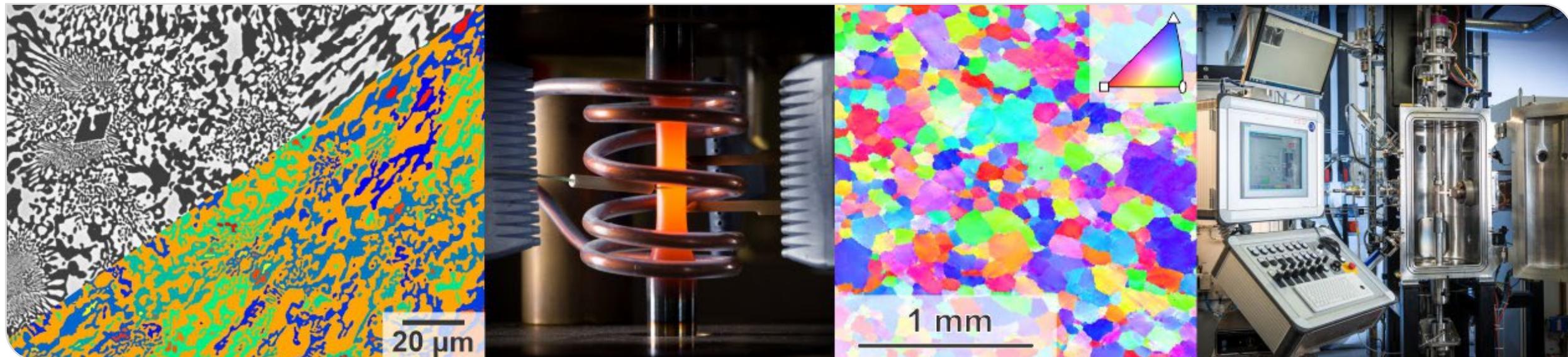# Phase Transformations in Materials

Lecture for "Mechanical Engineering" and "Materials Science and Engineering"
Dr.-Ing. Alexander Kauffmann (Bldg. 10.91, R. 375)
Dr. Sandipan Sen (Bldg. 10.91, R. 311)
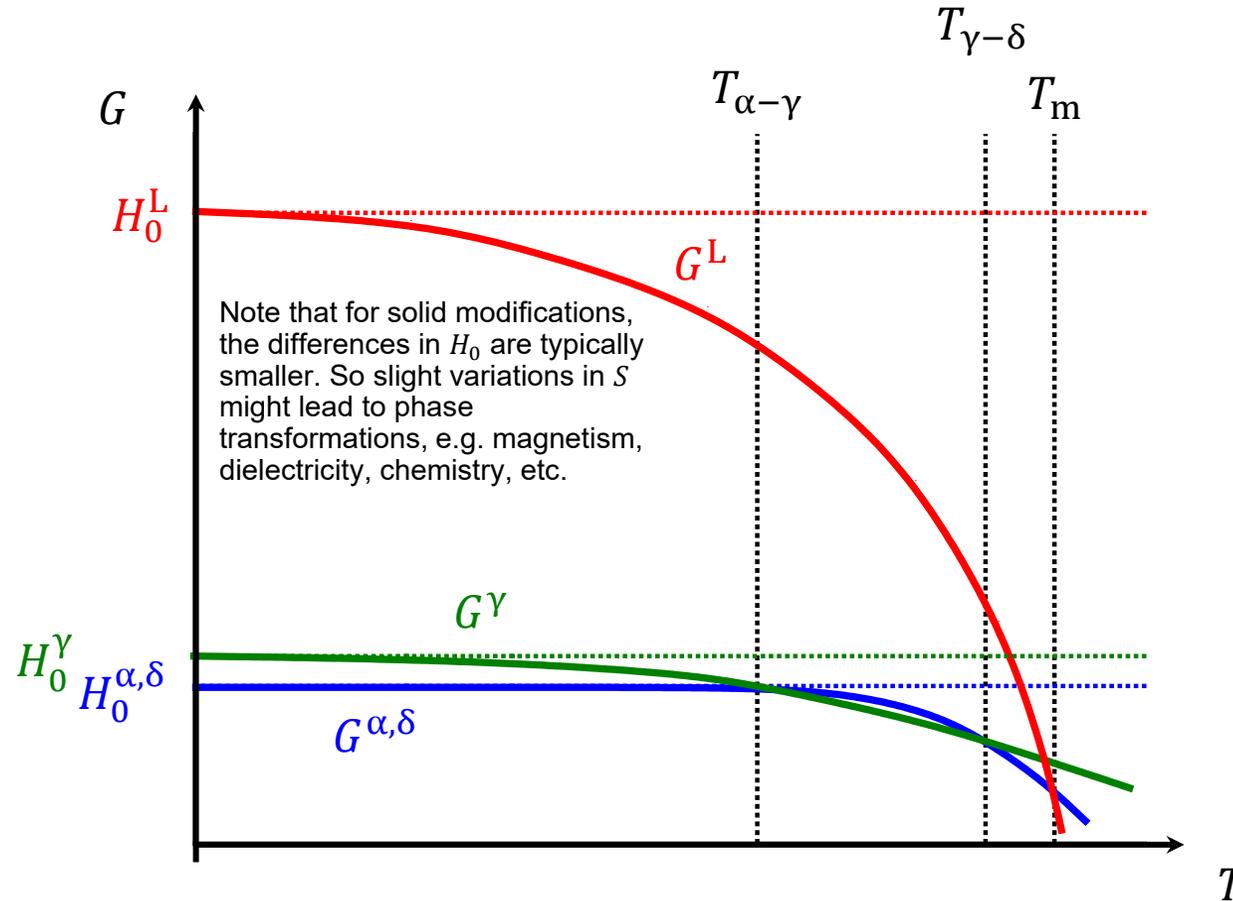
Version 23-12-15

www.kit.edu

Topics

- Allotropic Transformations
  - Driving Force and Latent Heat
  - Nucleation, Impact of Strain Energy
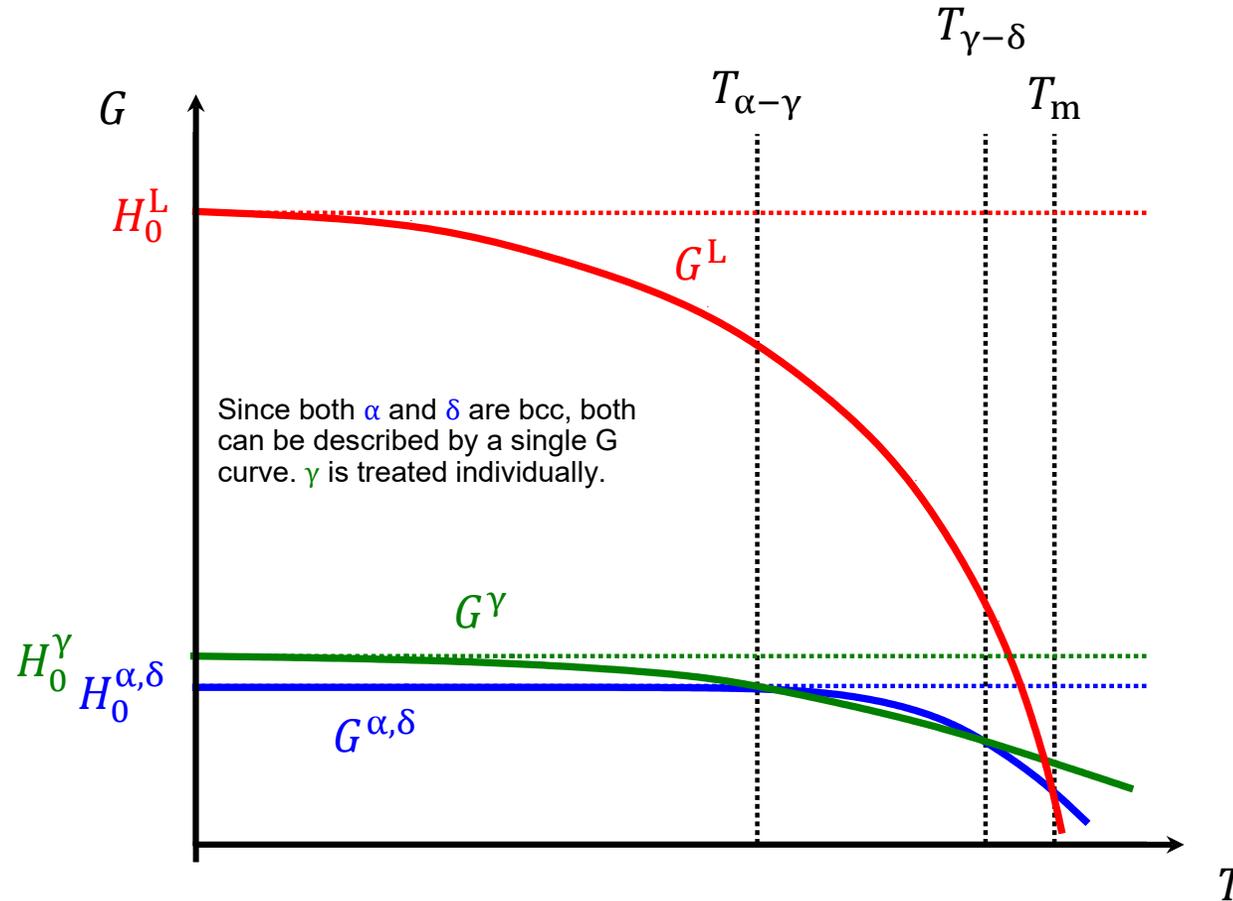
Extension to Solidification

- For allotropic transformations, the same considerations on phase transformations as for solidification need to be considered but with taking into account

  - that the newly formed and surrounding phase are elastically stiff and, hence, strain energy of both need to be considered during both, nucleation and growth,

  - and that the growing phase cannot rearrange when getting in contact. (The nucleation sites in the liquid are free and can move, in the solid they are fixed and cannot move. This needs to be considered during integration to obtain the transformed volume)

Driving Force and Latent Heat

Note that for solid modifications, the differences in H_0 are typically smaller. So slight variations in S might lead to phase transformations, e.g. magnetism, dielectricity, chemistry, etc.

Iron Fe

Driving Force and Latent Heat

Since both α and δ are bcc, both can be described by a single G curve. γ is treated individually.

Iron Fe

Phase Transformations in Materials

Driving Force and Latent Heat

α exhibits ferromagnetic order at $T < T_C$. Above T_C, the ferrite is paramagnetic.

At low temperatures, the ferromagnetic order causes slightly lower S of α over γ. By the transition to the paramagnetic state, the S contribution to G of α increases.

Iron Fe

Phase Transformations in Materials

Homogeneous Nucleation

liquid to solid

$\Delta G^{\mathrm{I}} \propto +r^2$

ΔG

0

$\Delta G^{\mathrm{hom}} = -V^{\mathrm{N}} \Delta g^{\mathrm{D}} + A^{\mathrm{I}} \gamma^{\mathrm{I}}$

$\Delta G^{\mathrm{D}} \propto -r^3$

complete solid →

r

super-cooled
liquid

Revision of Ch. 3a

Phase Transformations in Materials

IAM
Institute for Applied Materials

Homogeneous Nucleation

solid to solid

$$\Delta G^{\mathrm{hom}} = -V^{\mathrm{N}}\,\Delta g^{\mathrm{D}} + V^{\mathrm{N}}\,\Delta g^{\mathrm{S}} + A^{\mathrm{I}}\,\gamma^{\mathrm{I}}$$

$\Delta G^{\mathrm{I}} \propto +r^2$

$\Delta G^{\mathrm{D}} - \Delta G^{\mathrm{S}} \propto -r^3$

$\Delta G^{\mathrm{D}} \propto -r^3$

In the case of a transformation within the solid, the newly formed phase is of different shape and volume than the matrix. Hence, an adaption by elastic strain of the newly formed phase and the matrix occurs. The total strain energy ΔG^{S} associated with this scales with the volume of the newly formed phase.

super-cooled, solid high temperature phase

completely transformed →

Note the subtle impact of ΔG^{S} on the $\propto -r^3$ dependence but the significant shift of ΔG^{hom} over the strain-free case on the slide before.

Homogeneous Nucleation

$$\frac{\mathrm{d}\Delta G}{\mathrm{d}r} = -4\pi r^2 \left(\Delta g^{\mathrm{D}} {\color{red}- \Delta g^{\mathrm{S}}}\right) + 8\pi r\, \gamma^{\mathrm{I}}$$

$$-r^{\mathrm{c}2}\, \Delta g^{\mathrm{D}} + 2r^{\mathrm{c}}\, \gamma^{\mathrm{I}} = 0$$

$$r^{\mathrm{c}} = \frac{2\, \gamma^{\mathrm{I}}}{\Delta g^{\mathrm{D}} {\color{red}- \Delta g^{\mathrm{S}}}}$$

The strain energy term essentially acts like a reduced driving force for the transformation to occur.

$$\Delta G^{\mathrm{c}} =$$

$$\Delta G(r^{\mathrm{c}}) = -\frac{4}{3}\pi \left(\frac{2\, \gamma^{\mathrm{I}}}{\Delta g^{\mathrm{D}}}\right)^3 \Delta g^{\mathrm{D}} + 4\pi \left(\frac{2\, \gamma^{\mathrm{I}}}{\Delta g^{\mathrm{D}}}\right)^2 \gamma$$

$$= \frac{16\pi}{3} \frac{\gamma^{\mathrm{I}3}}{(\Delta g^{\mathrm{D}} {\color{red}- \Delta g^{\mathrm{S}}})^2}$$

Phase Transformations in Materials

Strain Energy

- The strain contribution to the transformation depends on the type of interface of the newly formed phase:
  - **Coherent**: **atomic positions in the interface** between the two phases **match** and accommodation of the different lattice types is needed.
  - Semi-coherent: at least some atomic positions in the interface match.
  - **Incoherent**: **the atomic positions of the two phases do not match within the interface**.

Phase Transformations in Materials

Strain Energy

- Coherent interface:

| Matrix | stress-free Nucleus | constraint N. |
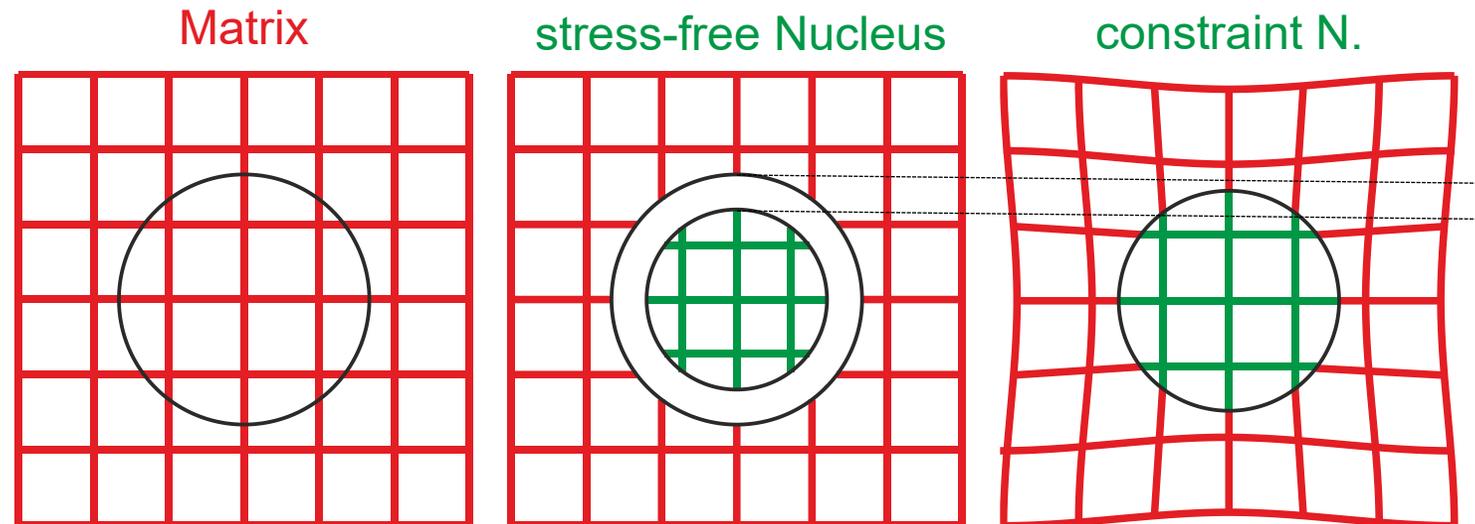
The newly formed phase has a similar crystal structure but with slightly different dimensions and a lattice misfit δ. There is an according volume misfit Δ.

$$\delta = \frac{a^N - a^M}{a^M}$$

$$\Delta = \frac{V^N - V^M}{V^M} \approx 3\delta$$

see Ch. 2

$$\varepsilon = \frac{a'^N - a^M}{a^M}$$

When embedded in the matrix, both matrix and nucleus are strained in order to get matching lattice positions (maintaining coherency).

Strain Energy

- Coherent interface:

  - With typically $0.5\delta < \varepsilon < \delta$, for example $\varepsilon \approx \frac{2}{3}\delta$, for $\nu^{\mathrm{M}} = \nu^{\mathrm{N}} = \nu \approx \frac{1}{3}$ and $G^{\mathrm{M}} = G^{\mathrm{N}} = G$.

  - For a spherical nucleus, the distortion of the nucleus is hydrostatic (uniform in all directions) while being concentrated along the thin axis for a thin plate-like nucleus.

  - The **volume-specific elastic strain energy** can be estimated **for isotropic elastic behavior of both the matrix and the newly formed phase**:

    - $G^{\mathrm{M}} = G^{\mathrm{N}} = G$: $\Delta g^{\mathrm{S}} = \frac{\Delta G^{\mathrm{S}}}{V} = 2\,G\,\delta^2\,\frac{1+\nu}{1-\nu}$ (independent of its shape)

    - $G^{\mathrm{M}} < G^{\mathrm{N}}$: Δg^{S} gets minimized for a flat ellipsoid

    - $G^{\mathrm{M}} > G^{\mathrm{N}}$: Δg^{S} gets minimized for a sphere

    - **In any case, Δg^{S} is a constant.** V denotes the unconstraint volume of the hole.

Phase Transformations in Materials

Strain Energy

- Coherent interface:

  - For anisotropic elastic behavior, minimization of the shape also depends on the crystallographic arrangement of the shape within the lattice.

  - For most metallic materials, positive Zener anisotropies are observed, e.g. $\langle 001 \rangle$ are more compliant than the stiff $\langle 111 \rangle$. Under these conditions, discs parallel to $\{001\}$ are favorable to accommodate most strain in the compliant direction.

Phase Transformations in Materials

Compliance & Stiffness

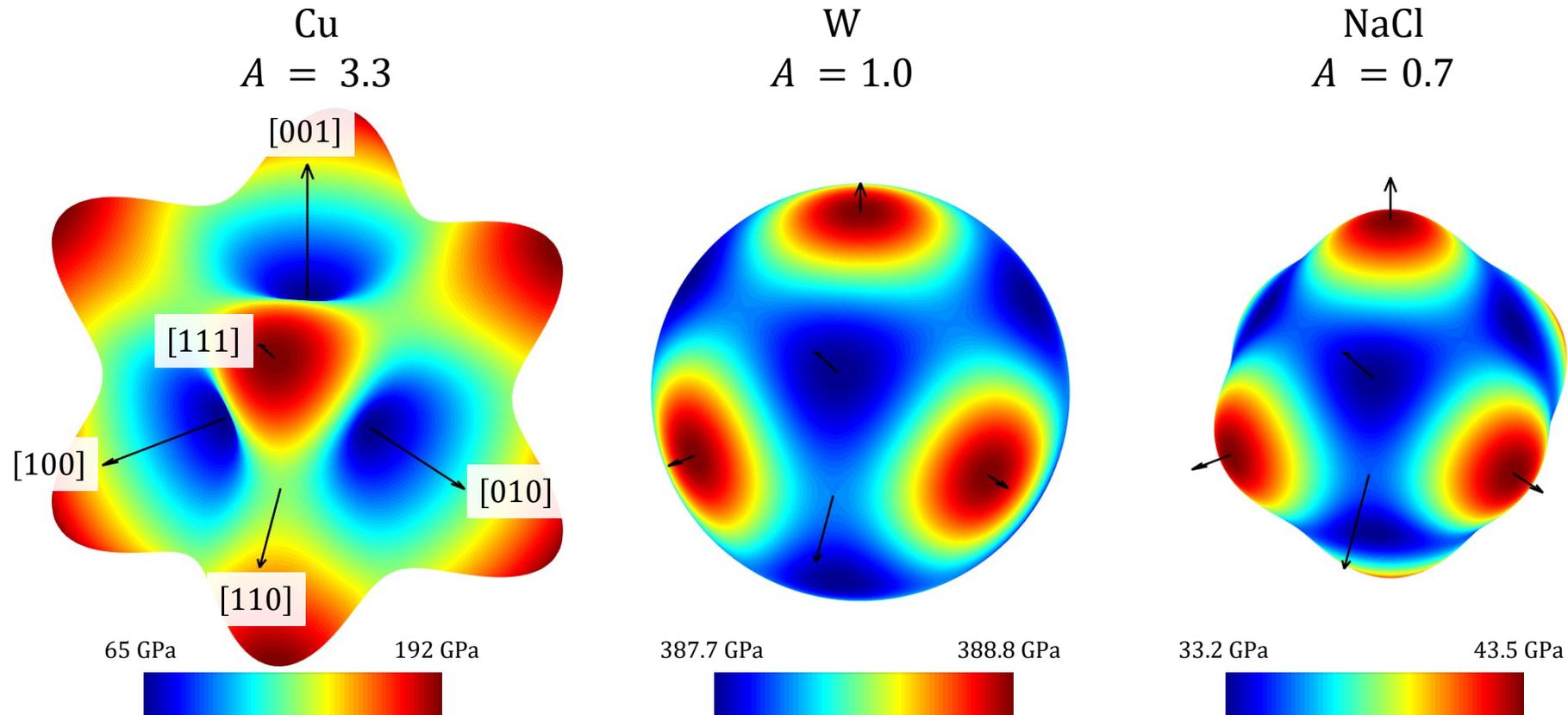| material	prototype	Struktur-bericht	C_{11} / GPa	C_{12} / GPa	C_{44} / GPa	A
Cu	Cu	A1	**166**	**120**	**76**	**3.3**
Al			106	60	28	1.2
Au			193	164	42	2.9
Ni			251	150	124	2.5
$\alpha - $ Fe	W	A2	230	135	117	2.5
W			**501**	**198**	**151**	**1.0**
Si	diamond	A4	166	64	80	1.6
NaCl	NaCl	B1	**49**	**13**	**13**	**0.7**

C. Teodosiu: „Elastic Models of Crystal Defects", Berlin, Heidelberg: Springer-Verlag (1982)
R. E. Newnham: „Properties of materials", Oxford: Oxford University Press (2004)
G. E. Dieter: „Mechanical Metallurgy", London: McGraw-Hili Book Company (1988)
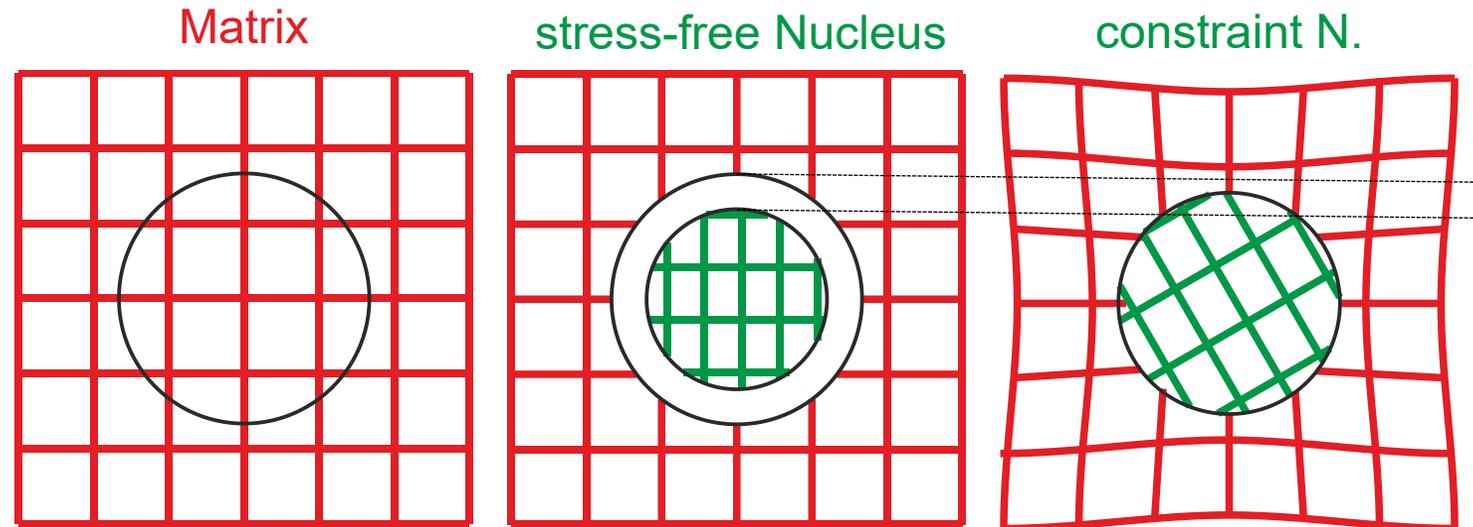
Phase Transformations in Materials

Compliance & Stiffness

- Visualization of the anisotropic Young's moduli of single crystals deformed uniaxial along certain axes:

Cu
$A = 3.3$

W
$A = 1.0$

NaCl
$A = 0.7$

Phase Transformations in Materials

Strain Energy

- Incoherent interface:

Matrix   stress-free Nucleus   constraint N.

The newly formed phase is of different crystal structure and a different volume.

$$\Delta = \frac{V^{\text{N}} - V^{\text{M}}}{V^{\text{M}}} \neq 3\delta$$

Notice the different number of lattice sites. In the nucleus vs. the matrix before making the hole.

Due to the incoherency, no coherence strain of the nucleus occurs, but still the phases need to be deformed to accommodate the different volume. Note that a rigid body rotation might occur to accommodate anisotropic interface energy.
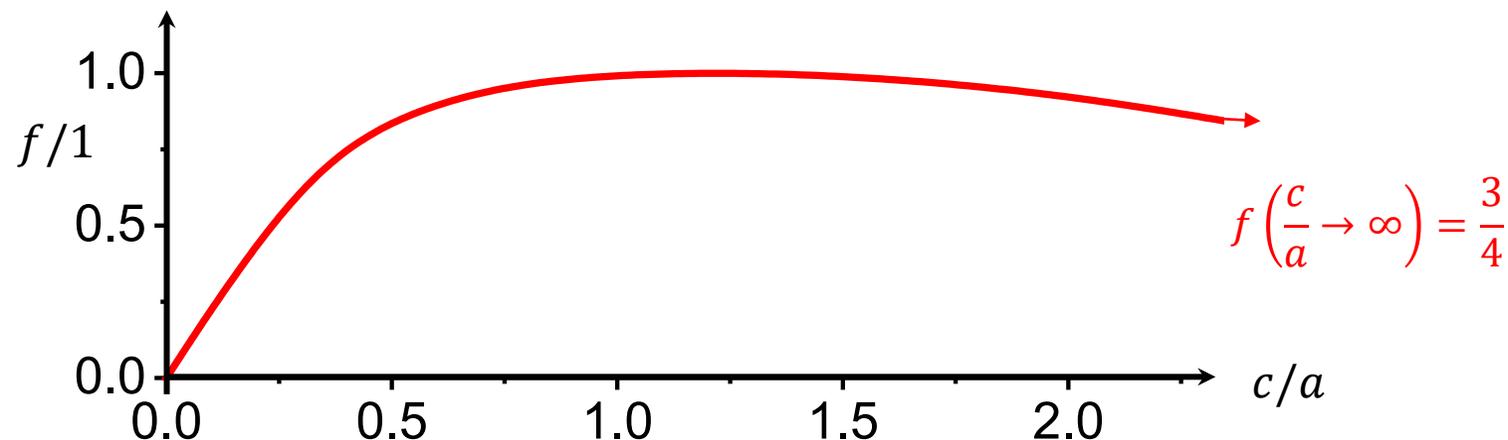
Strain Energy

- Incoherent interface:

  - The volume-specific elastic strain energy can be estimated for isotropic elastic behavior of both the matrix and an incompressible, spheroidal nucleus (cigar-like of the dimensions a and c):

    - $G^{\mathrm{M}} = G^{\mathrm{N}} = G, \nu^{\mathrm{M}} = \nu^{\mathrm{N}} = \nu \approx \frac{1}{3}$: $\Delta g^{\mathrm{S}} = \frac{\Delta G^{\mathrm{S}}}{V} = \frac{2}{3} G \Delta^2 f(\frac{c}{a})$

  - Hence, sphere and disc have maximum and minimal strain energy, respectively.

  - Anisotropy has only small impact on the elastic strain energy in this case.

$$f\left(\frac{c}{a} \to \infty\right) = \frac{3}{4}$$

Phase Transformations in Materials

Strain Energy

- Semi-coherent interface:

    - For the case of semi-coherent interfaces, the strain energy by the incorporation of misfit dislocations needs to be considered. This strain energy contribution must be smaller than the energy contribution for the coherent interface to allow for the formation of misfit dislocations.

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:

cap-shape nucleus

L

S

Θ

flat catalyst

C

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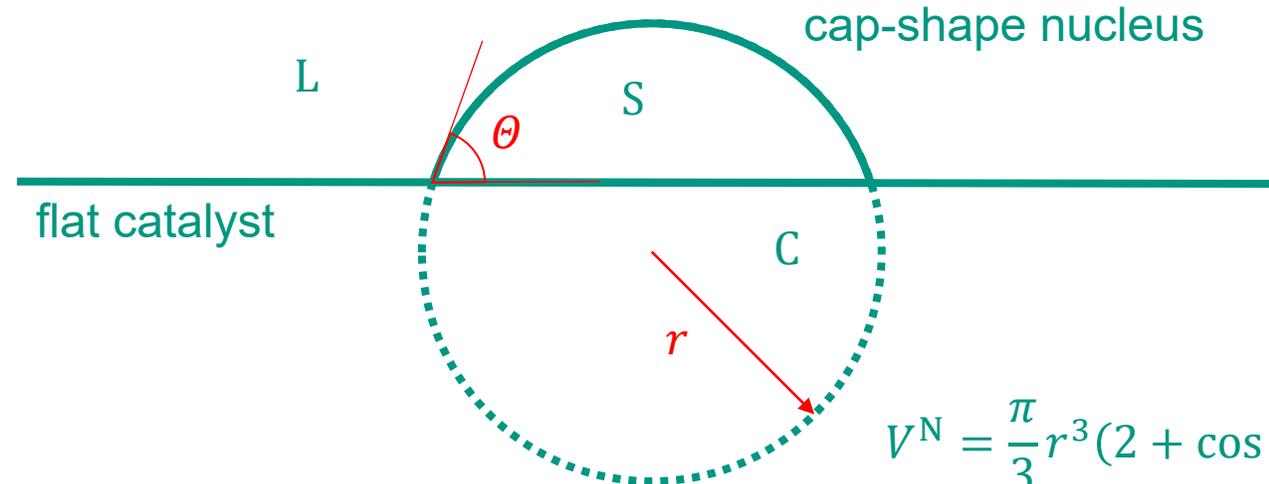
$$V^{\mathrm{N}} = \frac{\pi}{3}r^3(2 + \cos\Theta)(1 - \cos\Theta)^2$$

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

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

Revision of Ch. 3a

liquid to solid

■ The situation for the solid-solid transformation is similar but with a double cap nucleus nucleating at a boundary present in the matrix:

$$2\gamma^{\mathrm{I}} \cos \varTheta = \gamma^{\mathrm{GB}}$$

double cap-shape nucleus

γ^{I}

M

γ^{GB}

$\varTheta$

N

grain boundary

$$V^{\mathrm{N}} = \frac{2\pi}{3} r^3 (2 + \cos \varTheta)(1 - \cos \varTheta)^2$$
$$A^{\mathrm{I}} = 4\pi \, r^2 \, (1 - \cos \varTheta)$$
$$A^{\mathrm{GB}} = \pi \, r^2 \, (1 - \cos^2 \varTheta)$$

solid to solid
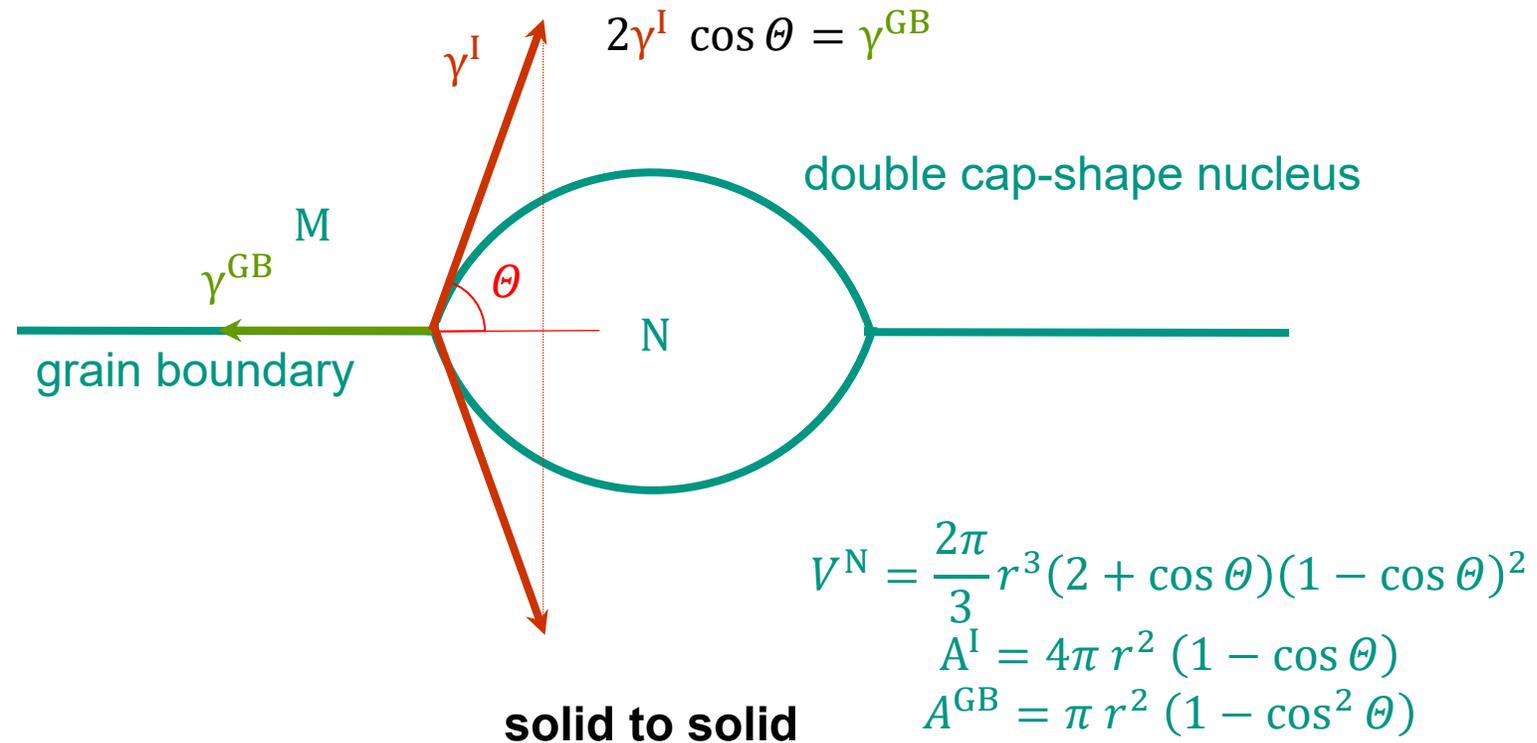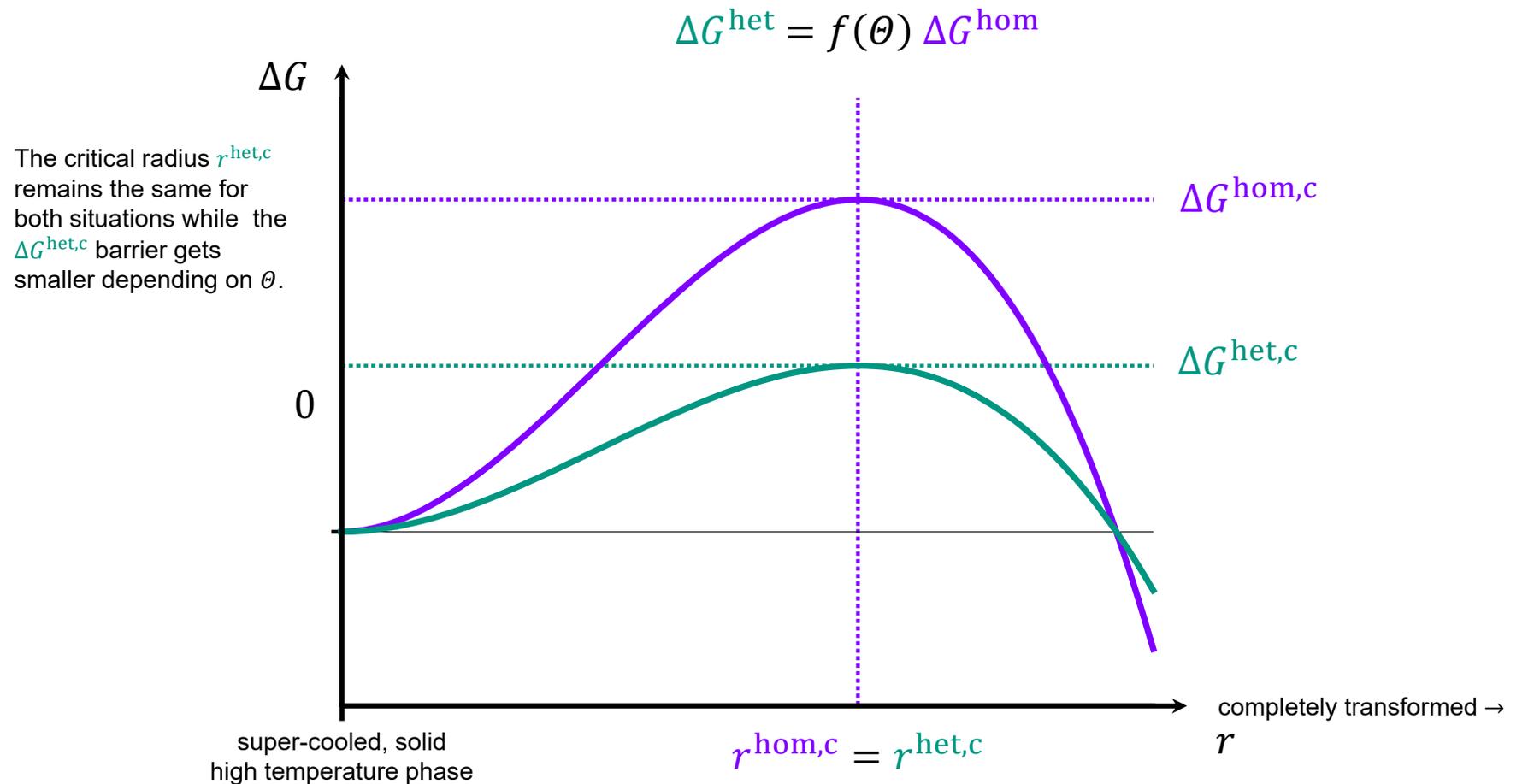
Heterogeneous Nucleation

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

$$\Delta G^{\text{het}} = -V^{\text{N}} \left(\Delta g^{\text{D}} - \Delta g^{\text{S}}\right) + A^{\text{I}} \gamma^{\text{I}} - A^{\text{GB}} \gamma^{\text{GB}}$$

$$= -\frac{2\pi}{3} r^3 (2 + \cos \Theta)(1 - \cos \Theta)^2 \left(\Delta g^{\text{D}} - \Delta g^{\text{S}}\right) + 4\pi r^2 (1 - \cos \Theta) \gamma^{\text{I}} - \pi r^2 (1 - \cos^2 \Theta) \gamma^{\text{GB}}$$

$$= -\frac{2\pi}{3} r^3 (2 + \cos \Theta)(1 - \cos \Theta)^2 \left(\Delta g^{\text{D}} - \Delta g^{\text{S}}\right) + 4\pi r^2 (1 - \cos \Theta) \gamma^{\text{I}} - \pi r^2 (1 - \cos^2 \Theta) 2\gamma^{\text{I}} \cos \Theta$$

$$= -\frac{2\pi}{3} r^3 \left(\Delta g^{\text{D}} - \Delta g^{\text{S}}\right)(2 - 3 \cos \Theta + \cos^3 \Theta) + 2\pi r^2 \gamma^{\text{I}} (2 - 3 \cos \Theta + \cos^3 \Theta)$$

$$= \left(-\frac{4}{3} \pi r^3 \left(\Delta g^{\text{D}} - \Delta g^{\text{S}}\right) + 4\pi r^2 \gamma^{\text{I}}\right) \frac{1}{2} (2 - 3 \cos \Theta + \cos^3 \Theta)$$

Phase Transformations in Materials

Heterogeneous Nucleation

$$\Delta G^{\text{het}} = f(\Theta)\, \Delta G^{\text{hom}}$$

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.

ΔG

$\Delta G^{\text{hom,c}}$

$\Delta G^{\text{het,c}}$

0

completely transformed →

r

super-cooled, solid high temperature phase

$r^{\text{hom,c}} = r^{\text{het,c}}$

with $f(\Theta) = \dfrac{1}{2}(2 - 3\cos\Theta + \cos^3\Theta),\ 0 \leq f(\Theta) \leq 0.5$

Heterogeneous Nucleation

The heterogeneous nucleation becomes more effective for high energy boundaries γ^{GB}, e.g. arbitrary high angle grain boundaries.
The nucleation at grain edges and corners is even more feasible. The formation of coherent or semi-coherent facets might further reduce the nucleation barrier close to grain boundaries.

$$f(\Theta) = \frac{1}{2}(2 - 3\cos\Theta + \cos^3\Theta)$$
$$= \frac{1}{2}(2 + \cos\Theta)(1 - \cos\Theta)^2$$

$$\cos\Theta = \frac{\gamma^{GB}}{2\gamma^{I}}$$

Phase Transformations in Materials