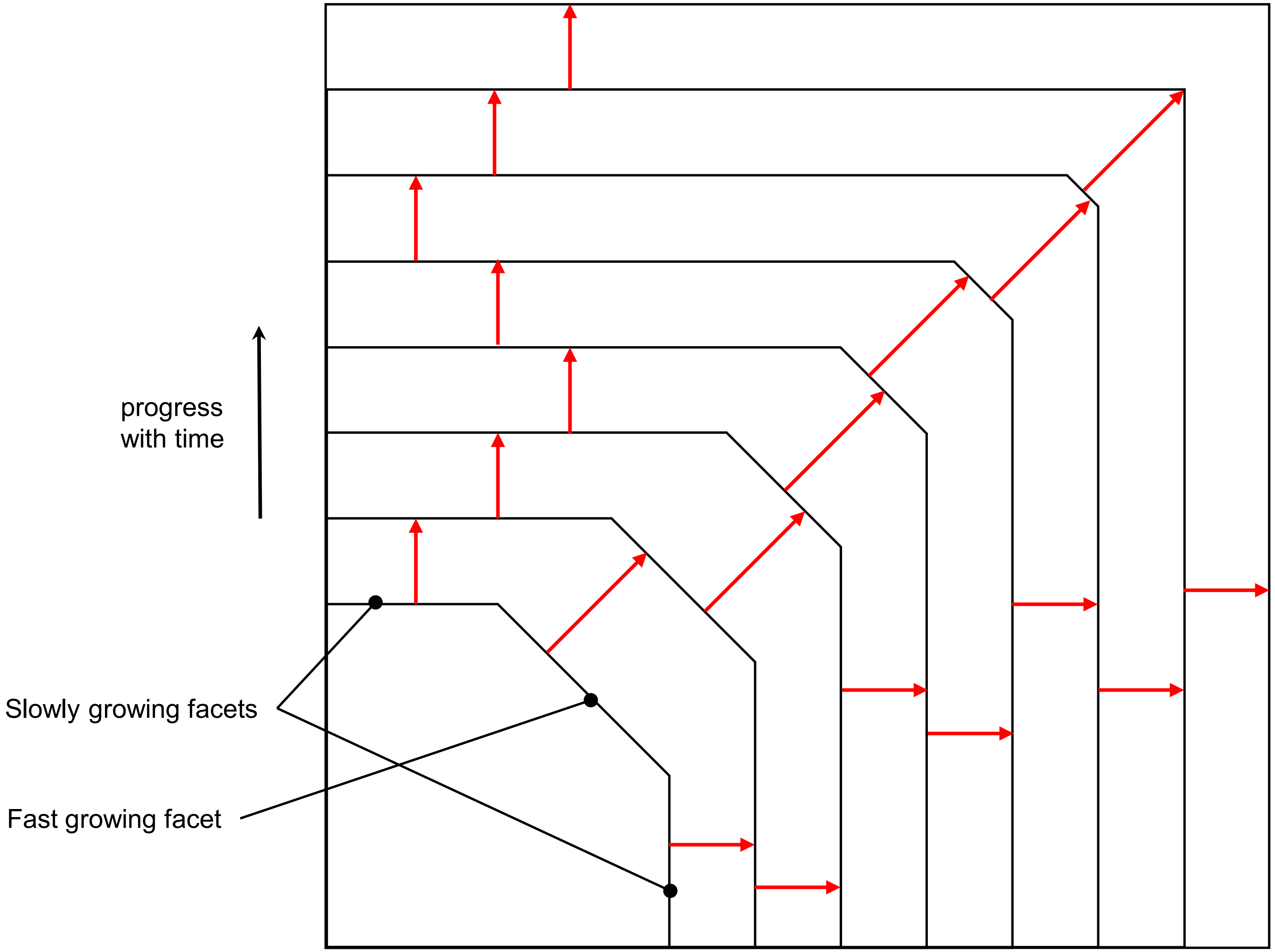
- Cu prototype structure (fcc, A2)



Facet Growth

- As pointed out in Chs. 1a & b, energy considerations are not relevant as long as the process is unable to kinetically proceed.
- In general, the growth of a facet is mediated by adding atoms to the surface. Hence, the growth velocity (see v on the previous slides) is higher for surface facets with low packing factor since a smaller number of atoms is needed to form a monolayer of the facet. For closed packed facets it is vice versa.
- There is a resulting competition of fast and slowly growing facets, the latter one prevailing in the long run.
- A similar construction principle as for the surface/interface energies exists but for polar plots of the growth velocity.

Facet Growth

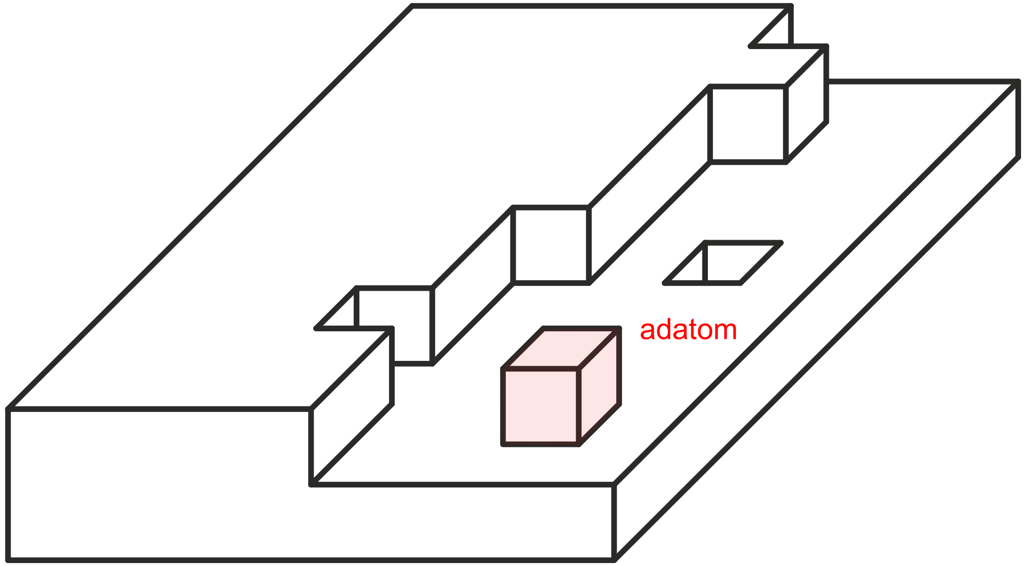


The relative proportion of the fast growing facet to the total surface of the crystal becomes smaller and smaller until it completely disappears.

Crystal facets growing at different velocities at different time steps.

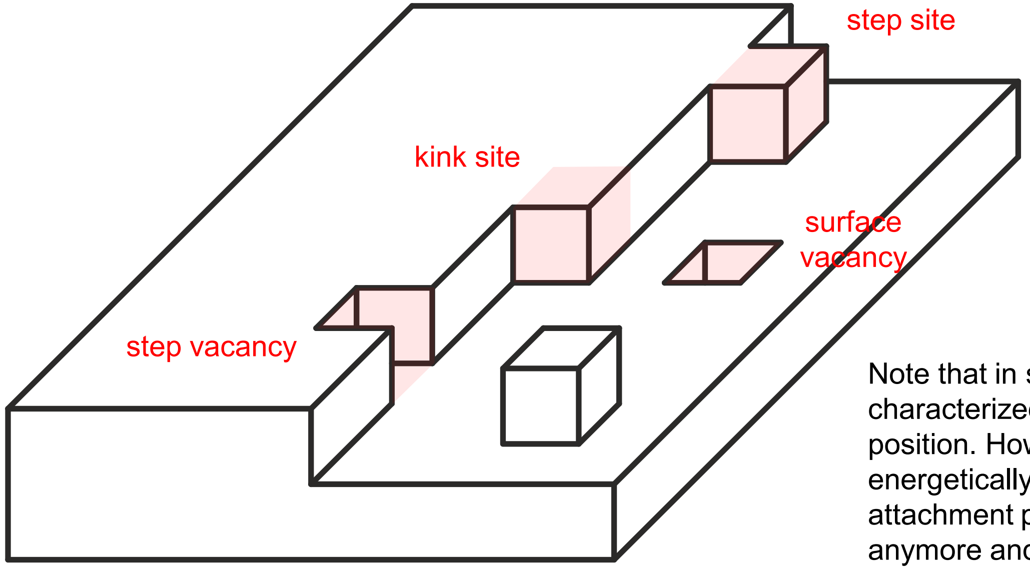
Growth

- On atomistic scale, the attachment process is also of relevance. Again the surface of a simple cubic crystal with dominant NN interactions might be considered.
- The adsorption of a free atom the flat surface has only little energy gain since only a single bond gets saturated.



Growth

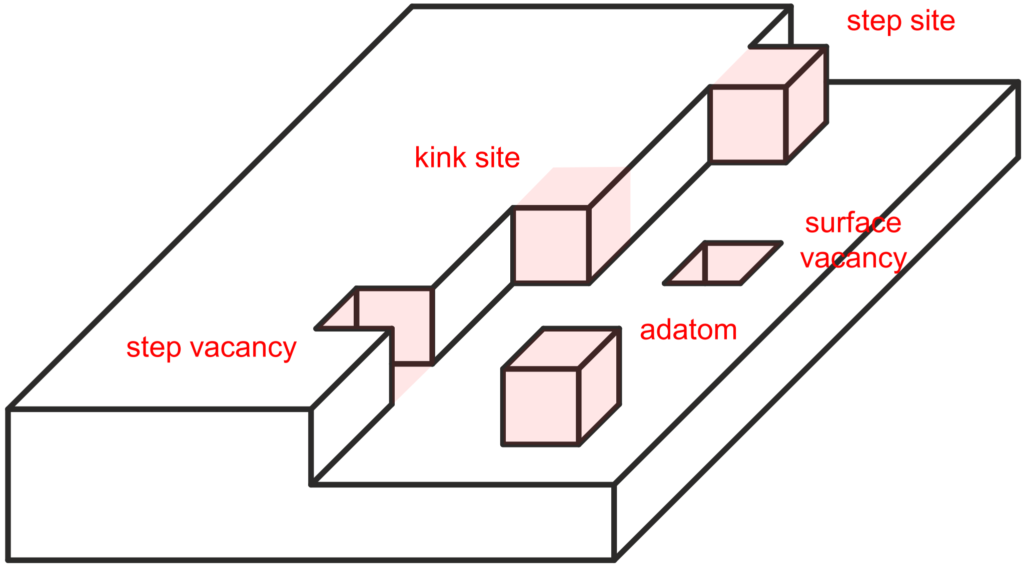
- Other attachment sites, like surface vacancy, step vacancy, kink site, or step site are more favorable since more bonds get saturated.
- The kink site is of specific interest since it is self-reproducing! When attaching an atom to a kink site, the kink site does not vanish and is still available for further growth.



Note that in some textbooks the kink site is characterized as the energetically feasible position. However, other positions are energetically of greater value but after the attachment process, they are not available anymore and need to be formed again. Hence, the importance for crystal growth is not only the energetic consideration but also the kinetic one.

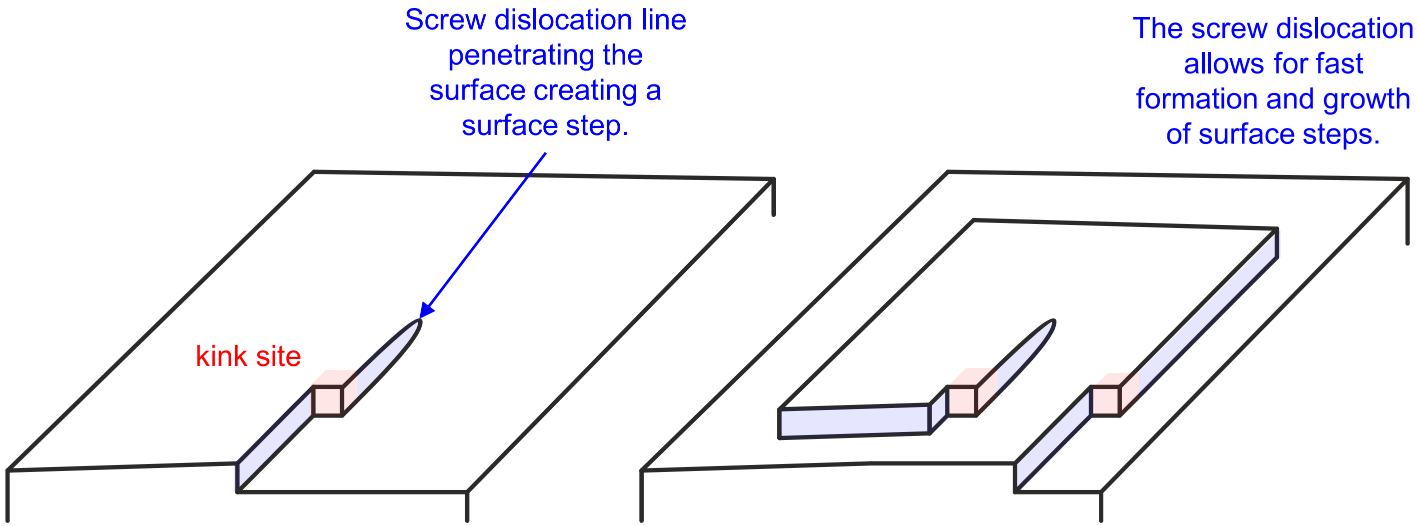
Growth

- The process is majorly influenced by adsorption to the surface (with a certain energy barrier) and afterwards surface diffusion towards the aforementioned surface sites (again connected with a specific energy barrier).



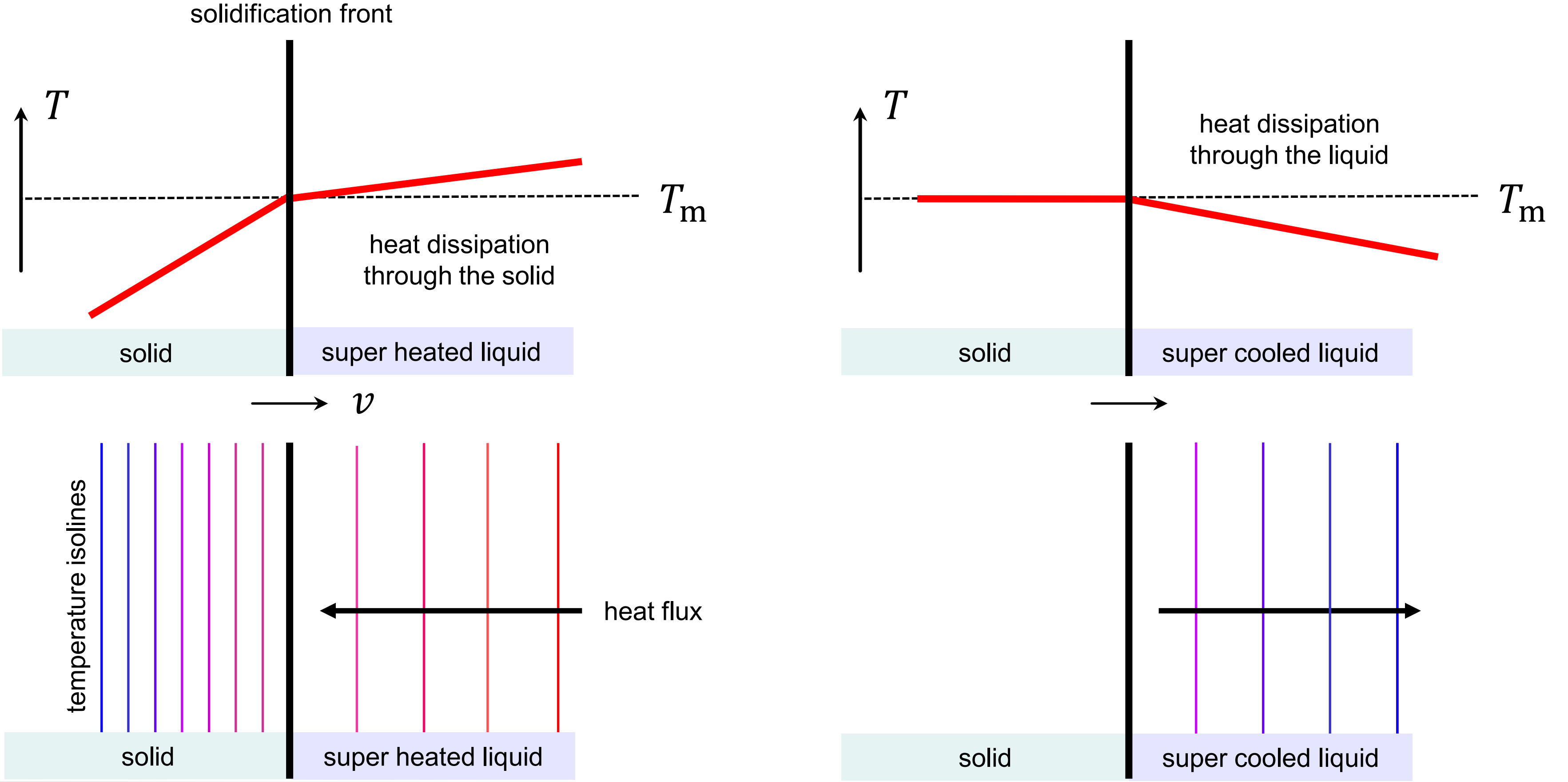
Growth

- Note that the presence of other defects, for example growth dislocations, might mediate an even faster growth by avoiding losing the step for attachment of additional atoms during growth:



Heat Transfer

- In general, two situations might be considered when it comes to **heat transfer at a flat solidification front**:



Note: Thermal Conduction

- Similar to diffusion in Ch. 1b:

heat flux: $q = -\lambda \cdot \nabla T$

continuity: $\rho c \frac{\partial T}{\partial t} - \nabla q = 0$

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho c} \Delta T$$

$$[T] = \mathrm{K},\ [\nabla T] = \frac{\mathrm{K}}{\mathrm{m}},\ [\lambda] = \frac{\mathrm{W}}{\mathrm{m\ K}},\ [q] = \frac{\mathrm{W}}{\mathrm{m}^2},\ [\rho] = \frac{\mathrm{kg}}{\mathrm{m}^3},\ [c] = \frac{\mathrm{J}}{\mathrm{kg\ K}}$$

Note: Thermal Conduction

- Similar to diffusion in Ch. 1b:

steady-state $\frac{\partial T}{\partial t} = 0$, linear: $\frac{\partial^2 T}{\partial x^2} = 0$

$$T(x) = T_0 + k\,x,\ \nabla T = k$$

steady-state $\frac{\partial T}{\partial t} = 0$, cylindrical in radial direction: $\frac{\partial}{\partial r}\left(r\,\frac{\partial T}{\partial r}\right) = 0$

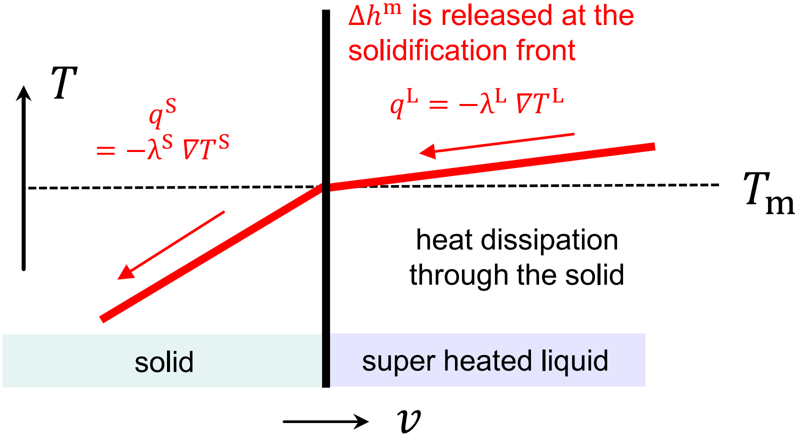
$$T(r) = T_0 + k \ln r,\ \nabla T = \frac{k}{r}$$

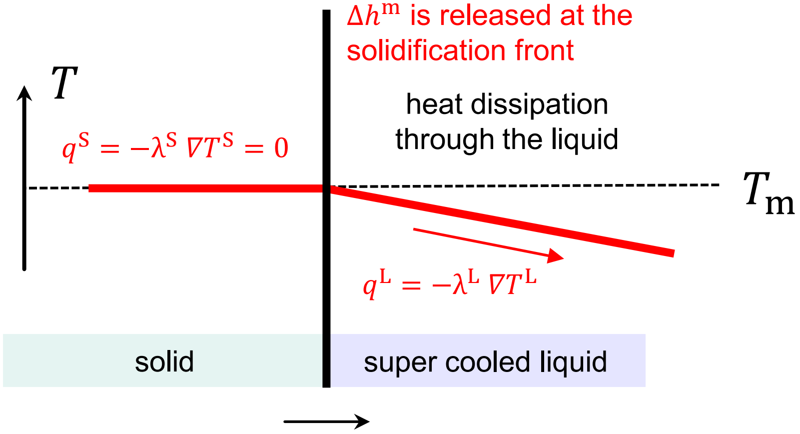
steady-state $\frac{\partial T}{\partial t} = 0$, spherical in radial direction: $\frac{\partial}{\partial r}\left(r^2\,\frac{\partial T}{\partial r}\right) = 0$

$$T(r) = T_0 + \frac{k}{r},\ \nabla T = -\frac{k}{r^2}$$

Stationary Situation

- For the situation of a stationary, planar solidification front, nucleation has already taken place, so the interface contribution can be neglected. If the interface is flat, no super cooling at the interface occurs. The assumption of local equilibrium is reasonable. The following balance of heat fluxes needs to be obtained for a stationary growth:





$$\lambda^{\mathrm{S}}\,\nabla T^{\mathrm{S}} = \lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L}} + v\,\Delta h_{\mathrm{m}}$$

$$v = \frac{\lambda^{\mathrm{S}}\,\nabla T^{\mathrm{S}} - \lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L}}}{\Delta h_{\mathrm{m}}}$$

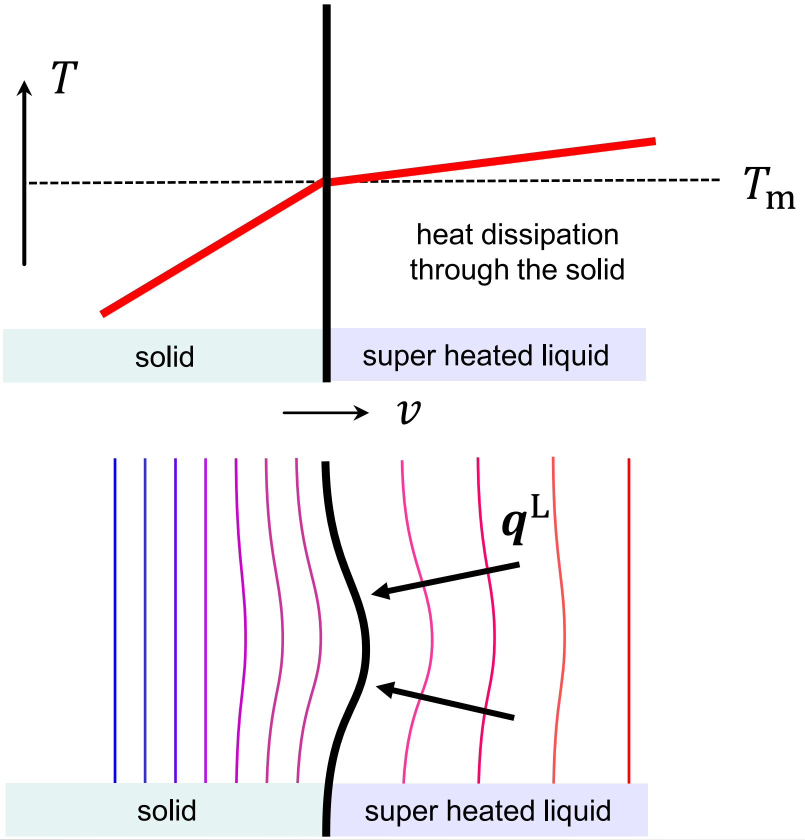
λ^{S}, λ^{L} are the thermal conductivities
∇T^{S}, ∇T^{L} are the temperature gradients
Δh_{m} is the volumetric latent heat
$[\lambda] = \frac{\mathrm{W}}{\mathrm{m\,K}}, [\nabla T] = \frac{\mathrm{K}}{\mathrm{m}}, [\Delta h_{\mathrm{m}}] = \frac{\mathrm{J}}{\mathrm{m}^3} = \frac{\mathrm{Ws}}{\mathrm{m}^3}, [v] = \frac{\mathrm{m}}{\mathrm{s}}$

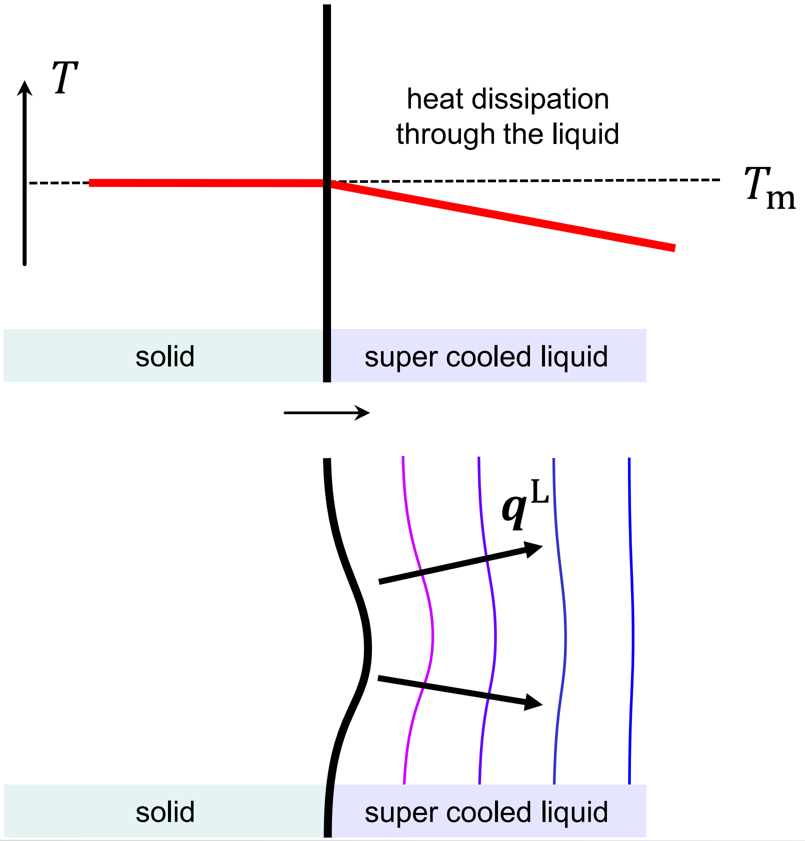
Heat Transfer

- **Heat conduction follows the exact same equations as seen for diffusion** in Ch. 1b! Heat flux is opposite to temperature gradients (and perpendicular to the temperature isolines in the figures).
- The important **two cases for solidification** are:
  - **Heat dissipation through the solid**, that is the most realistic case for solidification in a container which is typically colder than the solidifying material and the liquid.
  - **Heat dissipation through the liquid** occurs far away from the container walls when nucleation takes place free.
- The temperature profile is determined by:
  - In any case both, solid and liquid can only be in equilibrium at T_m (considering a flat interface and nucleation with super cooling already took place). We consider "local equilibrium" where the phases are contact! Due to the contact, there is no time lag to obtain equilibrium. Hence, at the solidification front $T = T_\mathrm{m}$.
  - For heat dissipation through the solid, the ability to dissipate the latent heat determines the progress of solidification. The liquid has $T > T_\mathrm{m}$. For heat dissipation through the liquid, the liquid is significantly super cooled since latent heat needs to be conducted away. If this would not be the case, there would be no solidification progress.

Heat Transfer

- Consider a perturbation/protrusion of the solidification front:



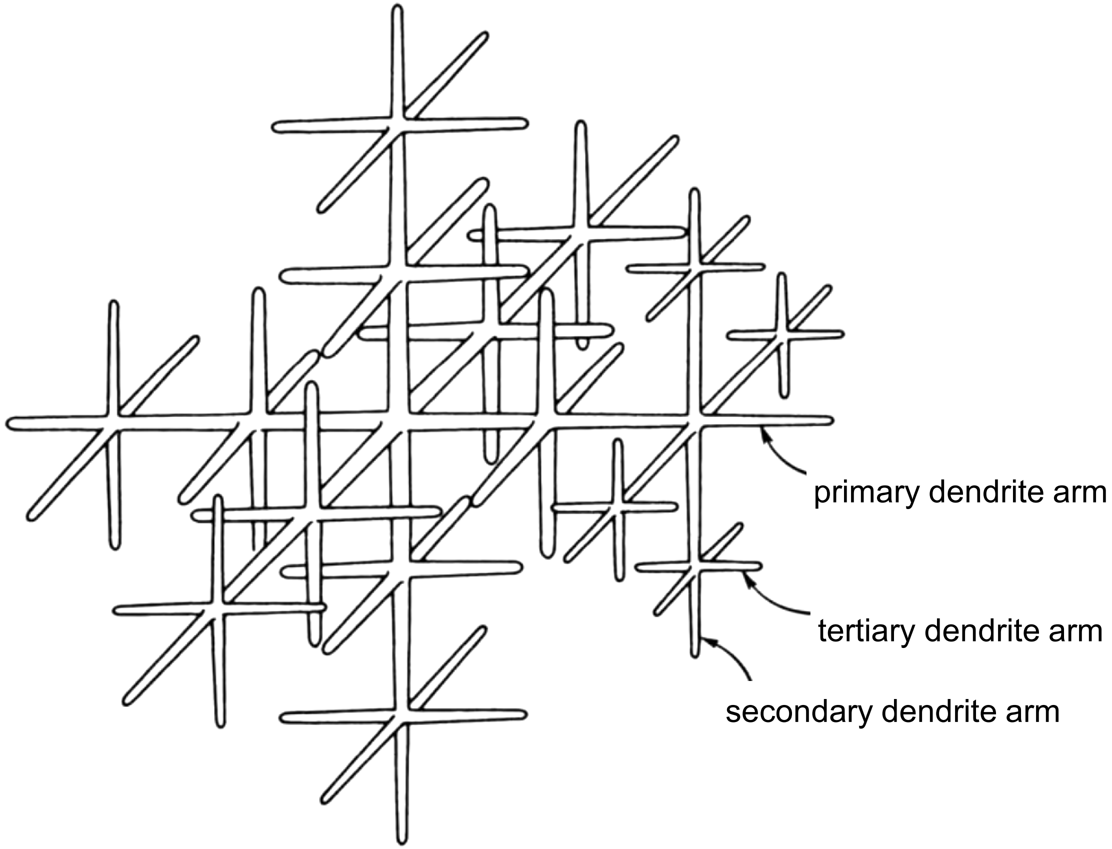


Heat Transfer

- The heat dissipation has important consequence on the **stability of the solidification front**:
  - In case some **portion of solid penetrates the liquid when the heat is dissipated through the solid**, the changing **heat flux acts against the protrusion**! The further growth of the protrusion is restricted.
  - **In case some portion of the solid penetrates the super cooled liquid**, the **generated heat flux further facilitates the situation** and the solidification front becomes unstable (it does not remain planar).

Heat Transfer

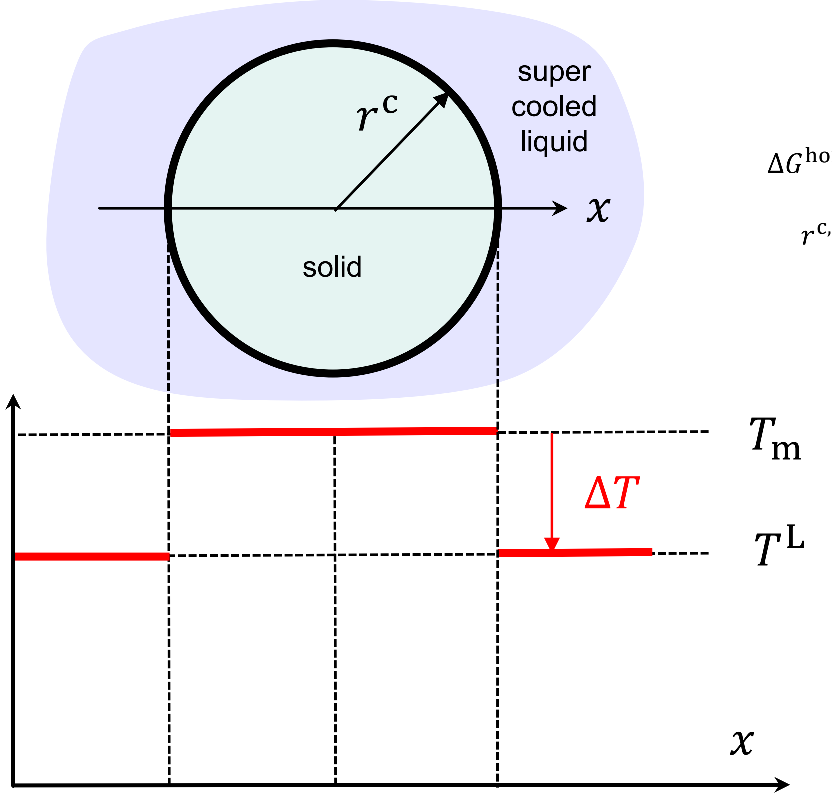
- Due to the instability of the solidification front, dendritic growth can occur:



D. A. Porter und K. E. Easterling: “Phase Transformations in Metals and Alloys”, Berlin, Heidelberg: Springer-Science+Business Media (1992)

Revision of Free Nucleation

- For homogeneous nucleation of a sphere, we have seen (Ch. 3a):



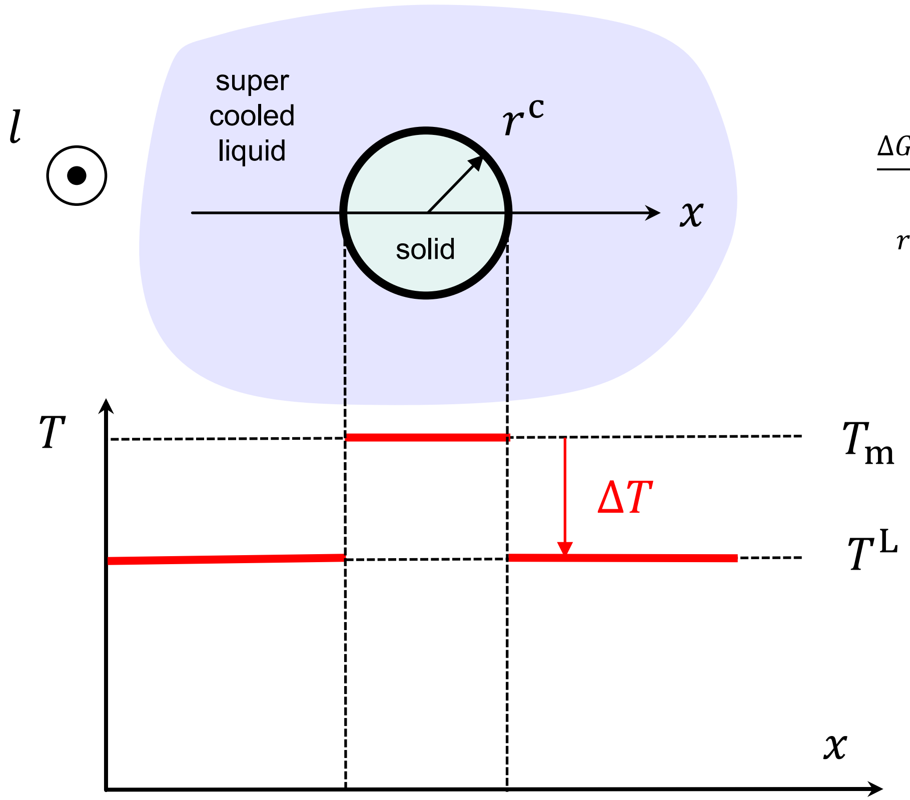
$$\Delta G^{\mathrm{hom}} = -\frac{4}{3}\pi r^3\, \Delta g^{\mathrm{D}} + 4\pi r^2\, \gamma^{\mathrm{SL}}$$

$$r^{\mathrm{c,sphere}} = \frac{2\,\gamma^{\mathrm{SL}}}{\Delta g^{\mathrm{D}}} = \frac{2\,\gamma^{\mathrm{SL}}\,T_{\mathrm{m}}}{\Delta h_{\mathrm{m}}\,\Delta T}$$

No growth occurs since the released heat Δh_{m} is not dissipated from the nucleus.

Extension of Free Nucleation

- For homogeneous nucleation of a cylinder, we obtain:



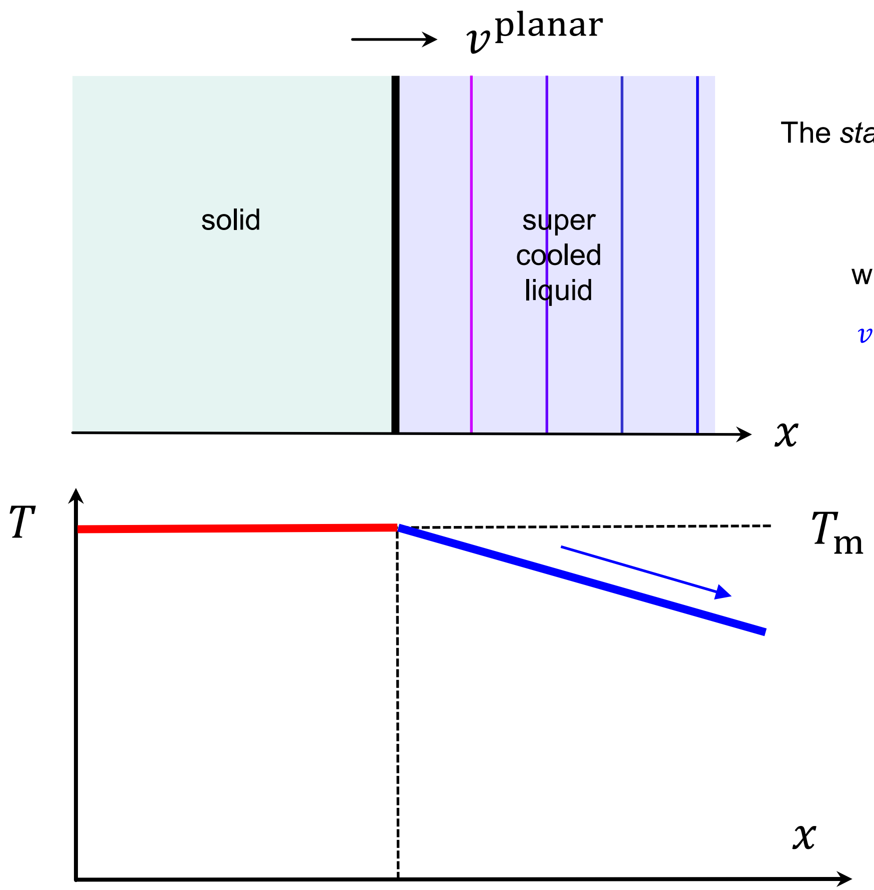
$$\frac{\Delta G^{\mathrm{hom}}}{l} = -\pi r^2\, \Delta g^{\mathrm{D}} + 2\pi r\, \gamma^{\mathrm{SL}}$$

$$r^{\mathrm{c,cylinder}} = \frac{\gamma^{\mathrm{SL}}}{\Delta g^{\mathrm{D}}} = \frac{\gamma^{\mathrm{SL}}\, T_{\mathrm{m}}}{\Delta h_{\mathrm{m}}\, \Delta T}$$

No growth occurs since the released heat Δh_{m} is not dissipated from the nucleus.

Heat Transfer

- For the planar, steady-state solidification front moving into the super cooled liquid, we obtain:



The *stationary* linear heat conduction problem yields:

$$\nabla T^{\mathrm{L}} = \mathrm{const.} < 0$$

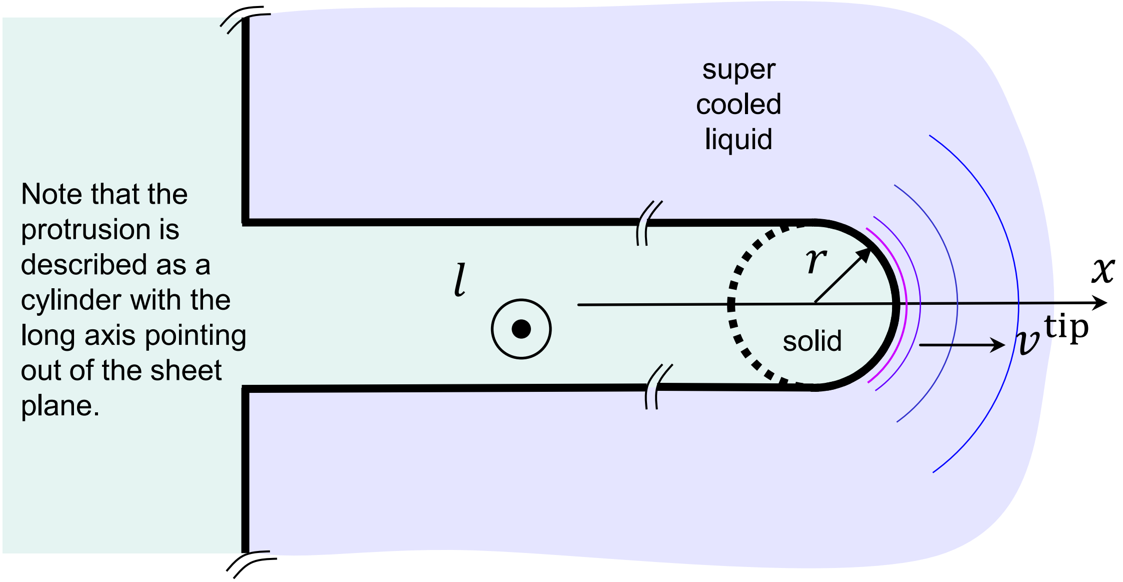
with the heat flux balance:

$$v^{\mathrm{planar}} = \frac{\lambda^{\mathrm{S}}\,\nabla T^{\mathrm{S}} - \lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L}}}{\Delta h_{\mathrm{m}}} = \frac{-\lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L}}}{\Delta h_{\mathrm{m}}}$$

No super cooling is needed since the interface remains flat and does not change during solidification. Growth is mediated by the stationary heat dissipation.

Thermal Dendrites – Heat Transfer

- Protrusion at the initially flat solidification front:



Note that the protrusion is described as a cylinder with the long axis pointing out of the sheet plane.

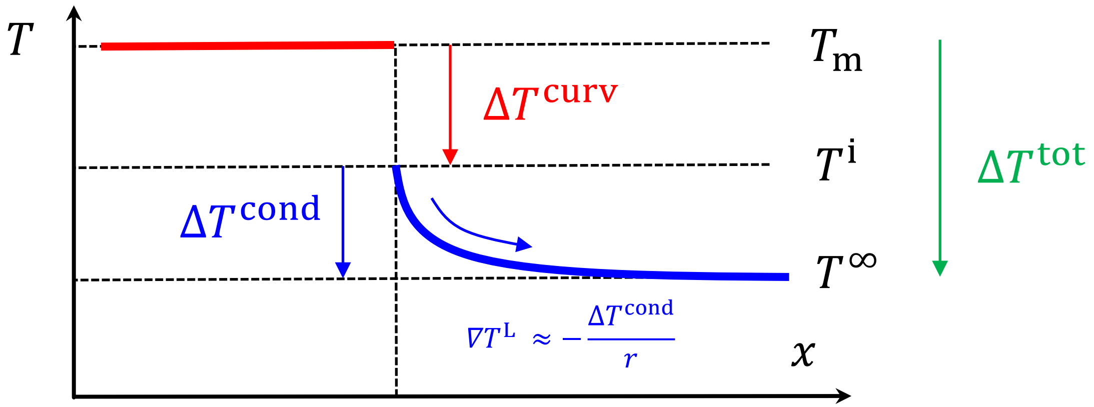
The *stationary* cylindrical heat conduction problem in radial direction yields for $x = r$:

$$\nabla T^{\mathrm{L}} = -\frac{\Delta T^{\text{cond}}}{r}$$

The heat flux balance yields a stationary growth at ($\lambda^{\mathrm{S}}\,\nabla T^{\mathrm{S}} = 0$):

$$v^{\text{tip}} = \frac{\lambda^{\mathrm{S}}\,\nabla T^{\mathrm{S}} - \lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L}}}{\Delta h_{\mathrm{m}}} = \frac{\lambda^{\mathrm{L}}\,\Delta T^{\text{cond}}}{\Delta h_{\mathrm{m}}\,r}$$

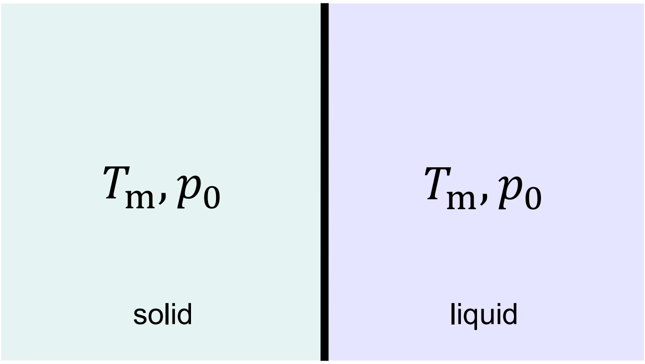
Quick growth occurs for small r.



Note: Gibbs-Thomson Equation

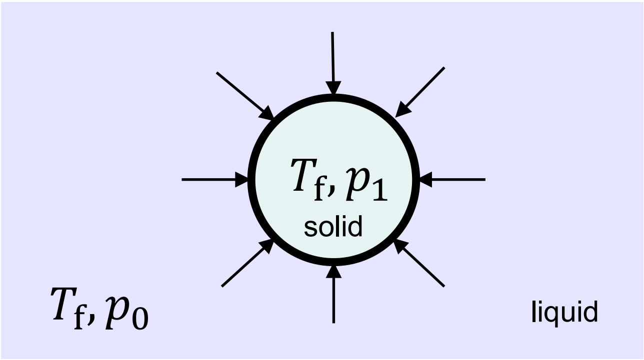
- Similar to what is observed for bubbles, a curved surface/interface applies a pressure to the volume due to trend to minimize the surface/interface energy contribution (Laplace pressure).
- The treatment of the problem of a solid sphere or cylinder in a liquid in this respect is another representation of the free nucleation problem:

equilibrium
at planar interface



$$G^S(T_m, p_0) = G^L(T_m, p_0)$$

equilibrium
at curved interface



$$G^S(T_f, p_1) = G^L(T_f, p_0)$$

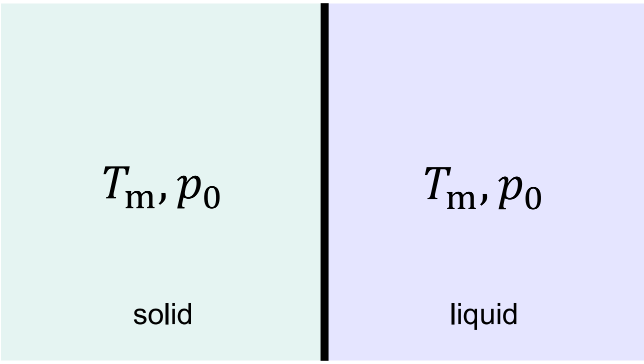
Note: Gibbs-Thomson Equation

- By using the integration form of $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$ (Ch. 1a):

$$G^{\mathrm{S}}(T_{\mathrm{f}}, p_1) = G^{\mathrm{L}}(T_{\mathrm{f}}, p_0)$$

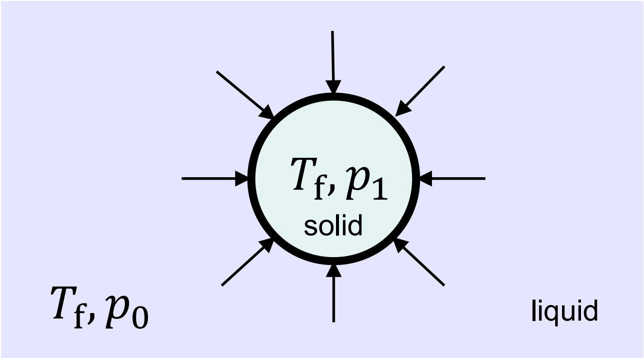
$$G^{\mathrm{S}}(T_{\mathrm{m}}, p_0) + \int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} -S^{\mathrm{S}}\,\mathrm{d}T + \int_{p_0}^{p_1} V^{\mathrm{S}}\,\mathrm{d}p = G^{\mathrm{L}}(T_{\mathrm{m}}, p_0) + \int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} -S^{\mathrm{L}}\,\mathrm{d}T$$

equilibrium
at planar interface



$$G^{\mathrm{S}}(T_{\mathrm{m}}, p_0) = G^{\mathrm{L}}(T_{\mathrm{m}}, p_0)$$

equilibrium
at curved interface



$$G^{\mathrm{S}}(T_{\mathrm{f}}, p_1) = G^{\mathrm{L}}(T_{\mathrm{f}}, p_0)$$

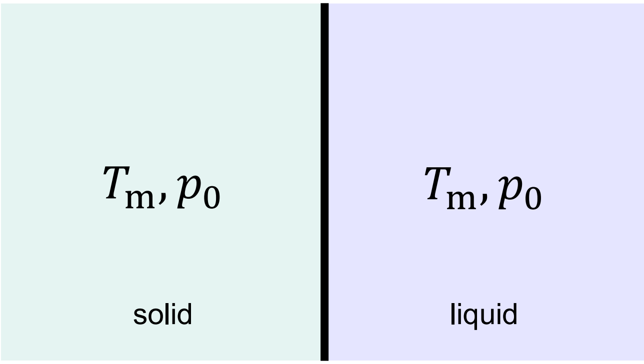
Note: Gibbs-Thomson Equation

- $G^{\mathrm{S}}(T_{\mathrm{m}}, p_0) = G^{\mathrm{L}}(T_{\mathrm{m}}, p_0)$ and $\Delta S_{\mathrm{m}} = S^{\mathrm{L}} - S^{\mathrm{S}} = \mathrm{const.}$ and $V^{\mathrm{S}} = \mathrm{const.}$:

$$+\int_{p_0}^{p_1} V^{\mathrm{S}}\,\mathrm{d}p = -\int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} \Delta S_{\mathrm{m}}\,\mathrm{d}T$$

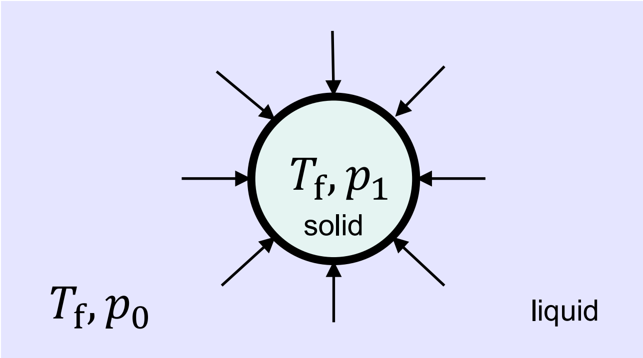
$$V^{\mathrm{S}}\,\Delta p = \Delta S_{\mathrm{m}}\,\Delta T$$

equilibrium
at planar interface



$$G^{\mathrm{S}}(T_{\mathrm{m}}, p_0) = G^{\mathrm{L}}(T_{\mathrm{m}}, p_0)$$

equilibrium
at curved interface



$$G^{\mathrm{S}}(T_{\mathrm{f}}, p_1) = G^{\mathrm{L}}(T_{\mathrm{f}}, p_0)$$

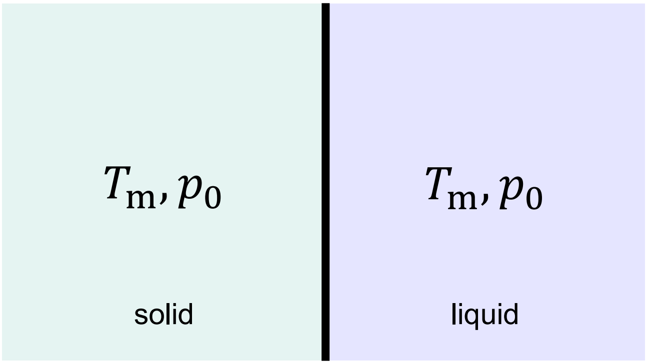
Note: Gibbs-Thomson Equation

- $\Delta S_\mathrm{m} = \frac{\Delta H_\mathrm{m}}{T_\mathrm{m}}$ (Ch. 1a) and $\Delta h_\mathrm{m} = \frac{\Delta H_\mathrm{m}}{V^\mathrm{S}}$:

$$\Delta T = \frac{V^\mathrm{S}\,\Delta p}{\Delta S_\mathrm{m}} = \frac{\Delta p\, T_\mathrm{m}}{\Delta h_\mathrm{m}}$$

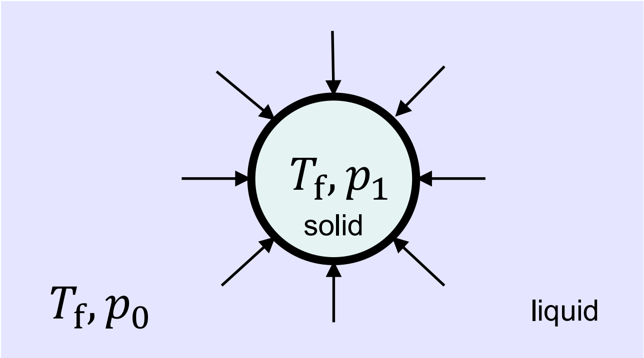
A "melting point depression" is observed when the freezing solid is finely dispersed in a liquid.

equilibrium
at planar interface



$$G^\mathrm{S}(T_\mathrm{m}, p_0) = G^\mathrm{L}(T_\mathrm{m}, p_0)$$

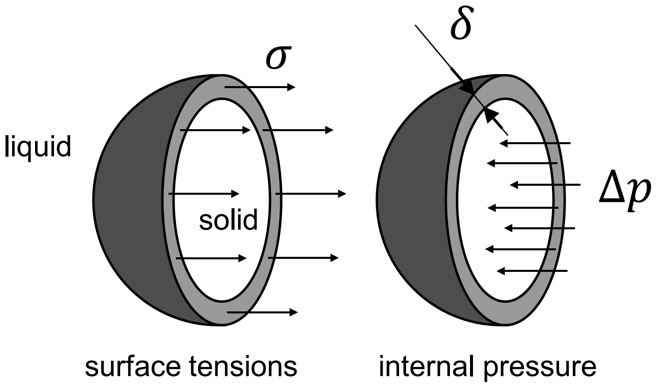
equilibrium
at curved interface

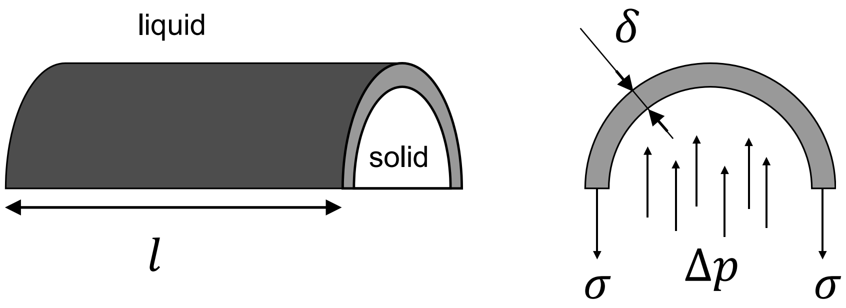


$$G^\mathrm{S}(T_\mathrm{f}, p_1) = G^\mathrm{L}(T_\mathrm{f}, p_0)$$

Note: Laplace Pressure

- The surface/interface tensions need to counter balance internal pressure:





$$\pi\left((r+\delta)^2 - r^2\right)\sigma - \pi r^2\,\Delta p = 0$$

$$\Delta p = \frac{2r\delta + \delta^2}{r^2}\sigma$$

with $\delta^2 \ll 2r\delta$:

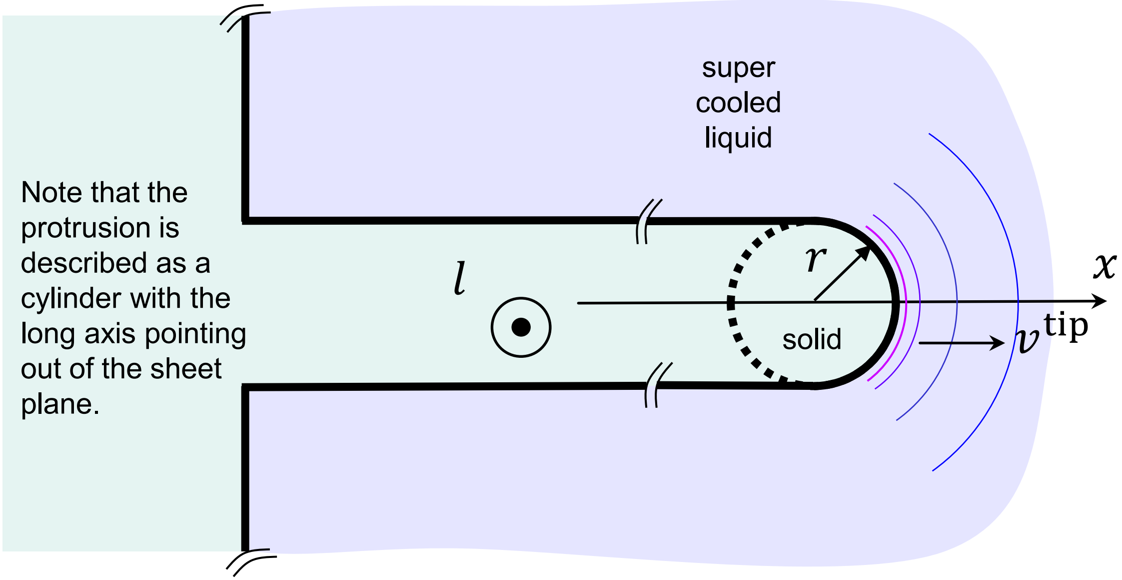
$$\Delta p \approx \frac{2\delta\sigma}{r} = \frac{2\gamma}{r}$$

$$2\delta l\,\sigma - 2rl\,\Delta p = 0$$

$$\Delta p = \frac{\delta}{r}\sigma = \frac{\gamma}{r}$$

Thermal Dendrites – Interface Curvature

- Protrusion at the initially flat solidification front:



Note that the protrusion is described as a cylinder with the long axis pointing out of the sheet plane.

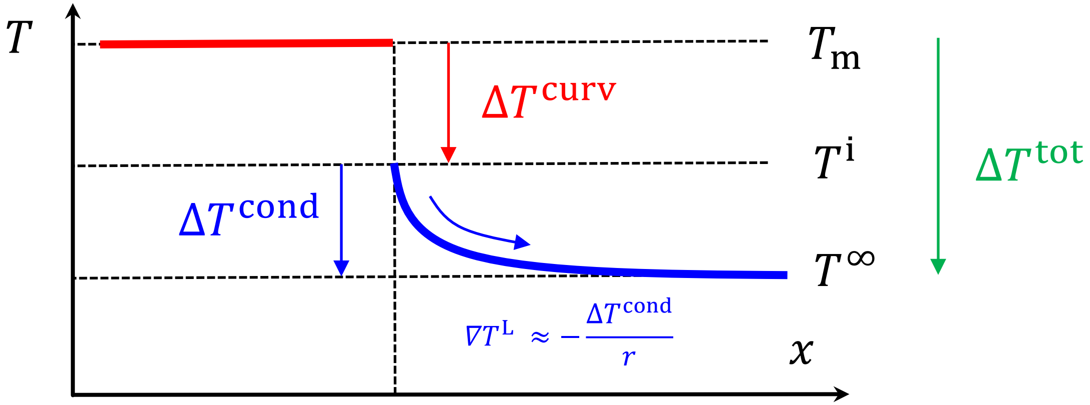
Similar to the conditions of homogeneous nucleation, the curved surface of the (cylinder) tip requires super cooling due to the acting interface energies/tensions (see Ch. 3a):

$$\Delta T^{\text{curv}} = \frac{\Delta p\, T_{\text{m}}}{\Delta h_{\text{m}}} = \frac{\gamma^{\text{SL}}\, T_{\text{m}}}{\Delta h_{\text{m}}\, r}$$

Hence, the minimum tip radius r^{c} is determined by $\Delta T^{\text{tot}} = \Delta T^{\text{curv}} + \Delta T^{\text{cond}}$ with $\Delta T^{\text{cond}} = 0$:

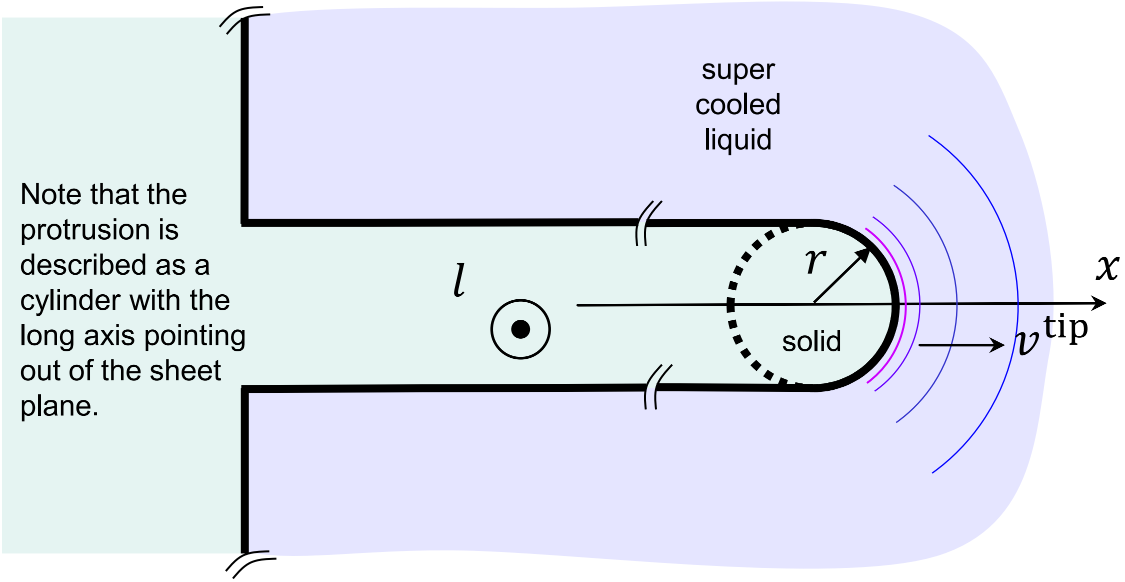
$$r^{\text{c}} = \frac{\gamma^{\text{SL}}\, T_{\text{m}}}{\Delta h_{\text{m}}\, \Delta T^{\text{tot}}}$$

corr. to the critical radius in the case of homogenous nucleation case



Thermal Dendrites

- Protrusion at the initially flat solidification front:



Note that the protrusion is described as a cylinder with the long axis pointing out of the sheet plane.

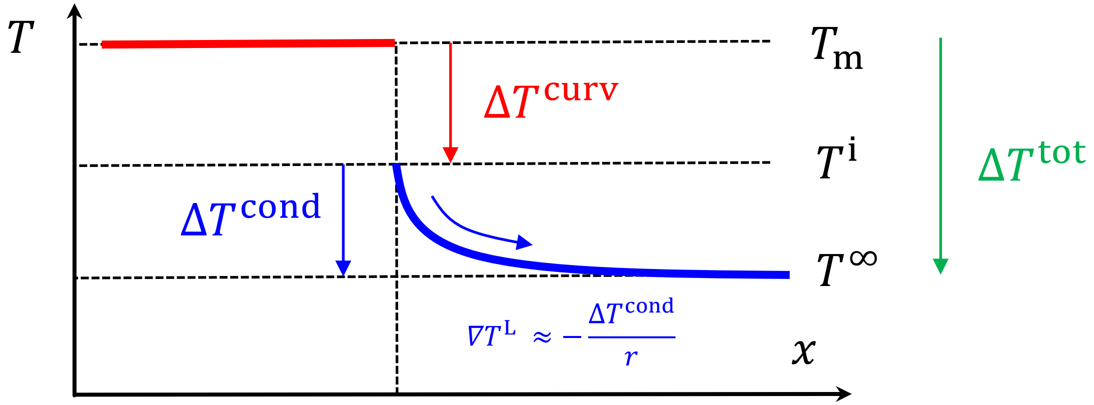
Based on this, the equations can be reformulated:

$$\Delta T^{\mathrm{curv}} = \frac{\gamma^{\mathrm{SL}}\, T_{\mathrm{m}}}{\Delta h_{\mathrm{m}}\, r} = \Delta T^{\mathrm{tot}} \frac{r^{\mathrm{c}}}{r}$$

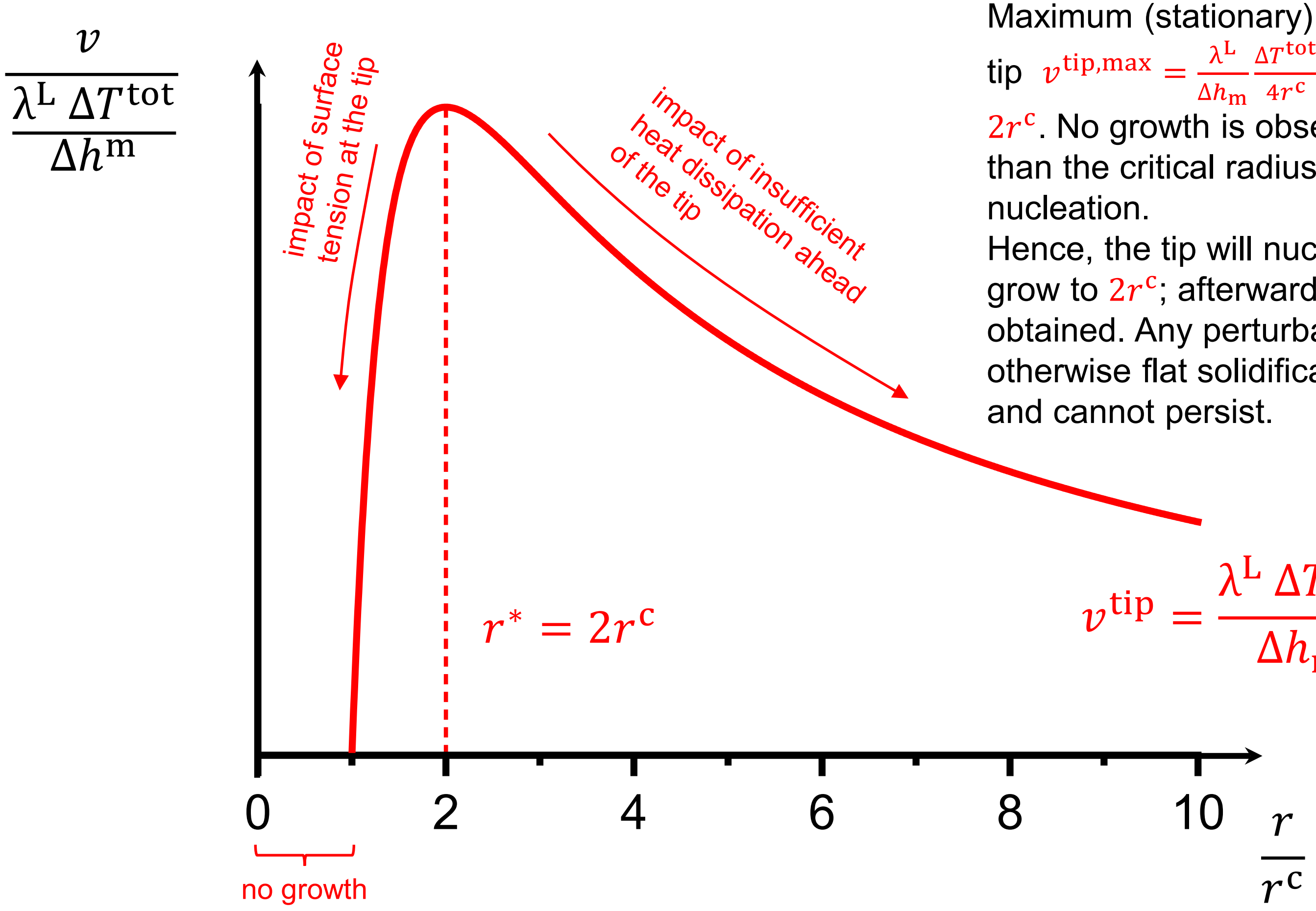
Hence,

$$v^{\mathrm{tip}} = \frac{\lambda^{\mathrm{L}}\, \Delta T^{\mathrm{cond}}}{\Delta h_{\mathrm{m}}\, r} = \frac{\lambda^{\mathrm{L}}}{\Delta h_{\mathrm{m}}} \frac{1}{r} \left(\Delta T^{\mathrm{tot}} - \Delta T^{\mathrm{curv}}\right)$$

$$= \frac{\lambda^{\mathrm{L}}}{\Delta h_{\mathrm{m}}} \frac{\Delta T^{\mathrm{tot}}}{r} \left(1 - \frac{r^{\mathrm{c}}}{r}\right)$$



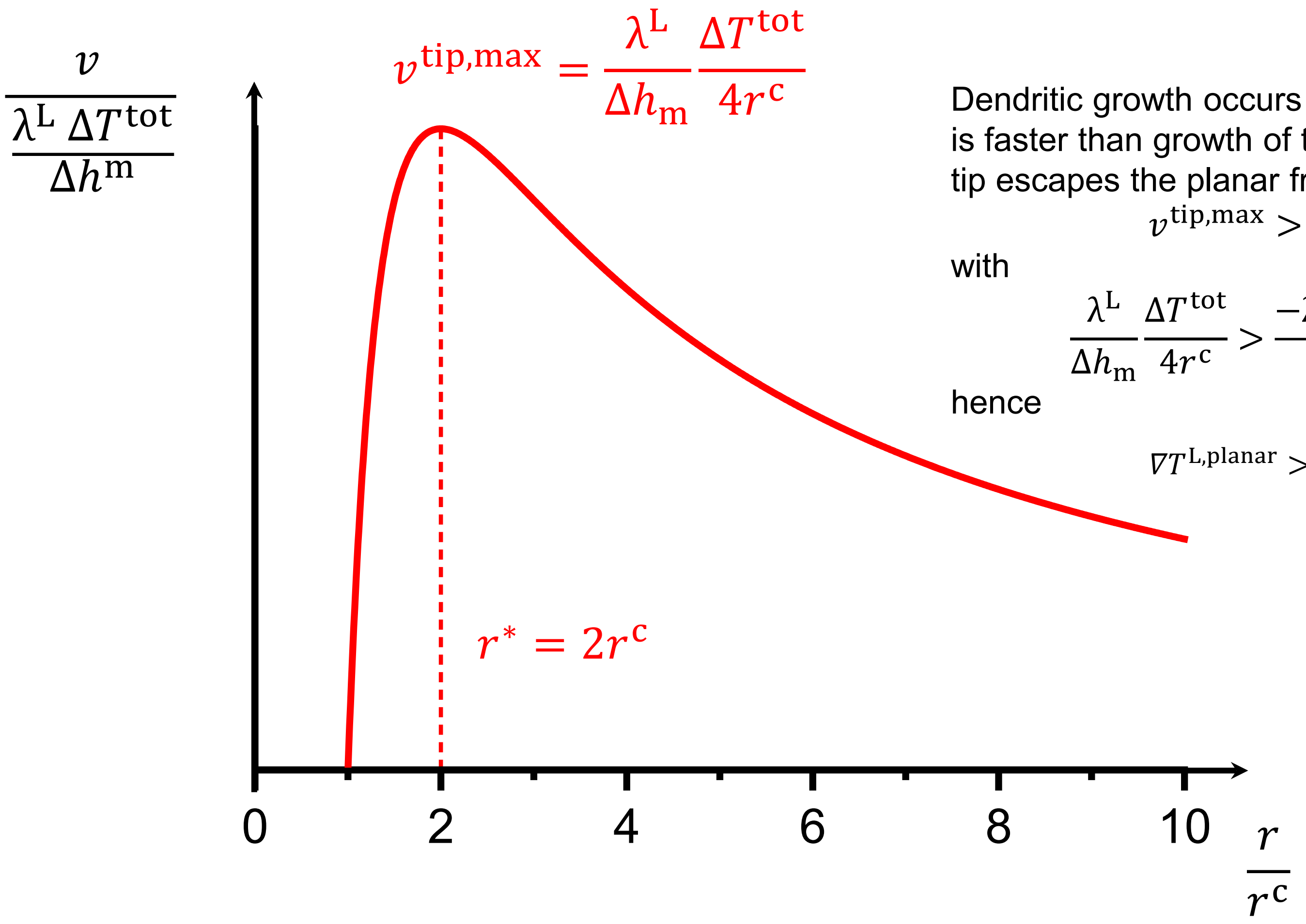
Thermal Dendrites



$$v^{\mathrm{tip}} = \frac{\lambda^{\mathrm{L}}\,\Delta T^{\mathrm{tot}}}{\Delta h_{\mathrm{m}}}\frac{1}{r}\left(1 - \frac{r^{\mathrm{c}}}{r}\right)$$

Maximum (stationary) growth velocity of the tip $v^{\mathrm{tip,max}} = \frac{\lambda^{\mathrm{L}}}{\Delta h_{\mathrm{m}}}\frac{\Delta T^{\mathrm{tot}}}{4r^{\mathrm{c}}}$ is observed for $r^* = 2r^{\mathrm{c}}$. No growth is observed for tip radii lower than the critical radius of homogeneous nucleation.
Hence, the tip will nucleate at r^{c} and quickly grow to $2r^{\mathrm{c}}$; afterwards stationary growth is obtained. Any perturbation with $r < r^{\mathrm{c}}$ of an otherwise flat solidification front is unstable and cannot persist.

Thermal Dendrites



Dendritic growth occurs when the tip growth is faster than growth of the planar front (the tip escapes the planar front):

$$v^{\mathrm{tip,max}} > v^{\mathrm{planar}}$$

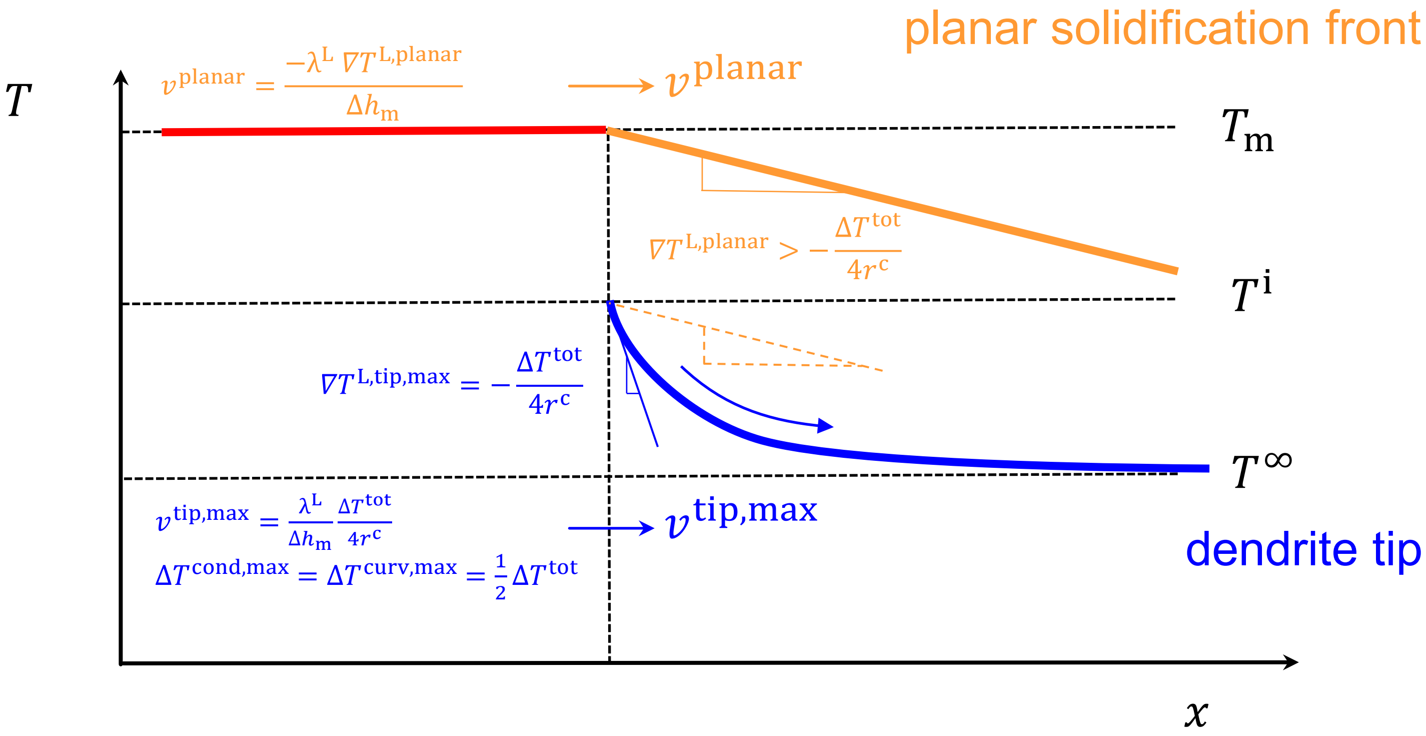
with

$$\frac{\lambda^{\mathrm{L}}}{\Delta h_{\mathrm{m}}}\,\frac{\Delta T^{\mathrm{tot}}}{4r^{\mathrm{c}}} > \frac{-\lambda^{\mathrm{L}}\,\nabla T^{\mathrm{L,planar}}}{\Delta h_{\mathrm{m}}}$$

hence

$$\nabla T^{\mathrm{L,planar}} > -\frac{\Delta T^{\mathrm{tot}}}{4r^{\mathrm{c}}}$$

Thermal Dendrites



$v^{\text{planar}} = \frac{-\lambda^{\text{L}}\,\nabla T^{\text{L,planar}}}{\Delta h_{\text{m}}}$

$\nabla T^{\text{L,planar}} > -\frac{\Delta T^{\text{tot}}}{4r^{\text{c}}}$

$\nabla T^{\text{L,tip,max}} = -\frac{\Delta T^{\text{tot}}}{4r^{\text{c}}}$

$v^{\text{tip,max}} = \frac{\lambda^{\text{L}}}{\Delta h_{\text{m}}}\frac{\Delta T^{\text{tot}}}{4r^{\text{c}}}$

$\Delta T^{\text{cond,max}} = \Delta T^{\text{curv,max}} = \frac{1}{2}\Delta T^{\text{tot}}$