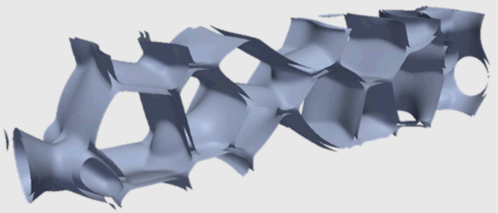
SAND2015-1761C



$$v_n = M\gamma H$$

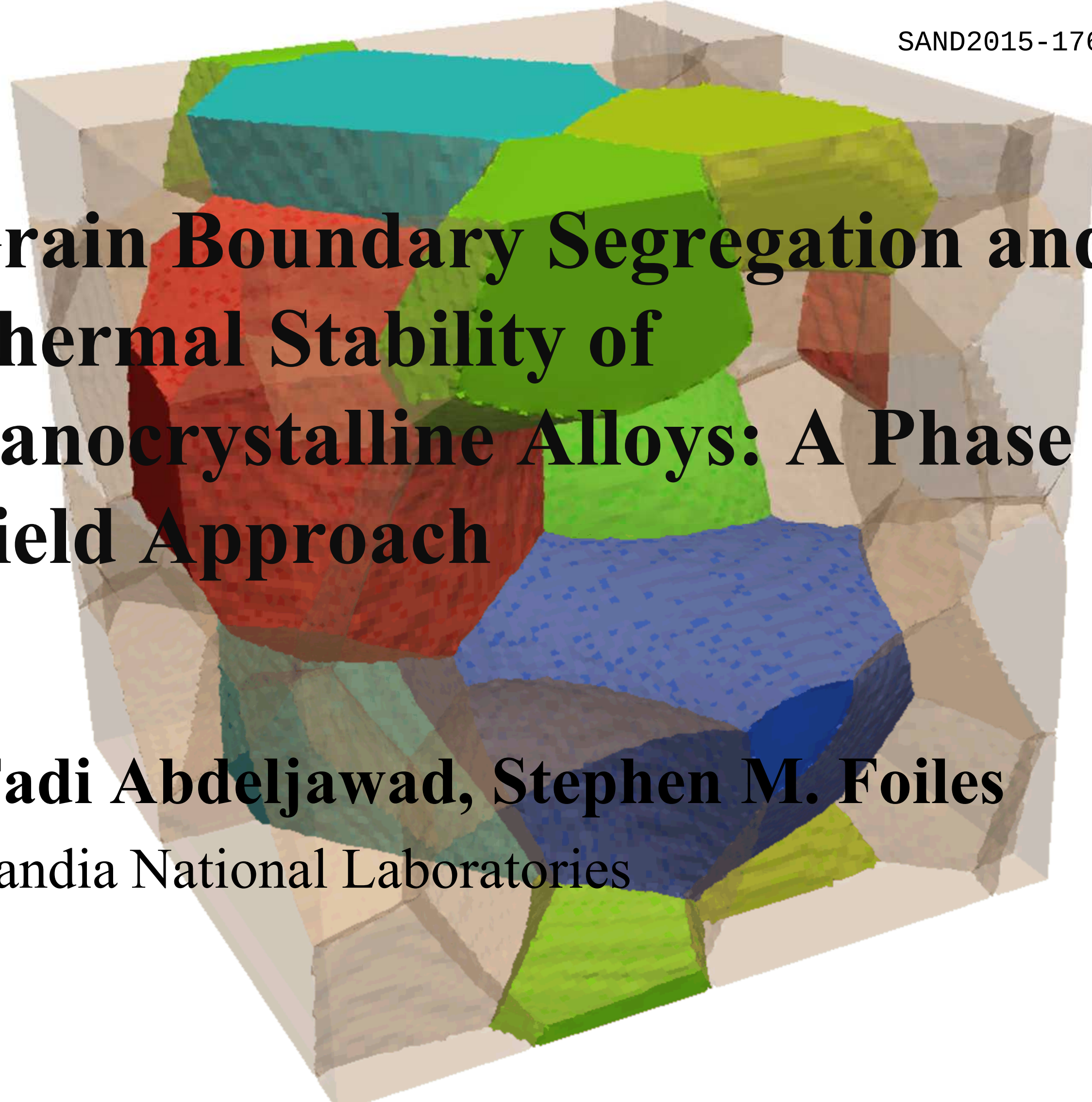
$$\frac{\partial \phi_i}{\partial t} = -L_i \frac{\delta \mathcal{F}_{tot}}{\delta \phi_i}$$

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

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

Sandia National Laboratories

Exceptional service in the national interest



Grain Boundary Segregation and Thermal Stability of Nanocrystalline Alloys: A Phase Field Approach

Fadi Abdeljawad, Stephen M. Foiles

Sandia National Laboratories

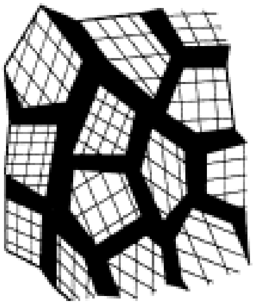
U.S. DEPARTMENT OF ENERGY · NNSA National Nuclear Security Administration · U.S. DEPARTMENT OF ENERGY Office of Science

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

The Case for Nanostructured Alloys

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

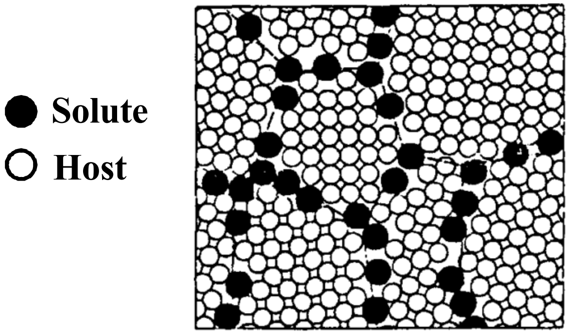
$$\mathcal{V}_n = M_{gb}\gamma_{gb}\mathcal{K}$$



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

- **Possible solution:** Solute segregation to GBs
  - Solute atoms preferentially occupy GB sites (mechanical or chemical)
  - **Kinetic** and/or **thermodynamic** stabilization

Kinetic → GB mobility; thermodynamic → GB energy

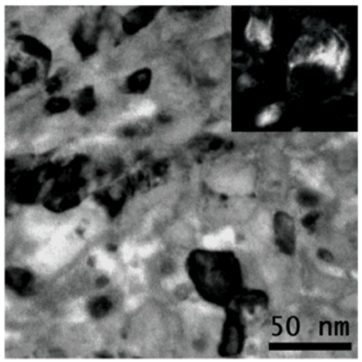


J. Weissmüller, Nanostruct. Mater. **3** (1993)

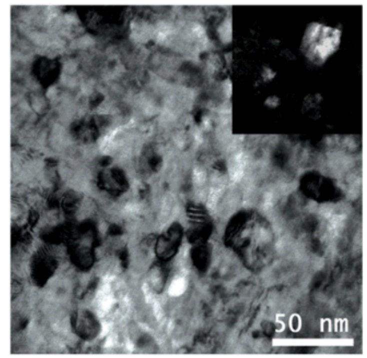
Experimental Observation

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

As milled



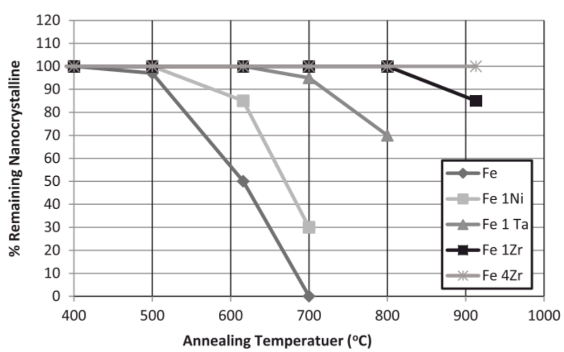
Annealed, 1 week at 1100°C

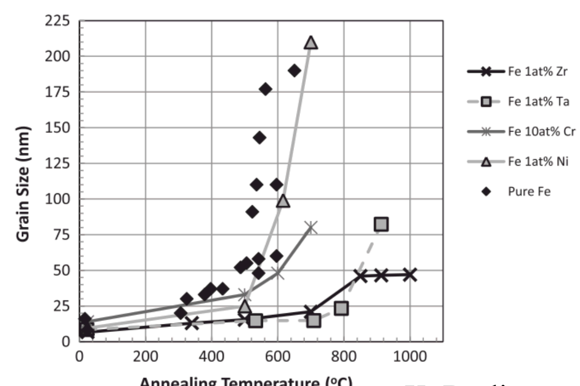


T. Chookajorn et al., Science. **337** (2012)
T. Chookajorn et al., Acta Mater. **73** (2014)

- Alloy selection in Fe-based systems

Addition of Ta, Cr, Ni and Zr





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

Theoretical/Analytical

- 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)

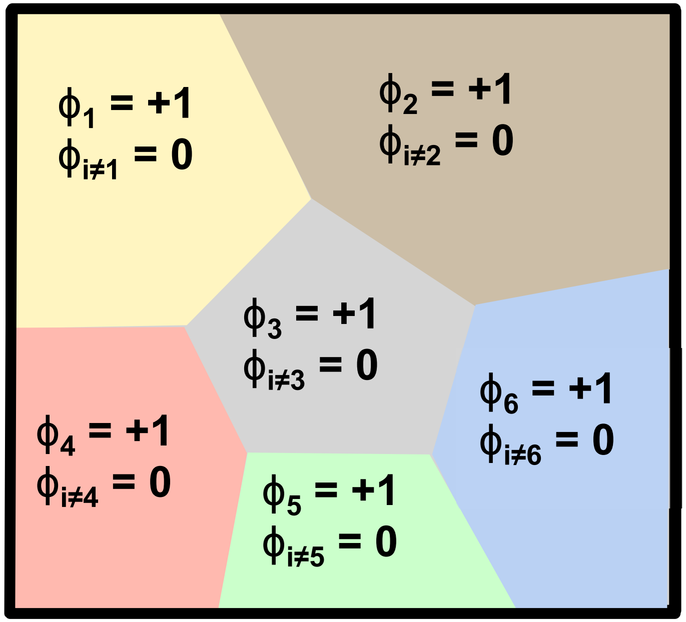
Key Questions

- 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

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[f_{mix}(c,T) + W_\phi f_{grain}(\phi_i) + \sum_i^{n_\phi} \frac{\epsilon_i^2}{2} |\nabla \phi_i|^2 + \frac{\kappa^2}{2} |\nabla c|^2 - (\xi_0 + \xi_1 c + \xi_2 c^2) f_{grain}(\phi_i) \right]$$

Bulk — **Grain microstructure** — **GB energy** — **Compositional domains** — **Assigns interaction energy to GBs**

- Dynamics

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

Cahn-Hilliard Eq. (conservation of mass)

M_c: Atomic mobility

- Model A: $\frac{\partial \phi_i}{\partial t} = -L_i \left(\frac{\delta \mathcal{F}_{tot}}{\delta \phi_i} \right)$

Allen-Cahn Eq. (Gradient flow of $\mathcal{F}_{tot}$)

L_i: GB mobility

Model C*

* P. Hohenberg and B. Halperin, Rev. Mod. Phys. 49, (1977)

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

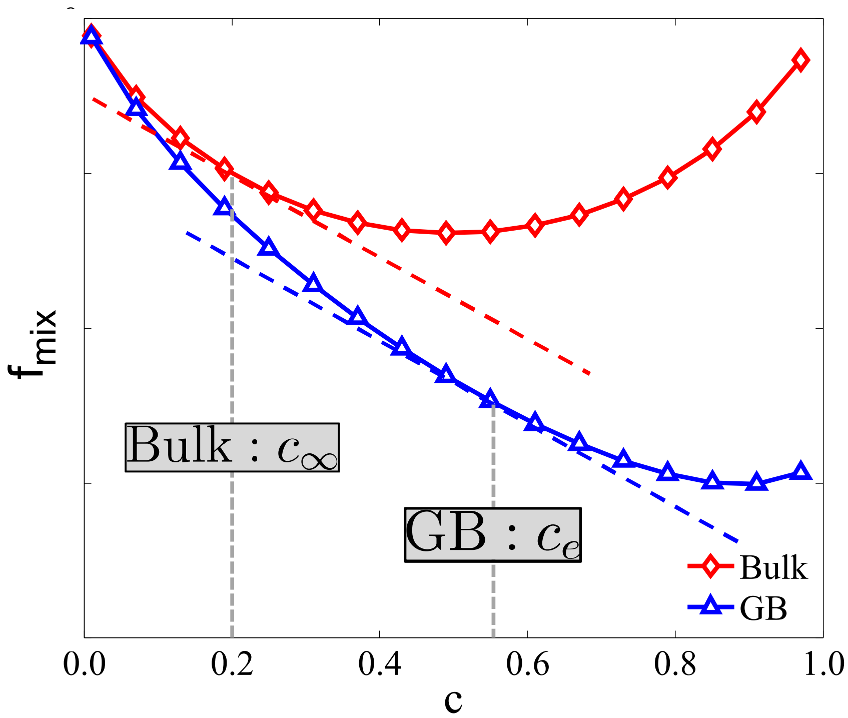
J. von Neumann

F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)

Equilibrium Properties

- Equilibrium Concentration
  - Equal chemical potential $\mu = \frac{\delta \mathcal{F}_{tot}}{\delta c}$

$$\mu\Big|_{bulk} = \mu\Big|_{GB}$$



- GB segregation isotherm

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

ξ_1 and ξ_2 set GB concentration relative to bulk one

F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)

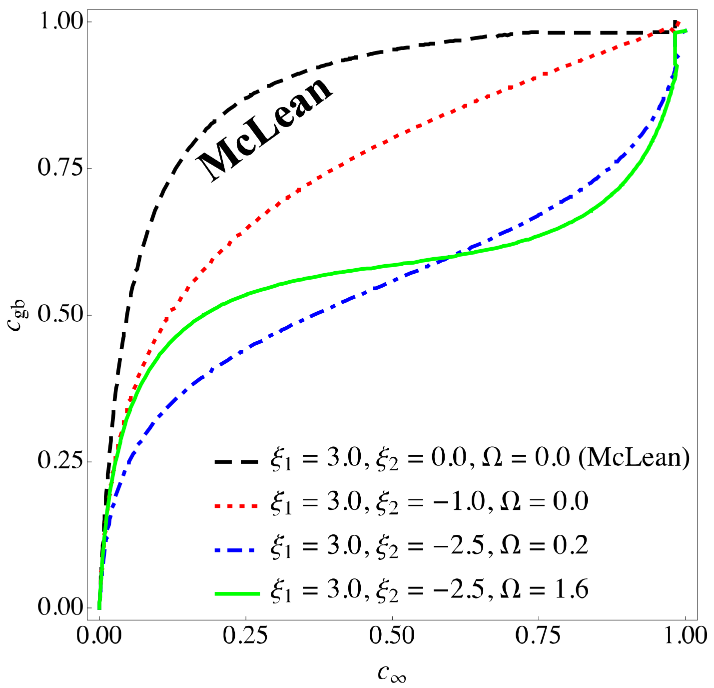
Equilibrium Properties (Cont.)

- GB segregation isotherm

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

Langmuir-McLean isotherm*

Fowler-Guggenheim isotherm**



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

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

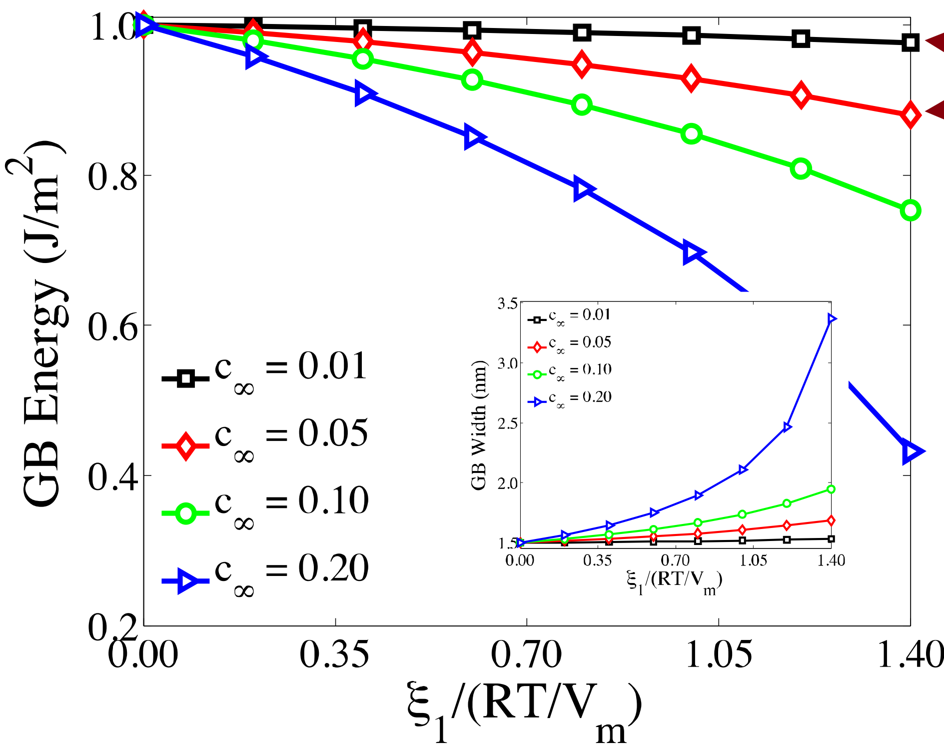
Observations:

1) Classic McLean when $\Omega = 0$, $\xi_2 = 0$
2) In the dilute limit: ξ_1 sets heat of segregation
3) ξ_2 sets solute-solute interactions at GBs

1D Equilibrium Properties

- **No solute-solute interactions within GBs**

Role of ξ_1 (McLean isotherm)



Dilute limit

Concentration away from dilute limit

Considerable reduction in GB energy

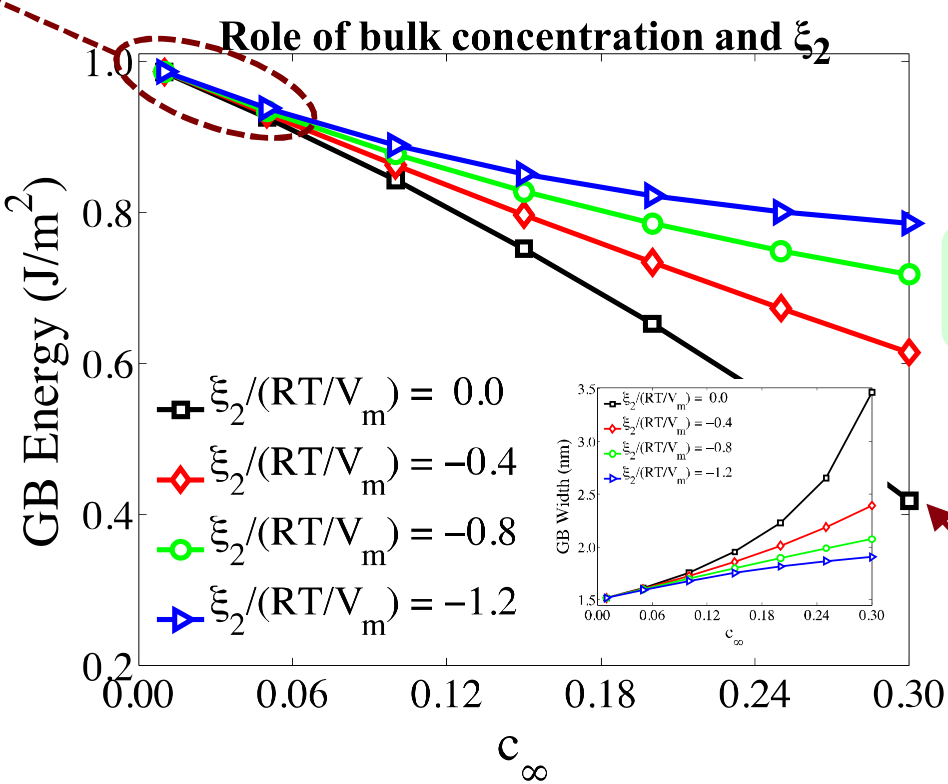
Increasing segregation tendency

F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)

1D Equilibrium Properties (cont.)

- **Solute-solute interactions within GBs: $\xi_2 \neq 0$**

Dilute limit



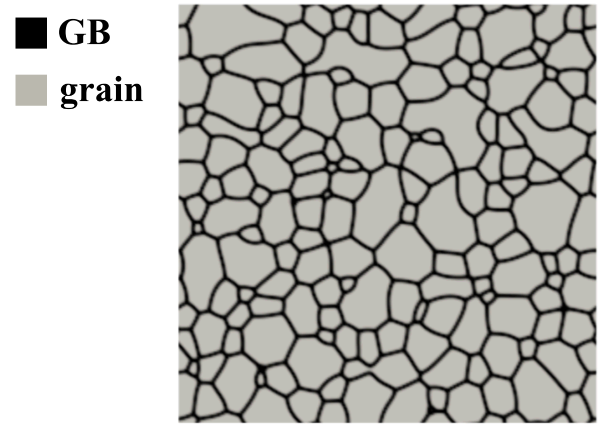
Increasing repulsive interactions

No interactions

F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)

Grain Microstructure

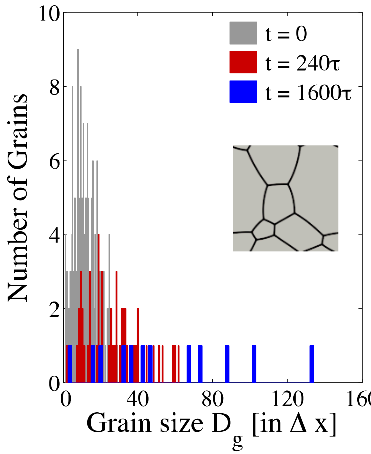
- Polycrystalline aggregates
  - At t = 0, a total of 185 grains
  - Track grain size distribution and avg. grain size $\langle D_g \rangle$



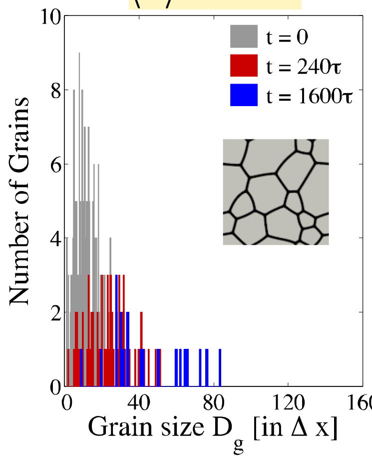
Grain size distribution

$\xi_1 = 0.8$, $\xi_2 = -0.1$, $\Omega = 1.6$

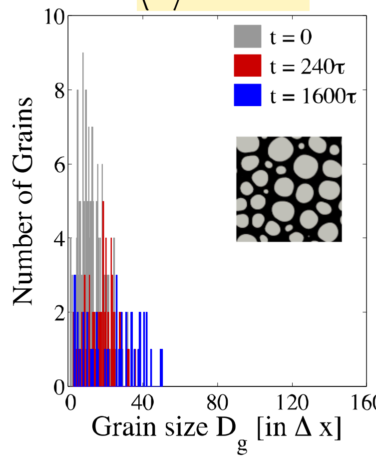
No segregation



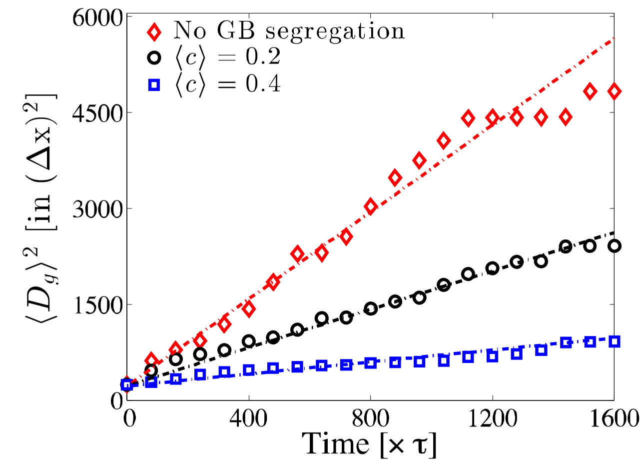
$\langle c \rangle = 0.2$



$\langle c \rangle = 0.4$



Avg. grain area



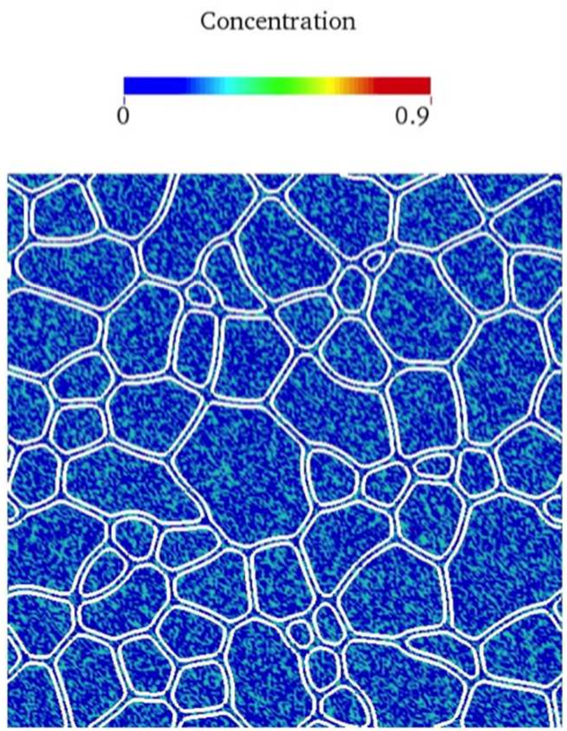
F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)

Combined Processes

- GB segregation in phase-separating systems
  - Initial concentration inside miscibility gap

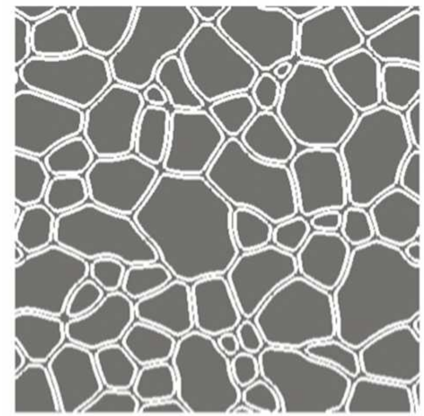
> - Slower dynamics
> - Interfacial energy due to phase boundaries
> - Duplex microstructures

GB segregation

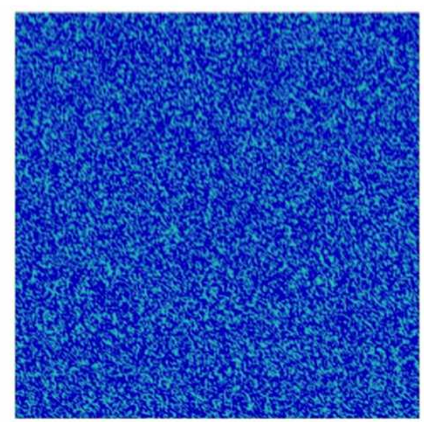


No segregation

GB network



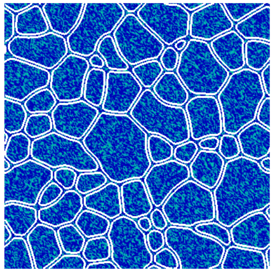
Concentration



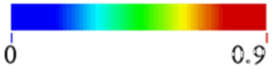
Combined Processes (cont.)

- Heat of GB segregation vs. phase separation
  - Fix heat of phase separation (bulk thermodynamics): $\Omega/(RT/V_m) = 4.5$
  - Vary heat of GB segregation
  - Initially: $\langle c \rangle = 0.3$

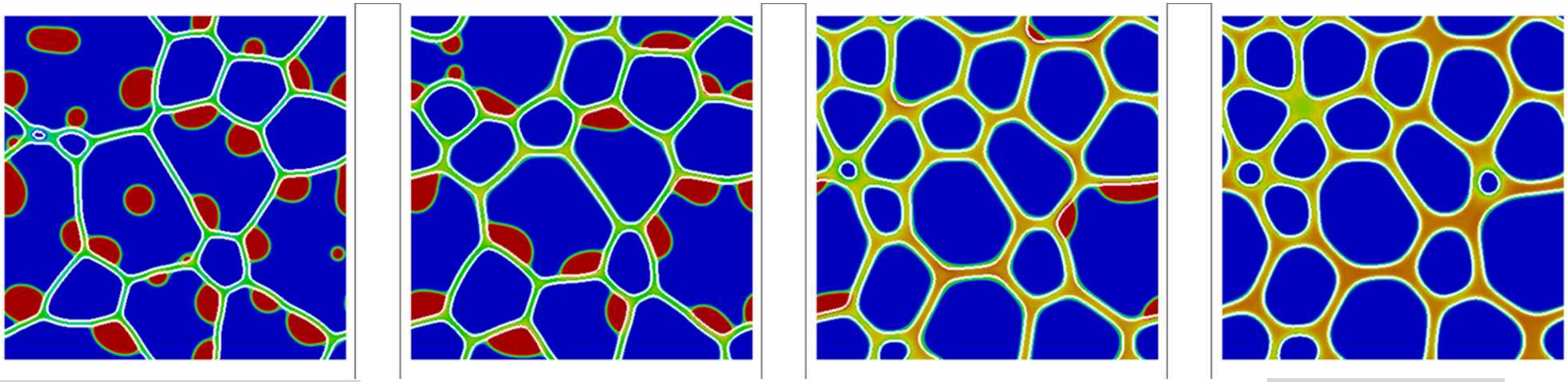
Initial



Concentration



Increasing heat of segregation for a given heat of separation



Duplex (Grains within grains)

Brick-Mortar

Conclusion 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
  - Examine anisotropy in GB energy, mobility and segregation

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. FA and SMF would like to acknowledge the financial support from the US department of Energy, Office of Basic Energy Sciences.

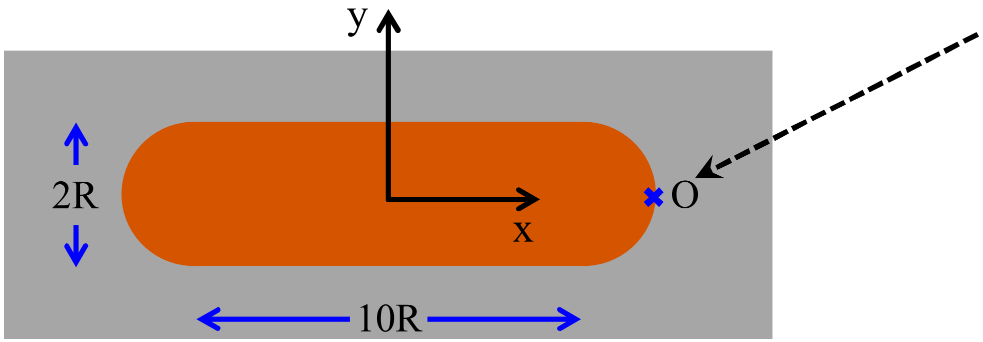
Sandia National Laboratories

Backup Slides

“Racetrack” Grain Geometry

- Eliminates role of curvature in driving force

Track the evolution of
- Concentration profile at GB
- Spatial position of GB point “O”



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

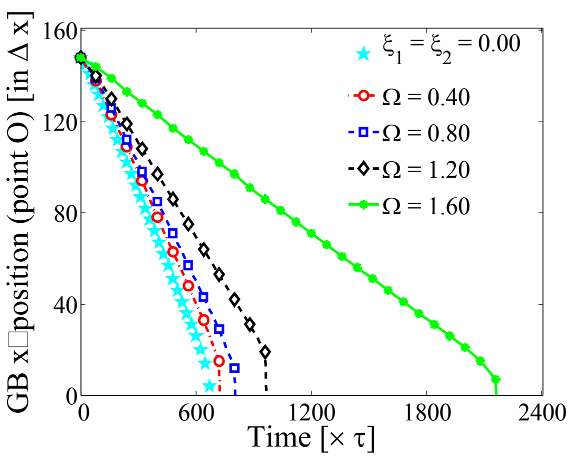
Non-ideality: $\Omega, \Omega^{gb} \neq 0$

Sandia National Laboratories

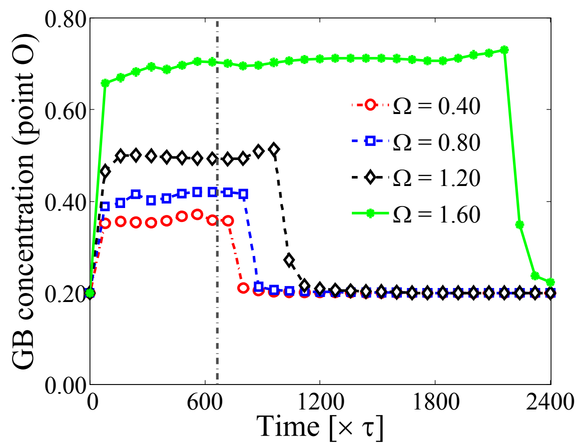
- Regular solution approximation
  - Enthalpic (heat of mixing) term via Ω

$$\Omega^{gb} = \Omega + \xi_2$$

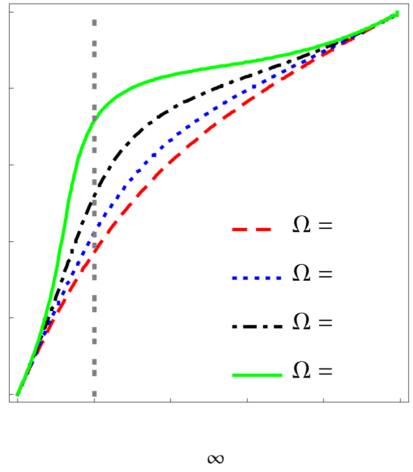
GB position (Point O)

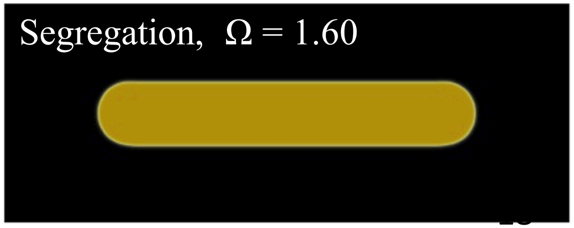


GB concentration



GB isotherm





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

F. Abdeljawad and S. M. Foiles, To be submitted to Acta Mat. (2015)