Solute drag and diffusion processes in the interface

E. Gamsjäger[1], J. Svoboda[2], Y. Liu[1], F.D. Fischer[1]

[1]Montanuniversität Leoben, Institute of Mechanics, Leoben, Austria

[2]Institute of Physics of Materials, Brno, Czech Republic

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Contents

Principle of maximum dissipation Q of the Gibbs energy

Onsager 1931 (Equations for heat conduction)
Onsager 1945 (Equations for diffusion)
Svoboda & Turek 1991 (Evolution equations for characteristic variables q_i)

Closed system, isothermal and isobaric process:
appropriate thermodynamic potential:
Gibbs energy $G(q_1, \ldots, q_N)$

$$\dot{G} = \sum_{i=1}^{N} \frac{\partial G}{\partial q_i} \dot{q}_i$$

Assumption: Dissipation Q of Gibbs energy is a quadratic form of N rates $\dot{q}_i$ of the characteristic variables q_i.

$$Q = \sum_{i=1}^{N} \sum_{k=1}^{N} B_{ik} \dot{q}_i \dot{q}_k$$

B_{ik} considers the kinetic parameter of the material (diffusion coefficients) and the geometry of the system.

Principle of maximum dissipation *Q* of the Gibbs energy

$$\dot{G} = \sum_{i=1}^{N} \frac{\partial G}{\partial q_i} \dot{q}_i$$

$$Q = \sum_{i=1}^{N} \sum_{k=1}^{N} B_{ik} \dot{q}_i \dot{q}_k$$

The extremal principle asserts that the rates $\dot{q}_i$ of the characteristic variables correspond to a maximum of the Gibbs energy dissipation *Q* constrained by the energy balance $Q = -\dot{G}$ and by *m* further constraints.

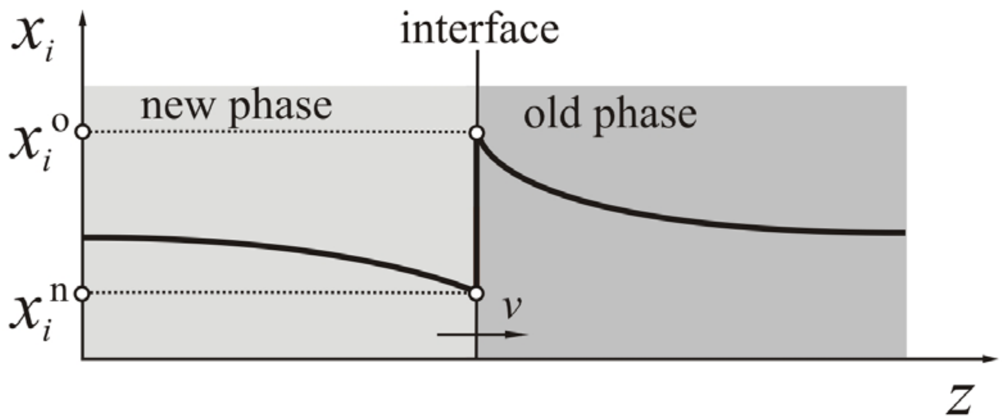
$$\sum_{i=1}^{N} a_{ik}(q_1, ..., q_N) \dot{q}_i = 0$$

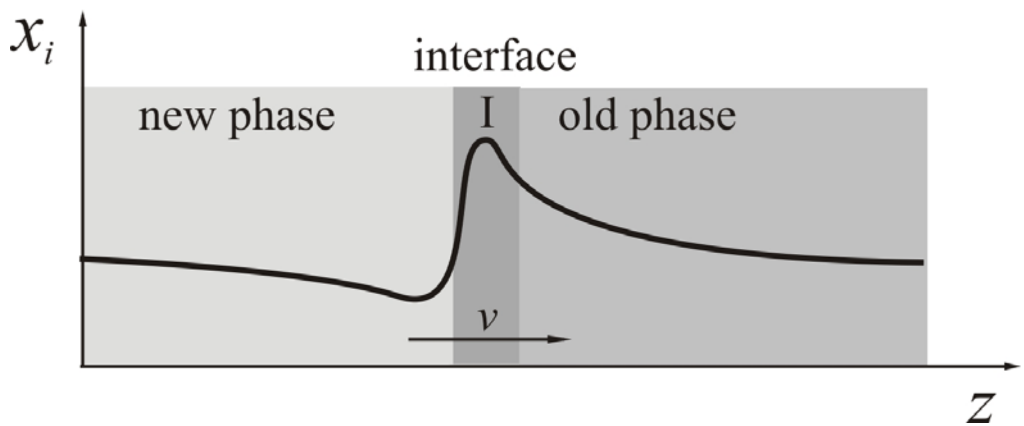
$$\frac{\partial}{\partial \dot{q}_i} \left[Q + \lambda \left(Q + \dot{G} \right) + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0$$

$$\frac{\partial}{\partial \dot{q}_i} \left[\dot{G} + \frac{Q}{2} + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0$$

$$\sum_{j=1}^{N} B_{ij} \dot{q}_j + \sum_{k=1}^{m} a_{ik} \beta_k = -\frac{\partial G}{\partial q_i}$$

Sharp interface - thick interface





Contact conditions at the sharp interface

$$\dot{G}_{\mathrm{int}} = -\sum_{i=1}^{N} \frac{v}{\Omega} \cdot x_i^{\mathrm{I}} [[\mu_i]]$$

$$x_i^{\mathrm{I}} = x_i^{\mathrm{o}} - \frac{j_i^{\mathrm{o}}}{v}\Omega$$

$$\dot{G}_{\mathrm{int}} = \sum_{i=1}^{N} j_i^{\mathrm{o}} [[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\mathrm{o}}}{\Omega} v [[\mu_i]]$$

$$Q_{\mathrm{int}} = v^2/M$$

Fluxes of the substitutional components (*i* = 1, … , *s*)

$$\frac{\partial}{\partial j_i^{\mathrm{o}}} \left[\dot{G}_{\mathrm{int}} + \frac{Q_{\mathrm{int}}}{2} + \kappa \left(\sum_{k=1}^{s} j_k \right) \right] = 0 \longrightarrow \kappa = -[[\mu_i]] \longrightarrow [[\mu_1]] = [[\mu_2]] = \ \dots \ = [[\mu_s]]$$

E. Gamsjäger, *Phil. Mag. Lett.* **88** (2008) 363-369.

Contact conditions at the sharp interface

$$\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^{\text{o}} [[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\text{o}}}{\Omega} v [[\mu_i]]$$

$$Q_{\text{int}} = v^2 / M$$

Fluxes (interstitial components *i*=*s* + 1, …, *N*)

$$\frac{\partial}{\partial j_i^{\text{o}}} \left[\dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2} \right] = 0 \longrightarrow [[\mu_{s+1}]] = [[\mu_{s+2}]] = \ \ldots \ = [[\mu_N]] = 0$$

Contact conditions at the sharp interface

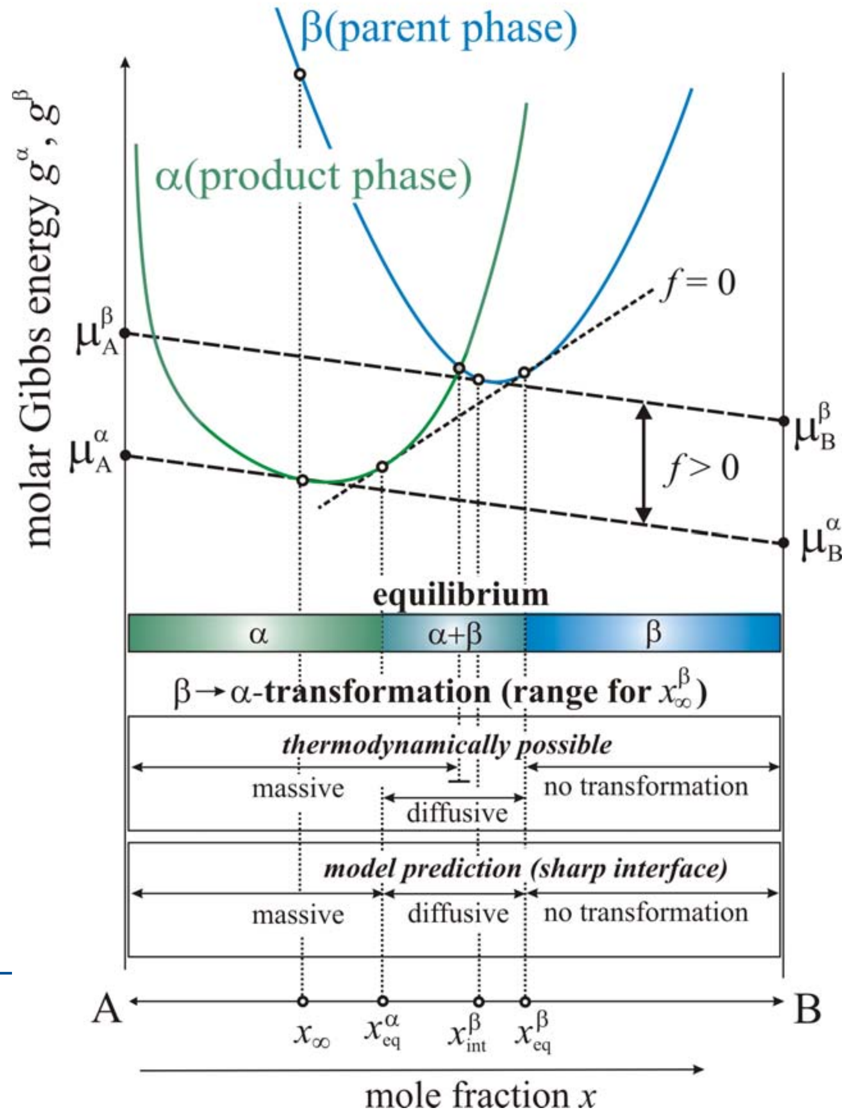
$$\dot{G}_{\text{int}} = \sum_{i=1}^{N} j_i^{\text{o}}[[\mu_i]] - \sum_{i=1}^{N} \frac{x_i^{\text{o}}}{\Omega} v[[\mu_i]]$$

$$Q_{\text{int}} = v^2/M$$

Interface velocity v

$$\frac{\partial}{\partial v}\left[\dot{G}_{\text{int}} + \frac{Q_{\text{int}}}{2}\right] = 0 \longrightarrow v = \frac{M}{\Omega}\sum_{i=1}^{N} x_i^{\text{o}}[[\mu_i]] = M\Delta f$$

Sharp interface - thick interface



„Spike“- thicknesses for different systems

$$d_i \sim \frac{D_i}{v}$$

- Cu-Zn: $\gamma \rightarrow \alpha$: 0.6nm, $v_{Cu\text{-}Zn} \approx$1-2 cm/s [1], [2]

→ **Sharp interface model (Massive growth occurs in the single phase region.)**

- Fe-Ni: $\gamma \rightarrow \alpha$: 10^{-6}nm or less [3], [4]

→ **Thick interface model (Massive growth occurs in the two phase region.)**

[1] D. A. Karlyn, J. W. Cahn, M. Cohen, *Trans. Am. Inst. Min. Engrs.*, **245**, 1969, 197-207.

[2] M. Hillert, *Metall. Trans. A*, **15A**, 1984, 411-419.

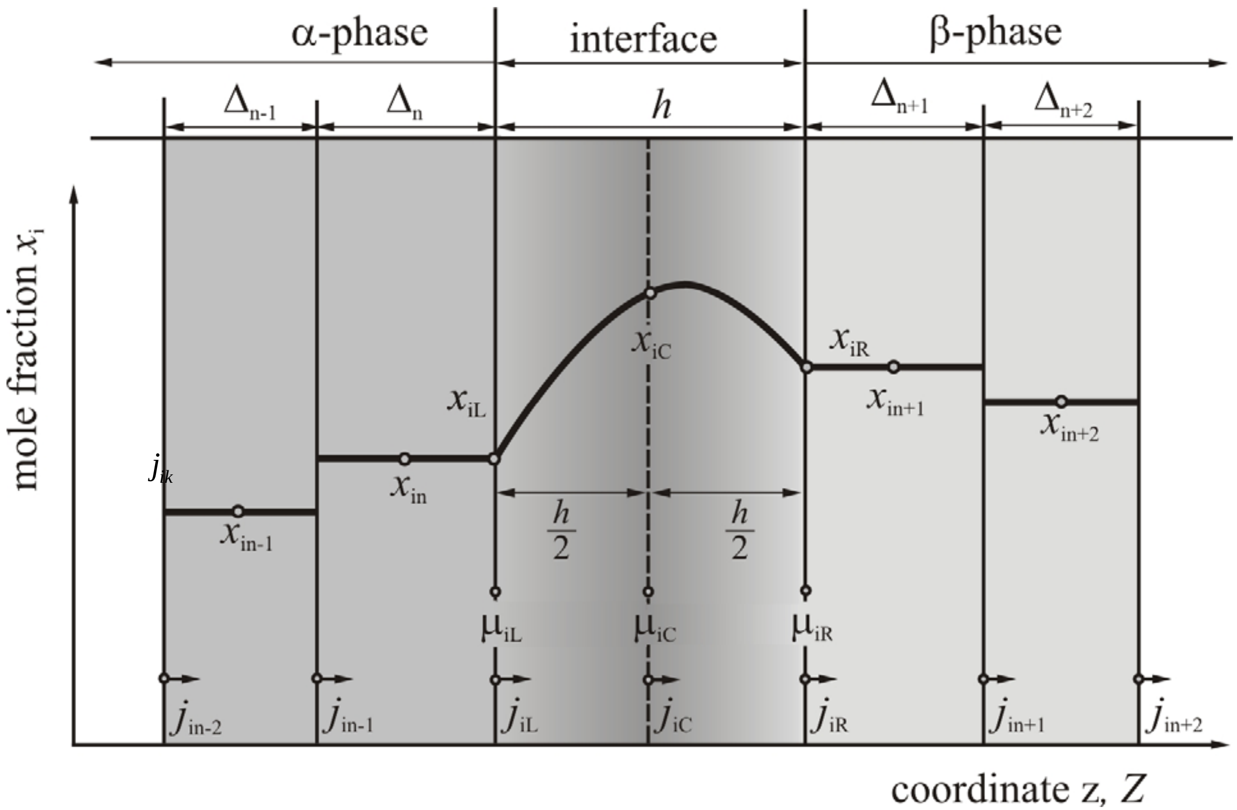
[3] M. Hillert, *Metall. Mater. Trans. A*, **33A** (2002) 2299-2308.

[4] A. Borgenstam, M. Hillert, *Acta mater.* **48** (2000) 2765-2775.

Thick interface model

Parabola describing the interface thickness. Additional state parameters x_{iC}

$$\sum_{i=1}^{s} j_i = 0$$



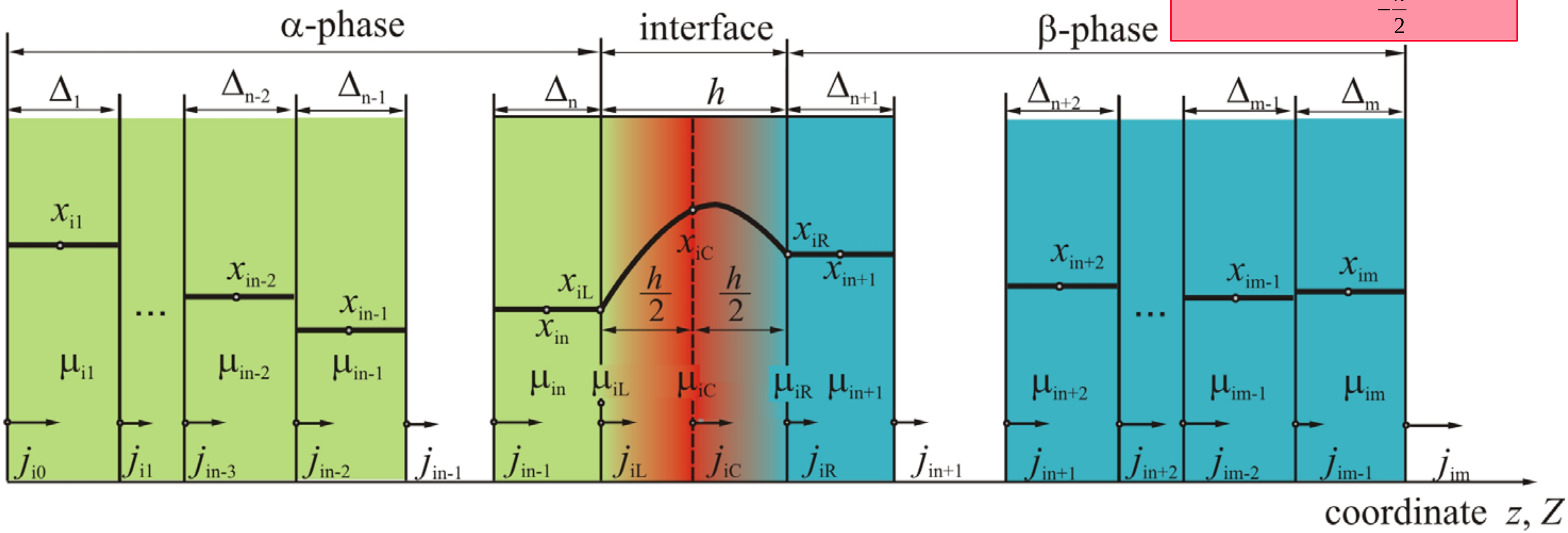
Kinetics [$\dot{x}_{ik}$, (i=1,…,s-1, k=1,…,m) and $\dot{x}_{iC}$ (i=1,…,s-1) and v]

or [j_{ik} (i=1,…,s-1, k=1,…,m) and $\dot{x}_{iC}$ (i=1,…,s-1) and v]

Thick interface model: Gibbs energy

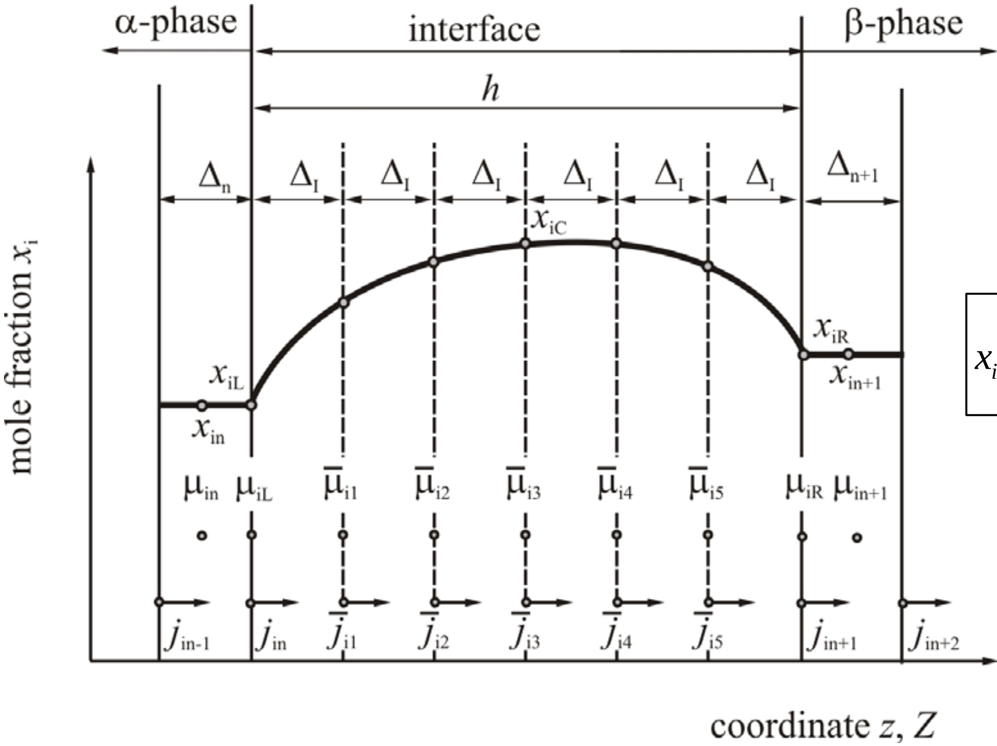
$$G = G(x_{i1}, x_{i2}, \ldots, x_{im}, x_{iC})$$

$$G_{inter} = \frac{1}{\Omega}\sum_{i=1}^{s}\int_{-\frac{h}{2}}^{\frac{h}{2}} x_i\,\mu_i\,dz$$



$$G_{bulk} = \frac{1}{\Omega}\cdot\left(\sum_{i=1}^{s}\sum_{k=1}^{n-1}\Delta_k x_k \mu_{ik}^{\alpha} + \sum_{i=1}^{s}\sum_{k=n+2}^{m}\Delta_k x_k \mu_{ik}^{\beta} + \sum_{i=1}^{s}\Delta_n x_n \mu_{in}^{\alpha} + \sum_{i=1}^{s}\Delta_{n+1} x_{n+1} \mu_{in+1}^{\beta}\right)$$

Thick interface model: Gibbs energy



$$x_i = x_{iC} - \left(x_{in} - x_{in+1}\right)\frac{Z}{h} + 2\left(x_{in} - 2x_{iC} + x_{in+1}\right)\left(\frac{Z}{h}\right)^2$$

$$G_{\text{int}} = \frac{\Delta_I}{3\Omega}\left(\sum_{i=1}^{s} x_{in}\mu_{in}^{\alpha} + \sum_{i=1}^{s} x_{in+1}\mu_{in+1}^{\beta} + 4\sum_{i=1}^{s}\sum_{j=odd} \overline{x}_{ij}\,\overline{\mu}_{ij} + 2\sum_{i=1}^{s}\sum_{k=\alpha,I,\beta}\sum_{j=even} \overline{x}_{ij}^{k}\,\overline{\mu}_{ij}^{k}\right)$$

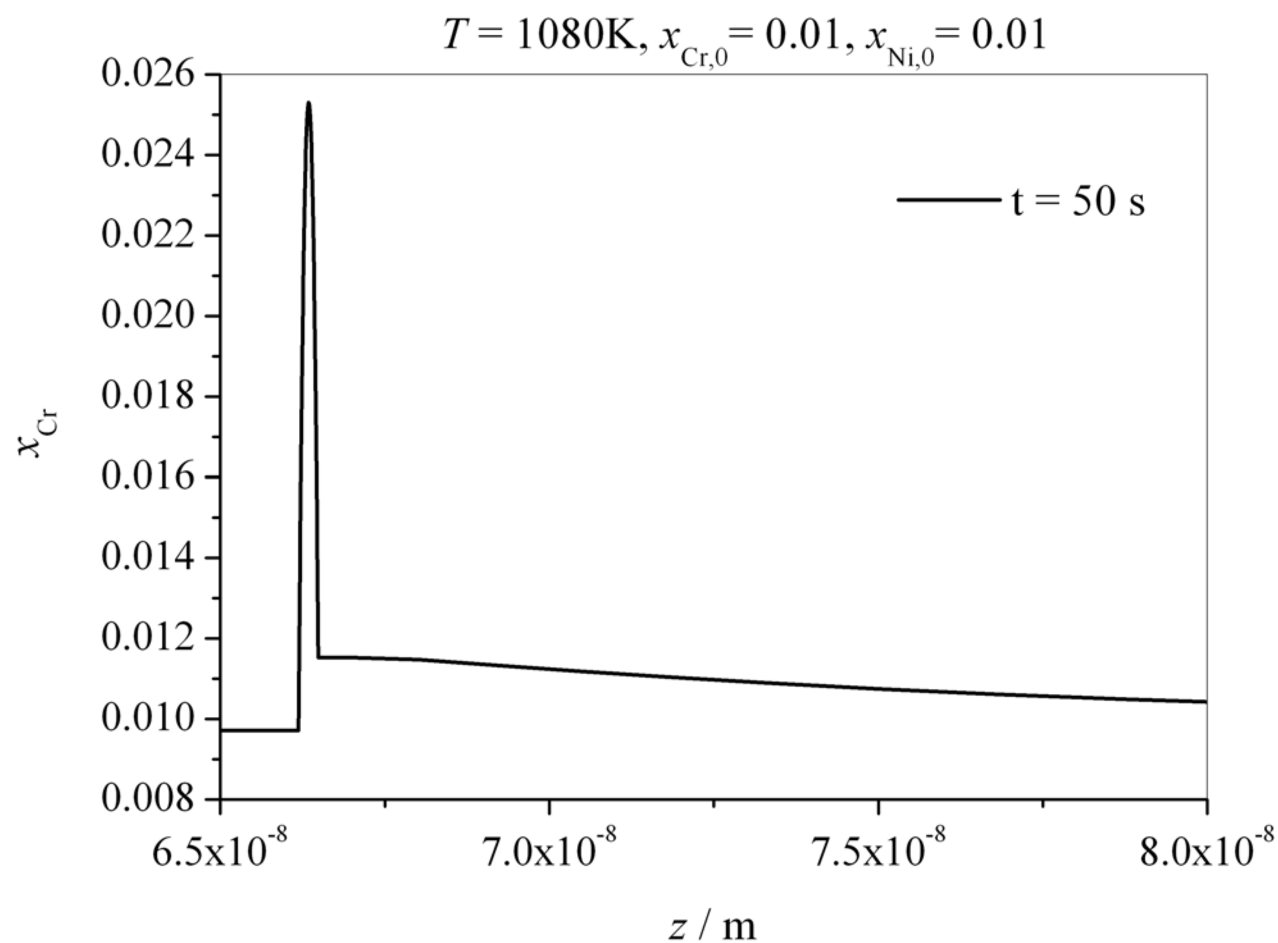
Rate of Gibbs energy $\dot{G}$ and dissipation Q

$\dot{G}$ (from G)

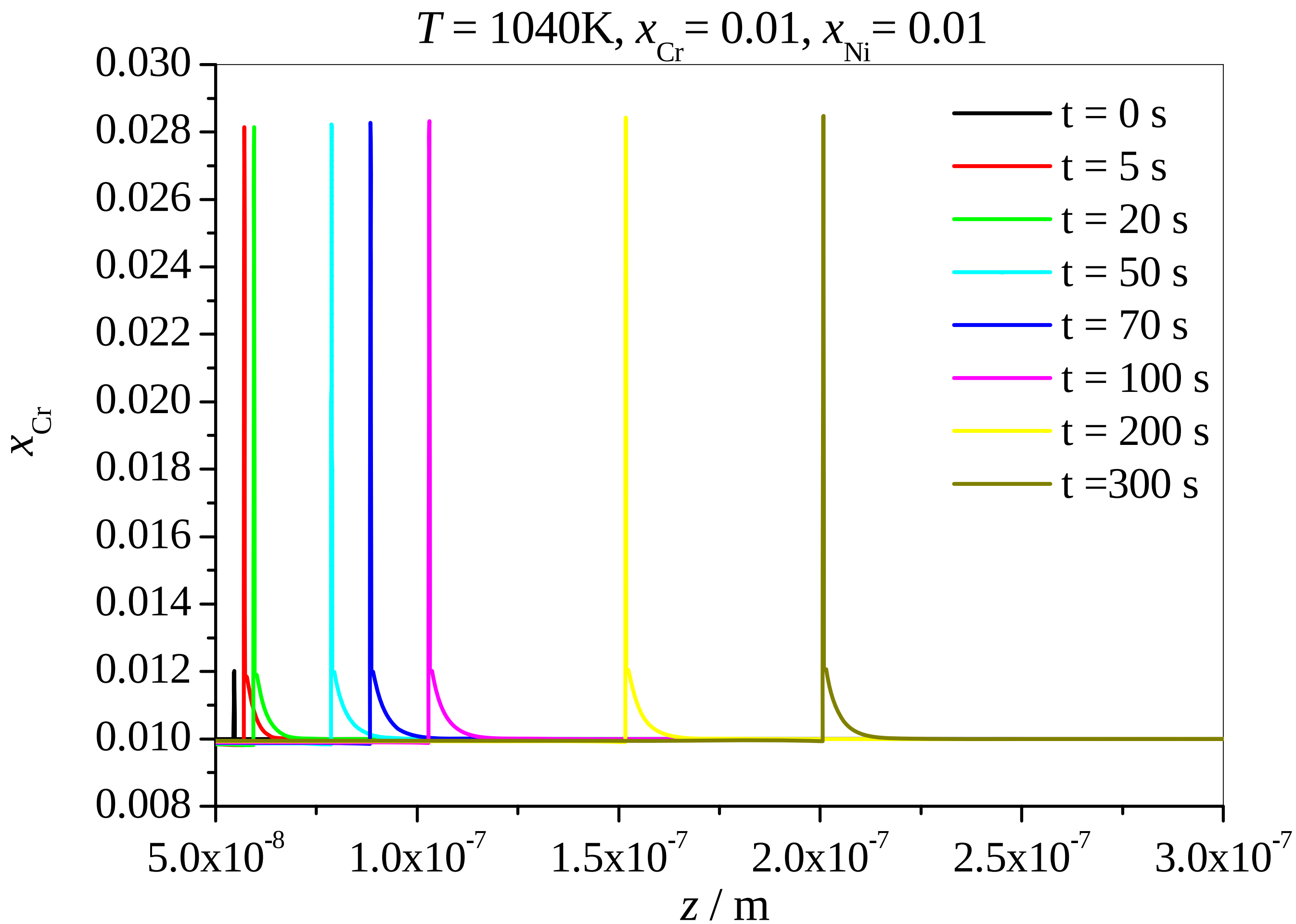
$$Q = \frac{v^2}{M} + \sum_{k=1}^{m} Q_k + Q_I$$

$$Q_k = \sum_{i=1}^{s} \frac{RT\Omega}{D_i x_{ik}} \int_0^{\Delta_k} j^2(z)\mathrm{d}z \approx \sum_{i=1}^{s} \frac{RT\Omega\Delta_k}{2D_i x_{ik}} \left(j_{ik-1}^2 + j_{ik}^2 \right)$$

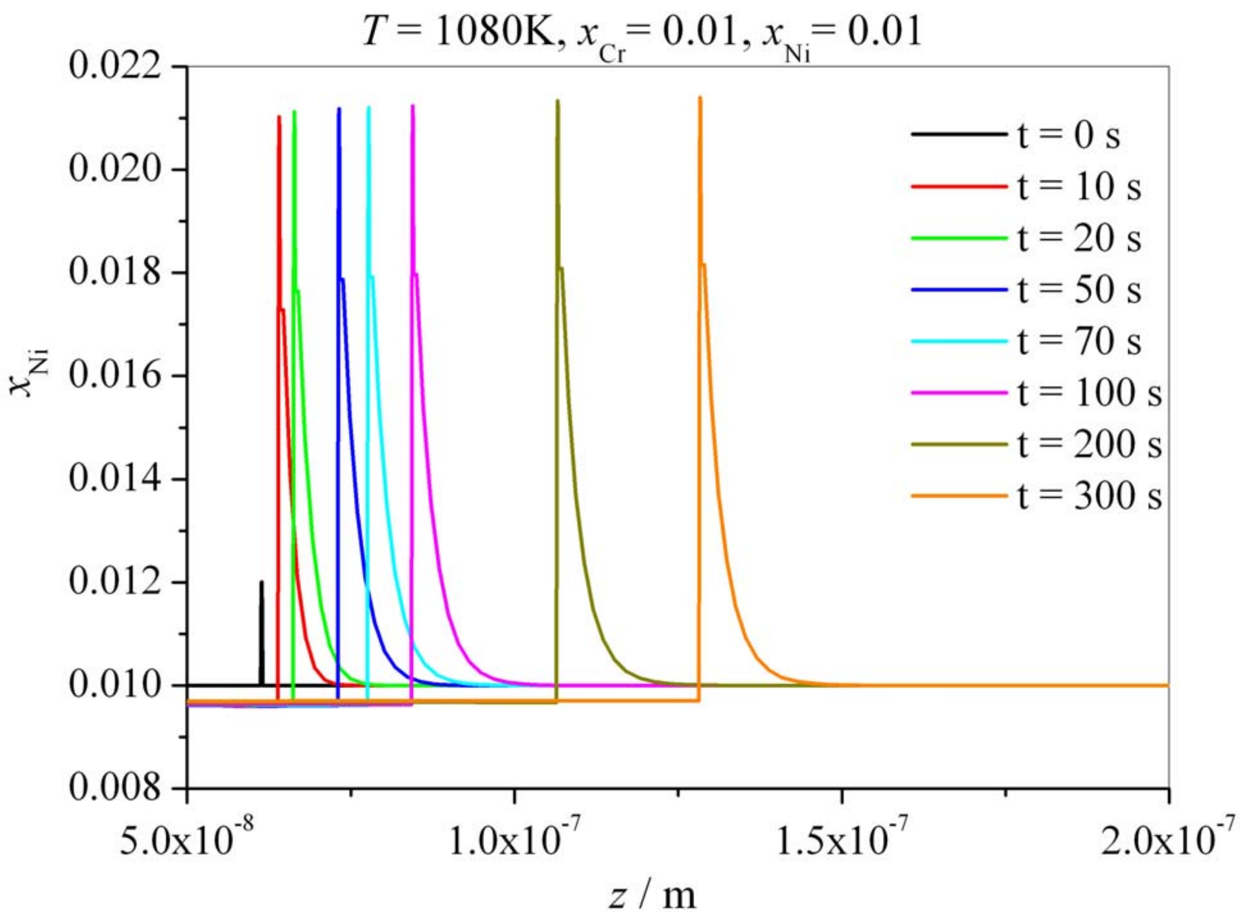
$$\frac{1}{2}\frac{\partial Q}{\partial \dot{q}_l} = -\frac{\partial \dot{G}}{\partial \dot{q}_l}$$



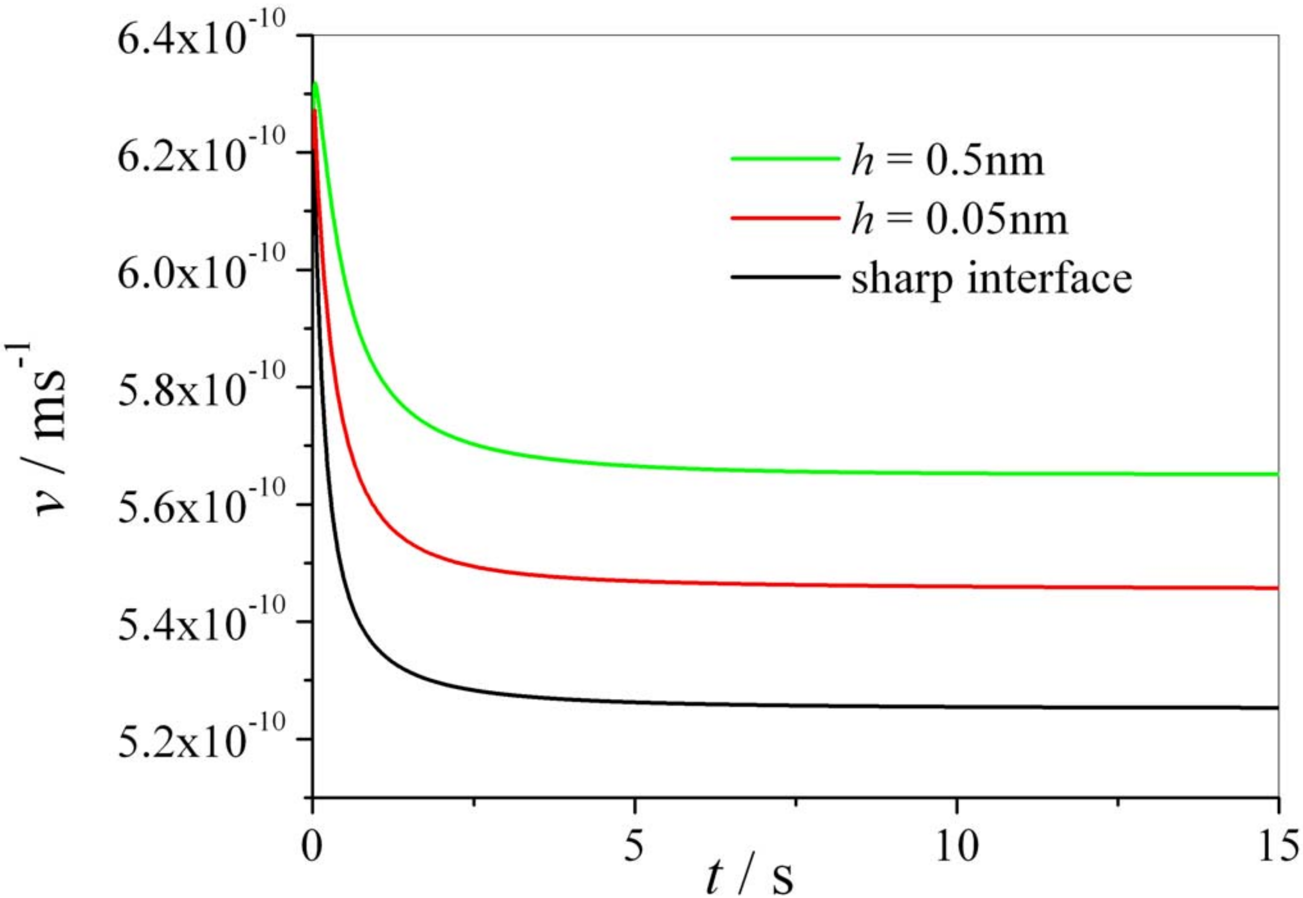
T = 1080K, x_Cr,0 = 0.01, x_Ni,0 = 0.01
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
x_Cr
t = 50 s
6.5x10^-8
7.0x10^-8
7.5x10^-8
8.0x10^-8
z / m



T = 1040K, x_Cr = 0.01, x_Ni = 0.01
x_Cr
0.030
0.028
0.026
0.024
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
5.0x10^-8
1.0x10^-7
1.5x10^-7
2.0x10^-7
2.5x10^-7
3.0x10^-7
z / m
t = 0 s
t = 5 s
t = 20 s
t = 50 s
t = 70 s
t = 100 s
t = 200 s
t =300 s



T = 1080K, x_Cr = 0.01, x_Ni = 0.01
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
x_Ni
t = 0 s
t = 10 s
t = 20 s
t = 50 s
t = 70 s
t = 100 s
t = 200 s
t = 300 s
5.0x10^-8
1.0x10^-7
1.5x10^-7
2.0x10^-7
z / m



6.4x10^-10
6.2x10^-10
6.0x10^-10
5.8x10^-10
5.6x10^-10
5.4x10^-10
5.2x10^-10
v / ms^-1
0
5
10
15
t / s
h = 0.5nm
h = 0.05nm
sharp interface

Results and outlook

- *Preliminary results*
  - give qualitatively correct trends.
- *Evaluation of the results*
  - Unrealistic low interface mobility.
  - Further check of the modelling results.
- *Comparison with experimental data*
  - Limit of massive growth (e. g. Fe-Ni)

Maxima and Minima
(subject to constraints: Lagrange multipliers)

Determine: Extremum of $F(x_1, x_2, \ldots, x_N)$

m constraints $g_j(x_1, x_2, \ldots, x_N) = 0$

$j = 1,2, \ldots, m$; $(m < N)$

By **Lagrange multipliers** λ_j:

Extremum of $F + \sum_{j=1}^{m} \lambda_j g_j$

$$\frac{\partial}{\partial x_i}\left(F + \sum_{j=1}^{m} \lambda_j g_j \right) = 0; \quad i = 1, \ldots, N$$

$N + m$ equations

for m unknown λ_j

N unknown x_i

Lagrange: Théorie des Fonctions Analytiques (p. 198, 1797)