

# **Fundamentals of MPF Modelling**

## **Formulation of the Free Energy Functional and the Relaxation Approach**

**Janin Eiken**

# General Multi-phase Free Energy Functional

$\{\phi_\alpha\} = \phi_{\alpha=1..\nu}$      $\tilde{\nu}$  = reduced number of locally interacting phases (  $|\nabla\phi| > 0$ .)

$$F = \int_V \left[ \underbrace{\sum_{\alpha}^{\nu} \phi_{\alpha} f_{\alpha}}_{\text{bulk contributions}} + \underbrace{\sum_{\alpha}^{\tilde{\nu}} \sum_{\beta=\alpha+1}^{\tilde{\nu}} \sigma_{\alpha\beta} \left( \frac{4}{\eta} \phi_{\alpha} \phi_{\beta} - \frac{4\eta}{\pi^2} \nabla\phi_{\alpha} \nabla\phi_{\beta} \right)}_{\text{interface contributions}} \right] dV$$

General formulation of a multiphase free energy functional:

$$F(\{\phi_{\alpha}\}) = \underbrace{\sum_{\alpha=1}^{\nu} F_{\alpha}(\phi_{\alpha})}_{\text{bulk energies}} + \underbrace{\sum_{\alpha=1}^{\tilde{\nu}} \sum_{\beta=\alpha}^{\tilde{\nu}} F_{\alpha\beta}(\phi_{\alpha}, \phi_{\beta})}_{\text{interface energies}} + \underbrace{\sum_{\alpha=1}^{\tilde{\nu}} \sum_{\beta=\alpha}^{\tilde{\nu}} \sum_{\gamma=\beta}^{\tilde{\nu}} F_{\alpha\beta\gamma}(\phi_{\alpha}, \phi_{\beta}, \phi_{\gamma})}_{\text{triple junction energies}} + \dots$$

# General Relaxation Approach for Multiphase systems

General relaxation approach:

$$\dot{\phi}_\alpha = \underbrace{\sum_\alpha^v \mathbf{M}_\alpha^\phi \left( \frac{\delta F}{\delta \phi_\alpha} \right)}_{\text{bulk mobilities}} \overset{0.}{\cancel{\left( \frac{\delta F}{\delta \phi_\alpha} \right)_{\phi_{\delta \neq \alpha}}}} + \underbrace{\sum_\alpha^{\tilde{v}} \sum_{\beta=\alpha+1}^{\tilde{v}} \mathbf{M}_{\alpha\beta}^\phi \left[ \left( \frac{\delta F}{\delta \phi_\beta} \right)_{\phi_{\delta \neq \alpha}} - \left( \frac{\delta F}{\delta \phi_\alpha} \right)_{\phi_{\delta \neq \beta}} \right]}_{\text{interface mobilities}} + \text{triple junction mobilities} + \dots$$

- A phase cannot change its state without interaction to another phase (→ zero bulk mobility  $M_\alpha$ ).
- interface mobilities  $M_{\alpha\beta}$  have to be specified for pairwise phase interaction. (Cannot be separated into individual phase mobilities  $M_\alpha$  and  $M_\beta$ .)
- Higher order junctions terms can be used to model local deviation from Young's law. (→ Zero junction terms under assumption of negligible junction drag.)

J. Eiken: thesis (2009)

# Handling of dependent PF parameters in two-phase formulation

**There generally exist two equivalent ways to handle two phase systems:**

1.) Free energy of two-phase system described based on **single independent parameter**

$$F_{\alpha\beta}(\phi_\beta) = \int_V \left[ (1 - h_{\alpha\beta}(\phi_\beta)) f_\alpha + h_{\alpha\beta}(\phi_\beta) f_\beta + W_{\alpha\beta} g(\phi_\beta) + \frac{\varepsilon_{\alpha\beta}^2}{2} |\nabla \phi_\beta|^2 \right] dV$$

2.) Free energy of two-phase system described based on **two dependent parameters**

**with constraint:**

$$F(\phi_\alpha, \phi_\beta) = \int_V \left[ (h(\phi_\alpha, \phi_\beta) f_\alpha + h_{\alpha\beta}(\phi_\alpha, \phi_\beta) f_\beta + W_{\alpha\beta} g(\phi_\alpha, \phi_\beta) + \frac{\varepsilon_{\alpha\beta}^2}{2} \nabla \phi_\alpha \nabla \phi_\beta) \right] dV$$

$$\begin{aligned} \dot{\phi}_\alpha &= -\dot{\phi}_\beta, \\ \phi_\alpha &= 1 - \phi_\beta \end{aligned}$$

**The relaxation approach depends on which of the two formulations was chosen!**

J. Eiken: thesis (2009)

# Relaxation Approach for Two-phase System

1.) Free energy of two-phase system described by **single independent parameter**

$$F_{\alpha\beta}(\phi_\beta) = \int_V \left[ (1 - h_{\alpha\beta}(\phi_\beta)) f_\alpha + h_{\alpha\beta}(\phi_\beta) f_\beta + W_{\alpha\beta} g(\phi_\beta) + \frac{\varepsilon_{\alpha\beta}^2}{2} |\nabla \phi_\beta|^2 \right] dV$$

$$\dot{\phi}_\beta = -M_{\alpha\beta} \frac{\partial F_{\alpha\beta}(\phi_\beta)}{\delta \phi_\beta} \quad (\dot{\phi}_\alpha = -\dot{\phi}_\beta)$$

2.) Free energy of two-phase system described by **two dependent parameters**

$$F(\phi_\alpha, \phi_\beta) = \int_V \left[ (h(\phi_\alpha, \phi_\beta) f_\alpha + h_{\alpha\beta}(\phi_\alpha, \phi_\beta) f_\beta + W_{\alpha\beta} g(\phi_\alpha, \phi_\beta) + \frac{\varepsilon_{\alpha\beta}^2}{2} \nabla \phi_\alpha \nabla \phi_\beta) \right] dV$$

constraint:

$$\begin{aligned} \dot{\phi}_\alpha &= -\dot{\phi}_\beta, \\ \phi_\alpha &= 1 - \phi_\beta \end{aligned}$$

$$\dot{\phi}_\alpha = M_{\alpha\beta} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\beta} \right)_{\phi_\alpha} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\alpha} \right)_{\phi_\beta} \right]$$

$$\dot{\phi}_\beta = M_{\alpha\beta} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\alpha} \right)_{\phi_\beta} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\beta} \right)_{\phi_\alpha} \right]$$

J. Eiken: thesis (2009)

# Short Consistency Check for Two-phase System

1.) Independent free energy functional and relaxation approach:

$$F_{\alpha\beta}(\phi_\beta) = \int_V [(1 - \phi_\beta) f_\alpha + \phi_\beta f_\beta + \dots] dV$$

$$\dot{\phi}_\beta = -M_{\alpha\beta} \frac{\partial F_{\alpha\beta}(\phi_\beta)}{\delta \phi_\beta}$$

$$= M_{\alpha\beta} (f_\alpha - f_\beta) + \dots \quad \dot{\phi}_\alpha = -\dot{\phi}_\beta = M_{\alpha\beta} (f_\beta - f_\alpha) - \dots$$

2.) Dependent free energy functional and relaxation approach

$$F(\phi_\alpha, \phi_\beta) = \int_V [\phi_\alpha f_\alpha + \phi_\beta f_\beta + \dots] dV$$

**In two-phase systems both formulations  
yield the same kinetic equations!**

$$\dot{\phi}_\alpha = M_{\alpha\beta} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\beta} \right)_{\phi_\alpha} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\alpha} \right)_{\phi_\beta} \right]$$

$$= M_{\alpha\beta} (f_\beta - f_\alpha) - \dots$$

$$\dot{\phi}_\beta = M_{\alpha\beta} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\alpha} \right)_{\phi_\beta} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta)}{\delta \phi_\beta} \right)_{\phi_\alpha} \right]$$

$$= M_{\alpha\beta} (f_\alpha - f_\beta) + \dots$$

$$F(\phi_\alpha, \phi_\beta) = \int_V [\phi_\alpha f_\alpha + \phi_\beta f_\beta + (1 - \phi_\alpha - \phi_\beta) f_\gamma] dV$$

implicit:

$$\phi_\gamma = 1 - \phi_\alpha - \phi_\beta$$

$$\dot{\phi}_\gamma = -\dot{\phi}_\alpha - \dot{\phi}_\beta$$

**Incomplete MPF relaxation approach** (widely spread in literature):

$$\dot{\phi}_\alpha = -M_\alpha \frac{\partial F(\phi_\gamma)}{\partial \phi_\alpha} = M_\alpha (f_\gamma - f_\alpha)$$

Only interactions of  $\alpha$  and  $\beta$  with reduced phase  $\gamma$ ,  
while  $\alpha\beta$  interactions are missing!

$$\dot{\phi}_\beta = -M_\beta \frac{\partial F(\phi_\alpha, \phi_\beta)}{\partial \phi_\beta} = M_\beta (f_\gamma - f_\beta)$$

Often used in solidification processes, where solid  
interactions are negligible, but even there leads to incorrect  
junction angles.

Complete equations with  $\alpha\beta$  interactions would be :

$$\dot{\phi}_\alpha = M_{\alpha\beta} (f_\beta - f_\alpha) + M_{\alpha\gamma} (f_\gamma - f_\alpha)$$
$$\dot{\phi}_\beta = M_{\beta\alpha} (f_\alpha - f_\beta) + M_{\beta\gamma} (f_\gamma - f_\beta)$$

**( Not suited for general MPF modelling. )**

# Complete Dependent Formulation of Three-Phase System

$$F(\phi_\alpha, \phi_\beta, \phi_\gamma) = \int_V [\phi_\alpha f_\alpha + \phi_\beta f_\beta + \phi_\gamma f_\gamma + \dots] dV$$

$$\begin{aligned} \dot{\phi}_\alpha &= M_{\alpha\beta} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\beta} \right)_{\phi_\alpha, \phi_\gamma} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} \right] + M_{\alpha\gamma} \left[ \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\gamma} \right)_{\phi_\alpha, \phi_\beta} - \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} \right] \\ &= M_{\alpha\beta} (f_\beta - f_\alpha) + M_{\alpha\gamma} (f_\gamma - f_\alpha) \quad \text{(equivalent derivation for } \beta \text{ and } \gamma) \end{aligned}$$

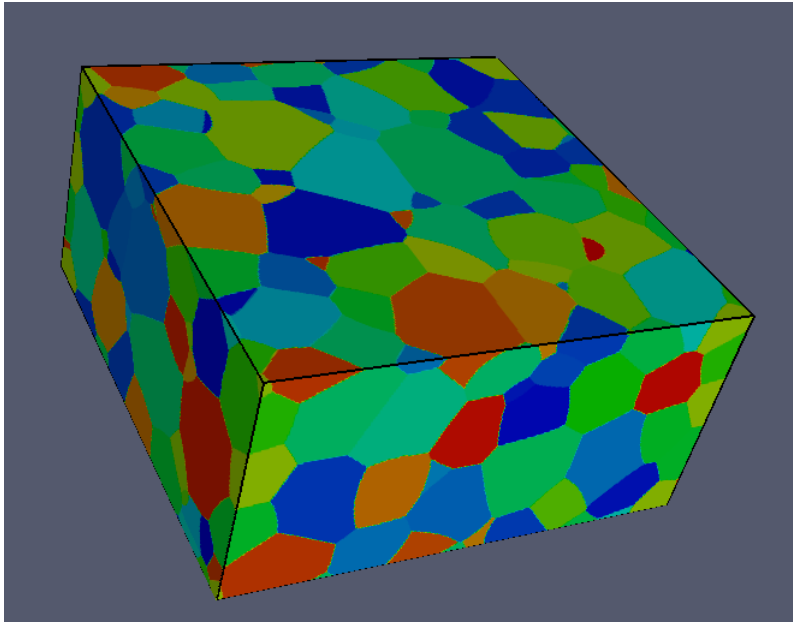
**Special case:**  $M = M_{\alpha\beta} = M_{\alpha\gamma}$

$$\begin{aligned} \frac{1}{M} \dot{\phi}_\alpha &= -2 \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} + \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\beta} \right)_{\phi_\alpha, \phi_\gamma} + \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\gamma} \right)_{\phi_\alpha, \phi_\beta} \\ \frac{1}{M} \dot{\phi}_\alpha &= -3 \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} + \underbrace{\left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} + \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\beta} \right)_{\phi_\alpha, \phi_\gamma} + \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\gamma} \right)_{\phi_\alpha, \phi_\beta}}_{3\lambda} \\ \tau \rightarrow \left( \frac{1}{3M} \right) \dot{\phi}_\alpha &= - \left( \frac{\delta F(\phi_\alpha, \phi_\beta, \phi_\gamma)}{\delta \phi_\alpha} \right)_{\phi_\beta, \phi_\gamma} + \lambda \end{aligned}$$

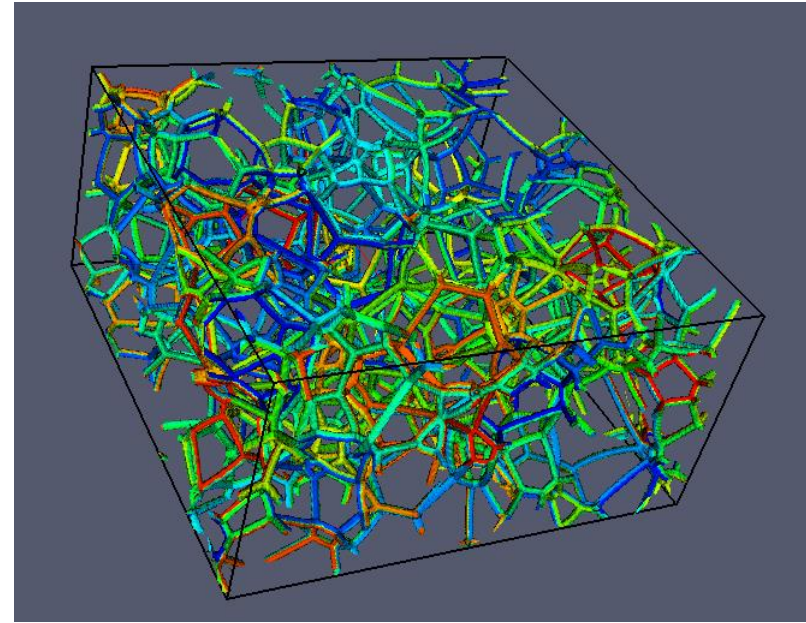
**Simplified handling of dependent terms by Lagrange multiplier  $\lambda$  only valid under assumption of equal interface mobilities !**



# MICRESS Free Energy Functional (based on dependent MPF parameters)



one phase-field for each grain:  $\phi_{\{\alpha\}} = \phi_{\alpha=1..v}$

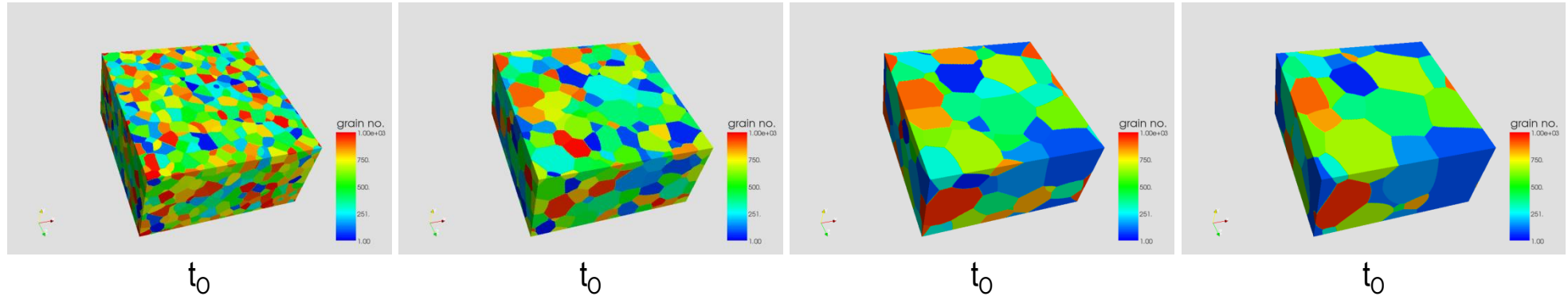


interfaces:  $\sum_{\alpha}^v \phi_{\alpha}(\bar{\mathbf{X}}, t) = 1$

$$F = \int_V \left[ \underbrace{\sum_{\alpha}^v \phi_{\alpha} f_{\alpha}}_{\text{thermodynamic contributions}} + \underbrace{\sum_{\alpha}^{\tilde{v}} \sum_{\beta=\alpha+1}^{\tilde{v}} \sigma_{\alpha\beta} \left( \frac{4}{\eta} \phi_{\alpha} \phi_{\beta} - \frac{4\eta}{\pi^2} \nabla \phi_{\alpha} \nabla \phi_{\beta} \right)}_{\text{interface contributions}} \right] dV$$

thermodynamic contributions + interface contributions

# MICRESS Relaxation Approach (based on dependent MPF parameters)



minimization of free energy with time

$$\dot{\phi}_{\alpha} = \sum_{\beta \neq \alpha}^v M_{\alpha\beta}^{\phi} \left[ \left( \frac{\delta F}{\delta \phi_{\beta}} \right)_{\phi_{\alpha}} - \left( \frac{\delta F}{\delta \phi_{\alpha}} \right)_{\phi_{\beta}} \right]$$

relaxation approach for dependent MPF parameter  
considering individual mobility of pairwise phase interaction

# Different Definition of MPF Mobility in Literature

J. Eiken, thesis, (2009)

$$\dot{\phi}_{\alpha} = \sum_{\beta \neq \alpha} \tilde{v} M_{\alpha\beta} \left[ \left[ \left( \frac{\delta F}{\delta \phi_{\beta}} \right)_{\phi_{\alpha}} - \left( \frac{\delta F}{\delta \phi_{\alpha}} \right)_{\phi_{\beta}} \right] \right]$$

former formulation in Steinbach F. Pezzolla, (1999), Physica D and Eiken et al. (2006):

$$\dot{\phi}_{\alpha} = \frac{1}{\tilde{v}} \sum_{\beta \neq \alpha} M_{\alpha\beta}^* \left[ \left[ \left( \frac{\delta F}{\delta \phi_{\beta}} \right)_{\phi_{\alpha}} - \left( \frac{\delta F}{\delta \phi_{\alpha}} \right)_{\phi_{\beta}} \right] \right]$$

$$M_{\alpha\beta}^* = \tilde{v} M_{\alpha\beta}$$

Models under assumption of equal mobility

$$M = \{M_{\alpha\beta}\}$$

$$\tau \dot{\phi}_{\alpha} = - \left( \frac{\delta F(\{\phi_{\alpha}\})}{\delta \phi_{\alpha}} \right)_{\phi_{\gamma \neq \alpha}} + \lambda$$

$$\tau = \frac{1}{\tilde{v}} \cdot \frac{1}{M}$$

$$\lambda = \frac{1}{\tilde{v}} \sum_{\alpha} \left( \frac{\delta F(\phi_{\alpha}, \phi_{\beta}, \phi_{\gamma})}{\delta \phi_{\alpha}} \right)_{\phi_{\gamma \neq \alpha}}$$

Consistency check for two phases

$$\frac{1}{2M} \dot{\phi}_{\beta} = - \frac{\partial F_{\alpha\beta}(\phi_{\beta})}{\delta \phi_{\beta}} + \frac{1}{2} \left[ \frac{\partial F_{\alpha\beta}(\phi_{\alpha}, \phi_{\beta})}{\delta \phi_{\alpha}} + \frac{\partial F_{\alpha\beta}(\phi_{\alpha}, \phi_{\beta})}{\delta \phi_{\beta}} \right]$$

$$\dot{\phi}_{\beta} = M \left[ \frac{\partial F_{\alpha\beta}(\phi_{\alpha}, \phi_{\beta})}{\delta \phi_{\beta}} - \frac{\partial F_{\alpha\beta}(\phi_{\alpha}, \phi_{\beta})}{\delta \phi_{\alpha}} \right]$$