Diffusion and redistribution at moving interfaces

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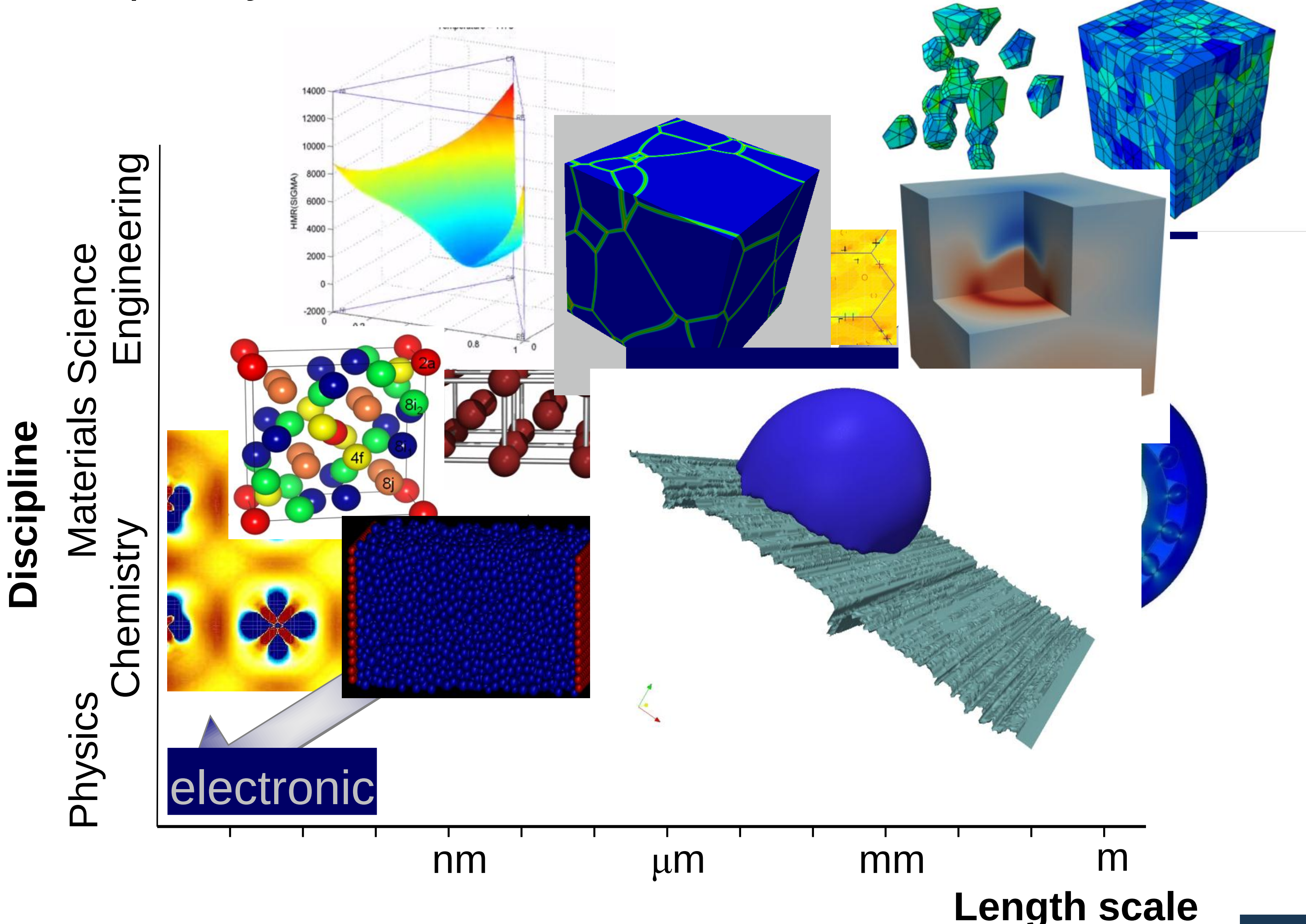
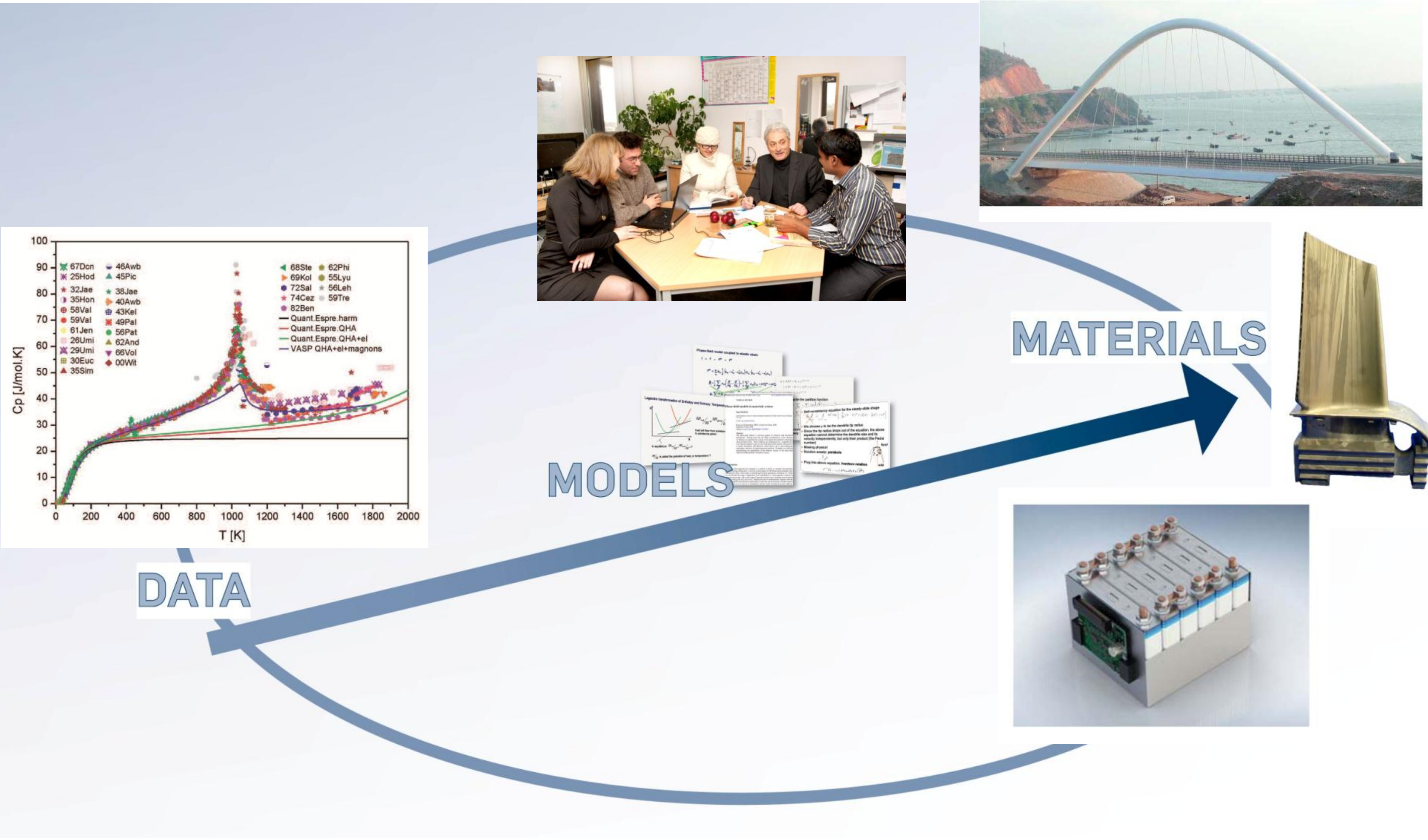


The materials designers needs



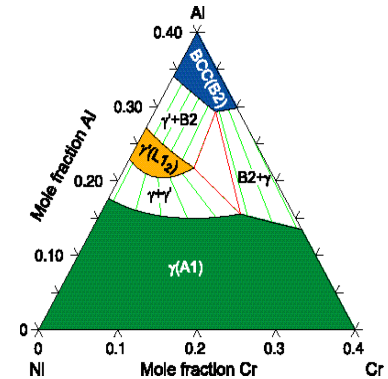
Outline

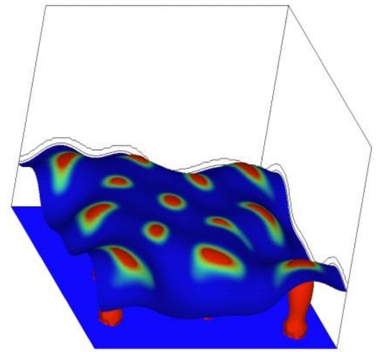
- Multi-Phase Field model for heterogeneous non (!) equilibrium
- Application:
    - rapid solidification
    - precipitation and diffusion
    - diffusion in Li-ion battery materials
- Questions and needs

Multi-phase field method + diffusion + mechanics

$$f = \sum_{\alpha,\beta} \frac{\sigma_{\alpha\beta}(\vec{n}_\alpha, \vec{n}_\beta)}{\eta_{\alpha\beta}} K^{\alpha\beta}(\Delta\phi_\alpha, \Delta\phi_\beta, \phi_\alpha, \phi_\beta) + \sum_\alpha \phi_\alpha f^\alpha(c_\alpha)$$

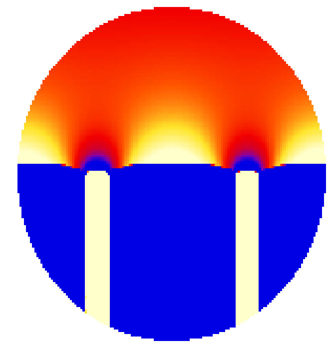
free energy functional





$$\dot{\phi}_\alpha = \frac{1}{n} \sum_\beta \mu_{\alpha\beta} \left(\frac{\delta f}{\delta \phi_\alpha} - \frac{\delta f}{\delta \phi_\beta} \right)$$

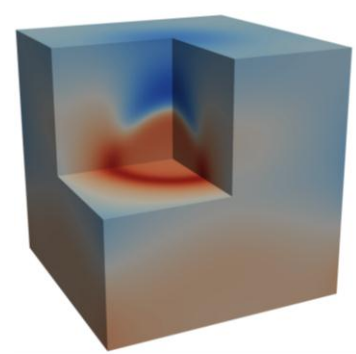
phase evolution



$$\dot{c}^i = \sum_k \nabla M^{ik} \nabla \frac{\partial f}{\partial c^i} = \sum_k \sum_\alpha \nabla D_\alpha^{ik} \nabla c_\alpha^k$$

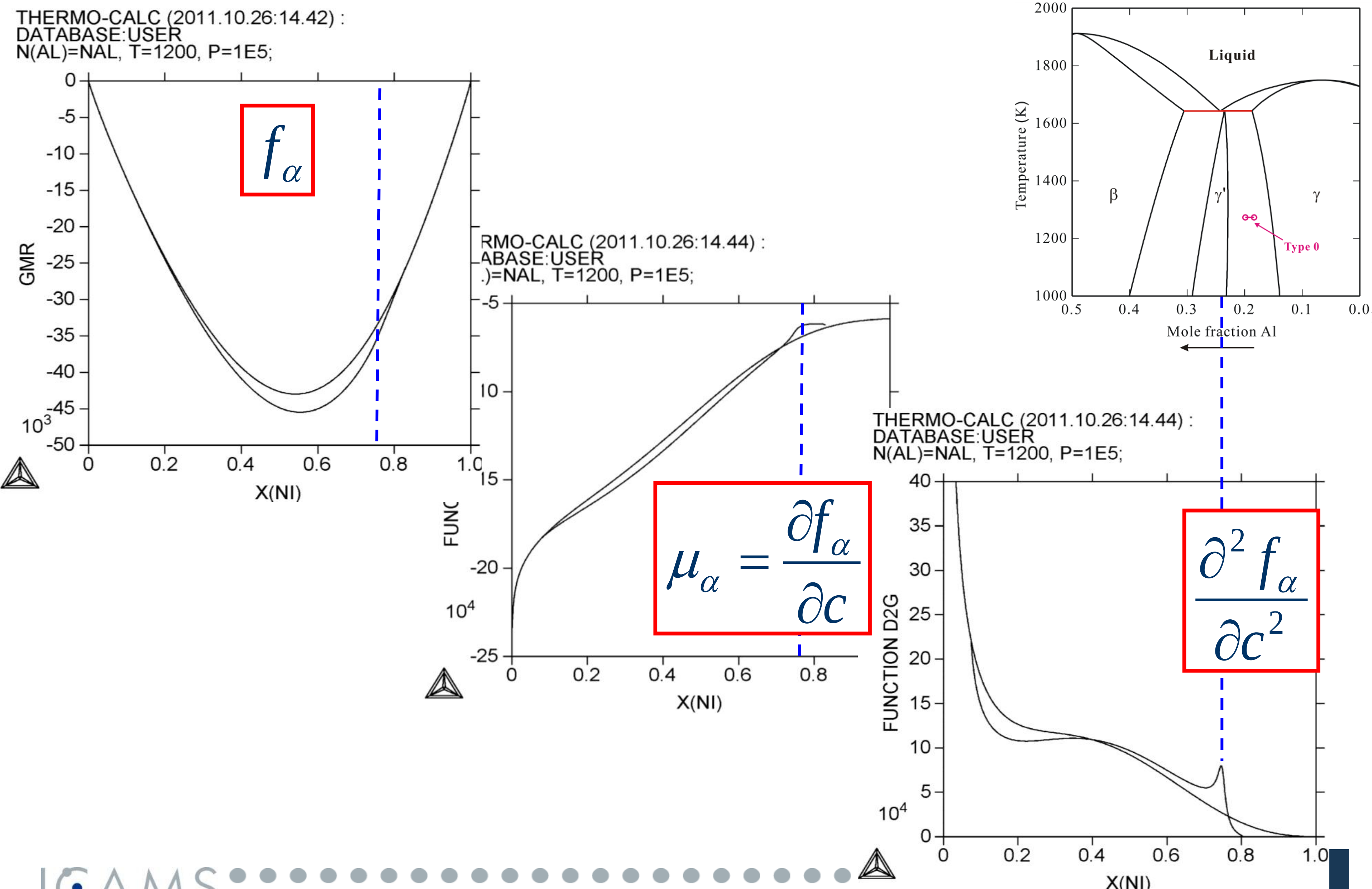
diffusion

$$0 = \nabla \frac{\partial f}{\partial \varepsilon} = \nabla \sigma = \sum_\alpha \nabla \phi_\alpha C_\alpha \left(\varepsilon_\alpha - \varepsilon_\alpha^* - \varepsilon_\alpha^1 c_\alpha \right)$$



mechanical equilibrium

Gibbs energies and their derivatives: Example Al-Ni



Phase field model for heterogeneous (non) equilibrium

$$\phi_\alpha \dot{c}_\alpha = \vec{\nabla}\left(\phi_\alpha M_\alpha \frac{\partial^2 f_\alpha}{\partial c^2} \vec{\nabla} c_\alpha \right) + \sum_\beta \left[P^{\alpha\beta} \phi_\alpha \phi_\beta \left(\tilde{\mu}_\beta - \tilde{\mu}_\alpha \right) + \phi_\alpha \dot{\phi}_\alpha (c_\alpha - c_\beta) \right]$$

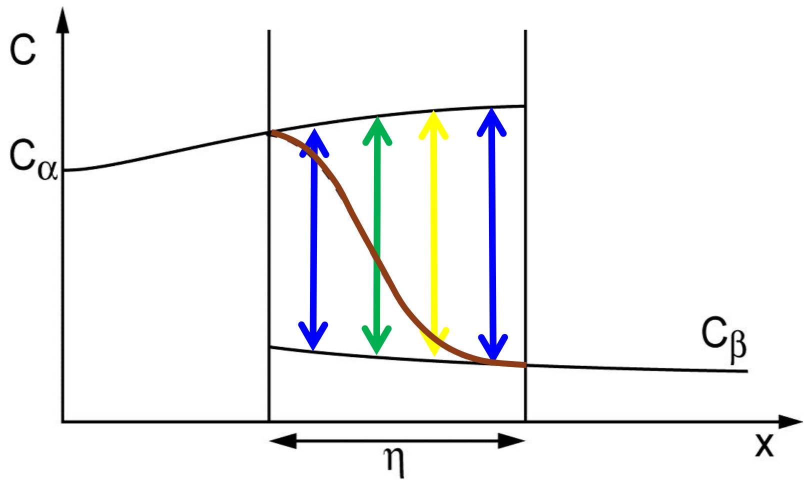
diffusion within the individual phases

redistribute solute if there is a chemical potential difference between the phases

phase concentrations change if there is a phase change

IS, L. Zhang, M. Plapp, Acta Mat 2012
L. Zhang, IS, Acta Mat 2012

Coars graining of the diffusion operator in the interface



$$\vec{\nabla} M \vec{\nabla} \mu \rightarrow \sum_{\alpha} \vec{\nabla} \phi_\alpha M_\alpha \vec{\nabla} \mu_\alpha + \sum_{\alpha,\beta} P^{\alpha\beta} \phi_\alpha \phi_\beta \left(\tilde{\mu}_\beta - \tilde{\mu}_\alpha \right)$$

long range diffusion

short range diffusion

$$P^{\alpha\beta} \approx \frac{\langle M \rangle^{\alpha\beta}}{\Delta x^2}$$

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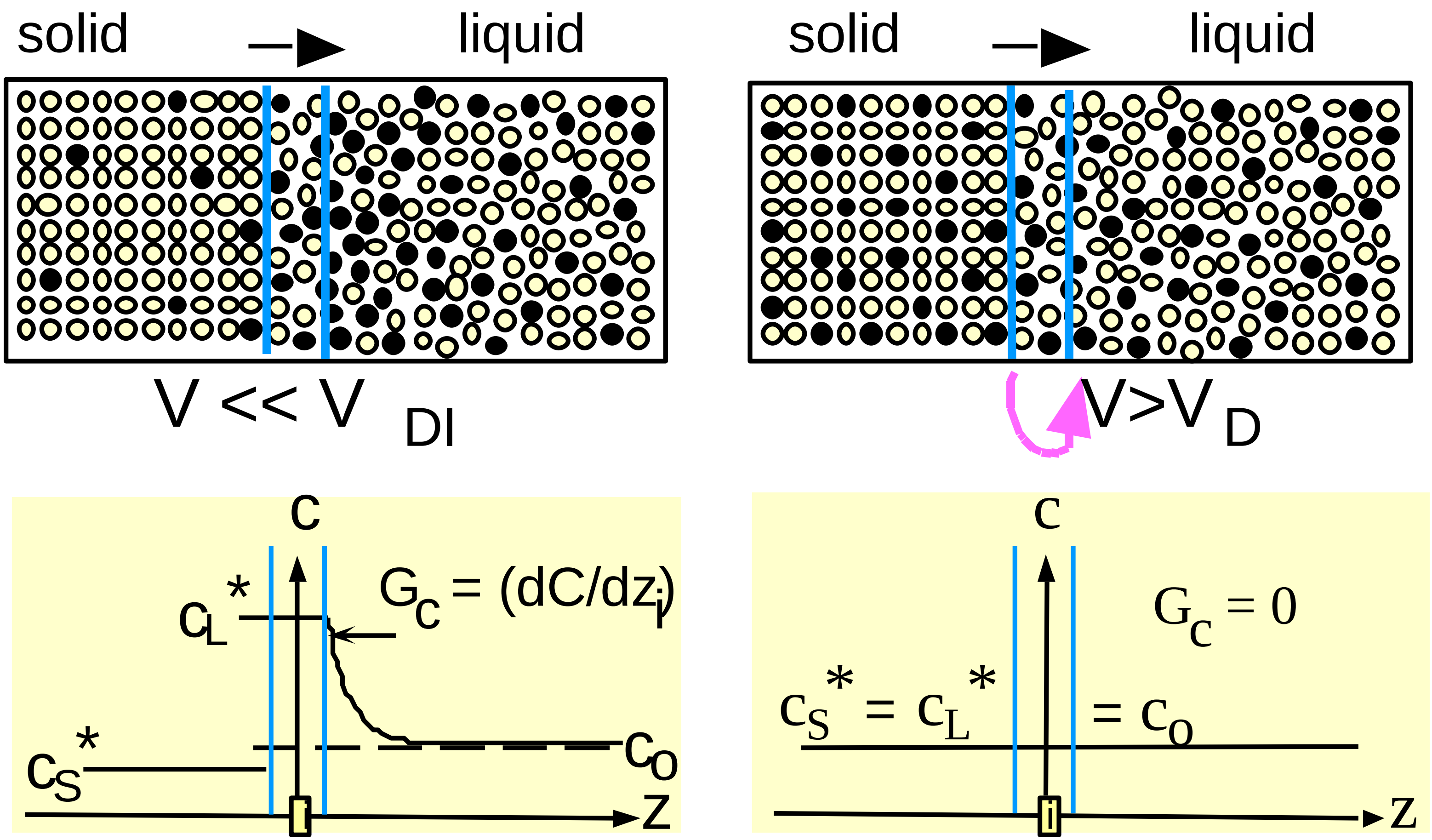
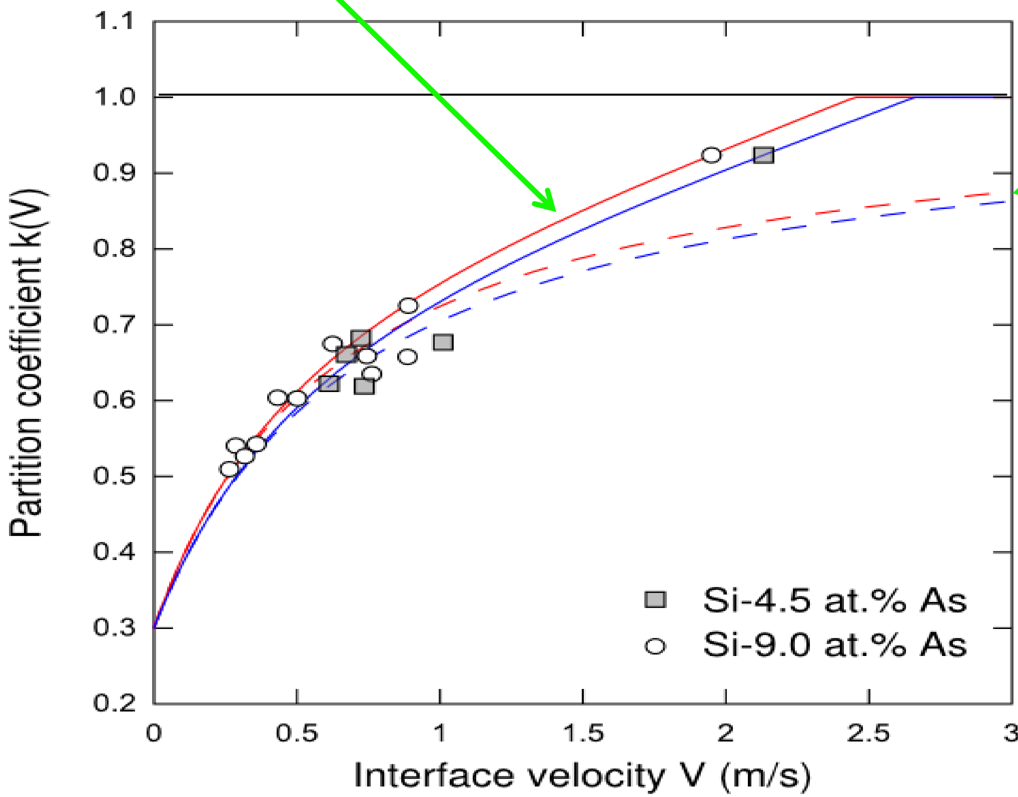
The physical problem: off equibrium in the interface



The physical problem: transition to complete trapping

Hyperbolic Model Galenko (2007)

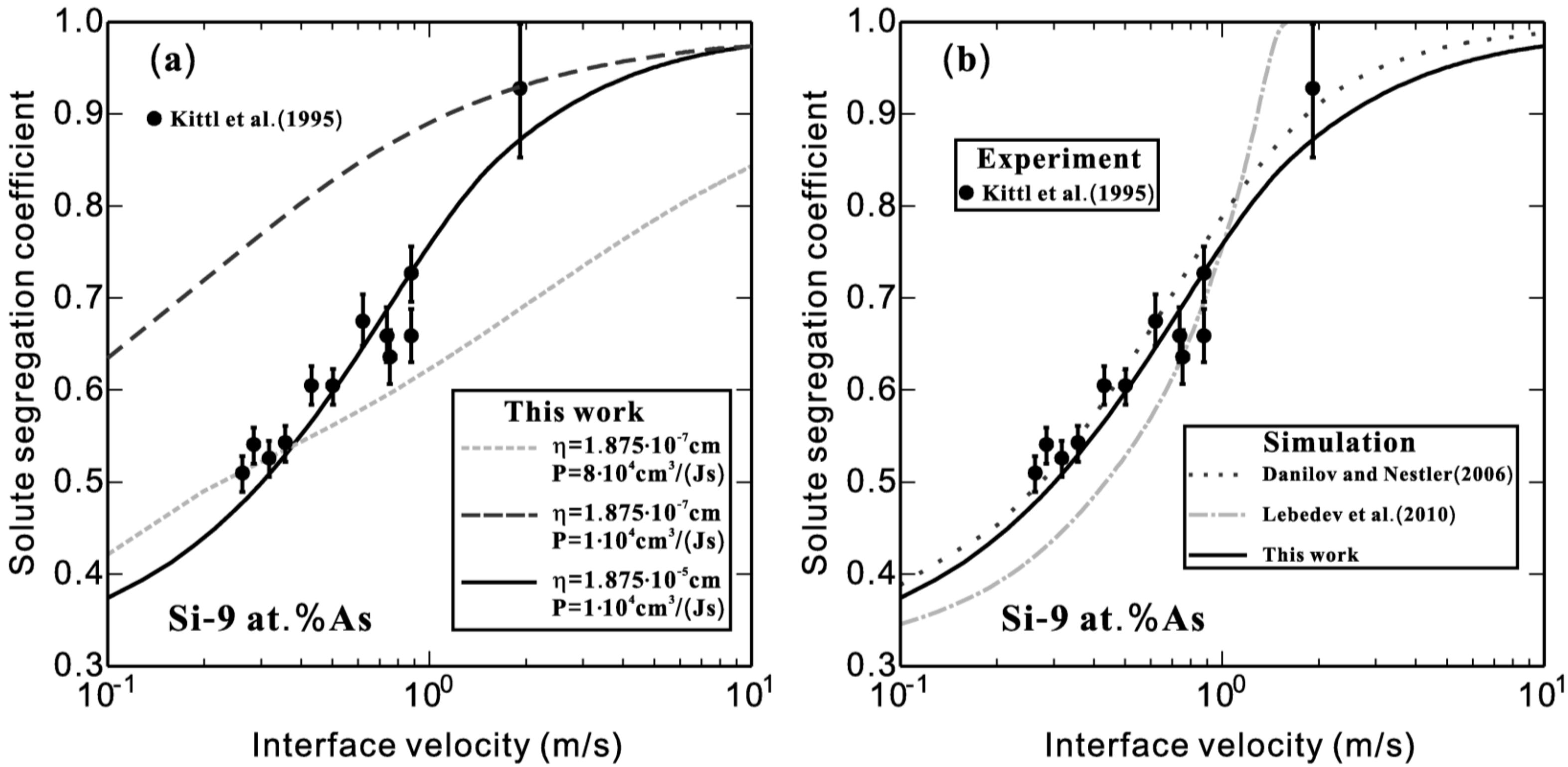
$$k(V) = \frac{k_e + V/V_D}{1 + V/V_D}$$



Aziz (1982)

experimental data: Kittl, Aziz et al (1995)

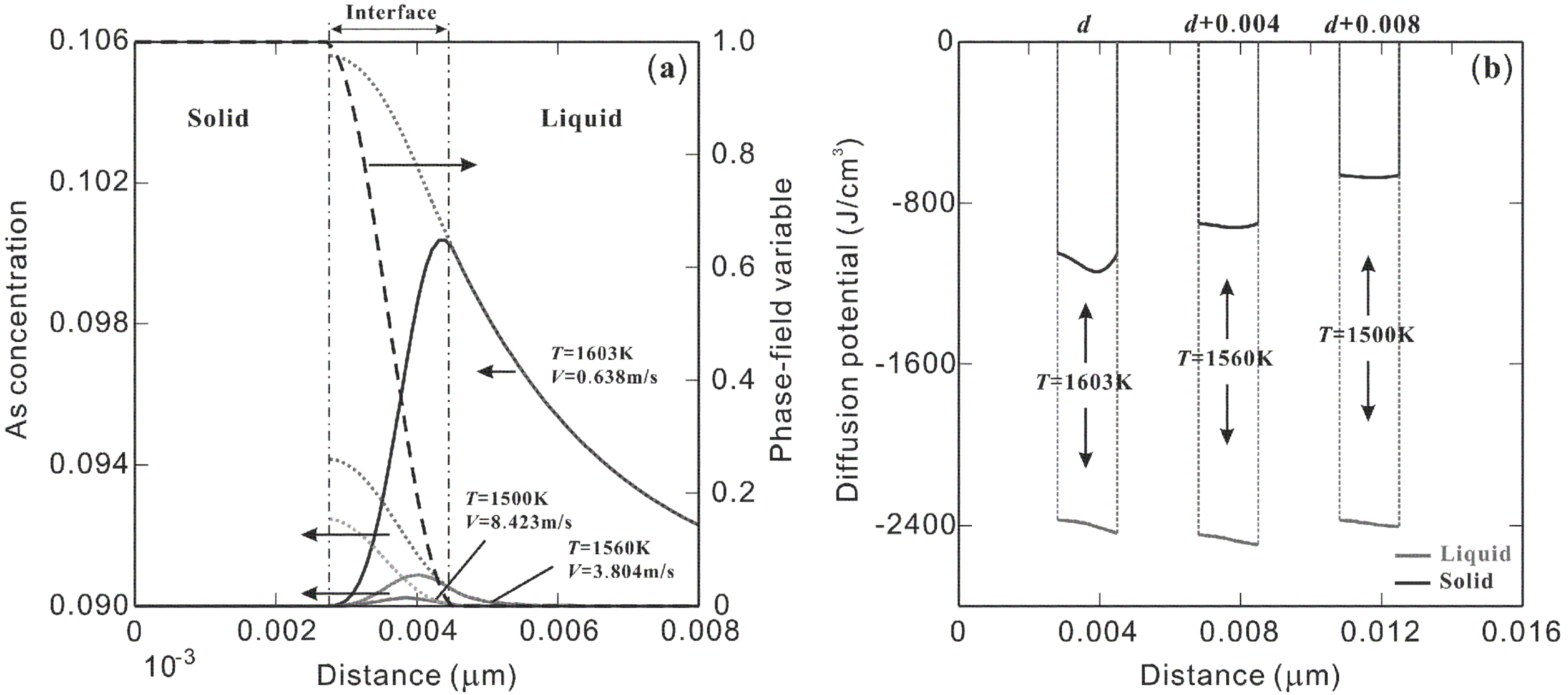
Variation of the interface width: Comparison with experiment and other models



IS, L. Zhang, M. Plapp, Acta Mat 2012

Potential jump at fast moving interfaces

Lijun Zhang



IS, L. Zhang, M. Plapp, Acta Mat 2012

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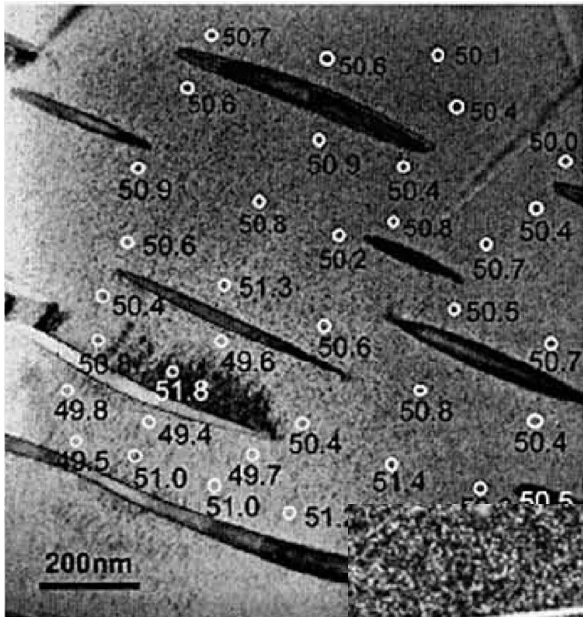
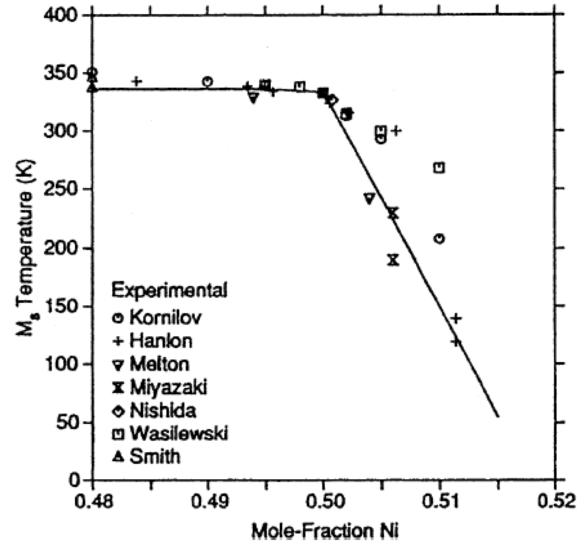
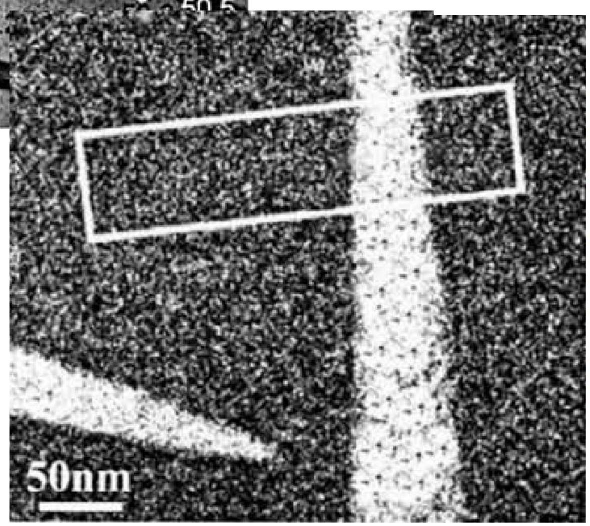
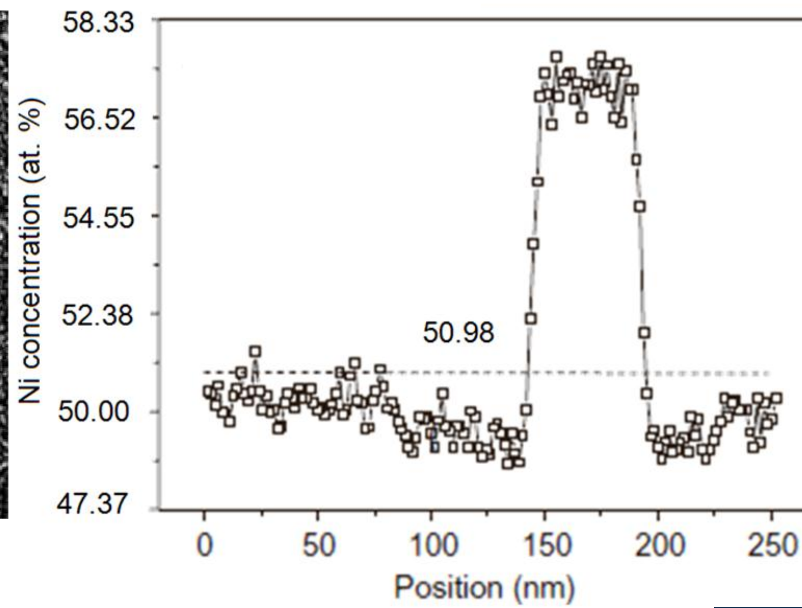
Ni4Ti3 precipitates in NiTi shape memory alloys





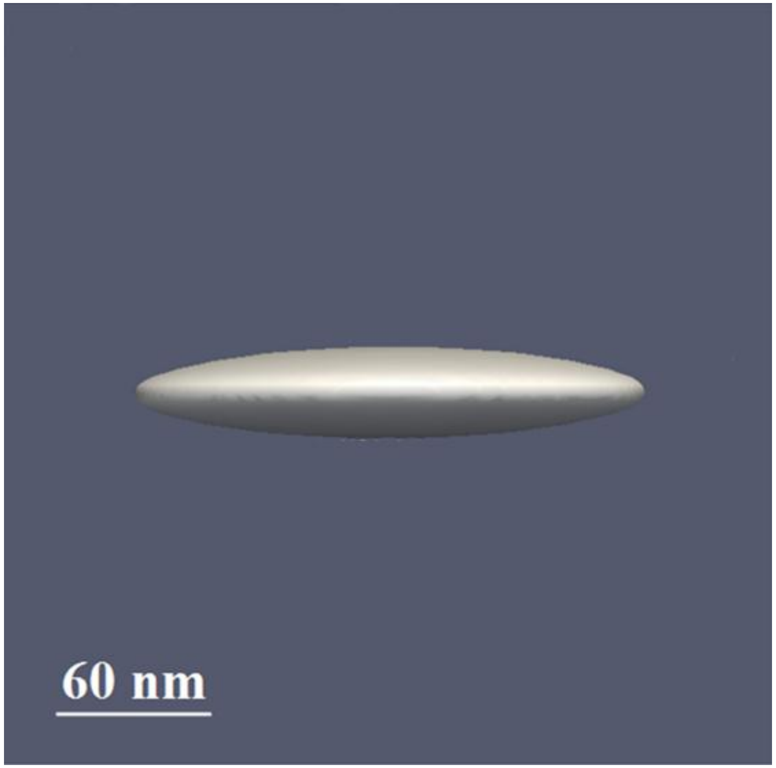
Otsuka, Ren
Progress in Material Science (2005)





Experiment:
Yang, Schryvers,
Intern. Journ. of
Appl. Electromagn.
and Mech (2006)

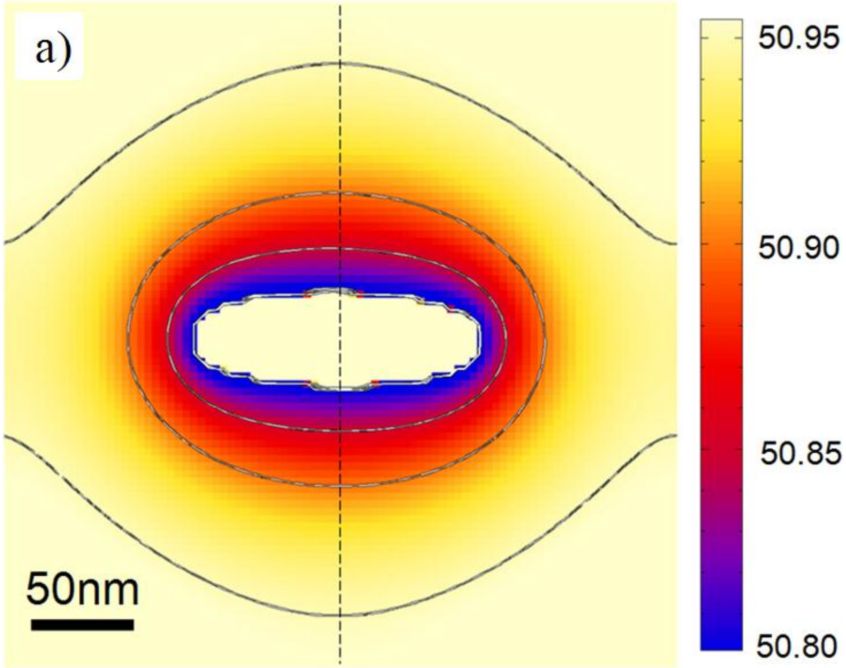
Shape and constitution (only Fick's diffusion)



Phase field

Wei Guo et al.,
Acta Mater. (2011)

Ni Concentration



Strain energy gradient driven diffusion

For a linear dependency between elastic constants and concentration field we have following terms:

$$\overset{=}{H}_c = \overset{=}{H}\ (1+kc) \longrightarrow \quad f_e = (\varepsilon - \varepsilon^*)\,\overset{=}{H}_c(\varepsilon - \varepsilon^*)$$

$$f_c = cf_\alpha(c) + (1-c)\,f_\beta(1-c)$$

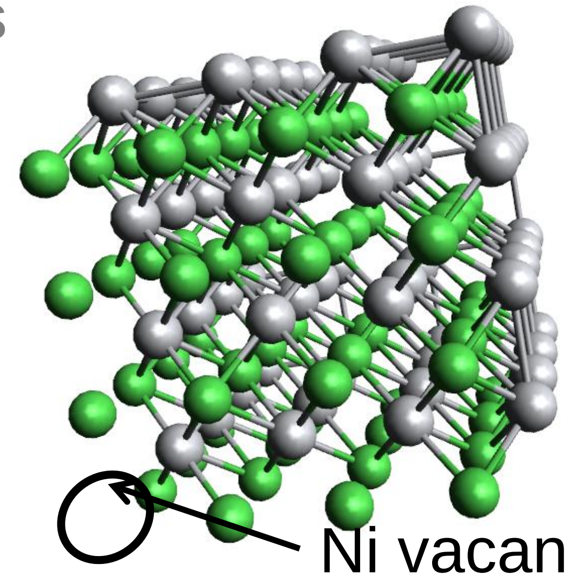
$$\dot{c} = \nabla.M\nabla\frac{\delta F}{\delta c} = \nabla.M\nabla\left(\frac{\delta f_c}{\delta c} + \frac{\delta f_e}{\delta c}\right)$$
$$= \nabla.M\nabla(c + k(\varepsilon - \varepsilon^*)\,\overset{=}{H}(\varepsilon - \varepsilon^*))$$

$$0 = \nabla^j\sigma^{ij} = \nabla^j(\overset{=}{H}_c(\varepsilon - \varepsilon^*))^{ij}$$

Larchet , Cahn 1982: The effect of self-stress on diffusion in solids

Elastic Properties of B2 Ni-Ti with Defects

- Perform full relaxation of B2 NiTi supercells with vacancies and substitutions to compare changes in elastic energy
- Obtain DFT elastic properties as a function of Ni-concentration
- Use DFT elastic properties and trends as inputs for phase-field (PF) models



1) Obtain DFT C_{ij} as function of Ni-concentration
2) Import concentration dependent C_{ij} into PF-model
3) Incorporate into PF mechanical energy term

$$E(V,\alpha) = E(V_o,0) + V_o\left(\sum_i \tau_i \alpha_i + \frac{1}{2}\sum_{i,j} C_{ij}\alpha_i \xi_i \alpha_j \xi_j\right)$$

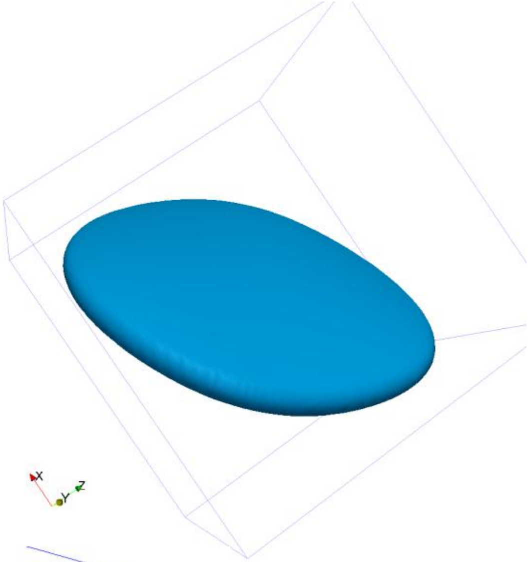
$$C^{ijkl} = \sum_{\alpha=1}^{N} \phi_\alpha C_\alpha^{ijkl} = \sum_{\alpha=1}^{N} \phi_\alpha C_{\alpha,0}^{ijkl}[1+\kappa_q^\alpha \Delta c^\alpha]$$

$$f^{\mathrm{mech}} = \frac{1}{2}\sum_{\alpha=1}^{N} \phi_\alpha [\epsilon_\alpha^{ij} - \epsilon_\alpha^{*ij}]\ C_\alpha^{ijkl}(\vec{c}_\alpha)\ [\epsilon_\alpha^{kl} - \epsilon_\alpha^{*kl}]$$

Nicholas Hatcher

Calculation results

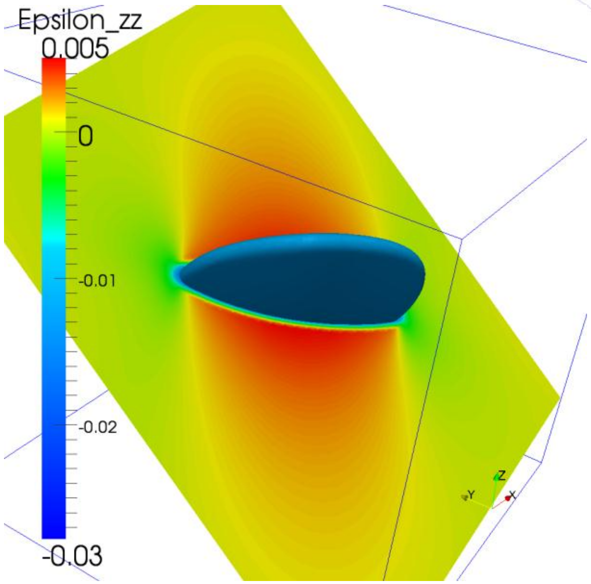
Efim Borukhovic

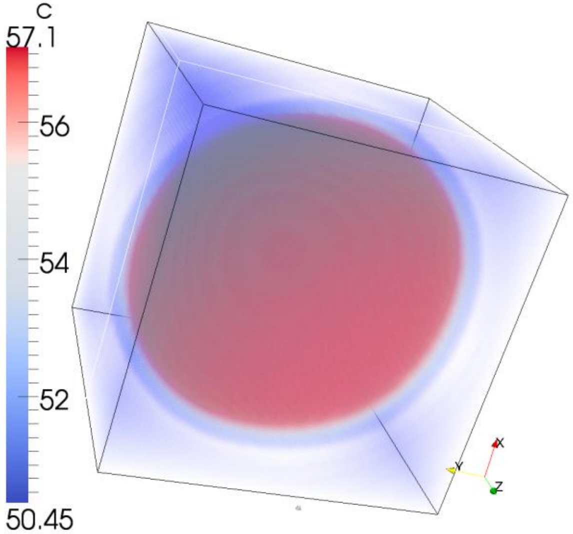


- Phasefield

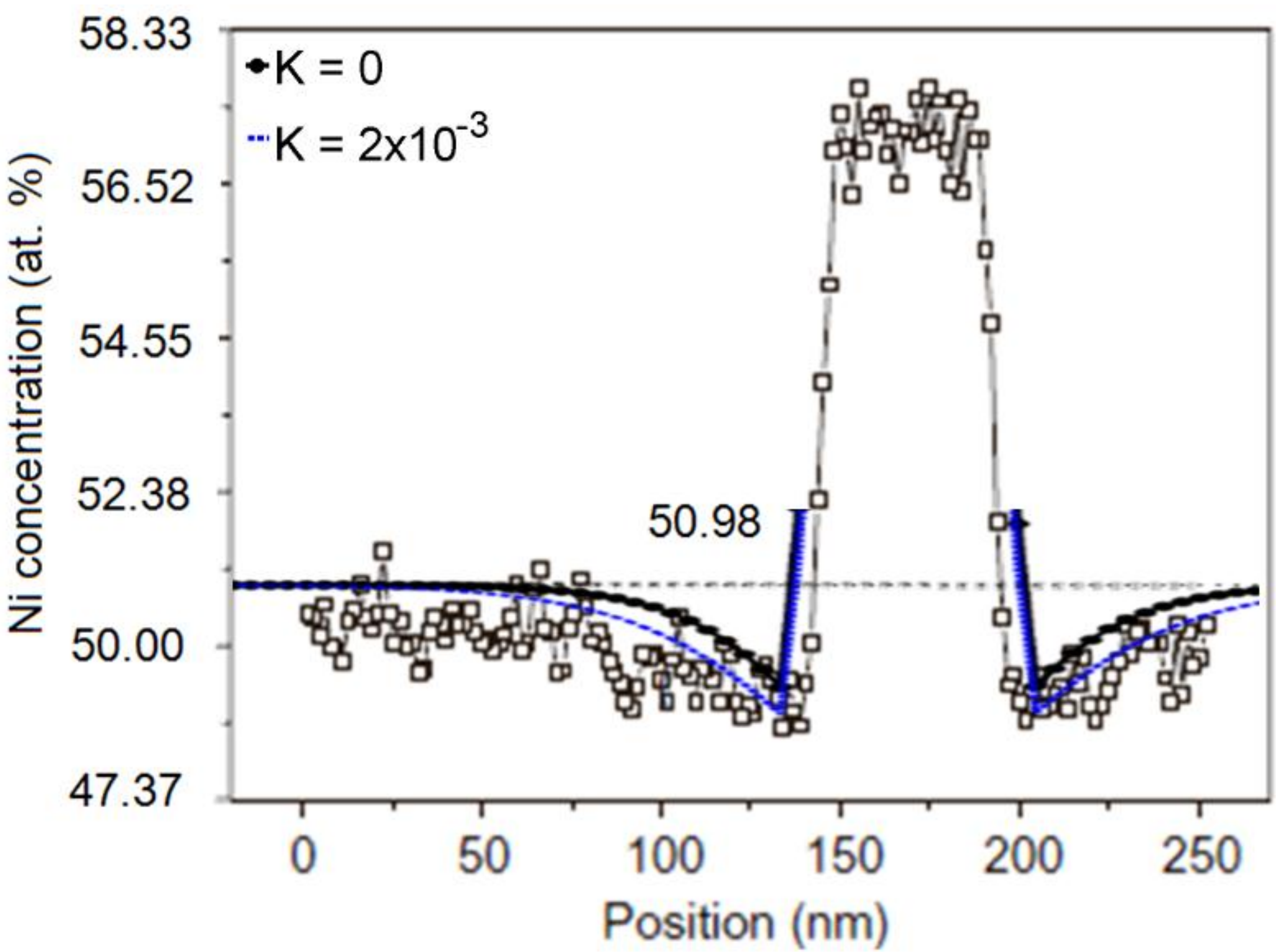
- Concentration

- Strain / Stress





Concentration profile in stress stabilized equilibrium



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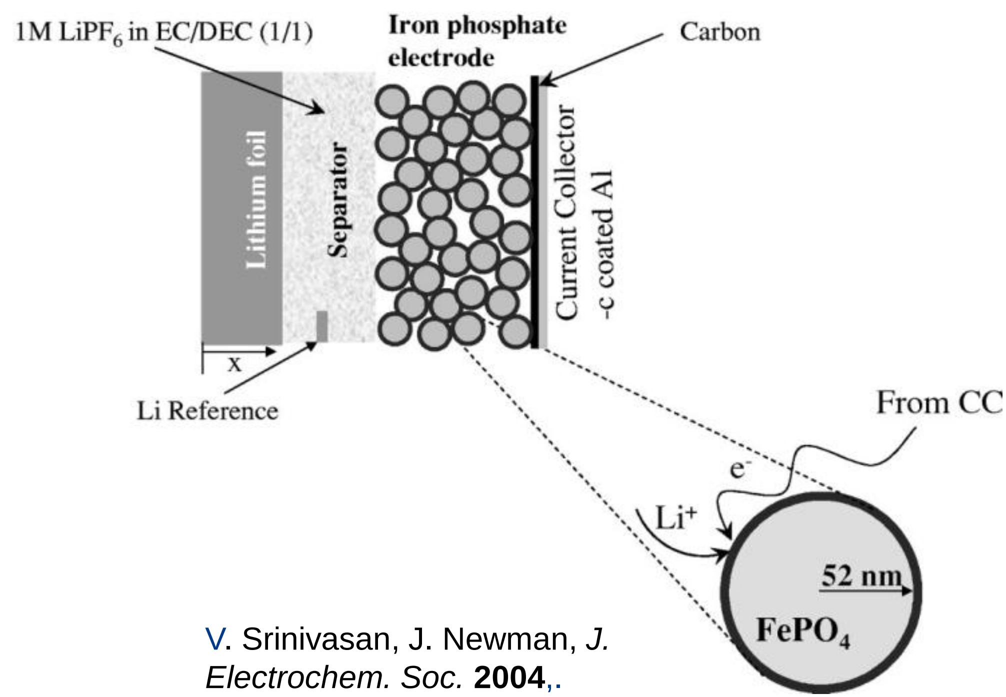
Scales in Batteries

- 100 pm: Li , $Li^{+}_{(solv)}$, point defect
- 1 nm: EDL, SEI
- 10 nm: electrode particle
- 10 µm: membrane, current collector
- 100 µm: cell, dendrite
- 1 mm: battery



V. Srinivasan, J. Newman, *J. Electrochem. Soc.* **2004**,.

How to obtain (effective) permeability *P*?

Ulrich Preiss

- from exchange current
- I_0 = electron flux in equilibrium
- assumption: $\dot{n}(\mathrm{Li}^+) = \dot{n}(\mathrm{e}^-)$
- then:

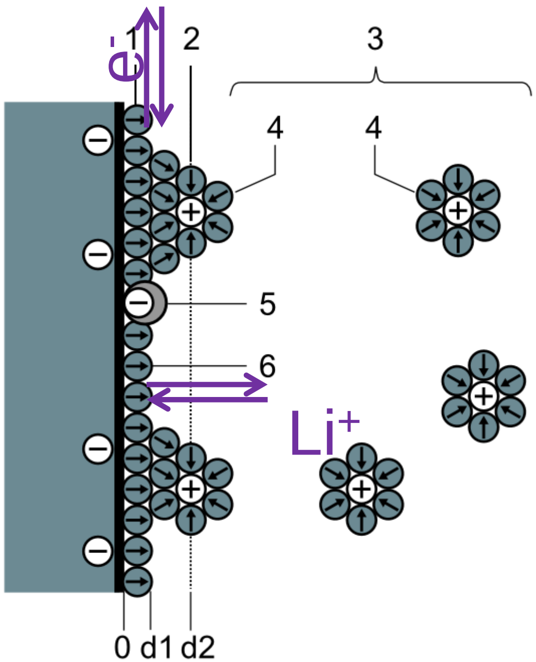
$$\frac{\dot{n}_\beta}{dA} = \frac{N_A}{F} \cdot \frac{I_{0,\beta}}{dA}$$

Nernst eqn.

$$E_\alpha - E_\beta = \pm \frac{R \cdot T}{z \cdot F} \cdot ln \frac{a_\alpha}{a_\beta}$$

$$P \approx 9.97 \frac{\mathrm{K} \cdot \mathrm{mol}^2 \cdot \mu\mathrm{V}}{\mathrm{J}^2} \cdot \frac{V_{mol}^2}{T \cdot \eta} \cdot \frac{I_{0,\beta}}{dA} \cdot \frac{x_\alpha \cdot x_\beta}{x_\alpha + x_\beta}$$

exchange current density (measurable)

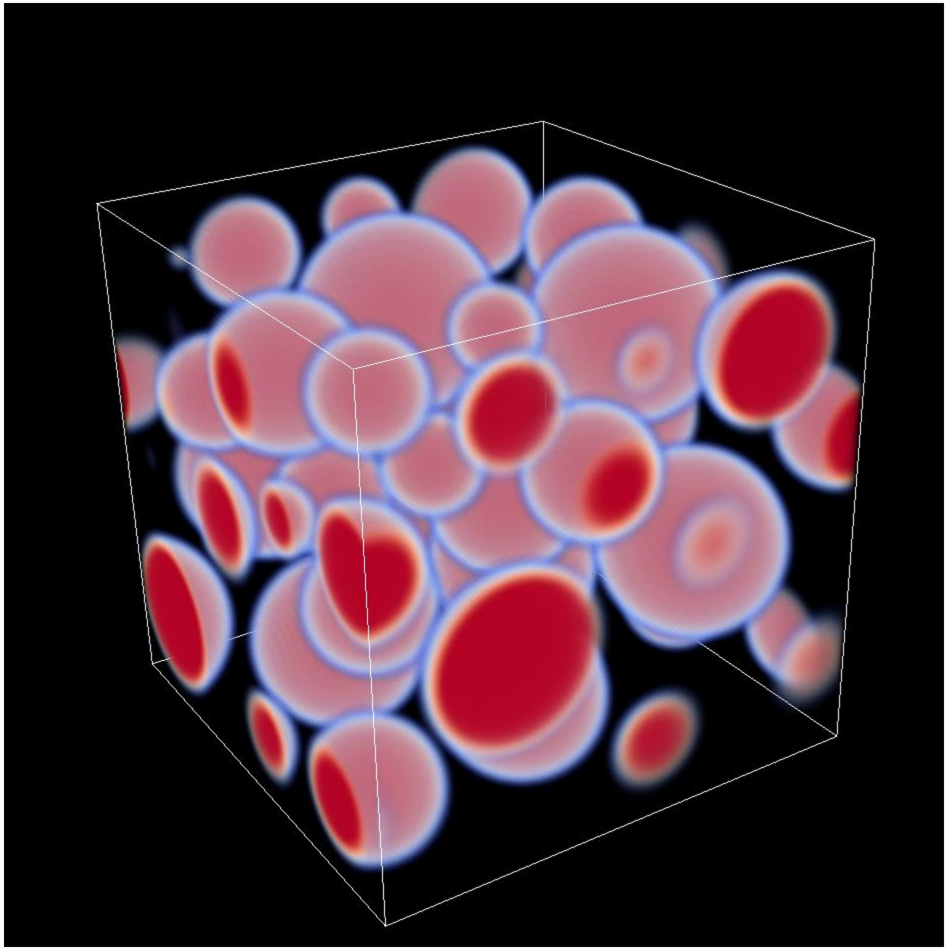


1 & 2 inner & outer Helmholtz layer,
3 diffusion layer,
4 solvated ions,
5 deposited material,
6 solvent

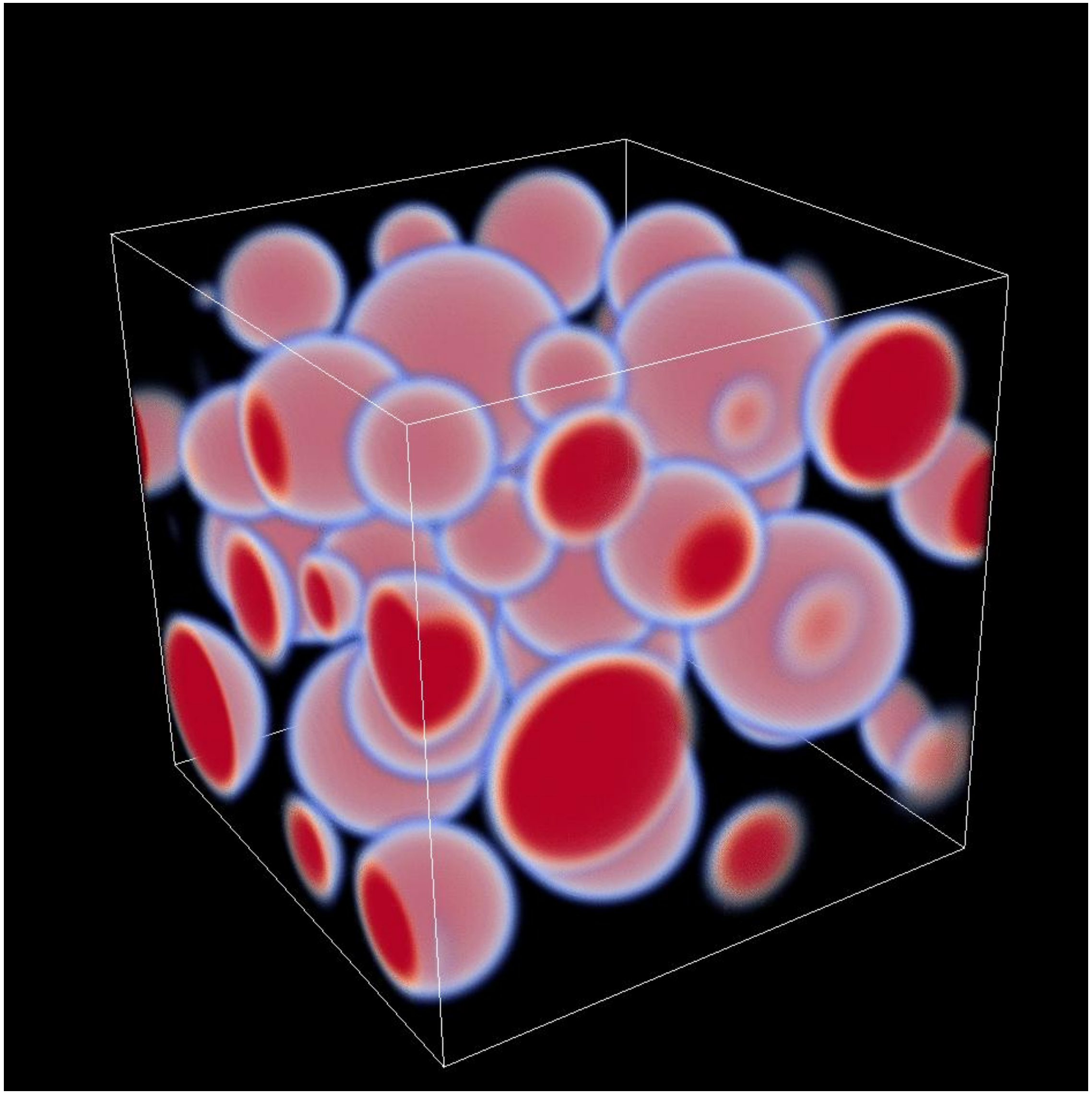
Li deintercalation from Si-anode material

- Initial Li concentration 63 at.%

- BC:
  - Top: c=0 at.%
  - Bottom: no flux
  - Walls: periodic



Li deintercalation from Si-anode material



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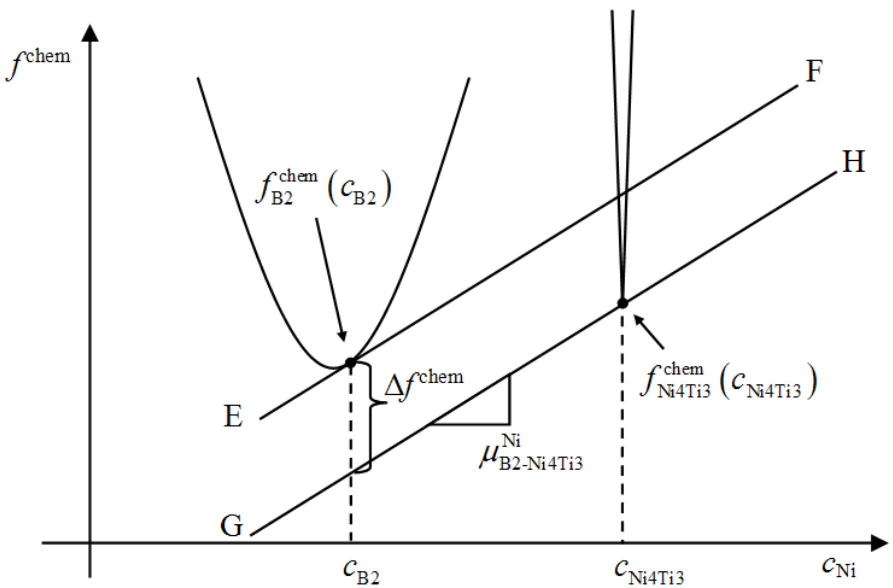
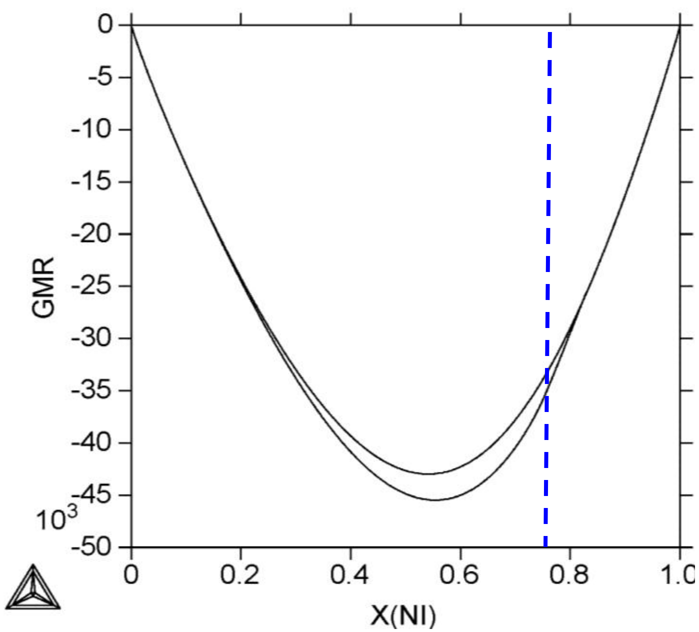
Diffusion in stoichiometric phases, ordered compounds

- Diffusion on different sublattices?
- Anisotropy?
- Dependence on the defect structure (vacancies)?
- Cross effects?

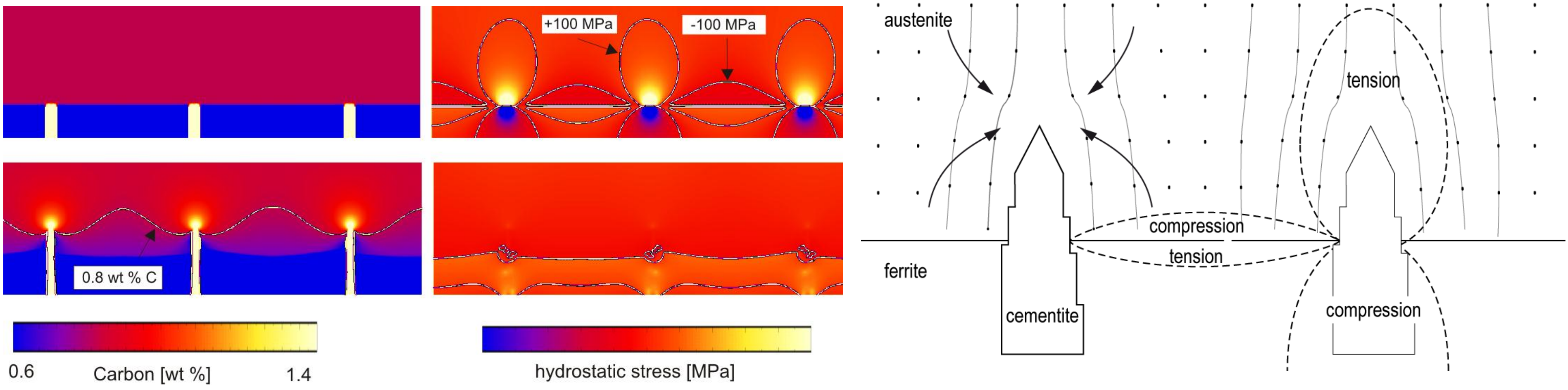




Questions and needs

Diffusion driven by outer fields

- Stress and strain: volumetric effect on the thermodynamic potential
- Gradients in the elastic energy (deviatoric stress)
- Electric field acting on charged species

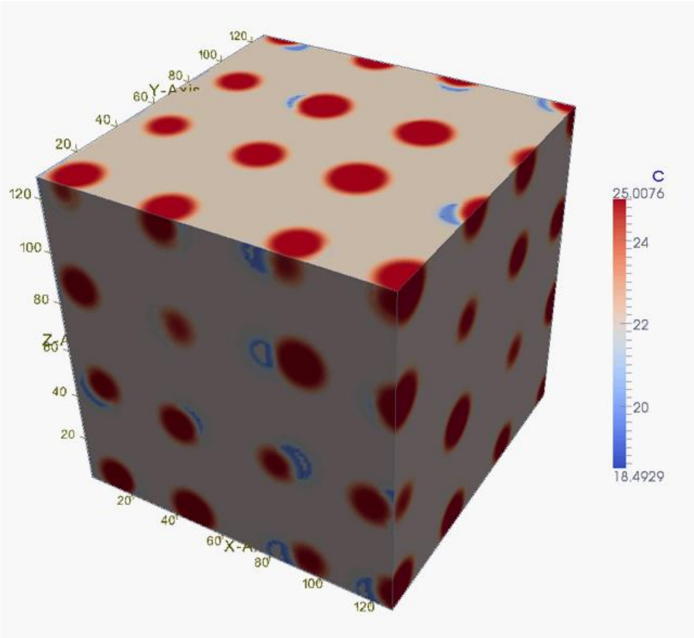


IS, Apel; Acta Mat 2007, IS, Plapp, Continuum Mech. Thermodyn 2012

Questions and needs

Diffusion in high temperature materials

- large atoms with large partition coefficient
- segregation to coherent interfaces
- role of misfit strain on diffusion
- pipe diffusion and creep



Mohan
Rajendran

Conclusion

- A phase-field model for heterogeneous (non) equilibria is established. It gives a thermodynamic consistent treatment of transformations with a potential jumps.
- Examples demonstrate the importance of well established kinetic coefficients, and the necessity to include stress driven diffusion.
- The designer's need are predictive models based on data suited for these models.

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