Methods to represent the interface conditions during austenite to ferrite transformation

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

Ackowledgement:
Joakim Odqvist, Henrik Larsson, Klara Grönhagen
Annika Borgenstam, Lars Höglund, Gerhard Inden
Mats Hillert

Content

1. The issue
2. Sharp interface
   - LENP
   - PARA
   - Interface kinetics
3. Finite thickness interface
   - Solute drag theories
   - Larsson-Hillert
4. Diffuse interface
   - Phase field
5. No interface at all
6. Conclusions

1. The issue

- We want to predict the rate of phase transformations (e.g. austenite -> ferrite)
- We want to calculate the rate from quantities which are ”easily” accesible.
- We want to tackle ”real” problems.
- Conditions for rapid transformation?

The mode of transformation?

- Partitional – composition change
  - Partitional for all elements (very slow)
  - Non partitional for substitutional elements (rapid)
- Non partitional for all elements
  - Massive (very rapid)
  - Martensitic (very-very rapid)
- Change in mode
  - Change in rate
  - Change in morphology

Rate controlling mechanisms

- Diffusion
  - in bulk
  - along grain boundaries and interfaces
  - across interfaces (trans-interface) – solute drag
- Interface migration – finite mobility
- Mixed mode (bulk-diffusion and interface mobility)

Modeling of the local state of phase interface

- 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.

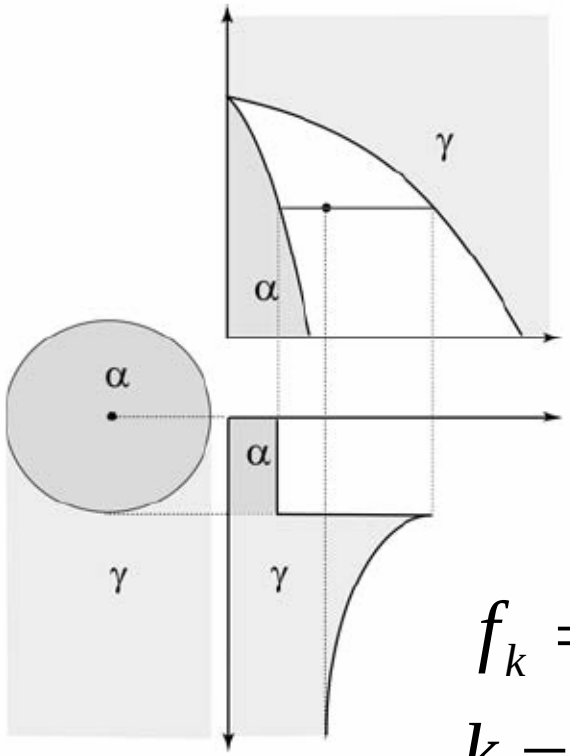
2. Sharp interface

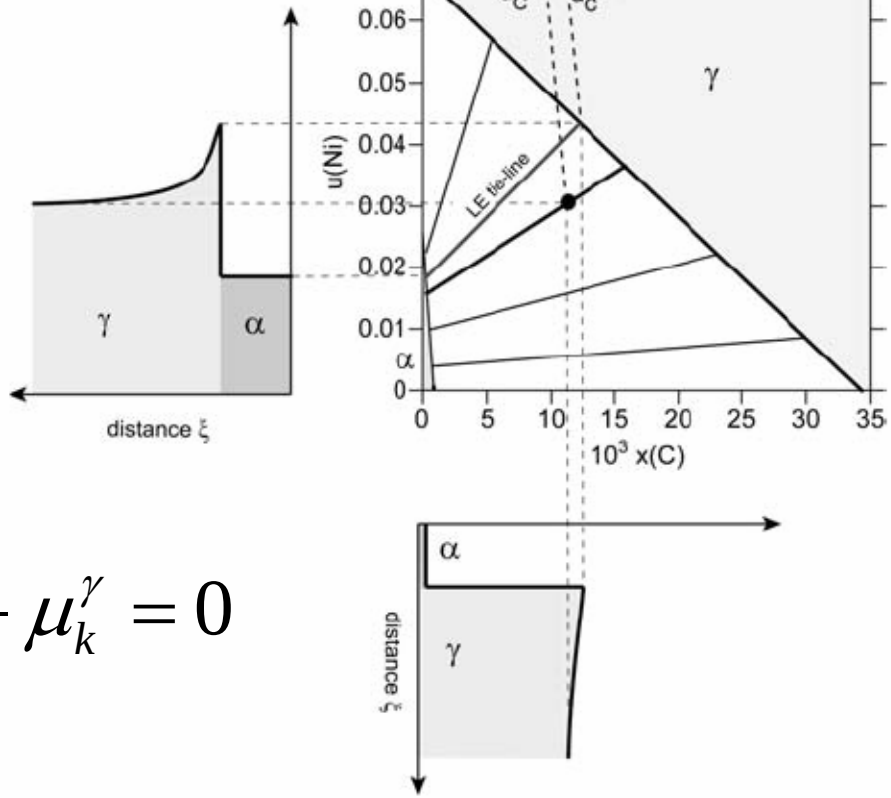
(Stefan Problem)

Transport equations in each phase solved.
In an *N* component system *N* extra conditions are needed at phase interface.

- Local equilibrium
- Para equilibrium
- Interface kinetics

Local equilibrium

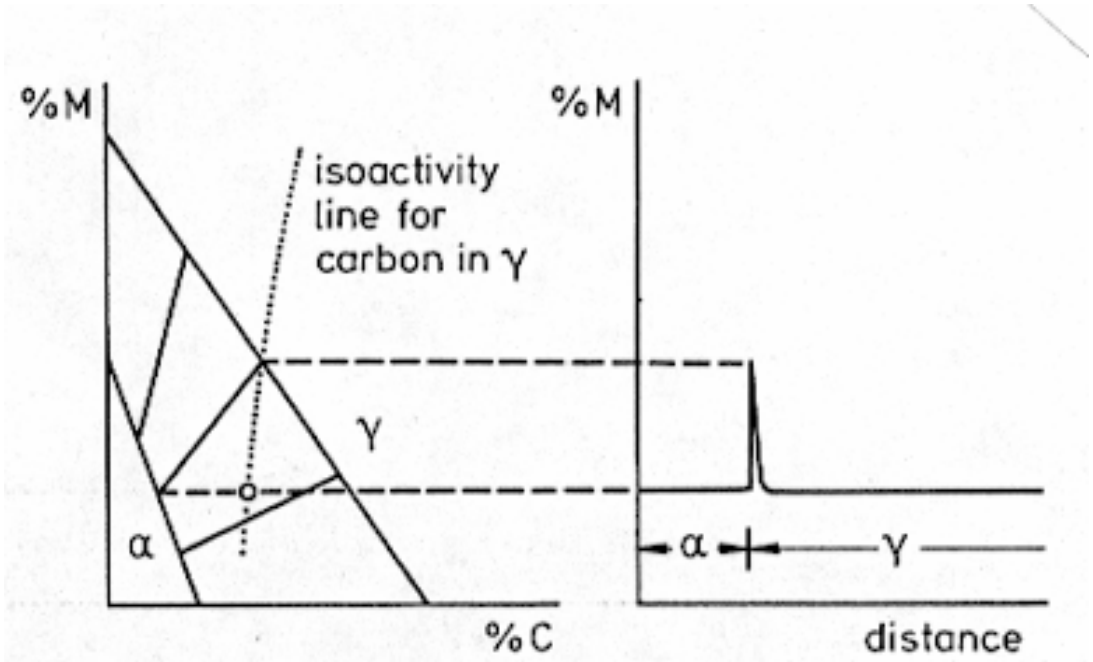


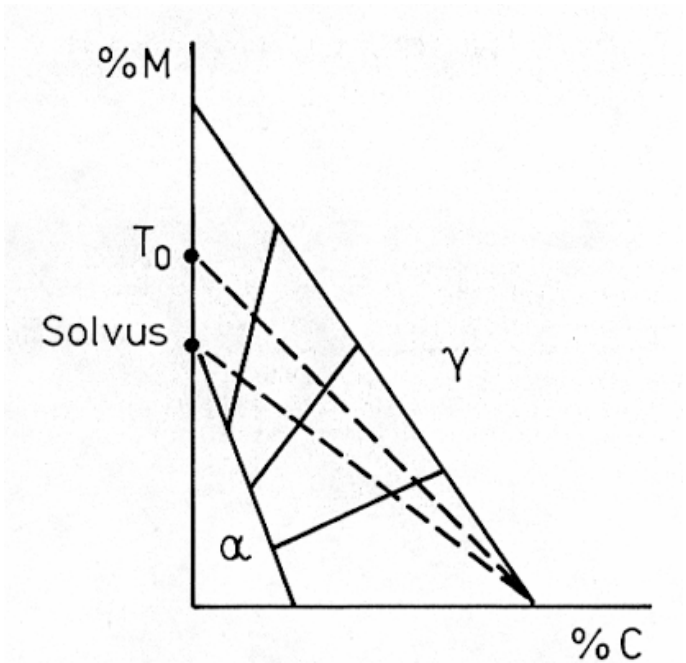


$$f_k = \mu_k^{\alpha} - \mu_k^{\gamma} = 0$$

$$k = 1,\ldots N$$

Local equilibrium non partitioning (LENP)
Ternary system Fe-M-C





”Quasi-paraequilibrium” (LENP)

Para equilibrium

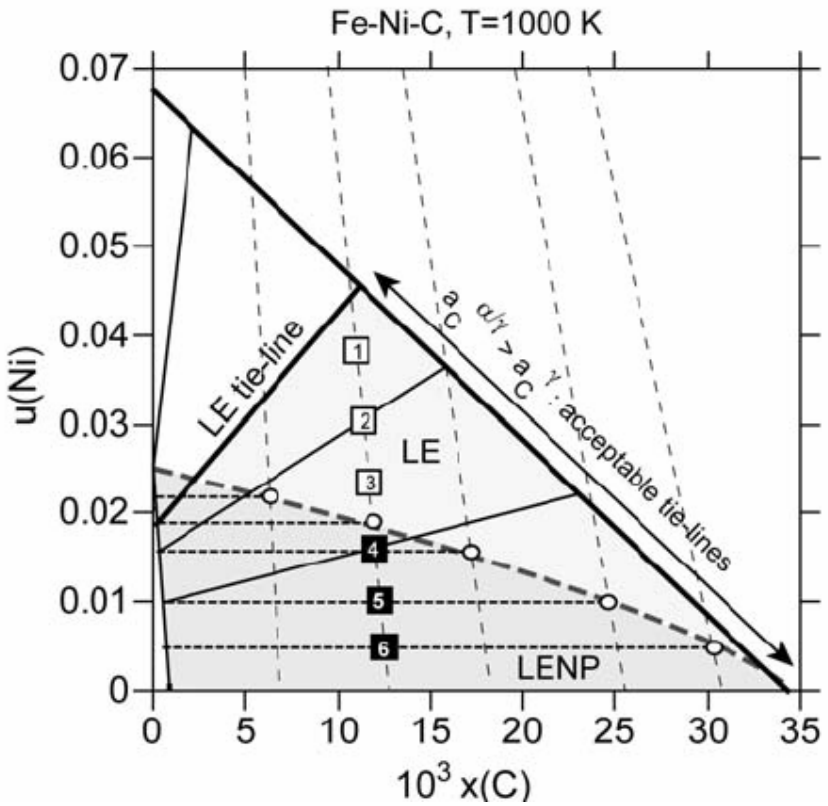
$$u_M = u_M^{\alpha} = u_M^{\gamma}$$

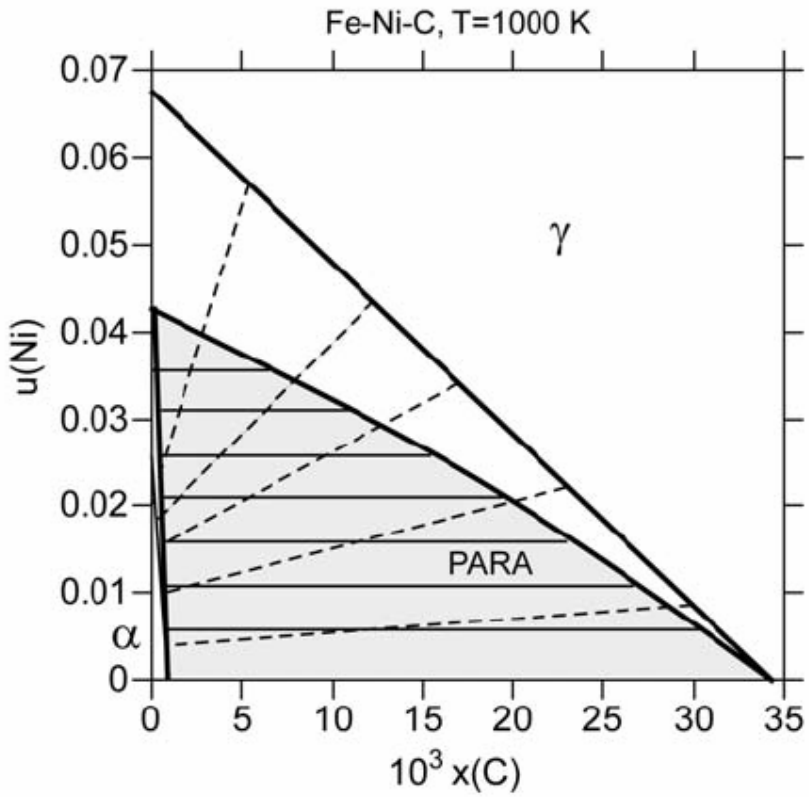
$X - C$ (2 effective components) $N = 2$

$$X = Fe_{(1-u_M)}M_{u_M} \Rightarrow \mu_X = (1-u_M)\mu_{Fe} + u_M \mu_M$$

$$f_1 = \mu_X^{\alpha}(u_C^{\alpha}, u_M, T) - \mu_X^{\gamma}(u_C^{\gamma}, u_M, T) = 0$$

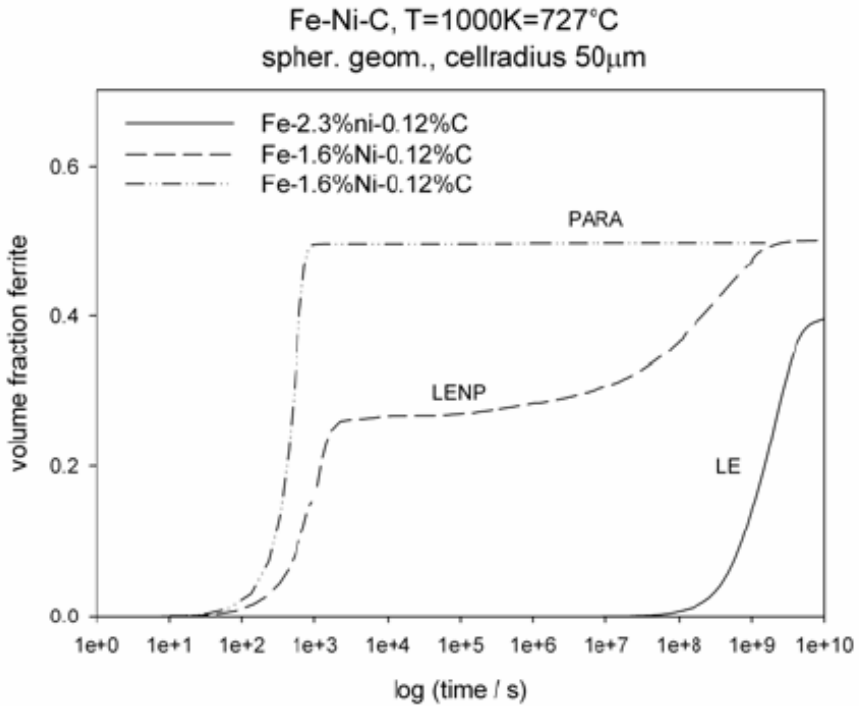
$$f_2 = \mu_C^{\alpha}(u_C^{\alpha}, u_M^{\alpha}, T) - \mu_C^{\gamma}(u_C^{\gamma}, u_M^{\gamma}, T) = 0$$

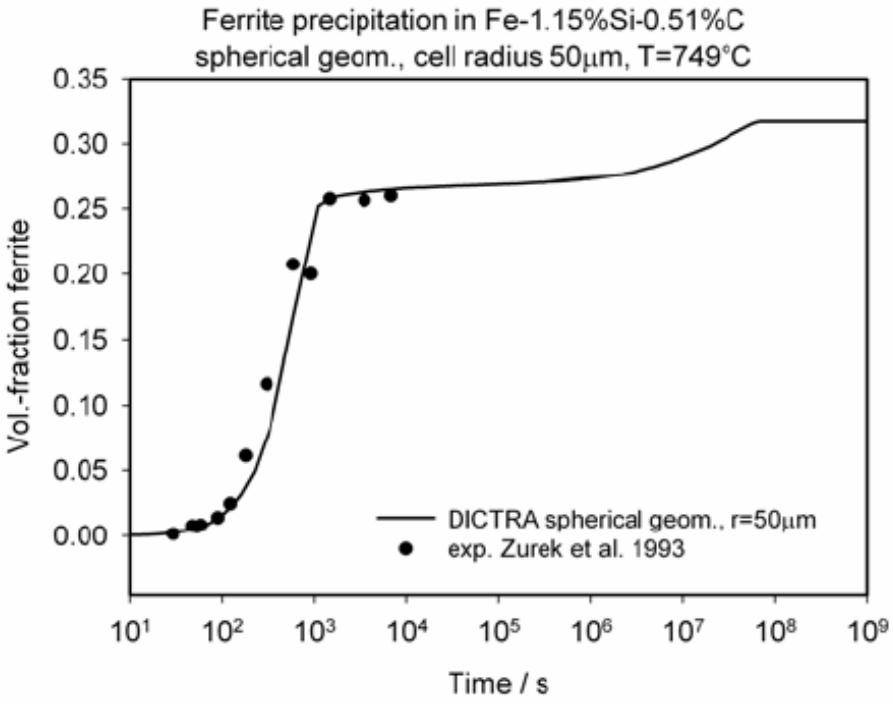

Fe-Ni-C, T=1000 K
u(Ni)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
25
30
35
10^3 x(C)
LE tie-line
LE
LENP
1
2
3
4
5
6
a_C
α/γ > a_C
γ : acceptable tie-lines


Fe-Ni-C, T=1000 K
u(Ni)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
α
0
0
5
10
15
20
25
30
35
10^3 x(C)
γ
PARA

LENP and PARA equilibrium very powerful methods because...

- Only involve bulk thermodynamic properties.
- Thermodynamic extremes. Truth in between?
- No information on interface needed.





From G. Inden 2008

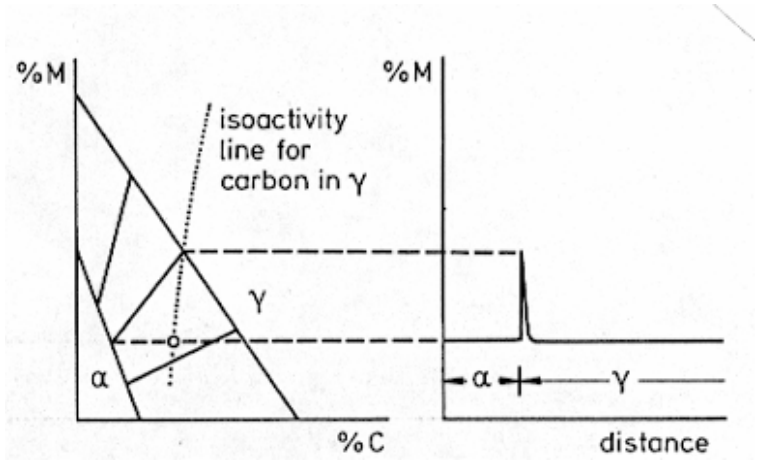
Transition para to LENP

- Thickness of alloy element spike

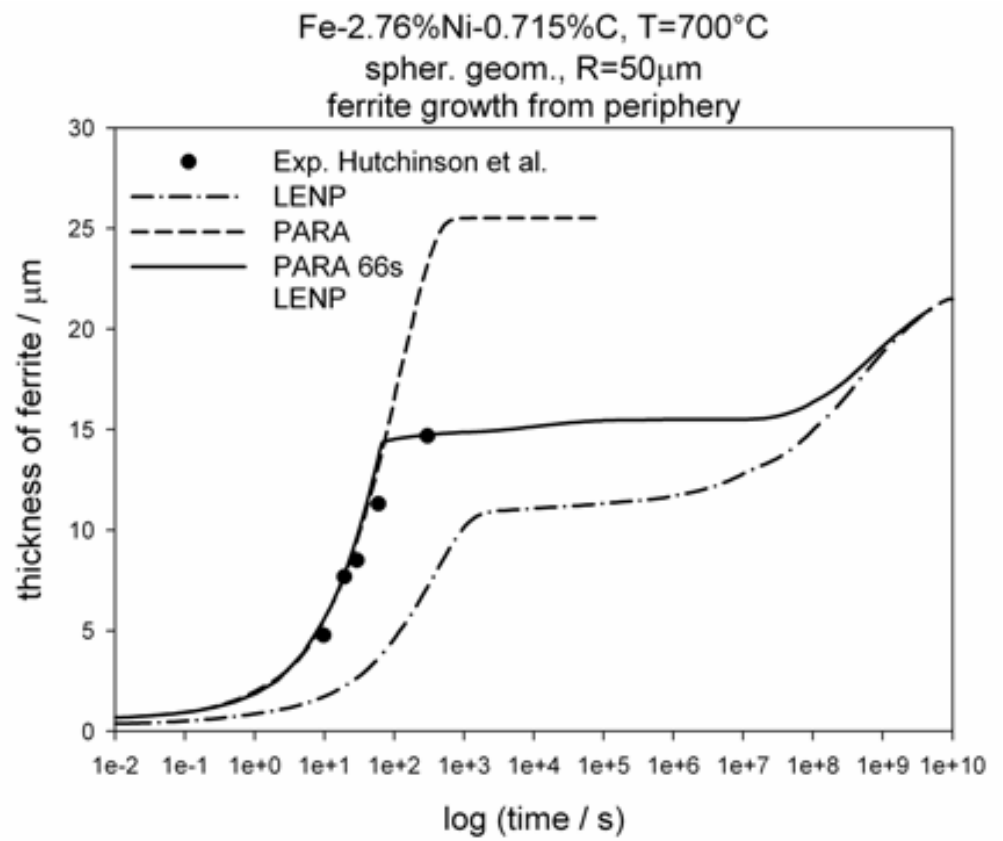
$$d \cong \frac{D}{v}$$

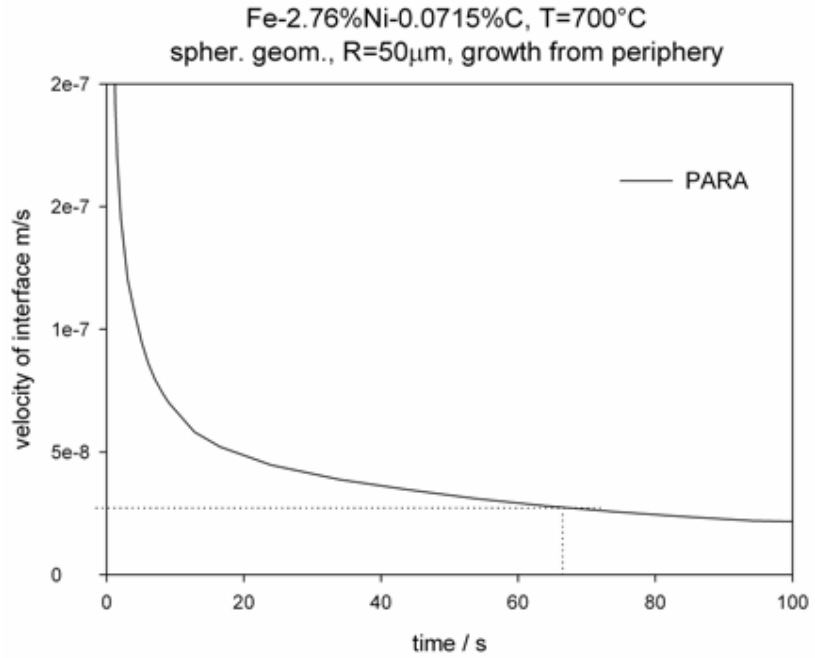
$d \leq 0.5$ nm : PARA

$d > 0.5$ nm LENP



- Early stages high growth rate: PARA
- Later stages lower rates change to LENP.


Fe-2.76%Ni-0.715%C, T=700°C
spher. geom., R=50μm
ferrite growth from periphery
Exp. Hutchinson et al.
LENP
PARA
PARA 66s
LENP
thickness of ferrite / μm
log (time / s)
0
5
10
15
20
25
30
1e-2
1e-1
1e+0
1e+1
1e+2
1e+3
1e+4
1e+5
1e+6
1e+7
1e+8
1e+9
1e+10


Fe-2.76%Ni-0.0715%C, T=700°C
spher. geom., R=50μm, growth from periphery
PARA
velocity of interface m/s
time / s
0
5e-8
1e-7
2e-7
2e-7
0
20
40
60
80
100

G. Inden 2008

Interface kinetics

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

- Transformation of crystalline lattice (finite interface mobility)
- Change in composition by trans-interface diffusion

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

$$f_k = \mu_k^{\alpha} - \mu_k^{\gamma} - (\Delta\mu_k^{cryst} + \Delta\mu_k^{trans}) = 0$$

Example: substitutional system *A - B*

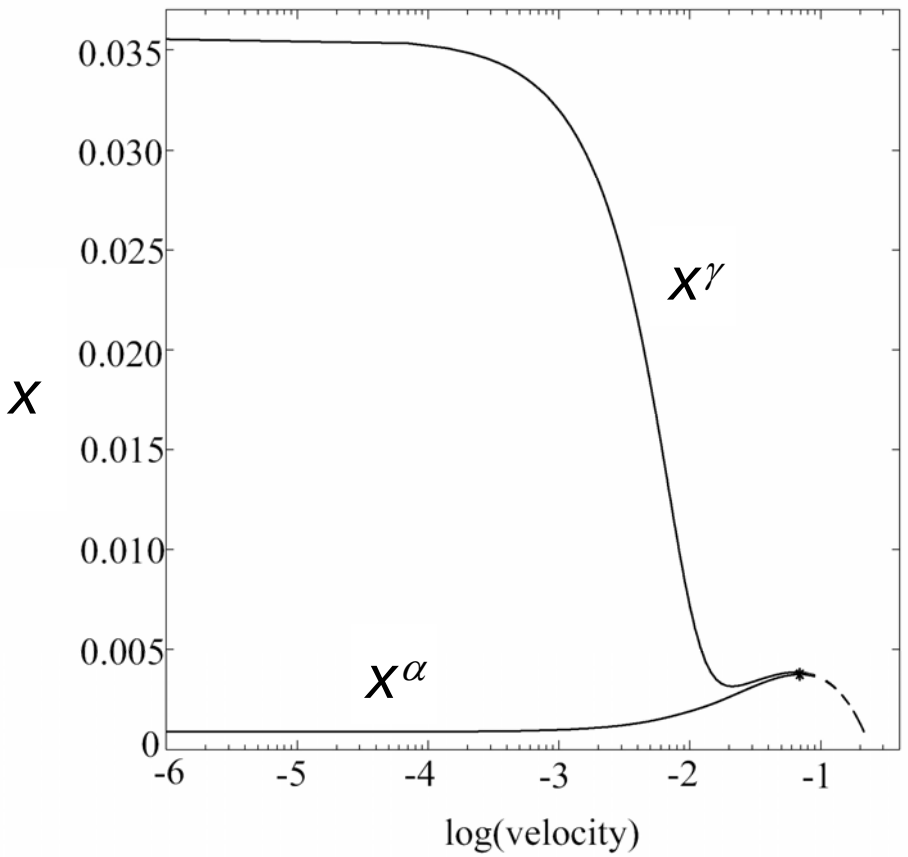
Transinterface diffusion and finite interface mobility yields:

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

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

$\Delta\mu_A$ 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.



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:

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

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

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

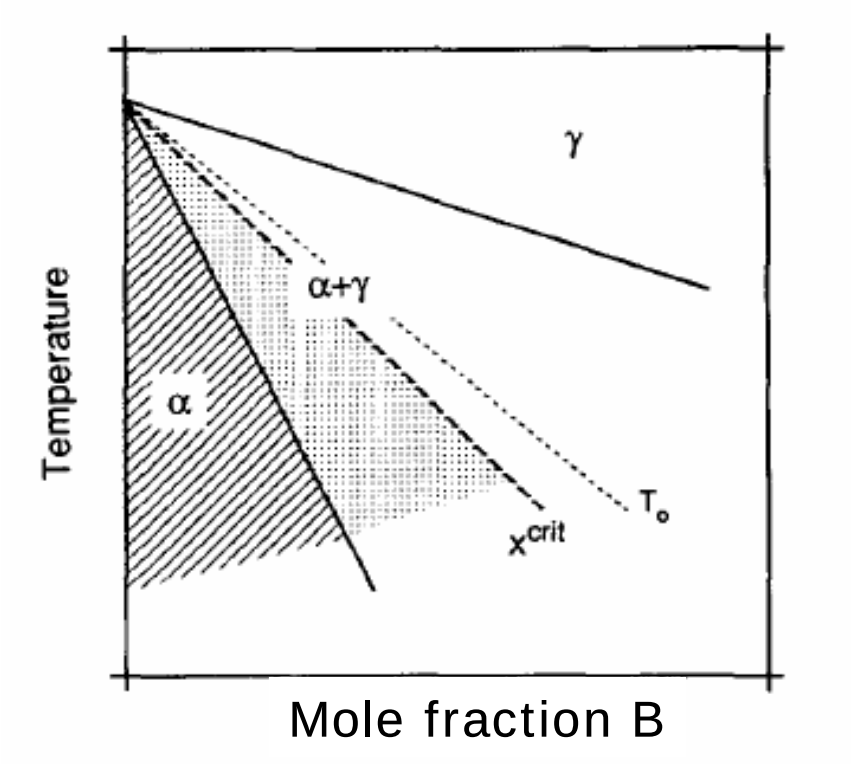
$$\Rightarrow \Delta G_m^{trans} = -\left(x_B^i - x_B^\alpha\right)\Delta(\mu_B - \mu_A)$$

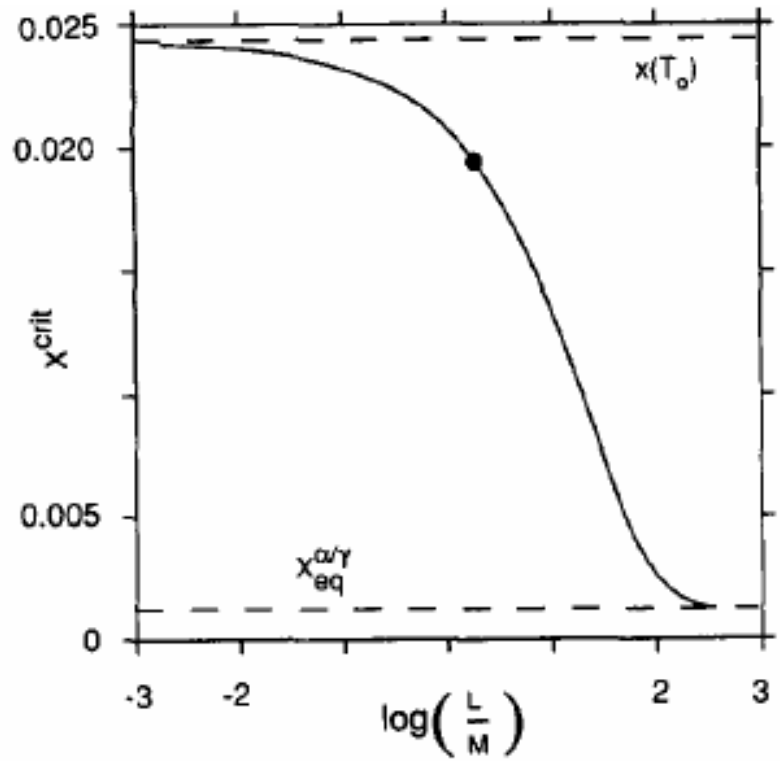
$$\Delta G_m^{cryst} = x_A^i \Delta\mu_A + x_B^i \Delta\mu_B$$

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

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

Limit for partitionless transformation

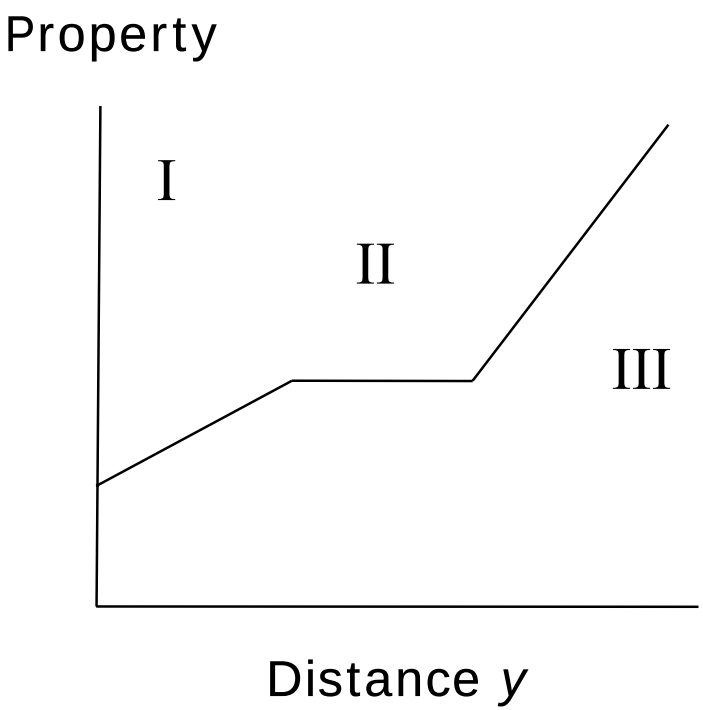




Jönsson and Ågren 1990

3. Finite interface thickness

Diffusion inside the interface → solute drag



Solute drag theory (Cahn, Hillert and Sundman, Brechet and Purdy)

- 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 $x_B^\alpha(y)$.

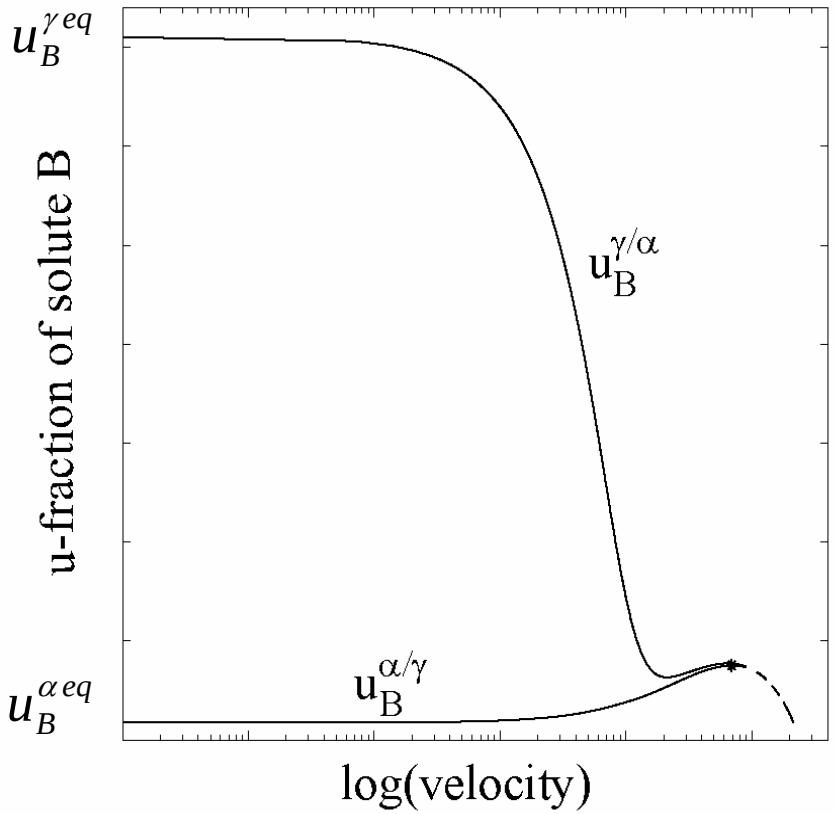
- Integration of dissipation over interface:

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

- Total driving force

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

Driving force = Dissipation:

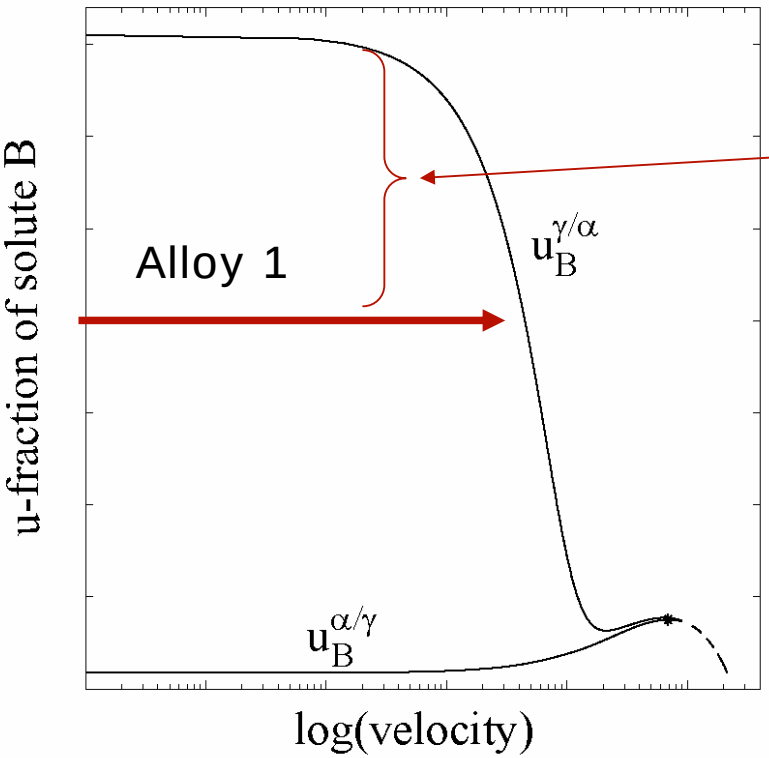


The compositions on each side of the phase interface depend on interface velocity and they approach each other.

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

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

Above a critical velocity transformation turns partitionless.



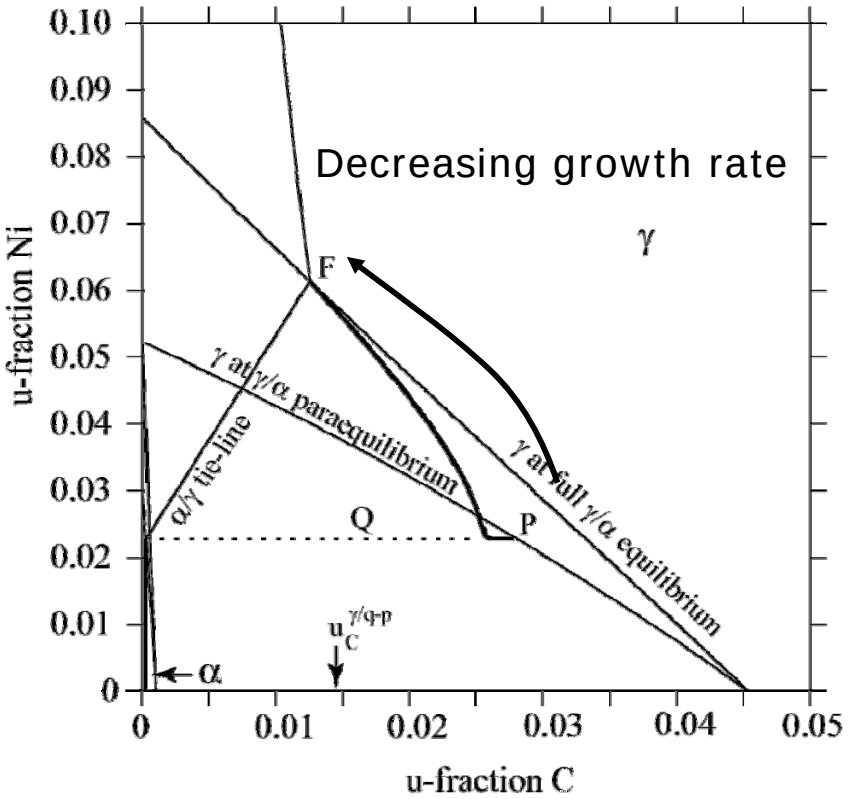
Driving diffusion in γ

Non-parabolic growth in early stages.

Maximum possible growth rate for alloy 1

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.

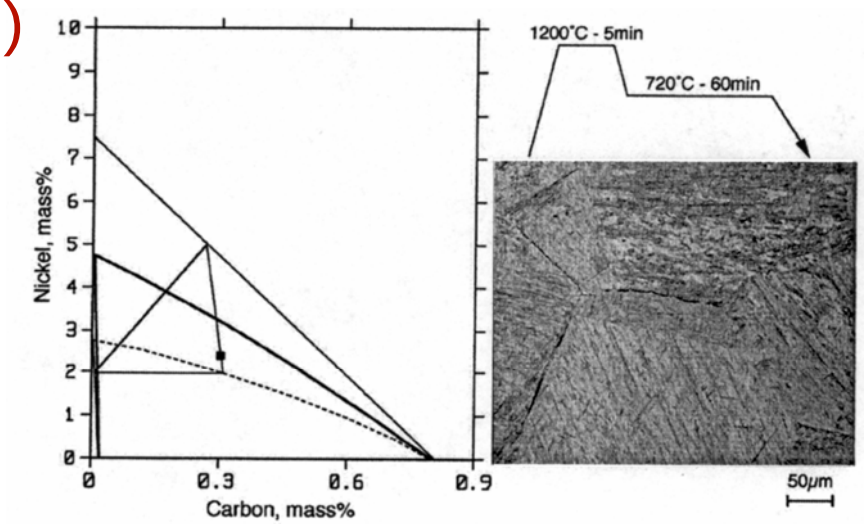
Ferrite formation under ”practical” conditions in Fe-Ni-C (Oi et al. 2000)

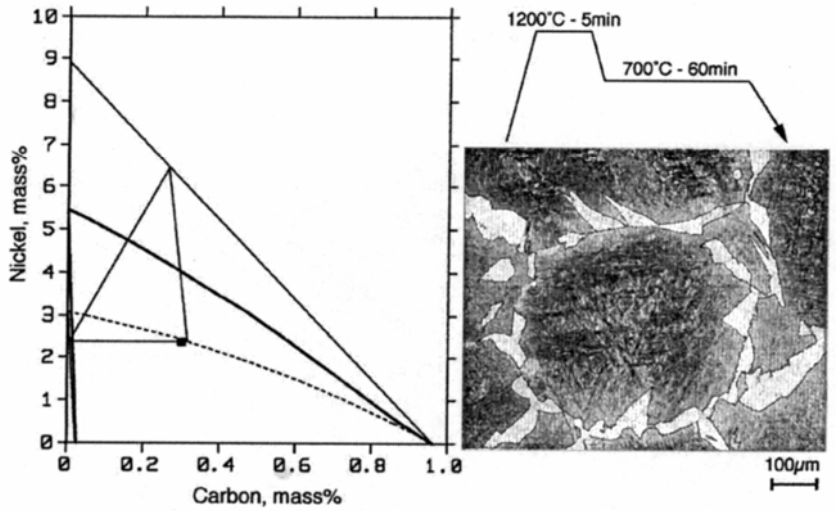
Thickness of M spike in γ:

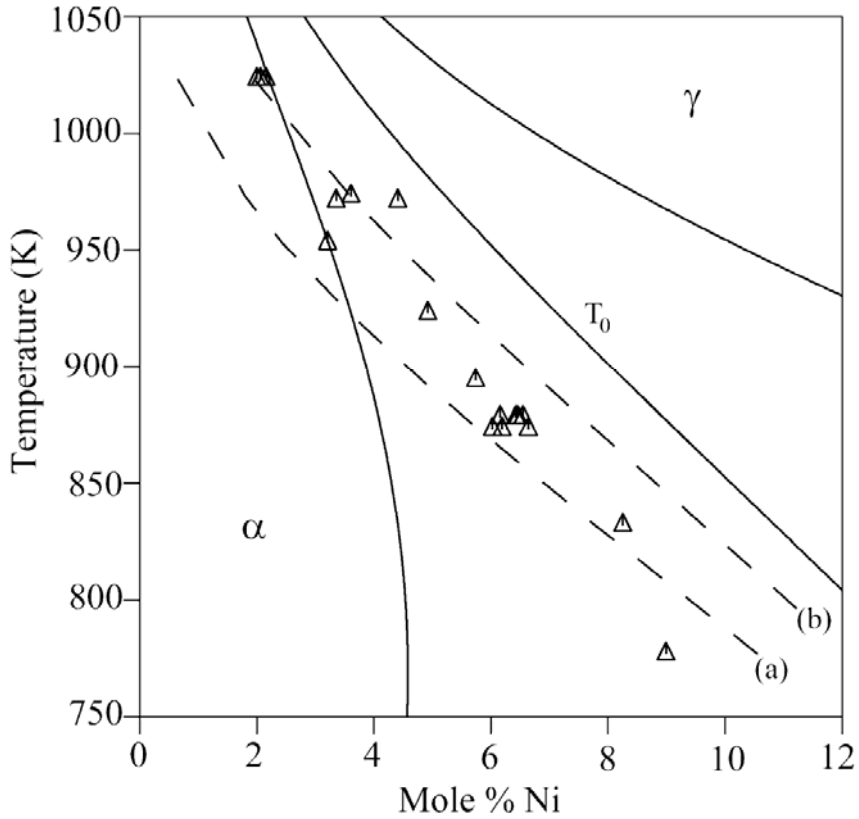
D_M / v.

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

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







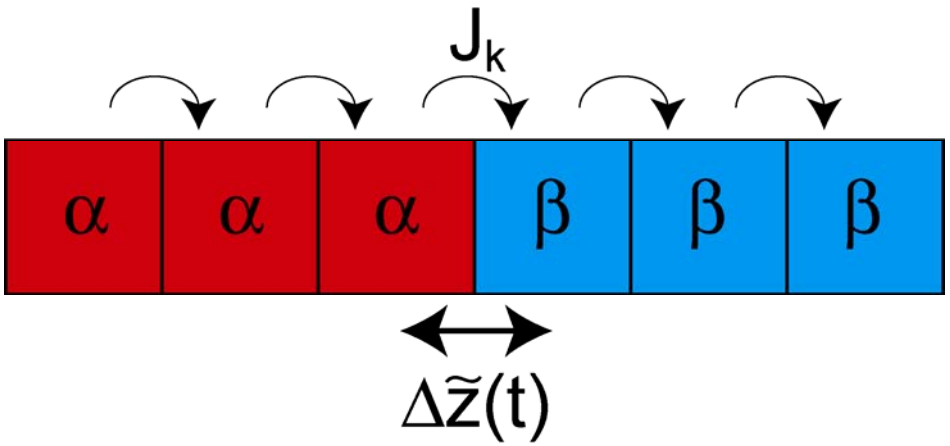
Calculated limit of the massive transformation in Fe-Ni alloys (dashed lines) calculated for two different assumptions on properties of interface.

(Odqvist et al. 2002)

Exp: Borgenstam and Hillert 2000

Larsson-Hillert (2005)

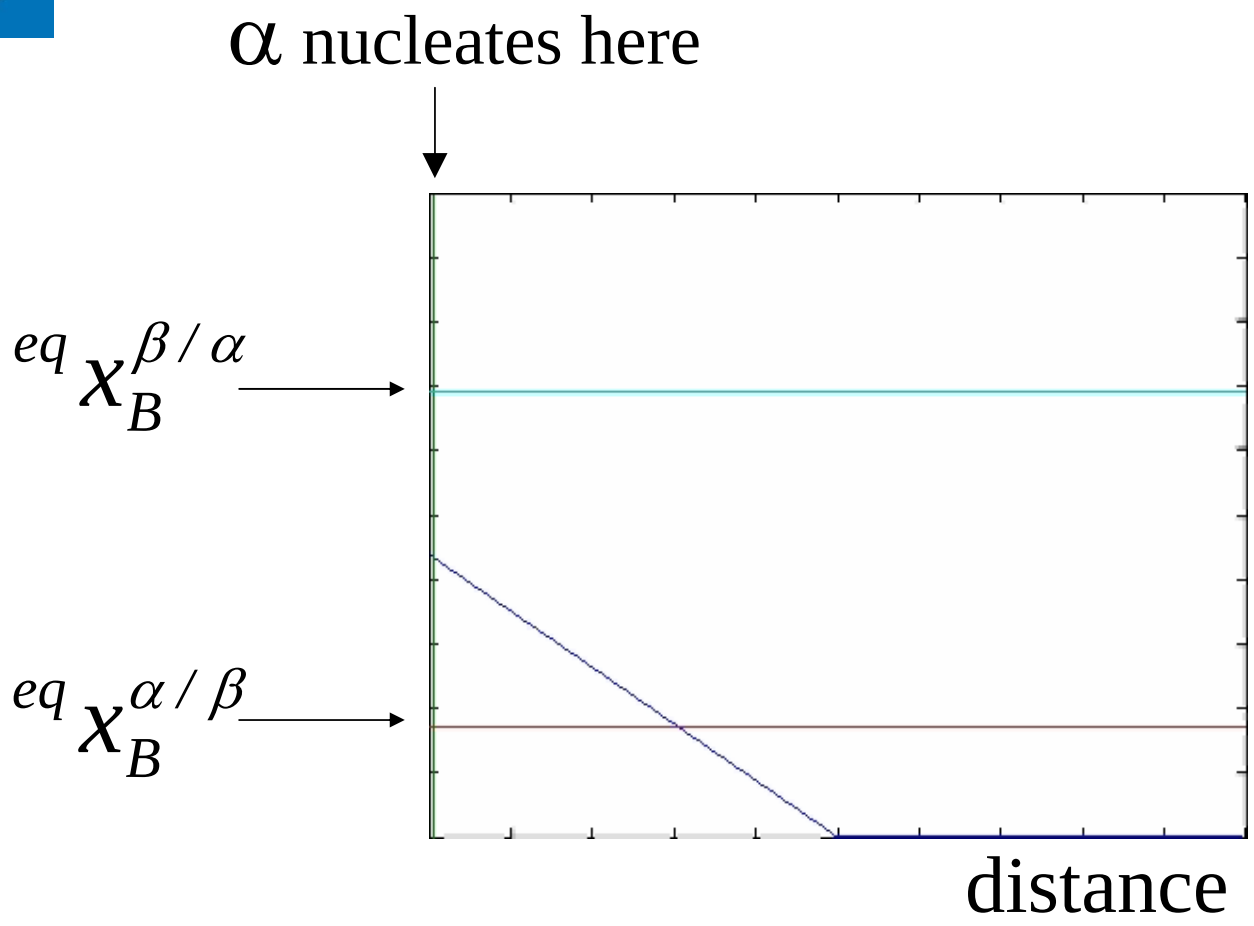
Finite volume technique

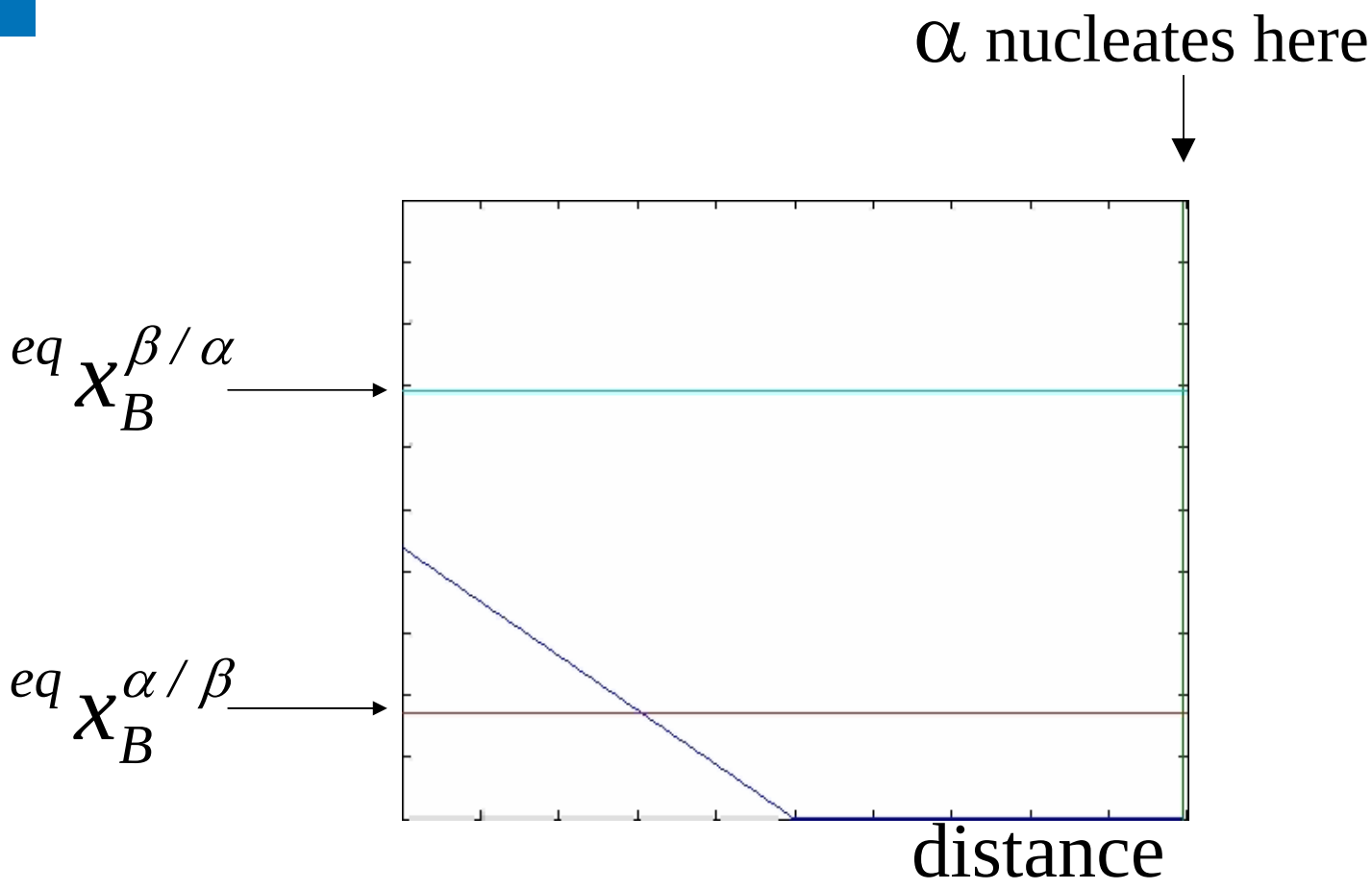


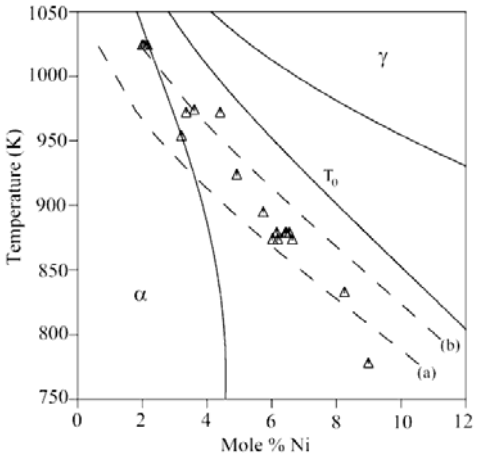
Absolute reaction rate theory of vacancy diffusion:

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

$$-\frac{M_k' RT}{V_m \Delta\tilde{z}} \sqrt{x_k^1 x_k^2} \left[\exp\left(\frac{\sum x_j^1 \Delta\mu_j}{RT}\right) - \exp\left(\frac{-\sum x_j^2 \Delta\mu_j}{RT}\right) \right]$$


α nucleates here
$eq\ x_B^{\beta/\alpha}$
$eq\ x_B^{\alpha/\beta}$
distance


α nucleates here
$x_B^{eq\,\beta/\alpha}$
$x_B^{eq\,\alpha/\beta}$
distance



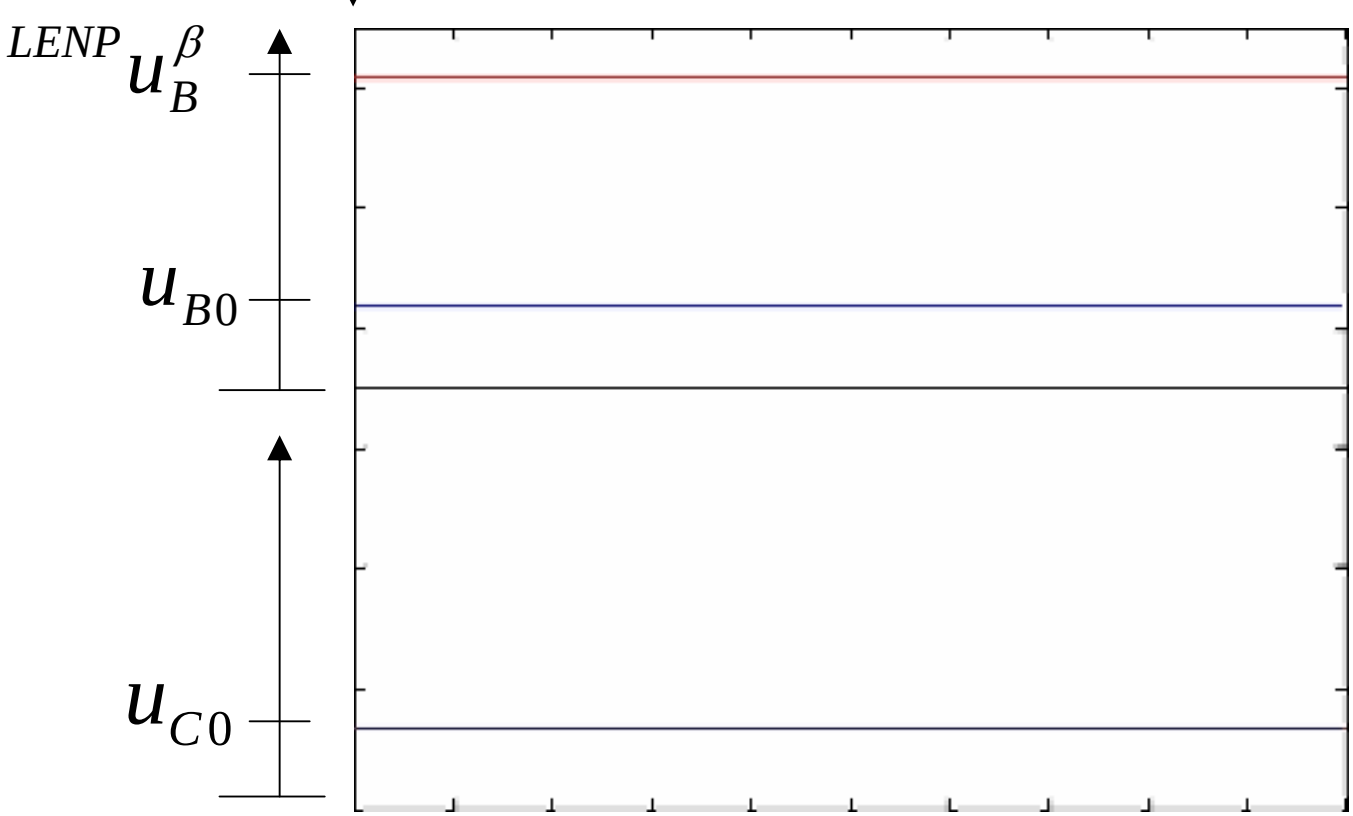
- Larsson and Borgenstam analyzed the critical limit for the massive transformation in Fe-Ni and found
  - high diffusivity across phase interface displaces critical limit towards one-phase field.
  - High interface mobility displaces critical limit towards T_0.

  These results are in agreement with Jönssons analysis.

Ternary system *A – B – C (interstitial)*

α nucleates here

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

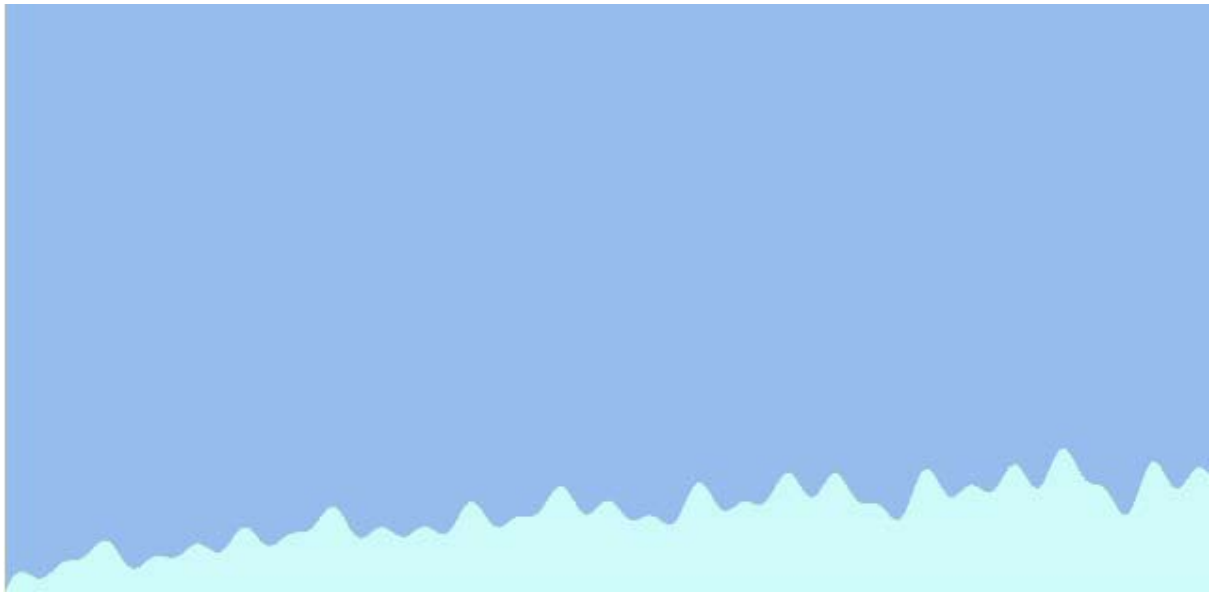


4. Diffuse interfaces – phase-field method

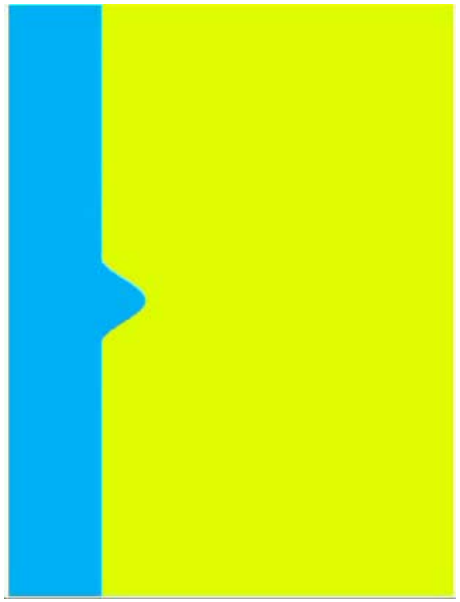
- Some properties of interface modelled.
- Solution of a diffusion equation to obtain concentreation profile.
- Cahn-Allen equation plays a similar role as the equation for interfacial friction.

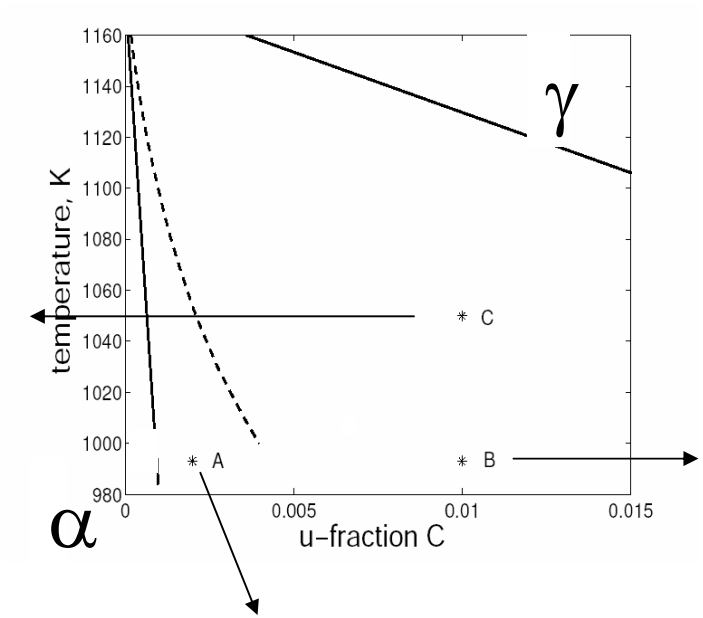
But: Thickness of interface must be treated not only as a numerical parameter but as a physical quatity.

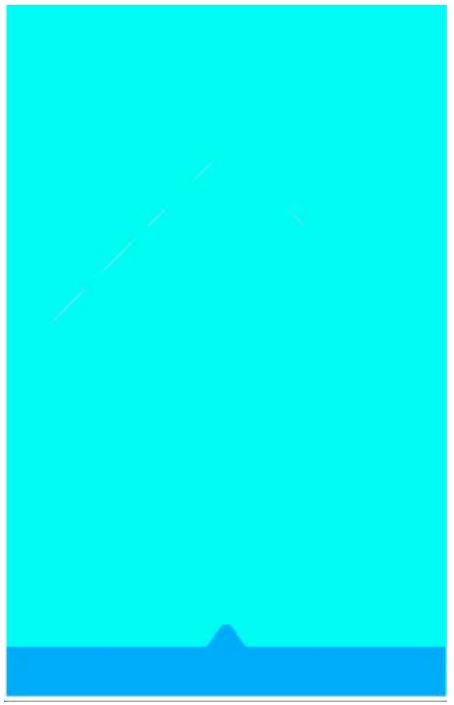
Example: Formation of WS-ferrite in steels



Loginova et al. 2004







Loginova et al. 2004

5. 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.
- Satisfactory accuracy for low supersaturation, less good for high.

6. 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, limited accuracy.