Melting and Solidification

Asymmetries and Consequences

M. Rettenmayr
Friedrich-Schiller-University Jena
Materialwissenschaft und Werkstofftechnologie
Metallische Werkstoffe

acknowledgements
Dr. O. Warkentin, Dr. B. Dutta, Dr. M. Buchmann, M. Fink

outline

- motivation: 2 examples for melting in technical applications

- asymmetries in solidification / melting
  - supercooling vs. superheating
  - nucleation
  - melting theories: ’catastrophes‘
  - solute redistribution
  - diffusion kinetics in parent/product phase
  - (- structural aspects)

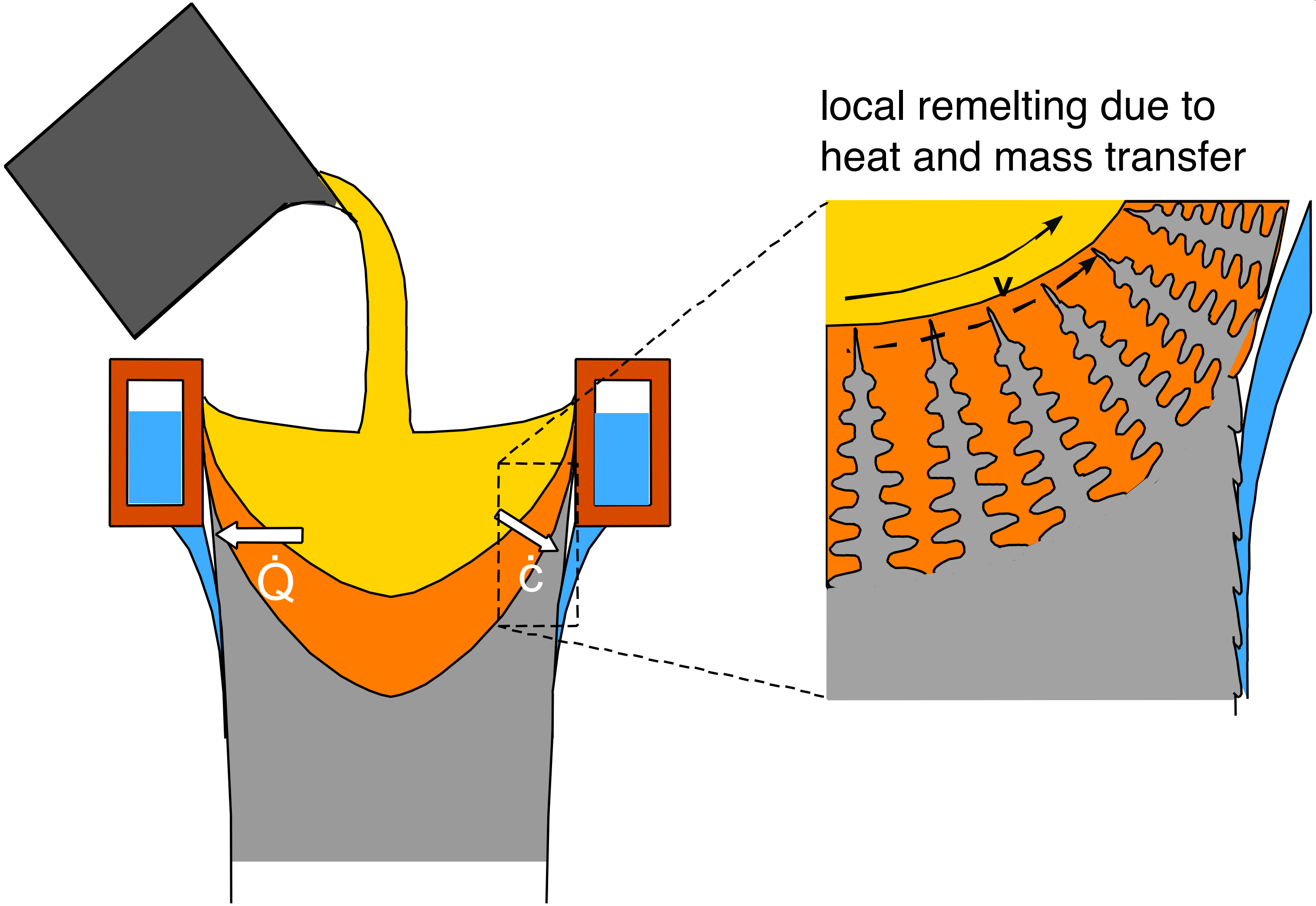
- solutal melting
  - experiment and results
  - generalized non-equilibrium thermodynamics

”convection ... can cause the remelting of large sections of the casting that solidified earlier. Such remelting can occur over extended periods of time, especially in large castings. Simplified solidification models that do not consider this effect are likely to be grossely inaccurate.“

J. Campell, ’Castings‘

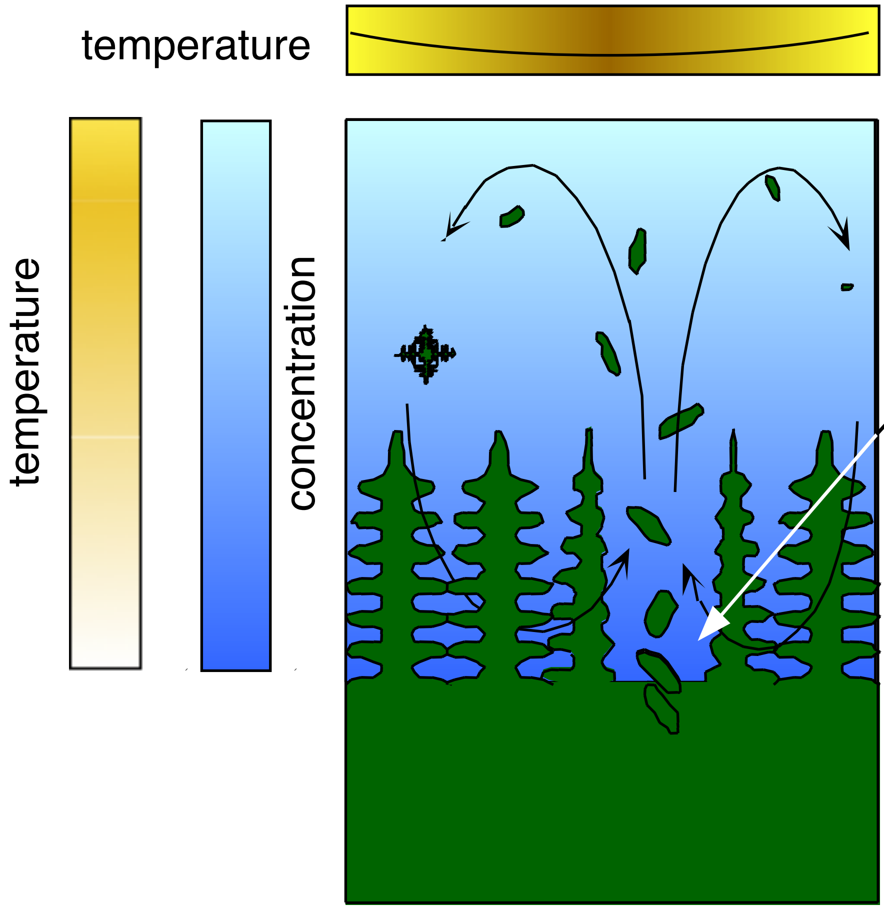
exudation, (semi-)continuous casting

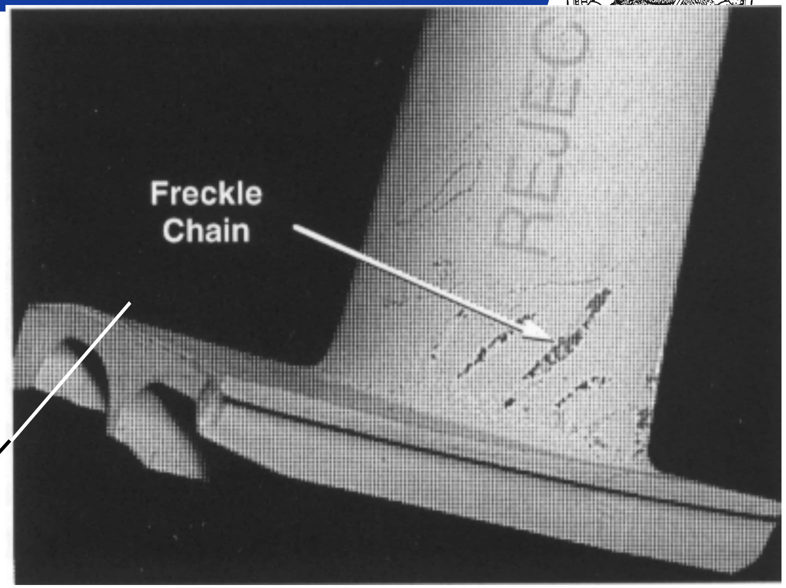
local remelting due to heat and mass transfer

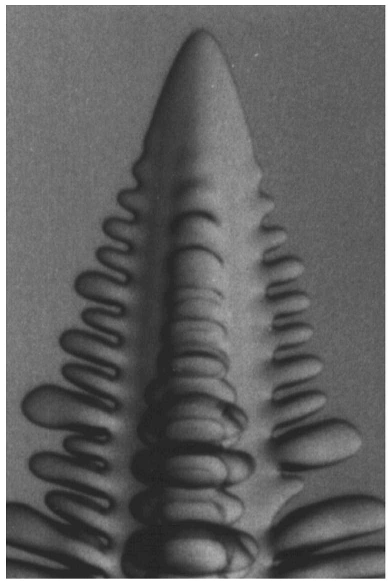


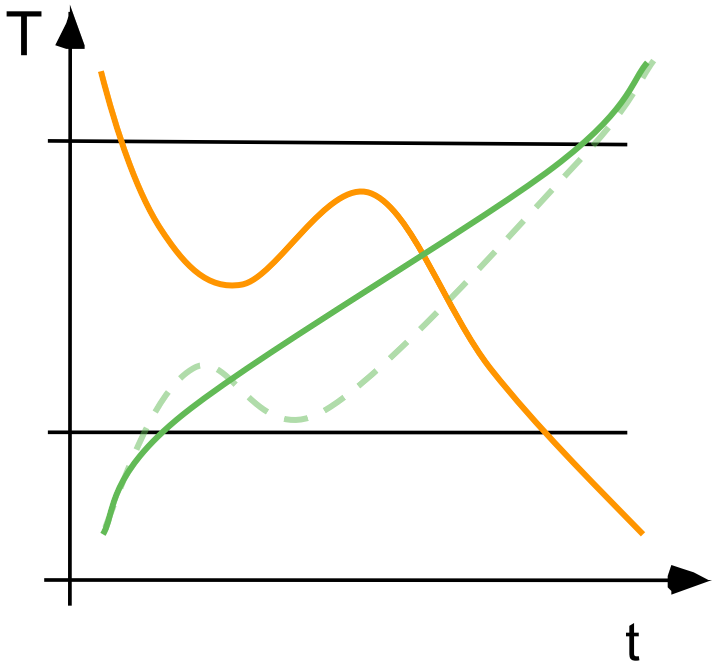
freckles, investment casting

"double diffusive instability"









supercooling:

hard to *avoid* in
liquid ⇒ solid transformations

superheating:

hard to *obtain* in
solid ⇒ liquid transformations

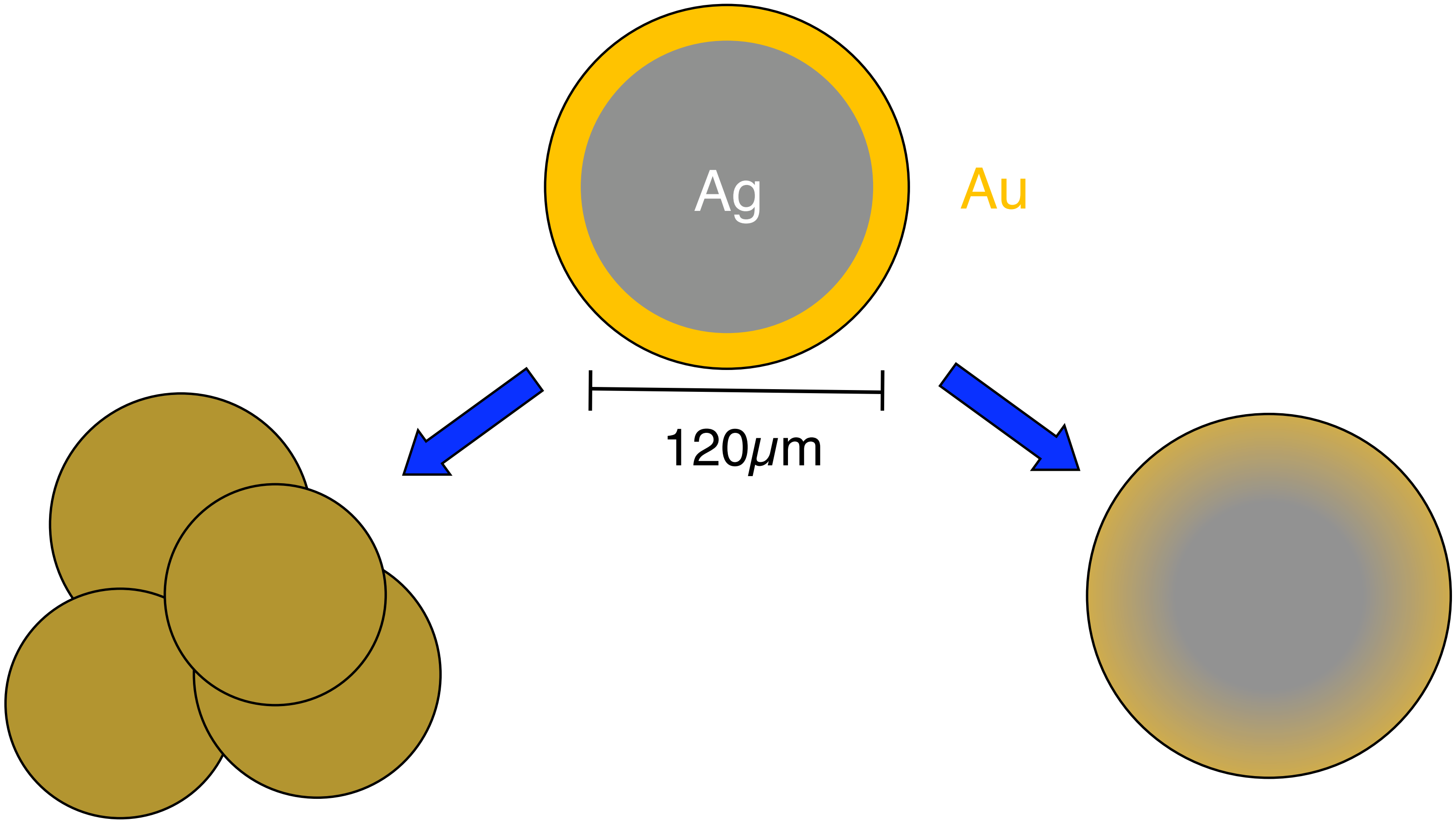
superheating experiments:

1930ies: Ga at 0.1K above T_m, 'dislocation assisted' (1960ies)
1960ies: Turnbull et al.: substances that form viscous melts (SiO_2, P_2O_5...)
(⇒ transfer results on melting from organic alloys to metals with care)
1960ies: ice at 0.4K above T_m
1986: Daeges, Gleiter, Perepezko: Ag 25K above T_m

Gleiter Daeges experiment

Au coated Ag particles

- external Ag surfaces eliminated
- small particles, relatively few defects



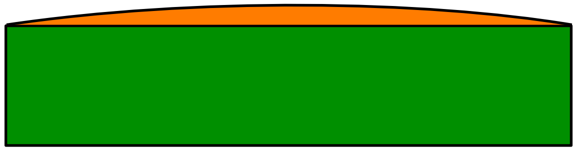
is nucleation responsible?

easy nucleation

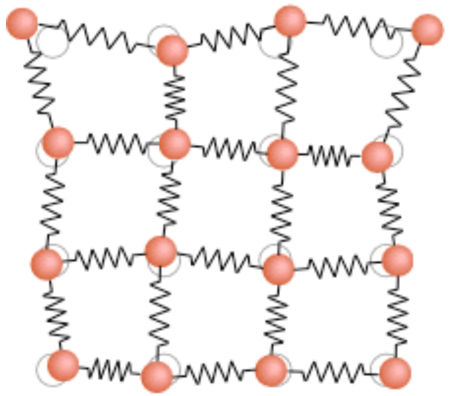
perfect wetting

$\sigma_{g/L} + \sigma_{L/S} < \sigma_{g/S}$

→ pre-melting



surface instability



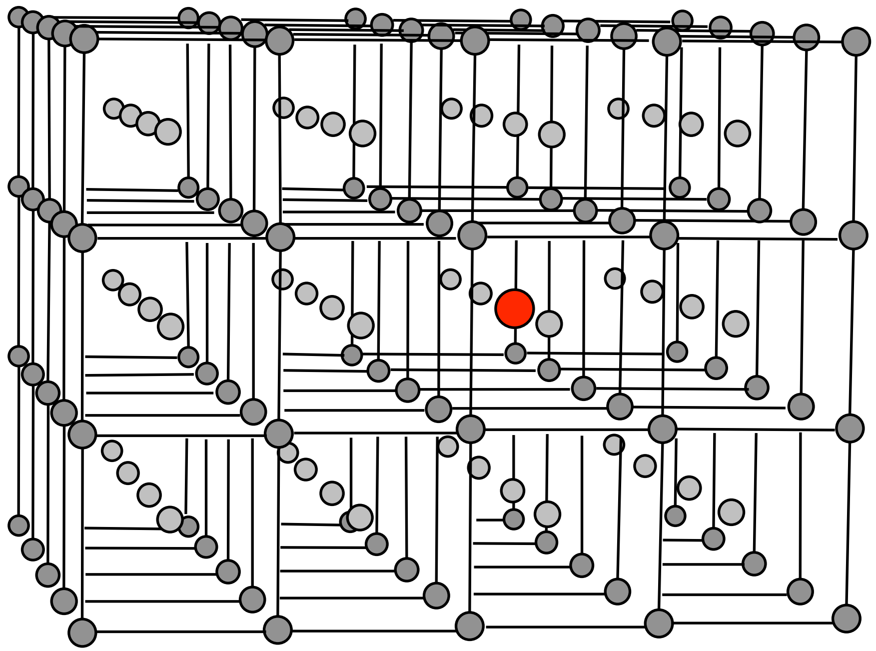
Lindemann 1910

nucleation at areal defects

nucleation at dislocations?

vacancy controlled nucleation

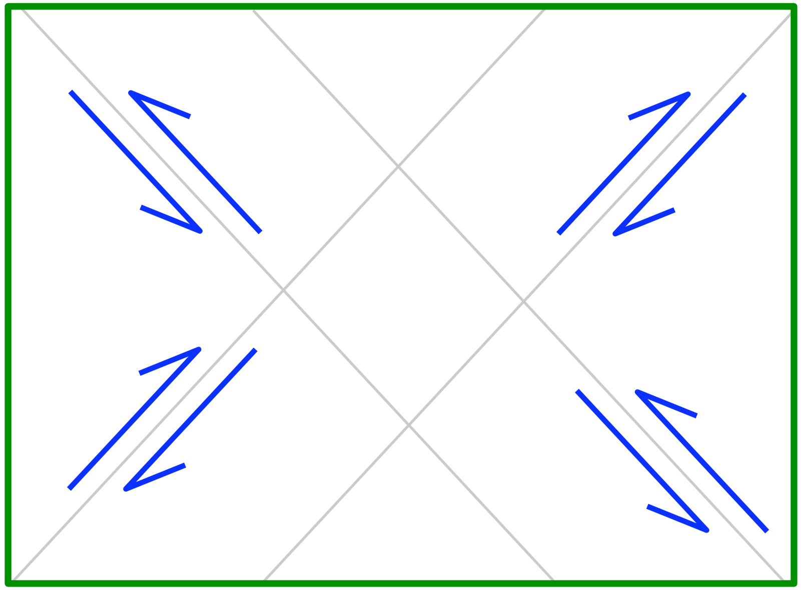
Gorecki 1974/76



148 atoms

no nucleation necessary: catastrophes

rigidity catastrophe

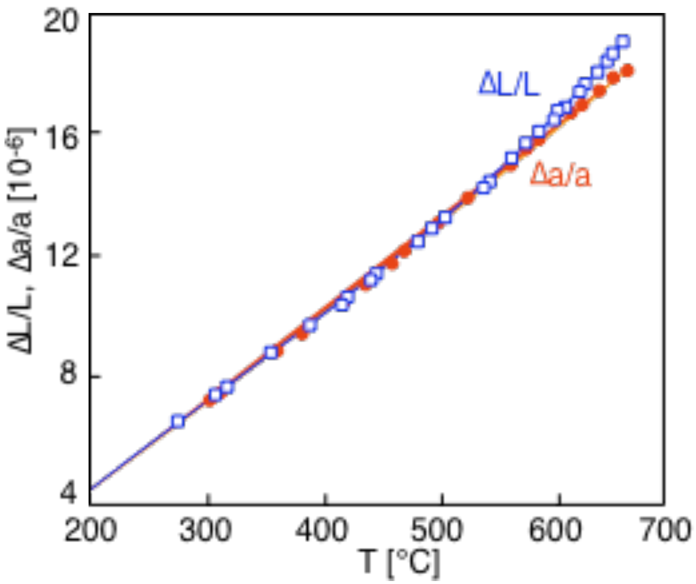


Born 1939

single phase theory, experimentally falsified

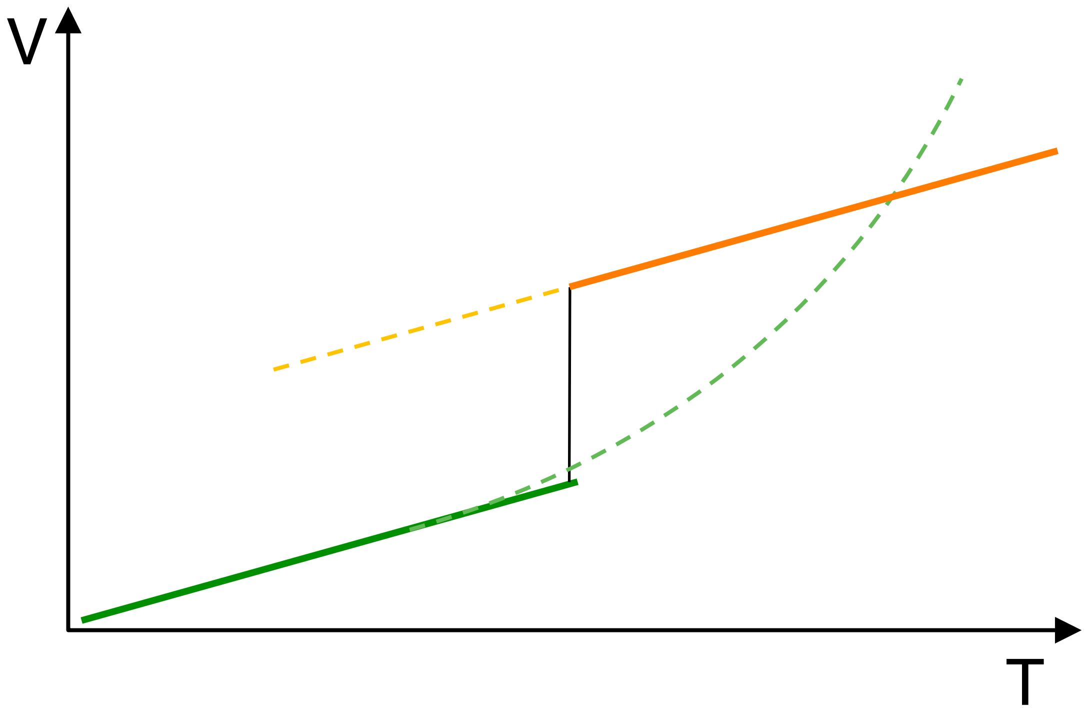
→ melting at the limit of superheating

melting at the limit of superheating

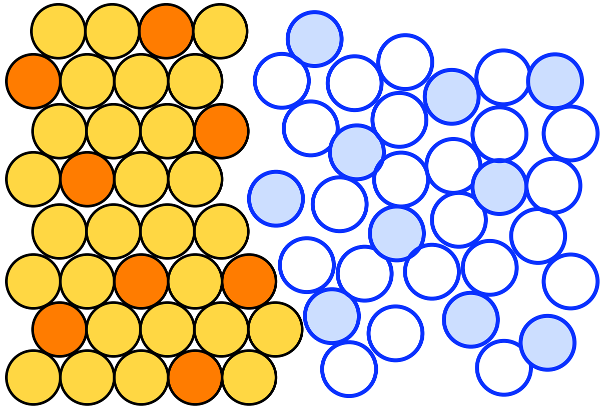


hierarchy of instability points

- isochoric catastrophe
- isenthalpic catastrophe
- isentropic catastrophe

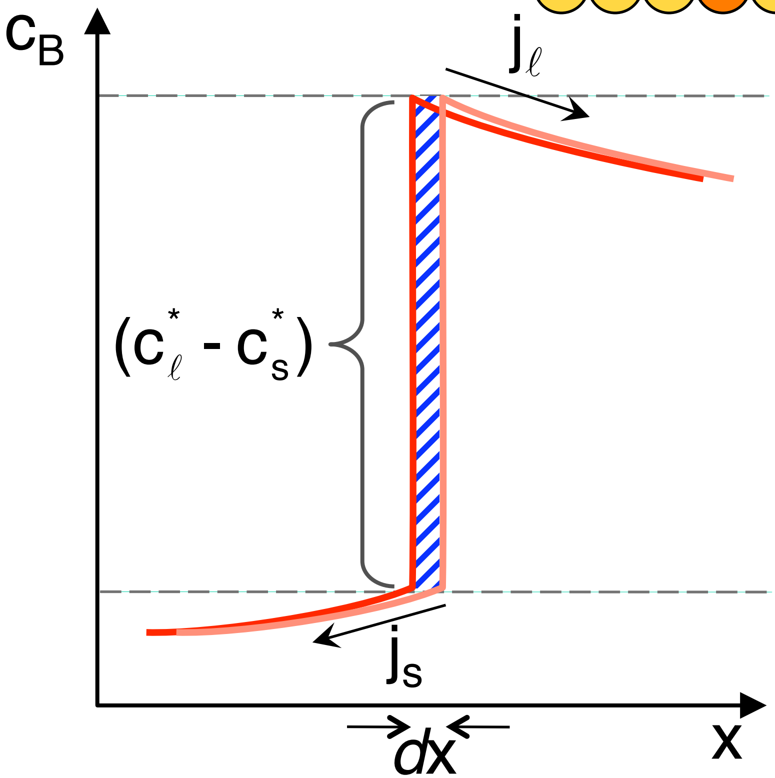


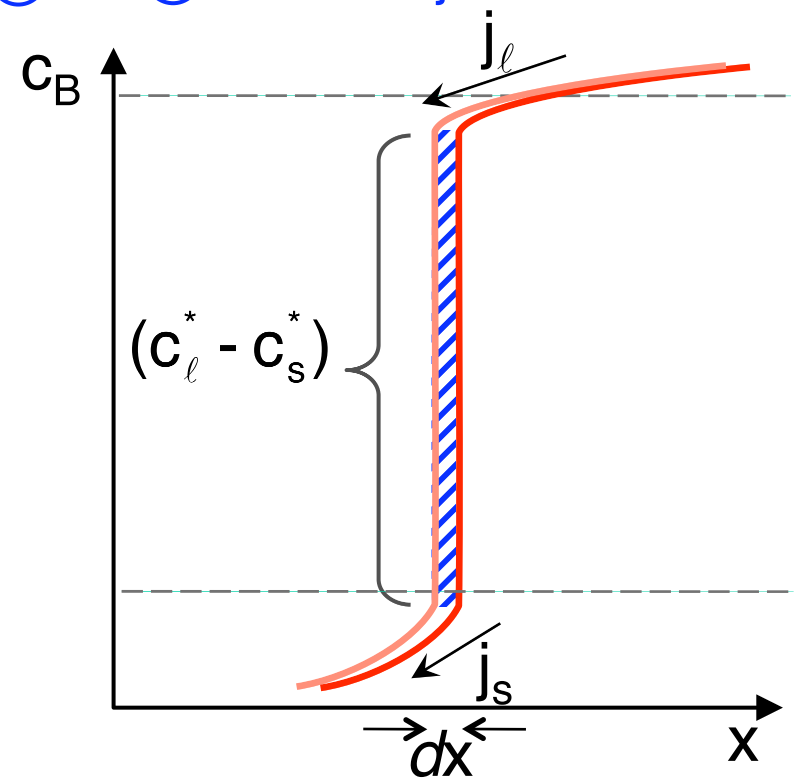
solute repartitioning



parent phase (liquid):
absorb solute

parent phase (solid):
eject solute?





further symmetry breaking:
$D_\ell \gg D_s$

solidification

parent phase (liquid): fast solute diffusion

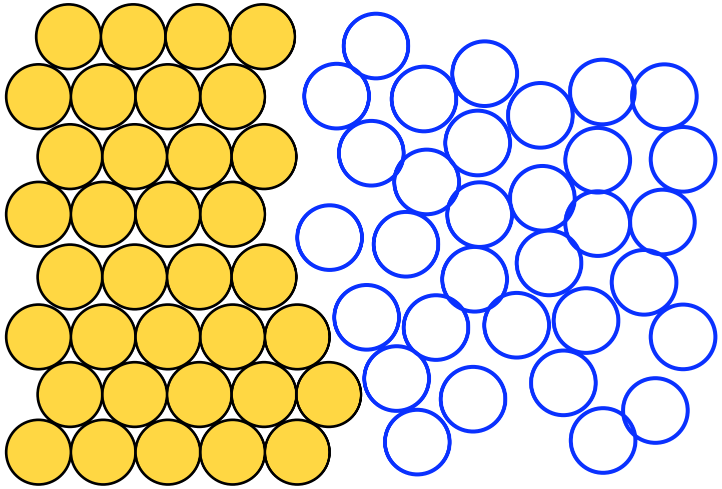
melting

parent phase (solid): slow solute diffusion

⇒ diffusion in melt controls both solidification *and* melting processes (migration of interface, interface stability...)

⇒ diffusion in melt influences phase transformation thermodynamics (thermodynamics and kinetics are coupled)

faceting: crystal structure and ΔS_f
(K.A. Jackson)



accomodation at lattice position
(B. Chalmers)

⇒ short range order in melt, long range order in crystal
(melt dynamics, structual changes close to interface)
⇒ rough interface of melt, rough or faceted interface of crystal
(additional undercooling due to faceting)

experimental difficulties

melting is hard to observe

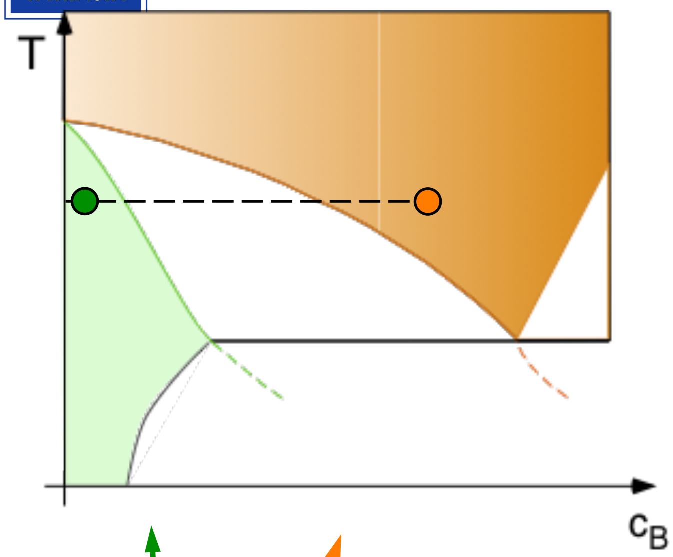
- shape of the sample not steady
- reactivity at high temperature: oxide layers
- evaporization
- gas absorption
- internal energy U and atomic mobility are high
- buoyancy

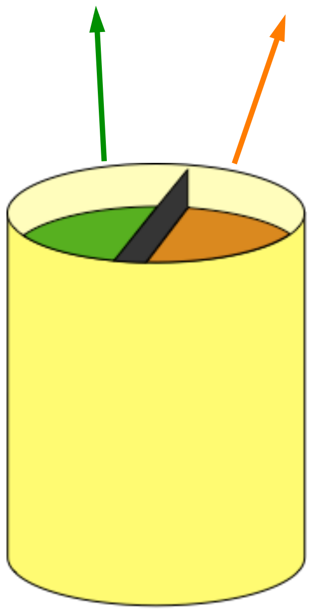
melt ‘microstructure‘ is not visible after solidification

experimental possibilities:

- thermal analysis (rapid melting)
- directional melting
- solutal melting
- gradient melting/resolidification
- metatectic equilibria, retrograde solidus

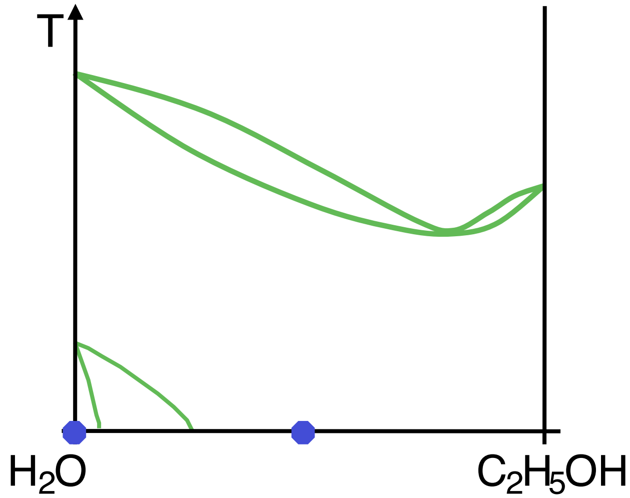
solutal melting experiment





- adiabatic conditions
  $\Delta T \Rightarrow v_F$
- discontinuity at interface
  (concentration and chem. potential)

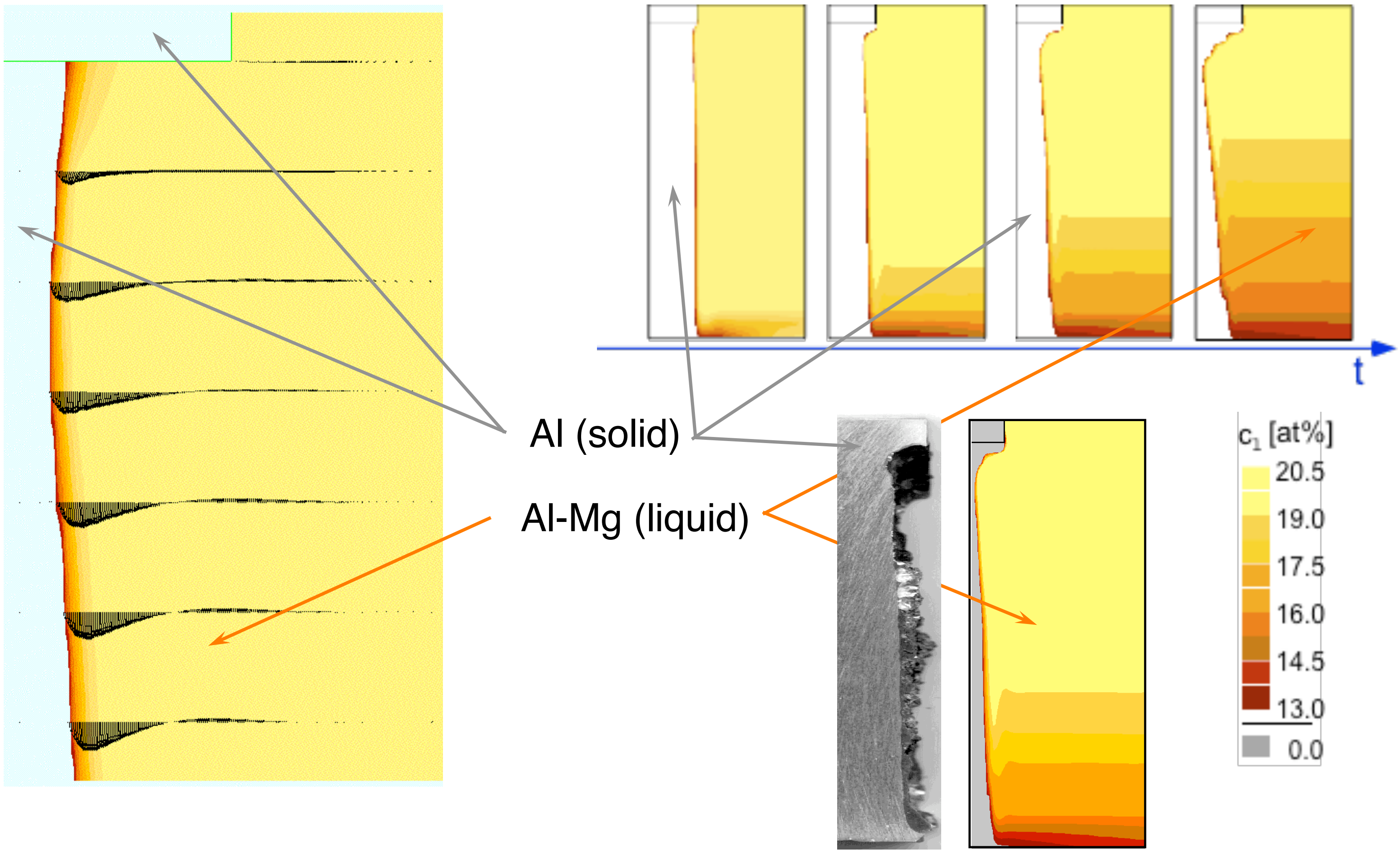
further example:



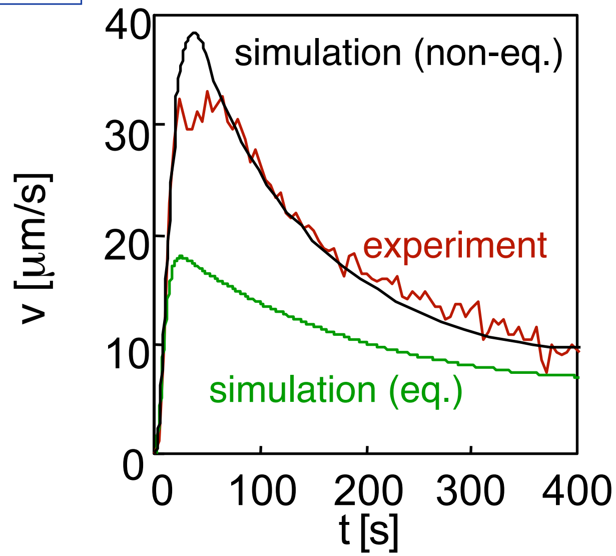
Metallische Werkstoffe

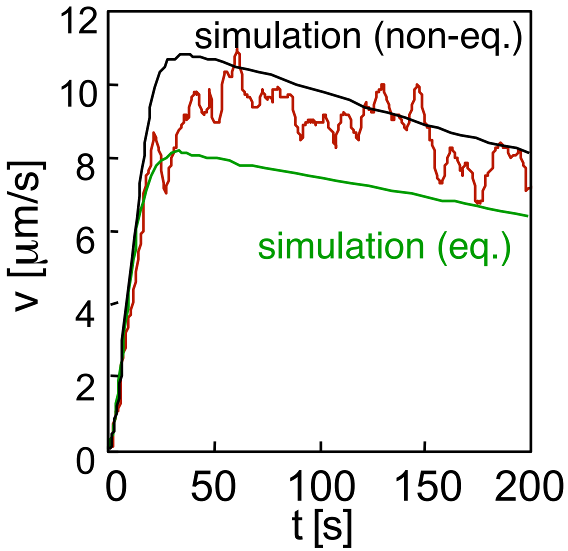
solutal melting - FEM simulation

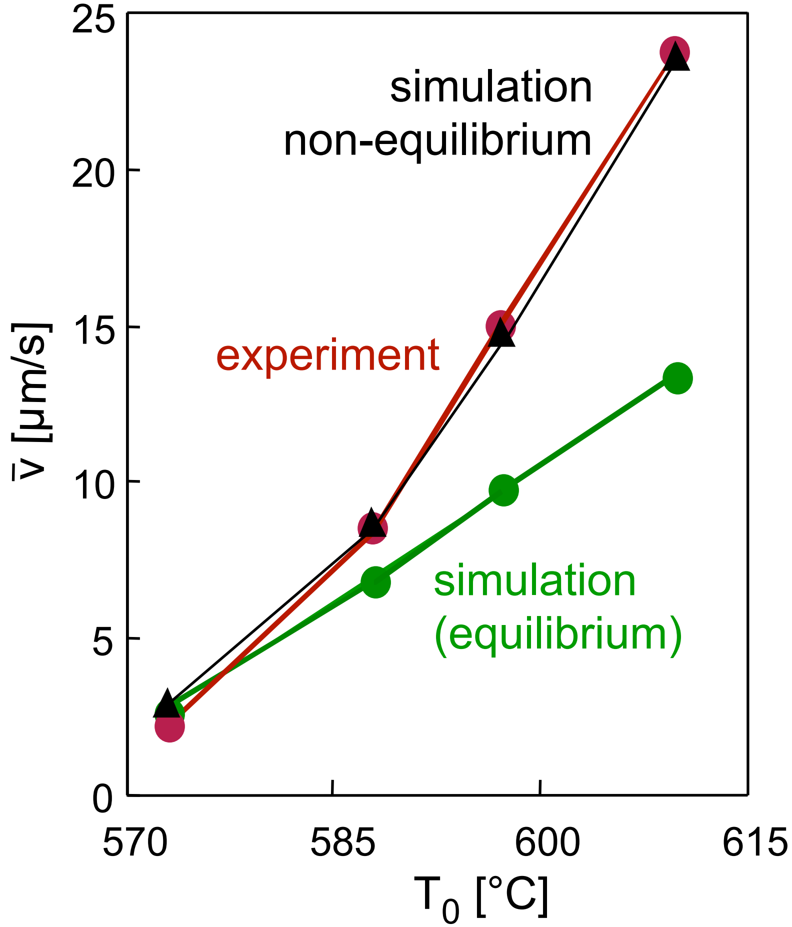
concentrations



simulation FE - FD - interface compositions

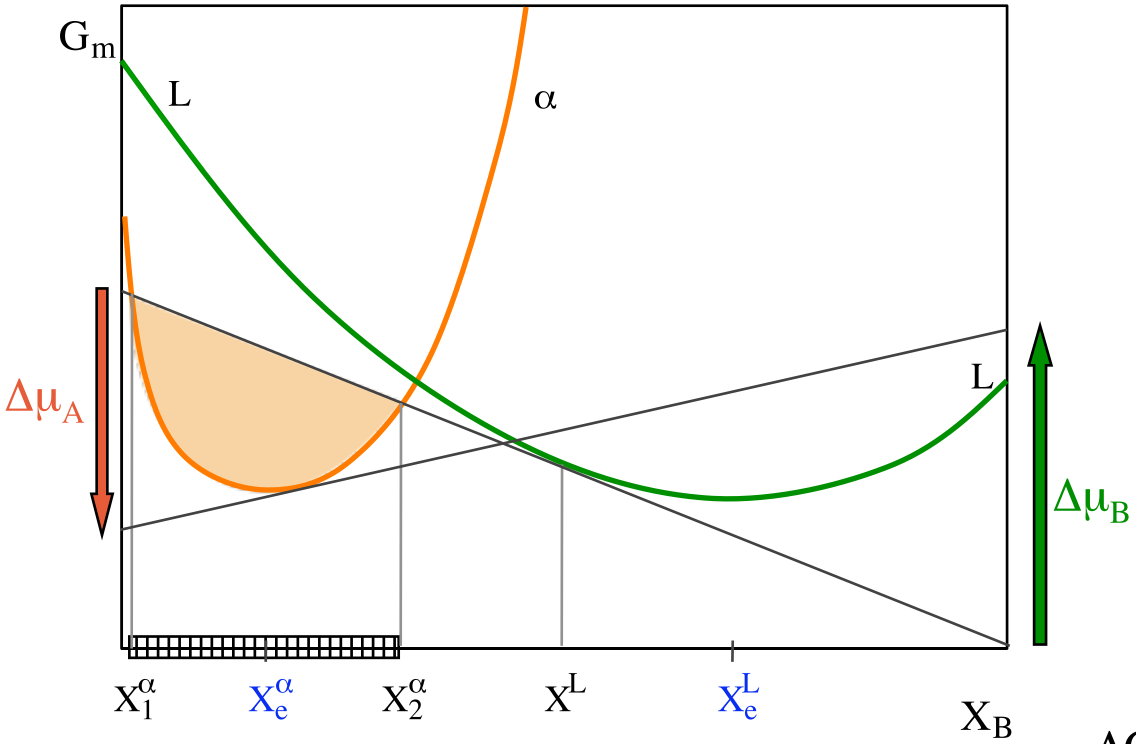






major findings

J. Baker, J. Cahn, 1971



define thermodynamically possible concentration range

$$X_1^\alpha < X^\alpha < X_2^\alpha$$

chemical potential of one of the components may increase

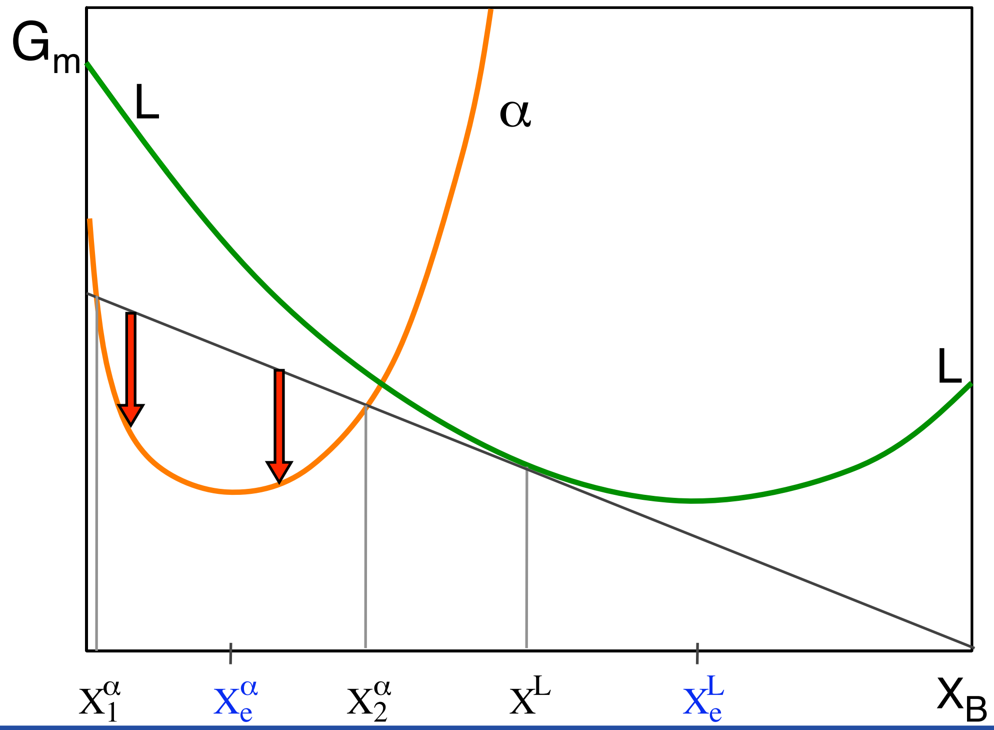
$$\Delta G = (1-X^\alpha)(\mu_A^L - \mu_A^\alpha) + X^\alpha(\mu_B^L - \mu_B^\alpha)$$

further graphical interpretation:

⇒ expand equation in several terms

linear relation driving force - velocity?

			kinetic constant	driving force
• diffusion (Fick‘s 1st law)	j	=	$-D$	$\partial c / \partial x$
• grain growth	v_{GB}	=	M_{GB}	p
• off-equilibrium solidification?	v_F	=	M_F	ΔG



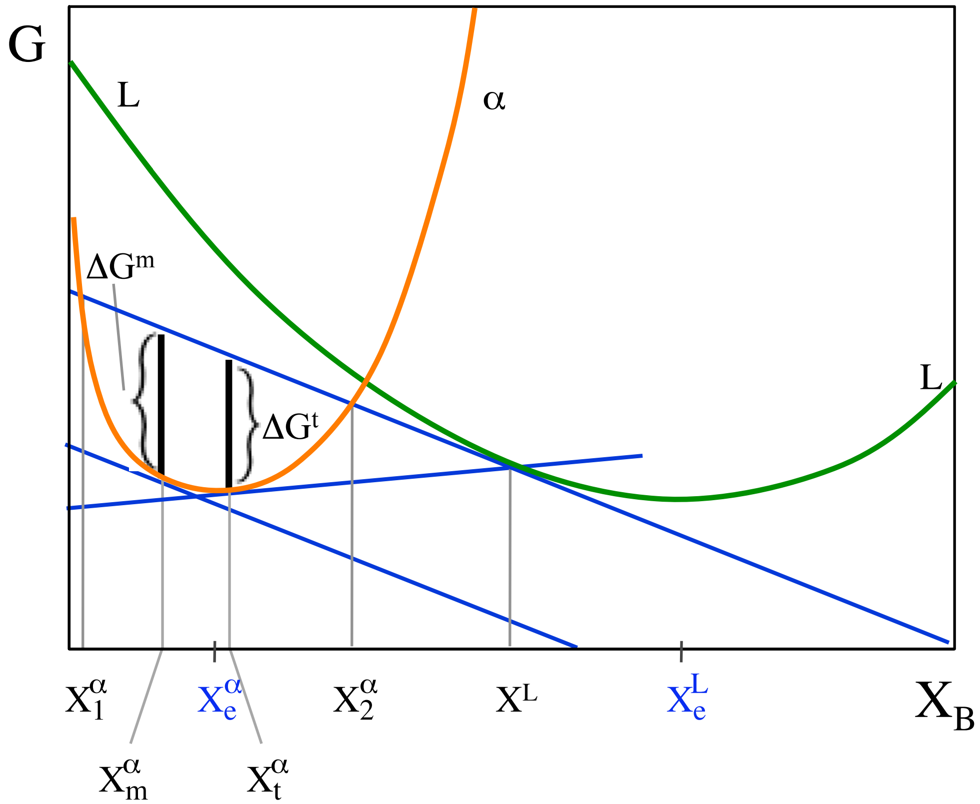
driving force subdivision

$$\Delta G = (1-X^{\alpha})(\mu_A^{L}-\mu_A^{\alpha}) + X^{\alpha}(\mu_B^{L}-\mu_B^{\alpha})$$

transforms to:

$$\Delta G = (1-X^{L})(\mu_A^{L}- \mu_A^{\alpha}) + X^{L}(\mu_B^{L}-\mu_B^{\alpha}) + (X^{L}-X^{\alpha})((\mu_A^{L}-\mu_A^{\alpha}) - (\mu_B^{L}-\mu_B^{\alpha}))$$

$\Delta G =$ ΔG^{m} ΔG^{t}



based on assumption:
no gradients in
product phase!

$$\Delta G^{m} = (1-X^{L})\Delta\mu_A + X^{L}\Delta\mu_B$$

$$\Delta G^{t} = (X^{L}-X^{\alpha})(\Delta\mu_A - \Delta\mu_B)$$

Hillert, Rettenmayr, Acta materialia 2003

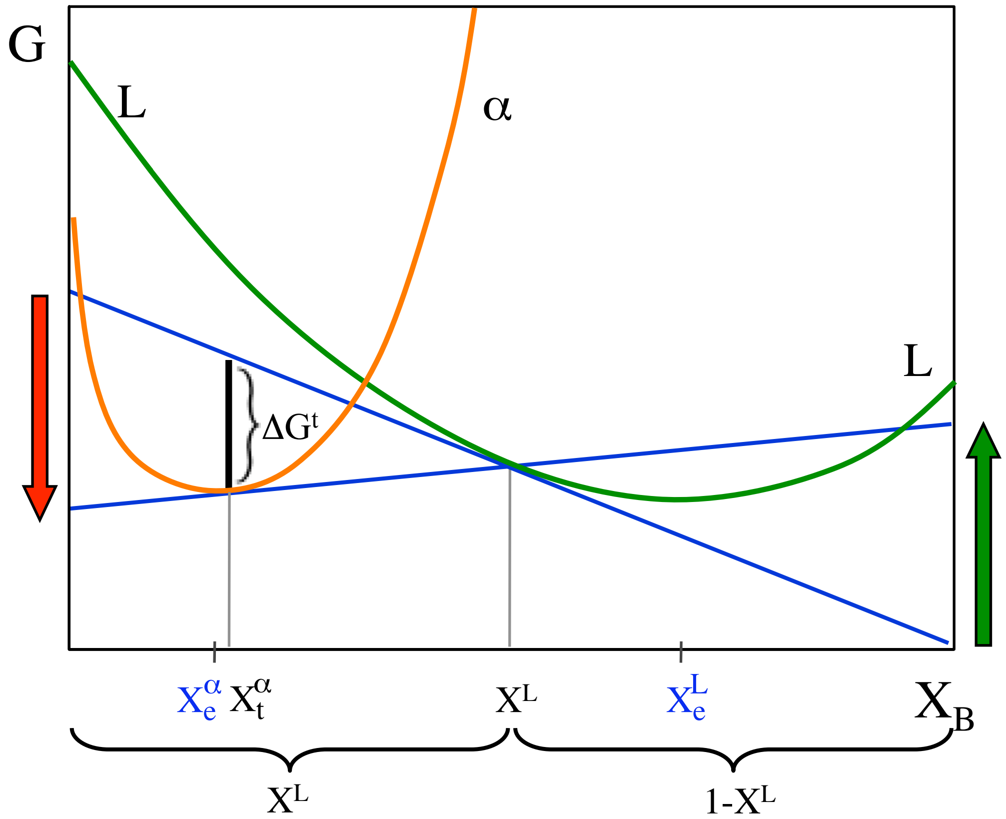
driving force subdivision - trans-interface diffusion

$$\Delta G = (1-X^{\alpha})(\mu_A^L-\mu_A^{\alpha}) + X^{\alpha}(\mu_B^L-\mu_B^{\alpha})$$

transforms to:

$$\Delta G = (1-X^L)(\mu_A^L-\mu_A^{\alpha}) + X^L(\mu_B^L-\mu_B^{\alpha}) + (X^L-X^{\alpha})((\mu_A^L-\mu_A^{\alpha}) - (\mu_B^L-\mu_B^{\alpha}))$$

$\Delta G =$ ΔG^m ΔG^t



based on assumption:
no gradients in
product phase!

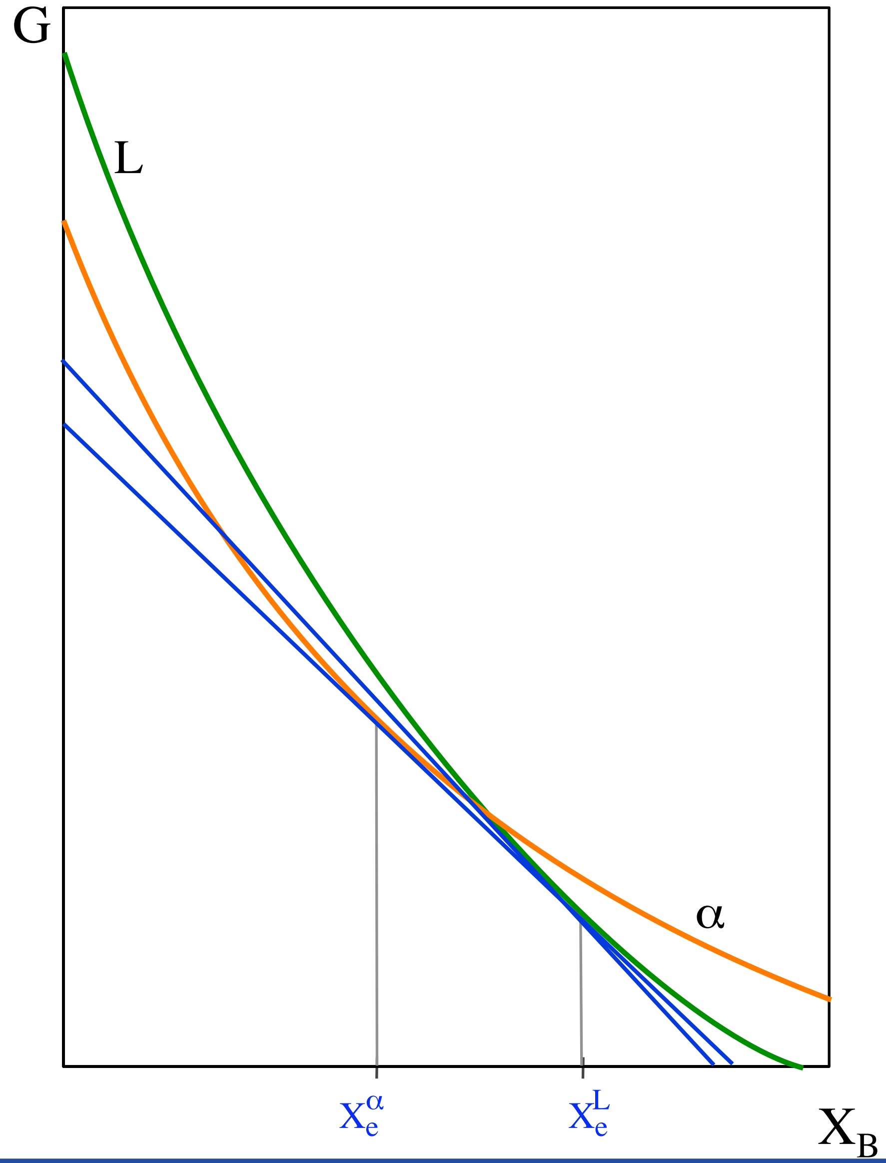
$$\Delta G^m = (1-X^L)\Delta\mu_A + X^L\Delta\mu_B$$

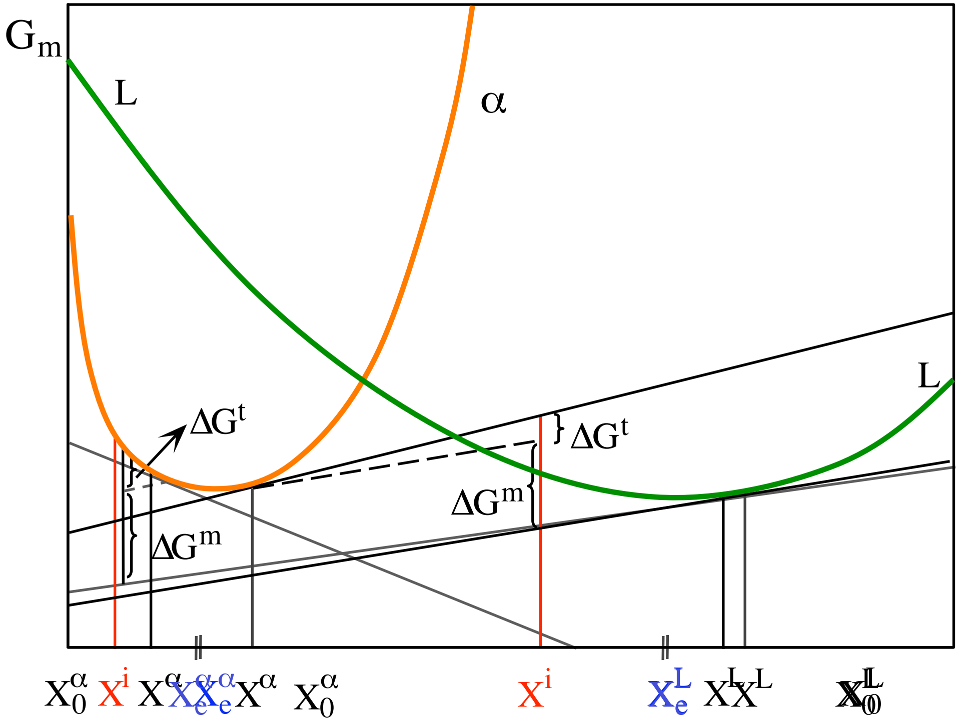
$$\Delta G^t = (X^L-X^{\alpha})(\Delta\mu_A - \Delta\mu_B)$$

generalization:
⇒ introduce composition
of transforming layer

Hillert, Rettenmayr, Acta materialia 2003

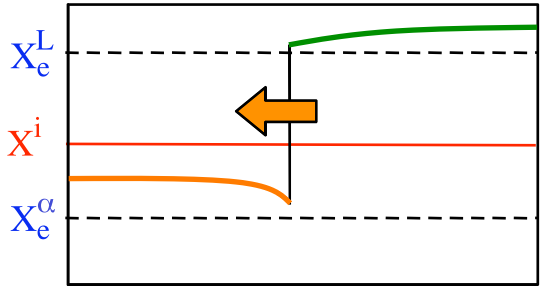
schematic vs. real G-X curves





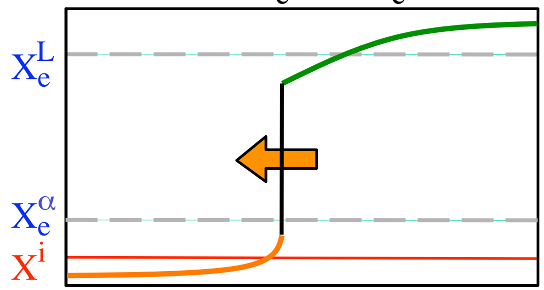
thermal melting

$X_e^{\alpha} < X^i < X_e^{L}$



solutal melting

$X^i < X_e^{\alpha} < X_e^{L}$



$$\Delta G = (1-X^{\alpha})(\mu_A^{\alpha} - \mu_A^{L}) + X^{\alpha}(\mu_B^{\alpha} - \mu_B^{L}) + (X^{\alpha} - X^{i})(\mu_A^{\alpha} - \mu_A^{L} - \mu_B^{\alpha} + \mu_B^{L})$$

$\Delta G =$ ΔG^m ΔG^t

X^i dependent on kinetic coefficients

Hillert, Rettenmayr, Acta materialia 2003

“fast“ melting

$$\Delta G = (1-X^{\alpha})(\mu_A^{\alpha}-\mu_A^{L}) + X^{\alpha}(\mu_B^{\alpha}-\mu_B^{L}) + (X^{\alpha}-X^{i})(\mu_A^{\alpha}-\mu_A^{L}-\mu_B^{\alpha}-\mu_B^{L})$$

$\Delta G =$ ΔG^m ΔG^t

for melting

$$X^{\alpha} - X^{i} = \frac{X^{\alpha} - X^{L}}{1 - \left(\frac{J^{L}}{J^{\alpha}}\right)}$$

$$X^{L} - X^{i} = \frac{X^{L} - X^{\alpha}}{1 - \left(\frac{J^{\alpha}}{J^{L}}\right)}$$

solidification: $J^{\alpha} = 0$

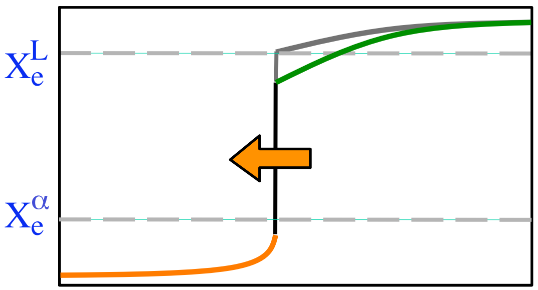
$\Rightarrow X^{L} - X^{i} = X^{L} - X^{\alpha}$

melting: $J^{\alpha} \approx 0$

$\Rightarrow X^{\alpha} - X^{i} \approx 0$

thermodynamics

→ $D_{\ell} >> D_s$ additional driving force



kinetics

→ steeper concentration gradients

conclusions

melting and solidification: numerous aspects of asymmetry

generalized theory for liquid/solid phase transformations

- sharp interface
- connects thermodynamics and kinetics
- no subdivision of domain (similar to phase field)
- unique solution for interface compositions
  (no assumptions / model at the interface necessary)
- for slow and rapid processes
- is applicable to both solidification and melting

questions

- kinetic coefficients during transient melting
- non-linear irreversible thermodynamics