Modelling of the motion of phase interfaces; coupling of thermodynamics and kinetics

John Ågren
Dept of Materials Science and Engineering
Royal Institute of Technology
S-100 44 Stockholm

Ackowledgement:
Joakim Odqvist, Henrik Larsson, Klara Asp
Annika Borgenstam, Lars Höglund, Mats Hillert

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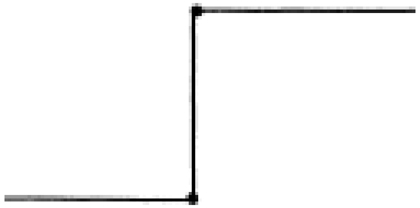
Content

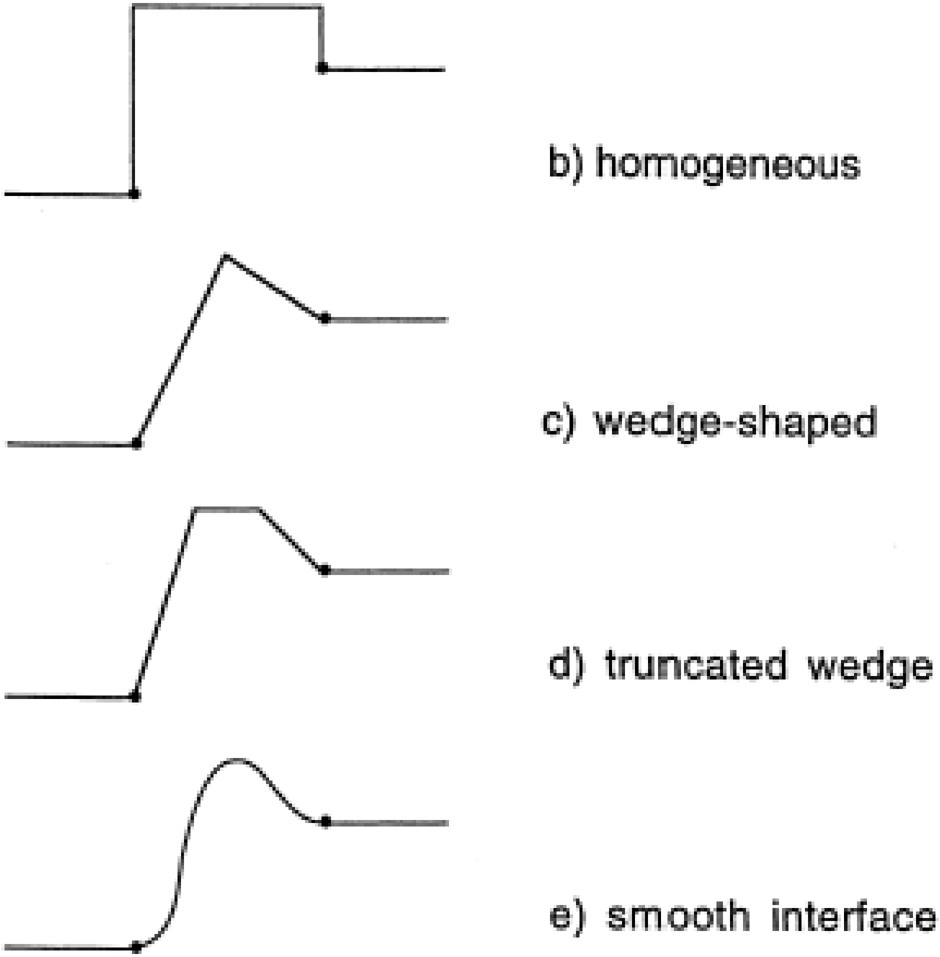
- Sharp interface
- Finite thickness interface
  - solute drag theories
  - Larsson-Hillert
- Diffuse interface
  - phase field
- No interface
- Conclusions

Modeling of the local state of phase interface (Hillert 1999)

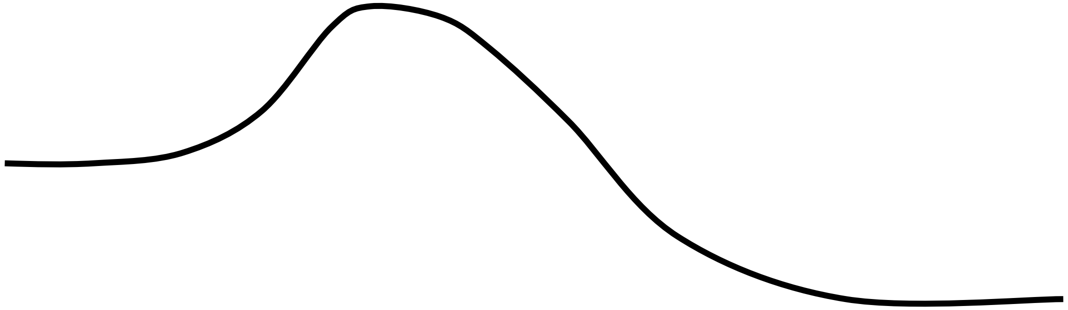
Sharp interface
- no thickness



Finite interface thickness – continuous variation in properties



Diffuse interface: no sharp boundary between interface and bulk (phase-field method)



No interface: Only bulk properties
are used, i.e. not even an operating interfacial
tieline calculated.

Sharp interface

(Stefan Problem)

The rate of isobarothermal diffusional phase transformations in an *N* component system may be predicted by solving a set of
N-1 diffusion equations in each phase : 2(*N*-*1*)

Boundary conditions at interface:

- Composition on each side	2(*N*-1)
- Velocity of interface	$\underline{+1}$
	2*N*-*1*
These boundary conditions must obey:	
Flux balance equations	$\underline{N\text{-}1}$
Net number of extra conditions needed at phase interface:	*N*

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How to formulate the *N* extra conditions?

Baker and Cahn (1971): *N* response functions. For example in a binary system β → α:

$$f_1(x_{B,}^{\alpha} x_{B,}^{\beta} v, T) = 0$$

$$f_2(x_{B,}^{\alpha} x_{B,}^{\beta} v, T) = 0$$

Simplest case: **Local equilibrium**.

- The interfacial properties do not enter into the problem except for the effect of interfacial energy of a curved interface (Gibbs-Thomson) and the interface velocity does not enter.

$$\Delta\mu_A = \mu_A^{\alpha}(x_B^{\alpha}, T) - \mu_A^{\beta}(x_B^{\beta}, T) = 0$$

$$\Delta\mu_B = \mu_B^{\alpha}(x_B^{\alpha}, T) - \mu_B^{\beta}(x_B^{\beta}, T) = 0$$

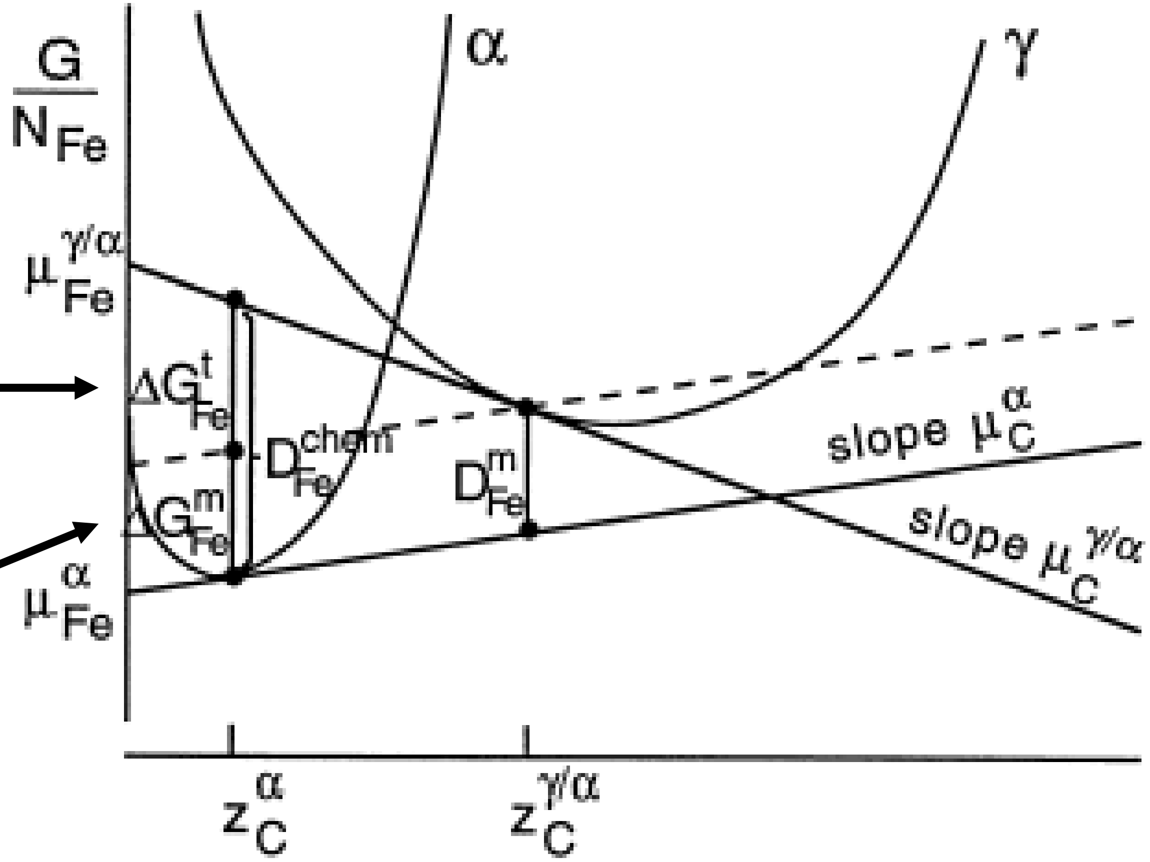
Dissipation of driving force at phase interface

The driving force across the interface is consumed by two independent processes:

- Transformation of crystalline lattice
- Change in composition by trans-interface diffusion

The processes are assumed independent and thus each needs a positive driving force.

Carbon diffuses across interface from α to γ.



Driving force for trans-interface diffusion:

Driving force for change of crystalline lattice:

All quantities expressed per mole of Fe atoms.

$$z_C = N_C / N_{Fe} = x_C / x_{Fe}$$

Trans-interface diffusion (Hillert 1960)

Combination with finite interface mobility yields:

$$J_C^t = -L_{CC}\Delta\mu_C$$

$$\Delta\mu_C = -\frac{v}{V_s L_{CC}}\left(z_C^{\gamma/\alpha} - z_C^{\alpha}\right)$$

$$\Delta\mu_{Fe} = \frac{v}{V_s}\left(\frac{V_s^{\,2}}{M} + \frac{z_C^{\gamma/\alpha}}{L_{CC}}\left(z_C^{\gamma/\alpha} - z_C^{\alpha}\right)\right)$$

$\Delta\mu_C$ and $\Delta\mu_{Fe}$ are functions of the composition on each side of the interface and may be described by suitable thermodynamic models of the γ and α phase, respectively.

Trans-interface diffusion substitutional system

Combination with finite interface mobility yields:

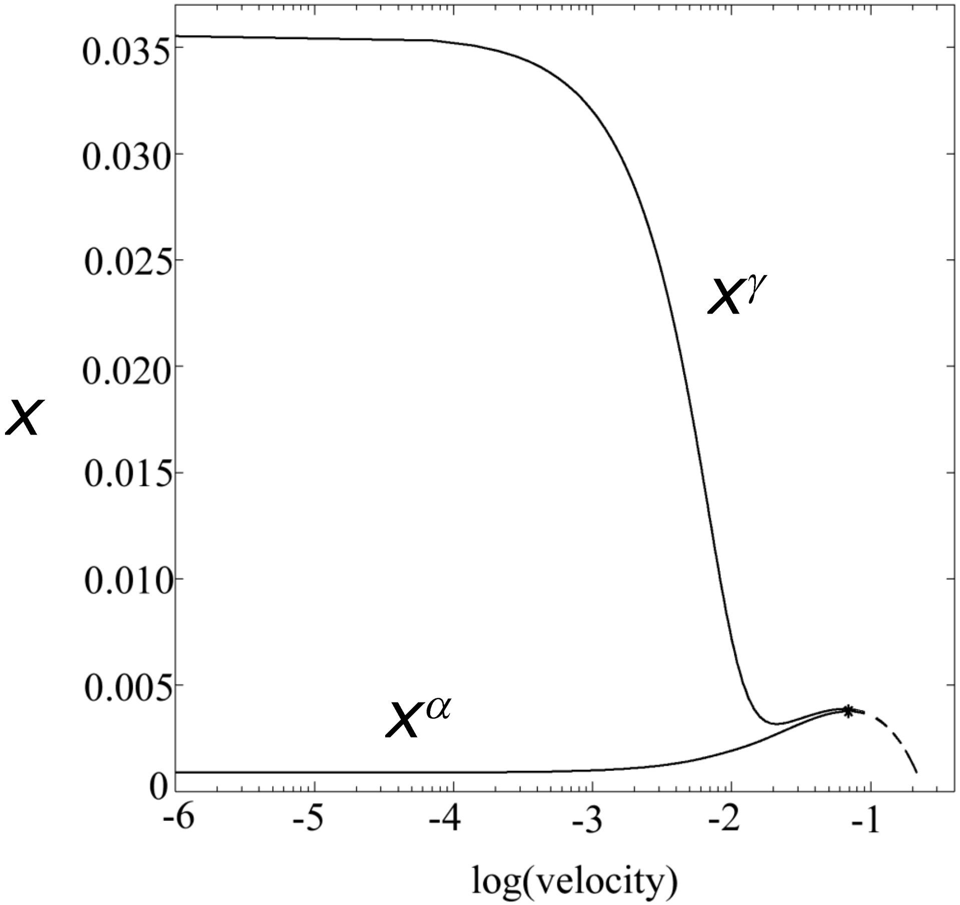
$$\Delta\mu_A = \frac{v}{V_m}\left[\frac{V_m^{\;2}}{M} + \frac{x_B^{\gamma/\alpha}}{L_{BB}}\left(x_B^{\gamma/\alpha} - x_B^{\alpha}\right)\right] > 0$$

$$\Delta\mu_B = \frac{v}{V_m}\left[\frac{V_m^{\;2}}{M} - \frac{(1 - x_B^{\gamma/\alpha})}{L_{BB}}\left(x_B^{\gamma/\alpha} - x_B^{\alpha}\right)\right]$$

Since $\Delta\mu_A > 0$ $\Delta\mu_B < 0$.

$\Delta\mu_A$ and $\Delta\mu_B$ are functions of the composition on each side of the interface and may be described by suitable thermodynamic models of the γ and α phase, respectively.

For a given interface velocity the equations may be solved to yield the composition on each side of interface.



”Sharp” interface with with representative composition (Ågren 1989)

$$-J_A^t = J_B^t = -L_{BB}\Delta(\mu_B - \mu_A) = \frac{v}{V_m}\left(x_B^i - x_B^\alpha\right)$$

$$\Rightarrow \Delta G_m^t = -\left(x_B^i - x_B^\alpha\right)\Delta(\mu_B - \mu_A)$$

$$\Delta G_m^m = x_A^i \Delta\mu_A + x_B^i \Delta\mu_B$$

$$\Delta\mu_A = \frac{v}{V_m}\left[\frac{V_m^2}{M} + \frac{x_B^i}{L_{BB}}\left(x_B^i - x_B^\alpha\right)\right]$$

$$\Delta\mu_B = \frac{v}{V_m}\left[\frac{V_m^2}{M} - \frac{(1 - x_B^i)}{L_{BB}}\left(x_B^i - x_B^\alpha\right)\right]$$

Aziz model (1982)

Similar as the previous sharp interface models but:

$$-J_A^t = J_B^t = -\frac{D^i}{V_m f^\alpha}(a_B^{\gamma/\alpha} - a_B^\alpha)/\lambda$$

where

$a_B^{\gamma/\alpha}$ and a_B^α : B activity on γ and α side of interface

f^α : activity coefficient in α, D^i : diffusivity in interface

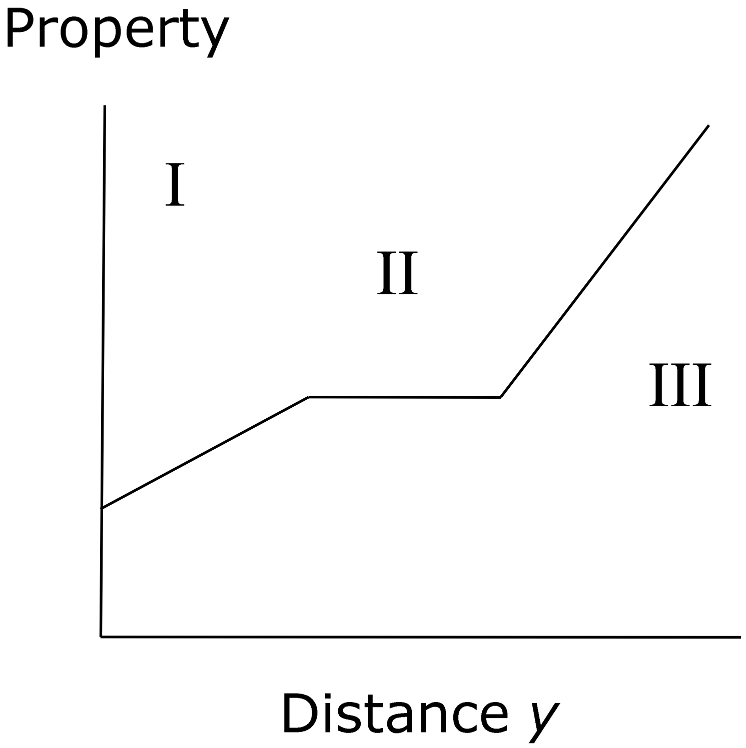
λ : Thickness of interface

Assuming activity coefficients constant one finds:

$$k_B^{\alpha/\gamma} = \frac{\beta + {}^{eq}k_B^{\alpha/\gamma}}{\beta + 1} \qquad \beta = \frac{v}{D^i/\lambda}$$

Finite interface thickness

Diffusion inside the interface → solute drag



Solute drag theory (Cahn, Hillert and Sundman etc)

- Solution of steady state equation inside interface.

$$-J_A^t = J_B^t = -L_{BB}\frac{\partial(\mu_B - \mu_A)}{\partial\, y} = \frac{v}{V_m}\left(x_B - x_B^{\alpha}\right)$$

A specific model yields $(\mu_B - \mu_A) = f(y, x_B)$.

For given v and x_B^{α} we may thus calculate

$x_B^{\alpha}(y)$.

- Integration of dissipation over interface:

$$\Delta G_m^{sd} = -\frac{V_m}{v}\int_{\delta} J_B^t \frac{d(\mu_B - \mu_A)}{dy}\,dy$$

- Total driving force

$$\Delta G_m^{tot} = \sum_{k=1}^{n} x_k^{\mathrm{int}}(\mu_k^{\gamma} - \mu_k^{\alpha})$$

Available driving force across phase-interface (Hillert et al. 2003)

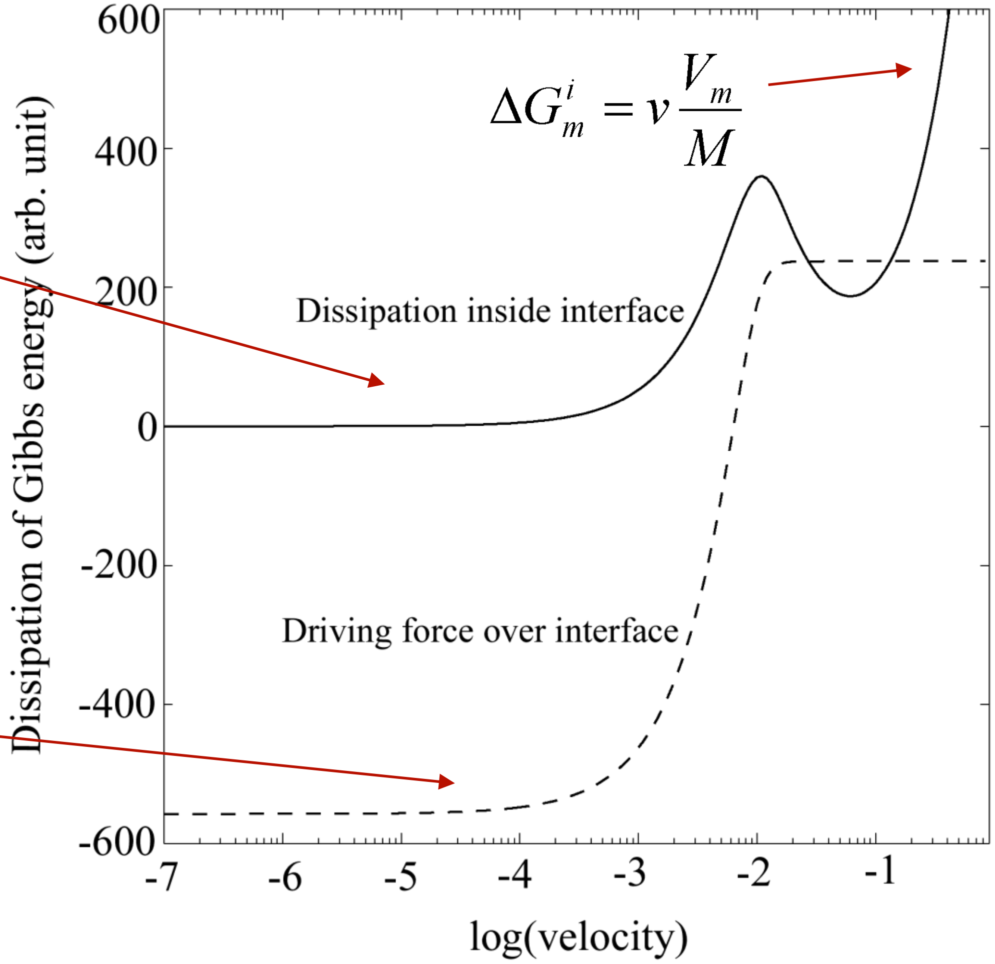
$$\Delta G_m^{tot} = \sum_{k=1}^{n} x_k^{\text{int}} (\mu_k^\gamma - \mu_k^\alpha)$$

$$x_k^{\text{int}} = \frac{x_k^\gamma J_k^\alpha - x_k^\alpha J_k^\gamma}{J_k^\alpha - J_k^\gamma} = x_k^\alpha \quad \text{when } J_k^\alpha = 0$$

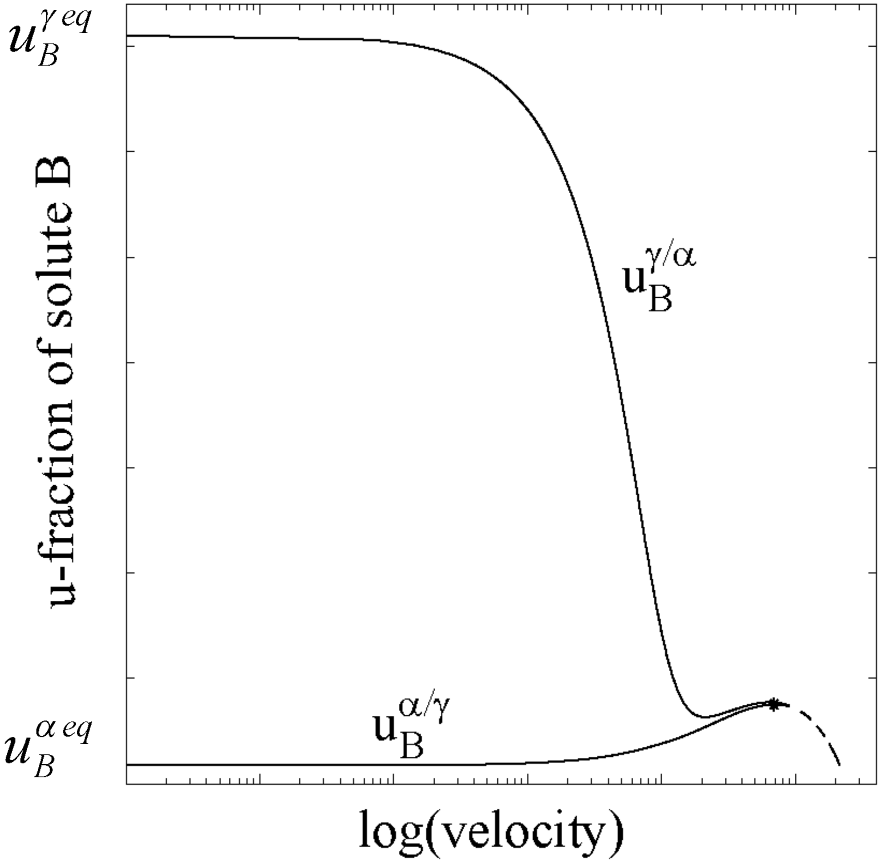
For a given composition of growing α:

$$\Delta G_m^{sd} = -\frac{V_m}{v}\int_{\delta} J_B^t \frac{d(\mu_B-\mu_A)}{dy}\,dy$$

$$\Delta G_m^{tot} = \sum_{k=1}^{n} x_k^{\mathrm{int}}(\mu_k^{\gamma}-\mu_k^{\alpha})$$



Driving force = Dissipation:

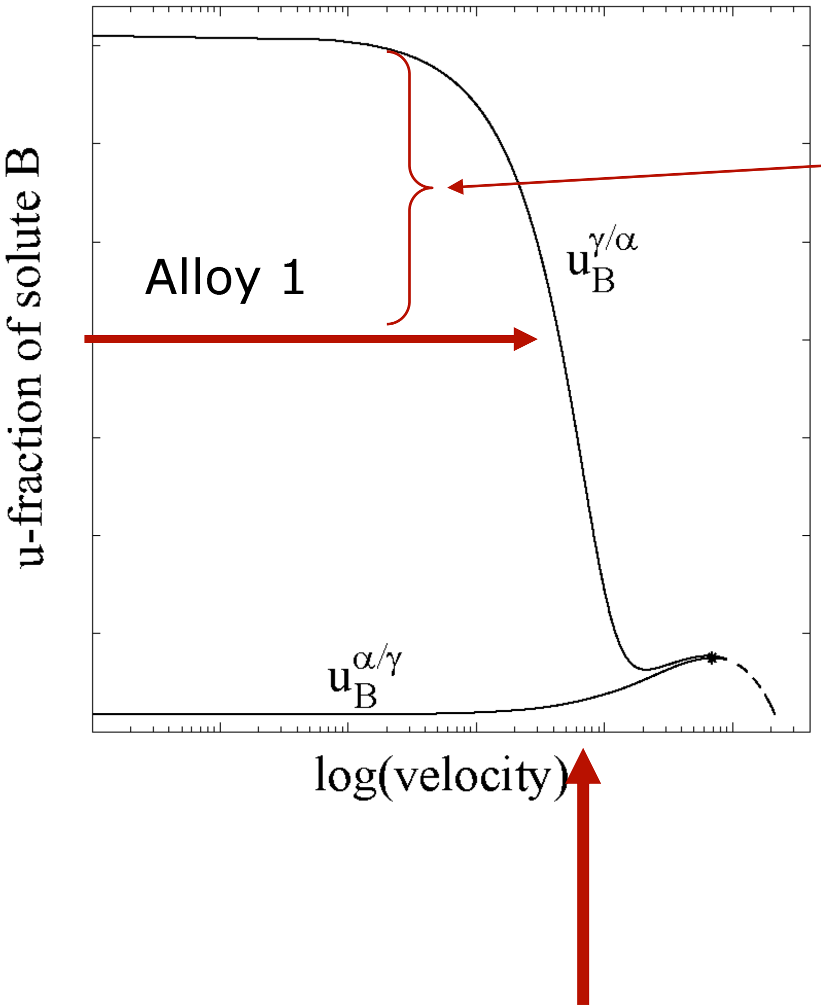


The compositions on each side of the phase interface depend on interface velocity and they approach each other.

$$u_B^{\alpha} = f(T,v) \rightarrow u_B^{\alpha\, eq} \quad \text{as } v \rightarrow 0$$

$$u_B^{\gamma} = g(T,v) \rightarrow u_B^{\gamma\, eq} \quad \text{as } v \rightarrow 0$$

Above a critical velocity transformation turns partitionless.



Driving diffusion in γ

Non-parabolic growth in early stages.

Maximum possible growth rate for alloy 1

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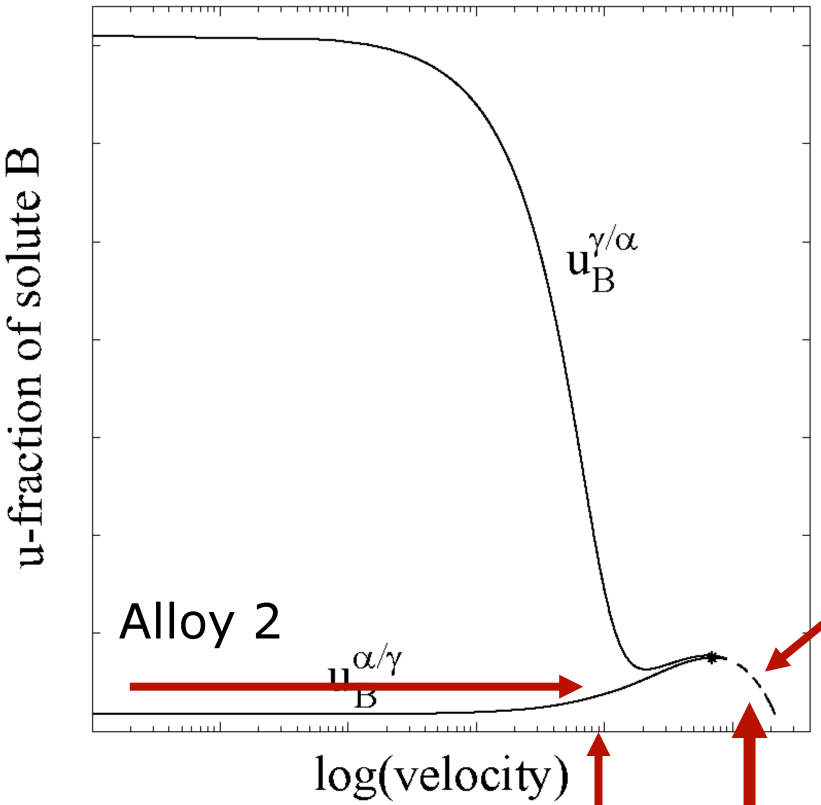
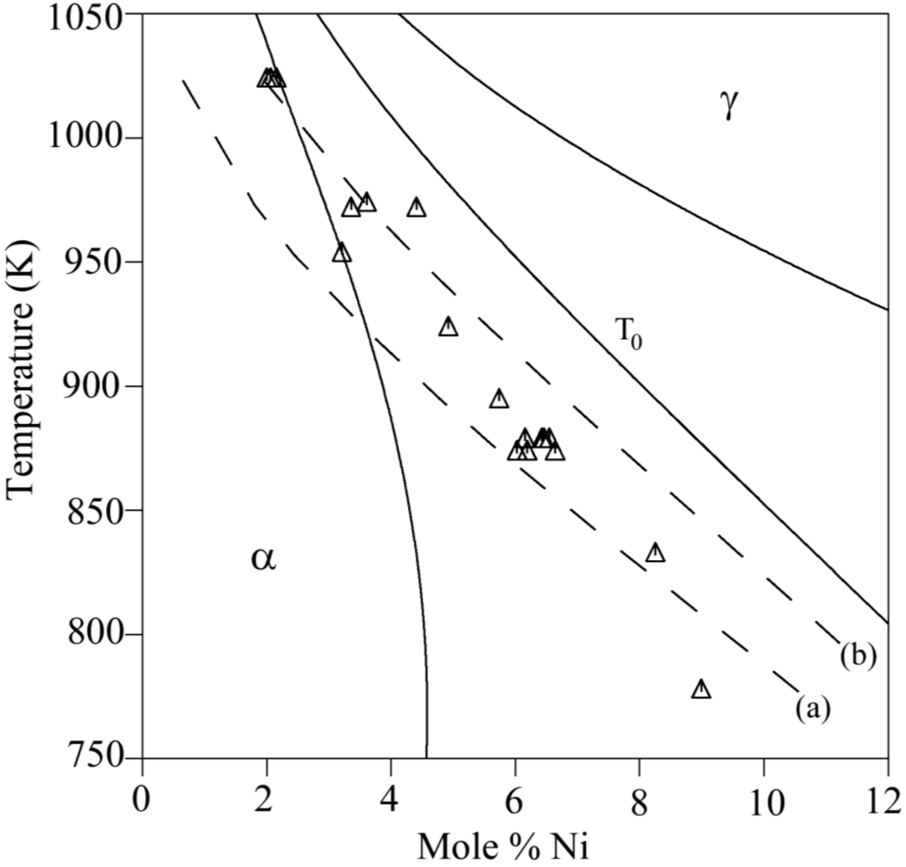


partitionless growth possible

partitionless growth with spike
in γ possible

Maximum possible (partitionless) growth rate
for alloy 2



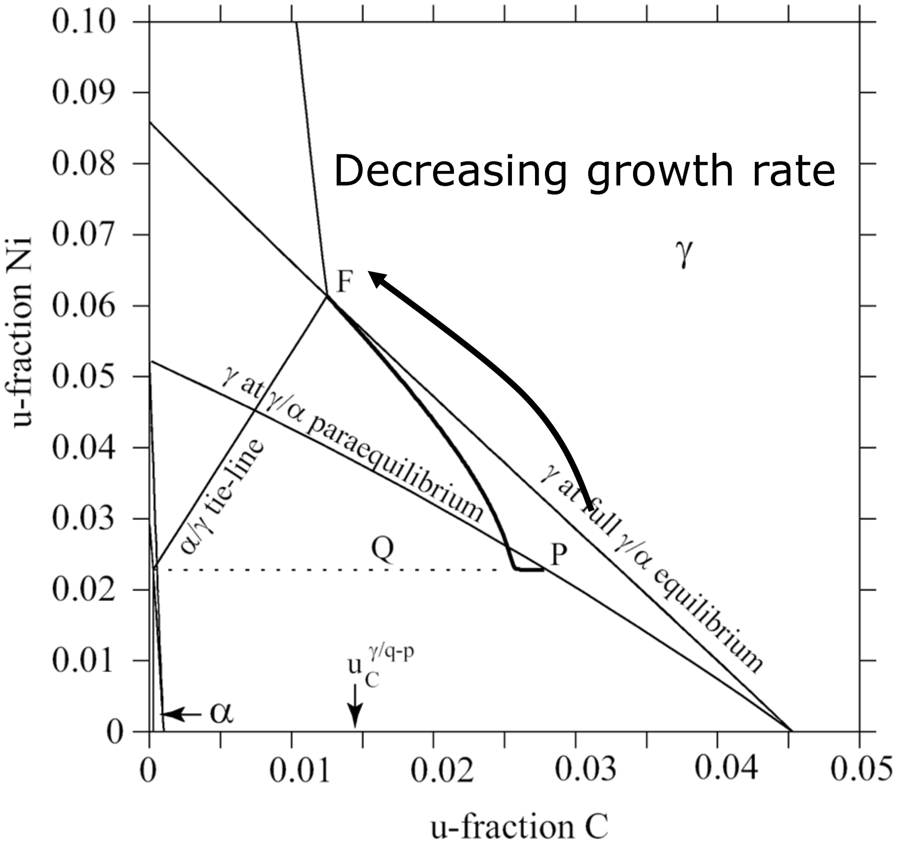
Calculated limit of the massive transformation in Fe-Ni alloys (dashed lines) calculated for two different assumptions on properties of interface.

(Odqvist et al. 2002)

Exp: Borgenstam and Hillert 2000

Fe-Ni-C

The interfacial tieline depends on the growth rate. (Odqvist et al. 2002)



- At high growth rates the state is close to paraequilibrium.

- At slower rates there is a gradual change towards NPLE.

- For each alloy composition there is a maximum size which can be reached under non-partitioning conditions.
  This size may be reached before there is carbon impingement.
  See also Srolovitz 2002.

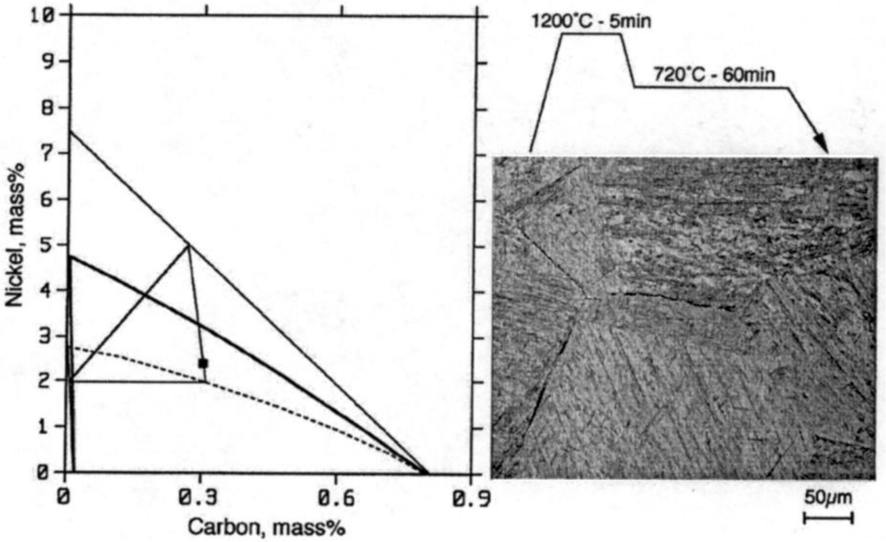
Ferrite formation under ”practical” conditions in Fe-Ni-C (Oi et al. 2000)

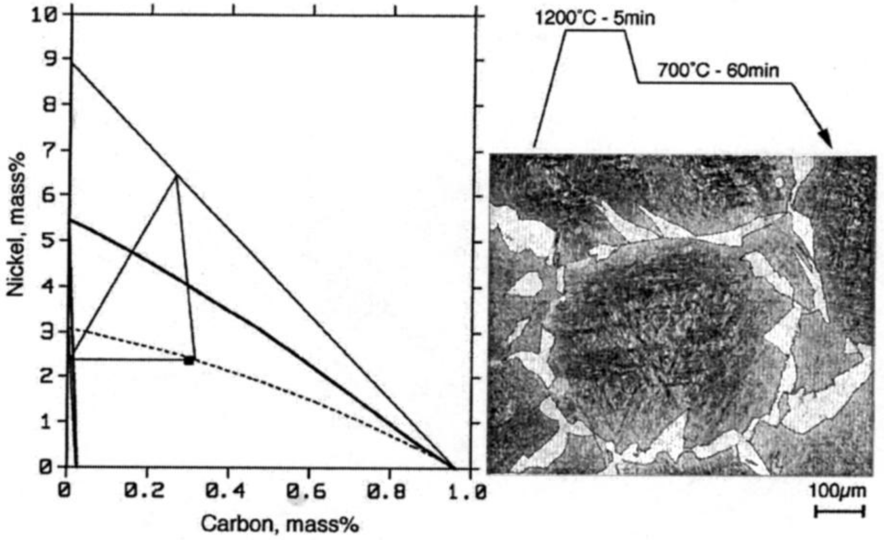
Thickness of M spike in γ:

D_M / v.

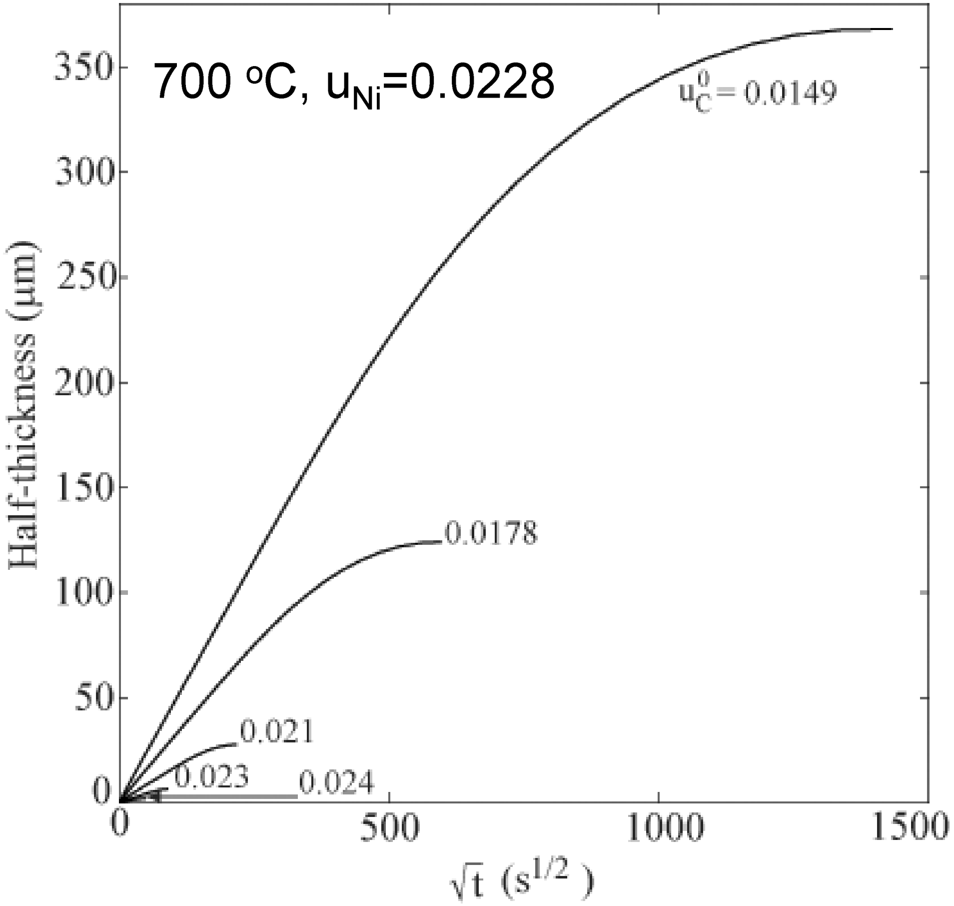
Local equilibrium, i.e. quasi paraequilibrium impossible if D_M / v < atomic dimensions.

$$v = 4.8\ 10^{-7}\ \mathrm{ms}^{-1}$$
$$D_M / v = 3.5\ 10^{-14}\ \mathrm{m}$$





Simulations Fe-Ni-C Odqvist et al. 2002



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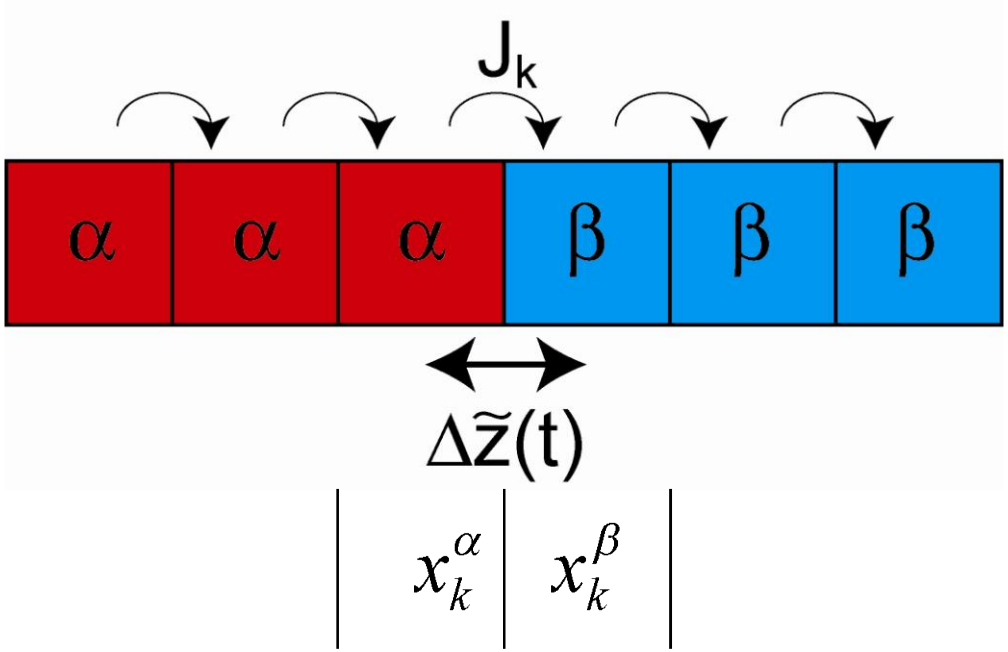
Larsson-Hillert (2005)

Lattice-fixed frame
of reference

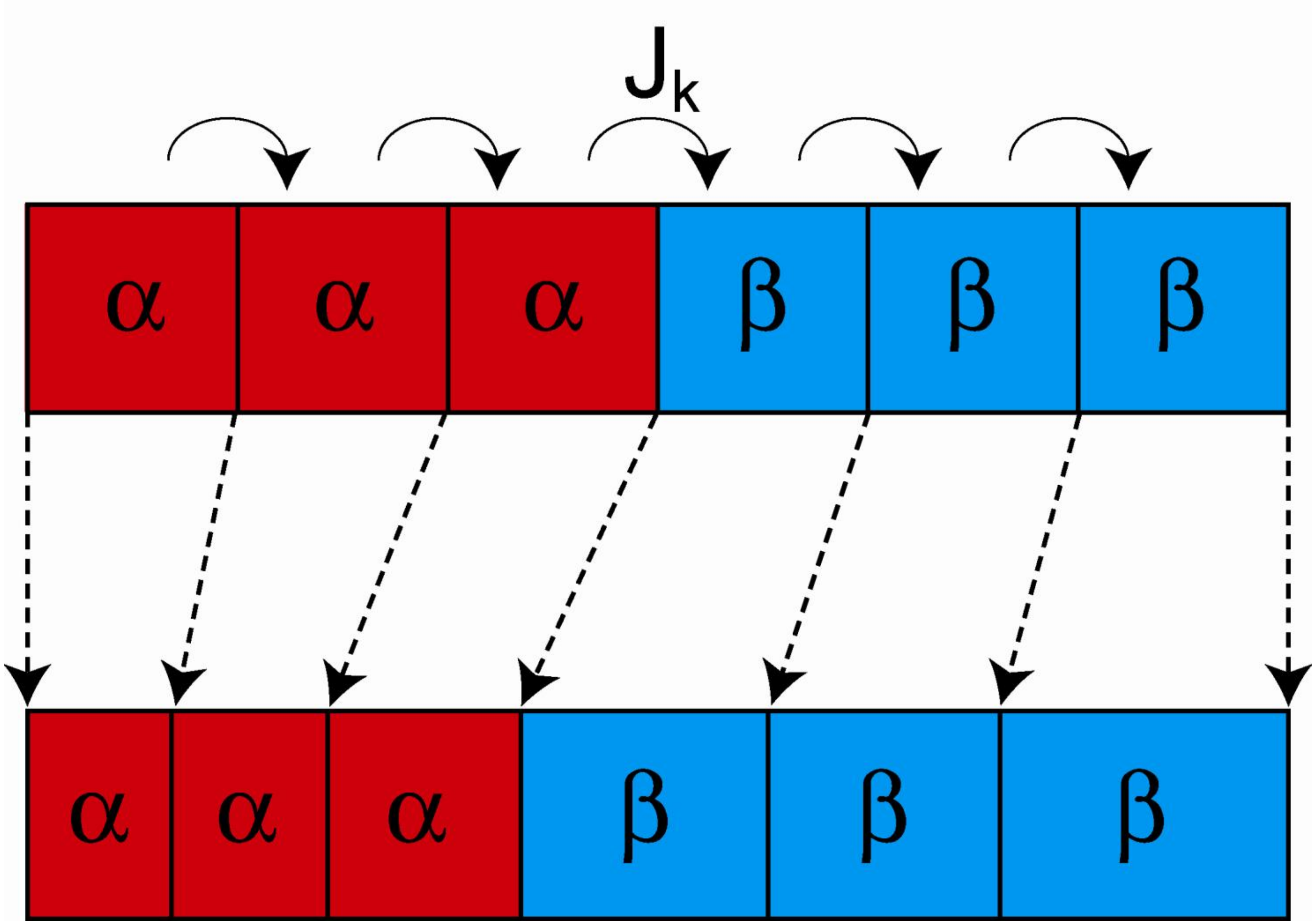


Absolute reaction rate theory of vacancy diffusion:

$$J_k = \frac{-M_k RT}{V_m \Delta\tilde{z}} \left[x_k^\alpha \, exp\left(\frac{\Delta\mu_k^*}{2RT} \right) - x_k^\beta \, exp\left(\frac{\Delta\mu_k^*}{2RT} \right) \right]$$

$\Delta\mu_k^* = \Delta\mu_k$ less ideal entropy of mixing

$$v = -V_m \sum J_k$$



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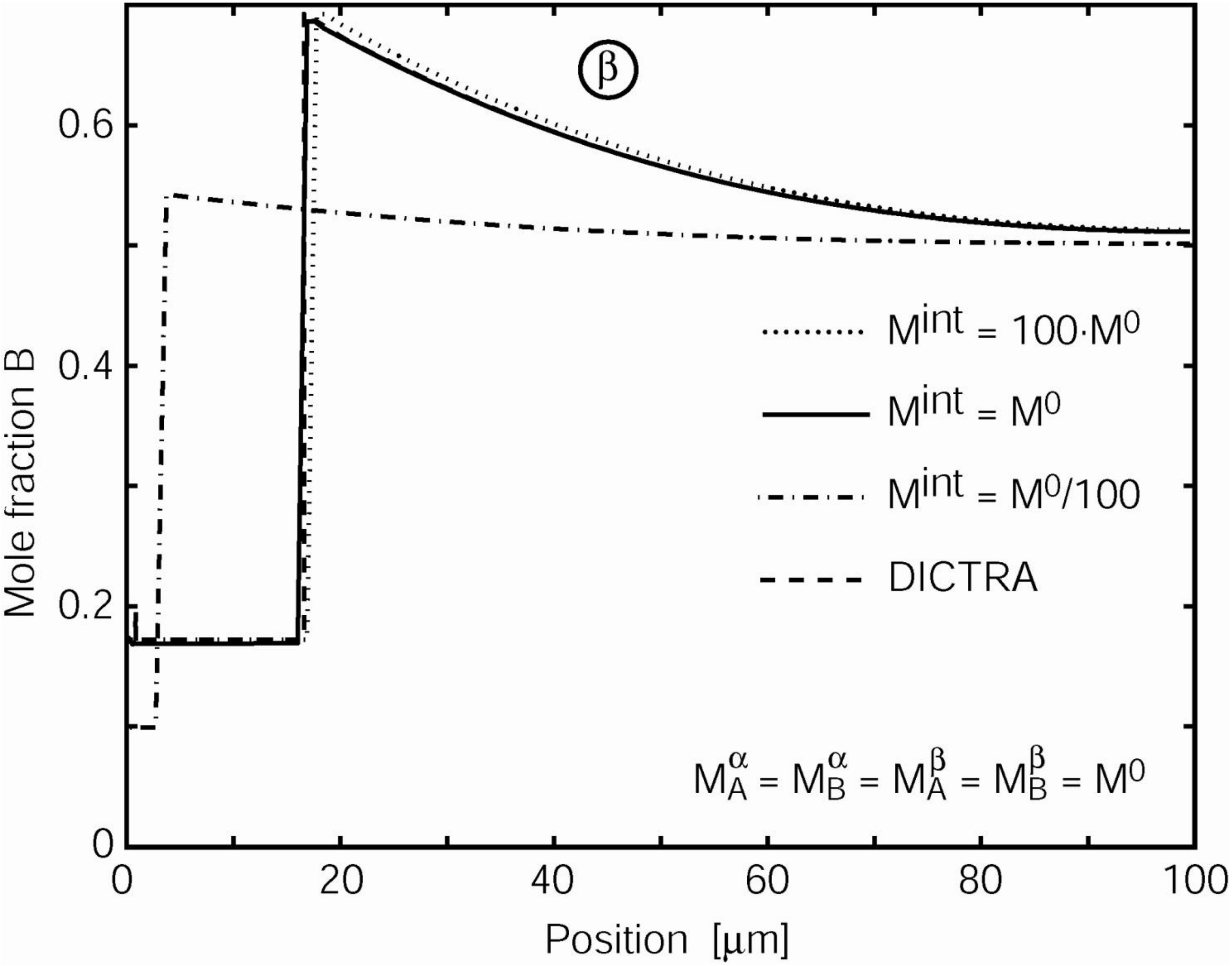
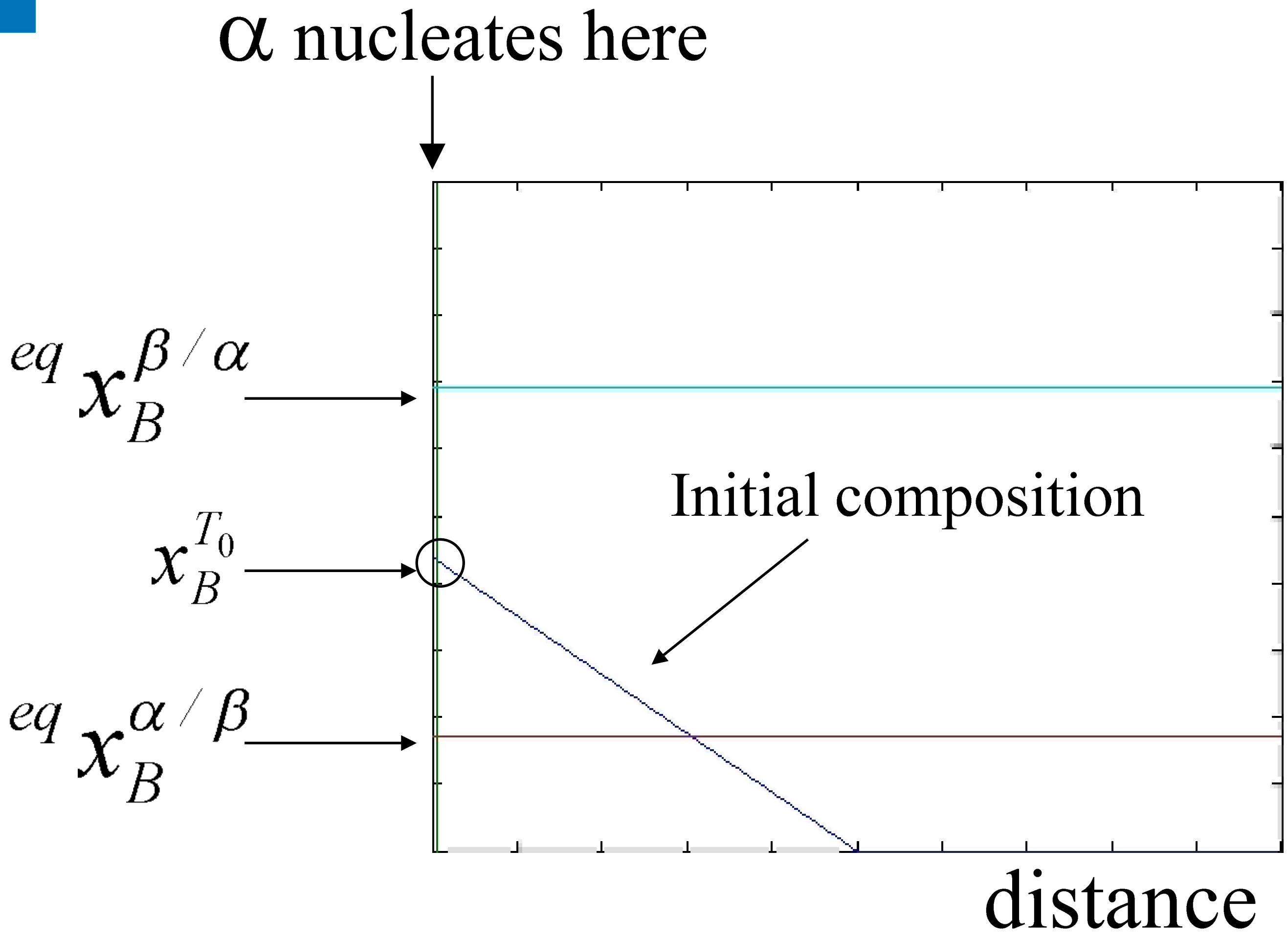
Simulation 1 (close to local equilibrium)



Simulation 2a vacancy diffusion with composition gradient



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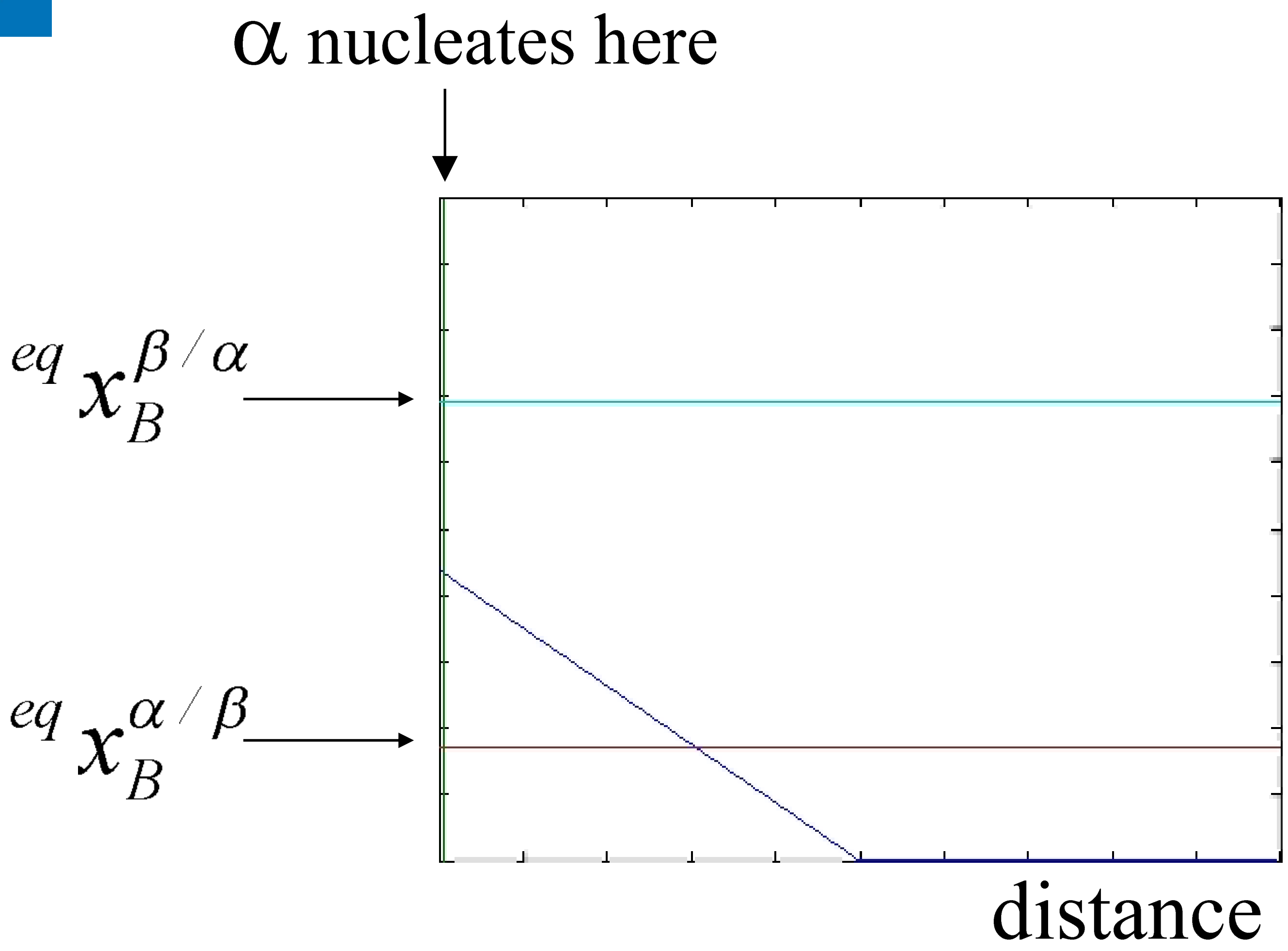
Solute trapping impossible!

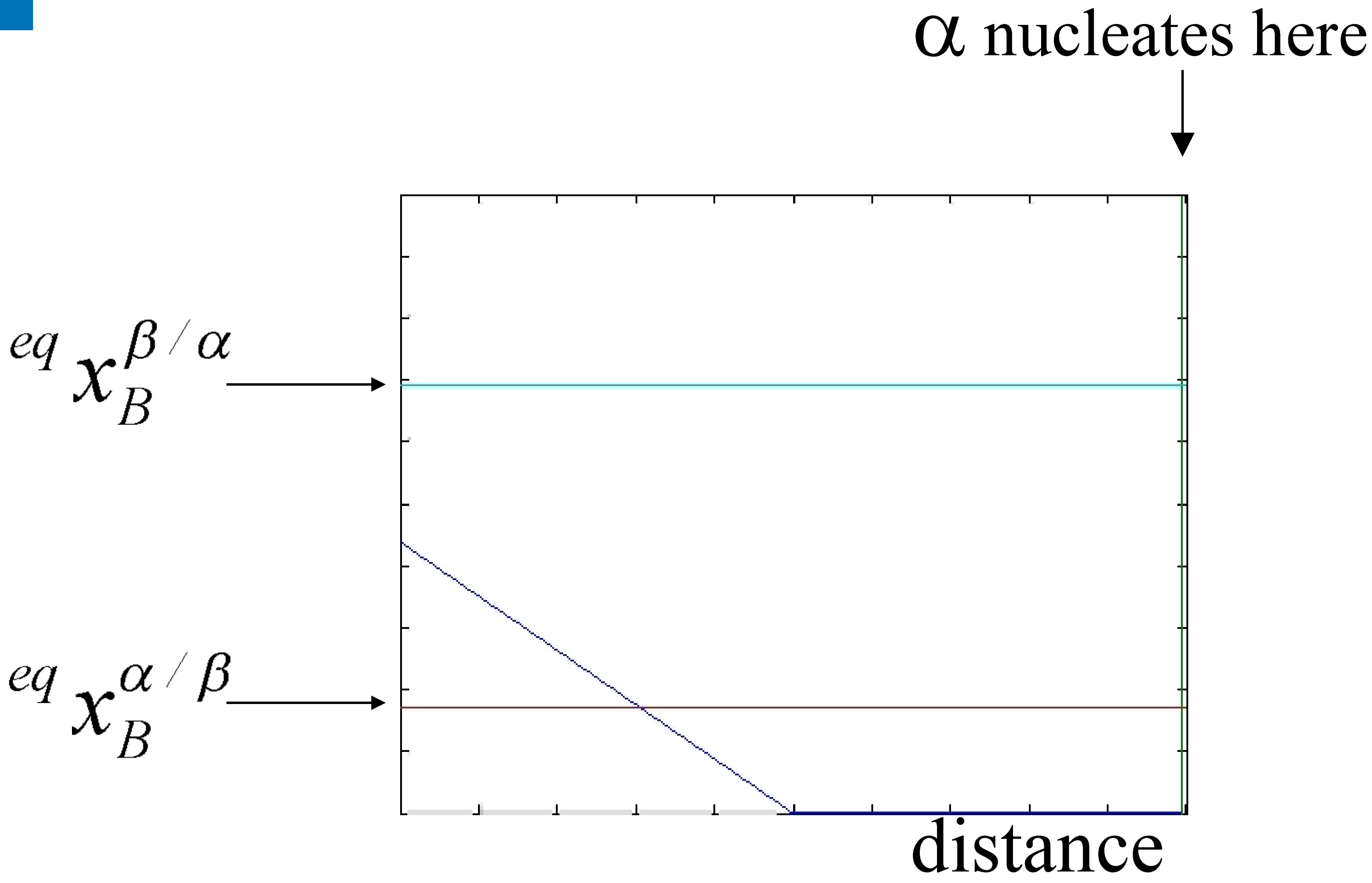
Add term for cooperative mechanism

$$J_k = \frac{-M_k RT}{V_m \Delta z}\left[x_k^1\, exp\left(\frac{\Delta\mu_k^*}{2RT}\right) - x_k^2\, exp\left(\frac{\Delta\mu_k^*}{2RT}\right)\right]$$

Simulation 2b
vacancy + cooperative mechanism

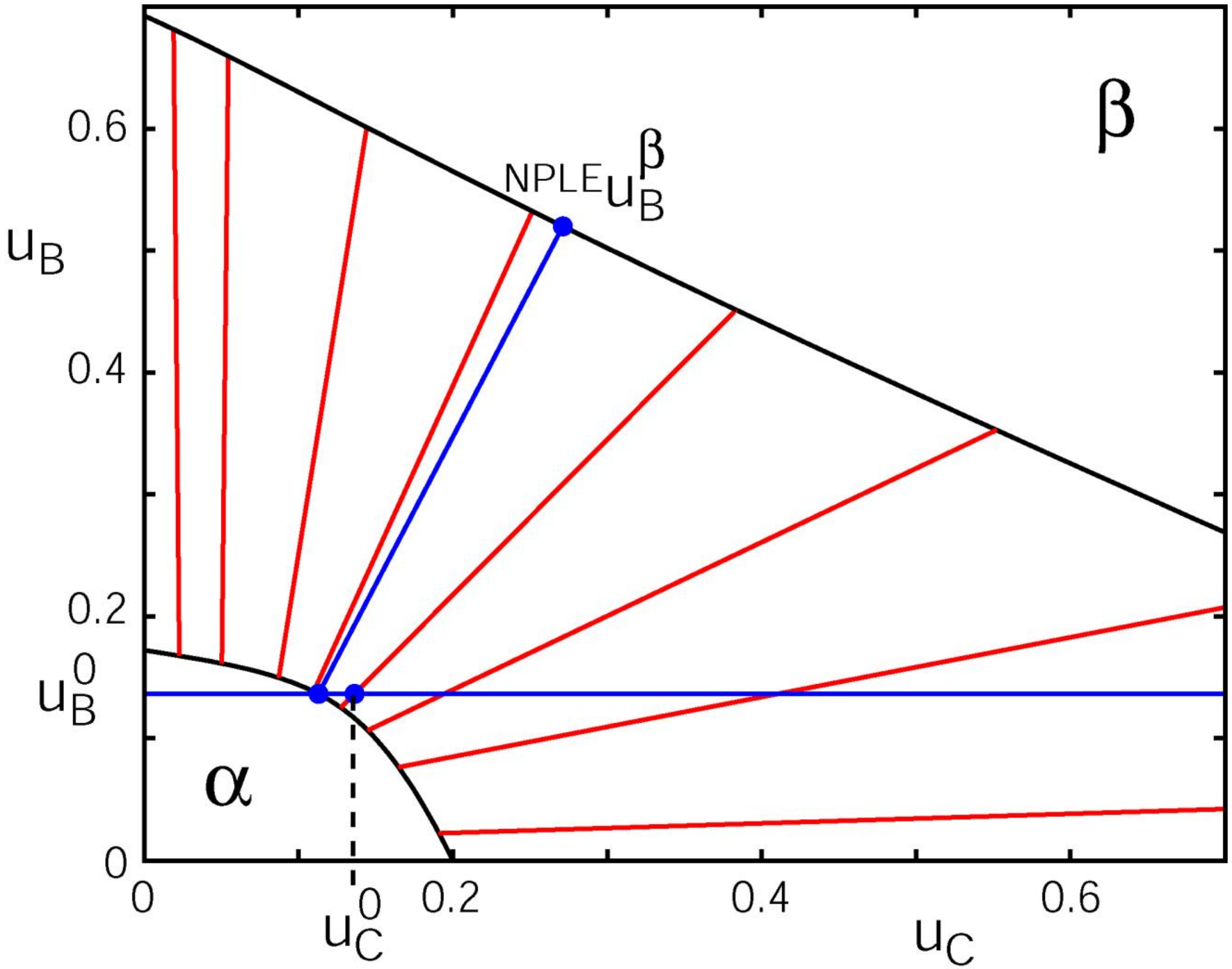


Simulation 2c - other direction vacancy + cooperative mechanism



Simulation 3
Ternary system A-B-C, C is interstitial

$$u_k = \frac{x_k}{1 - x_C}$$



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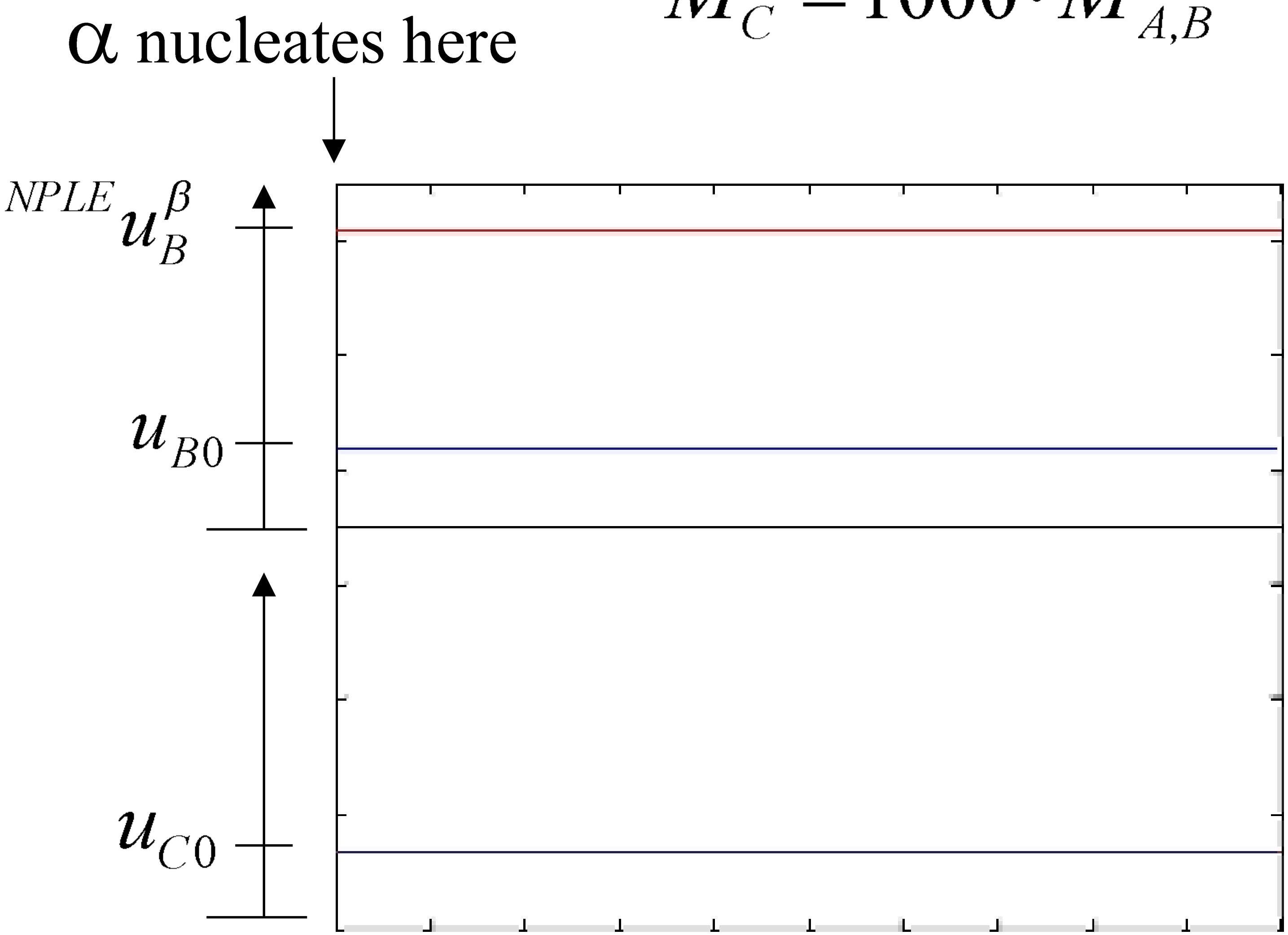
Simulation 3

$$M_C = 1000 \cdot M_{A,B}$$



Diffuse interfaces – phase-field method

ϕ not conserved

Cahn - Allen equation :

$$\dot{\phi} = -M_{\phi}\frac{\delta G}{\delta \phi} = -M_{\phi}\left(\frac{1}{V_m}\frac{\partial G_m}{\partial \phi} - \varepsilon^2 \nabla^2 \phi\right)$$

Concentration conserved :

$$\dot{c}_k = -\nabla \vec{J}_k \qquad \text{(n - 1 equations)}$$

$$\vec{J}_k = -\sum L''_{kj} \nabla \frac{\delta G}{\delta c_j}$$

$$\frac{\delta G}{\delta c_j} = \left(\frac{1}{V_m}\frac{\partial G_m}{\partial c_j} - \kappa_j^2 \nabla^2 c_j\right)$$

Thermodynamic and kinetic properties of diffuse interfaces are needed, e.g.

$$G_m(\phi, c_k)/V_m.$$

Phase-field modelling of solute drag in grain-boundary migration (Asp and Ågren 2006)

$$G_m = G_m^\alpha + \phi^2\left(1-\phi\right)^2 W(x_B)$$

$$W(x_B) = x_B W_B + (1 - x_B) W_A$$

Example 1 – grain boundary segregation

Equilibrium solute segregation

$$\nabla \frac{\partial G_m}{\partial x_B} = 0 \Rightarrow$$

$$x_B^{gb} = x_B^{\alpha} \exp\left(\frac{-\phi^2 (1-\phi)^2 (W_B - W_A)}{RT} \right)$$

$$W_A = 18 V_m \left(\frac{\sigma_A}{\varepsilon} \right)^2$$

$$W_B = W_A - 16 RT \ln k^{gb/\alpha}$$

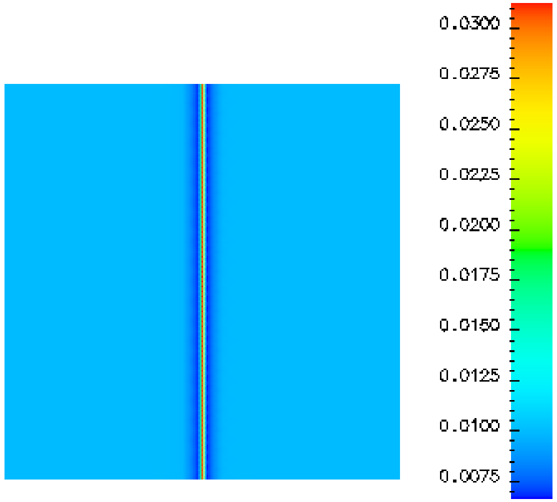
Equilibrium solute segregation by Cahn

$$C = C_0 \exp\left(\frac{-E(x)}{kT} \right)$$

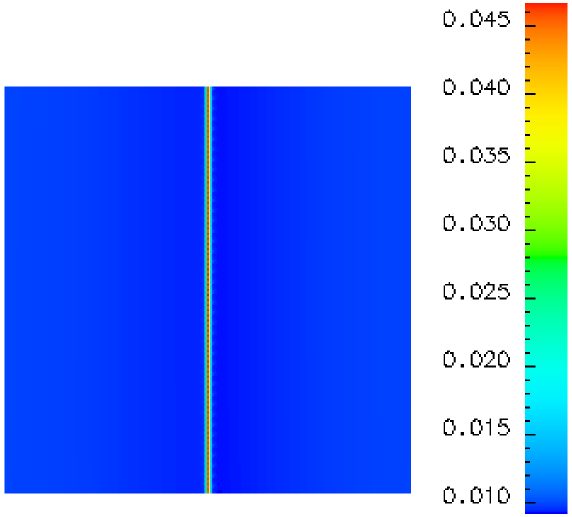
Example 1 – grain boundary segregation

Two grains devided by a planar grain boundary

- Concentration distribution at t1=30 sec and t2=1 h



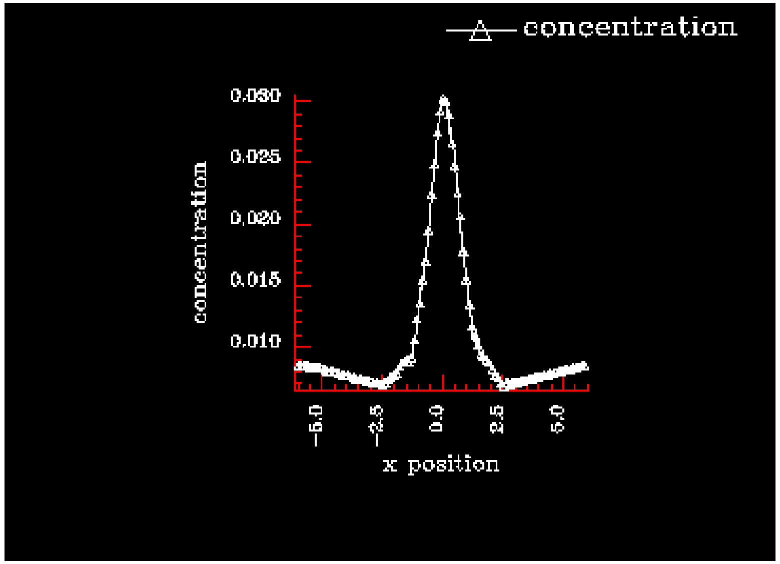
t1



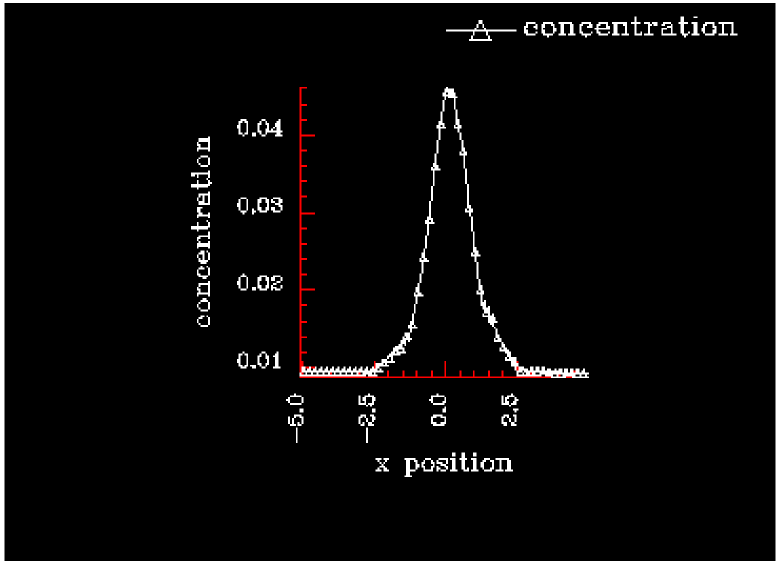
t2

Example 1 – grain boundary segregation

- Concentration profile at t1=30 sec and t2=1 h

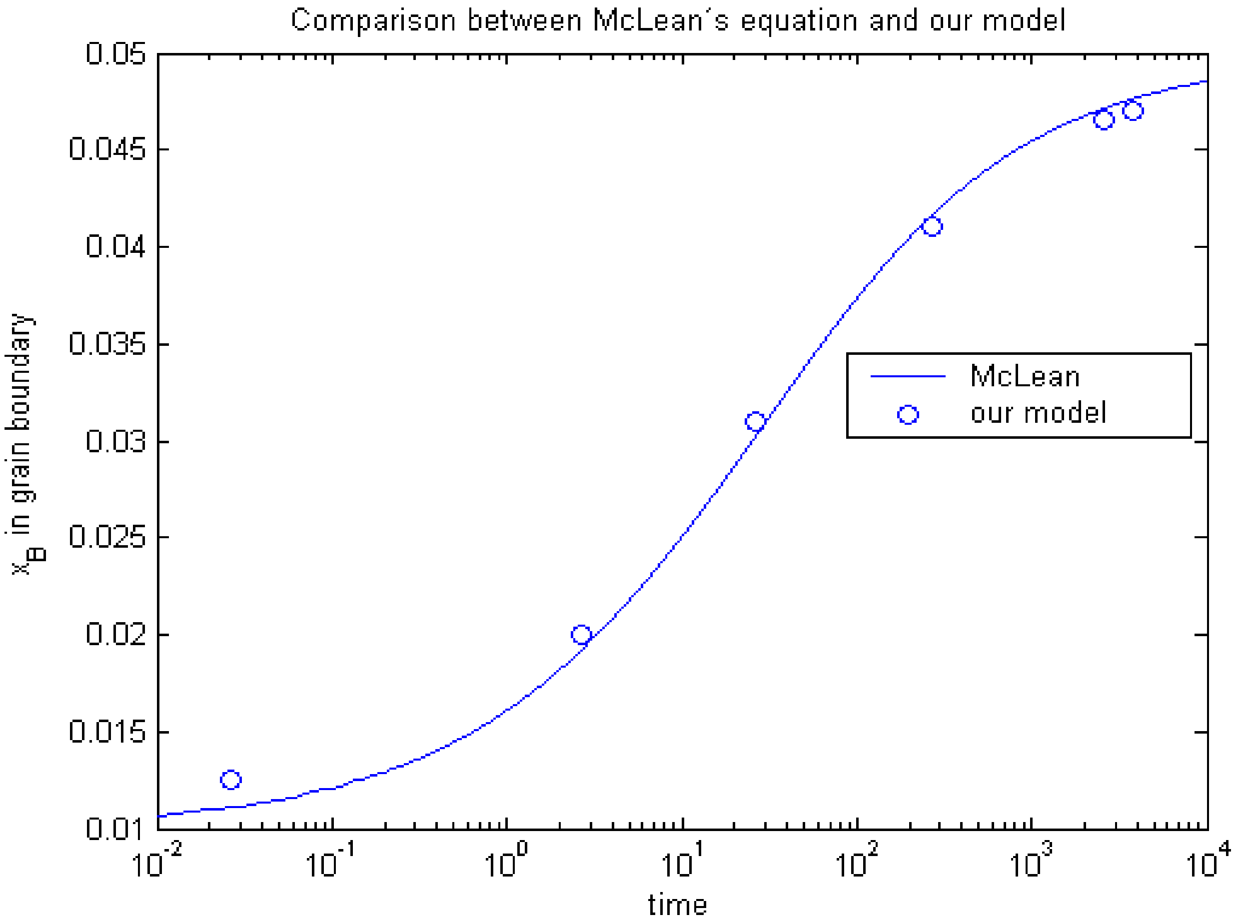


t1



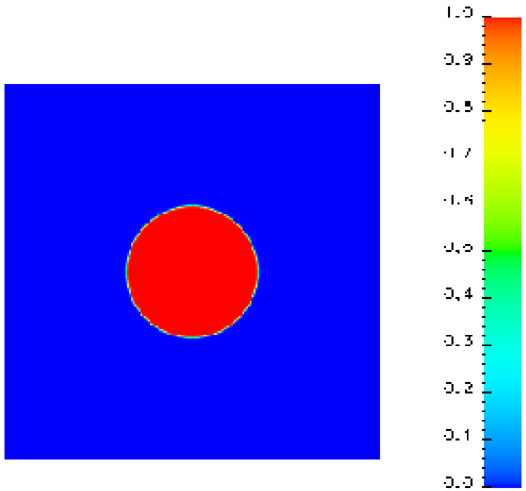
t2

Example 1 – grain boundary segregation



Example 2 – dynamic solute drag

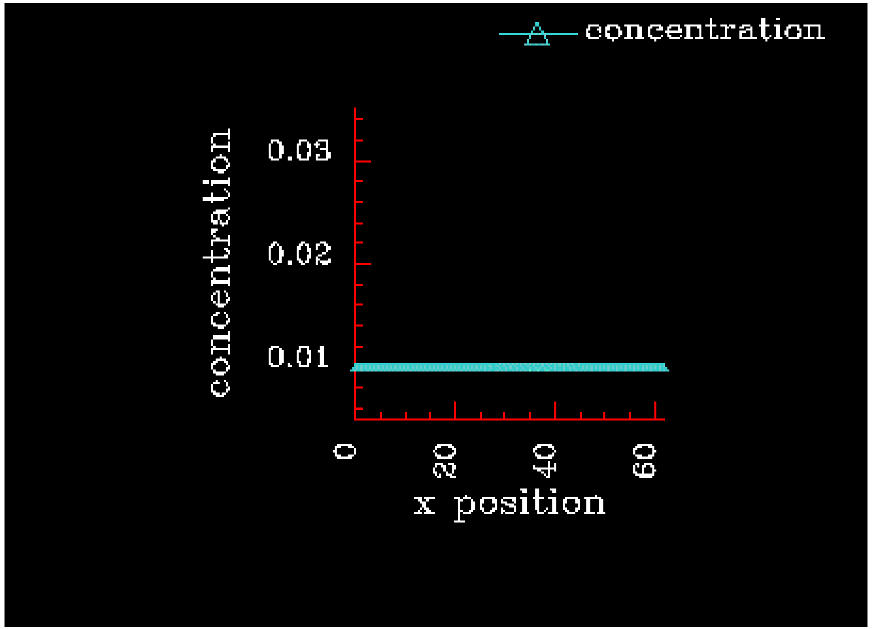
- Initial state: A circular grain with ϕ=1 surrounded by another grain where ϕ =0. Homogenous concentration of x_B=0.01.



Phase-field at t=0

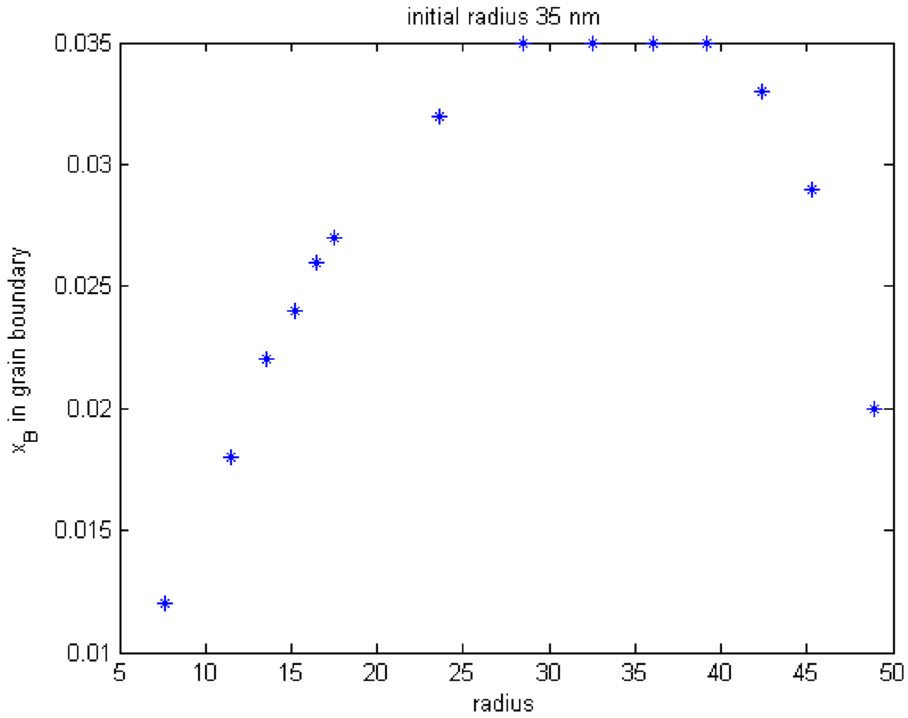
Example 2 – dynamic solute drag

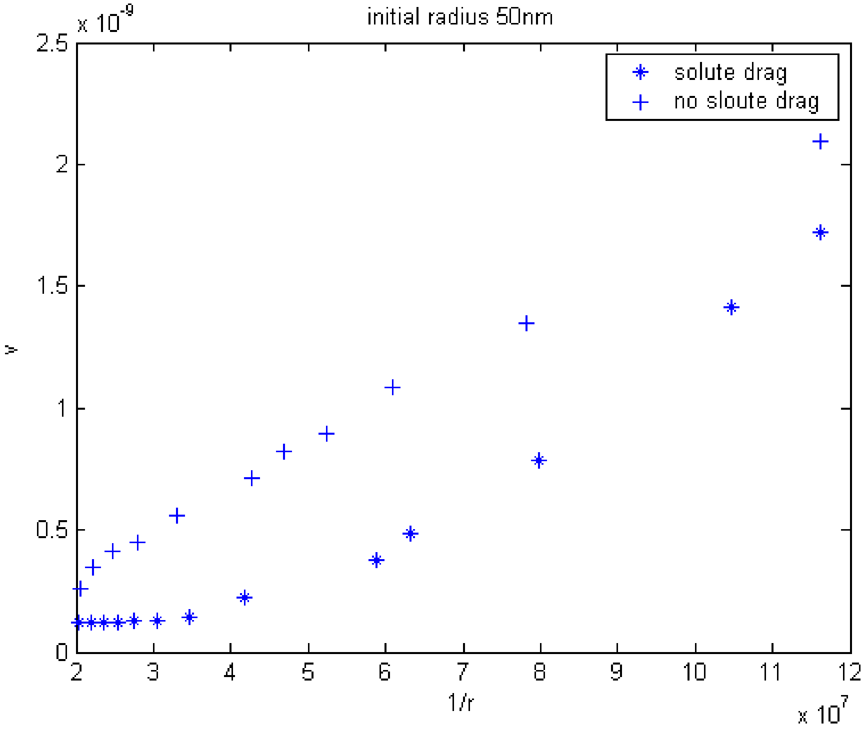
- Concentration profile as a function of time



Example 2 – dynamic solute drag

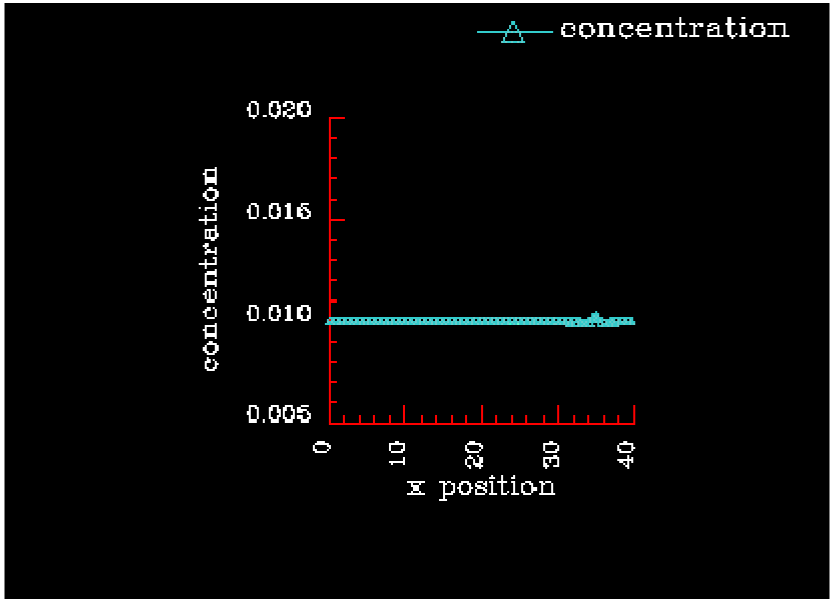
- Velocity as a function of curvature
- Concentration x_B in the grain boundary





Example 2 – dynamic solute drag

- Smaller initial grain
- Concentration profile as a function of time



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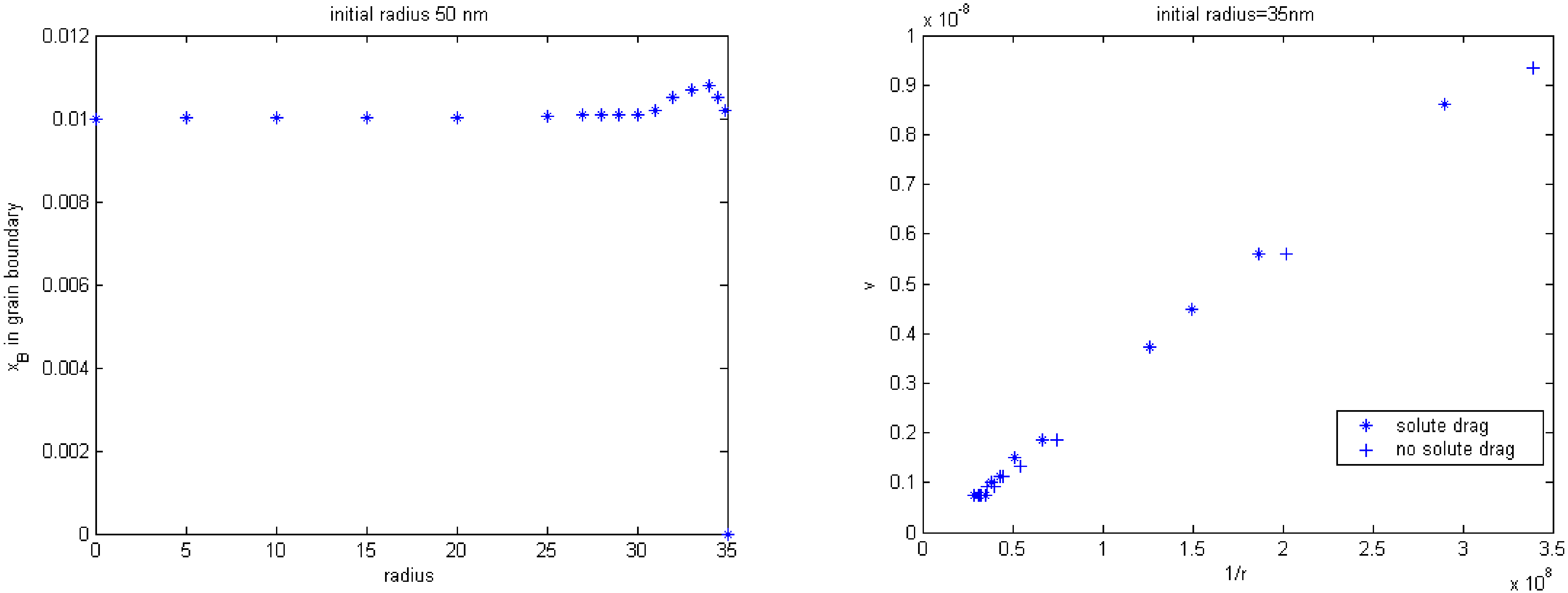
Example 2 – dynamic solute drag

- Smaller initial grain



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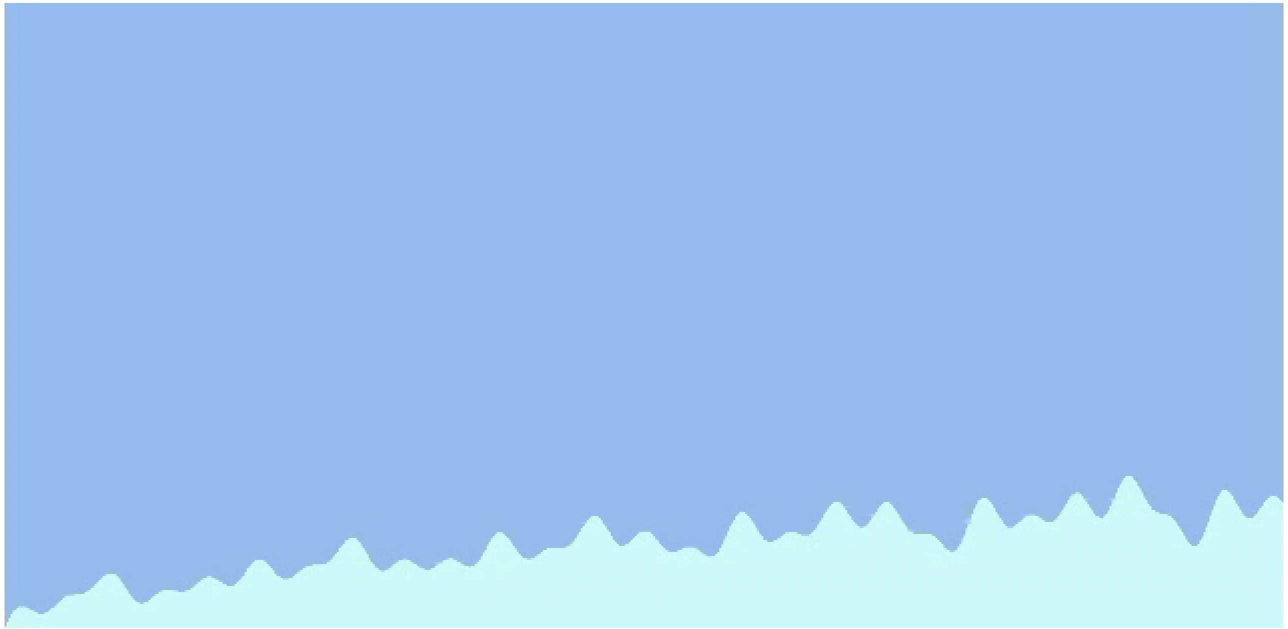
Phase-field method contains similar steps as in sharp and finite interface modelling:

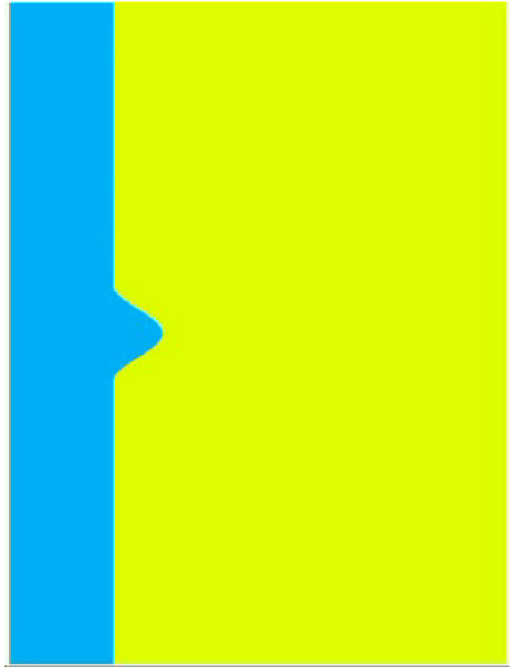
- Some properties of interface modelled.
- Solution of a diffusion equation to obtain concentreation profile.
- Cahn-Allen equation plays a similar role as the equation for interfacial friction.

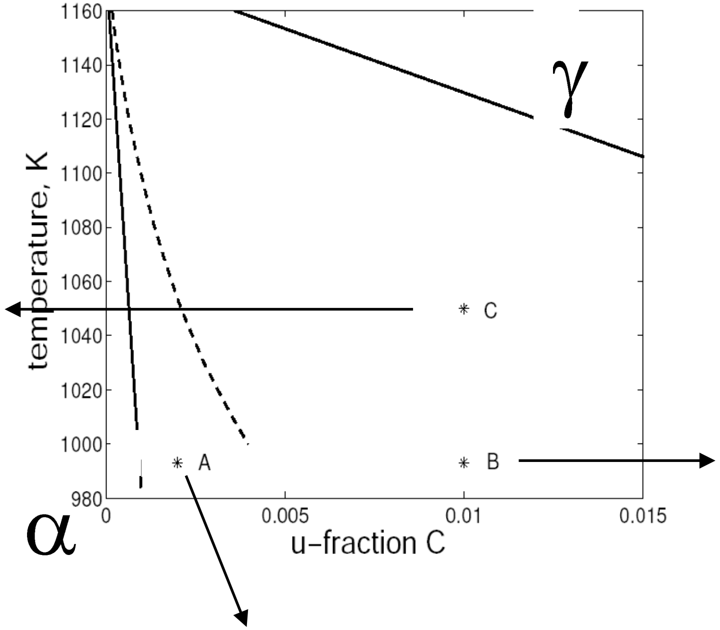
But: Thickness of interface must be treated not only as a numerical parameter but as a physical quatity.

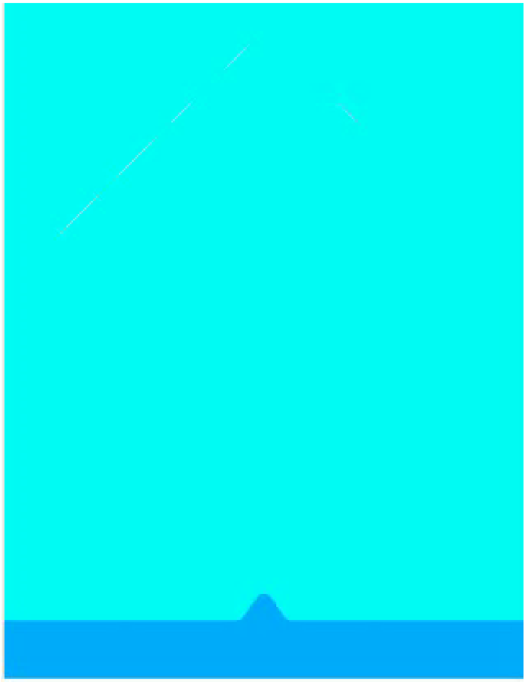
Example: Formation of WS-ferrite in steels

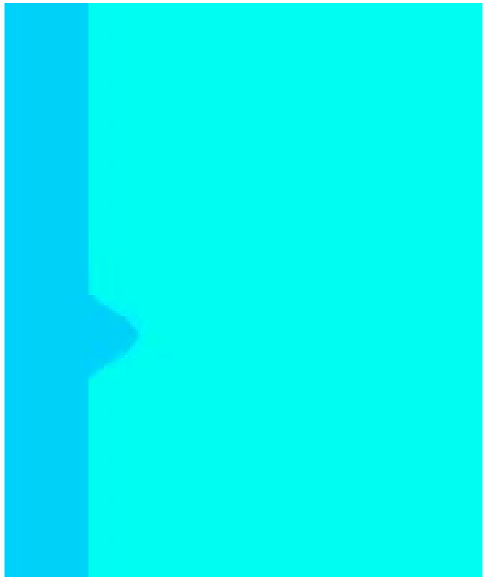


Loginova et al. 2004









Loginova et al. 2004

No Interface at all

Svoboda et al. 2004 (by Onsager extremum principle)

Ågren et al. 1997 (from other principles)

$$\frac{d\Re}{dt}=\frac{1}{\Re}M_{eff}\left(\sum_{i=1}^{C}x_i^{\beta}\mu_i^{\alpha}-G_m^{\beta}-\frac{2\sigma V_m^{\beta}}{\Re}-\frac{\dot{\Re}}{M}V_m\right)$$

where

$$M_{eff}=\frac{1}{\sum_{i=1}^{C}\frac{\left(x_i^{\beta}-x_i^{\alpha}\right)^2}{x_i^{\alpha}M_i}}$$

- Very efficient method – quite simple calculations.
- No details about the phase interface.
- Remains to investigate its accuracy.

Conclusions

- Sharp interface methods are computationally simple but may show problems with convergency.
- Solute drag models may be better than sharp interface models but have similar convergency problems.
- Larsson-Hillert method very promising
- Phase-field approach very powerful – no convergency problems – heavy computations.
- No-interface methods – quick calculations, accuracy remains to be investigated.