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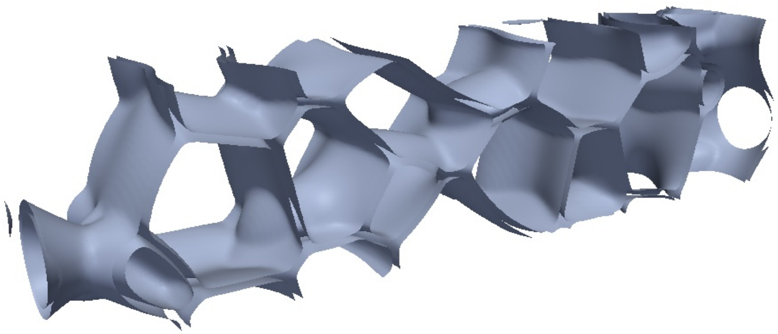

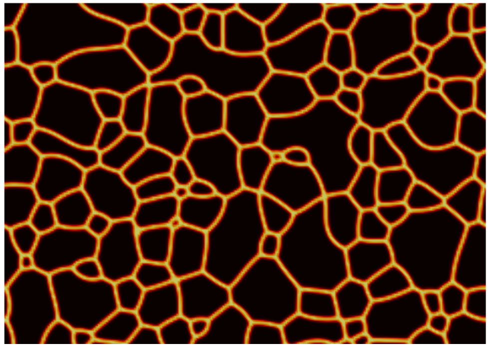

$$v_n = M\gamma H$$

$$\gamma = \Delta F - \Gamma \frac{\partial f_{mix}}{\partial c}\Big|_{eq}$$

$$\frac{\partial \phi_i}{\partial t} = -L_i \frac{\delta \mathcal{F}_{tot}}{\delta \phi_i}$$

$$\frac{\partial \mathbf{c}}{\partial \mathbf{t}} = \nabla \cdot \left[\mathbf{M_c} \nabla \left(\frac{\delta \mathcal{F}_{\mathbf{tot}}}{\delta \mathbf{c}} \right) \right]$$

Grain boundary segregation as a route to stabilize nanocrystalline alloys: A phase field study

Fadi Abdeljawad, Stephen M. Foiles

Computational materials and data science

U.S. DEPARTMENT OF ENERGY | Office of Science

NNSA National Nuclear Security Administration

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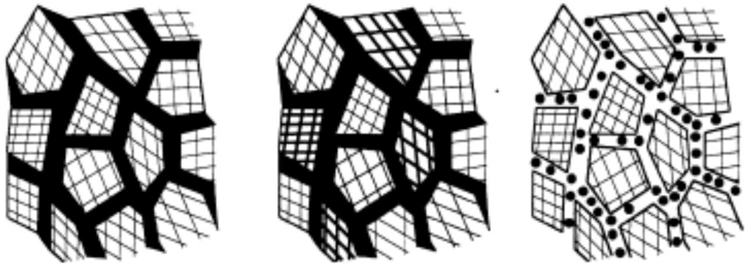
Introduction

- Nanostructured Materials (NMs)
  - Nanometric characteristic feature size

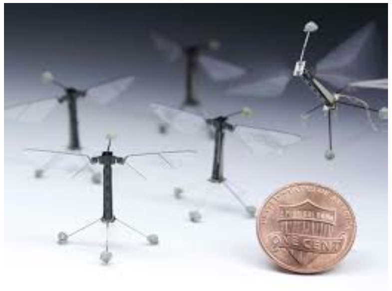
Chemical composition



H. Gleiter, Acta Mater. **48** (2000)

- Properties and applications
  - Strength, hardness and wear resistance
  - Thin film coatings
  - Miniaturization for biomedical and nanoelectronics

RoboBee



Ma et al., Science. **340** (2013)

- But …

Introduction

- **Problem:** Large portion of conjugation interfaces
  - Highly non-equilibrium states
  - Excess free energy: $\partial G = \gamma \partial A$
  - Grain-growth and homogenization processes

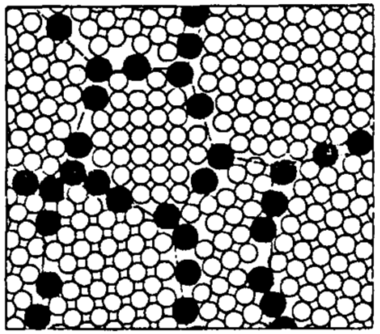
$$v_n = M_{gb} P_o = M_{gb} \gamma_{gb} H$$

Porter and Easterling (2004)

v_n	: Normal velocity
M	: GB mobility
γ	: GB energy
H	: Mean curvature

- **Possible solution:** solute segregation to GBs
  - Solute atoms preferentially occupy GB sites (mechanical or chemical)
  - $\underbrace{\text{Kinetic}}_{\text{GB mobility}}$ and/or $\underbrace{\text{thermodynamic}}_{\text{GB energy}}$ stabilization

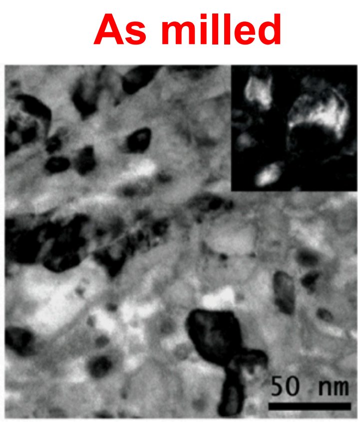
● **Solute**
○ **Host**

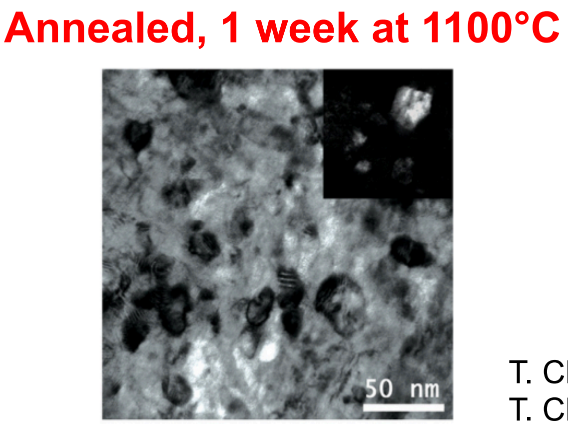


J. Weissmüller, Nanostruct. Mater. **3** (1993)

GB segregation: Experimental

- Sluggish growth dynamics: W-20 at.% Ti

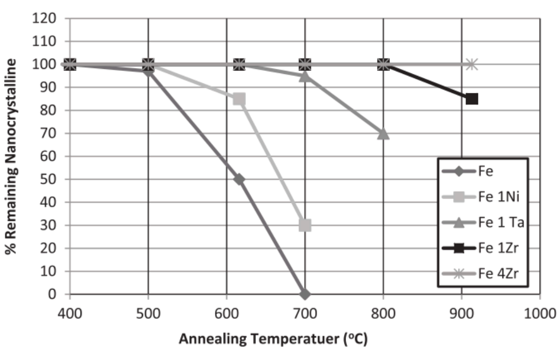


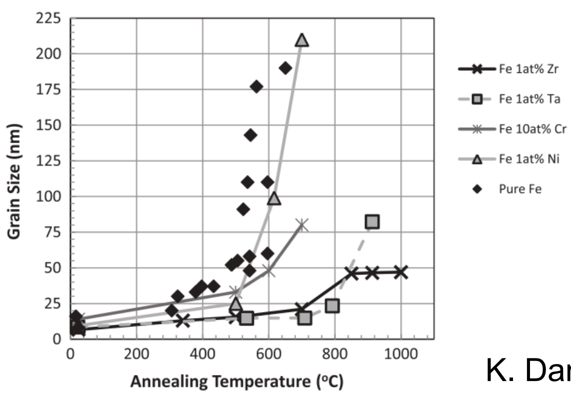


T. Chookajorn et al., Science. **337** (2012)
T. Chookajorn et al., Acta Mater. **73** (2014)

- Alloy selection in Fe-based systems

Addition of Ta, Cr, Ni and Zr





K. Darling et al., Mat. Sci. Eng. A **528** (2011)

GB segregation: Theory/Modeling

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- Analytical
  - Gibbs adsorption: $\Gamma = -\left(\frac{\partial \gamma_{gb}}{\partial \mu}\right)_{P,T}$
  - GB energy vs. solute concentration: J. Weissmüller, Nanostruct. Mater. **3** (1993)
  - Cahn's treatment of solute drag: J. Cahn, Acta Metall. **10** (1962)

Ideal and dilute systems with no solute-solute interactions at GBs

- Atomistic
  - Examine dependence of segregation on GB character (type, orientation)
  - Don't attain diffusive time scales to examine growth dynamics

A. Seki et al., Acta Metall. Mater. **39** (1991)
M. Hashimoto et al., Acta Metall. **32** (1984)

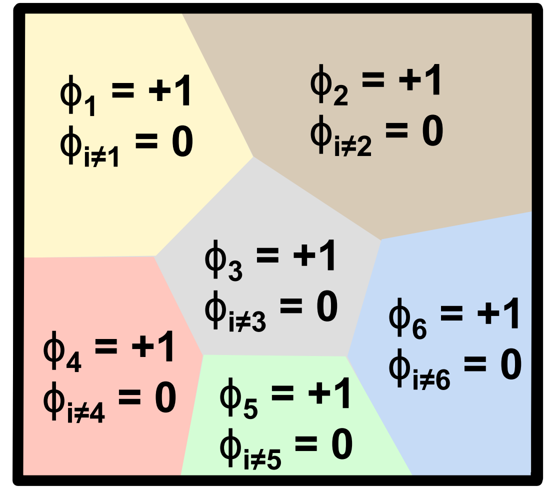
Key Questions

- GB segregation in NM binary alloys
- Grain growth and other processes (phase separation)
- Dependence of GB energy on segregation
- Incorporates anisotropy in GB energy, mobility and segregation

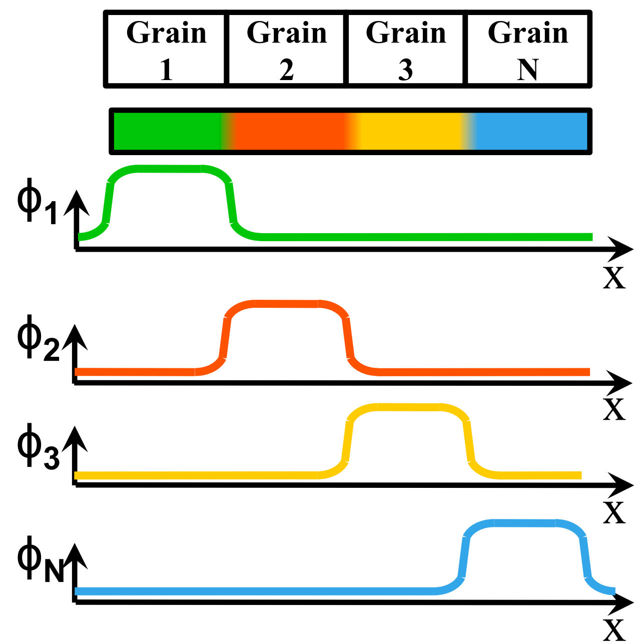
Phase field method

Phase Field Formalism

- Systems of interest
  - Binary alloys of A (host) and B (solute) elements
  - Polycrystalline: grains with various character



- Order parameters
  - c: solute concentration
  - ϕ_i: define grain microstructure



- Total free energy
  - Bulk thermodynamics
  - Interfacial energies and thermodynamics (Gibbs-Thomson boundary condition, GBs, anisotropy, …)
  - Dynamics driven by minimization of energy

Phase Field Formalism (cont.)

- Total free energy

$$\mathcal{F}_{tot} = \int \left[\underbrace{f_{mix}(c,T)}_{\text{Bulk}} + \underbrace{W_\phi f_{grain}(\phi_i)}_{\text{Grain microstructure}} + \underbrace{\sum_i^{n_\phi} \frac{\epsilon_i^2}{2} |\nabla \phi_i|^2}_{\text{GB energy}} - \underbrace{(\xi_o + \xi_1 c + \xi_2 c^2)\psi(\phi_i)}_{\text{Assigns interaction energy to GBs}} \right] d\mathbf{r}$$

- Dynamics

Concentration field: $$\frac{\partial c}{\partial t} = \nabla \cdot \left[M_c \nabla \left(\frac{\delta \mathcal{F}_{tot}}{\delta c} \right) \right]$$

Cahn-Hilliard Eq. (Model B)

Conservation of mass

M_c: solute atomic mobility

Evolution of grains: $$\frac{\partial \phi_i}{\partial t} = -L_i \frac{\delta \mathcal{F}_{tot}}{\delta \phi_i}$$

Allen-Cahn Eq. (Model A)

Gradient flow of $\mathcal{F}_{tot}$

L_i: GB mobility

With four parameters I can fit an elephant, and with five I can make him wiggle his trunk

J. von Neumann

Equilibrium Properties

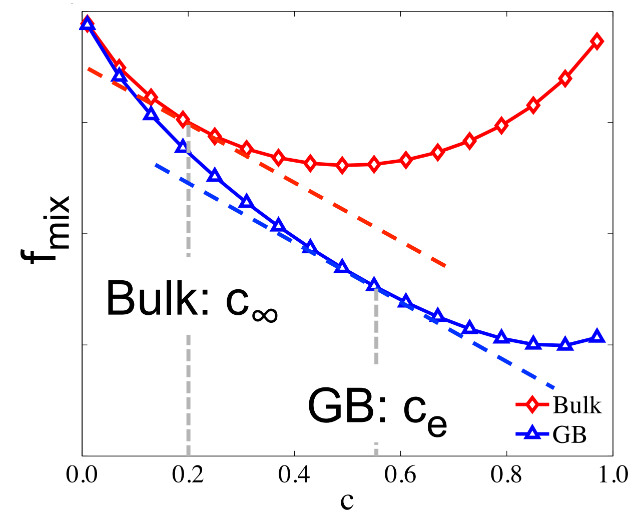
- Regular solution approximation

Bulk: $f_{mix}^{bulk} = G_B c + G_A(1-c) + \Omega c(1-c) + \frac{RT}{V_m}\left[c\ln c + (1-c)\ln(1-c)\right]$

GB: $f_{mix}^{gb} = G_B^{gb} c + G_A^{gb}(1-c) + \Omega^{gb} c(1-c) + \frac{RT}{V_m}\left[c\ln c + (1-c)\ln(1-c)\right]$

Effective GB thermodynamic properties

$$G_A^{gb} = G_A - \xi_0 \quad G_B^{gb} = G_B - \xi_0 - \xi_1 - \xi_2 \quad \Omega^{gb} = \Omega + \xi_2$$

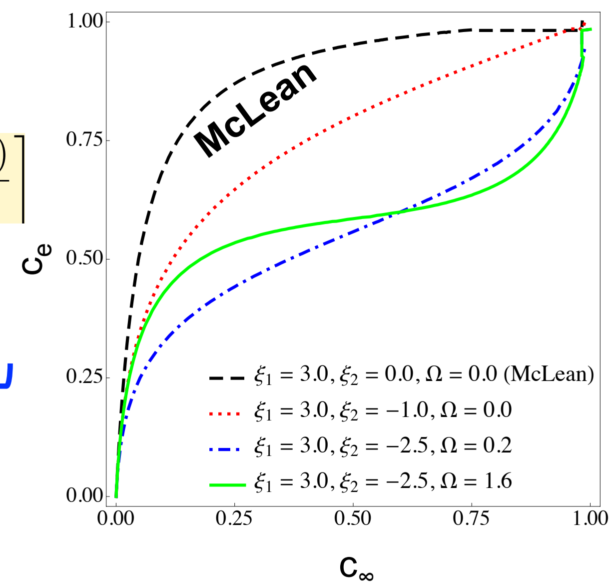


- GB segregation isotherm

$$\frac{c_e(\mathbf{r})}{1-c_e(\mathbf{r})} = \frac{c_\infty}{1-c_\infty}\exp\left[\frac{\overbrace{16\xi_1\phi_e^2(1-\phi_e)^2}^{\text{Langmuir-McLean isotherm*}} + 32\xi_2\phi_e^2(1-\phi_e)^2 c_e + 2\Omega(c_e - c_\infty)}{(RT/V_m)}\right]$$

Langmuir-McLean isotherm*

Fowler-Guggenheim isotherm**



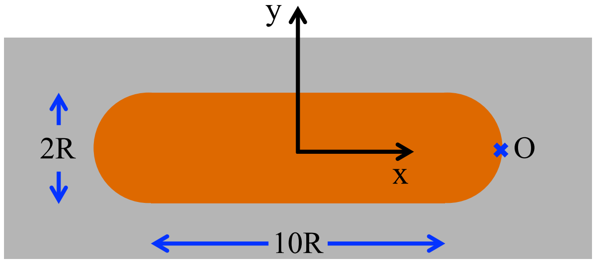
* D. McLean, Grain Boundaries in Metals (1957)

** R. Fowler and E. Guggenheim, Statistical Thermodynamics (1939)

Oval Racetrack Geometry

- Eliminates role of curvature in driving force

Track the evolution of
- Concentration profile at GB
- GB point "O"

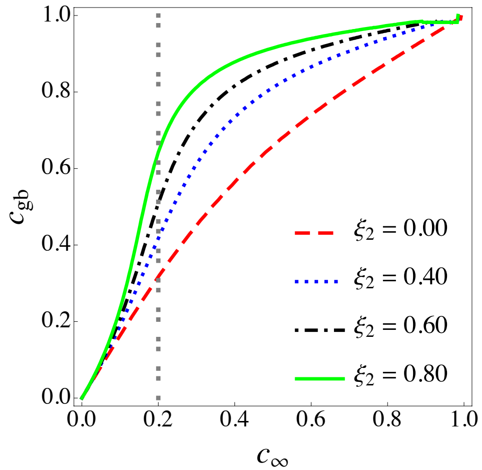


Upmanyu et al. Interface Science **6** (1998)

- Examine phase space of (ξ_1, ξ_2, Ω)

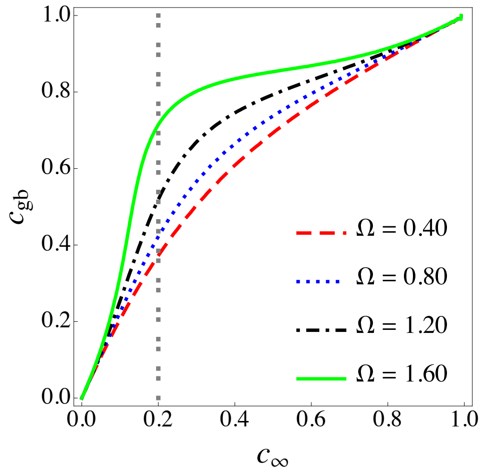
Case 1

GB solute-solute interactions



Case 2

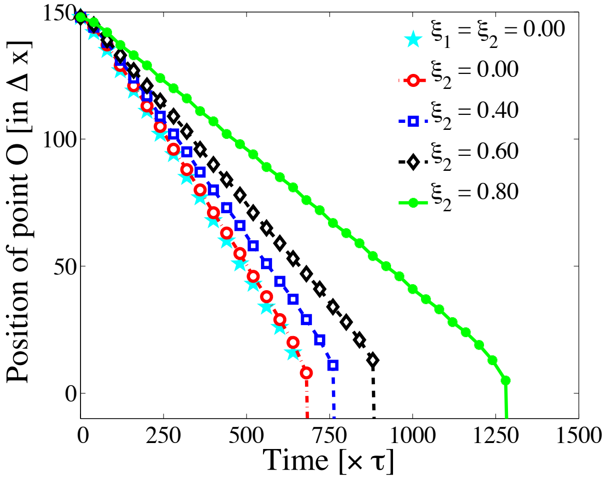
Degree of non-ideality



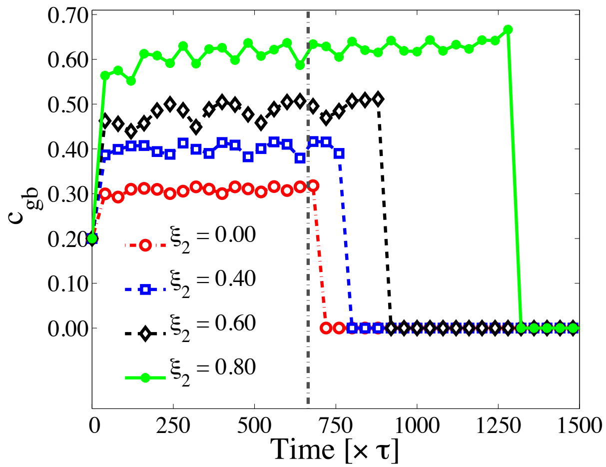
Case 1: $\xi_2 \neq 0$

- Solute-solute interactions at GBs
  - Dependence on concentration at GBs

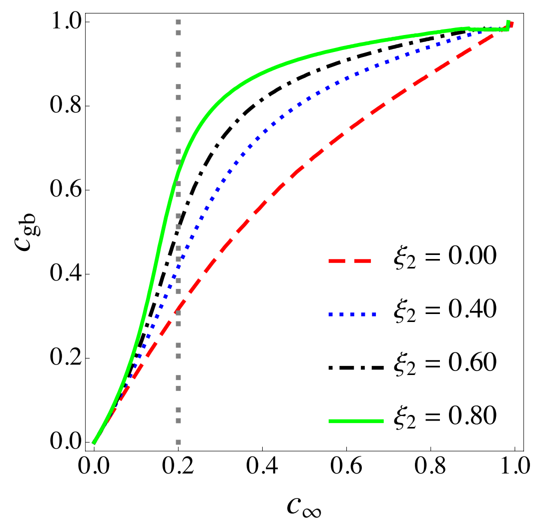
GB position



GB concentration



GB isotherm



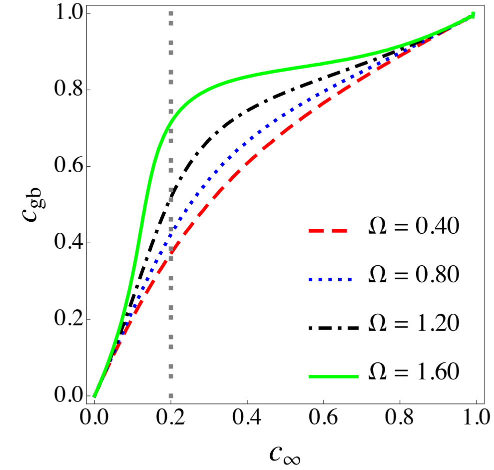
- Observations
  - Attractive interactions: **i)** increases c_{gb} **ii)** slower growth dynamics
  - Velocity: $v_n = dx/dt \sim M_{gb}\gamma_{gb}H$ ➔ $\xi_2 \uparrow, M_{gb}\gamma_{gb} \downarrow$

F. Abdeljawad and S. M. Foiles. Manuscript in preparation (2014)

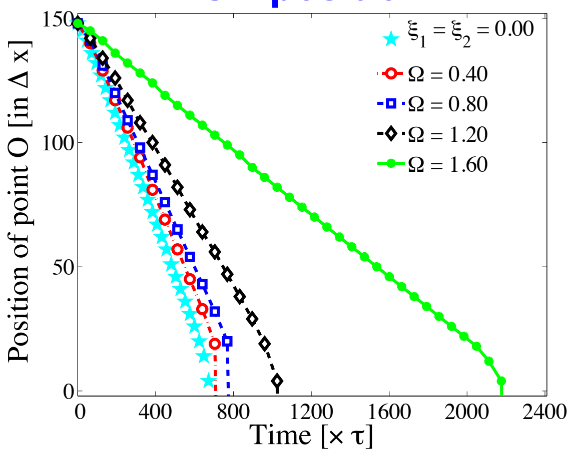
Case 2: Non-ideality

- Regular solution approximation
  - Enthalpic term via Ω

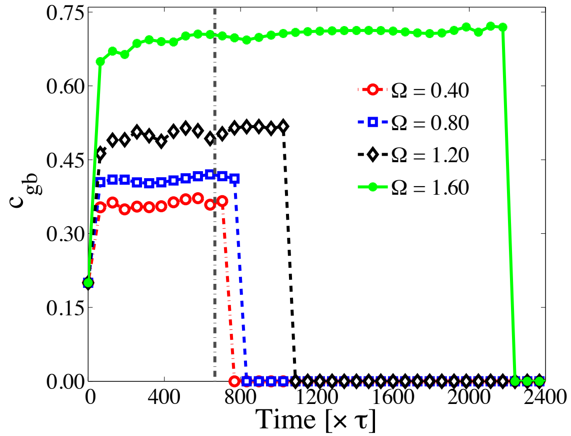
GB isotherm



GB position



GB concentration



No segregation

Ω = 1.60

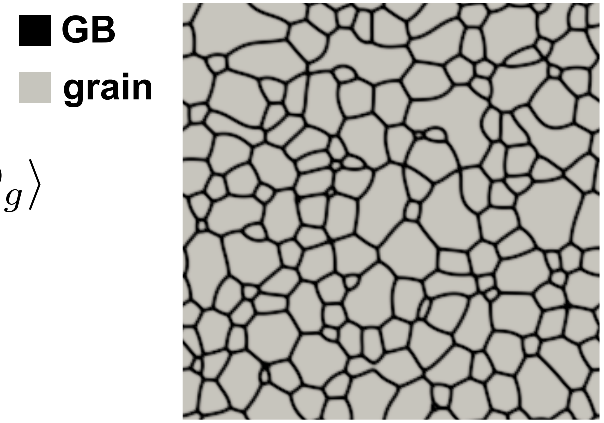
- Observations
  - Increasing Ω leads to slower dynamics
  - Phase separation when Ω is large enough

F. Abdeljawad and S. M. Foiles. Manuscript in preparation (2014)

Grain Microstructure

- Polycrystalline Aggregates
  - At t = 0, a total of 185 grains
  - Track grain size distribution and avg. grain size $\langle D_g \rangle$

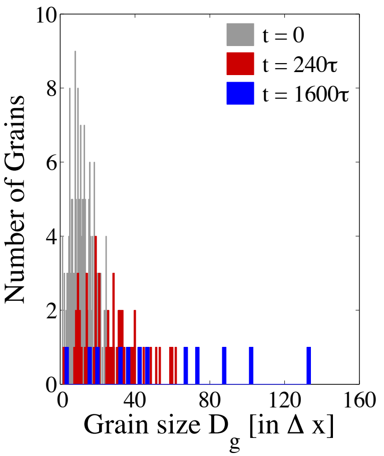
$$\langle D_g(t) \rangle^2 - \langle D_g(0) \rangle^2 \sim t$$



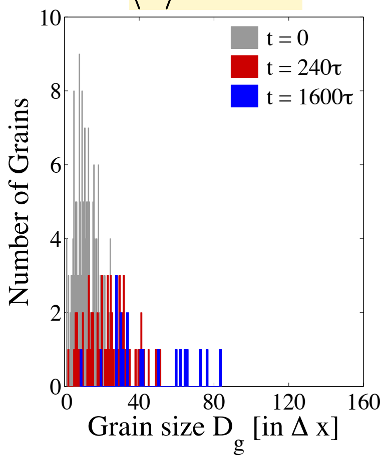
Grain size distribution

ξ_1= 0.8, ξ_2= -0.1, Ω = 1.6

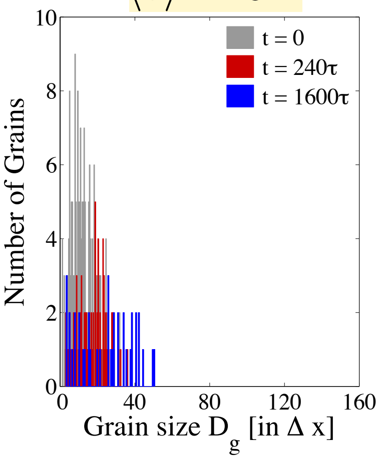
No segregation



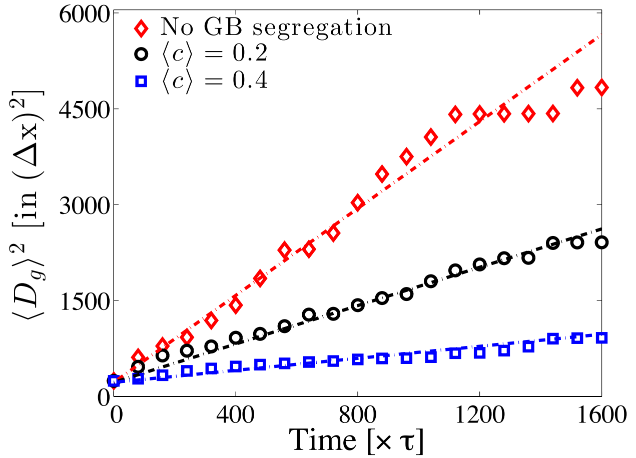
$\langle c \rangle = 0.2$



$\langle c \rangle = 0.4$



Avg. grain size



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Summary and Future Work

- Phase field framework
  - GB solute segregation
  - Bulk and interface thermodynamics
  - Phase-space of parameters controlling segregation

- Future work
  - Extension to thin films (addition of an OP to account for surface energy)
  - Examine anisotropy in GB energy, mobility and segregation
  - Growth in phase-separating systems (grain growth + phase-separation)

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Backup slides

Equilibrium Properties: 1D

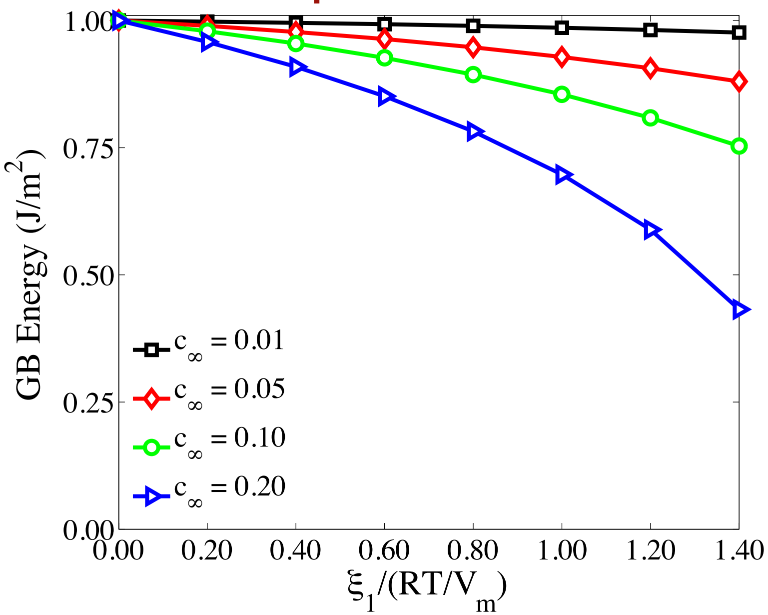
- GB energy: $\gamma = \Delta F - \Gamma \frac{\partial f_{mix}}{\partial c}\Big|_{eq}$ where $\Gamma = \int_{-\infty}^{+\infty} d\mathbf{r}[c - c_{grain}]$

- Phase field definition: $\gamma_{GB} = \epsilon^2 \int_0^1 \frac{d\phi}{dx} d\phi$

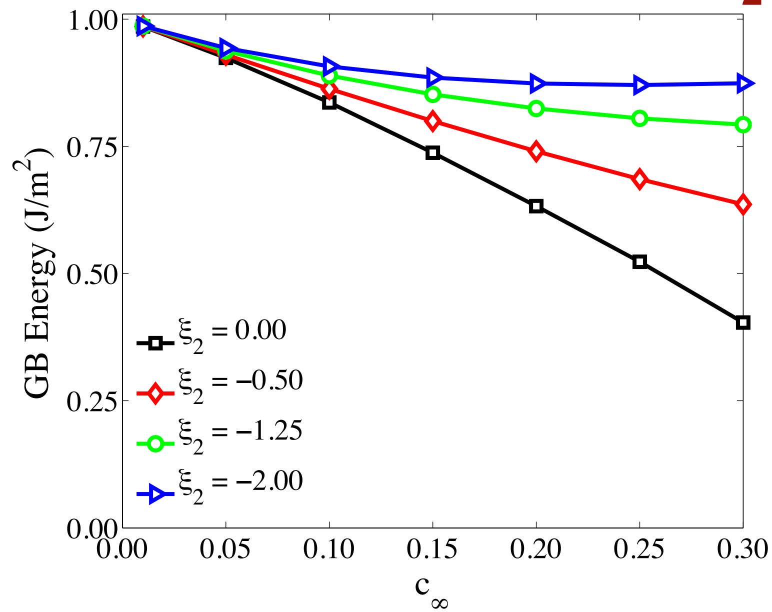
Solve by numerical integration

$$\frac{\epsilon^2}{2}\left(\frac{d\phi_e}{dx}\right)^2 = 16\phi_e^2(1-\phi_e)^2(W_\phi - (\xi_1 c_e + \xi_2 c_e^2)) + \Omega(2c_e c_\infty - c_\infty^2 - c_e^2) + \frac{RT}{V_m}\left[c_e \ln\left(\frac{c_e}{c_\infty}\right) + (1-c_e)\ln\left(\frac{1-c_e}{1-c_\infty}\right)\right]$$

Role of ξ_1 (McLean isotherm)



Role of bulk concentration and ξ_2



F. Abdeljawad and S. M. Foiles, Manuscript in preparation for Acta Materialia

Case 1: Varying ξ_1

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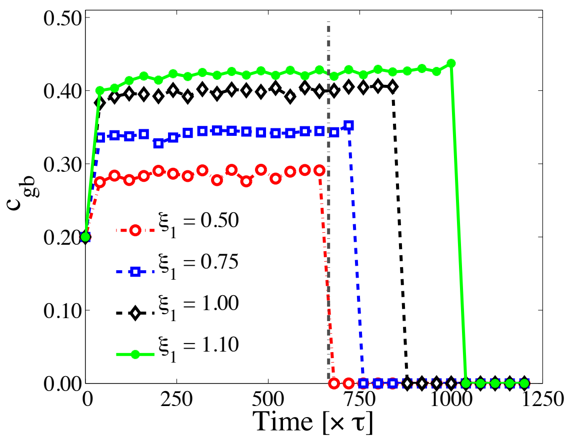
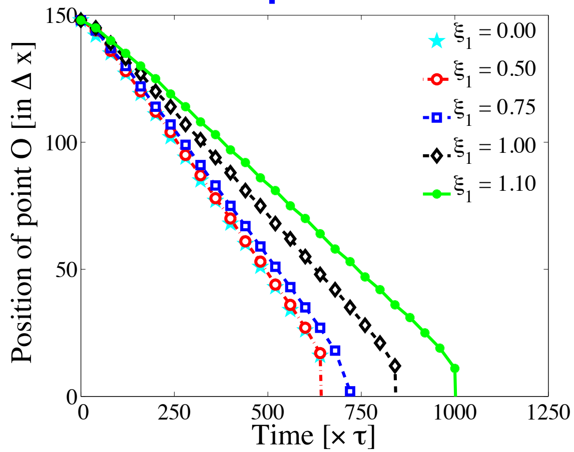
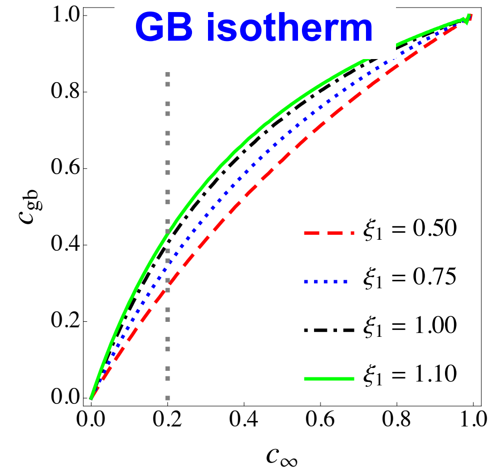
- Segregation Isotherm: $\xi_2 = \Omega = 0$
  - Independent of concentration at GBs
  - GBs are substitutional sites and equally available

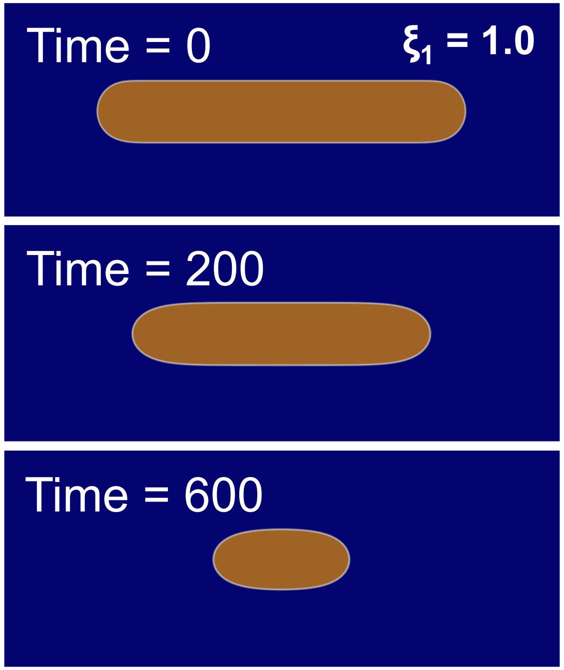
GB concentration



GB position







- Observations
  - Increasing ξ_1 leads to slower grain growth
  - Cahn's solute drag: Varying GB mobility

S. Kim et al., Acta Mat. **56** (2008)