From extremum principles in materials science to the kinetic coefficients such as the interface mobility

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ALEMI 2010
6. Juni 2010, Avignon, France

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- ***Interface mobility***
  - Estimation of the intrinsic mobility

Irreversible thermodynamics

Transport processes for systems out of global equilibrium are aimed to be described.

We need: complete set of extensive, independent variables A_i .

We define: Conjugate fluxes J_i and conjugate forces X_i .

$$\boxed{J_i = \mathrm{d}A_i / \mathrm{d}t} \qquad \boxed{X_i = \partial S / \partial A_i}$$

2nd law in terms of the local entropy production Ψ.

$$\boxed{\Psi = \sum_i J_i X_i \geq 0}$$

Each conjugate flux J_i is a linear combination of all forces X_i :

$$\boxed{J_i = \sum_i L_{ij} X_j}$$ with Onsager's reciprocal relations $$\boxed{L_{ij} = L_{ji}}$$

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.

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

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

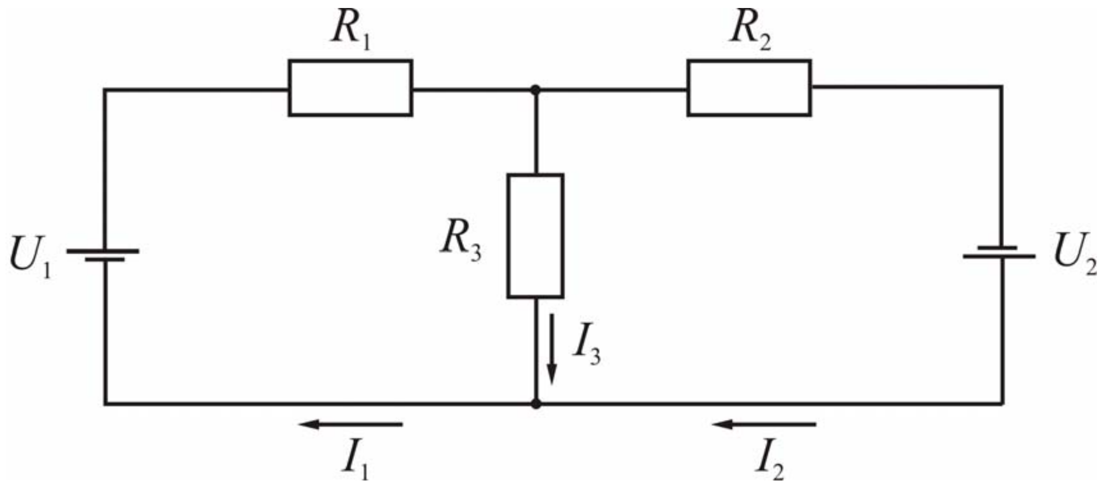
$$\frac{\partial}{\partial \dot{q}_i} \left[\dot{G} + \frac{Q}{2} + \sum_{k=1}^{m} \beta_k \sum_{i=1}^{N} a_{ik} \dot{q}_i \right] = 0$$

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

John Ågren‘s comparison

Newton‘s laws of motion	vs.	Hamilton and Lagrange
↕		↕
Balance of driving forces	vs.	Extremal principle

Application of the principle I
Electric circuits



Given: $R_1,\ R_2,\ R_3,\ U_1,\ U_2$

Unknown variables: $I_1,\ I_2,\ I_3$

$$\dot{G} = -U_1 I_1 - U_2 I_2$$

$$Q = R_1 I_1^2 + R_2 I_2^2 + R_3 I_3^2$$

$$I_1 - I_2 - I_3 = 0$$

$$\frac{\partial}{\partial I_i}\left[Q + \lambda(\dot{G} + Q) + \beta_1(I_1 - I_2 - I_3)\right] = 0$$

Electric circuits (Maple8)

===== Gibbs energy dissipation Q =====================

```
> Q:=R1*I1^2+R2*(I2)^2+R3*(I3)^2;
```

$$Q := R1\ I1^2 + R2\ I2^2 + R3\ I3^2$$

===== Rate of the Gibbs energy ======================

```
> Gdot:=-U1*I1-U2*I2;
```

$$Gdot := -U1\ I1 - U2\ I2$$

===== Method of Lagrange using two constraints ===========

```
> extrema( Q, {Gdot+Q,I1-I2-I3}, {I1,I2,I3},'s'):
> s;
```

$$\{\{I2 = 0, I1 = 0, I3 = 0\}, \{I2 = \frac{R3\ U2 + R3\ U1 + R1\ U2}{R3\ R2 + R1\ R2 + R3\ R1}, I1 = \frac{R3\ U2 + U1\ R2 + R3\ U1}{R3\ R2 + R1\ R2 + R3\ R1},$$
$$I3 = -\frac{-U1\ R2 + R1\ U2}{R3\ R2 + R1\ R2 + R3\ R1}\}\}$$

===== Check with Kirchhoff's current and voltage laws ========

```
> solve({R1*I1+R3*I3=U1, R2*I2-R3*I3=U2,I1-I2-I3=0}, {I1,I2,I3});
```

$$\{I2 = \frac{R3\ U2 + R3\ U1 + R1\ U2}{R3\ R2 + R1\ R2 + R3\ R1}, I1 = \frac{R3\ U2 + U1\ R2 + R3\ U1}{R3\ R2 + R1\ R2 + R3\ R1},$$
$$I3 = -\frac{-U1\ R2 + R1\ U2}{R3\ R2 + R1\ R2 + R3\ R1}\}$$

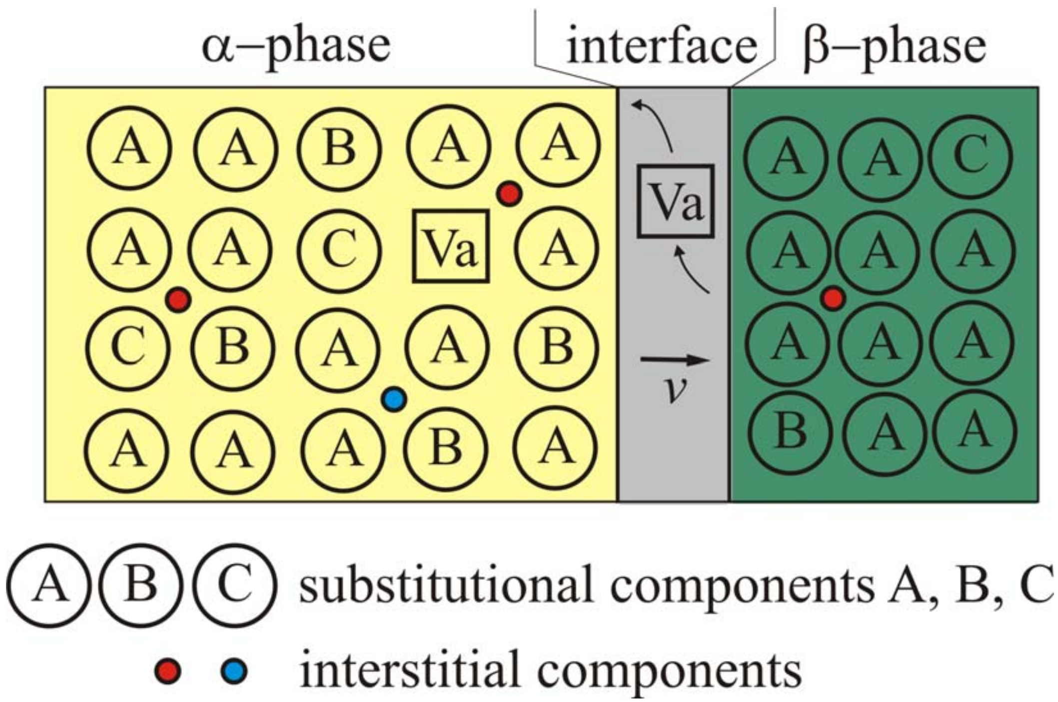
- ***Mathematic formulation***
  - **can be applied in several fields in a similar manner (mathematics, physics, biology, materials science…)**
  - **Symbolic computation.**

- ***Results***
  - **contribute to the insight of the considered phenomenon.**
  - **provide the solution of a technical problem.**

Application to diffusive phase transformations

Transformation kinetics depends on:
1, Diffusion of the components in the bulk material,
2, the rearrangement of the lattice and
3, on diffusion in the interface.

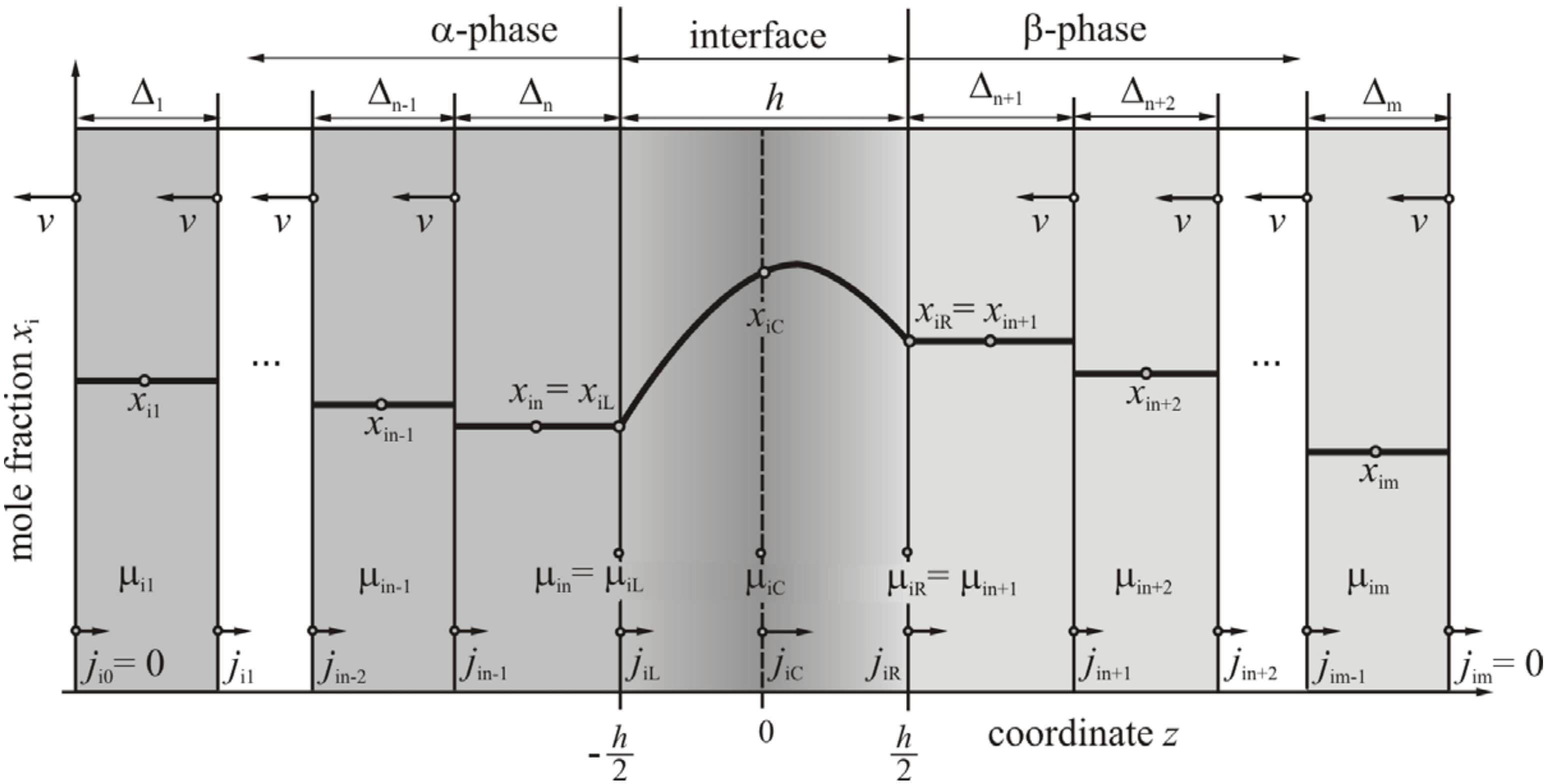
1: Dictra
1 + 2: first results are published.
1 + 2 + 3: current research.



Thick interface model

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

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



Bulk fluxes α: $j_{ik} \left(i = 1, \ldots, s-1;\ k = 1, \ldots, n-1\right)$

Bulk fluxes β: $j_{ik} \left(i = 1, \ldots, s-1;\ k = n+2, \ldots, m\right)$

Interface: $\dot{x}_{iL}, \dot{x}_{iC}, \dot{x}_{iR} \ \left(i = 1, \ldots, s-1\right),\ v$

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

$$G = \frac{1}{\Omega}\sum_{i=1}^{s}\int_{z_L}^{z_R} x_i \mu_i \mathrm{dz}$$

$$\dot{G} \quad (\text{from } G)$$

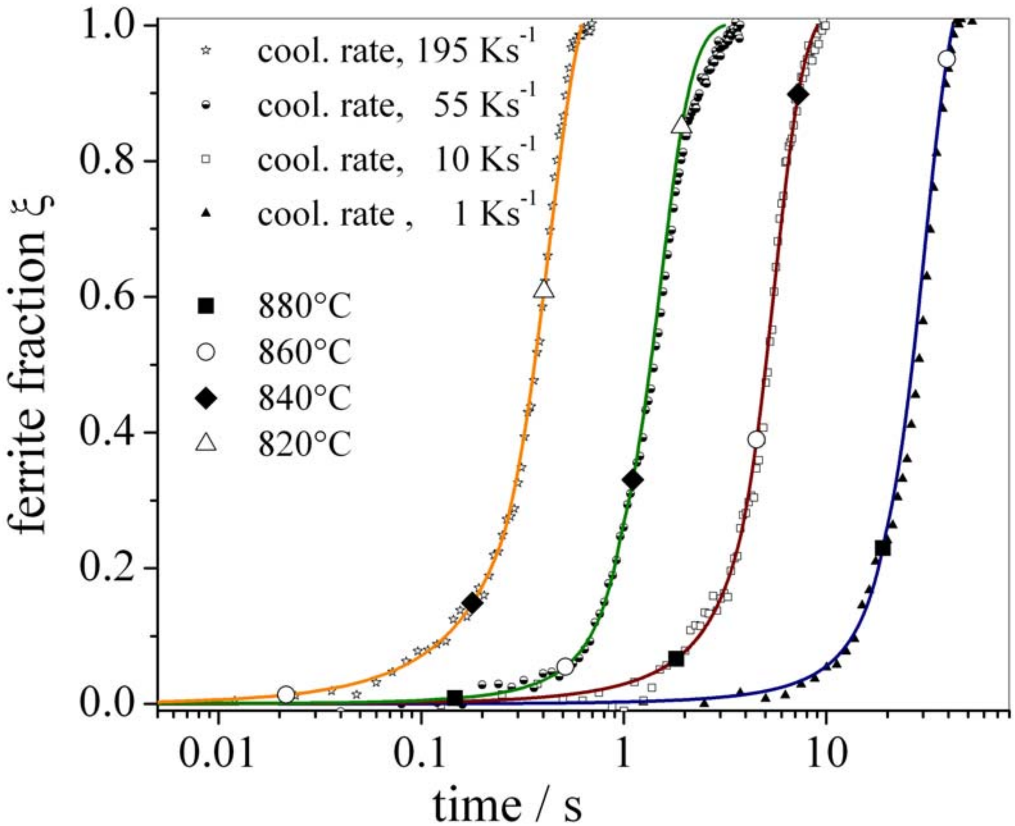
$$Q_k = \sum_{i=1}^{s}\frac{RT\Omega}{D_i x_{ik}}\int_{0}^{\Delta_k} j^2(z)\mathrm{dz}$$

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

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

$\Rightarrow$ Evolution equation for the fluxes and the rates of the mole fractions

Experiment 1: Ultra-low alloyed C-steel



$w_C = 20\text{ppm}$
$w_{Mn} = 0.11\%$

$$\xi(t) = \frac{a}{1 + b\exp(-ct)}$$

$$\frac{d\xi}{ds} \cdot \frac{ds}{dt} = \frac{d\xi}{ds}(\text{geometry}) \cdot \frac{ds}{dt}$$

$$v = M_{\text{eff}} \cdot \Delta f$$

M. Militzer, Austenite decomposition kinetics in advanced low carbon steels, Solid Phase Transformations 99, eds. M. Koiwa, K. Otsuka and T. Miyazaki, JIM, Sendai (1999) 1521-1524.

E. Gamsjäger, M. Militzer, F. Fazeli, J. Svoboda, F. D. Fischer: "Interface mobility in case of the austenite-to-ferrite phase transformation", *Comp. Mat. Sci*, **37** (2006) 94-100.

Solute drag

$$\boxed{v = M_{\mathrm{eff}} \Delta f} \longrightarrow \boxed{v = M\left(\Delta f - \Delta f_{\mathrm{sd}}\right)}$$

$$\boxed{M = M_0 \cdot \exp\left(-\frac{Q_\mathrm{M}}{RT}\right)} \longrightarrow Q_\mathrm{M} \approx 147\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$$

- $M_0 = 4800\,\mathrm{mol}\cdot\mathrm{s}\cdot\mathrm{kg}^{-1}\cdot\mathrm{m}^{-1}$

M. Hillert, Diffusion and interface control of reactions in alloys, Metallurgical Transactions 6A (1975) 5-19.

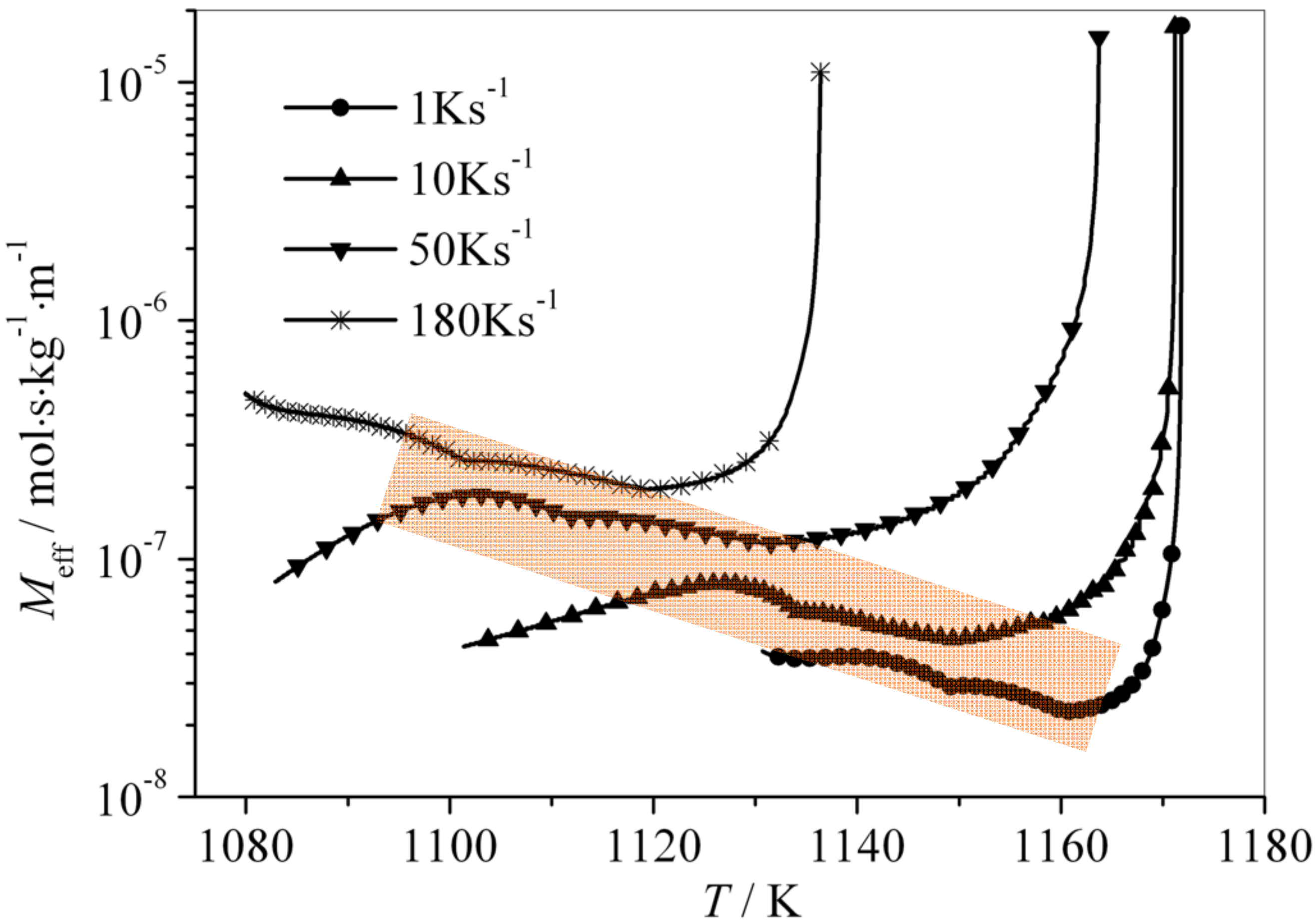
- $M_0 = 0.058\,\mathrm{mol}\cdot\mathrm{s}\cdot\mathrm{kg}^{-1}\cdot\mathrm{m}^{-1}$

G. P. Krielaart, S. van der Zwaag, Kinetics of γ/α phase transformations in Fe-Mn alloys containing low manganese, Materials Science and Technology 14 (1998) 10-18.

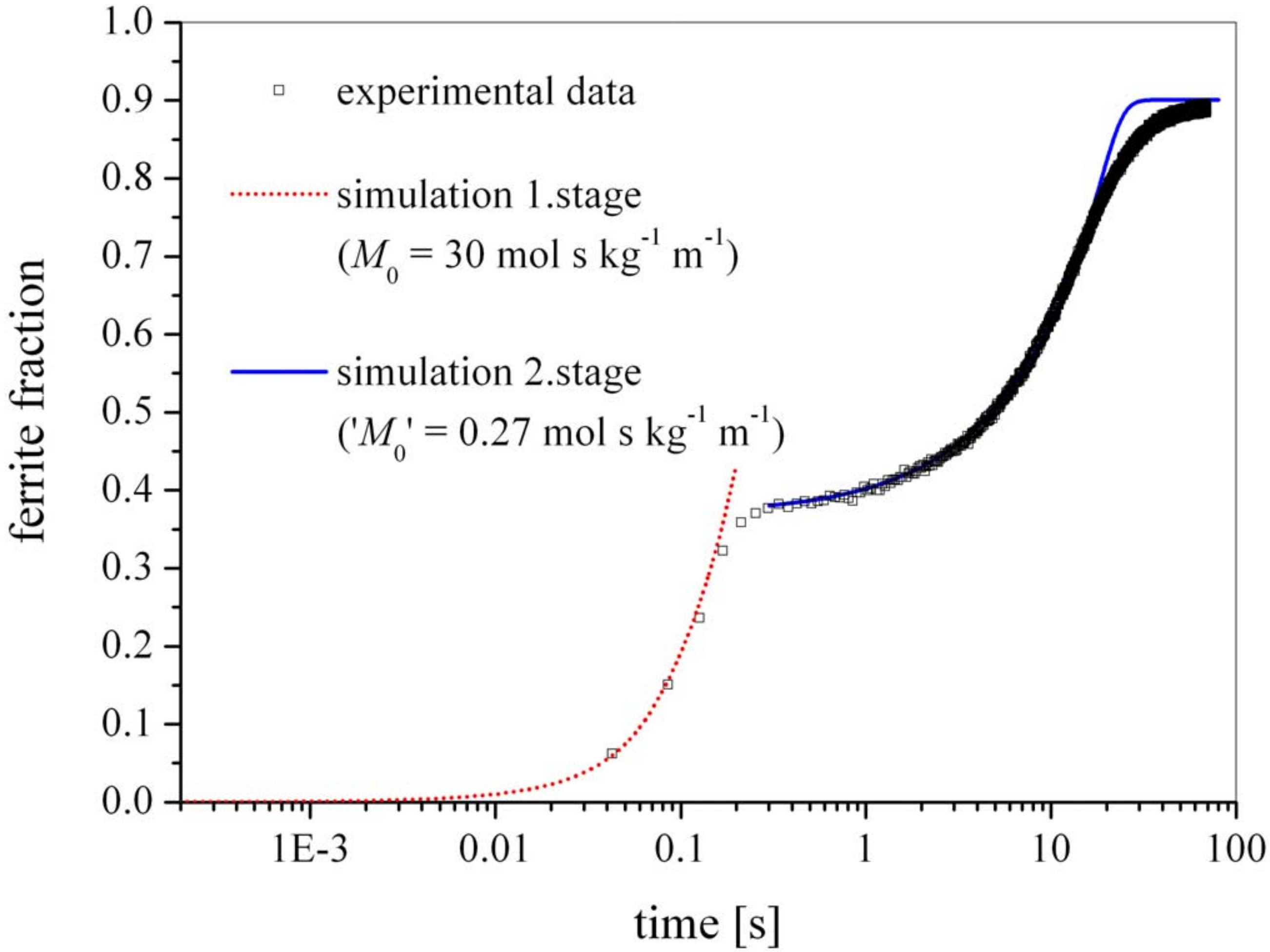
- $M_0 = (6 - 15)\,\mathrm{mol}\cdot\mathrm{s}\cdot\mathrm{kg}^{-1}\cdot\mathrm{m}^{-1}$

E. Gamsjäger, M. Militzer, F. Fazeli, J. Svoboda, F. D. Fischer, „Interface mobility in case of the austenite-to-ferrite phase transformation“, Comput. Mater. Sci. 37 (2006) 94-100.

Effective interface mobility as a result of the tetrakaidecahedron model

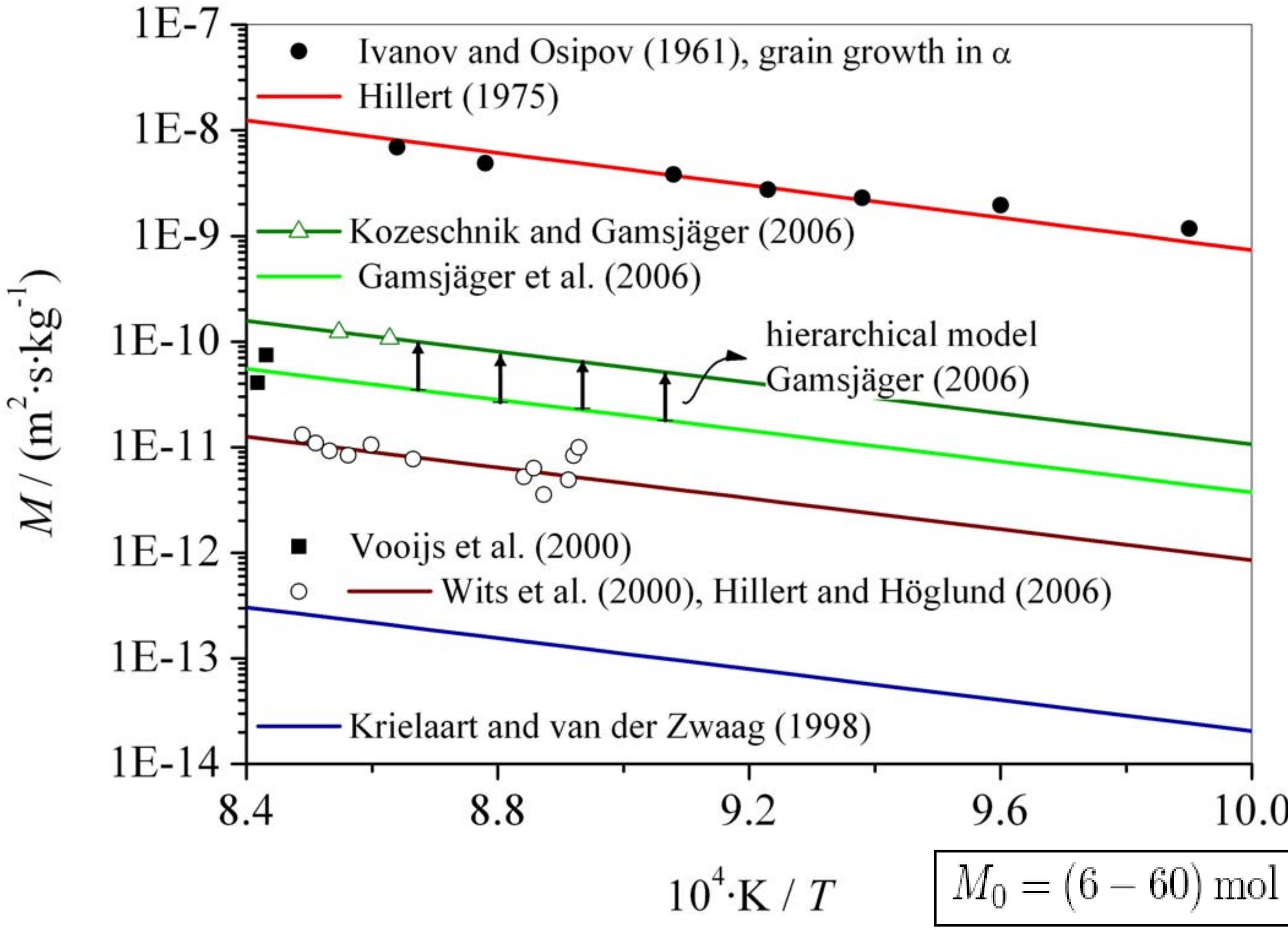


Experiment 2: Fe-C-alloy
1. stage and 2. stage



E. Kozeschnik, E. Gamsjäger, *Metall. Mater. Trans.* **37A** (2006) 1791-1797.

Intrinsic interface mobility *M*
A literature survey



$$M_0 = (6 - 60)\ \mathrm{mol \cdot s \cdot kg^{-1} \cdot m^{-1}}$$

Conclusions and Outlook

➔ **Extremum principle (applicable to equilibrium and to processes not too far away)**

- **Equilibrium conditions and evolution equations**
- **Thick interface simulation**

➔ **Estimation of the intrinsic mobility**

- Evaluation of experimental data by transformation models.

Next tasks:

➔ Application of the principle of maximum dissipation to further problems in materials science.

➔ Comparison with experimental results