Principe des modèles à champ de phase et utilisation dans les substances multi-composants

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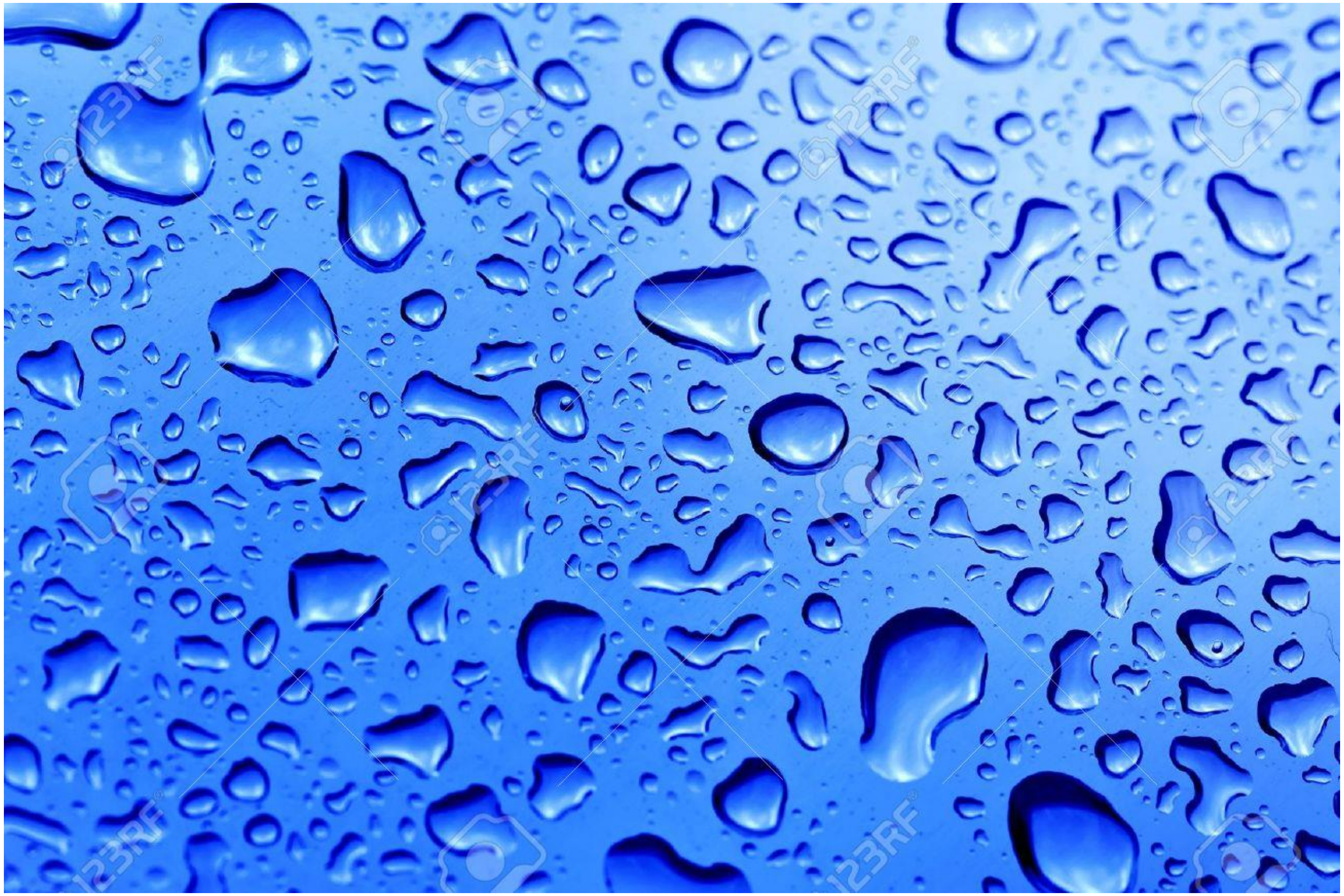
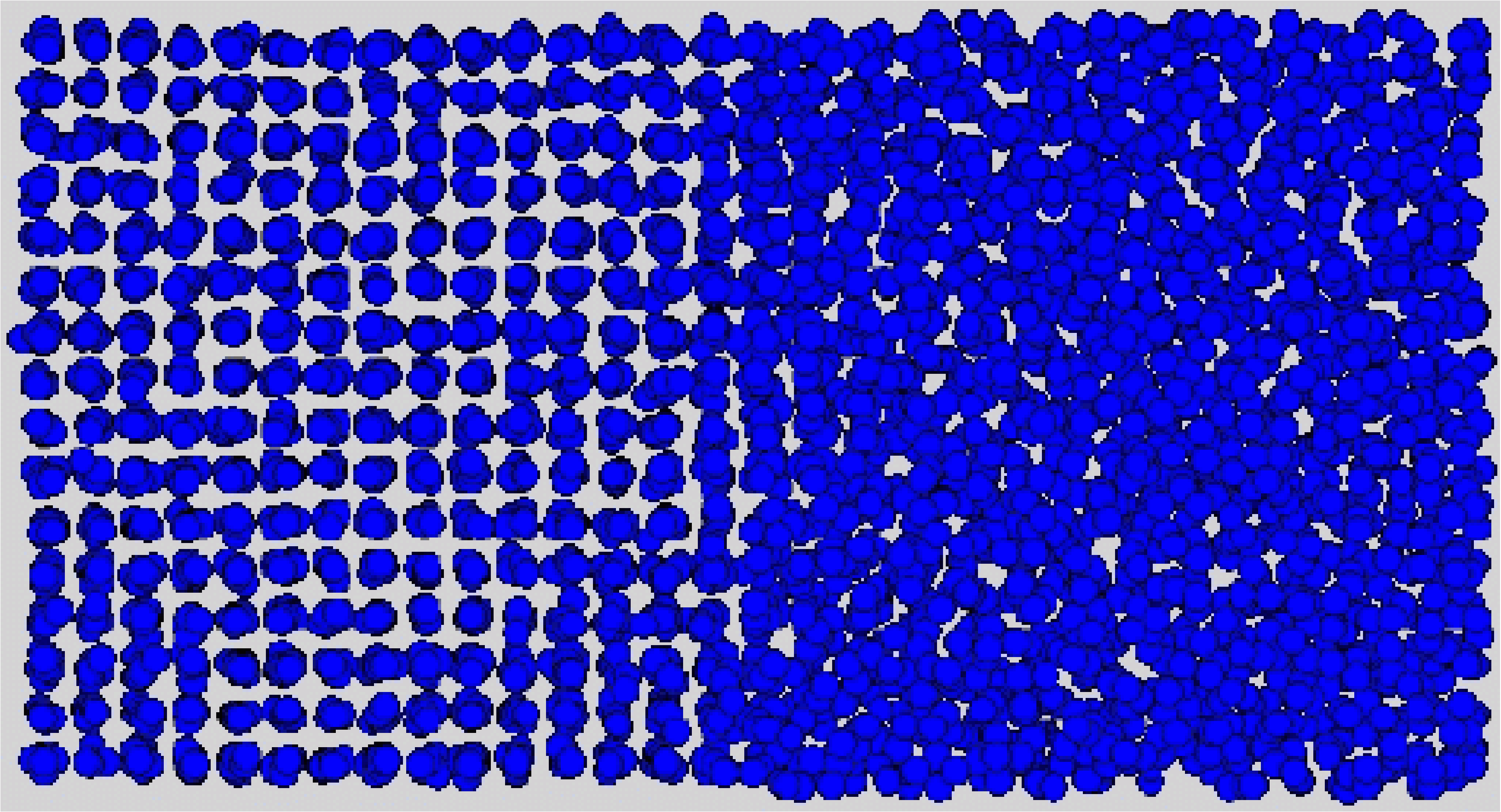
Interfaces



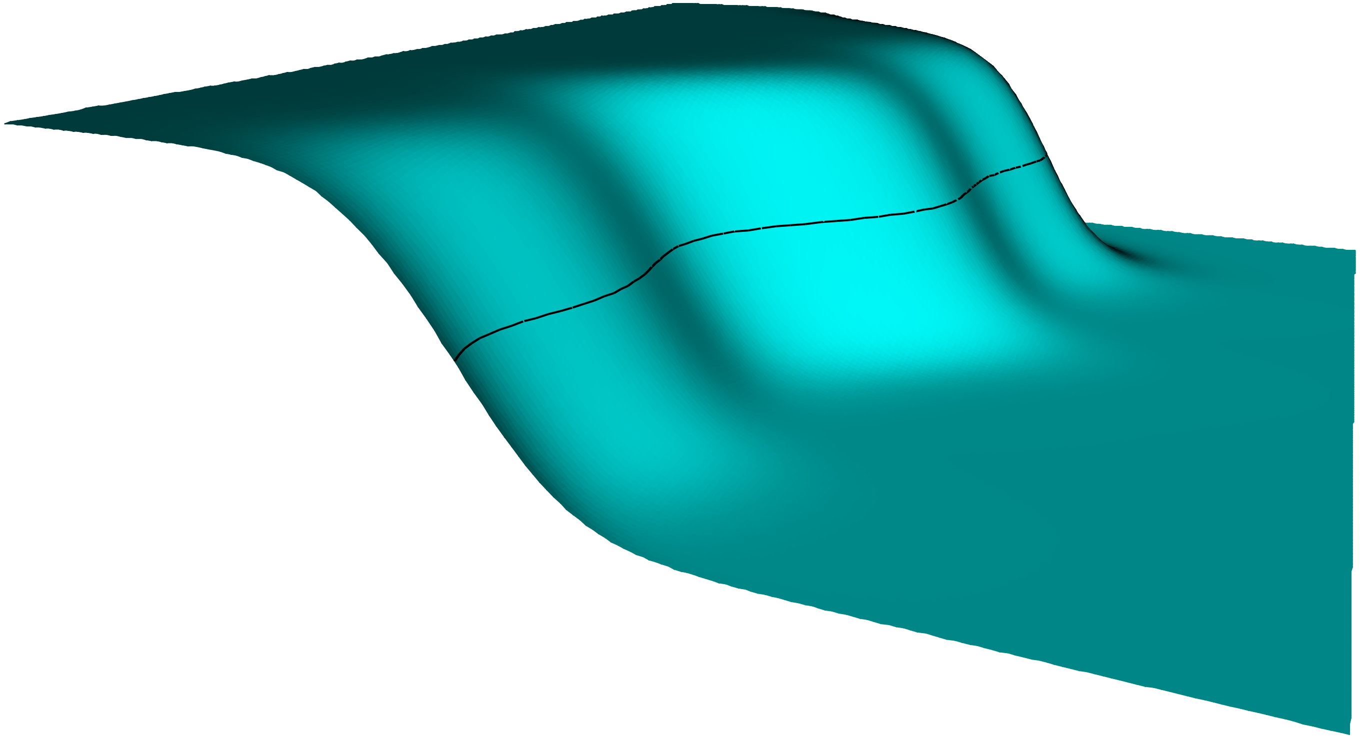
Macroscopic scale: an interface appears as a sharp dividing surface

Scales and descriptions



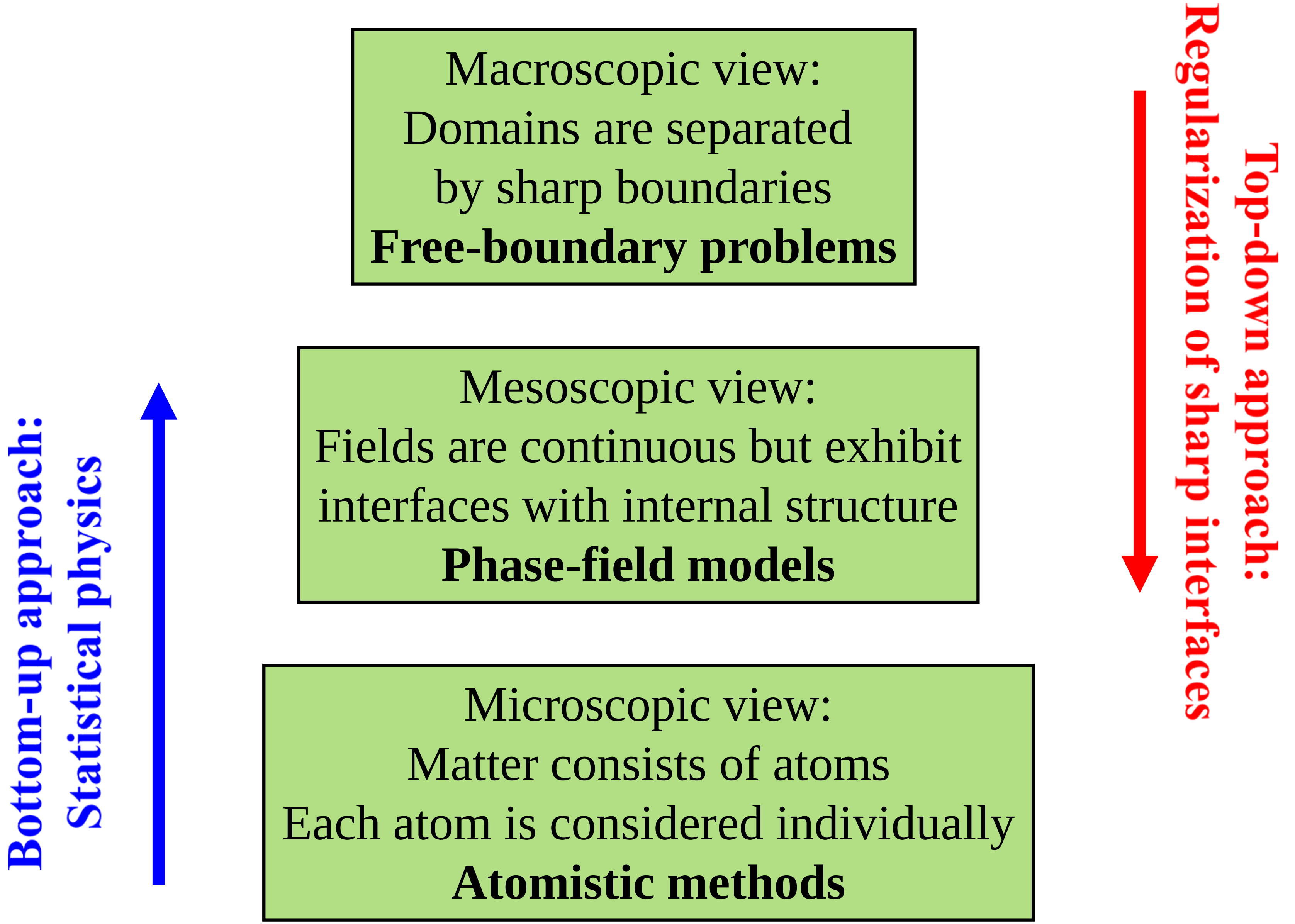
Microscopic scale: matter consists of atoms, which can exhibit spatial order (or not) (Molecular dynamics simulation, B. Laird)

Diffuse-interface picture



Mesoscopic scale: the interface can be described by a continuum theory, but has an internal structure and a finite width (picture: R. Folch)

Scales and descriptions



Macroscopic view:
Domains are separated
by sharp boundaries
Free-boundary problems

Mesoscopic view:
Fields are continuous but exhibit
interfaces with internal structure
Phase-field models

Microscopic view:
Matter consists of atoms
Each atom is considered individually
Atomistic methods

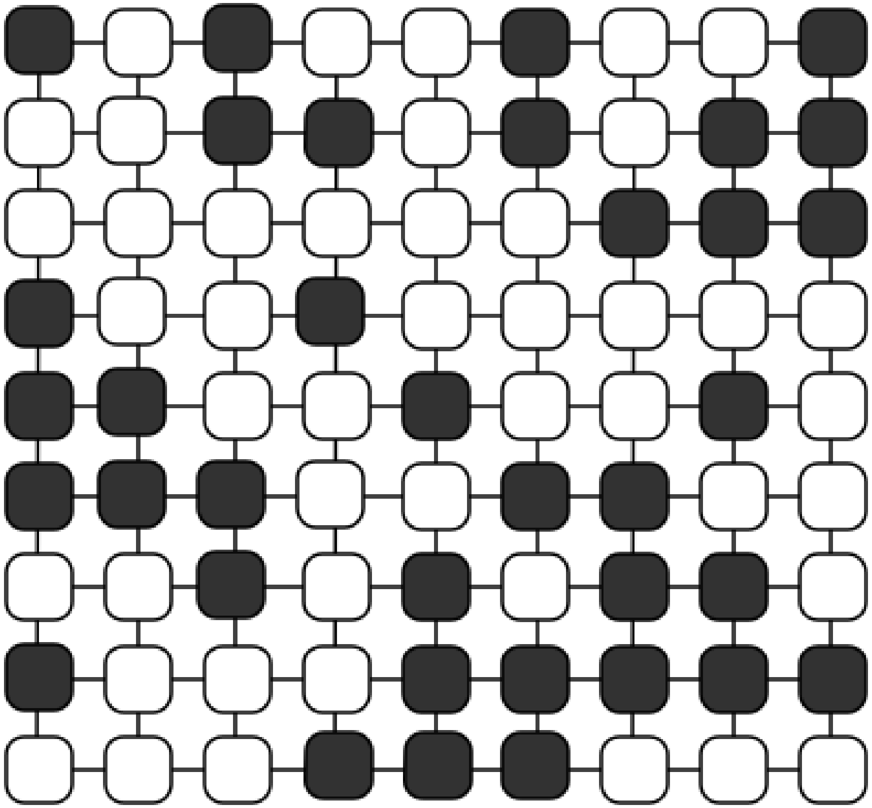
Bottom-up approach:
Statistical physics

Top-down approach:
Regularization of sharp interfaces

Bottom-up approach: physics of phase transitions

- J. S. Langer, « An introduction to the kinetics of first-order phase transitions », in *Solids far from equilibrium*, Cambridge university press
- M. Plapp, « Phase-field models », in *Multiphase microfluidics: The diffuse interface method*, CISM lectures 538, Springer 2012
- M. Plapp, « *Phase-field models* », in Handbook of Crystal Growth, Elsevier (2015)

Lattice alloy model



- Toy model for solid solutions
- Each lattice site can be occupied by an A atom (black) or a B atom (white)
- Atoms interact with their nearest neighbors
- Can be easily generalized to more species or longer range interactions

$$\mathbf{H} = \sum_{\langle \mathbf{i},\mathbf{j} \rangle} \mathbf{V}_{\mathbf{AA}} \mathbf{n}_{\mathbf{i}}^{\mathbf{A}} \mathbf{n}_{\mathbf{j}}^{\mathbf{A}} + \mathbf{V}_{\mathbf{BB}} \mathbf{n}_{\mathbf{i}}^{\mathbf{B}} \mathbf{n}_{\mathbf{j}}^{\mathbf{B}} + \mathbf{V}_{\mathbf{AB}} \left(\mathbf{n}_{\mathbf{i}}^{\mathbf{A}} \mathbf{n}_{\mathbf{j}}^{\mathbf{B}} + \mathbf{n}_{\mathbf{i}}^{\mathbf{B}} \mathbf{n}_{\mathbf{j}}^{\mathbf{A}} \right)$$

Free energy

By a simple mean-field approximation, we obtain

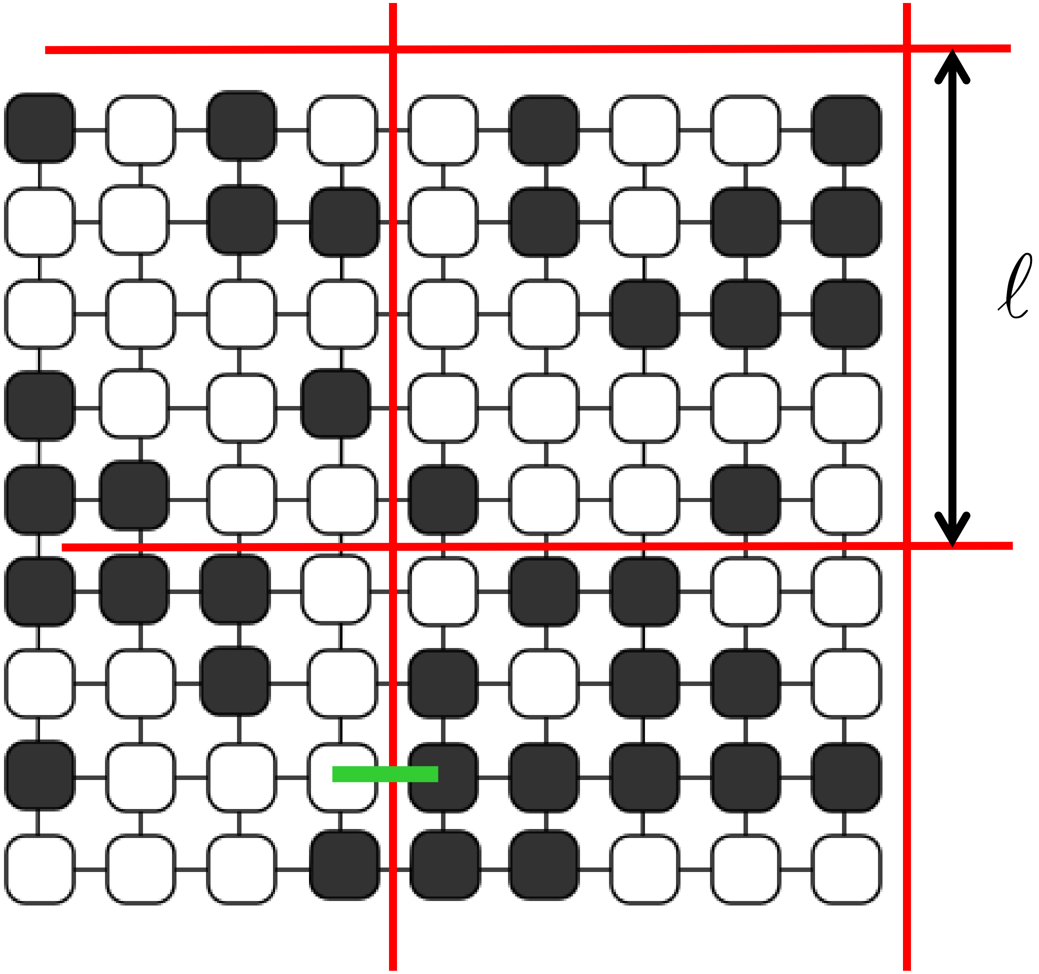
$$\frac{\mathbf{F}}{\mathbf{N}} = \frac{\mathbf{z}\tilde{\mathbf{V}}}{2}\mathbf{c}(1-\mathbf{c}) + \mathbf{k_B T}\left[\mathbf{c}\log\mathbf{c} + (1-\mathbf{c})\log(1-\mathbf{c})\right]$$

$$\tilde{\mathbf{V}} = \mathbf{V_{AA}} + \mathbf{V_{BB}} - 2\mathbf{V_{AB}} \qquad \mathbf{c} = \frac{\mathbf{N_B}}{\mathbf{N}}$$

Above the critical temperature: single well

Below the critical temperature: double well → phase separation

Inhomogeneous systems



- The concentration depends on space
- Idea: coarse-graining
- Need to take into account interactions between neighboring cells

!! Attention !! Supposes that there is a scale hierarchy:

Lattice spacing $\ll \ell \ll$ scales of interest

Free-energy functional

In the continuum limit: Ginzburg-Landau free energy functional

$$F = \int_V \left[\frac{K}{2} (\nabla c)^2 + f(c) \right] dV \qquad K \propto \tilde{V}$$

The square gradient coefficient is proportional to the interaction strength

Dynamics

Conserved dynamics: $$\frac{\partial c}{\partial t} = -\nabla \cdot J$$

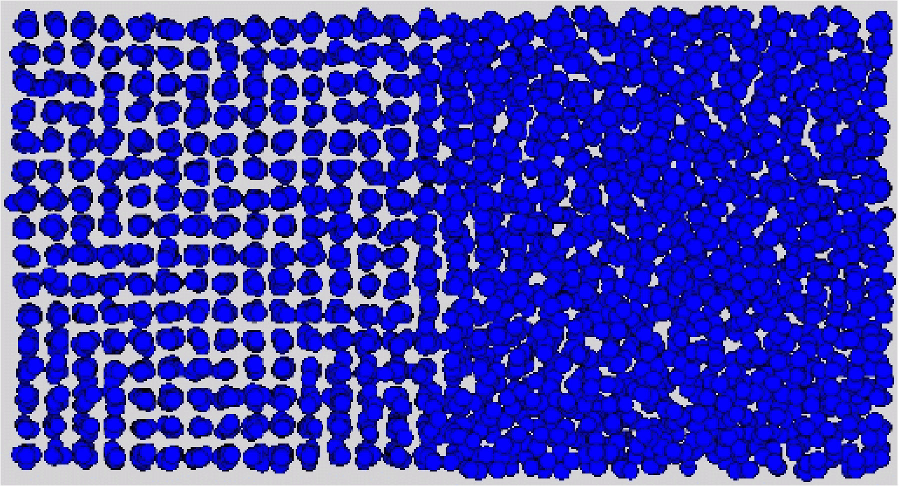
$$J = -M\nabla\mu \qquad \mu = \frac{\delta F}{\delta c}$$

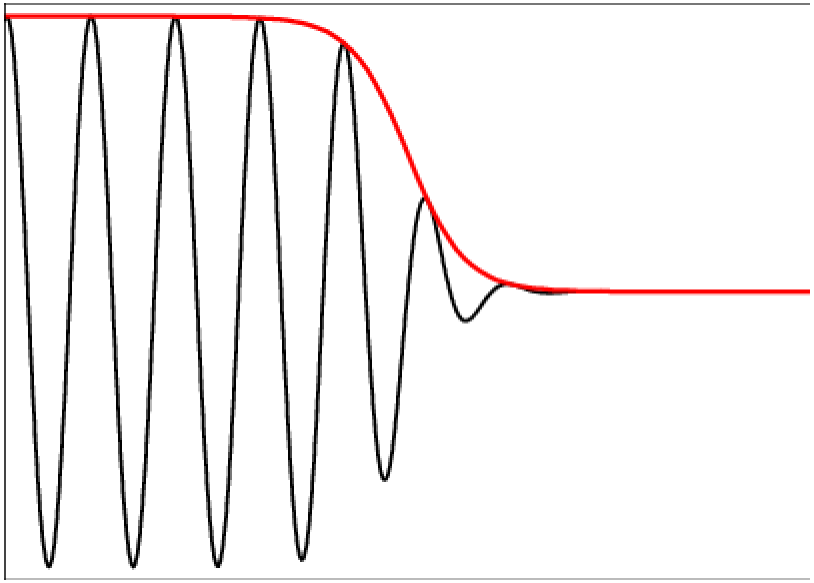
μ: diffusion potential

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M\nabla\left(-K\nabla^2 c + f'(c) \right) \right]$$

Cahn-Hilliard equation or **model B**

Order parameter for the solid-liquid transition





An order parameter ϕ
can be defined in several ways:

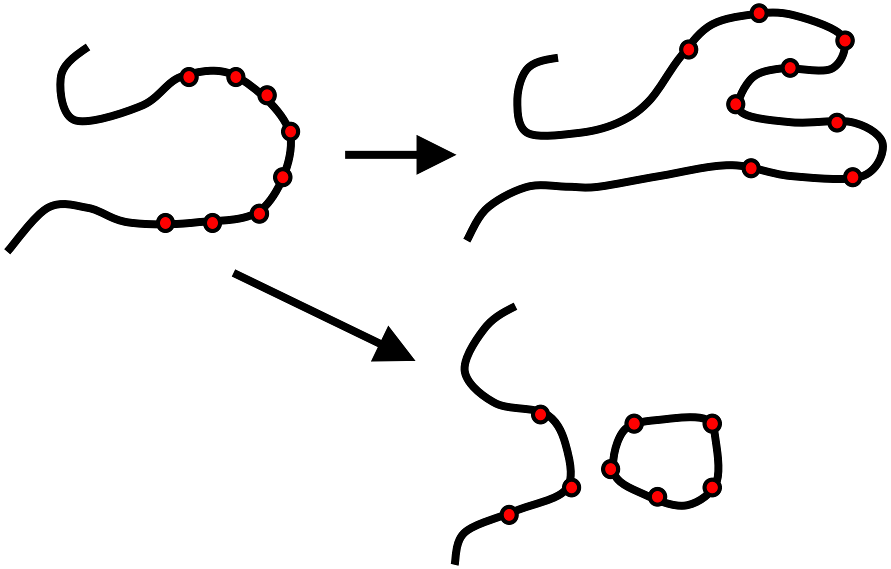
- Bond-angle order parameter (MD)
- Envelope of density oscillations

The latter can be calculated quite rigorously from DFT if the interface width is large compared to the lattice constant

ϕ: order parameter or indicator function

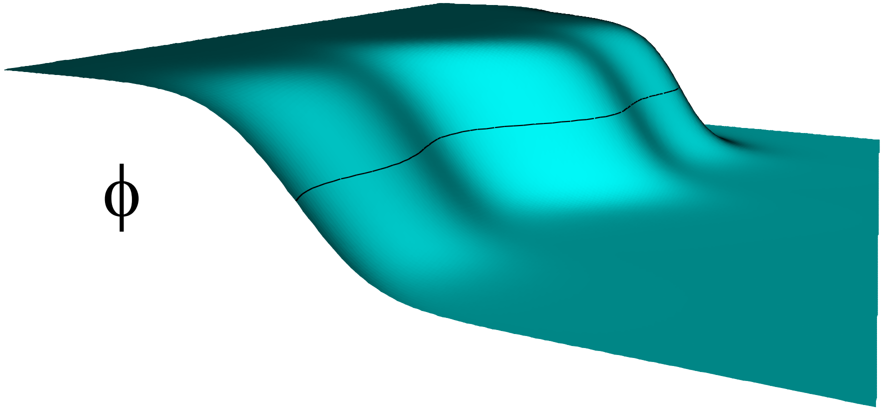
Top-down approach: matched asymptotics

Phase-field models : basic idea



Explicit
tracking of interfaces
+
Boundary conditions

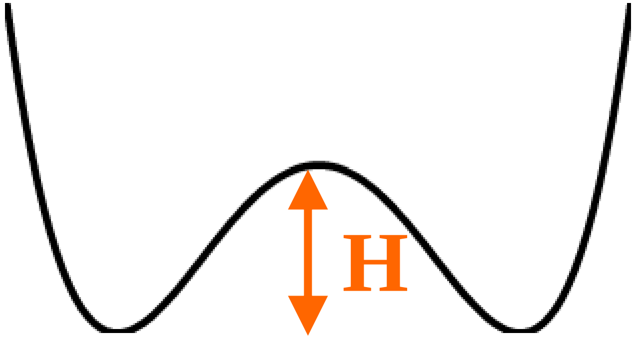
Implicit
description of interfaces
+
Evolution equation



Free energy functional

$$\mathbf{F} = \int_V \mathbf{K}(\nabla\phi)^2 + \mathbf{H}\mathbf{f}_{dw}(\phi)$$

For example : $$\mathbf{f}_{dw}(\phi) = -\phi^2/2 + \phi^4/4$$

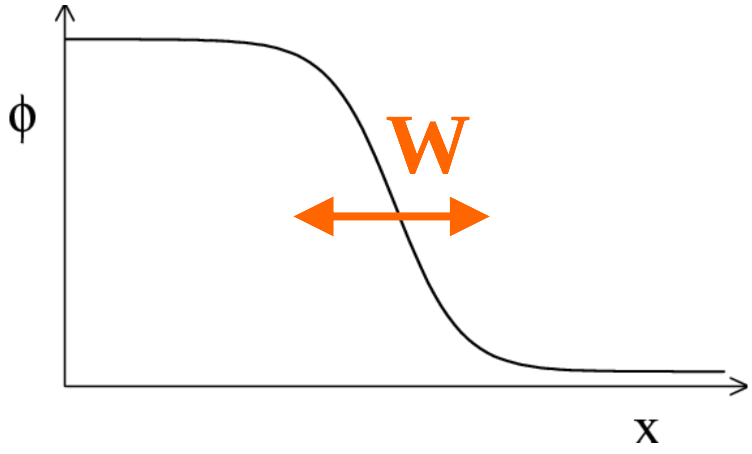


General scaling relations :

H : energy/volume
K : energy/length

$$\mathbf{W} \sim \sqrt{\mathbf{K}/\mathbf{H}}$$

$$\gamma \sim \sqrt{\mathbf{KH}} = \mathbf{HW}$$



Coupling to temperature

Free energy density :

$$\mathbf{f}(\mathbf{T},\phi)=\mathbf{f}(\mathbf{T_m},\phi)+\left.\frac{\partial \mathbf{f}(\mathbf{T},\phi)}{\partial \mathbf{T}}\right|_{\mathbf{T_m}}(\mathbf{T}-\mathbf{T_m})$$

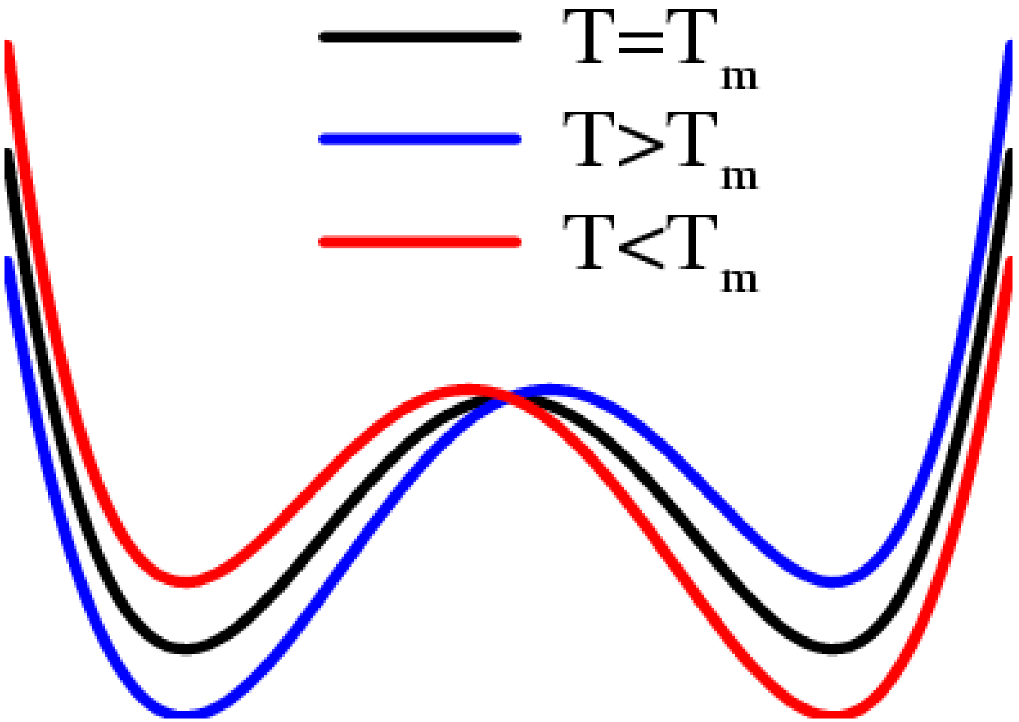
$$\left.\frac{\partial \mathbf{f}(\mathbf{T},\phi)}{\partial \mathbf{T}}\right|_{\mathbf{T_m}}=-\mathbf{s}(\mathbf{T_m},\phi)$$

$$\mathbf{s}(\phi)=\mathbf{s_S}\frac{\mathbf{1}+\mathbf{g}(\phi)}{\mathbf{2}}+\mathbf{s_L}\frac{\mathbf{1}-\mathbf{g}(\phi)}{\mathbf{2}}$$

g : tilting function

Must satisfy

$$\mathbf{g}'(\pm\mathbf{1})=\mathbf{0}$$
$$\mathbf{g}(\pm\mathbf{1})=\pm\mathbf{1}$$



Evolution equations

$$\partial_t \phi = -\Gamma \frac{\delta F}{\delta \phi}$$

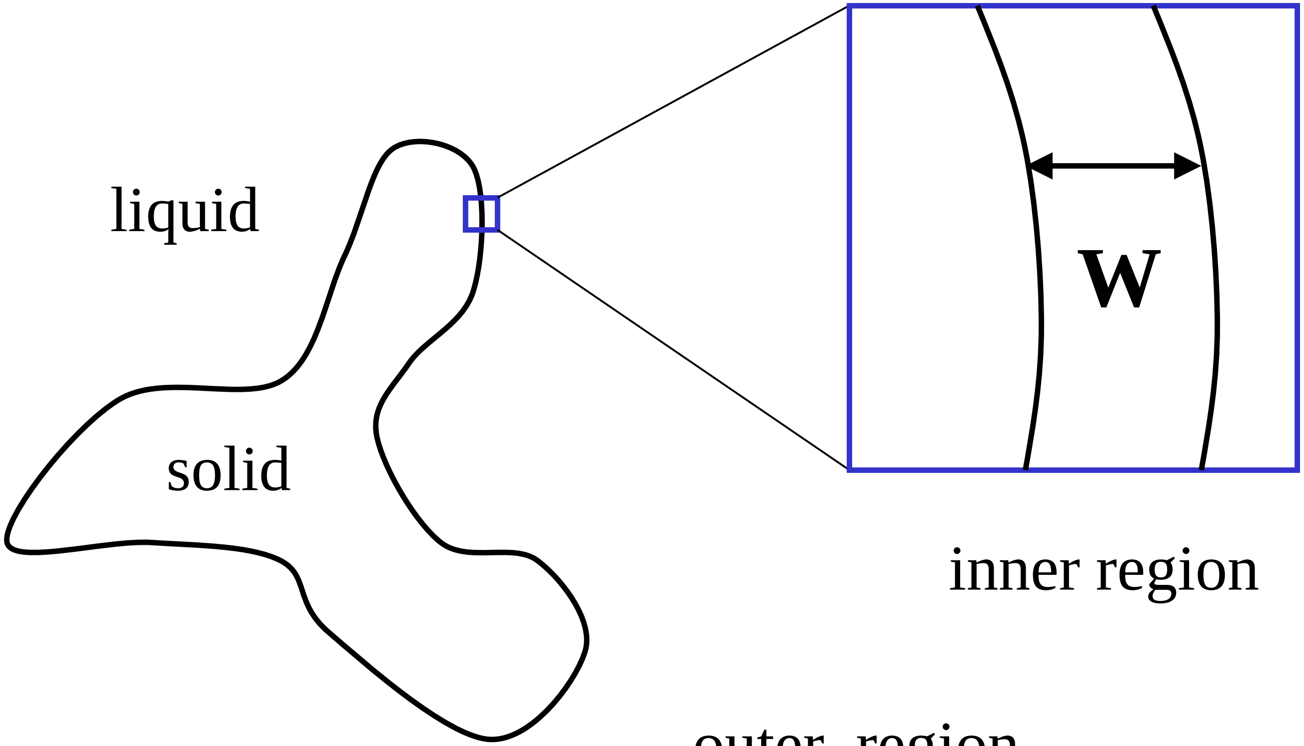
$$c = T\frac{\partial s}{\partial T}$$

$$\left.\begin{aligned} de &= T\,ds = T\left(\frac{\partial s}{\partial T}\,dT + \frac{\partial s}{\partial \phi}\,d\phi\right) \\ \partial_t e &= \nabla\left(\kappa \nabla T\right) \end{aligned}\right\}$$

$$cD$$

$$\Rightarrow \quad \partial_t T = \nabla\left(D\nabla T\right) + \frac{L}{2c}\,g'(\phi)\,\partial_t \phi$$

Principle of matched asymptotic expansions



liquid

solid

W

inner region

outer region

$$\mathbf{W \ll R}$$

$$\mathbf{W \ll D / v_n}$$

- inner region (scale **W**): calculation with constant $\boldsymbol{\kappa}$ and $\mathbf{v_n}$
- outer region (macroscale): simple solution because $\boldsymbol{\phi}$ constant
- matching of the two solutions close to the interface

Example in 3D: A dendrite

Anisotropy:

$$\mathbf{W} \rightarrow \mathbf{W}(\hat{\mathbf{n}})$$

$$\boldsymbol{\tau} \rightarrow \boldsymbol{\tau}(\hat{\mathbf{n}})$$

$$\hat{\mathbf{n}} = -\frac{\nabla\phi}{|\nabla\phi|}$$

Can be generalized to alloys in two ways:
two-phase approach (Kim-Kim-Suzuki 1999) or
grand-canonical formulation (Plapp 2011)

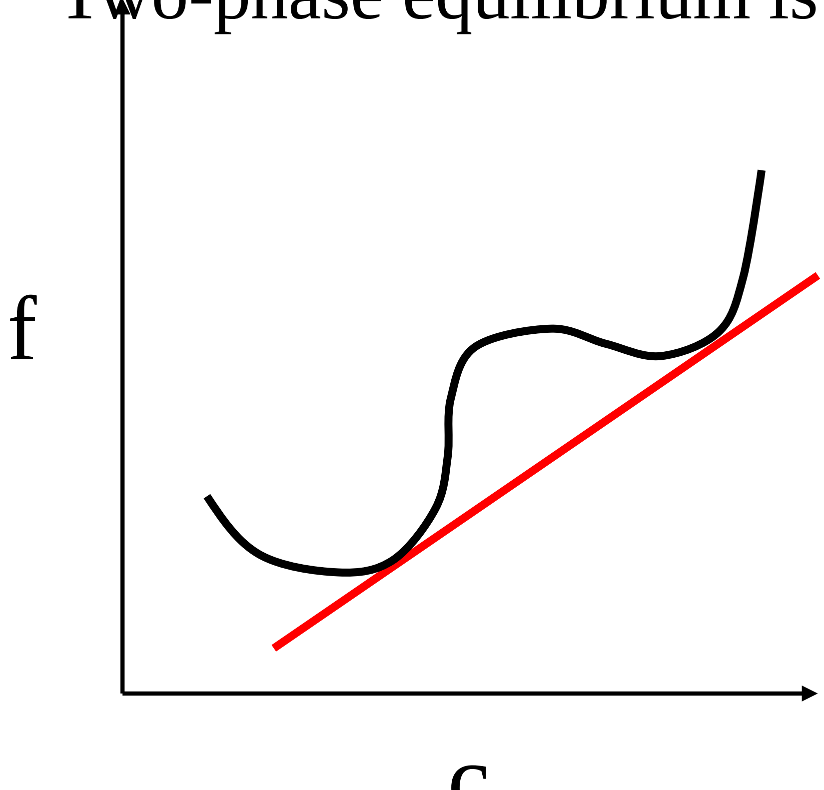
Coupling to CALPHAD

Cahn-Hilliard formulation

Suppose that CALPHAD gives us a free energy f(c):

$$\mathbf{F}=\int_V\left[\frac{K}{2}(\nabla c)^2+f(c)\right]dV$$

Two-phase equilibrium is given by the common tangent:

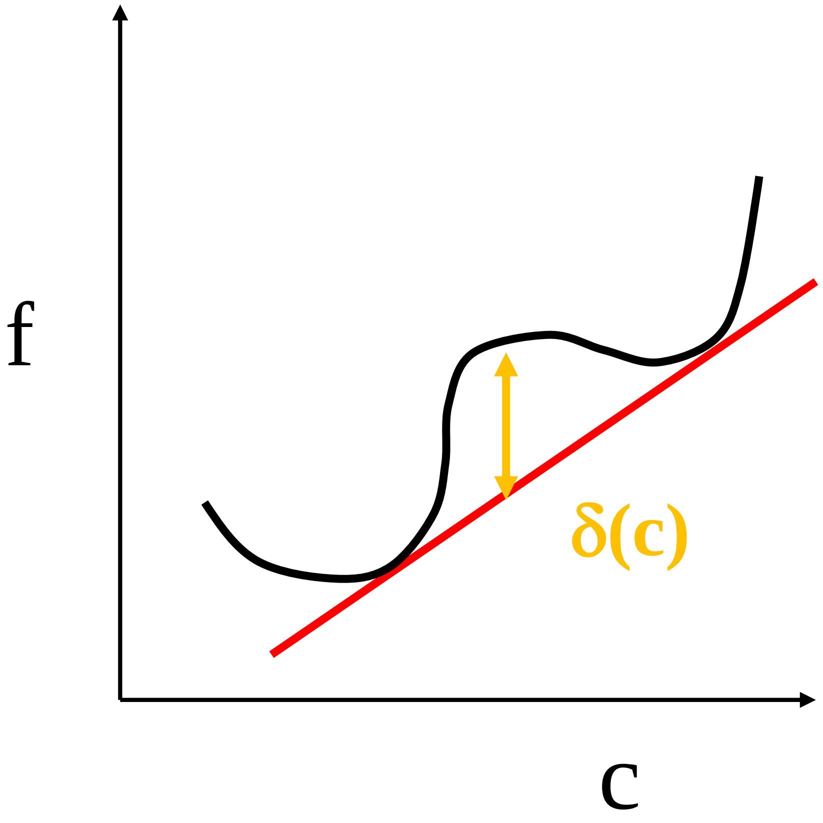


$$\mu_{eq}=\left.\frac{\partial f}{\partial c}\right|_{c_1}=\left.\frac{\partial f}{\partial c}\right|_{c_2}$$

$$f(c_1)-f(c_2)=\mu_{eq}(c_1-c_2)$$

Interface structure

The interface profile is determined by the equation



$$\frac{1}{2}K(\partial_x c)^2 = \delta(c(x))$$

Surface energy:

$$\gamma = \int_{-\infty}^{+\infty} K(\partial_x c)^2 dx$$

Consequence: the surface energy and the interface thickness are determined by K and f(c).

More flexibility ?

Possibility 1: introduce scaling coefficient for f(c)
(Ph.D. thesis of C. Cardon; Cardon, Le Tellier, Plapp 2016)

$$\mathbf{F} = \int_V \left[\frac{\mathbf{K}}{2} \left(\nabla \mathbf{c} \right)^2 + \mathbf{A f}\left(\mathbf{c} \right) \right] \mathbf{dV}$$

$$\Rightarrow \gamma \propto \sqrt{\mathbf{KA}} \quad \mathbf{W} \propto \sqrt{\mathbf{K/A}}$$

Possibility 2: describe each phase by a separate free energy function and use a phase-field description (as of yet unexplored)

Multi-component systems

Simplest case: ternary

Two independent composition variables c_A, c_B

$$\mathbf{F} = \int_V \left[\sum_{i,j=A,B} \frac{1}{2} K_{ij} \nabla c_i \cdot \nabla c_j + f(c_A, c_B) \right] dV$$

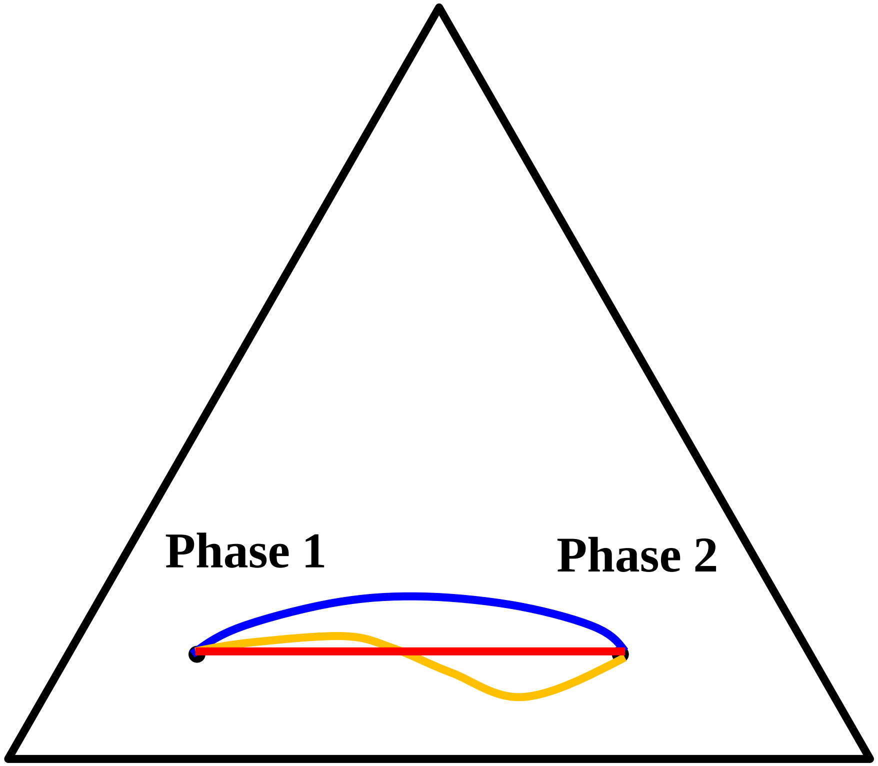
The coefficients K_{ij} form a symmetric 2×2 matrix

The interface profile is determined by two coupled equations

Problem: the surface energy is a function of K_{AA}, K_{AB}, and K_{BB}: the K matrix remains **undetermined**

Interface adsorption

Visualization of interface « trajectory » in the Gibbs simplex:



The interface structure and the total interface adsorption depend on the choice of the K matrix !

Solutions ?

Develop a CALPHAD description for the gradient energy coefficients that is consistent with the bulk description

Use a phase-field description: separate bulk free energies for the two phases and a single phase field for the interface

Dynamics

Conserved dynamics:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i$$

$$J_i = -\sum_j M_{ij} \nabla \mu_j \qquad \mu_i = \frac{\delta F}{\delta c_i}$$

Problem: mobility matrix Mij is needed. Can be related to diffusion matrix, but very little information is available.

Conclusions

Diffuse-interface methods are a useful tool for the modeling of interface dynamics

They are based on non-equilibrium thermodynamics

More work is needed to establish a solid relation to CALPHAD free energies in multi-component systems