SAND2015-1732C

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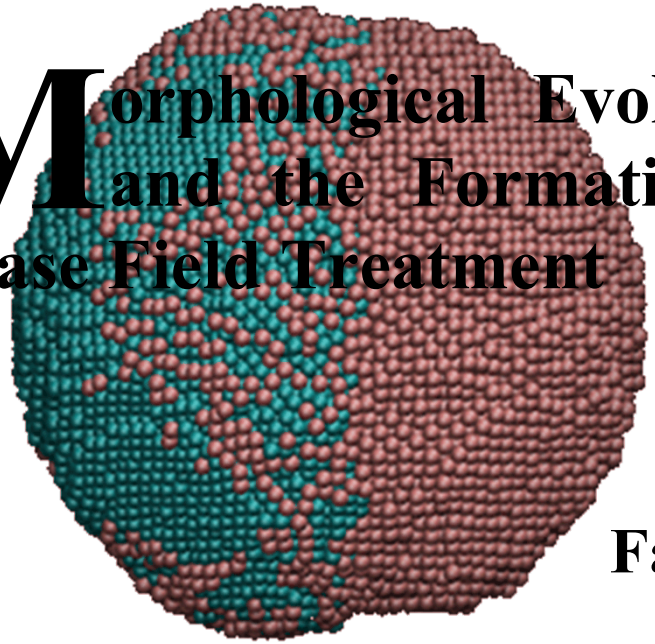
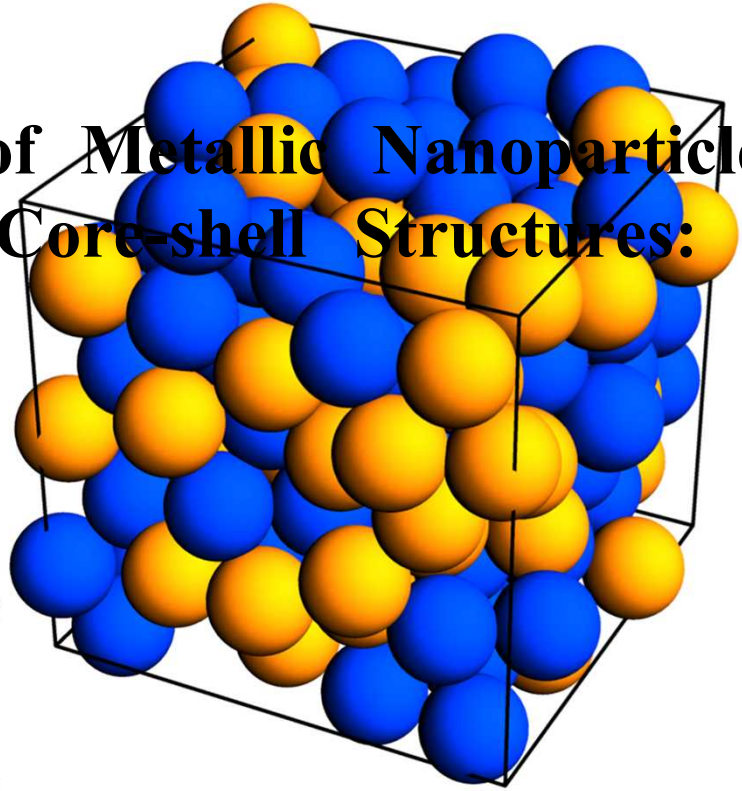


# Morphological Evolution of Metallic Nanoparticles and the Formation of Core-shell Structures: A Phase Field Treatment



**Fadi Abde**

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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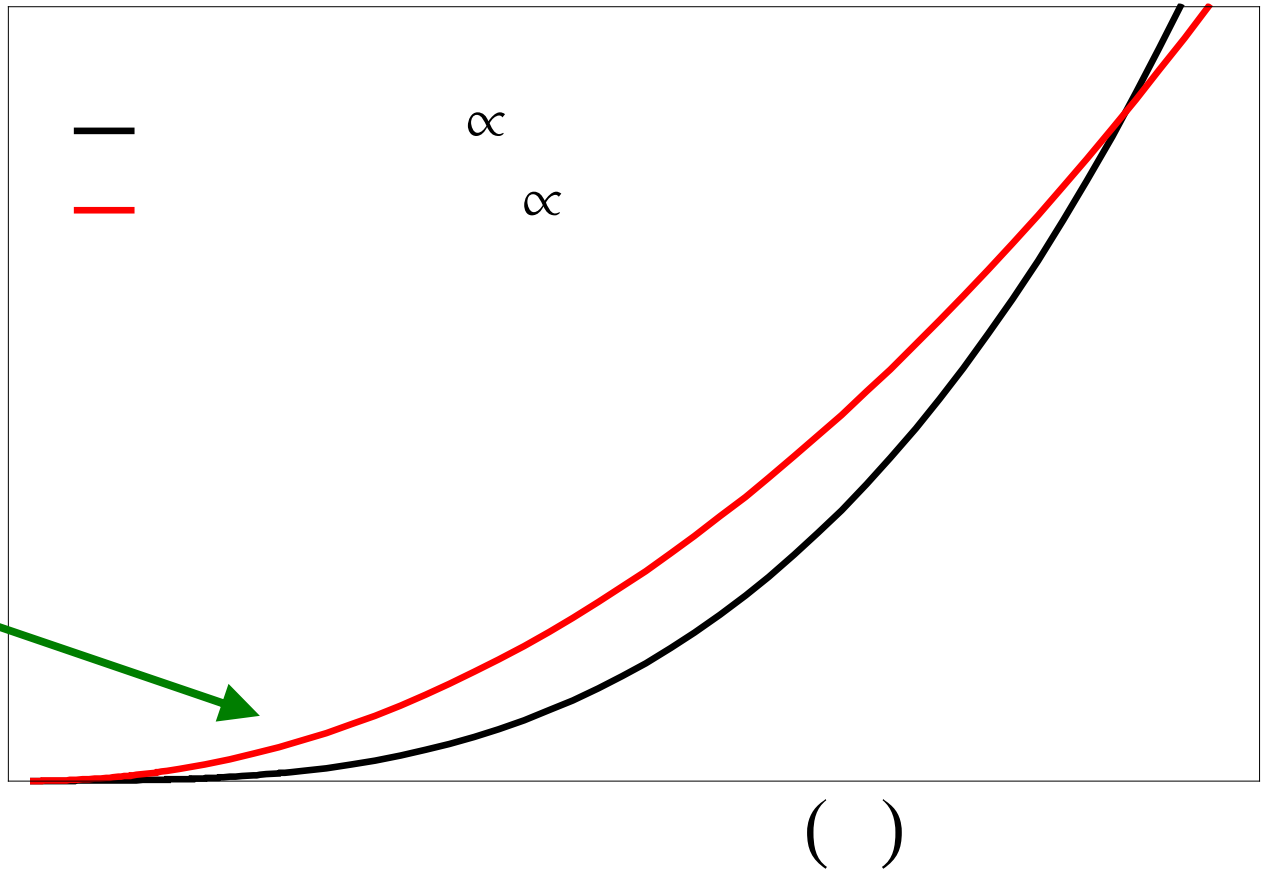
# The Nano in Nanomaterials

Sandia National Laboratories



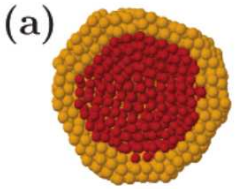

"There's plenty of room at the bottom" – R. Feynman

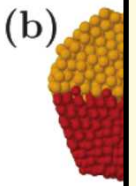
- **Capillary length:** $d_c \simeq \sqrt{\frac{\gamma}{\rho g}}$

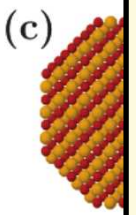
Water at room temperature: $d_c \sim 10^{-4} m$

# A Zoo of Morphologies

Sandia National Laboratories



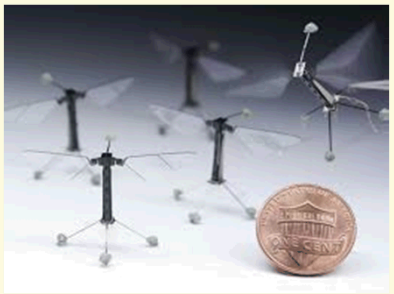

$t_0$

$t_1$

## Nanostructured Materials

- **Feature size at the nano-scale**
- **Characteristic size affects**
  - Geometric shape/morphology
  - Energetic stability
- **Potential applications**
  - Miniaturization for nano-electronics
  - Electrocatalysis (fuel cells and energy devices)
  - Materials joining and **solders**

RoboBee



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

Ferra (2005)

# Nanosolders

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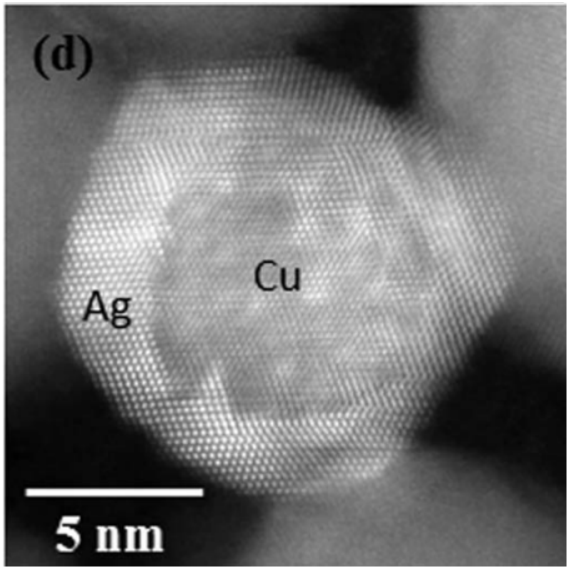
- Main advantages
  - Low processing temperatures
  - High service temperatures
  - Example: Ag/Cu
    - Bonding at ~ 200C
    - Applications above 350C




Lu et al. Appl. Phys. Lett. Mat. **2** (2014)

# Key Questions

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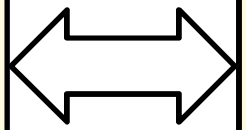
- Need to identify and understand
  - Factors controlling the formation of various morphologies
  - Interfacial energies and energetic stability

**Role of (micro)structure**

- Particle size and/or ratio, distribution
- Volume fractions
- Porosity
- Transport (surface vs. bulk)
- Design: patterned, graded, …



**Shape/Morphology**

- **Core-shell**
- Janus drops
- Mixed alloy
- Multi-core-shell

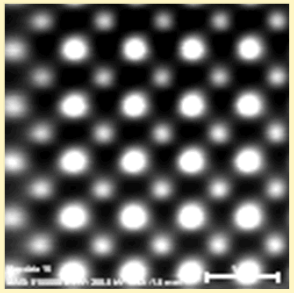
# Approach

T. Boyle, B. Clark, P. Lu
Sandia National Labs

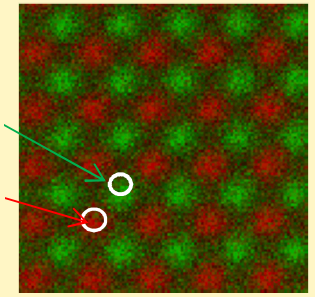
**Experimental**

- In-situ aberration-corrected STEM to obtain atomic-scale, compositional maps at a given (T, t)

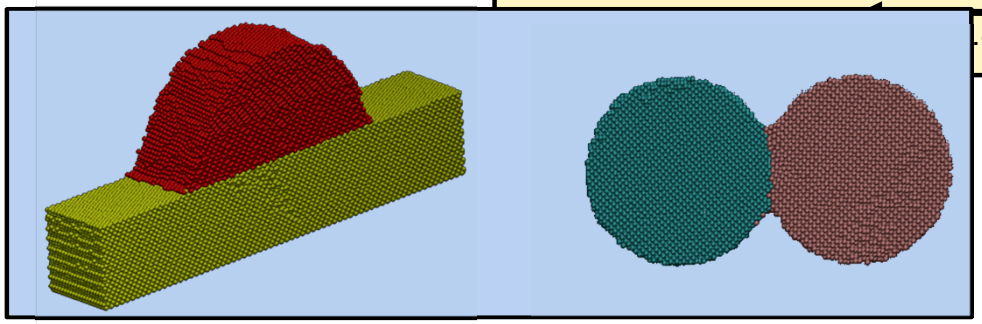

HAADF Z-contrast imaging

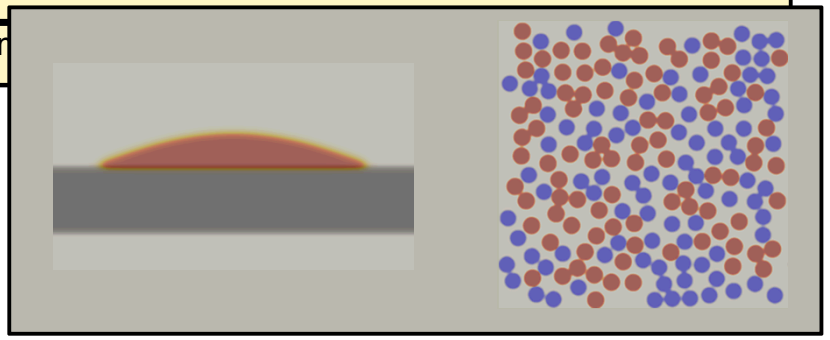


Atomic-scale element map









**Atomistic (MD, MC)**

- Interfacial energies
- Thermodynamic stability

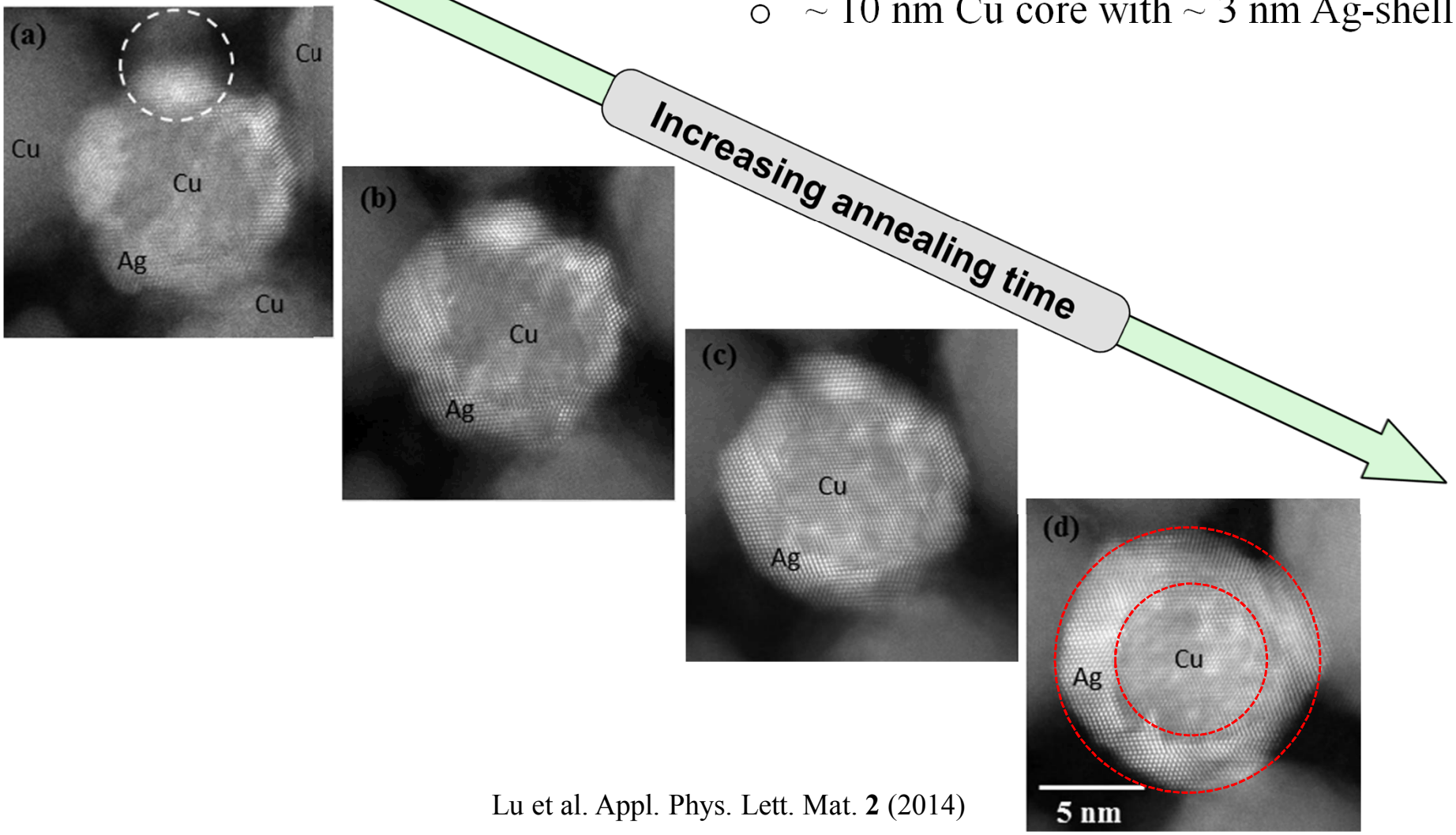
**Mesoscale (phase field)**

- Role of microstructure
- Diffusive scales

# Experimental Results: $Cu_{core}Ag_{shell}$

Sandia National Laboratories

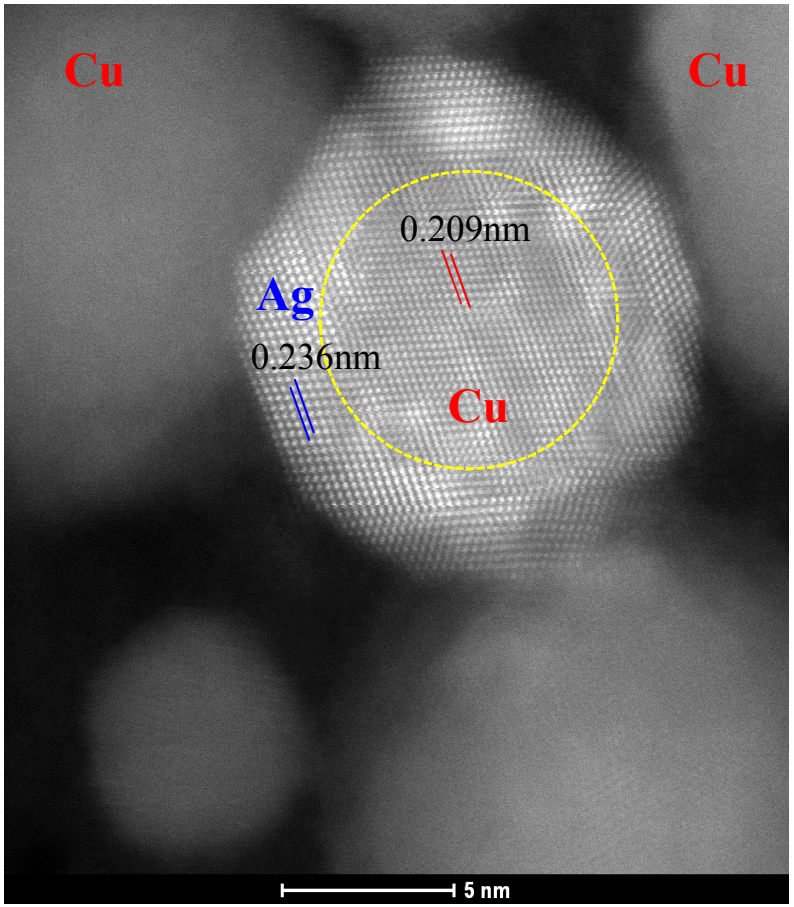
- Results from heating to 150 °C
- ~ 10 nm Cu core with ~ 3 nm Ag-shell

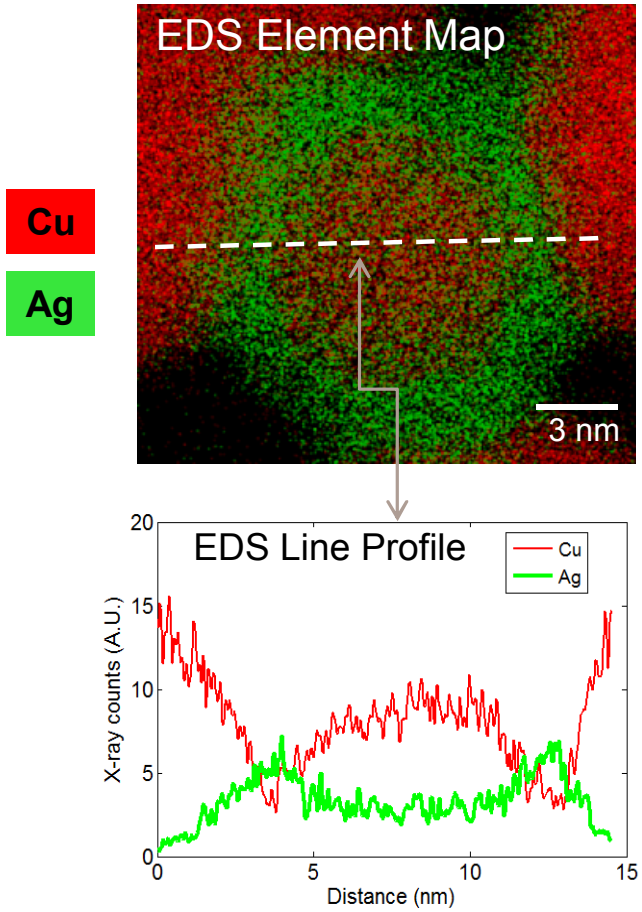



Lu et al. Appl. Phys. Lett. Mat. **2** (2014)

# Experimental Results: $Cu_{core}Ag_{shell}$

- Results from heating to 150 °C
- Carefully avoid electron beam heating
- ~ 10 nm Cu core with ~ 3 nm Ag-shell




Lu et al. Appl. Phys. Lett. Mat. **2** (2014)

# Experimental Results: $Cu_{core}Ag_{shell}$

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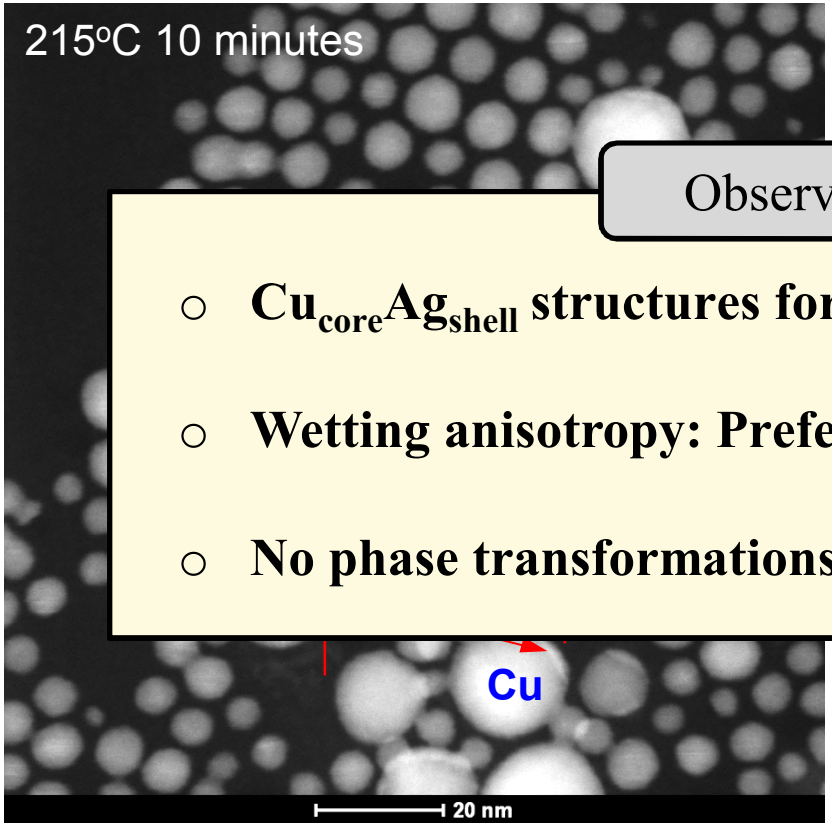
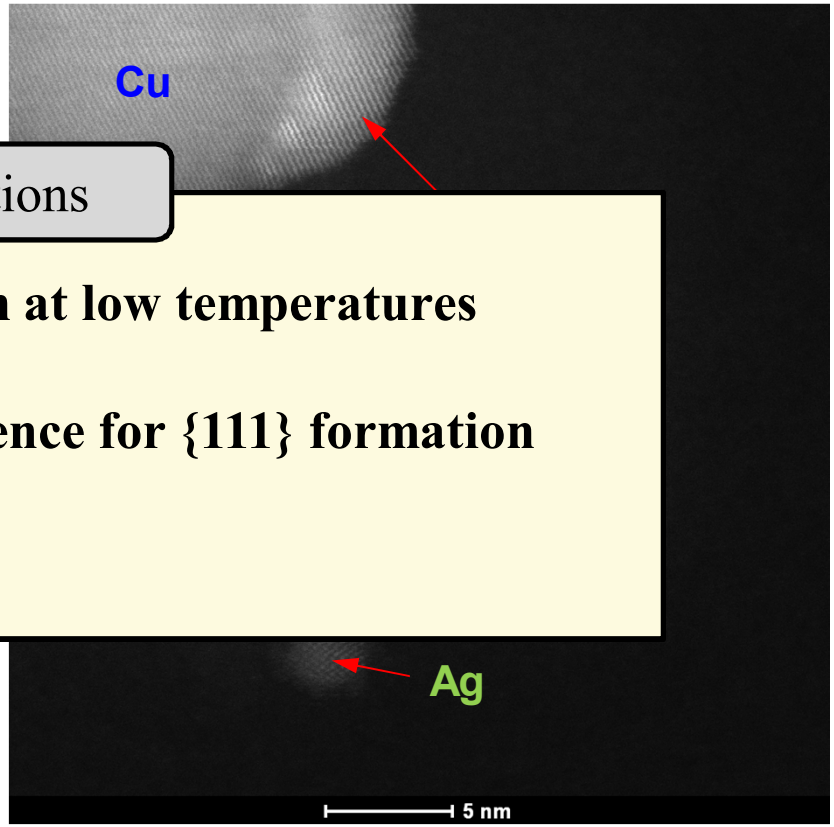
- Anisotropy
  - Slightly higher annealing temperature (215°C)
  - Preference for wetting along {111}



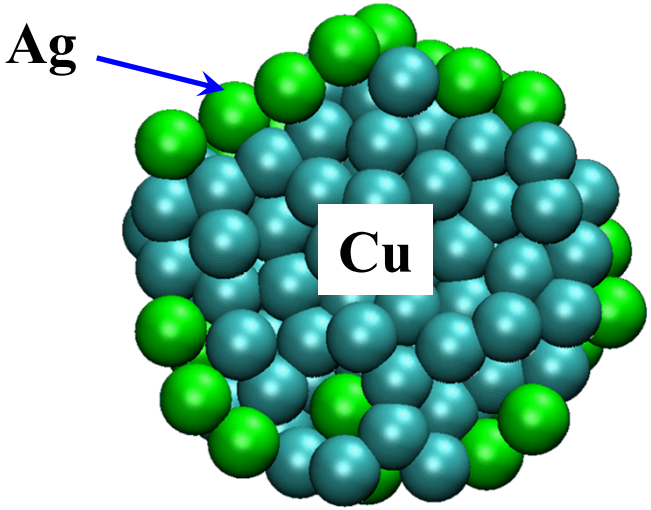

**Observations**

- **$Cu_{core}Ag_{shell}$ structures form at low temperatures**
- **Wetting anisotropy: Preference for {111} formation**
- **No phase transformations**

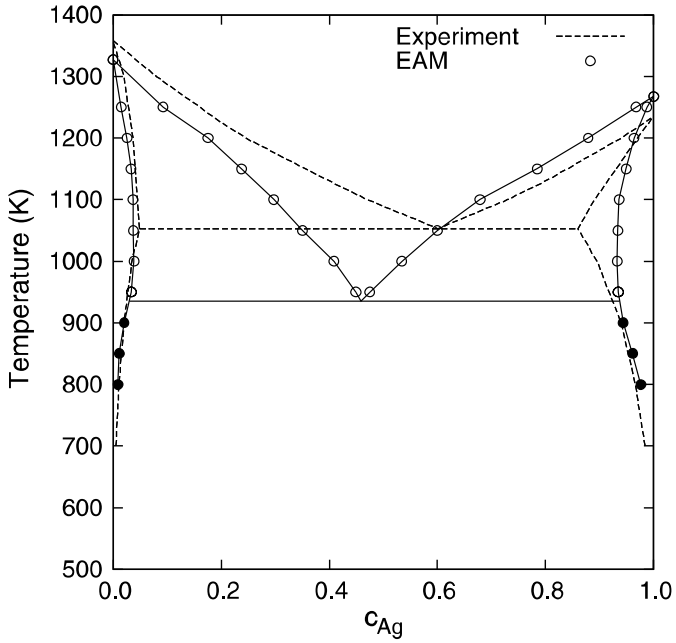
Lu et al. Appl. Phys. Lett. Mat. **2** (2014)

# Atomistic Results

- Start with very small particles
  - Ag-Cu EAM potential by Williams et al. (2006)
  - Typical time step ≈ 1fs
  - 2 nm Janus nanoparticle
  - Anneal at 800K for 12.5 ns (≈ 12.5 million steps)
  - Formation of $Cu_{core}Ag_{shell}$




Particle cut in half for detail




Williams et al. Mod. Simul. Mater. Sci. Eng. **14** (2006)

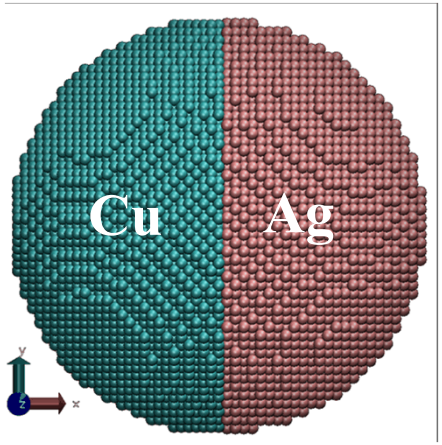
# Janus Nanoparticles

- Molecular Dynamics (MD)
  - 10nm Janus nanoparticles
  - At 800 K (below eutectic) for < 7 ns
  - Core-shell "wetting" starts to form
  - Equilibrium not yet reached. Need to run longer.

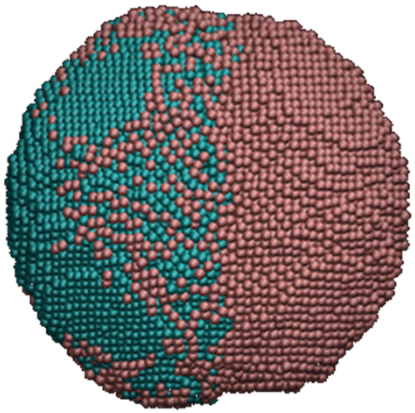
**Computationally expensive**

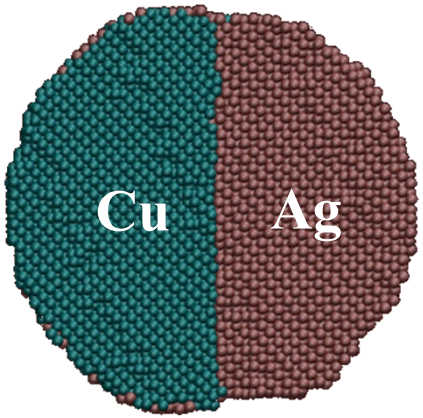
Try Monte Carlo (MC) with the Ag-Cu EAM potential by Williams et al. (2006)

Williams et al. Mod. Simul. Mater. Sci. Eng. **14** (2006)




Anneal at 800 K for
< 7 ns ≈ 7 million steps





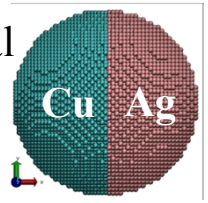

cross section

# Janus Nanoparticles

Sandia National Laboratories

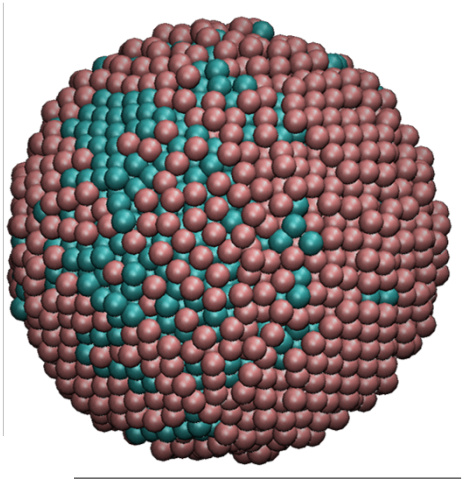
- Monte Carlo (MC)
  - Simulation is in MC steps (not real time )
  - Randomly pick two particles to swap (with small translation)
  - Accept move if energy is lower, or according to Boltzmann (Metropolis)

Initial

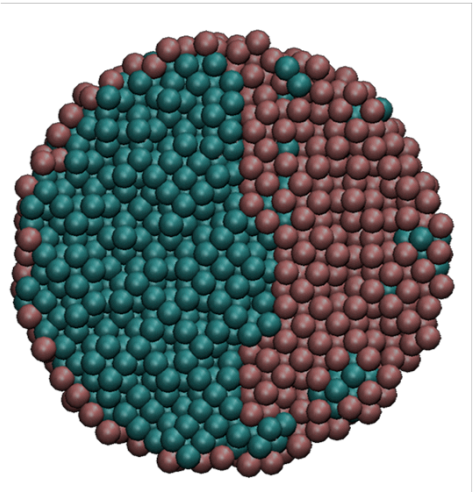



**5 nm Janus particle after 20 million MC steps**

Full view



Sliced in half



**Anyone who considers arithmetical methods of producing random digits is, of course, in a state of sin**

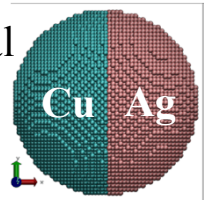
J. von Neumann

# Janus Nanoparticles

Sandia National Laboratories

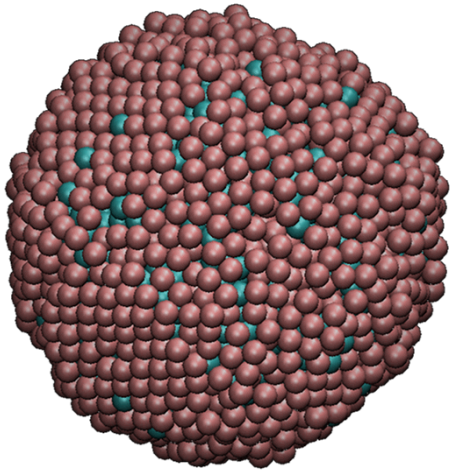
- Monte Carlo (MC)
  - Simulation is in MC steps (not real time )
  - Randomly pick two particles to swap (with small translation)
  - Accept move if energy is lower, or according to Boltzmann (Metropolis)

Initial

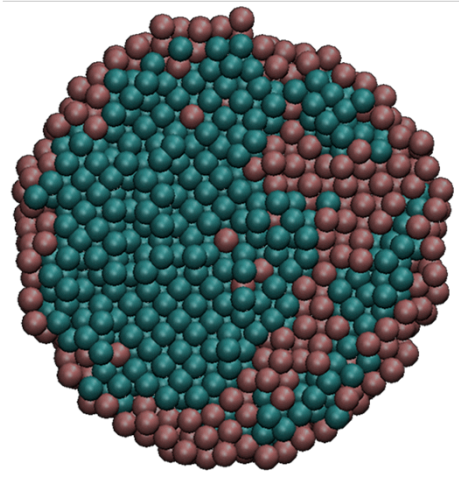



**5 nm Janus particle after 60 million MC steps**

Full view



Sliced in half



**Anyone who considers arithmetical methods of producing random digits is, of course, in a state of sin**

J. von Neumann

# Spreading along {111}

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- Preference for wetting along {111}
  - Balance of interfacial energies
  - Geometry: Slabs (periodic in two dimensions)
  - Tool: Molecular Statics (energy minimization)
  - Calculate all relevant interfacial energies

$$\gamma_{Ag(100)}, \gamma_{Ag(111)}, \gamma_{Cu(100)}, \gamma_{Cu(111)}$$
$$\gamma_{AgCu(100)}, \gamma_{AgCu(111)}$$

| $\gamma$ (J/m$^2$) | Cu(100) | Cu(111) | Surface Ag |
|---|---|---|---|
| Ag(100) | 0.532 | 0.433 | 0.940 |
| Ag(111) | 0.475 | **0.197** | 0.862 |
| Surface Cu | 1.345 | 1.239 | |

Chandross. Mod. Simul. Mater. Sci. Eng. **22** (2014)

The most energetic gain when I) Forming AgCu interfaces II) wetting along {111}

# Observations

Sandia National Laboratories

- Atomistic (MD, MC)
  - Ag-Cu: Formation of CucoreAgshell structures
  - Relatively low temperatures, no phase transformations
  - Anisotropy in spreading: preference along {111}
  - Balance of interfacial energies of $\gamma_{Ag}, \gamma_{Cu}, \gamma_{AgCu}$
  - Unable to attain diffusive scales

**Mesoscale treatment**

- Phase field formalism
- Incorporates the relevant physics (interfacial energies, wetting)
- Examine various aspects of (micro)structure
  - Particle size/ratio/distribution
  - Volume fractions
  - Transport paths (surface vs. bulk)

# Phase Field Formalism

Sandia National Laboratories

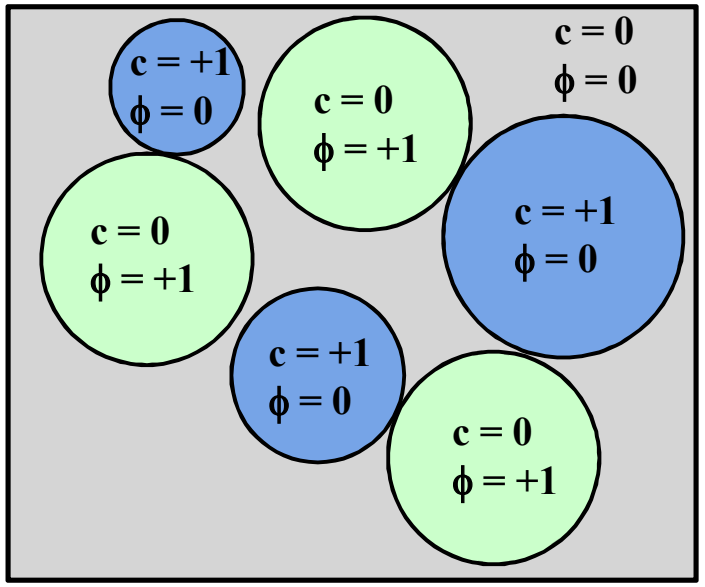
- Assumptions
  - Particles are single crystal
  - No phase transformations
  - Bulk phase are immiscible (positive heat of mixing)
  - Non-reactive wetting/spreading
  - (Micro)structure evolution is due to interfaces
  - Interfaces are isotropic (Anisotropy to added later)

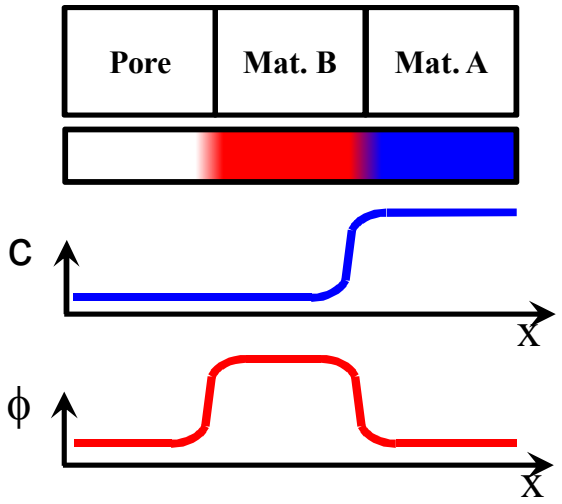
First, we assume a spherical cow

# Phase Field Formalism

Sandia National Laboratories

- Systems of interest
  - Ensemble of particles
  - Material A: Evolves in time
  - Material B: Static
- Order parameters
  - c: Evolving material (Material A)
  - $\phi$: Static material (Material B)
- Total free energy
  - Bulk thermodynamics
  - Interfacial energies and thermodynamics (Gibbs-Thomson condition, adsorption, wetting, …)
  - Dynamics driven by minimization of energy



# Phase Field Formalism (Cont.)

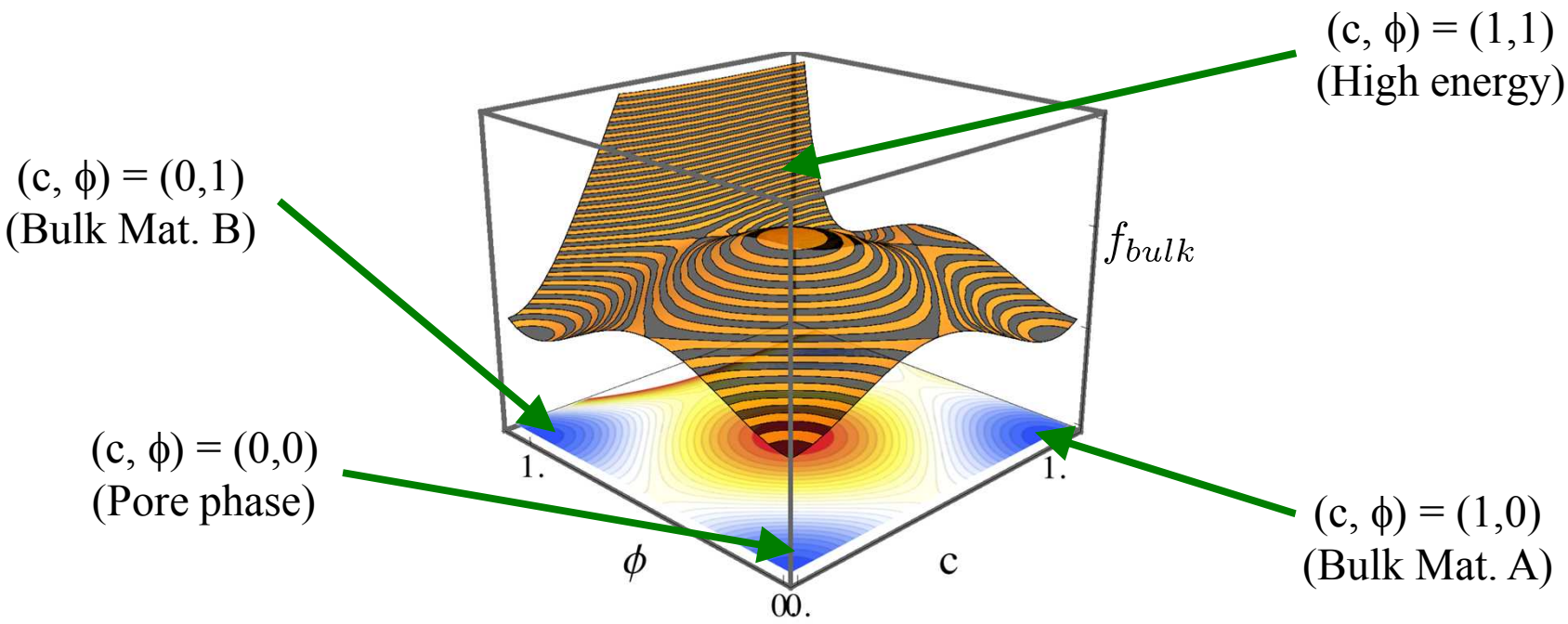
Sandia National Laboratories

- Total free energy

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[ f_{bulk}(c,\phi) + \frac{\kappa_c^2}{2}|\nabla c|^2 + \frac{\kappa_\phi^2}{2}|\nabla \phi|^2 - \xi_1 z_1(c,\phi) \right]$$

**Bulk** **Interfacial energy** **Wetting**
**Mat. A wets B**

$$f_{bulk}(c,\phi) = m_c g_1(c) + m_\phi g_2(\phi) + \xi_2 z_2(c,\phi)$$



# Phase Field Formalism (Cont.)

Sandia National Laboratories

- Total free energy

$$\mathcal{F}_{tot} = \int d\mathbf{r} \left[ f_{bulk}(c,\phi) + \frac{\kappa_c^2}{2}|\nabla c|^2 + \frac{\kappa_\phi^2}{2}|\nabla \phi|^2 - \xi_1 z_1(c,\phi) \right]$$

**Bulk** | **Interfacial energy** | **Wetting** — **Mat. A wets B**

- Dynamics

**- Mat. A (c 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. (conservation of mass)

$M_c$: (degenerate) atomic mobility $M_c = M_c(c, \phi, \cdots)$

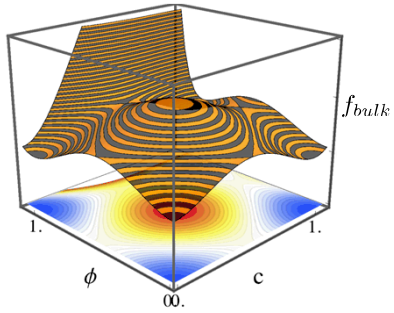
**Allow inhomogeneity in diffusion pathways (surface, bulk, …)**

# Model Parameters

- Bulk Phases

$m_c$
$m_\phi$
$\xi_2$

Three stable phases
(Mat. A, Mat. B, Pore)



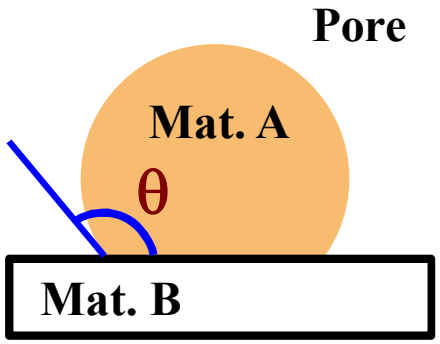

- Interfacial Energies and Widths

**Energies:** $\gamma_A \simeq \kappa_c \sqrt{m_c}$

**Widths** $\delta_A \simeq \dfrac{\kappa_c}{\sqrt{m_c}}$

- Wetting Behavior

$\xi_1$ : Equilibrium wetting angle

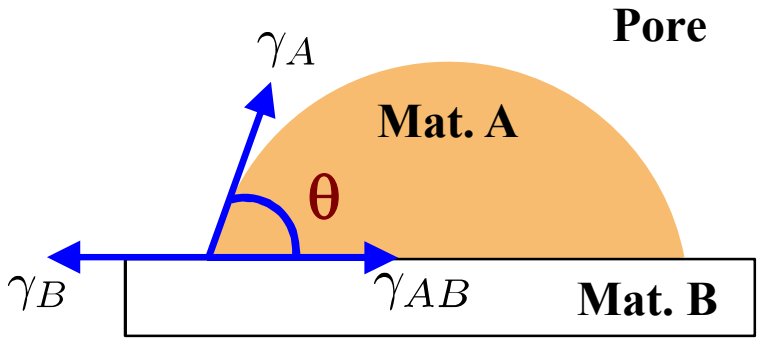



**With four parameters I can fit an elephant, and with five I can make him wiggle his trunk**

J. von Neumann

# Model Parameterization

- Wetting parameter
  - Material B: Static
  - Mat. A and B: Single crystals
  - Interfaces are isotropic




Young-Dupre Equation: $\cos(\theta) = \dfrac{\gamma_B - \gamma_{AB}}{\gamma_A}$

Definition of interface energy: $\gamma = \Delta\mathcal{F}$

$$\gamma_B - \gamma_{AB} = \int d\mathbf{r}\,[\xi_1 z_1(c,\phi) - \xi_2 z_2(c,\phi) - m_c g(c)]$$

$$\gamma_A = \int d\mathbf{r}\; m_c g(c)$$

No need to track the ϕ field

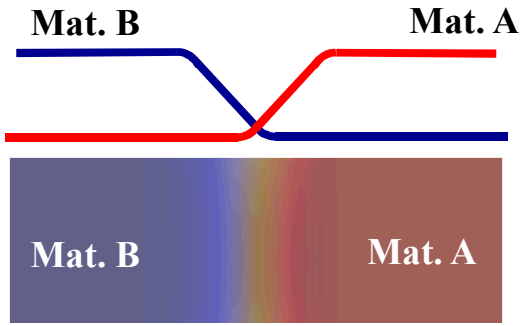
# Equilibrium Properties

- Equilibrium 1D solution for c and ϕ

$$c(x) = \frac{1}{2}\left[1.0 + \tanh\left(\frac{x+L}{\delta}\right)\right]$$

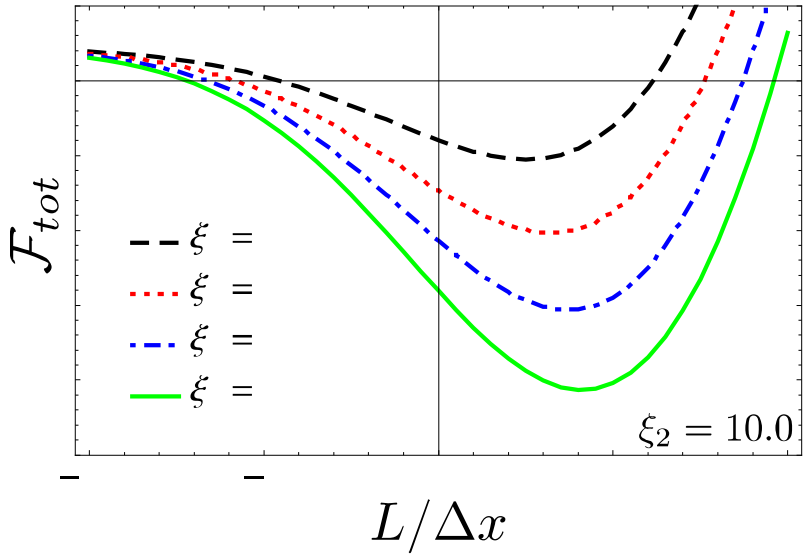
$$\phi(x) = \frac{1}{2}\left[1.0 - \tanh\left(\frac{x}{\delta}\right)\right]$$

δ: Interfacial width
L: Interfacial overlap

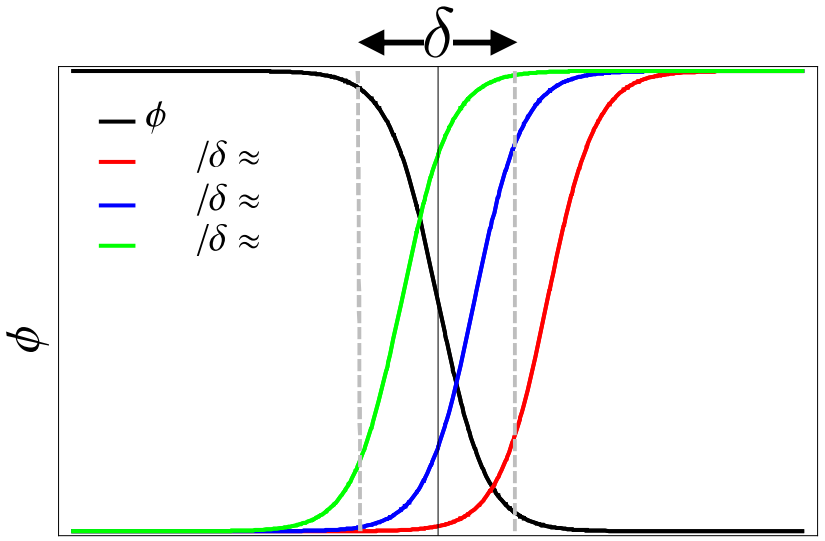



- Plug profiles in energy functional and set $\partial\mathcal{F}/\partial L = 0$ to find minimizers

Energy vs. L




1D solution



# Virtual Sessile Drops

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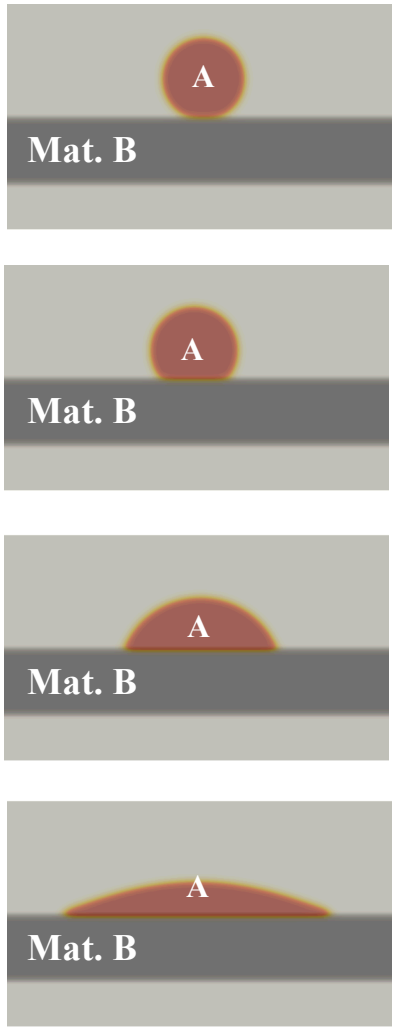
- Equilibrium wetting angle




$\xi_1 = 0.1$
$\theta \approx 155°$

$\xi_1 = 0.3$
$\theta \approx 135°$

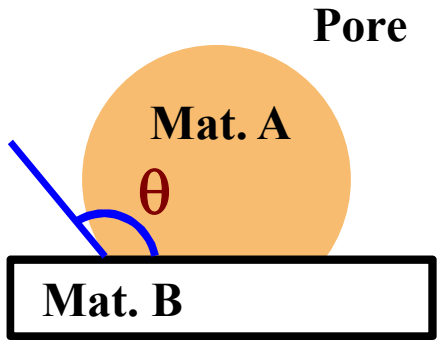
$\xi_1 = 0.9$
$\theta \approx 65°$

$\xi_1 = 1.2$
$\theta \approx 30°$

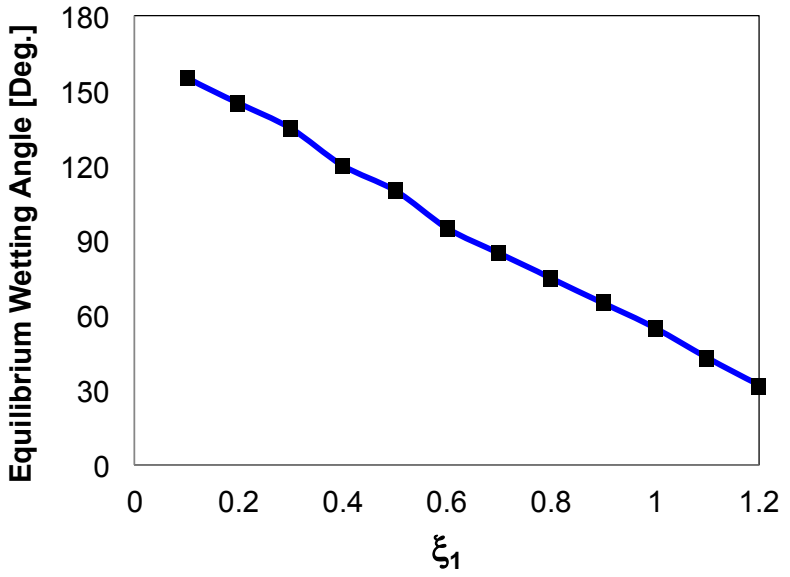
**Low wettability**
**Large θ**

Increasing wettability

**High wettability**
**Small θ**




Equilibrium wetting angle θ vs. $\xi_1$




Assuming values for Ag-Cu system

# A Two-particle System

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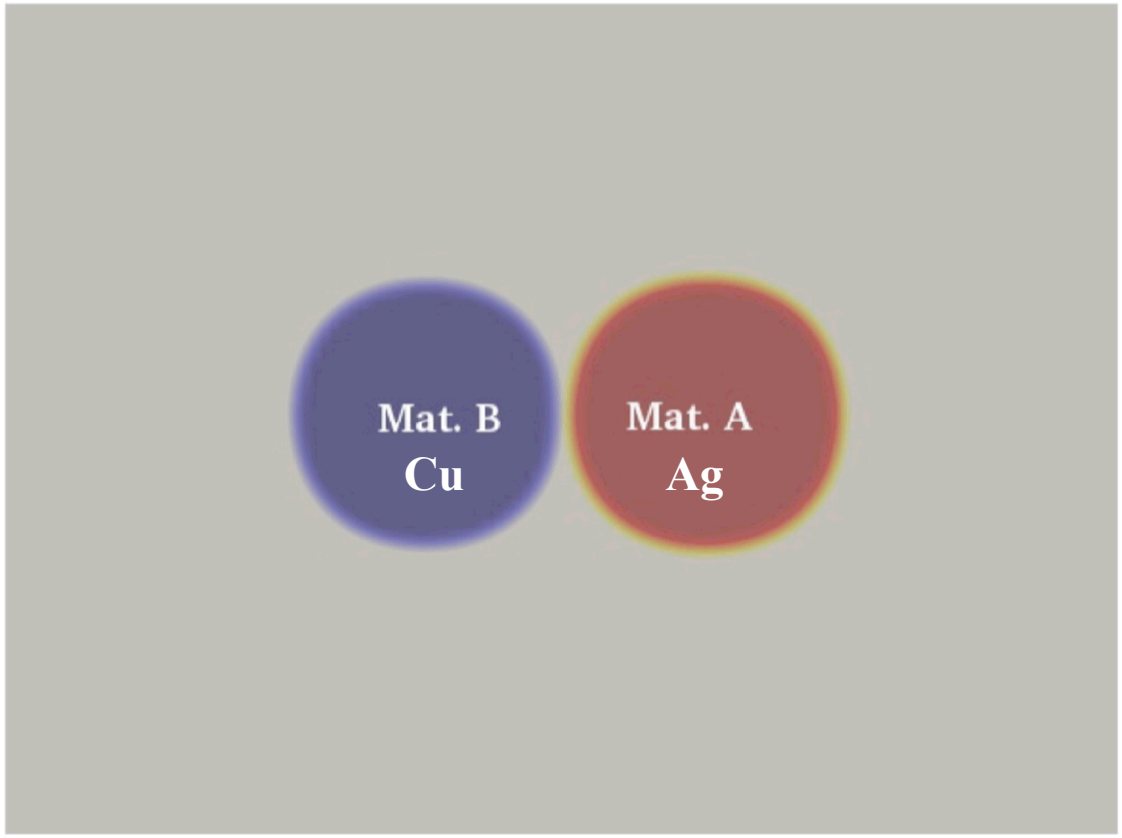
- Formation of core-shell structures
  - Interfacial energies representative of Ag-Cu system: $\gamma_{Ag}, \gamma_{Cu}, \gamma_{AgCu}$
  - $\xi_1 = 1.2$: $\theta \approx 30°$, assuming values for {100} planes

$\gamma_{Ag(100)} = 0.94$ J/m$^2$
$\gamma_{Cu(100)} = 1.345$ J/m$^2$
$\gamma_{AgCu(100)} = 0.532$ J/m$^2$



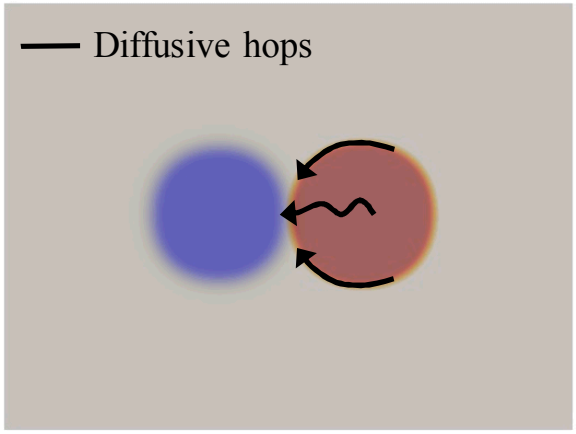
# Bulk vs. Surface Diffusion

- Fix wetting parameter $\xi_1$
- Coverage fraction $\lambda = \dfrac{\text{Volume elements of A-B interfacial region}}{\text{Total interfacial elements of Mat. B}}$

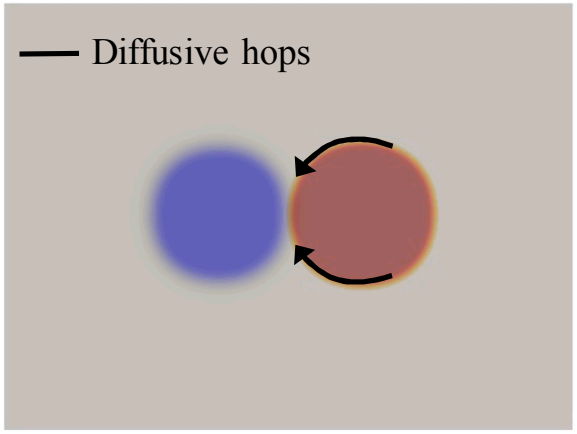
**Mat. A**

**Mat. B**

Bulk (all active)



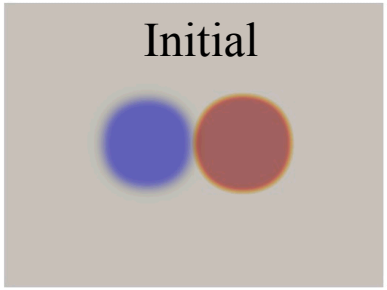

Surface

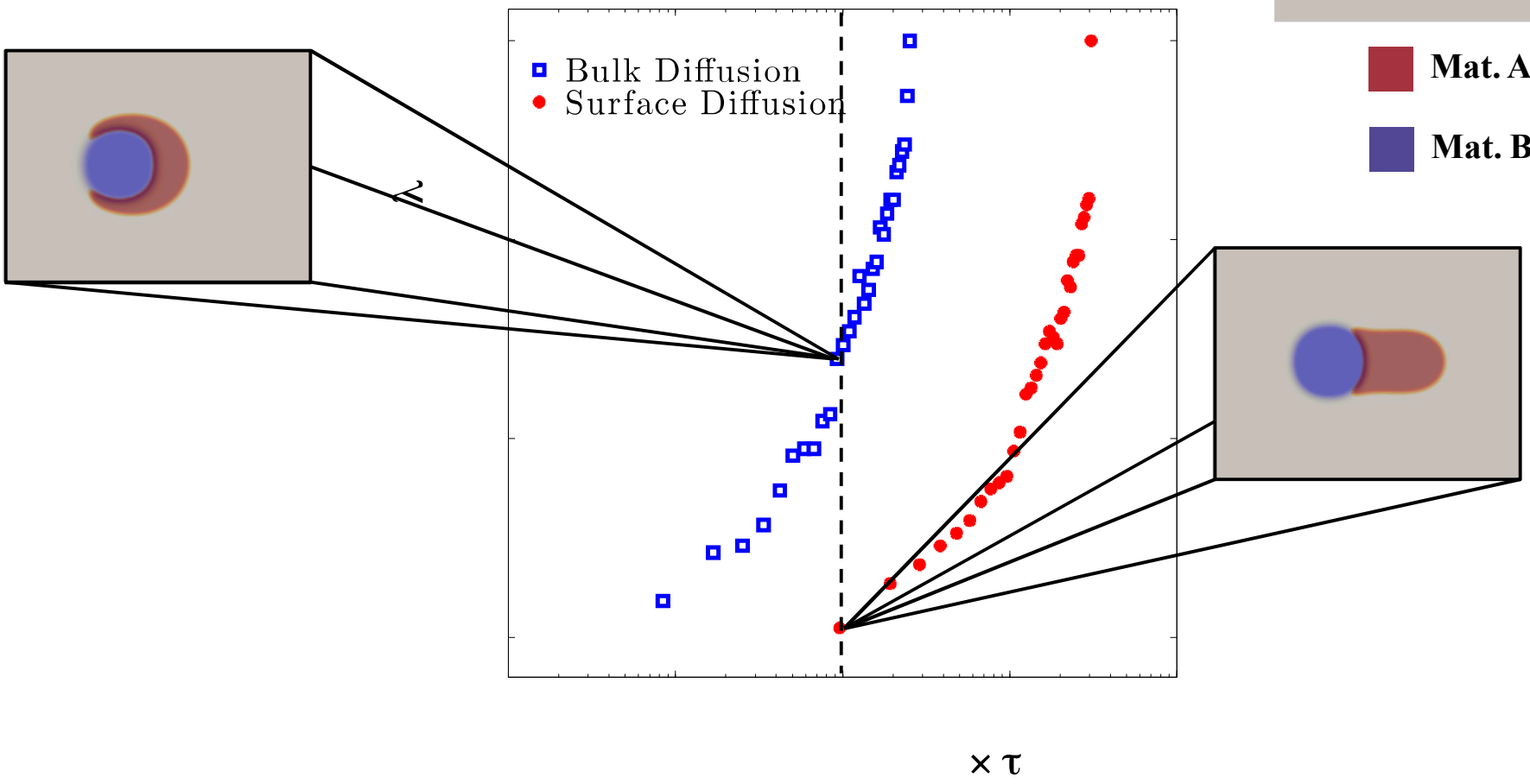


# Bulk vs. Surface Diffusion

Sandia National Laboratories

- Coverage fraction $\lambda = \dfrac{\text{Volume elements of A-B interfacial region}}{\text{Total interfacial elements of Mat. B}}$



# Role of Wettability

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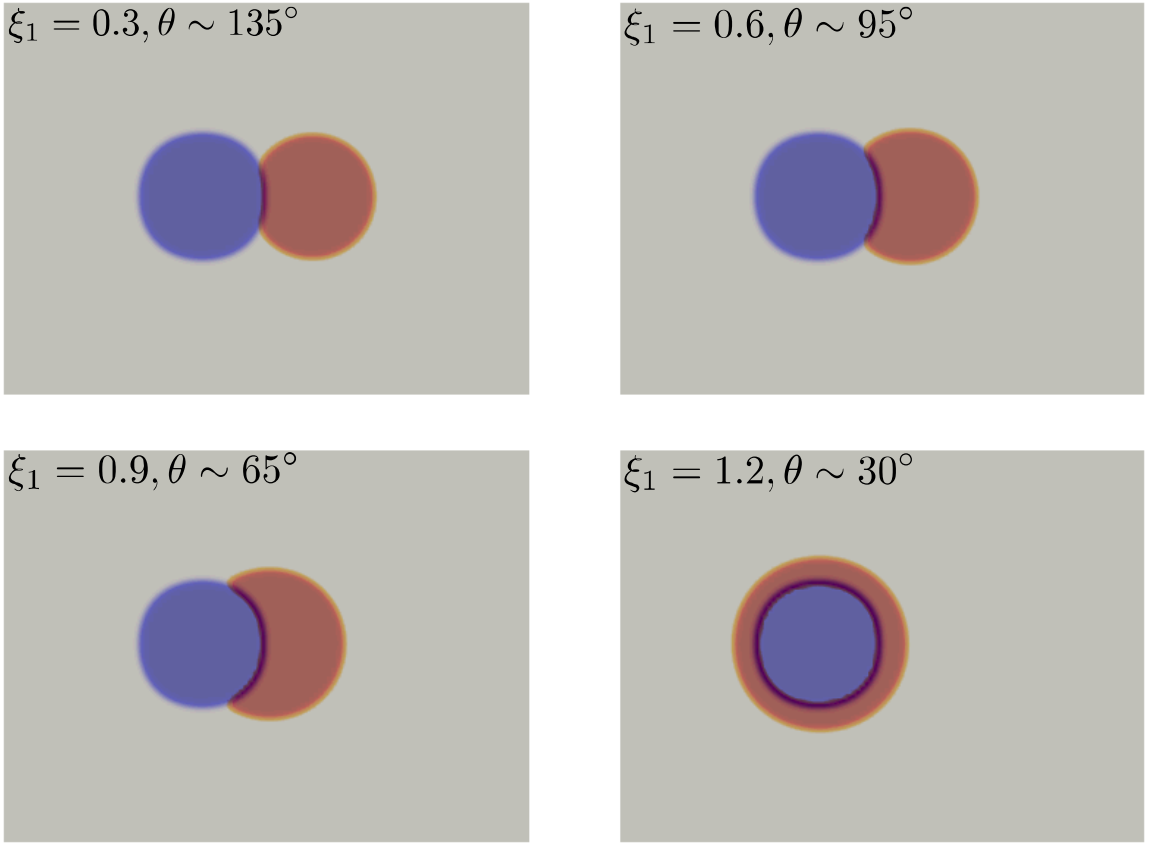
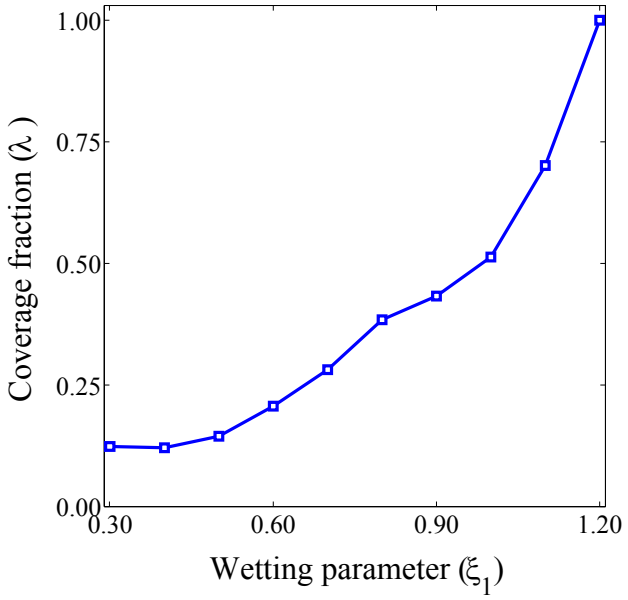
- Equilibrium Shapes vs. Wetting Angles
  - Coverage fraction $\lambda = \dfrac{\text{Volume elements of A-B interfacial region}}{\text{Total interfacial elements of Mat. B}}$

**Mat. A** **Mat. B**



# Dependence on Particle Size

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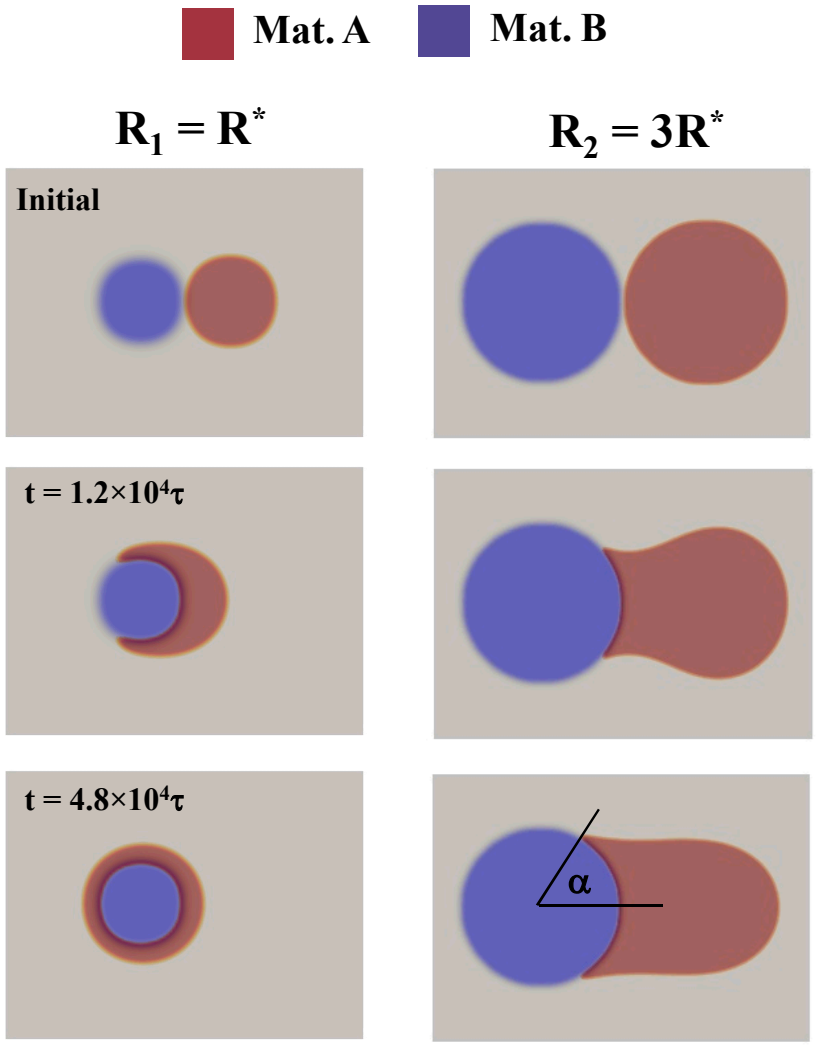
- Interplay between interfacial energies
  - Fix wetting parameter $\xi_1 = 1.2$ ($\theta \approx 30°$)
  - Vary particle size

**Simple scaling law**

- Diffusion distance: $l_d = \sqrt{Dt} \simeq 2R\Delta\alpha$
- Coverage fraction: $\lambda = \dfrac{l_d}{2\pi R}$

$$\frac{\Delta\alpha_2}{\Delta\alpha_1} = \frac{\lambda_2}{\lambda_1}$$

- Time: $t_2 = t_1 \left(\dfrac{R_2}{R_1}\right)^2 \left(\dfrac{\lambda_2}{\lambda_1}\right)^2$



# Dependence on Particle Size

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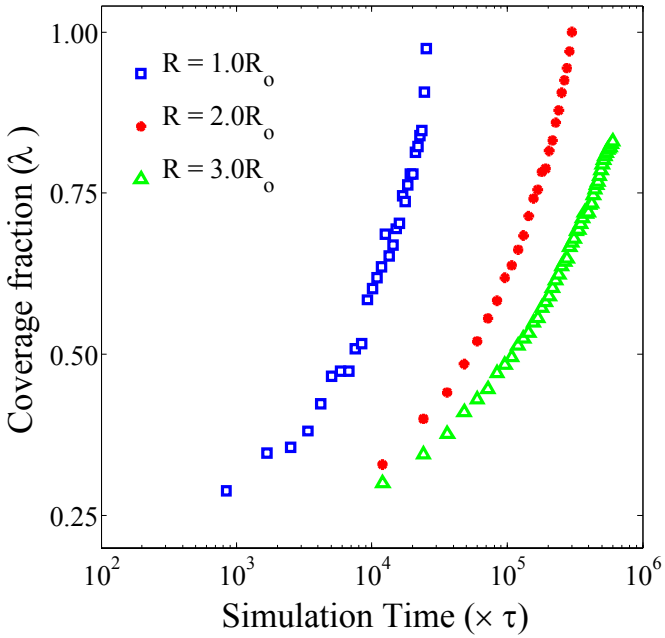
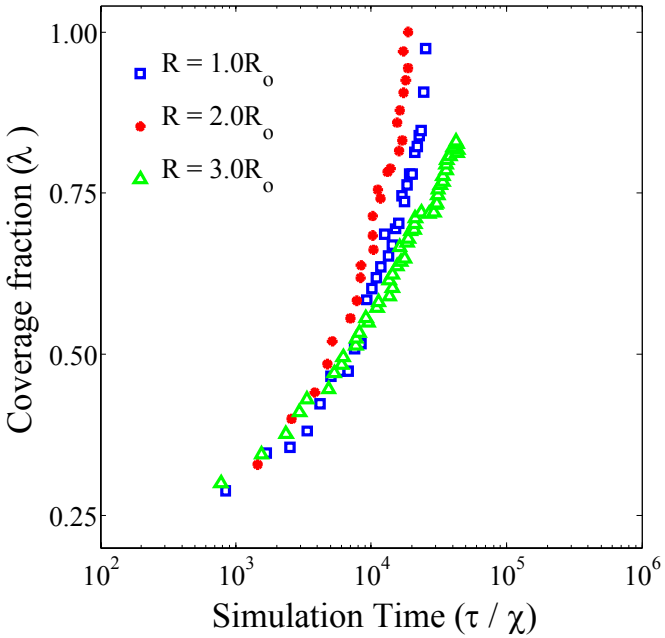
- Scaling law
  - For a system with particle size $R_i$
  - Time: $t_i = \left(\frac{R_i}{R_1}\right)^2 \left(\frac{\lambda_i}{\lambda_1}\right)^2 t_1 = \chi\, t_1$




Collapse using time $\chi$



# Summary and Future Outlook

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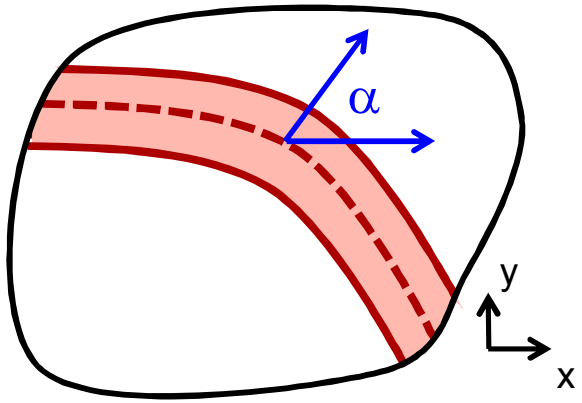
- Experimental/theoretical Treatment
  - Interface-driven processes in binary metallic systems
  - Conditions for the formation of core-shell structures
  - Various aspects of microstructure
- Atomistic
  - Atomic radius effects (various combinations of metals)
  - Parametric study using LJ-EAM potentials
- Mesoscale
  - Anisotropy in wetting/spreading: $\xi_1 = \xi_1(\alpha)$
  - Size-dependent interface energy: $\gamma = \gamma_o + \gamma_2 \mathcal{K}^2$



# Backup Slides

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