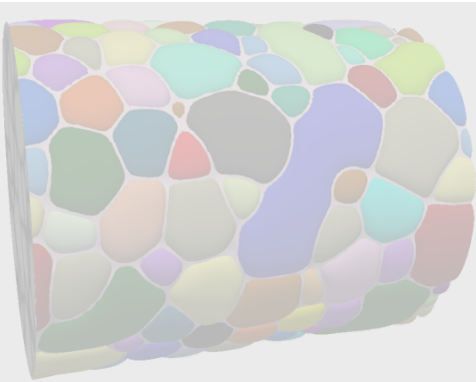


$$v_n = M\gamma H \quad \gamma = \Delta F - \Gamma \left. \frac{\partial f_{mix}}{\partial c} \right|_{eq}$$

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



Mesoscale Modeling of Grain Boundary Segregation: The Role of Anisotropy in Segregation

Fadi Abdeljawad¹, Stephen Foiles¹, Blas Uberuaga² and Enrique Martinez²

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² Material Science and Technology Division, MST-8, Los Alamos National Laboratory, Los Alamos, NM



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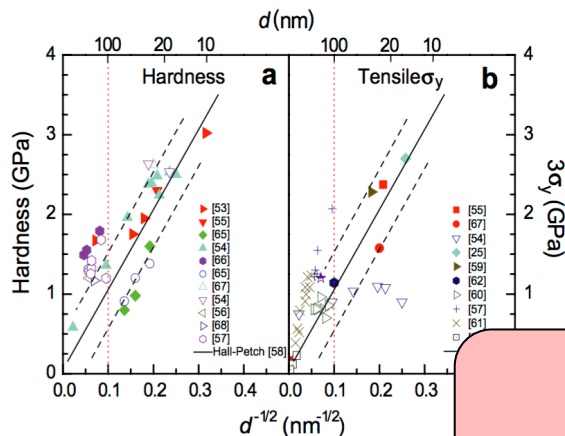
U.S. DEPARTMENT OF
ENERGY

Office of
Science

Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525

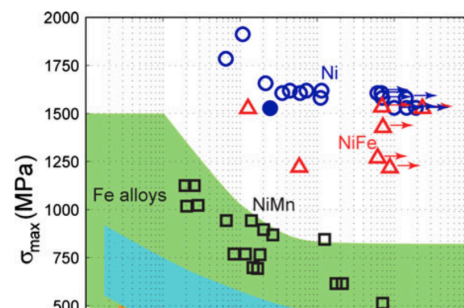
Nanocrystalline (NC) Metals

Hardness and Yield

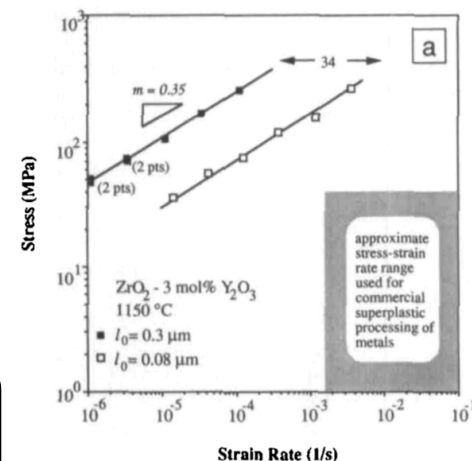


Dao *et al.*, Acta Mater. (2007)

Fatigue



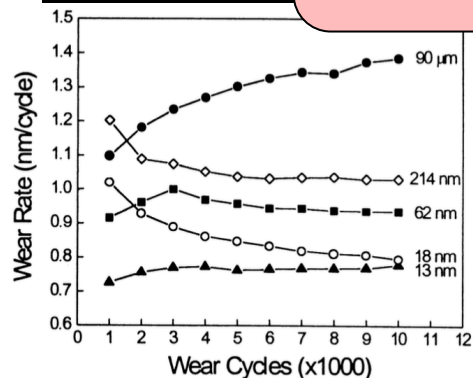
Strain Rate



Weertman *et al.*, MRS Bull. (1999)

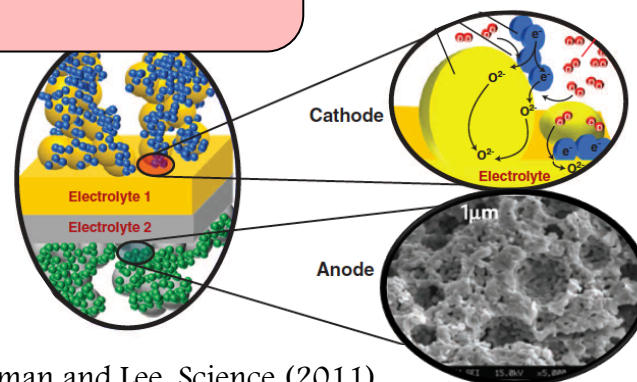
But ...

Wear (electrical)



Jeong *et al.*, Scripta Mat. (2001)

Solid oxide fuel cells



Wachsman and Lee, Science (2011)

Suzuki *et al.*, Science (2009)

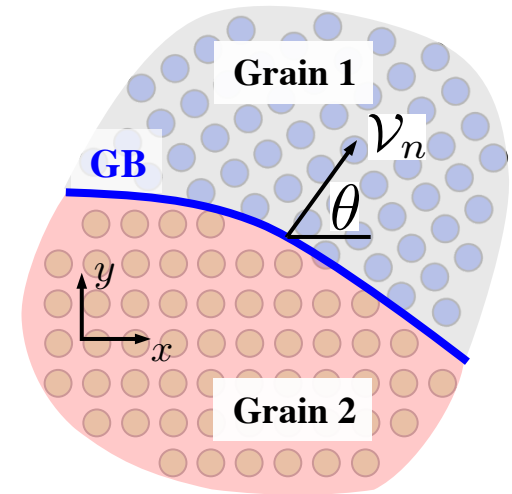
The Case for NC Metals

■ **Problem:** High density of grain boundaries (GBs)

- Excess free energy: $\Delta\mathcal{F} = \Delta(\gamma A)$
- Grain-growth and homogenization processes

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

Herring, Phys. Powd. Metall. (1951)
Burke and Turnbull, Prog. Metal. Phys. (1952)
Mullins, J. App. Phys. (1956)



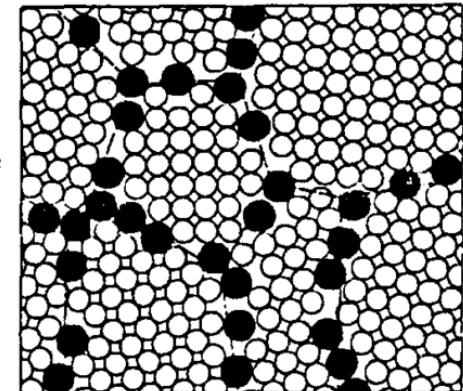
■ **Possible solution:** Solute segregation to GBs

- Solute atoms preferentially occupy GB sites
- **Kinetic** and/or **thermodynamic** stabilization

GB mobility
Solute drag

GB energy

● Solute
○ Host



Weissmüller, Nanostruct. Mater. (1993)

Phase Field Formalism

Free energy

- $c(\mathbf{r}, t)$: alloy concentration
- $\Phi_i(\mathbf{r}, t)$, $\{i = 1, \dots, n_\phi\}$: grain order parameters

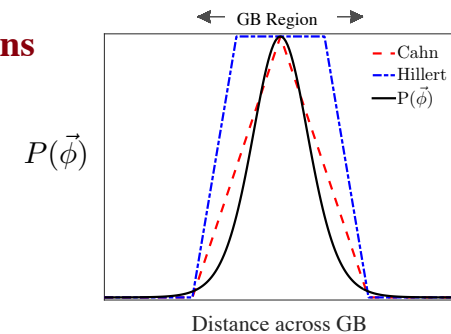
$$\mathcal{F}_{tot}[c, T] = \int d\mathbf{r} \left[f_{loc}(c, T) + \underbrace{\sum_i^{n_\phi} \frac{\epsilon^2}{2} |\nabla \phi_i|^2 + \frac{\kappa^2}{2} |\nabla c|^2}_{\text{Gradient terms for GBs and compositional damins}} \right]$$

Local energy density

Gradient terms for
GBs and compositional damins

$$f_{loc}(c, T) = P(\vec{\phi}) f_{gb}(c, T) + [1 - P(\vec{\phi})] f_b(c, T)$$

$P(\vec{\phi})$: interpolates free energy between bulk and GB

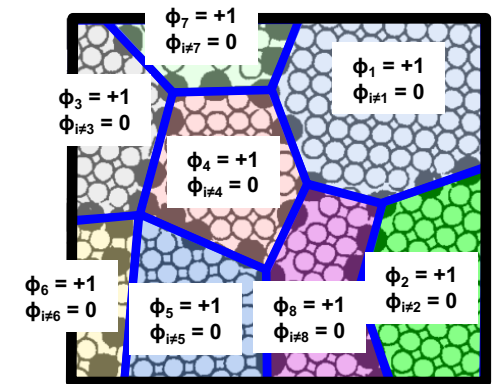


Dynamics

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[M_c \nabla \left(\frac{\delta \mathcal{F}_{tot}}{\delta c} \right) \right] \quad \begin{array}{l} \text{Mass conservation} \\ \text{Cahn-Hilliard Eq.} \end{array}$$

$$\frac{\partial \phi_i}{\partial t} = -L_i \left(\frac{\delta \mathcal{F}_{tot}}{\delta \phi_i} \right) \quad \begin{array}{l} \text{Gradient flow} \\ \text{Allen-Cahn Eq.} \end{array}$$

● Solute
○ Host



GB Segregation Isotherm

$$f_i^{mix}(c, T) = \mathbf{G}_i^B c + \mathbf{G}_i^A (1 - c) + \frac{RT}{V_m} \left[c \ln c + (1 - c) \ln(1 - c) \right] + \mathbf{\Omega}_i c(1 - c), \quad i = gb, bulk$$

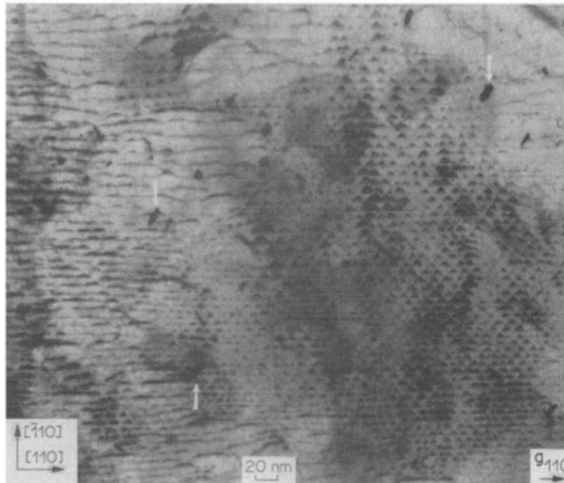
Free energy of pure states

Heat of mixing

A : Solvent
B : Solute atoms
 c_∞ : Alloy concentration

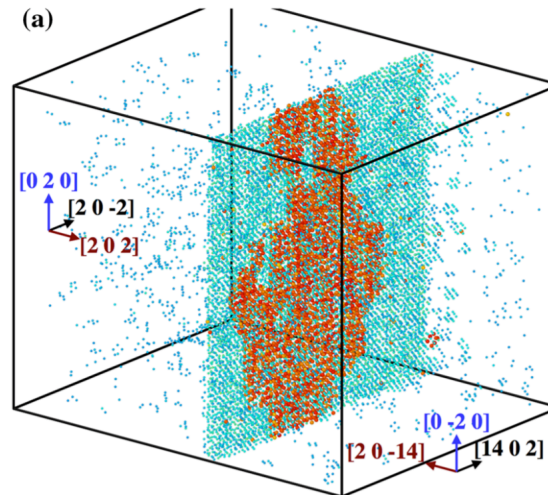
Bulk: G_b^A, G_b^B, Ω_b
GB: $G_{gb}^A, G_{gb}^B, \Omega_{gb}$

1.5° about [001], Fe-1.03 at.% Au



Sickafus and Sass, Acta Metall. (1987)

$\Sigma 5$, Pt-15 at.% Au



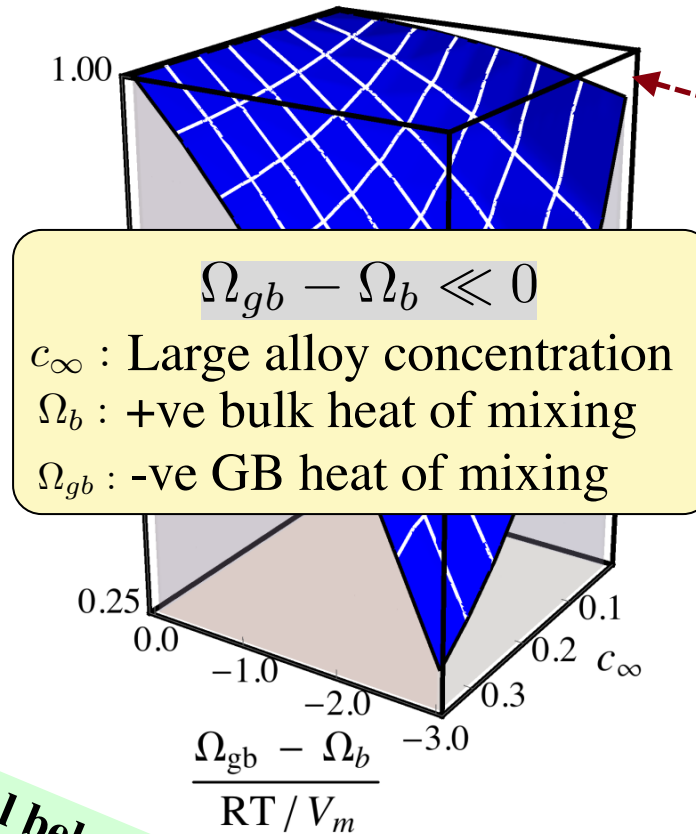
O'brien et al. J. Mater. Sci. (2017)

GB energy $\gamma_{gb} = \gamma_{gb}(c, \Omega_{gb})$

- Gibbs adsorption eq.:

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

c_{∞} : Alloy concentration
 Ω_b : Bulk heat of mixing
 Ω_{gb} : GB heat of mixing



Dilute limit

Non-ideal behavior

Concentration away from dilute limit

Considerable reduction in GB energy

Abdeljawad *et al.*, Acta Mater. (2017)

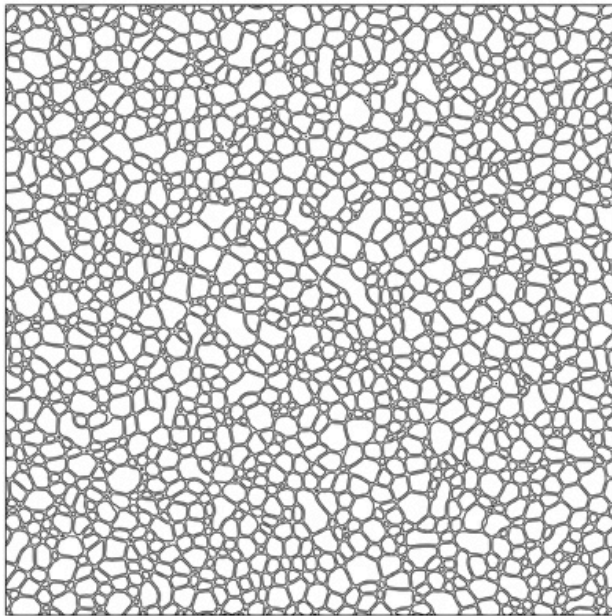
Murdoch *et al.*, Acta Mater. (2013)

Competing Processes

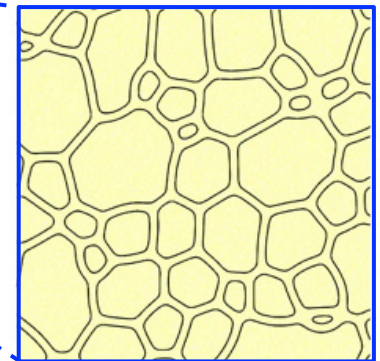
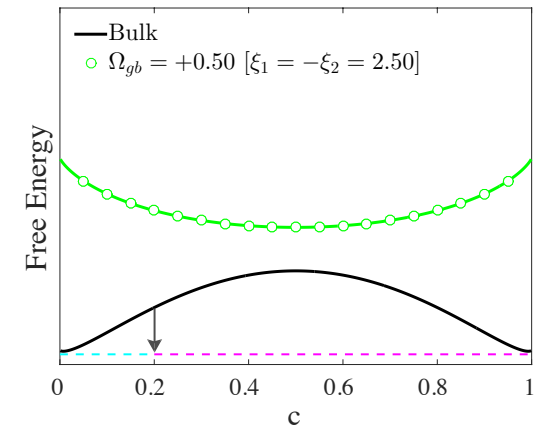
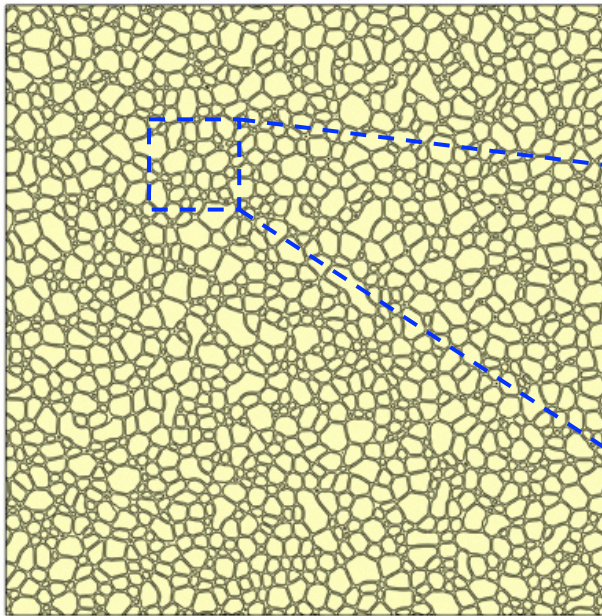
■ Polycrystalline systems

- Initially ($t=0$): **1560** grains
- $c(\mathbf{r}, t = 0) = \langle c \rangle = 0.2$

Normal grain growth
No segregation

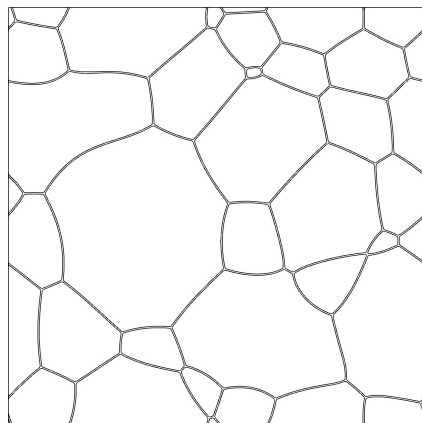


With GB segregation and
phase separation

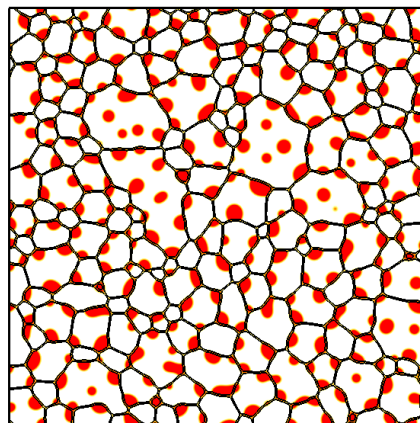


Role of GB Free Energy

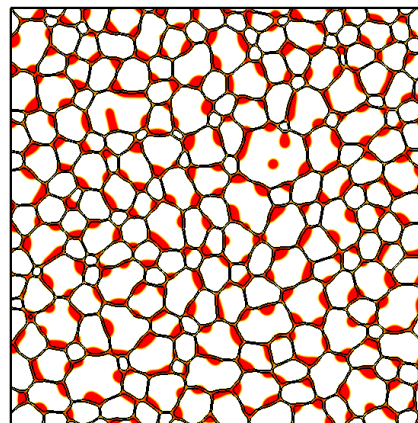
Normal grain growth
(No segregation)



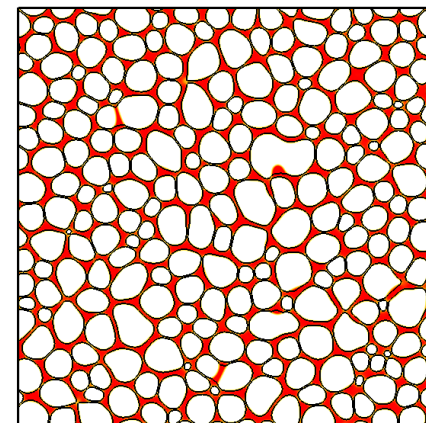
$$G_{gb}^B - G_b^B = 0.60$$



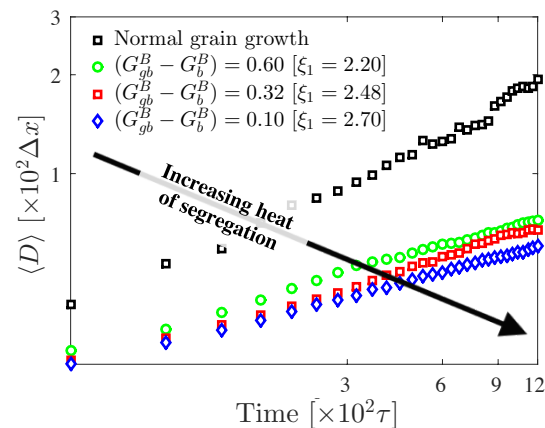
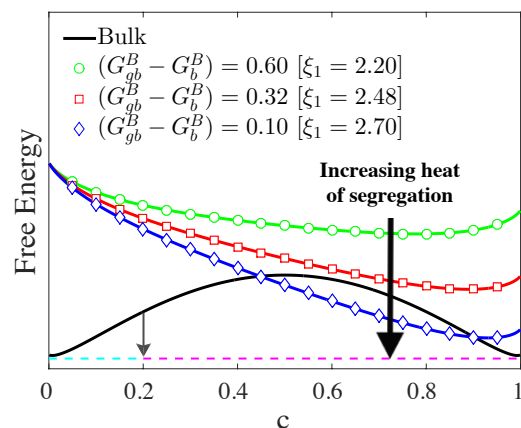
$$G_{gb}^B - G_b^B = 0.32$$



$$G_{gb}^B - G_b^B = 0.10$$



Increasing heat of segregation



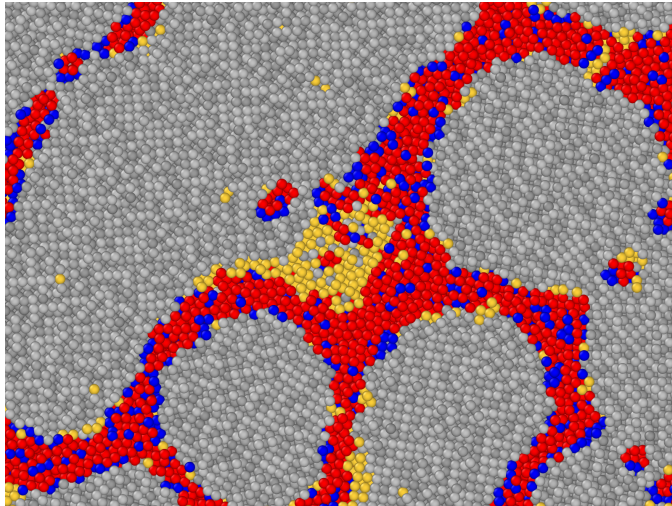
Observations

Atomistics: Pt-Au

Hybrid MC/MD, $T = 775\text{K}$, 15 at.% Au

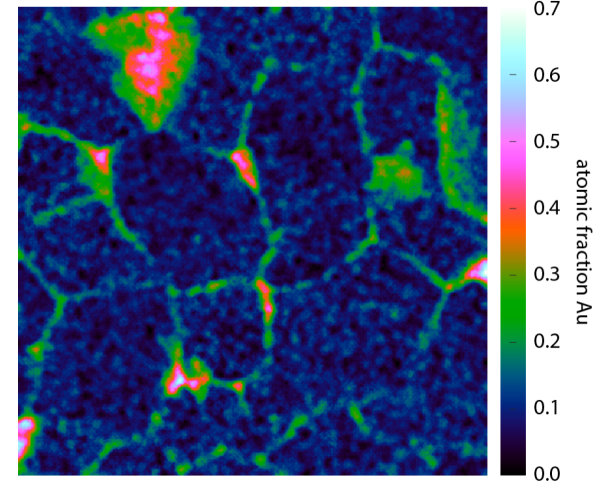
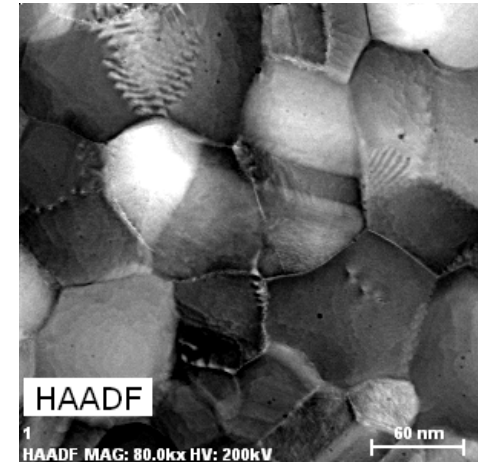
FCC Pt
Non FCC Pt

FCC Au
Non FCC Au



Foiles *et al.*, In preparation (2017)

Experimental: Pt-Au



Abdeljawad *et al.*, Acta Mater. (2017)

Anisotropy: Link to Atomistics

- GBs described by: $G_{gb}^A, G_{gb}^B, \Omega_{gb}$

Ni-Zr

$\Sigma 11s$ —■—
 $\Sigma 11a$ —○—

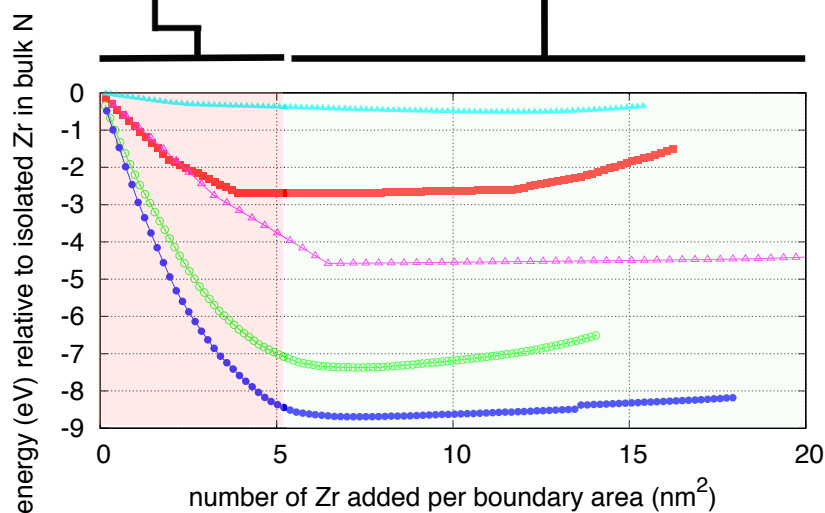
$\Sigma 45$ —●—
 $\Sigma 5t$ —▲—

$\Sigma 3$ —▲—

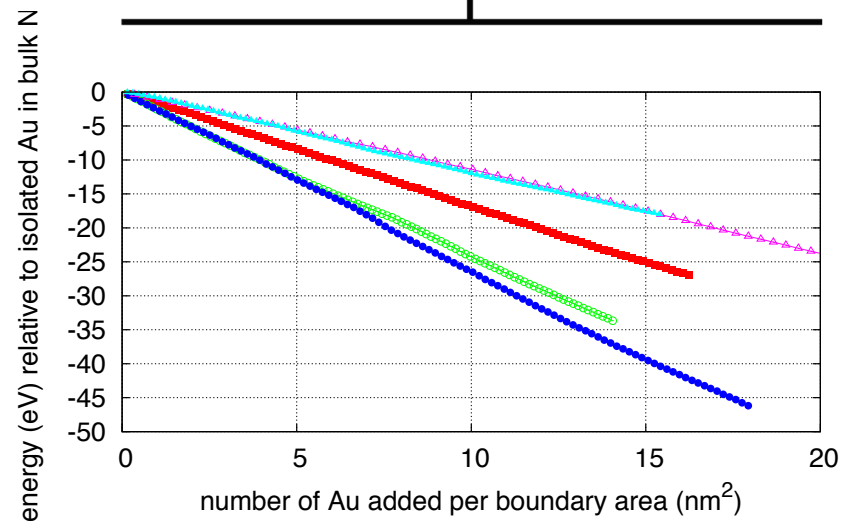
Ni-Au

Increasing heat
of segregation

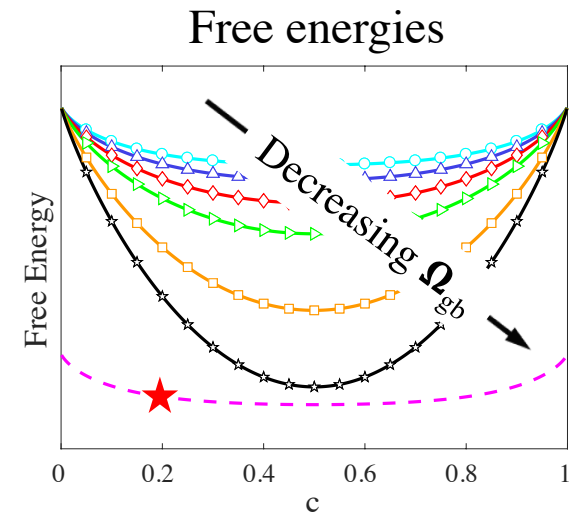
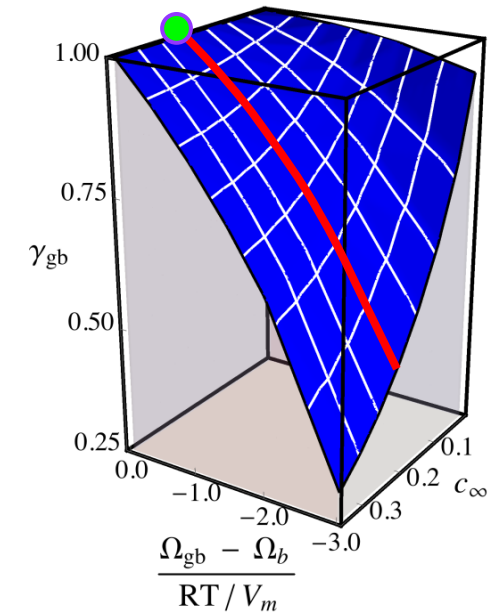
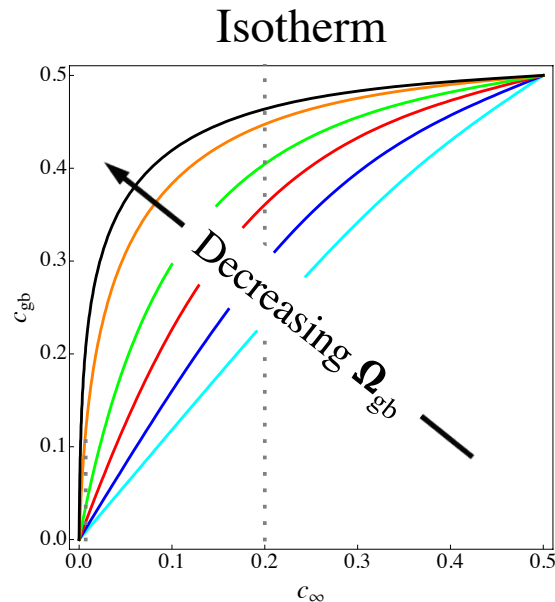
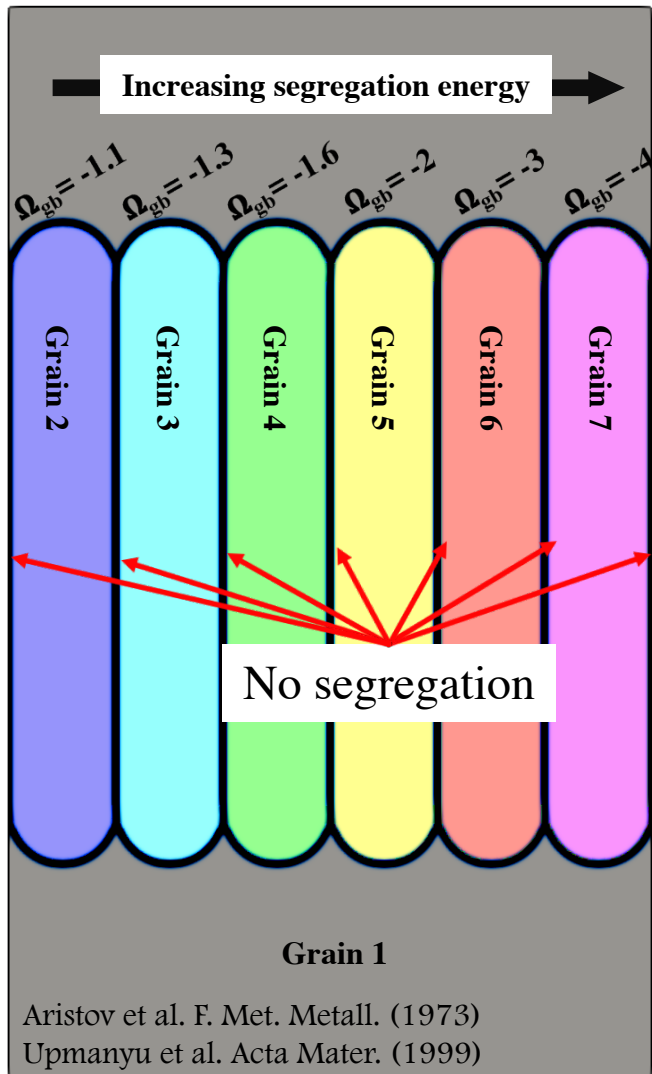
Saturation:
GB solute-solute interaction: $\Omega_{gb} > 0$



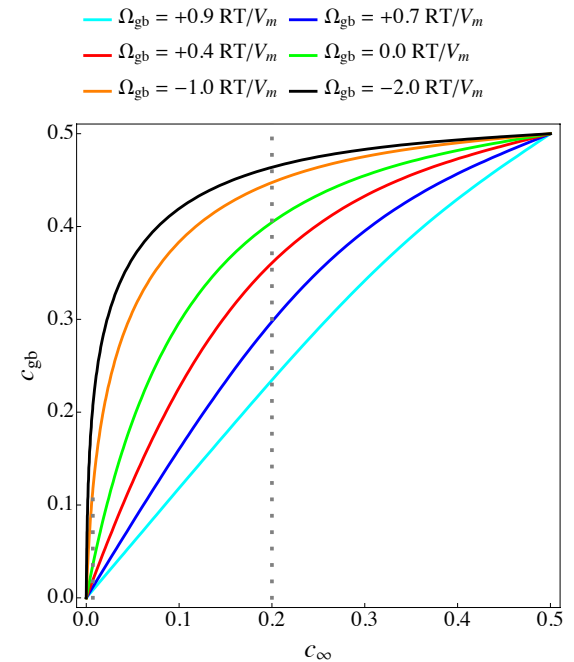
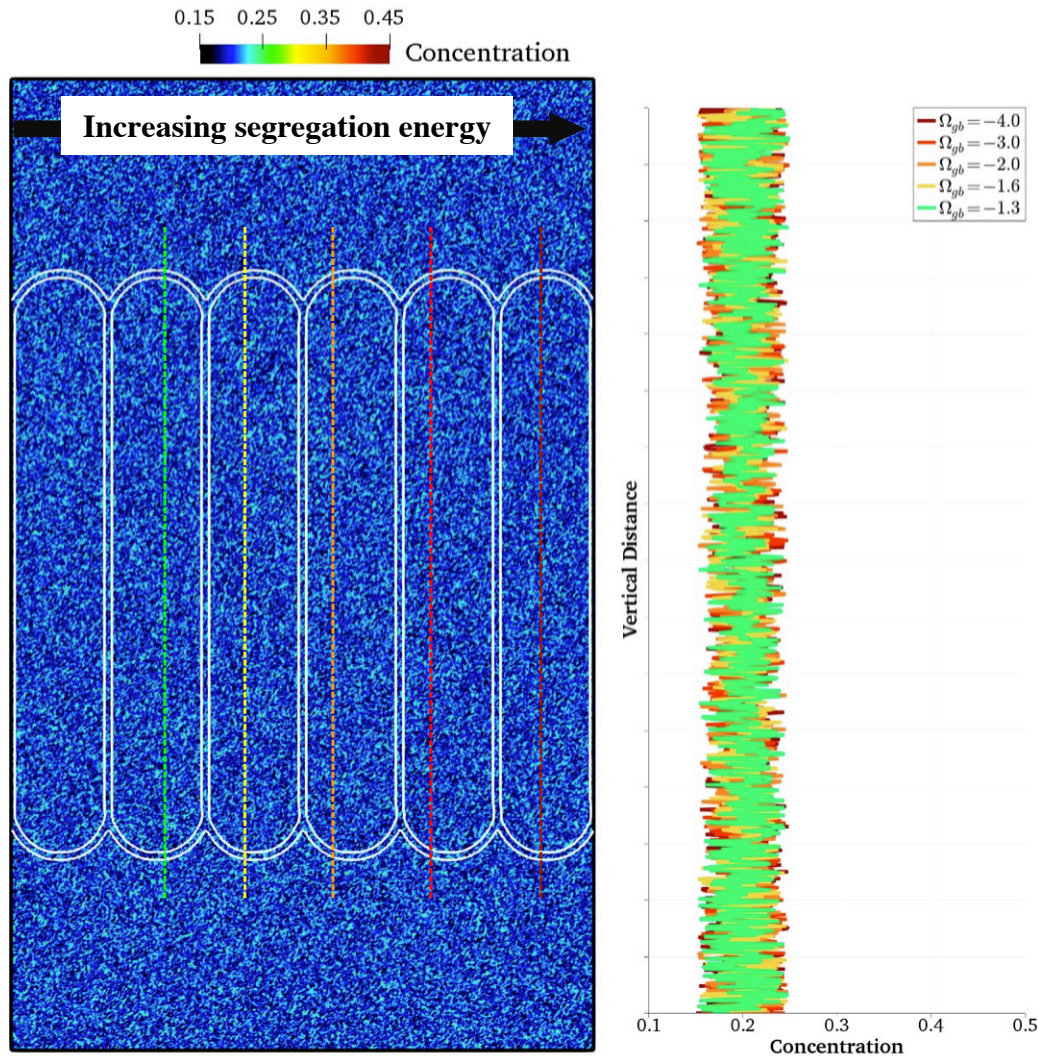
Segregation with no saturation: $\Omega_{gb} < 0$



Anisotropy: Half-loop Geometry



Anisotropy: Half-loop Geometry

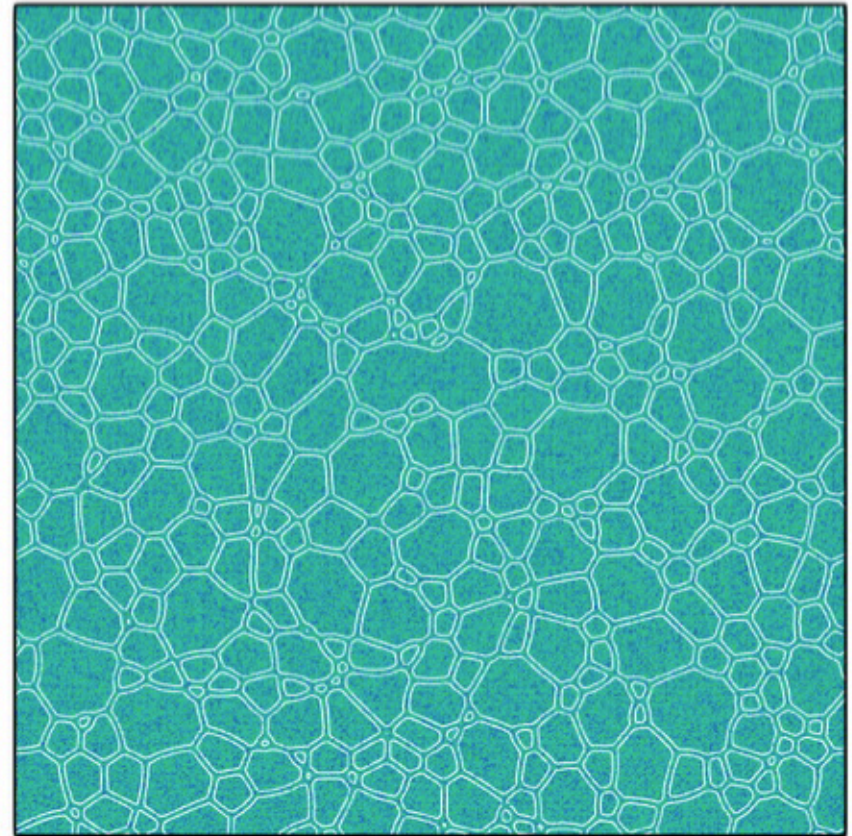
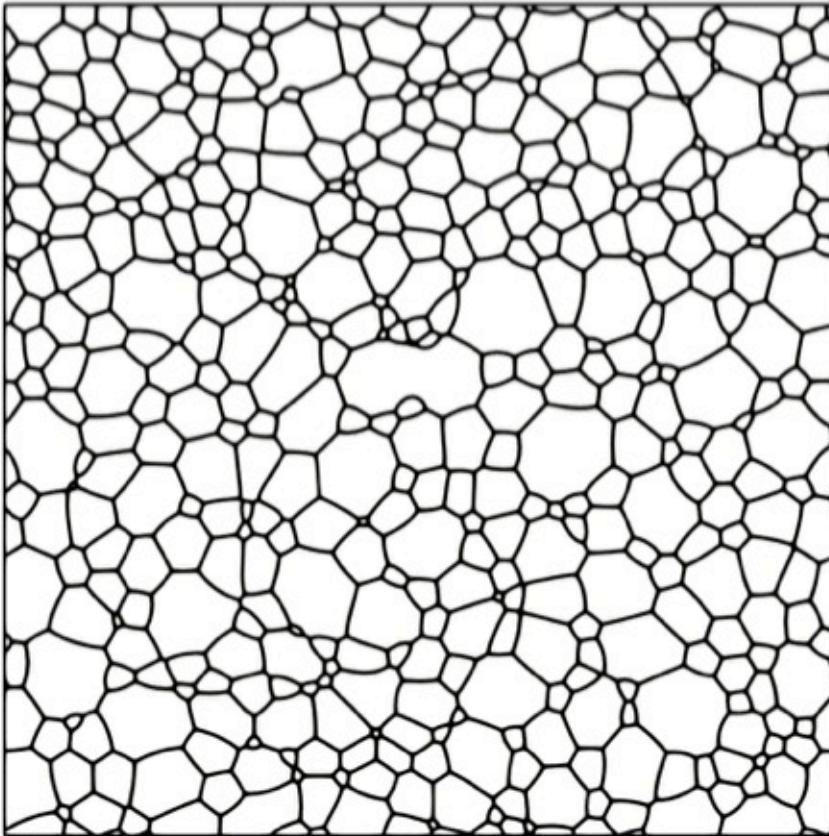


Anisotropy: Polycrystals

- Ω_{gb} Uniformly drawn and randomly assigned (spatially)

$$\Omega_b = \frac{5}{3} \frac{RT}{V_m} \quad \Omega_{gb} \in \left[-\frac{10}{3}, \frac{5}{3} \right] \frac{RT}{V_m}$$

Normal grain growth



Thank you

Publications relevant to this presentation

Argibay, et al. Under review in Acta Mater. (2018)

Abdeljawad, Lu, Argibay, Clark, Boyce and Foiles, Acta Mater. 127 (2017)

Abdeljawad, Medlin, Foiles, Hattar and Zimmerman, J. App. Phys. 119 (2016)

Abdeljawad and Foiles, Acta Mater. 101 (2015)

Acknowledgments

Funding:

Department of Energy (DOE) Basic Energy Sciences (BES)



Backup Slides

Equilibrium Properties

■ Regular solution model:

$$f_i^{mix}(c, T) = \mathbf{G}_i^B c + \mathbf{G}_i^A (1 - c) + \frac{RT}{V_m} \left[c \ln c + (1 - c) \ln(1 - c) \right] + \mathbf{\Omega}_i c(1 - c), \quad i = gb, bulk$$

Free energy of
pure states

Bulk: G_b^A, G_b^B, Ω_b GB: $G_{gb}^A, G_{gb}^B, \Omega_{gb}$

Heat of mixing

$$\begin{aligned} W &= W_\phi + (G_{gb}^A - G_b^A), \\ \xi_1 &= (G_{gb}^A - G_b^A) - (G_{gb}^B - G_b^B) - (\Omega_{gb} - \Omega_b), \\ \xi_2 &= (\Omega_{gb} - \Omega_b). \end{aligned}$$

■ Parallel tangent construction: Segregation isotherm

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

Langmuir-McLean isotherm*

Fowler-Guggenheim isotherm**

* McLean (1957)

** Fowler and Guggenheim(1939)

Competing Processes

■ Grain growth, GB segregation and phase separation

- Initially ($t=0$): **1560** grains
- $c(\mathbf{r}, t = 0) = \langle c \rangle = 0.2$ (unstable alloy)
- Vary GB free energies

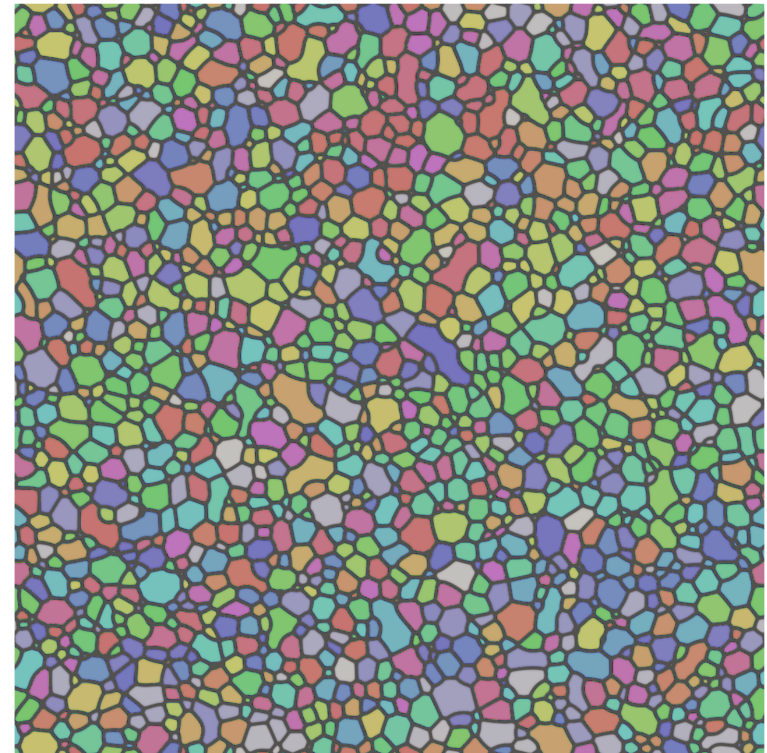
■ Metrics

- Average grain diameter $\langle D \rangle$
- Define solute partitioning factor

$$\Upsilon(t) = \frac{\int d\mathbf{r} \, c(\mathbf{r}, t) P(\vec{\phi})}{\int d\mathbf{r} \, c(\mathbf{r}, t)}$$

$$\Upsilon = \begin{cases} 0, & \text{No solute at GBs} \\ 1, & \text{GBs saturated with solute} \end{cases}$$

Initial ($t = 0$): Colors are for grain IDs



Relation to Solute Drag

- Sharp interface asymptotics (underway)

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[W f_{loc}(c, \phi, T) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right]$$

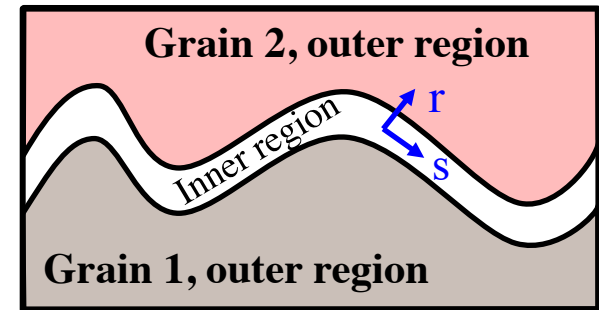
$$\frac{\partial \phi}{\partial t} = -L \left(\frac{\delta \mathcal{F}_{tot}}{\delta \phi} \right)$$

Normal grain growth

$$\mathcal{V}_n = M_{gb} \gamma_{gb} \mathcal{K} = L \epsilon^2 \mathcal{K}$$

With GB solute segregation

$$\mathcal{V}_n = \frac{L \epsilon^2}{1 + \left(\frac{LW}{D} \right) \frac{K_I}{K_{II}}} \mathcal{K} \simeq L \epsilon^2 \left(1 - \frac{LW}{D} \frac{K_I}{K_{II}} \right) \mathcal{K}$$



$$\phi = \phi_0 + \omega \phi_1 + \omega^2 \phi_2 + \dots$$

$$c = c_0 + \omega c_1 + \omega^2 c_2 + \dots$$

Provatas and Elder (2009)

Karma and Rappel, Phys. Rev. E **57** (1998)

$$K_I = \int_{-\infty}^{+\infty} \frac{\partial c_o}{\partial x} \int_0^x (c_o - c_\infty) dx' dx$$

$$K_{II} = \int_{-\infty}^{+\infty} \left(\frac{d\phi_0}{d\xi} \right)^2 d\xi$$

D: solute diffusivity

Young Man, in mathematics you don't understand things. You just get used to them

Relation to Solute Drag

- Phase field sharp interface asymptotics (underway)

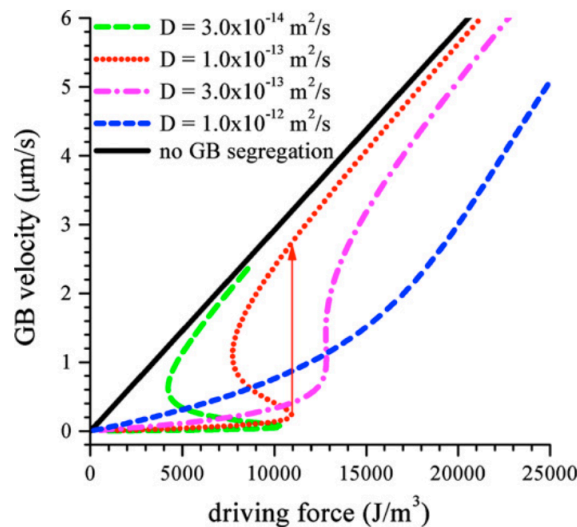
$$\mathcal{V}_n = \frac{L\epsilon^2}{1 + \left(\frac{LW}{D}\right) \frac{K_I}{K_{II}}} \mathcal{K} \simeq L\epsilon^2 \left(1 - \frac{LW}{D} \frac{K_I}{K_{II}}\right) \mathcal{K}$$

- Solute drag model [ideal, dilute alloys]

$$\mathcal{V}_n = M_{gb} \left(P - P^*(\mathcal{V}_n) \right)$$

$P = \gamma_{gb} \mathcal{K}$: Curvature driven flow

$P^*(\mathcal{V}_n)$: Drag pressure



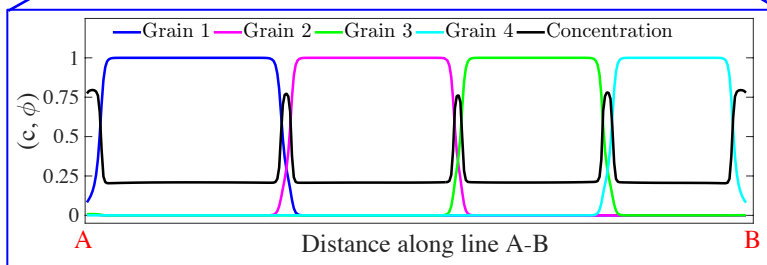
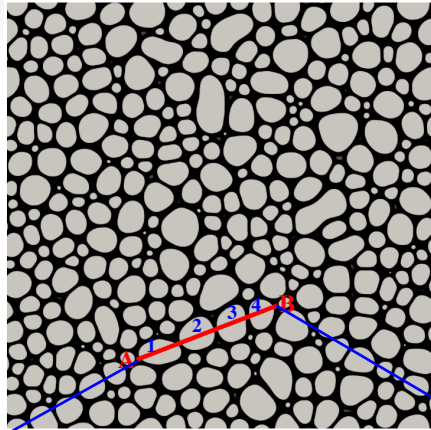
Cahn, Acta Metall. (1962)

Hillert and Sundman, Acta Metall. (1976)

Gottstein and Shvindlerman (1999)

Kim and Park, Acta Mater. (2008)

GB Widening?



$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[W f_{loc}(c, \phi, T) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right]$$

- Concentration-dependent energy barrier: $W = W(c)$
- Control GB width: $\epsilon \stackrel{?}{=} \epsilon(c)$

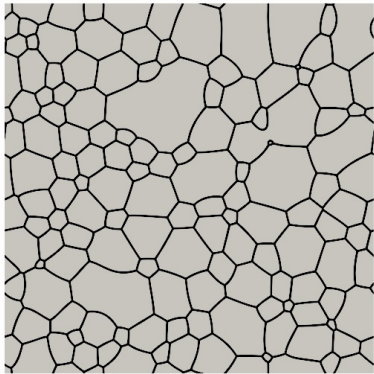
$$\text{Energy: } \gamma_{gb} \sim \epsilon \sqrt{W}$$

$$\text{Width: } \delta_{gb} \sim \frac{\epsilon}{\sqrt{W}}$$

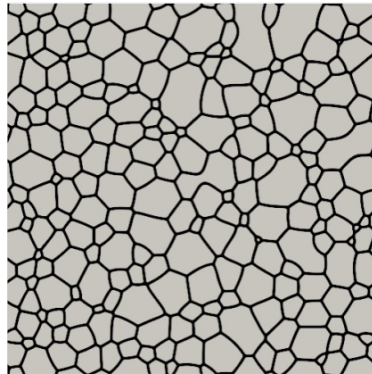
GB Widening?

- Fix free energy model parameters
- Vary the initial alloy concentration

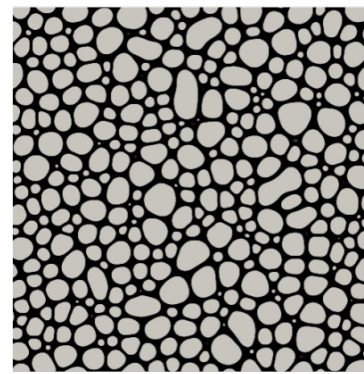
Normal grain growth



$\langle c \rangle = 0.2$

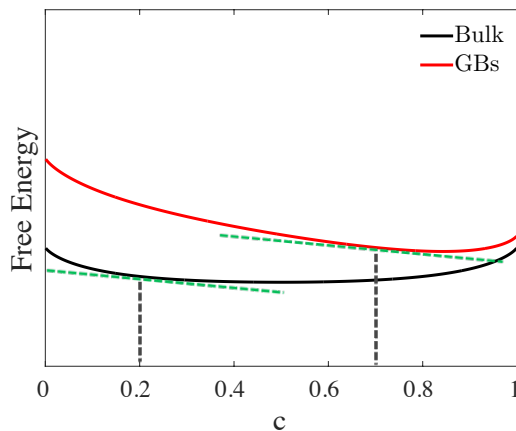


$\langle c \rangle = 0.35$

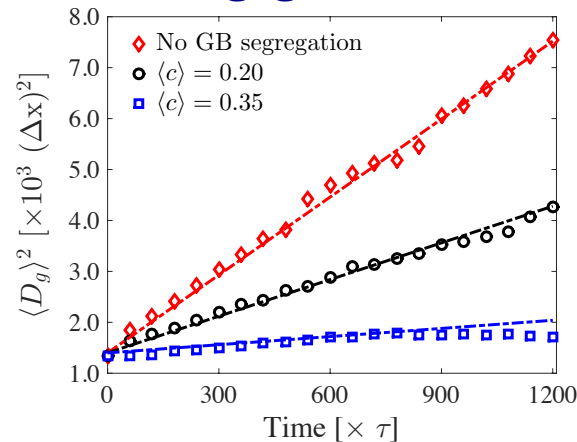


■ GB
■ grain

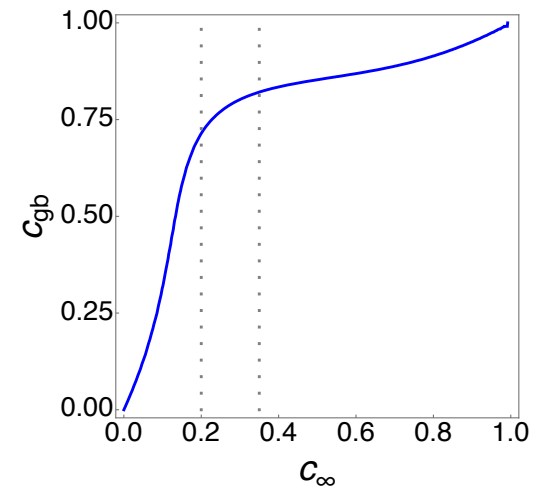
Free energies



Avg. grain area



GB segregation
isotherm



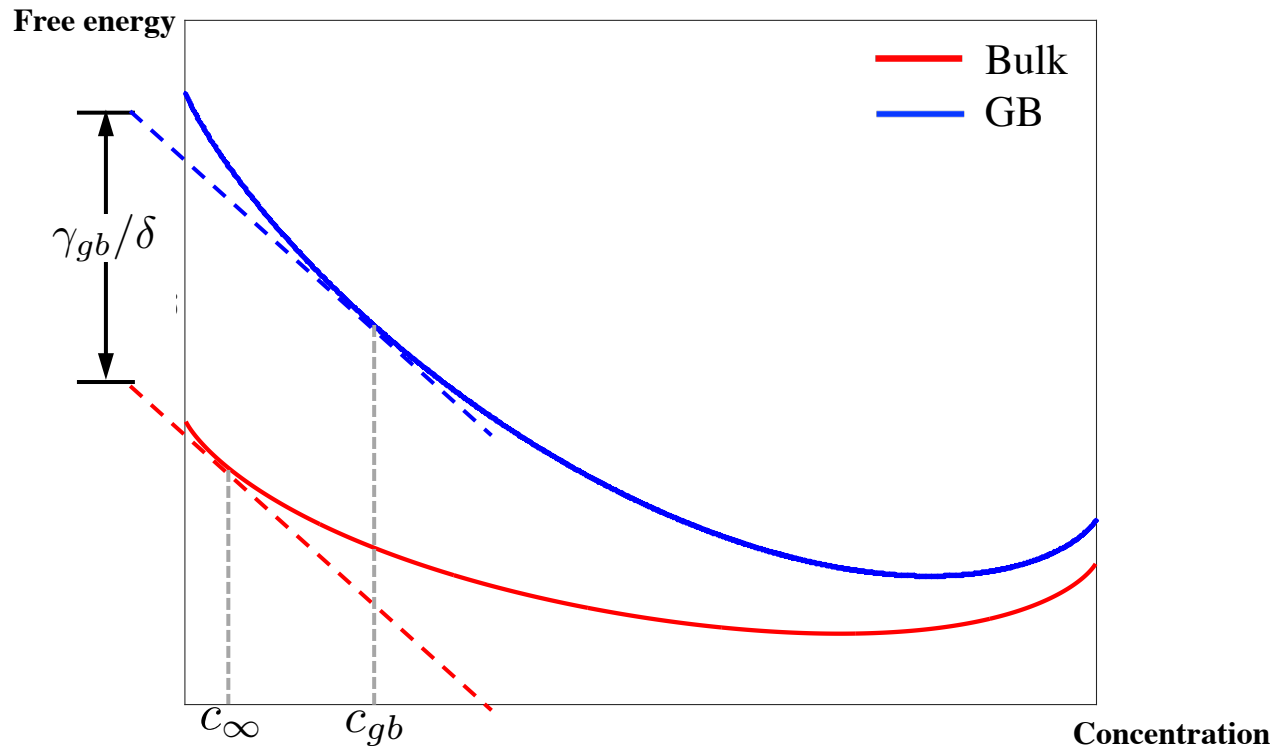
Segregation: Graphically

■ Parallel tangent construction

$$f_i^{mix}(c, T) = \mathbf{G}_i^B c + \mathbf{G}_i^A (1 - c) + \frac{RT}{V_m} \left[c \ln c + (1 - c) \ln(1 - c) \right] + \mathbf{\Omega}_i c(1 - c), \quad i = gb, bulk$$

Free energy of pure states

Heat of mixing



A: Solvent (matrix phase)

B: Solute atoms

Bulk: G_b^A, G_b^B, Ω_b

GB: $G_{gb}^A, G_{gb}^B, \Omega_{gb}$

c_∞ : Alloy concentration

δ : GB width

M. Hillert (2007)

P. Lejcek (2010)