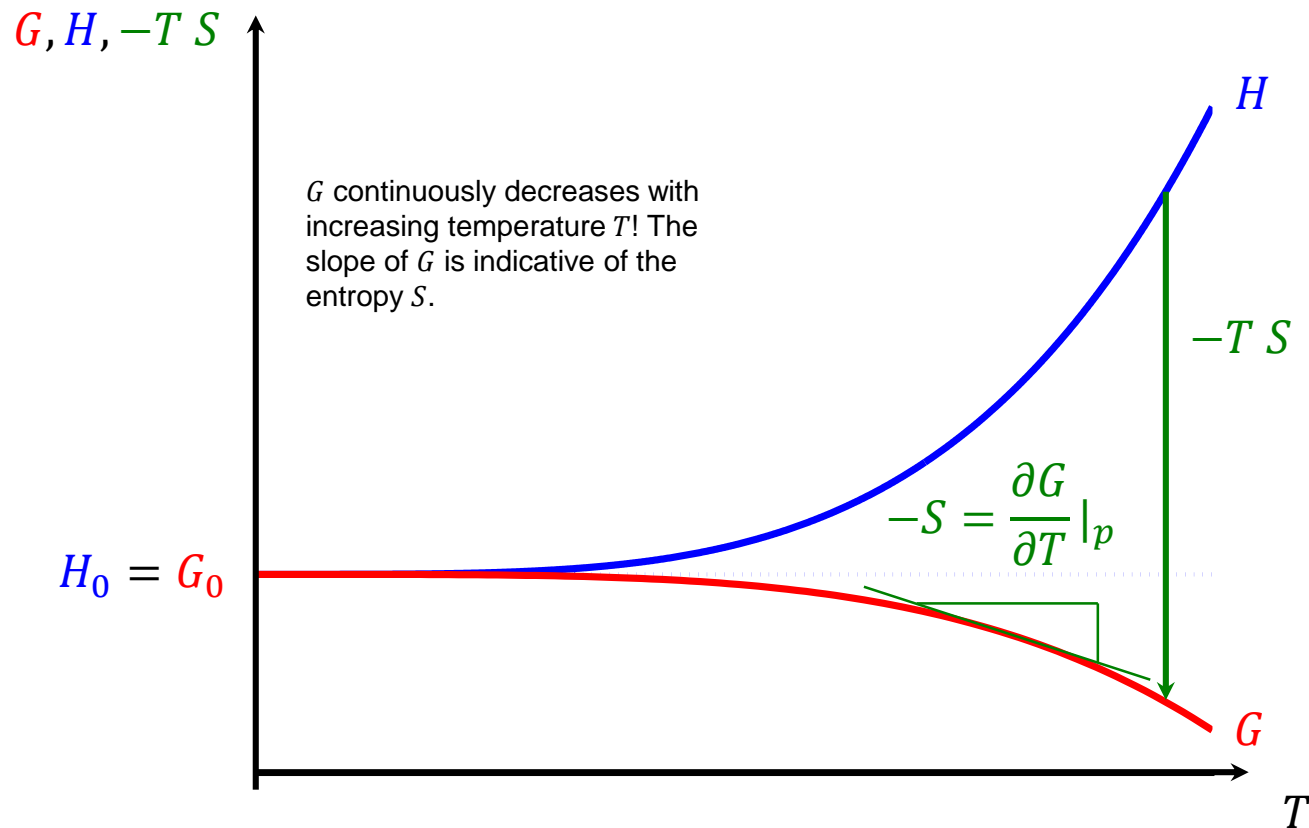


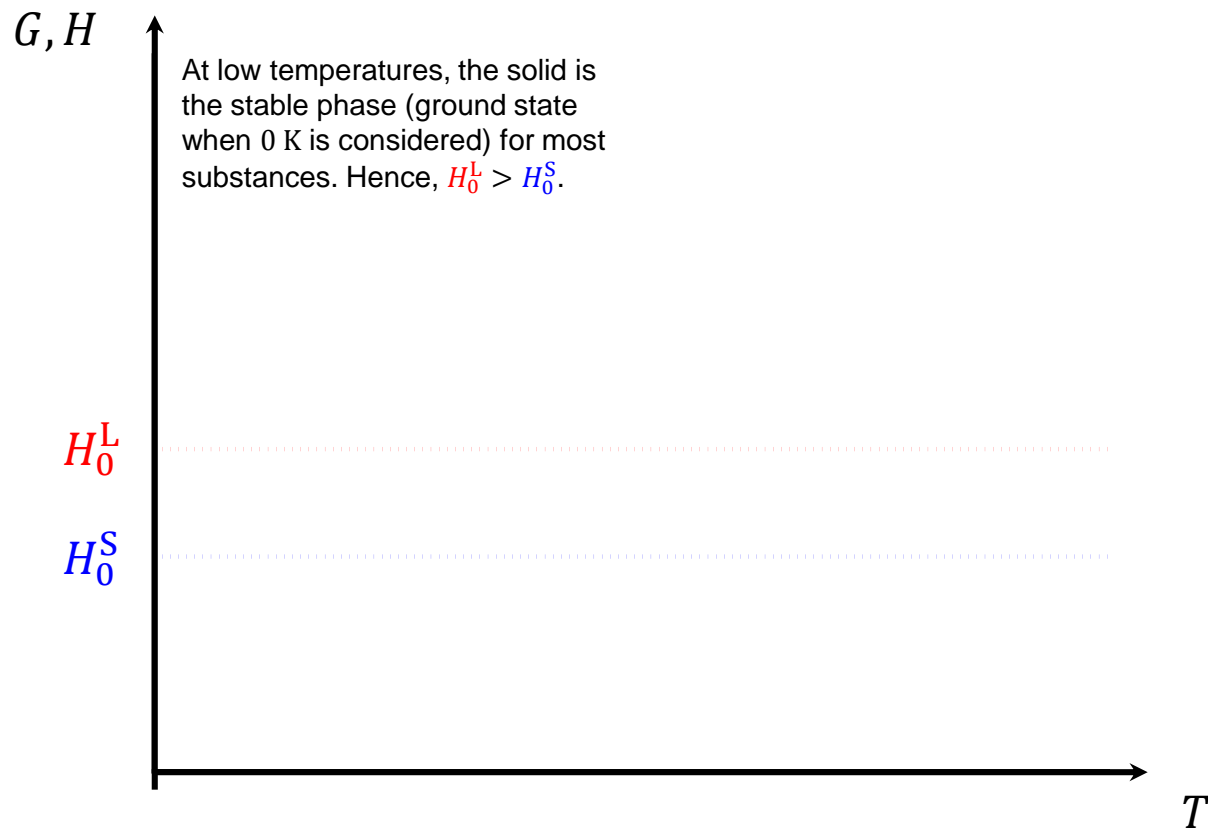
- Single-component systems
 - Solidification and Allotropic Transformations (discontinuous)
 - Temperature-Dependent Thermodynamic Potentials
 - Driving Force and Latent Heat
 - Nucleation
 - Temperature Dependence
 - Homogeneous vs. Heterogeneous

Temperature Dependence of G

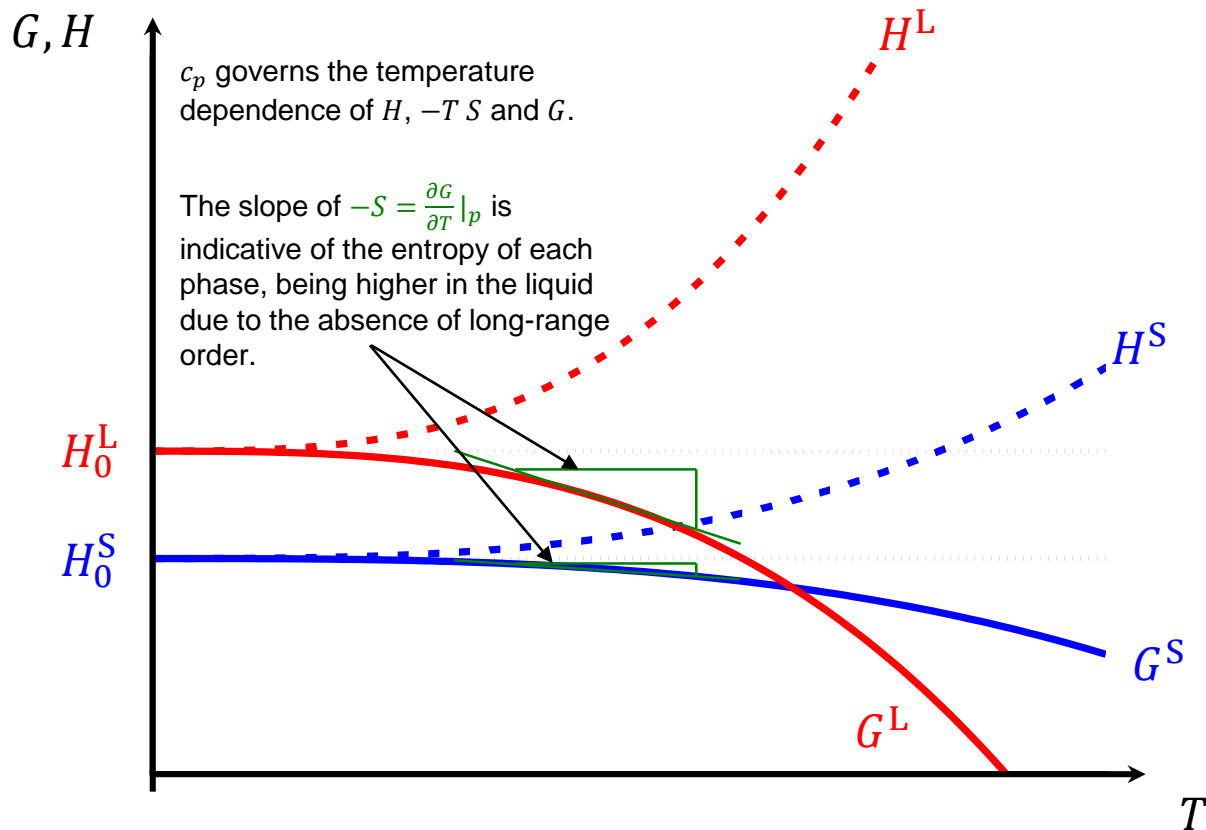


Revision of Ch. 1a

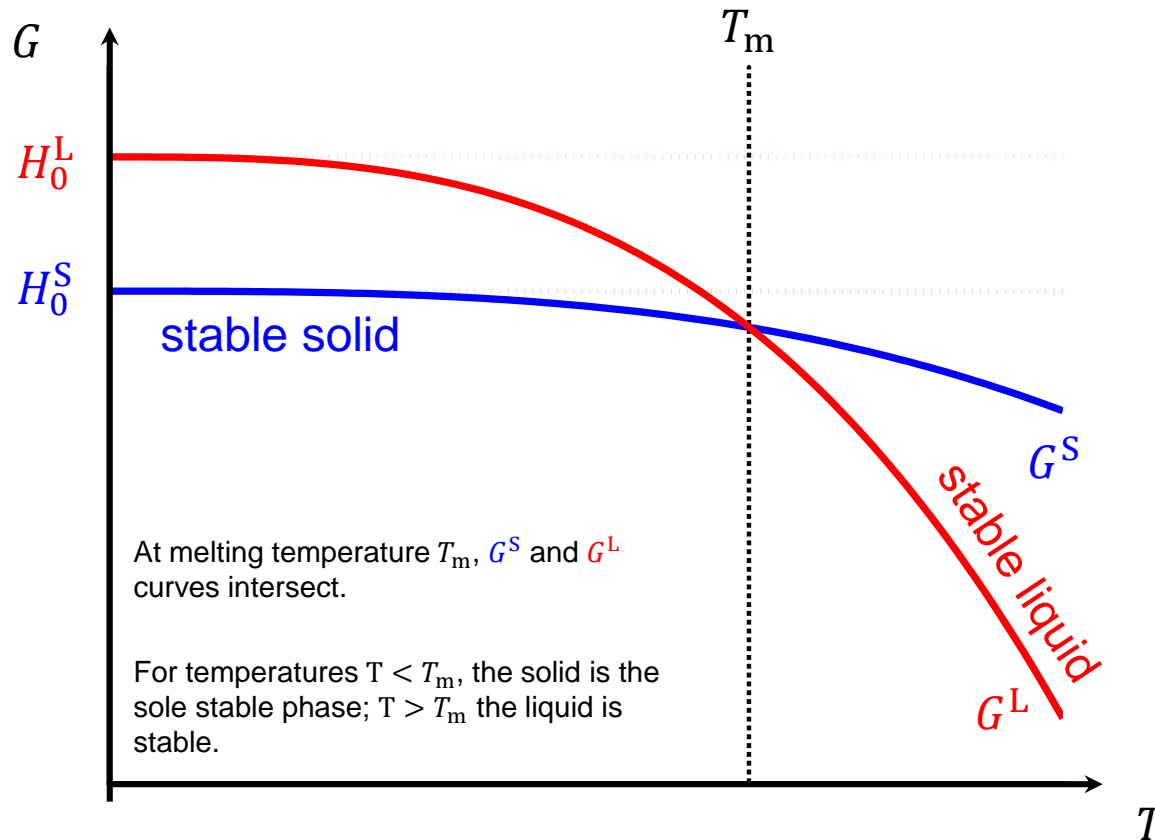
Solidification



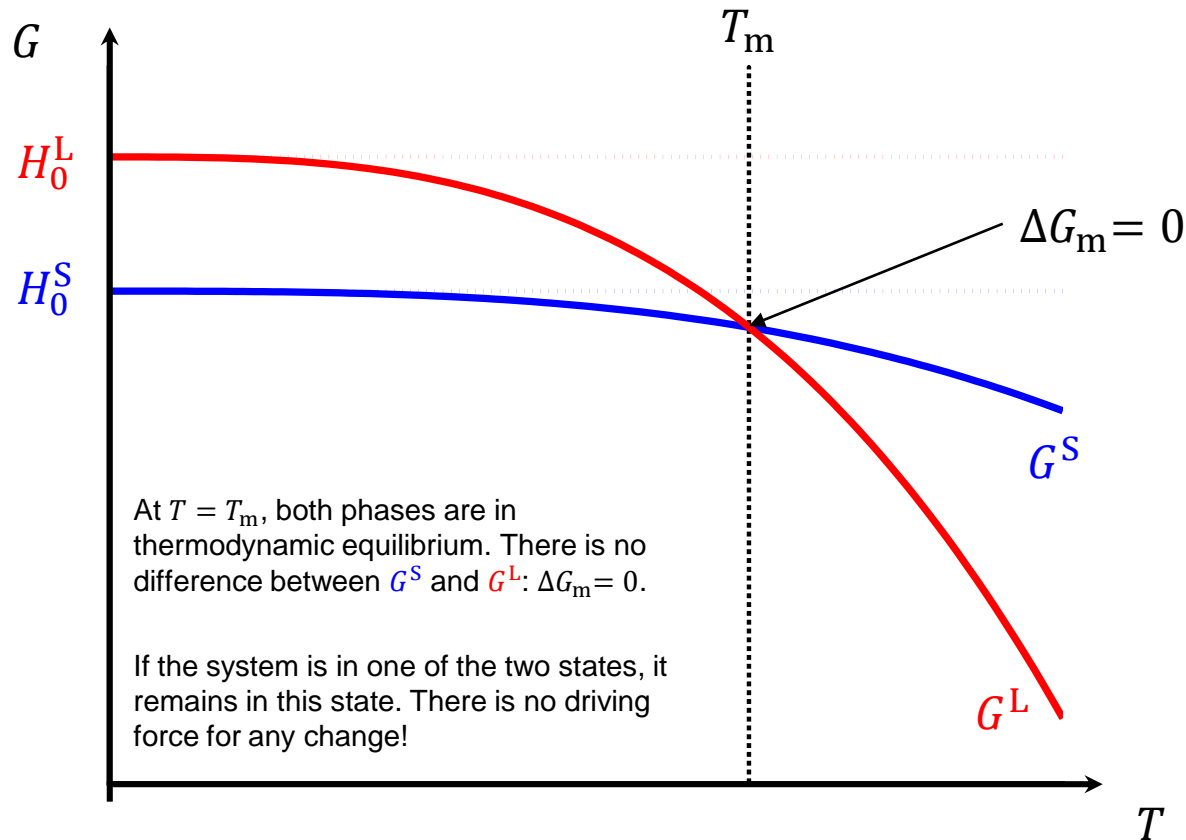
Solidification



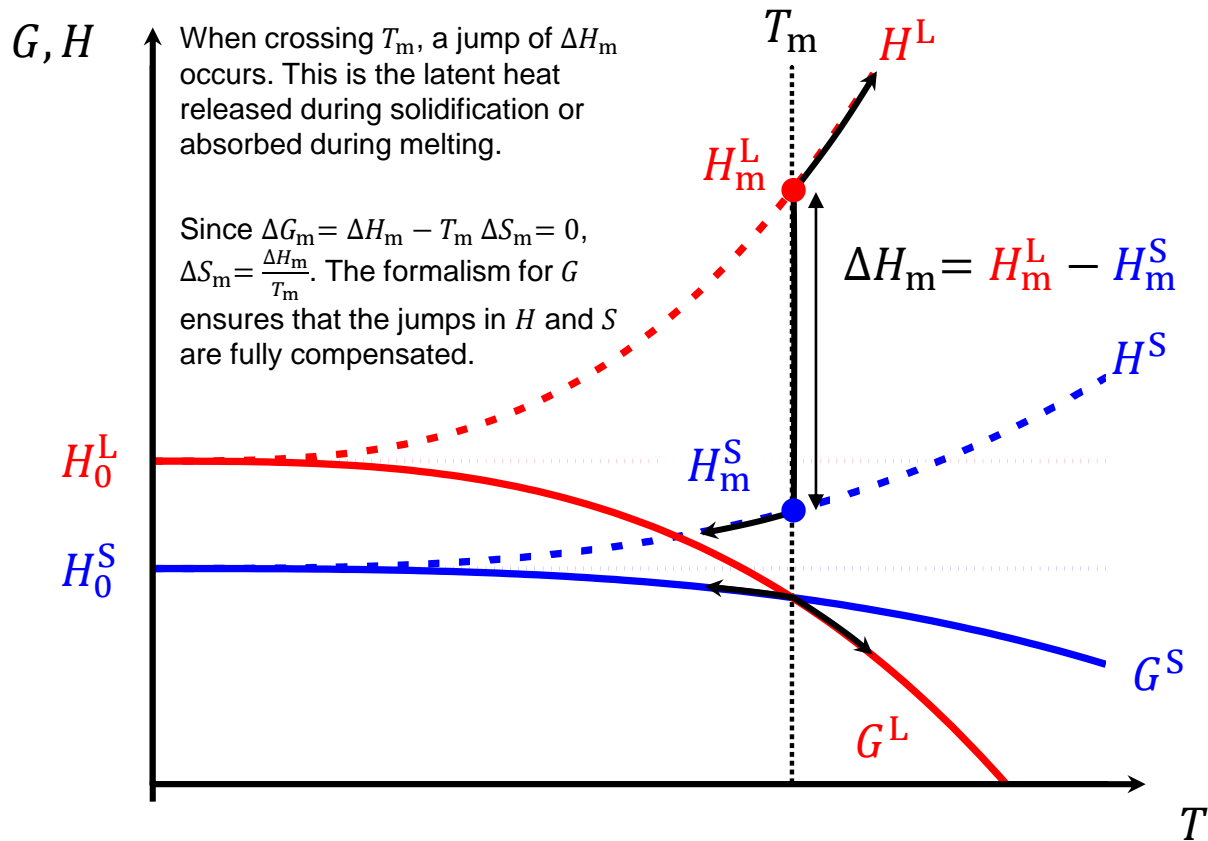
Solidification



Solidification



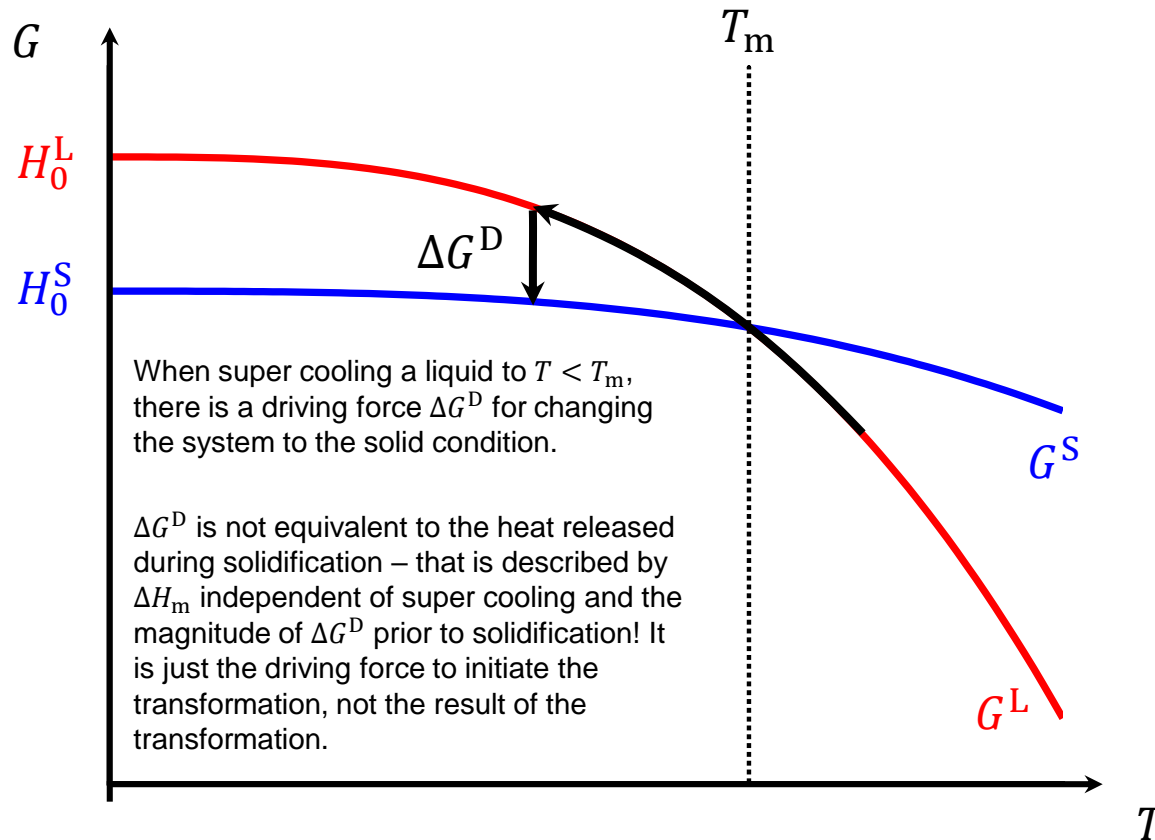
Solidification



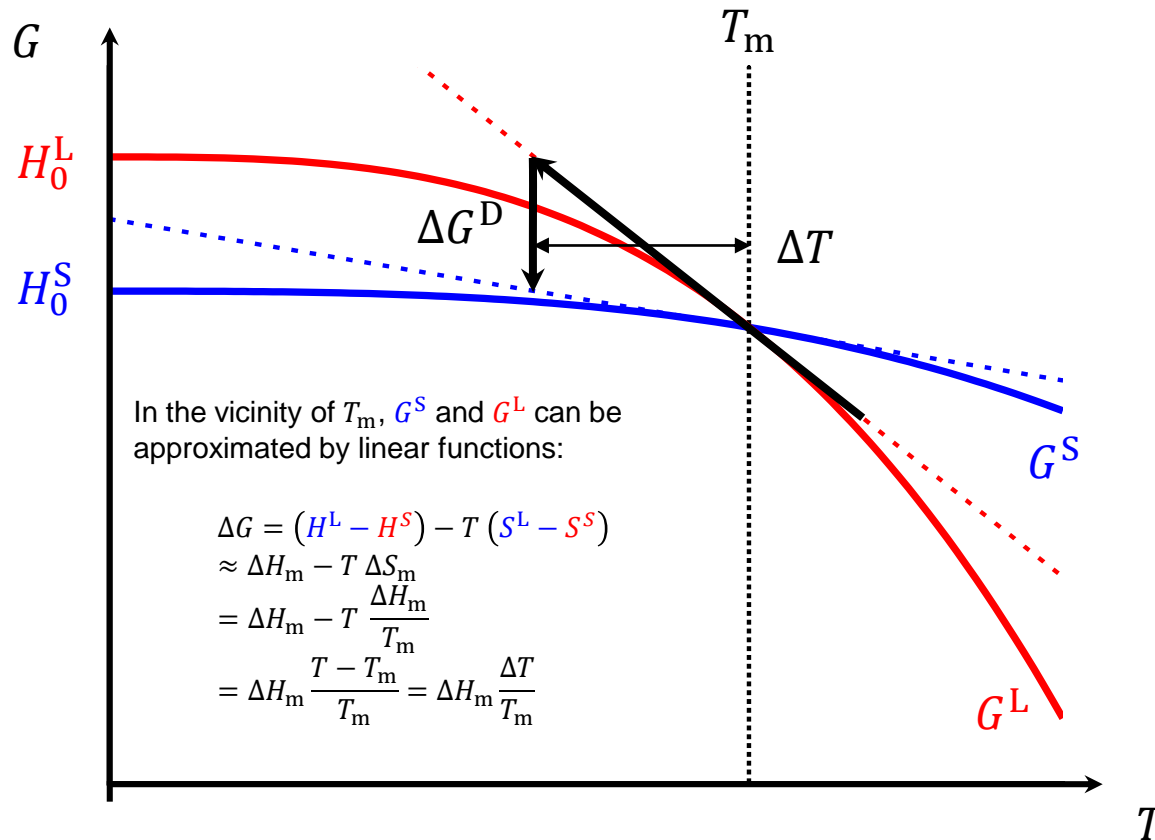
not shown here:

$$\Delta S_m = S_m^L - S_m^S$$

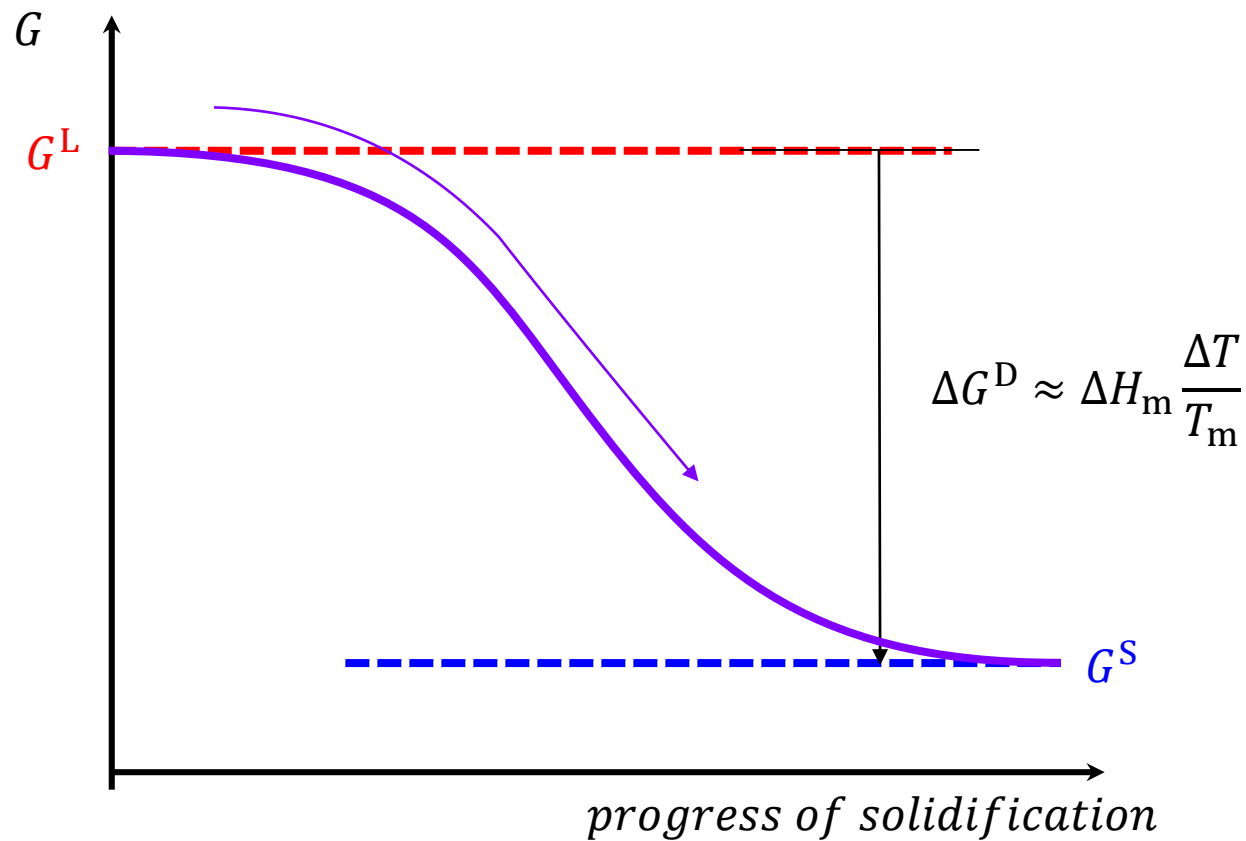
Solidification



Solidification

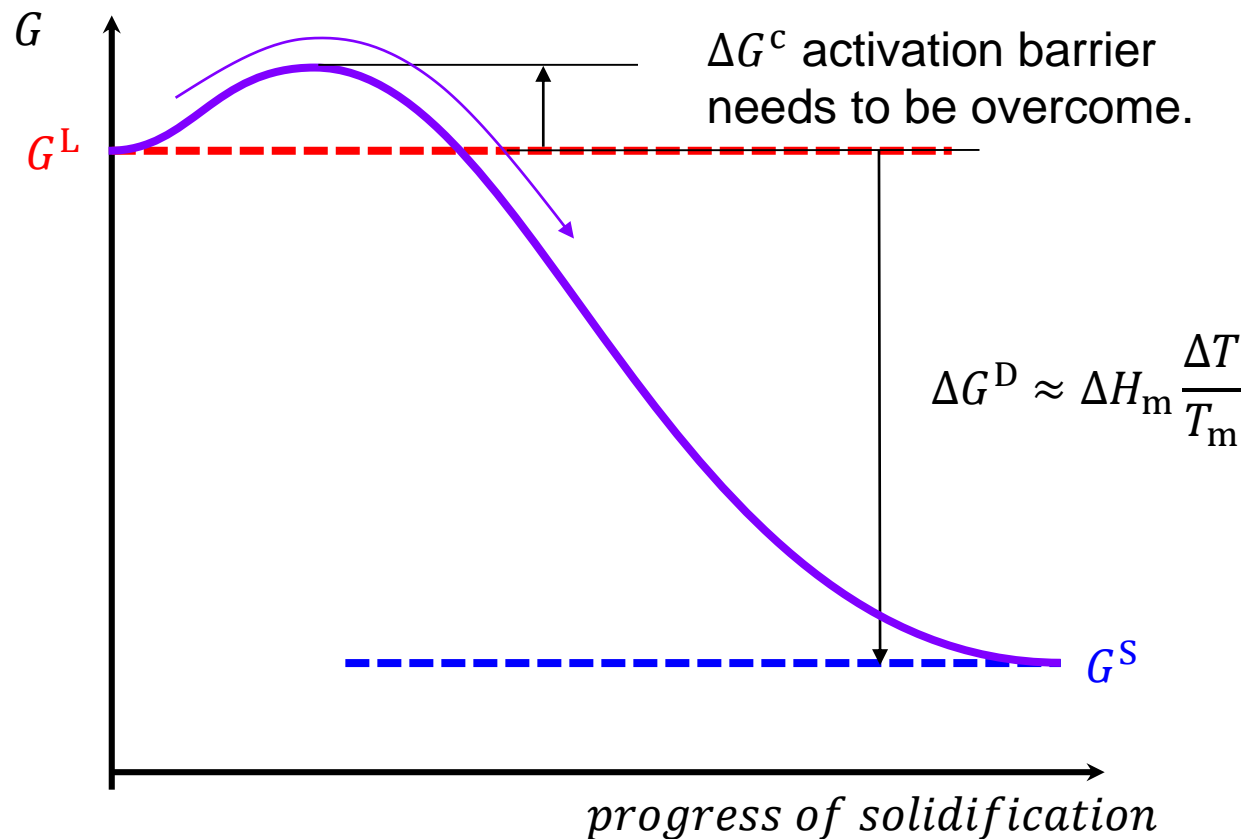


Progress of Solidification



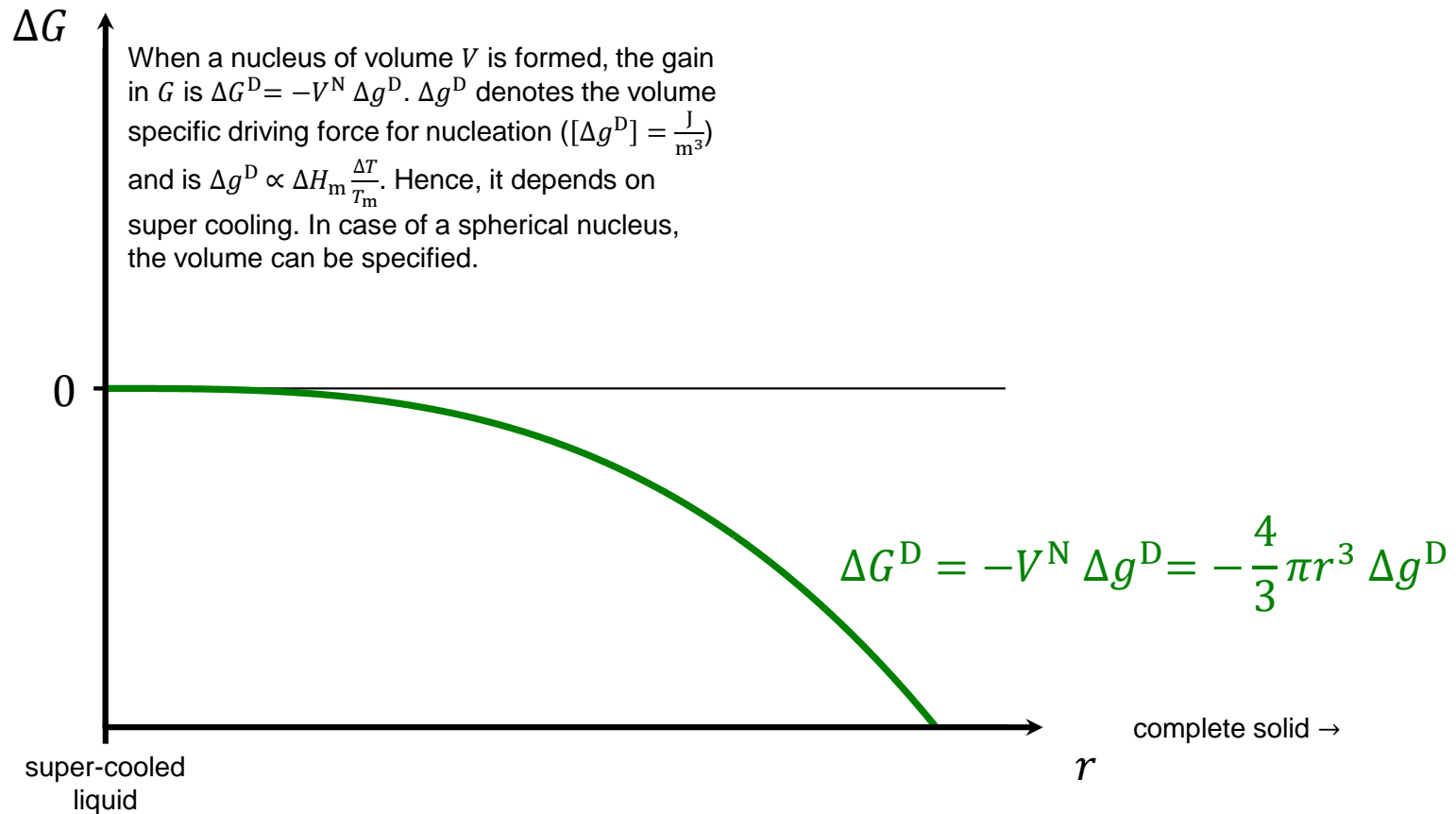
Spontaneous Solidification?

Progress of Solidification

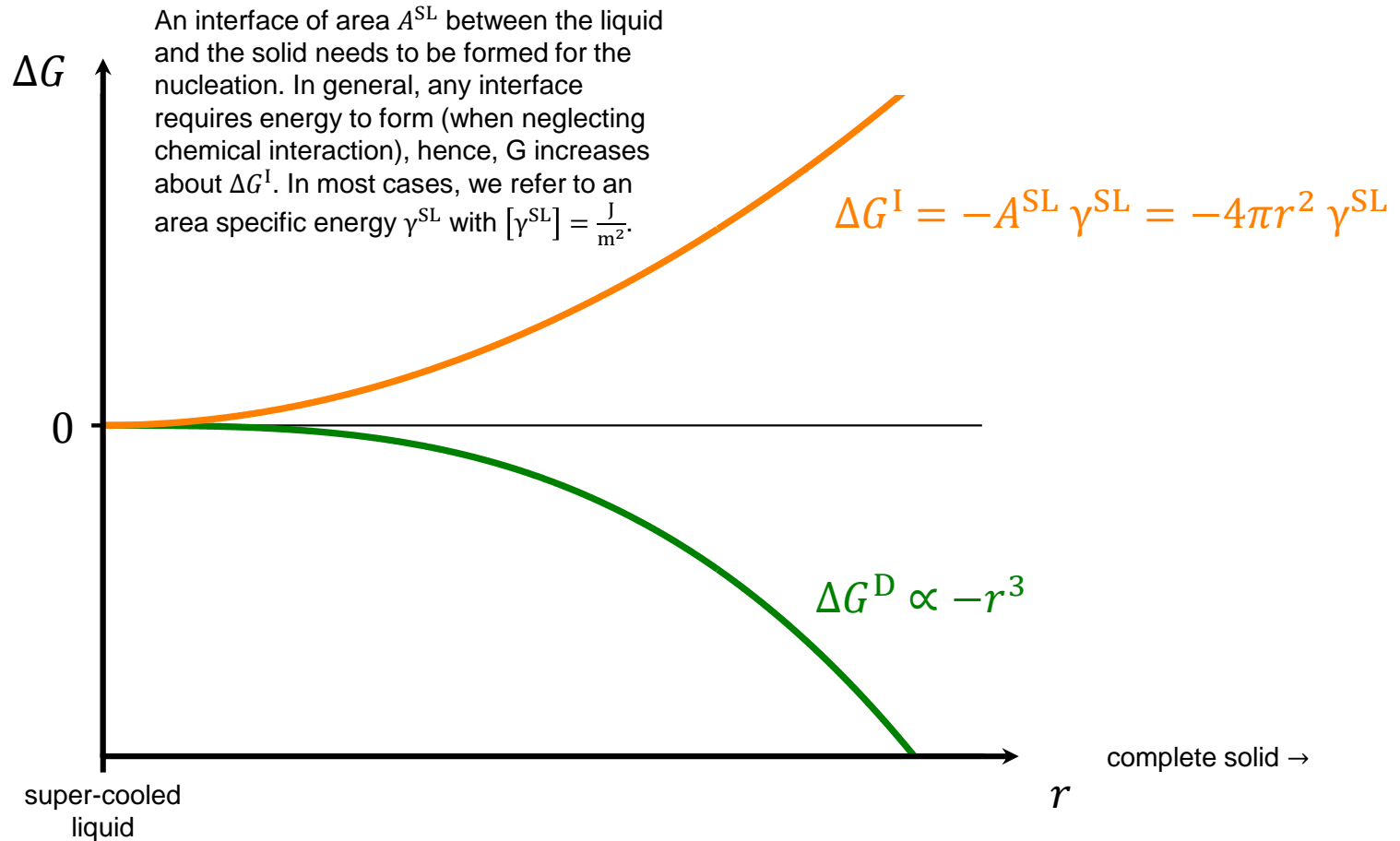


Metastable, super-cooled liquid!

Homogeneous Nucleation

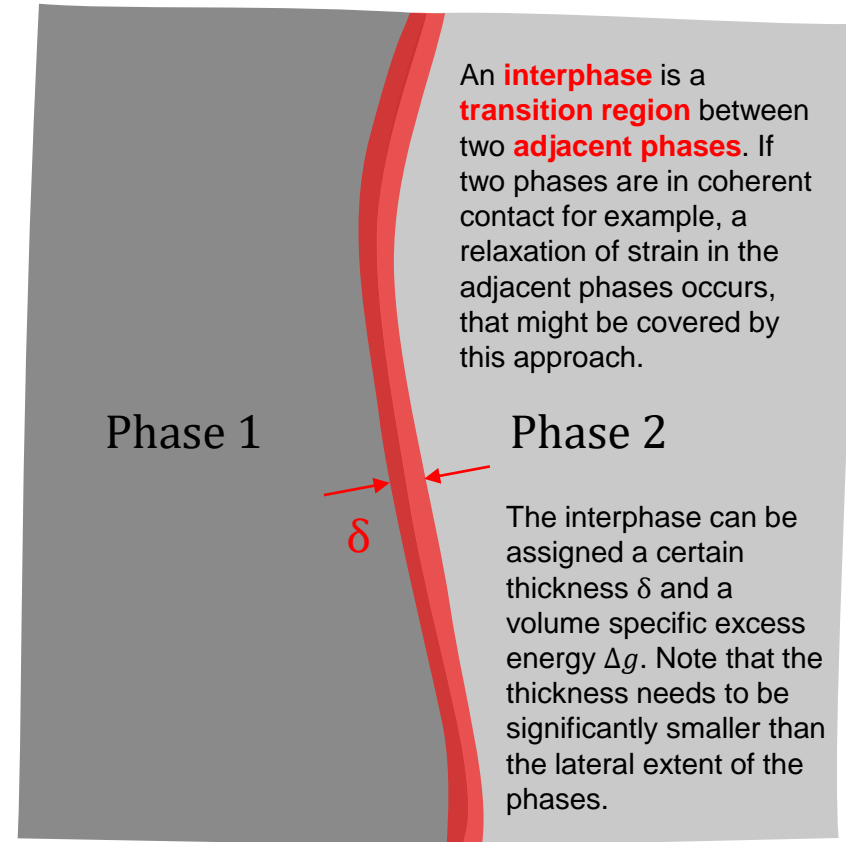
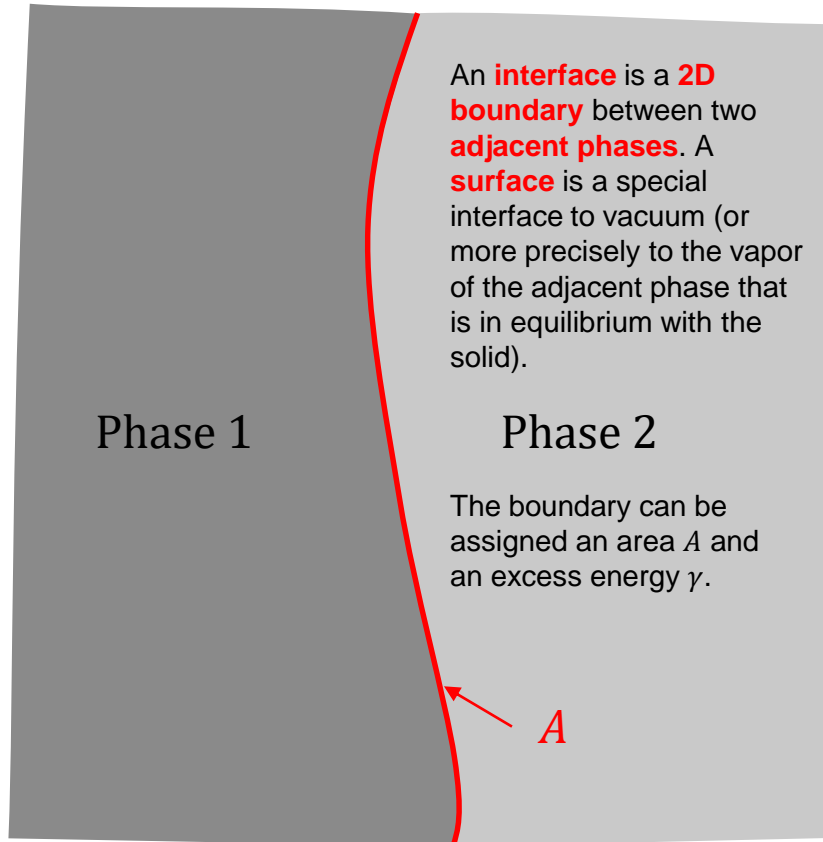


Homogeneous Nucleation



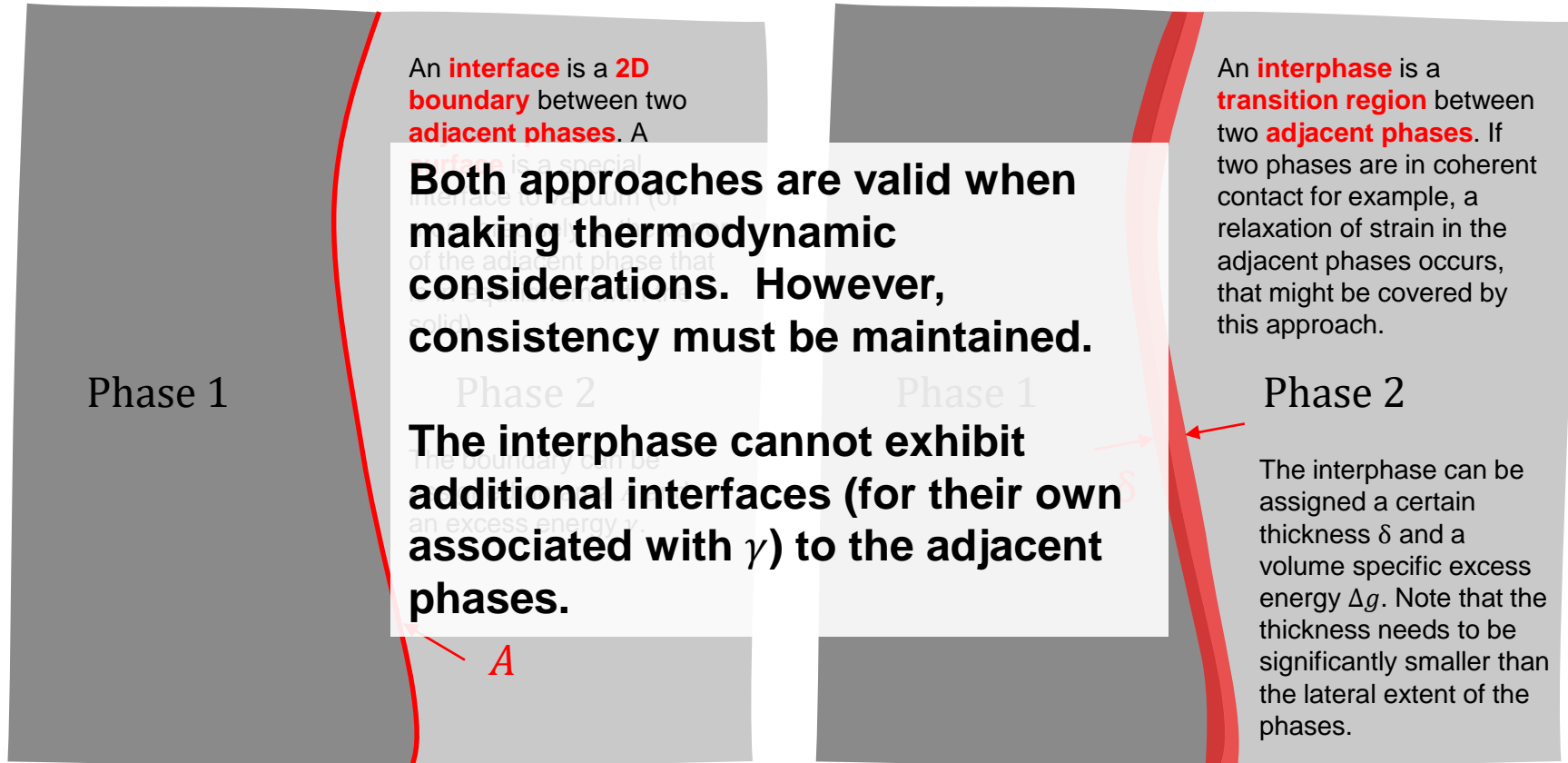
Concept of Interface and Interphase

- Some notes of the thermodynamic concepts on interfaces:

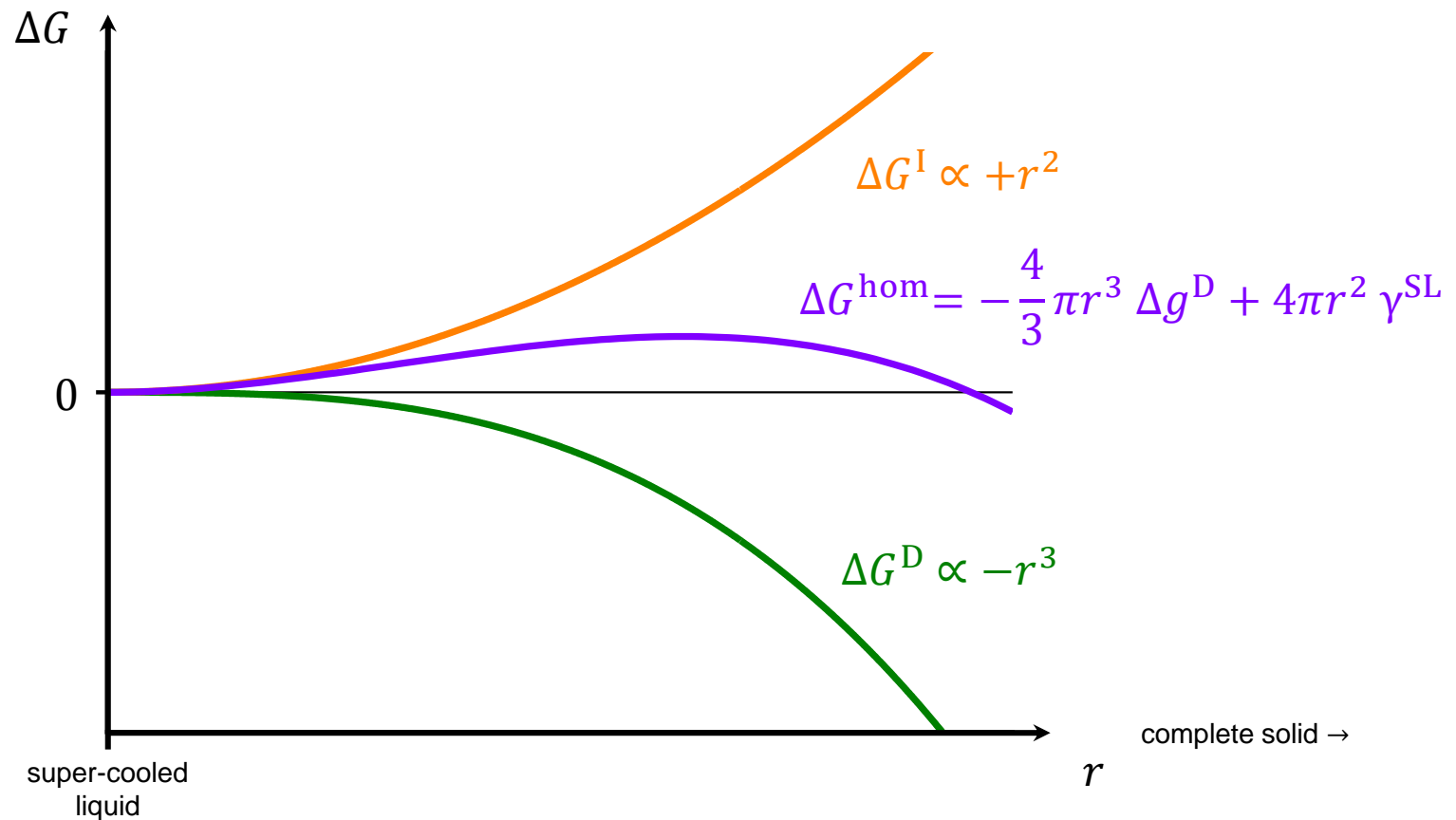


Concept of Interface and Interphase

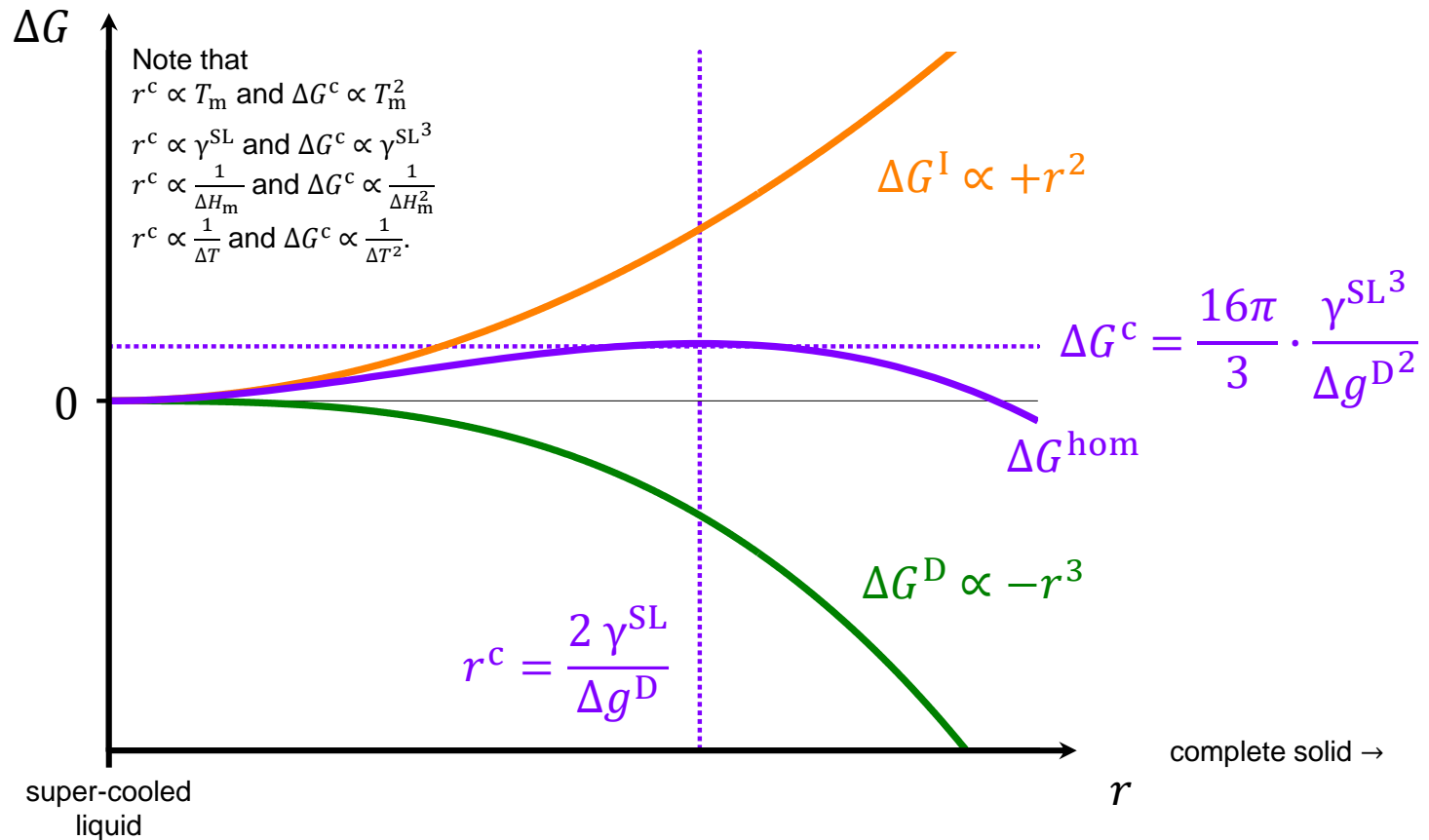
- Some notes of the thermodynamic concepts on interfaces:



Homogeneous Nucleation



Homogeneous Nucleation



Homogeneous Nucleation

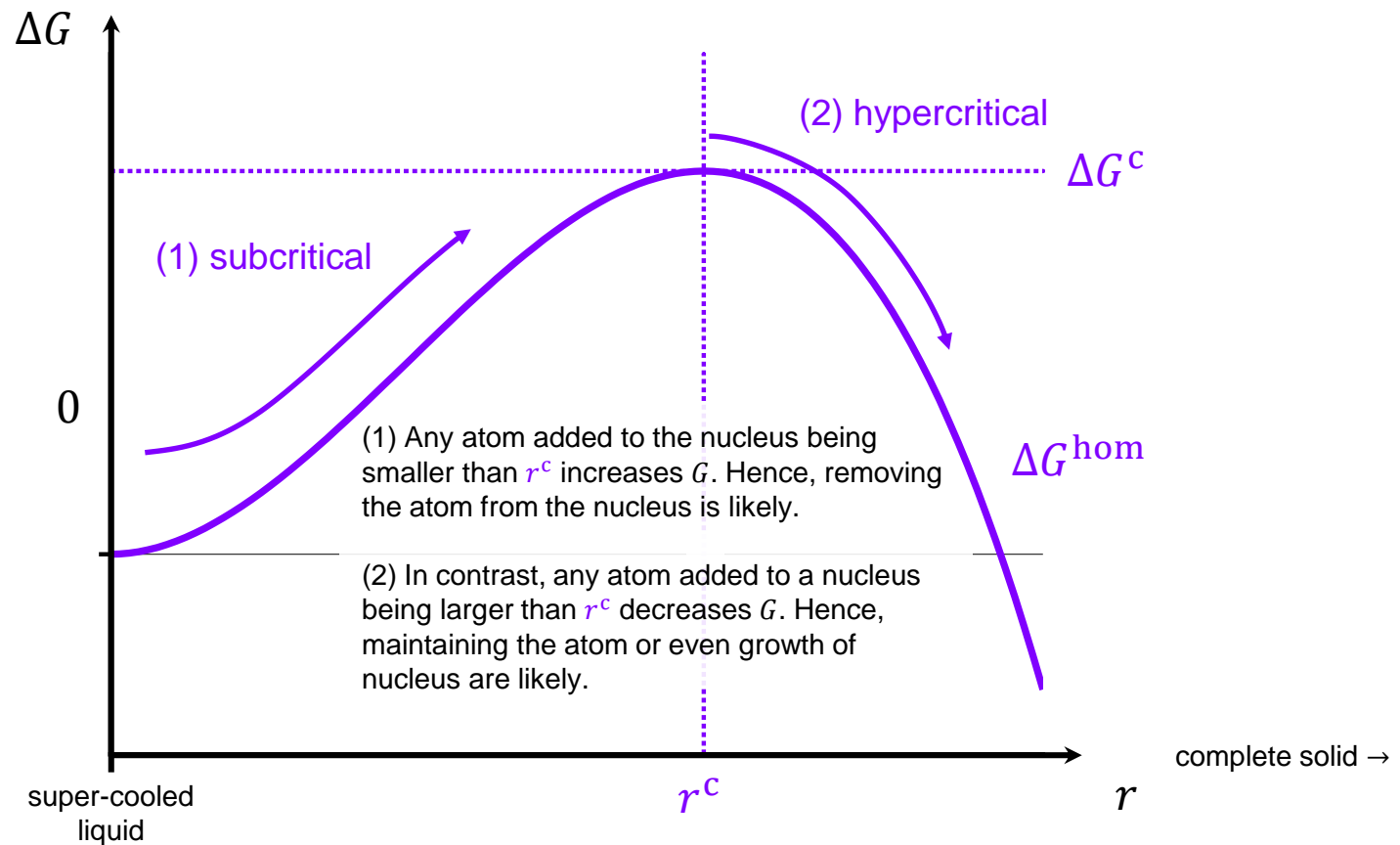
$$\frac{d\Delta G}{dr} = -4\pi r^2 \Delta g^D + 8\pi r \gamma^{SL}$$

$$-r^{c2} \Delta g^D + 2r^c \gamma^{SL} = 0$$

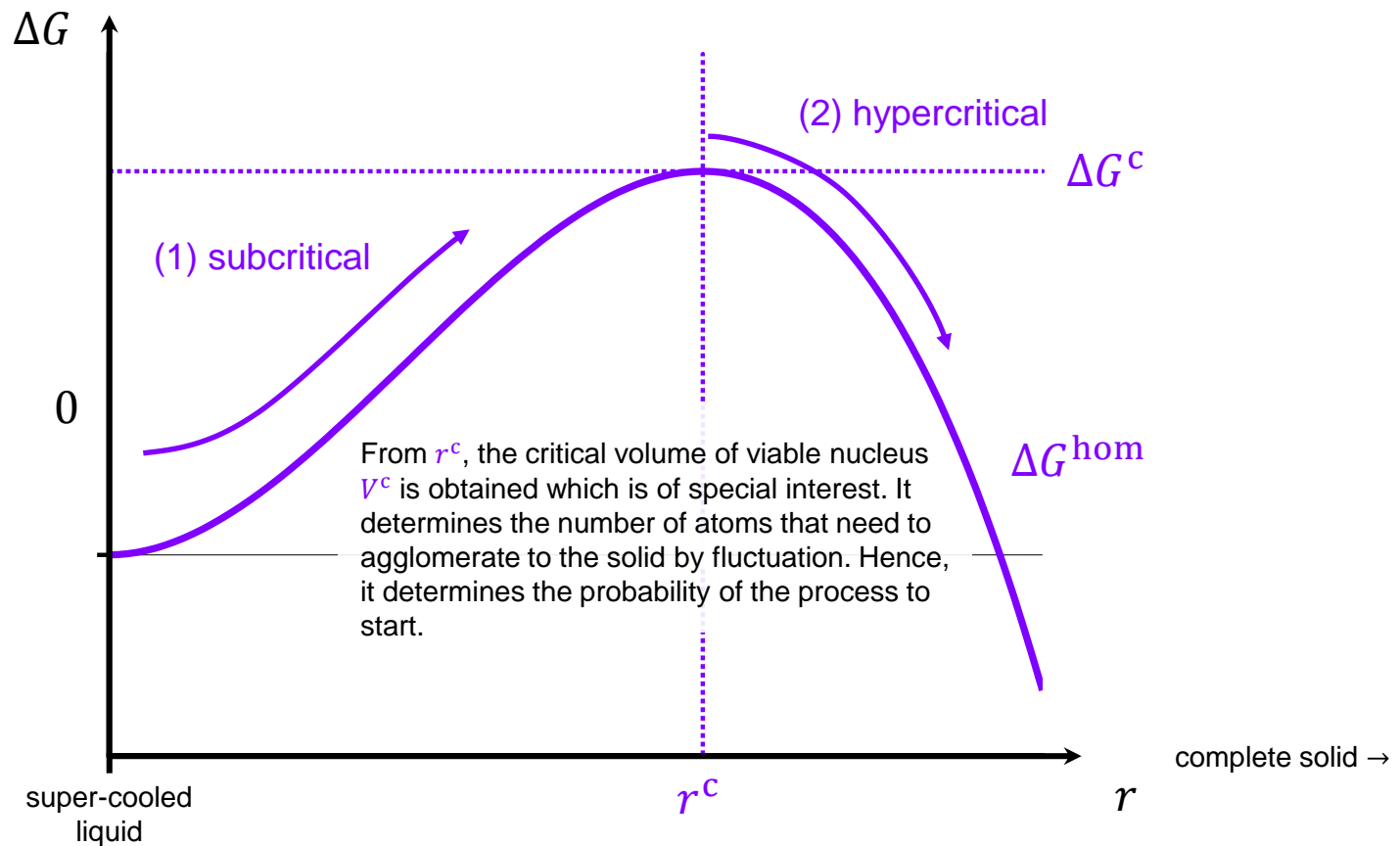
$$r^c = \frac{2 \gamma^{SL}}{\Delta g^D}$$

$$\begin{aligned} \Delta G^c &= \\ \Delta G(r^c) &= -\frac{4}{3} \pi \left(\frac{2 \gamma^{SL}}{\Delta g^D} \right)^3 \Delta g^D + 4\pi \left(\frac{2 \gamma^{SL}}{\Delta g^D} \right)^2 \gamma \\ &= \frac{16\pi \gamma^{SL3}}{3 \Delta g^{D2}} \end{aligned}$$

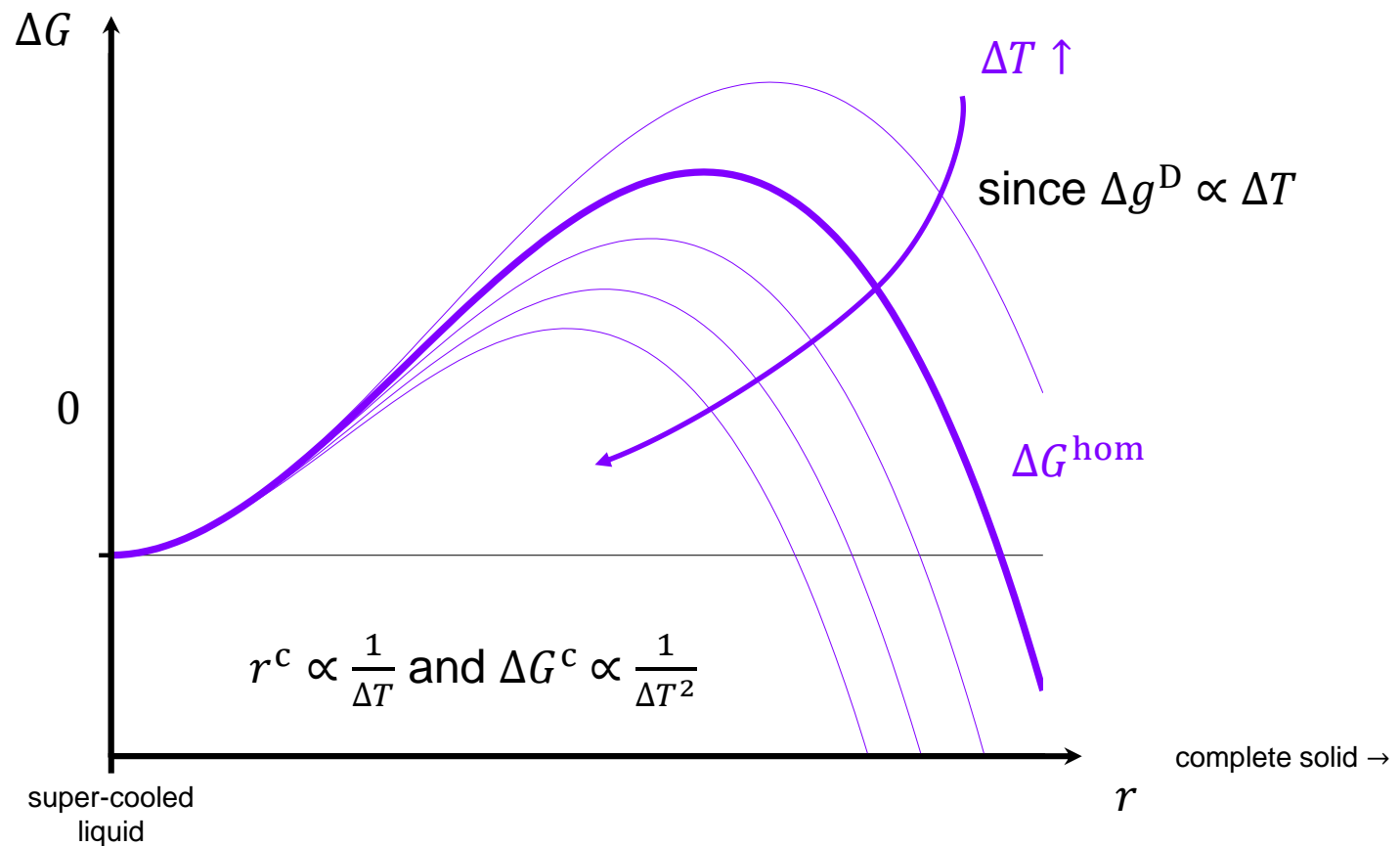
Homogeneous Nucleation



Homogeneous Nucleation

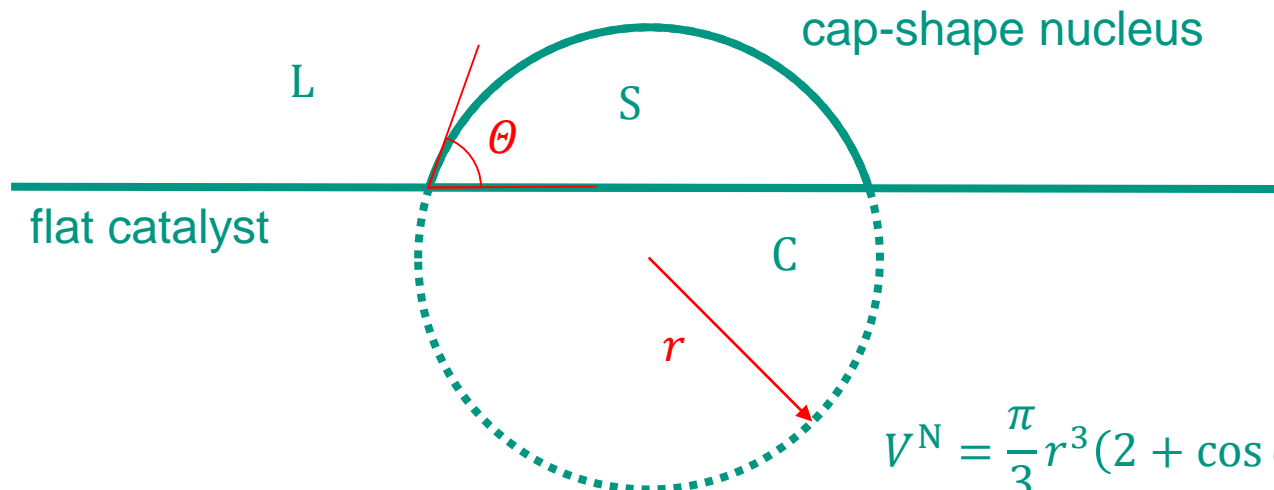


Homogeneous Nucleation



Heterogeneous Nucleation

- Apart from super cooling, ΔG can be manipulated by modification of the interface contribution.
- For example, wetting of the nucleus at an already existing catalyst (e.g. walls of molds and dies) can be assumed:



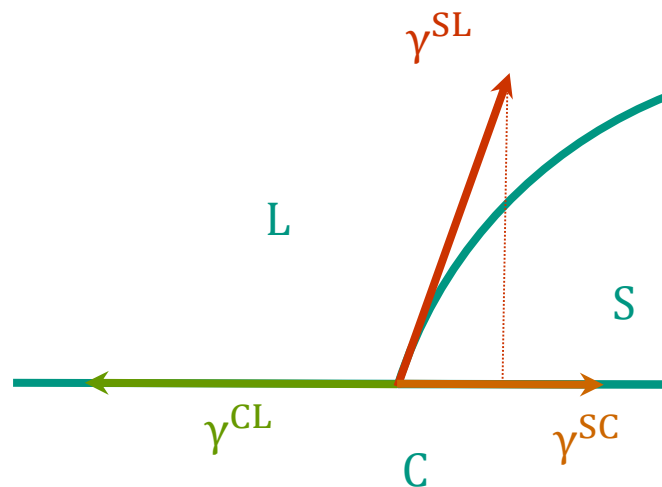
$$V^N = \frac{\pi}{3} r^3 (2 + \cos \theta)(1 - \cos \theta)^2$$

$$A^{SL} = 2\pi r^2 (1 - \cos \theta)$$

$$A^{CS} = \pi r^2 (1 - \cos^2 \theta)$$

Heterogeneous Nucleation

- In order to estimate the interface energies, Young's pseudo equilibrium can be considered:



$$\gamma^{CL} = \gamma^{SC} + \gamma^{SL} \cos \theta$$

Note that for mechanical equilibrium, the reaction force by the catalyst perpendicular to its surface needs to be considered by proper sectioning.

Heterogeneous Nucleation

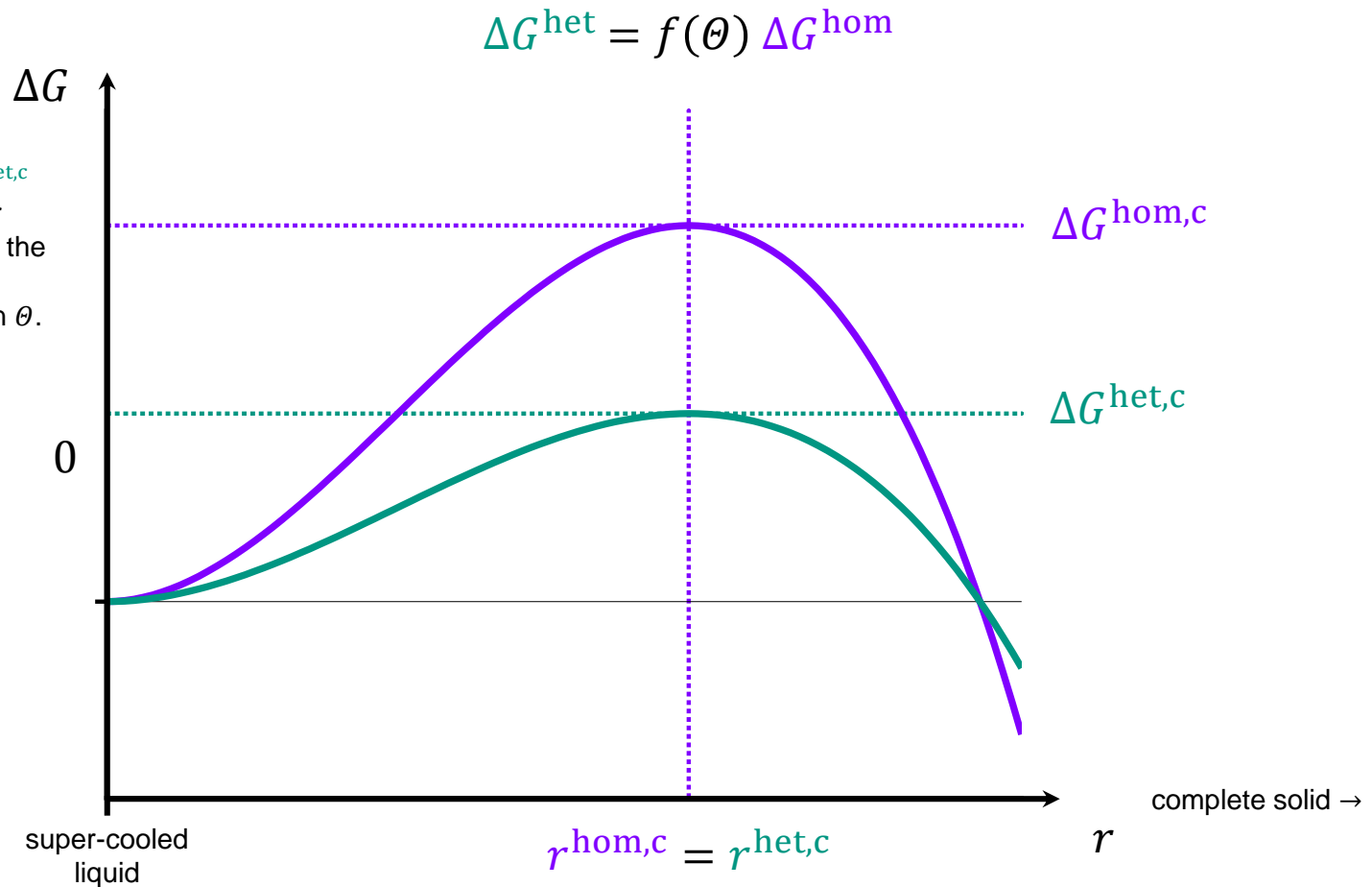
- In order to estimate the interface energies, Young's pseudo equilibrium can be considered:

Note that the interface **CL** exists before nucleation and is removed by nucleation. Instead, the interface **SC** is formed.

$$\begin{aligned}
 \Delta G^{\text{het}} &= -V^{\text{N}} \Delta g^{\text{D}} + A^{\text{SL}} \gamma^{\text{SL}} + A^{\text{SC}} \gamma^{\text{SC}} - A^{\text{CL}} \gamma^{\text{CL}} \\
 &= -\frac{\pi}{3} r^3 (2 + \cos \theta) (1 - \cos \theta)^2 \Delta g^{\text{D}} + 2\pi r^2 (1 - \cos \theta) \gamma^{\text{SL}} \\
 &\quad + \pi r^2 (1 - \cos^2 \theta) (\gamma^{\text{SC}} - \gamma^{\text{CL}}) \\
 &= -\frac{\pi}{3} r^3 (2 + \cos \theta) (1 - \cos \theta)^2 \Delta g^{\text{D}} + 2\pi r^2 (1 - \cos \theta) \gamma^{\text{SL}} \\
 &\quad - \pi r^2 (1 - \cos^2 \theta) \gamma^{\text{SL}} \cos \theta \\
 &= -\frac{\pi}{3} r^3 \Delta g^{\text{D}} (2 - 3 \cos \theta + \cos^3 \theta) + \pi r^2 \gamma^{\text{SL}} (2 - 3 \cos \theta + \cos^3 \theta) \\
 &= \left(-\frac{4}{3} \pi r^3 \Delta g^{\text{D}} + 4\pi r^2 \gamma^{\text{SL}} \right) \frac{1}{4} (2 - 3 \cos \theta + \cos^3 \theta)
 \end{aligned}$$

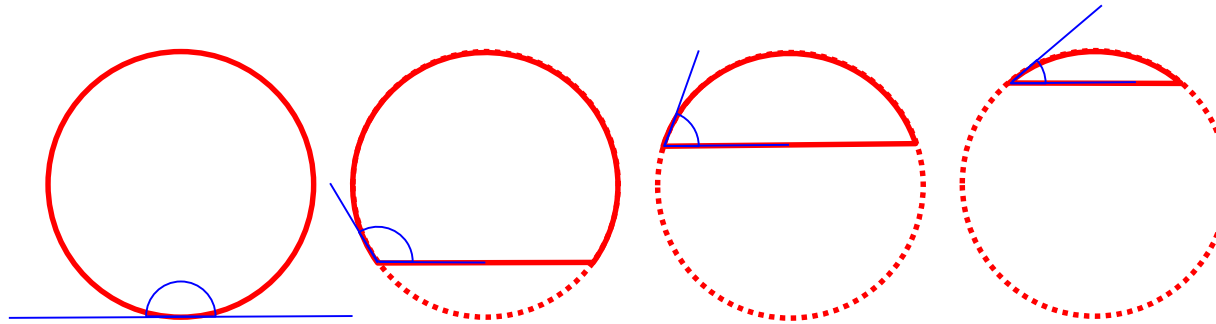
Heterogeneous Nucleation

The critical radius $r^{\text{het},c}$ remains the same for both situations while the $\Delta G^{\text{het},c}$ barrier gets smaller depending on θ .



with $f(\theta) = \frac{1}{4} (2 - 3 \cos \theta + \cos^3 \theta), 0 \leq f(\theta) \leq 1$

Heterogeneous Nucleation



critical volume $V^{\text{het},c}$ decreases with better wetting \longrightarrow

It might be counter-intuitive that the critical radius remains the same while the G barrier gets smaller.

The contradiction is resolved by considering the volume. Indeed, the volume of the critical nucleus gets smaller with decreasing θ .

$$V^{\text{het},c} = V^{\text{hom},c} f(\theta)$$

The volume determines how many atoms need to join by fluctuations to form a small crystal-like object of critical size. Hence, volume determines the probability of the process in contrast to the radius of cap-shaped nucleus.

Heat of fusion

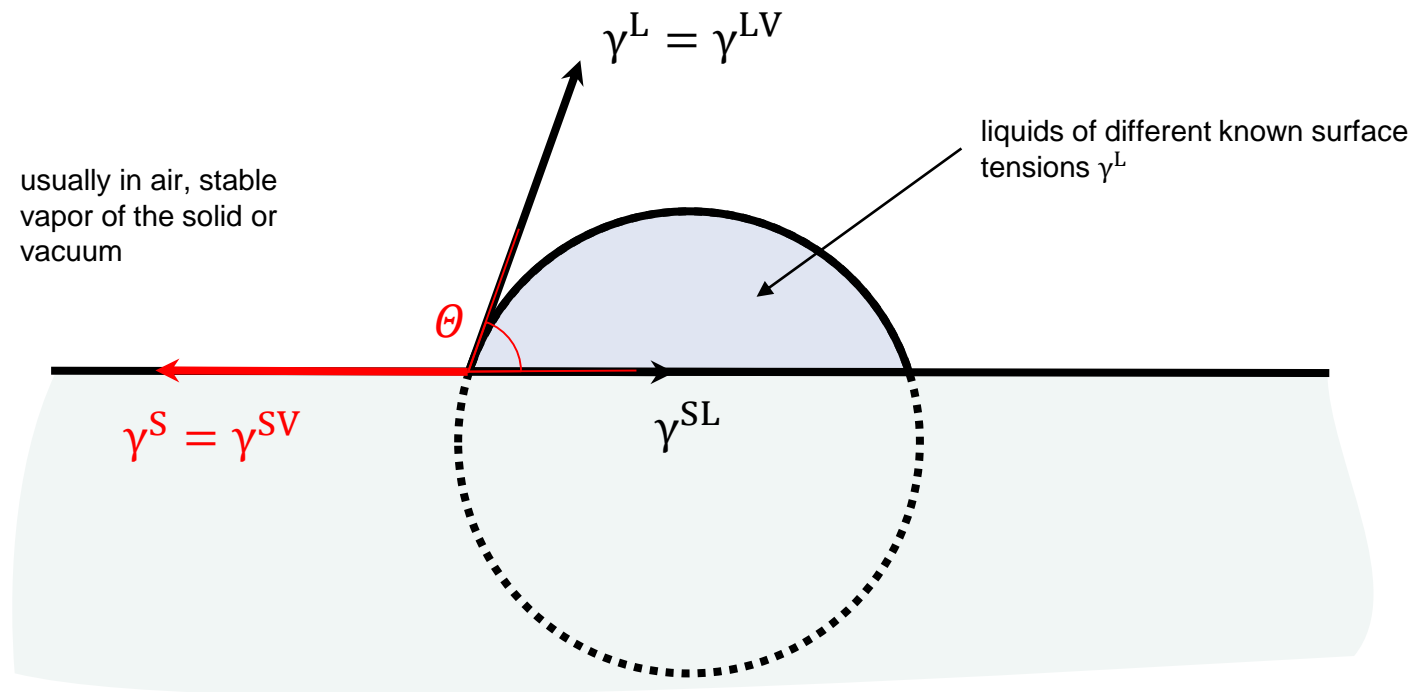
Metal	$\Delta H_m/\text{kJ/mol}$	$\Delta H_m/\text{meV}$	T_m/K	$\Delta S_m/k_B$
Al	10.79	112	933	11.6
Cu	12.93	134	1358	9.5
Fe	13.81	143	1811	7.6
Au	12.72	132	1337	9.5
Ag	11.28	117	1235	9.1
Pb	4.78	50	601	8.0
Pt	22.17	230	2042	10.9
Ni	17.04	177	1728	9.9
Mo	37.48	389	2896	12.9
W	52.31	542	3695	14.2

Note that for both melting and boiling, the entropy change ΔS_m or ΔS_b can be estimated using Trouton's rule: $\Delta S_m \approx \Delta S_b \approx 10.5 k_B$. It is related to the change in free volume associated with the phase transition. Deviations from this rough estimate provide indication to the binding state of the respective phases.

D. R. Lide (ed.): CRC Handbook of Chemistry and Physics, Boca Raton: CRC Press LLC (2003)

Surface/Interface Energy Determination

- Young's equation can be utilized by measuring (static) contact angles in images of wetted surfaces. There is a need for imaging contrast between substrate, droplet and surrounding medium:



Several methods exist to recalculate the surface energy of the solid. Most commonly, the Owens, Wendt, Rabel and Kaelble (OWRK) approach is applied.

Surface/Interface Energy Determination

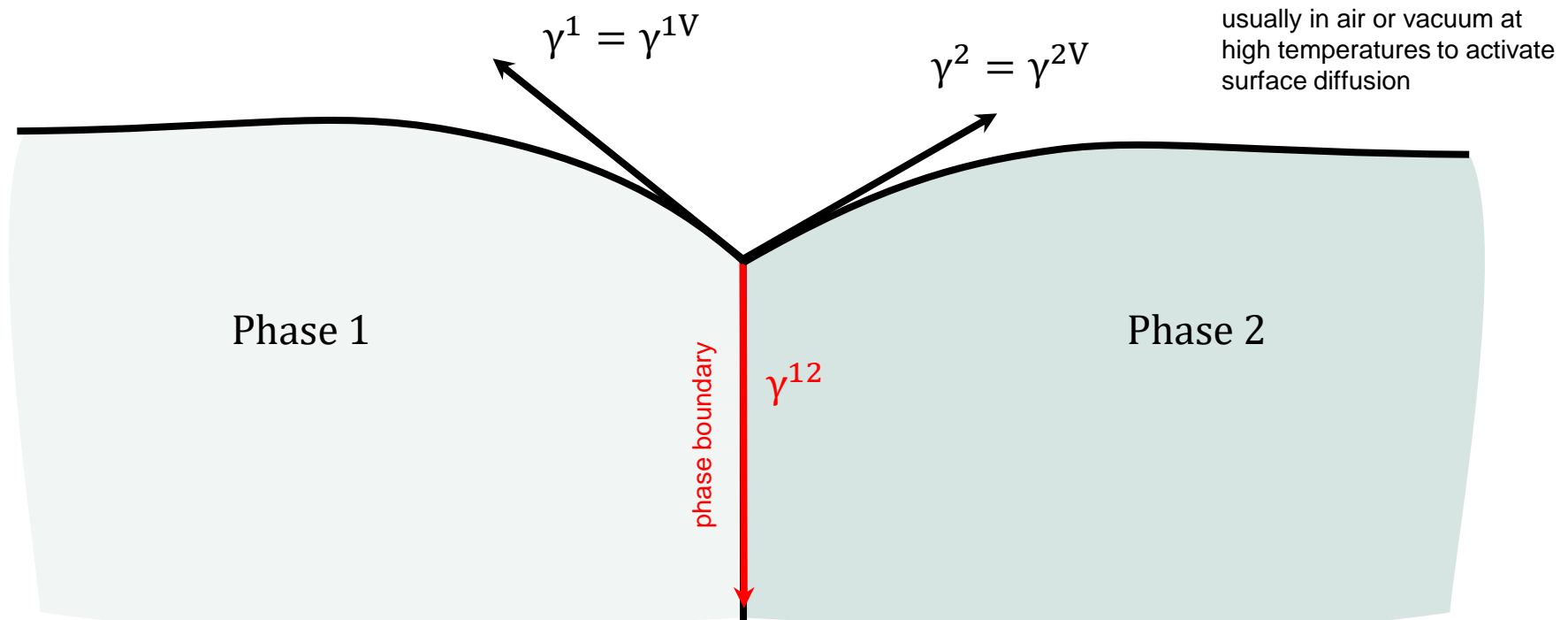


Contact angle image glycerol on polycarbonate glass in unstrained condition. Straining the polymer causes a change in surface energy of the polymer. The images are rescaled to have equal cap radii. The scale bars are 50 μm .

R. D. Schulman et al.: Surface energy of strained amorphous solids, Nature Communications 9 (2018) 982

Surface/Interface Energy Determination

- Similar to the contact angle determination, phase/grain boundary grooves can be analyzed. In the equilibrium state of phase/grain boundary breaking through the surface, the surface tensions are in mechanical equilibrium. Diffusion from the phase/grain boundary to the free surface of the phase regions lead to the formation of grooves when being subjected to sufficiently high temperatures:

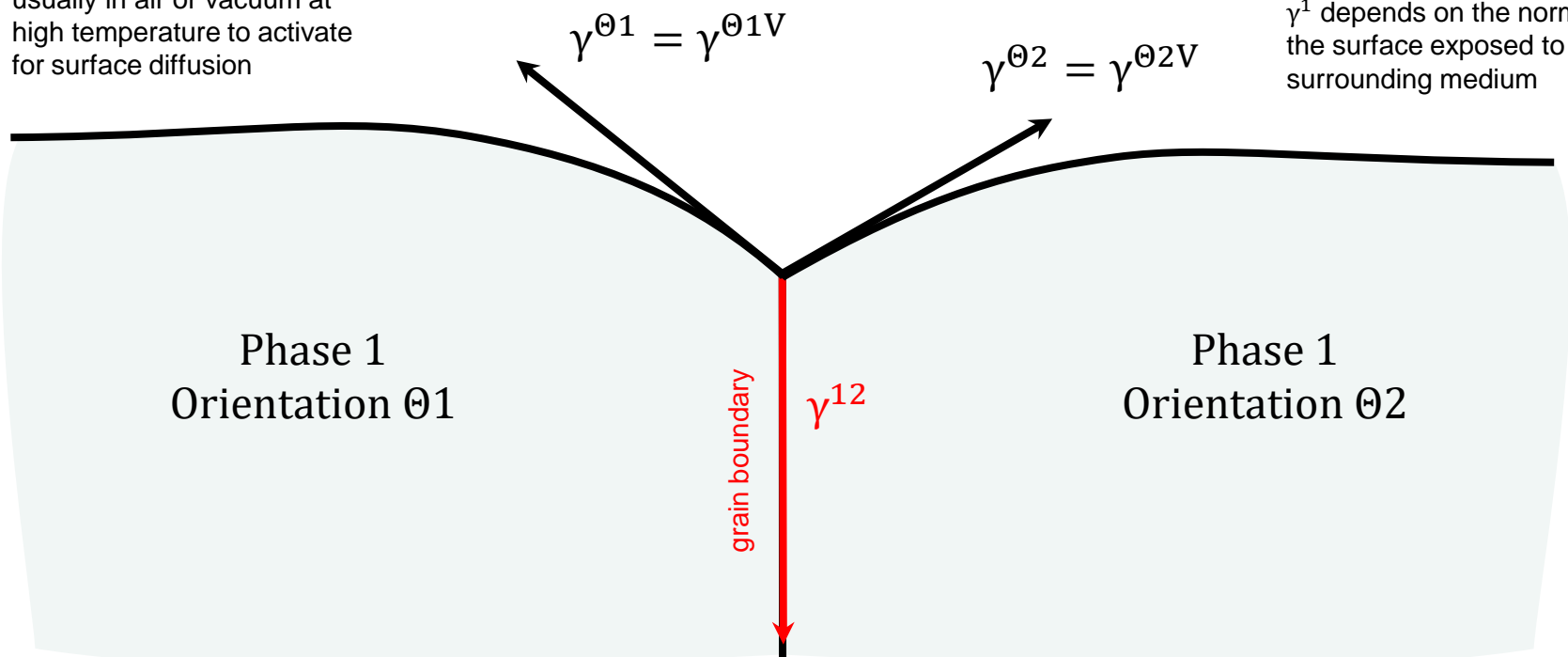


Surface/Interface Energy Determination

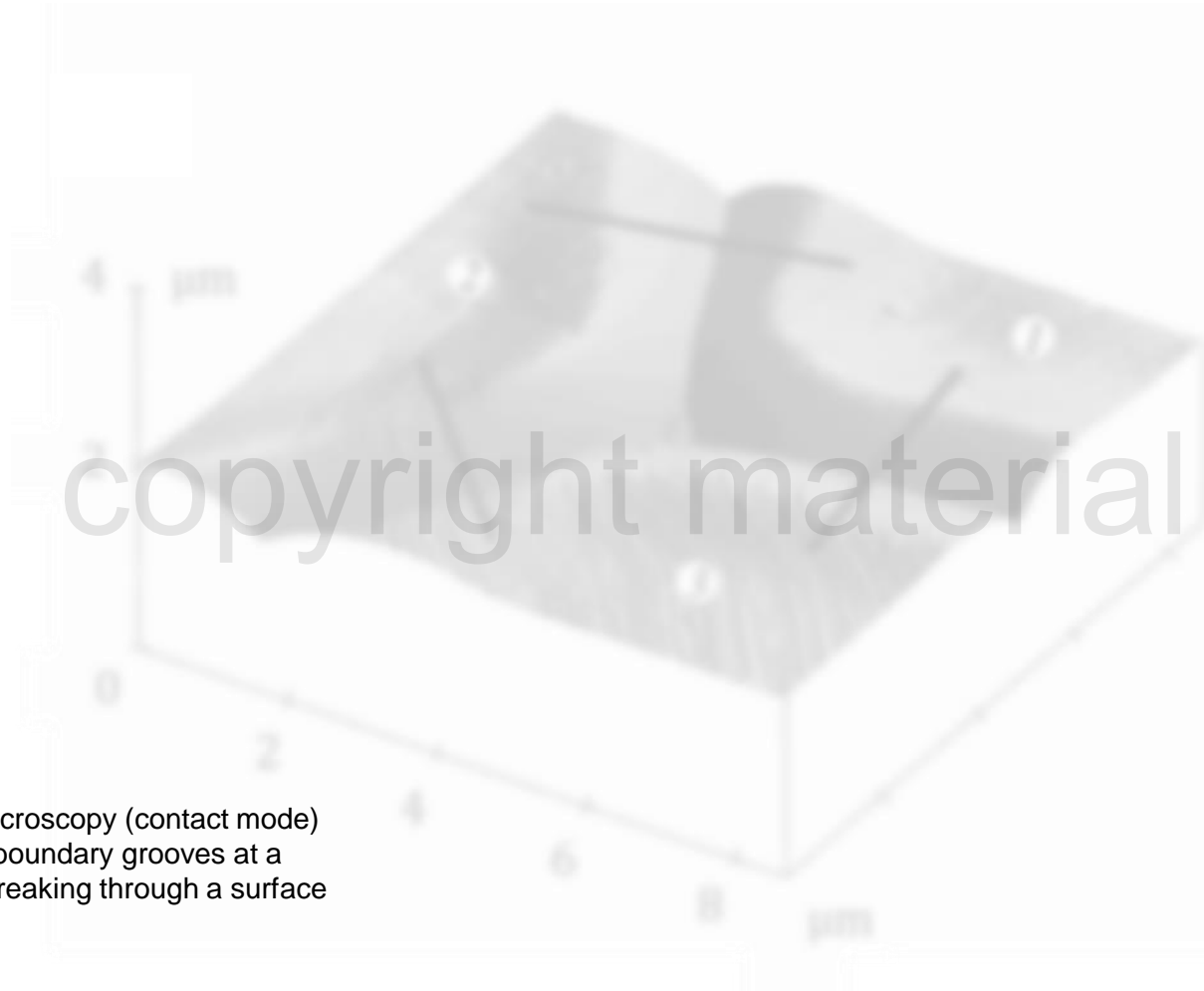
- Similar to the contact angle determination, phase/grain boundary grooves can be analyzed. The equilibrium state of phase/grain boundary penetrating the surface, the surface tensions are also in equilibrium. Diffusion from the phase/grain boundary to the free surface of phase regions lead to the formation of grooves when being subjected to sufficiently high temperatures:

usually in air or vacuum at high temperature to activate for surface diffusion

γ^1 depends on the normal of the surface exposed to the surrounding medium



Surface/Interface Energy Determination

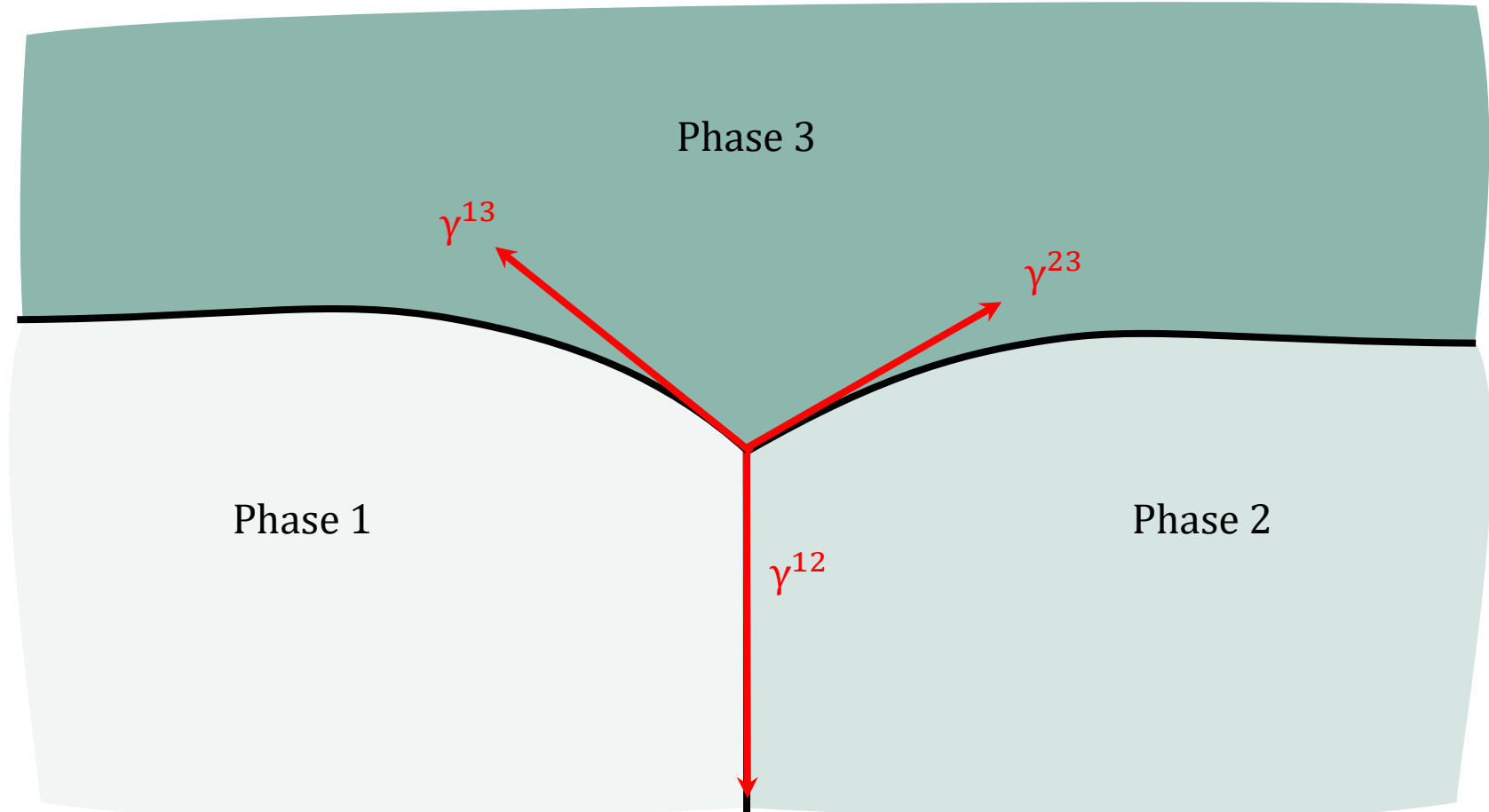


Atomic force microscopy (contact mode) image of grain boundary grooves at a triple junction breaking through a surface of Magnesia.

D. M. Saylor, G. S. Rohrer: Measuring the Influence of Grain-Boundary Misorientation on Thermal Groove Geometry in Ceramic Polycrystals, Journal of the American Ceramic Society 82 (1999) 1529-1536

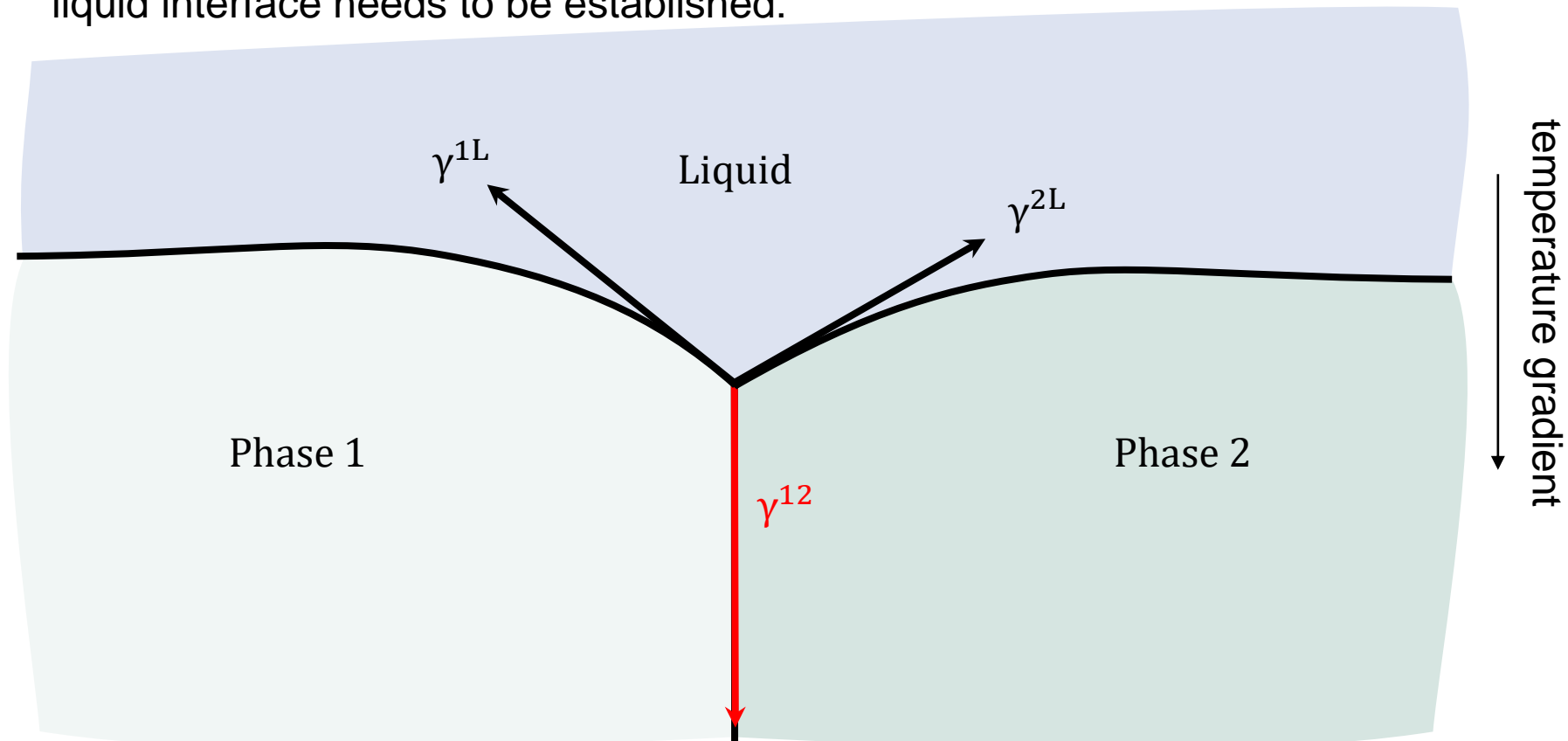
Surface/Interface Energy Determination

- Similarly, the surrounding phase can be another solid phase or the liquid in case of a three-phase equilibrium:



Surface/Interface Energy Determination

- Similarly, the surrounding phase can be another solid phase or the liquid in case of a three-phase equilibrium. In order to maintain the stable equ. of the liquid and the solid phases, a proper temperature gradient across the solid-liquid interface needs to be established:



Surface/Interface Energy Determination



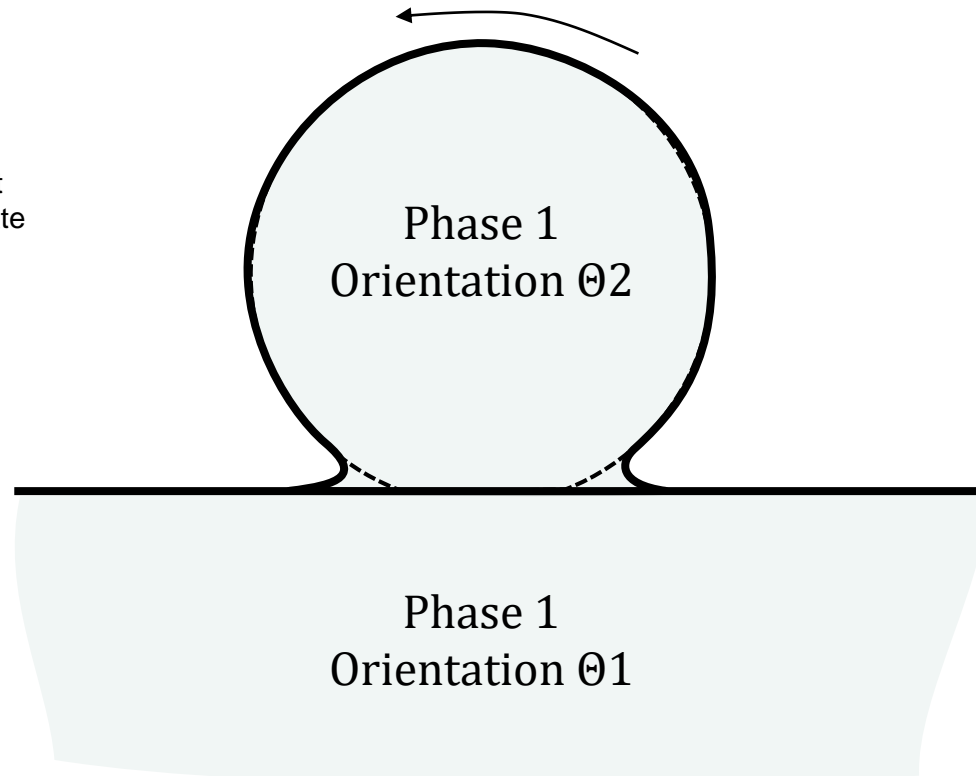
Grain boundary grooves in pro-eutectic phases obtained by quenching in a Bridgman type directional solidification apparatus.

S. Engin, U. Büyük, N. Maraşlı: Determination of interfacial energies in the Al–Ag and Sn–Ag alloys by using Bridgman type solidification apparatus, Journal of Alloys and Compounds 488 (2009) 138-143

Surface/Interface Energy Determination

- For sinter contacts, reorientation of sinter particles occurs to low energy grain boundaries:

usually in air or vacuum at high temperature to activate for surface diffusion



Super cooling

- Consider Fe with $\Delta H_m = 13.81 \text{ kJ/mol}$, $T_m = 1811 \text{ K}$ and a volume per atom at T_m of $V_A = 12.7 \text{ \AA}^3$ (see Ch. 2 on dilatometry). Typical values for γ^{SL} are in the order of $\approx 100 \text{ mJ/m}^2$.

- The volumetric $\Delta h_m = \frac{\Delta H_m}{V_m} = \frac{\Delta H_m}{V_A N_A} = 1.8 \cdot 10^9 \text{ J/m}^3$.

- The critical radii are then $r^c = \frac{2 \gamma^{SL}}{\Delta g^D} = \frac{2 \gamma^{SL} T_m}{\Delta h_m \Delta T}$ with:

$$\Delta T = 10 \text{ K: } r^c \approx 201 \text{ \AA}$$

$$\Delta T = 20 \text{ K: } r^c \approx 100 \text{ \AA}$$

$$\Delta T = 30 \text{ K: } r^c \approx 67 \text{ \AA}$$

- This corresponds to N^c atoms in the critical nuclei:

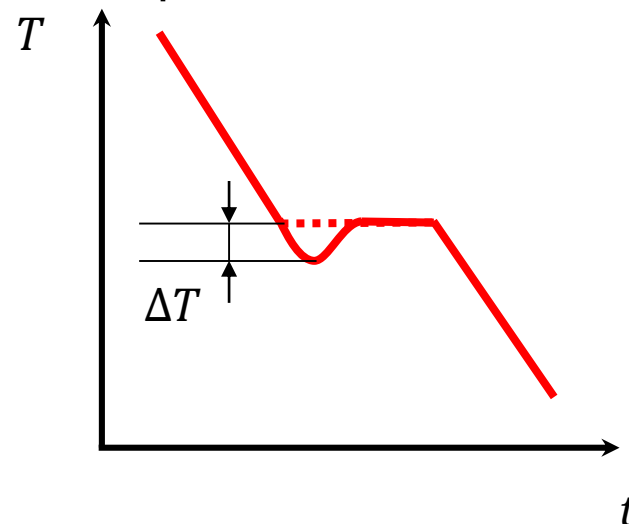
$$\Delta T = 10 \text{ K: } N^c \approx 2.7 \cdot 10^6$$

$$\Delta T = 20 \text{ K: } N^c \approx 3.3 \cdot 10^5$$

$$\Delta T = 30 \text{ K: } N^c \approx 9.9 \cdot 10^4$$

Super cooling

- Considering the high temperatures, only a very limited number of atoms need to join to a critical nucleus by fluctuations.
- In engineering systems, artificial or unintentional catalysts are always present (particles in the liquid or container walls) or perturbation of the system (convection, stirring, etc.) occurs leading to even smaller numbers of atoms to form critical nuclei, for example by heterogeneous nucleation, or to increased number of fluctuations.
- Hence, super cooling under practical conditions usually remains small.



Super cooling

- In order to maintain systems at large super cooling, special techniques are needed.
- There are experiments performed on International Space Station (ISS) that allow for container-less melting in low gravity conditions in order to achieve large super cooling:



Electro-magnetic levitation (ISS-EML)



Electro-static levitation furnace (ISS-ESL)

DLR (2014): https://www.dlr.de/content/de/bilder/2014/4/ohne-behaelter-schmelzen-mit-dem-eml-an-bord-der-iss-ist-das-moeglich_17106.html

NASA (2019): https://www.nasa.gov/mission_pages/station/research/news/b4h-3rd/it-levitating-without-container