Bonding of Metallic Nanoparticles

SAND2013-3557C

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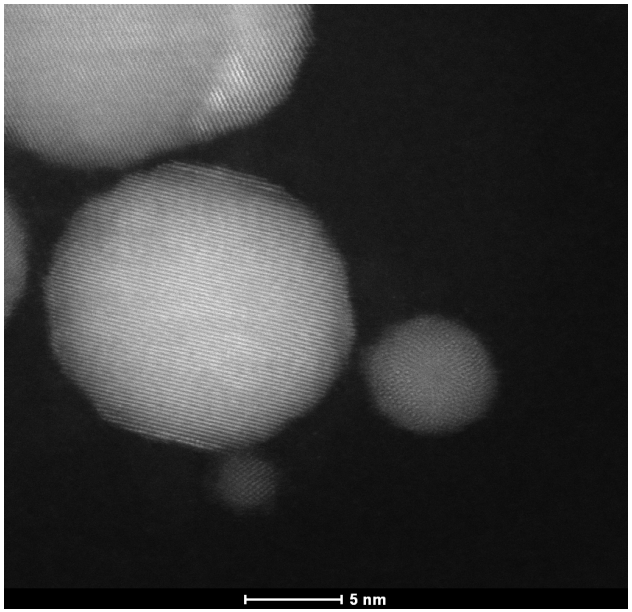

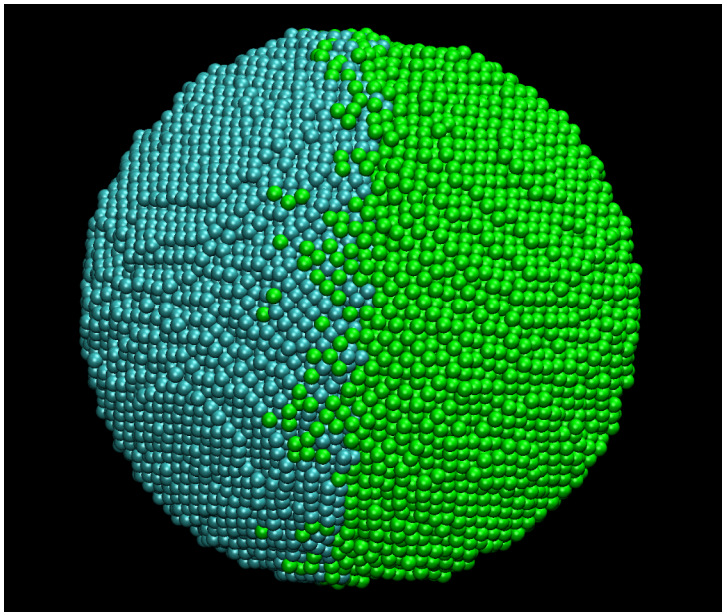

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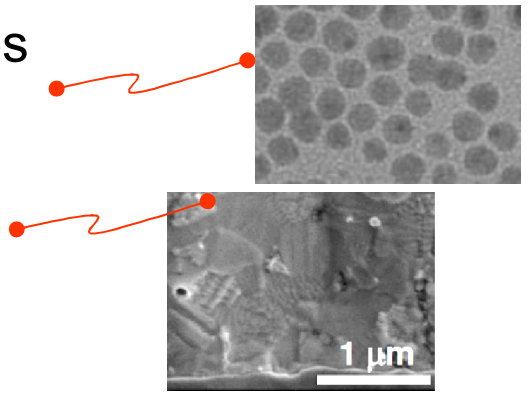
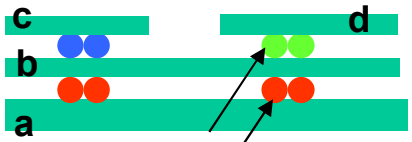
Nanoparticle Solders

- Metallic NP nanosolders offer two advantages
  - Low processing temperatures
  - High service temperatures
- Example: Ag/Cu
  - Bonding at ~200°C
  - Applications above 350°C





Different color shows different soldering steps

- Enable step-soldering for stacked (3D) package
  - Increases functionality, reliability
  - Does not increase footprint
- Critical parameters controling the metal/metal interfacial reactions are not understood

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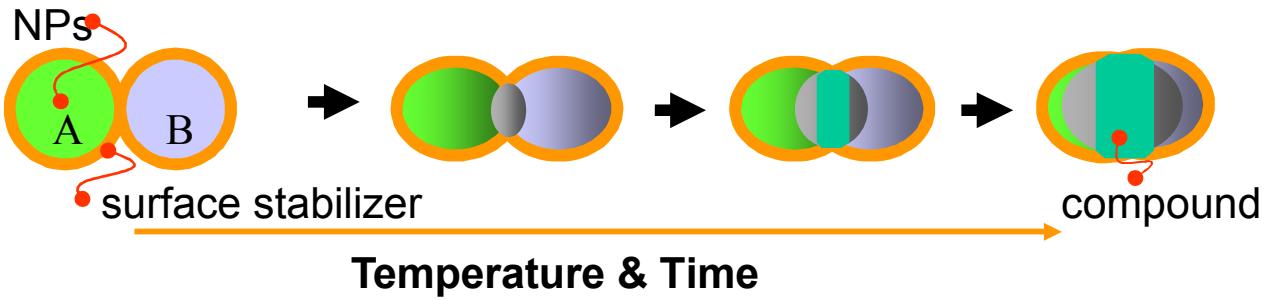
R&D Goals & Approach

Goals: ***Identify, understand and control*** **the key properties that affect bonding formations at NP metal interfaces**

- ***In-situ*****, dynamic TEM observation & Atomic-scale MD modeling**



- ***In-situ*****, aberration-corrected STEM will used to obtain** ***atomic-scale, compositional maps*** **(at T, t).**

- ***Direct comparison*** **between the experiment and theory (MD) will be used to understand the reaction model.**

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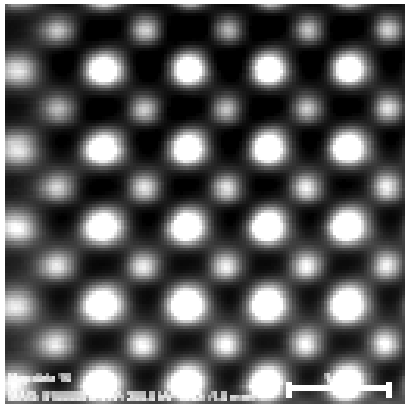
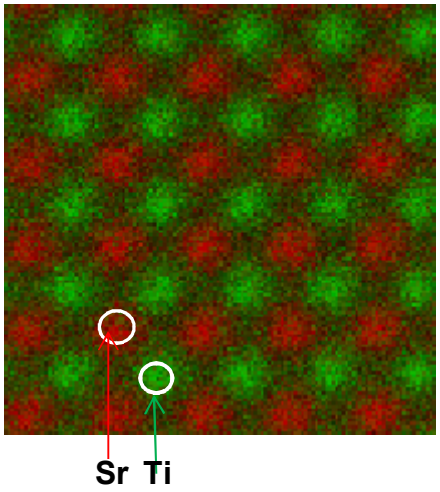
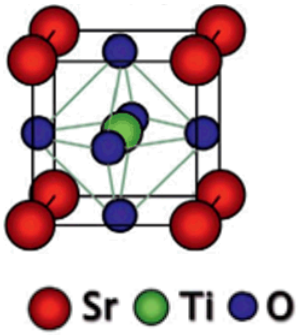
Aberration Corrected STEM

HAADF Z-contrast imaging



Atomic-scale element map





- FEI Titan G2 with *ChemiSTEM Technology*
  - Advanced spherical aberration correction
  - Super-bright field emission electron gun
  - Four Si drift detectors
  - 1000°C/sec thermal ramp
- Unprecendented capabilities
  - Sub-atomic scale STEM (80-120 pm)
  - Atomic scale chemical mapping
  - Light element detection
  - Low energy operation for sensitive materials

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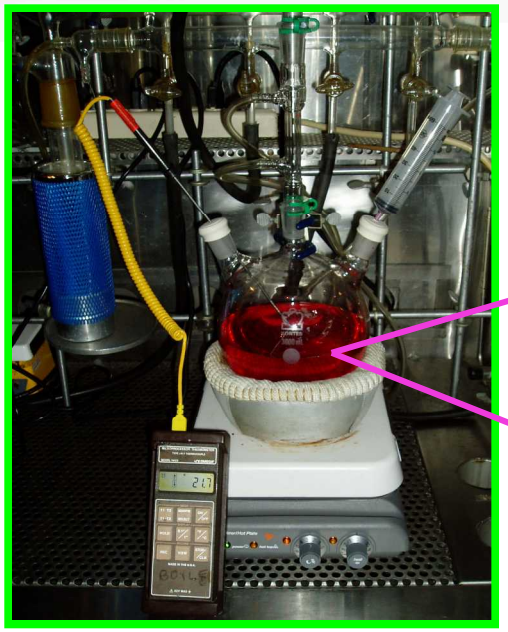
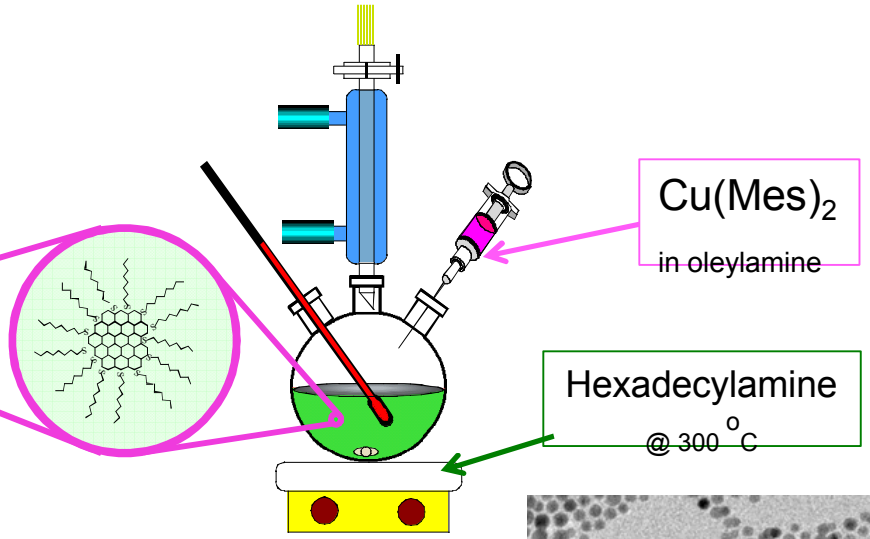
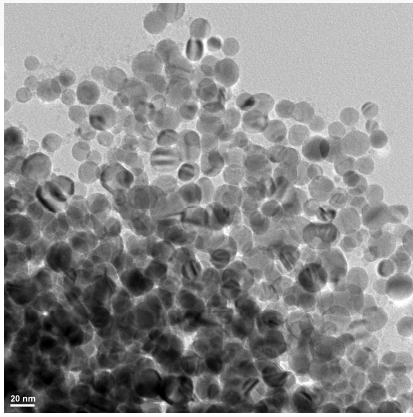
Nanoparticle Creation

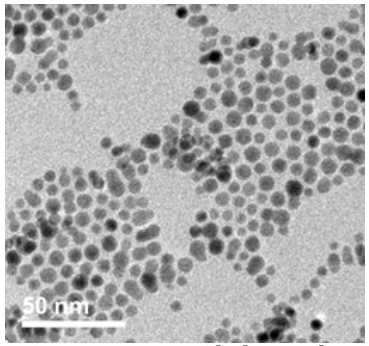




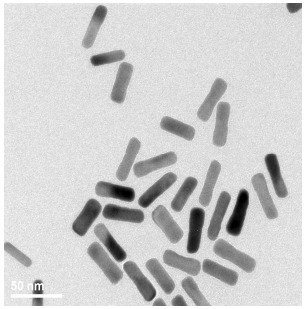
Cu NPs
~12nm-15nm



Ag NPs
~6nm



Au NP rods
~12nmx26nm



- Solution Precipitation – inject something cold into something hot
- Variety of particles
- Different shapes. sizes
  - Spheres
  - Rods

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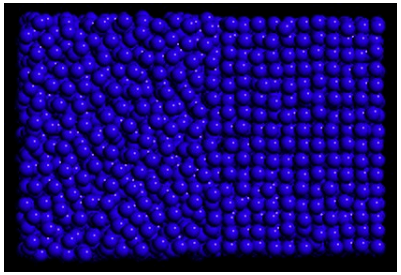
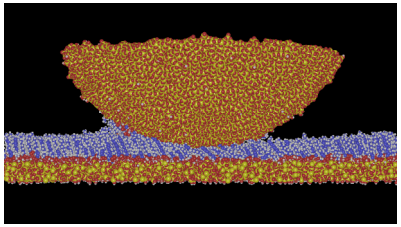
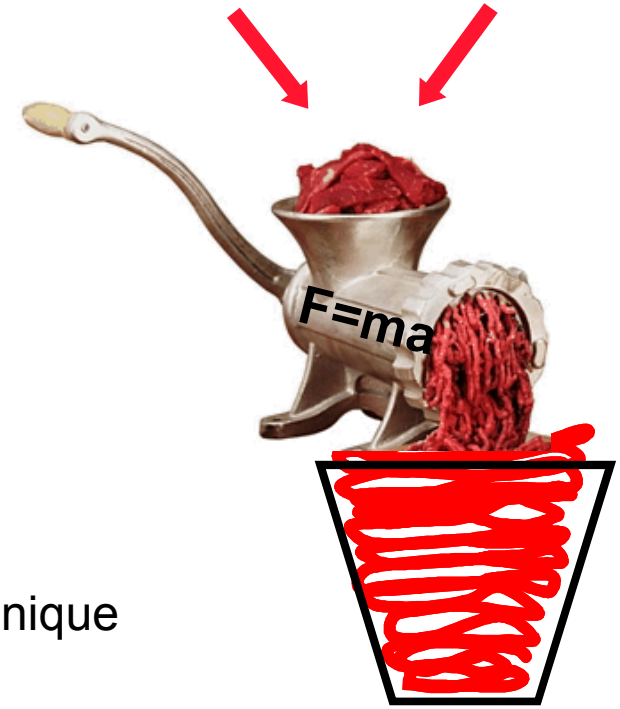
Molecular Dynamics Modeling

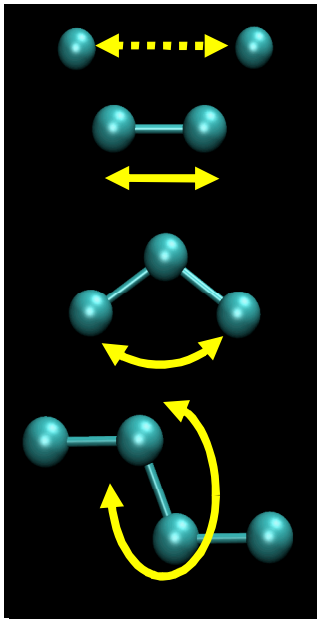




Initial positions and velocities

Interatomic potential





Positions and velocities at later times

- Classical simulation technique
- Empirical interactions
- Evolve system, analyze
- Also performed Monte Carlo substitutions

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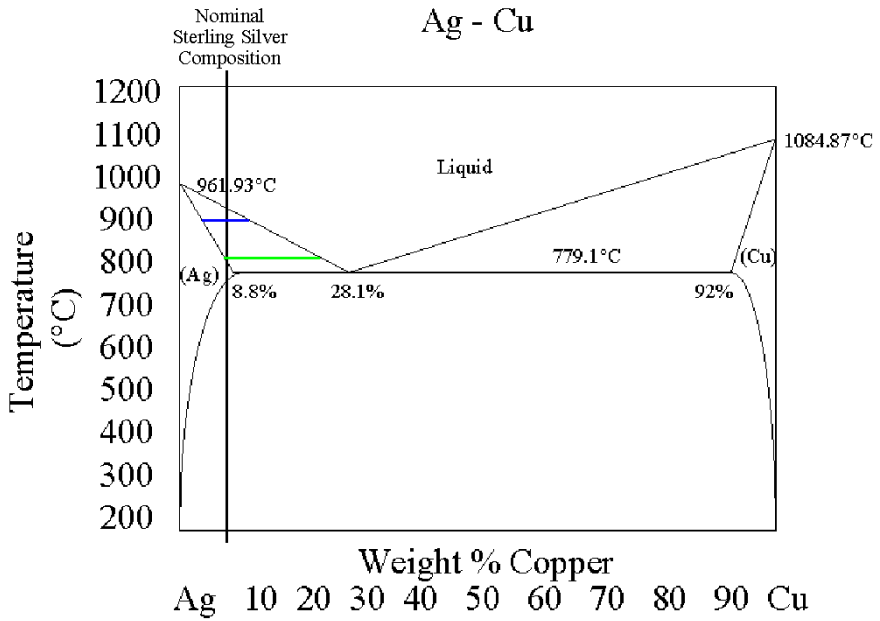
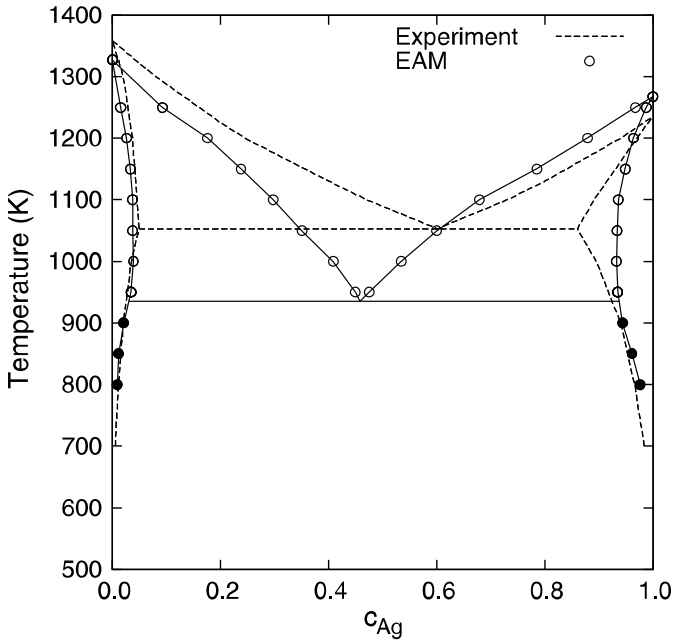
Ag/Cu Phase Diagram





- Eutectic system
- Not miscible
- This is bulk, is nanoscale different?
- Model phase diagram matches very well

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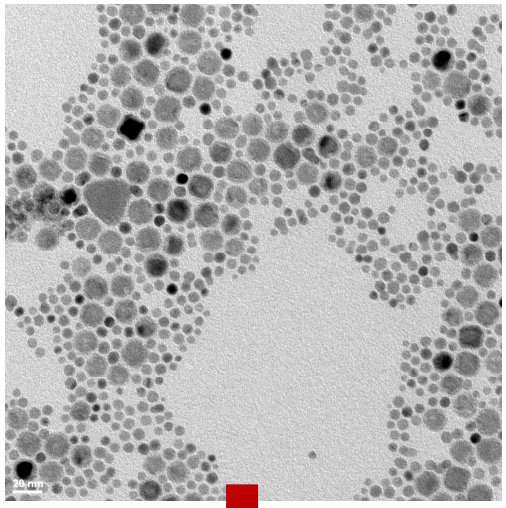
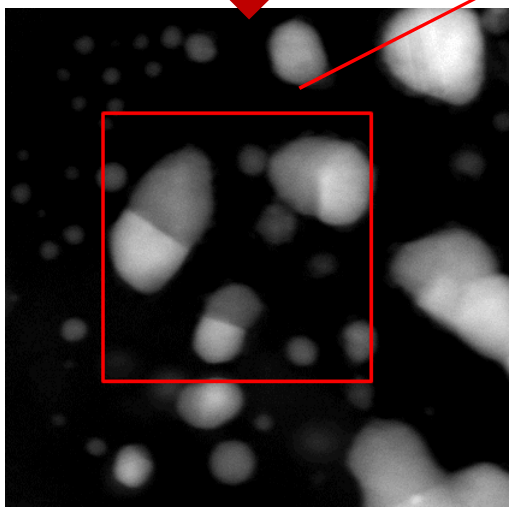
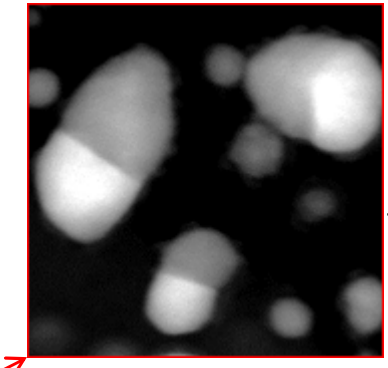
Initial Experiments

Cu/Ag dispersed on C film
Ag – 5-6 nm
Cu – 12-15nm

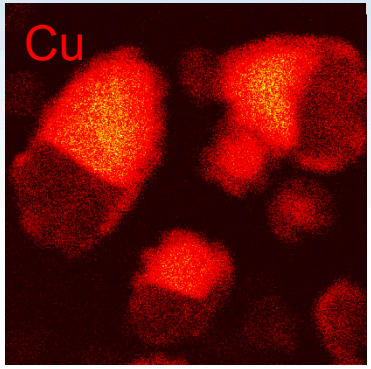


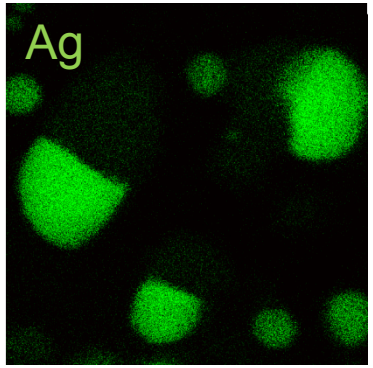
300°C
1 minute

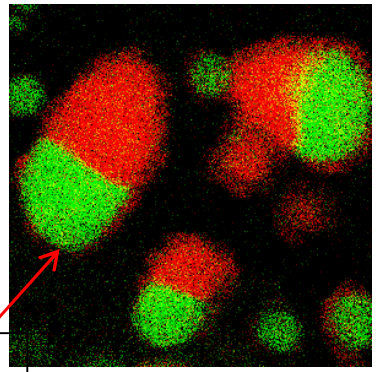




105nm







Thin layer of Cu around Ag !

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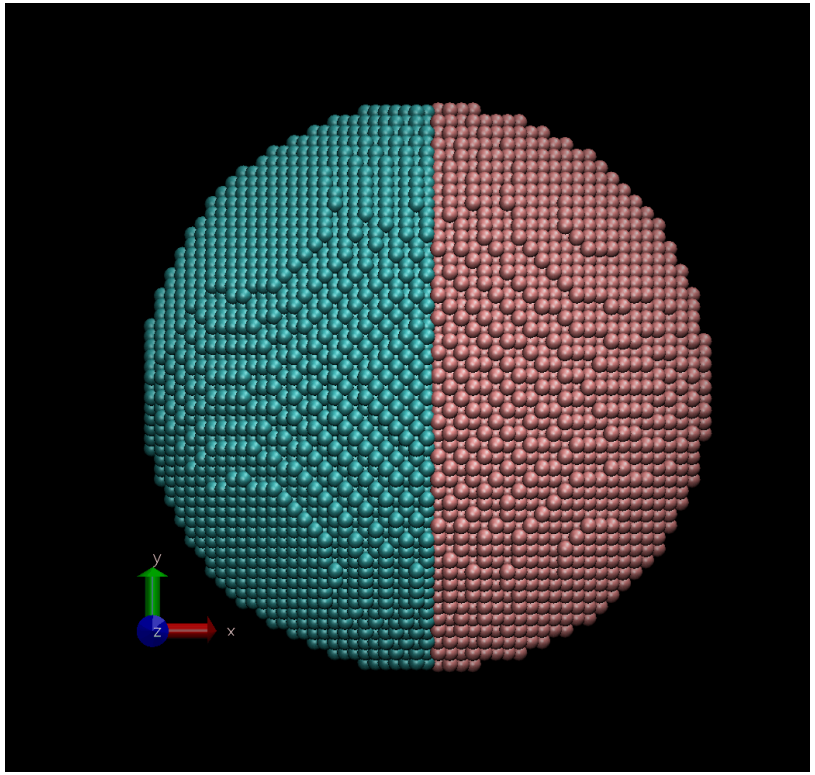
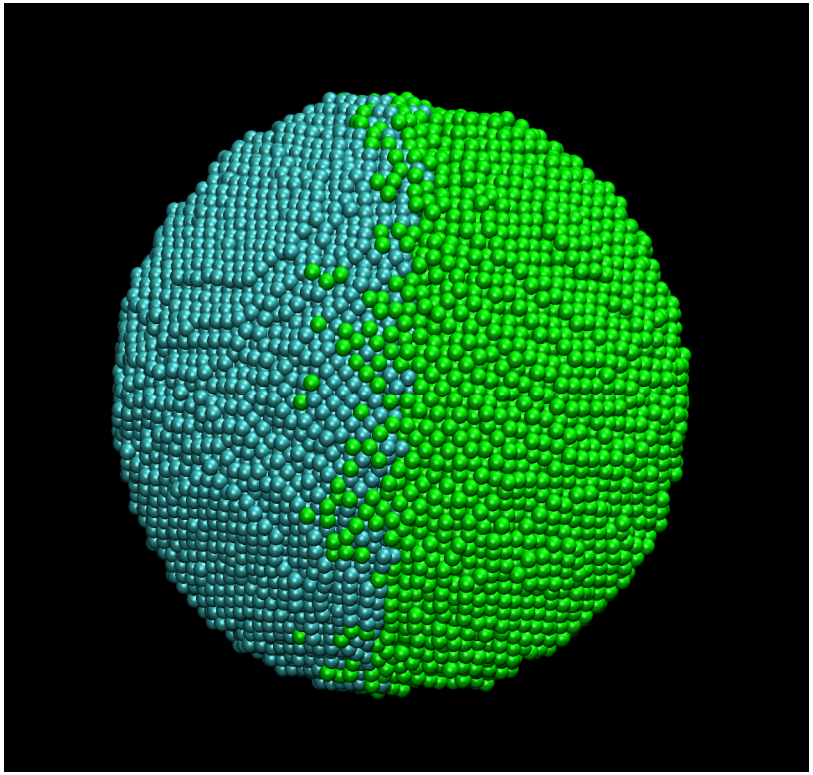
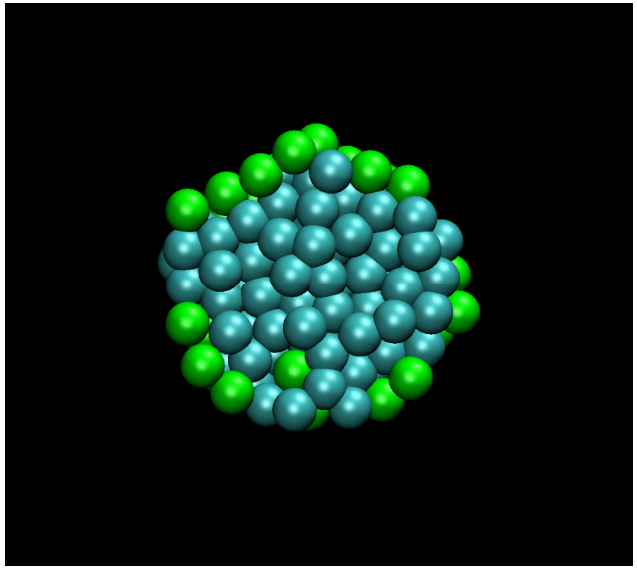
Simulation Results





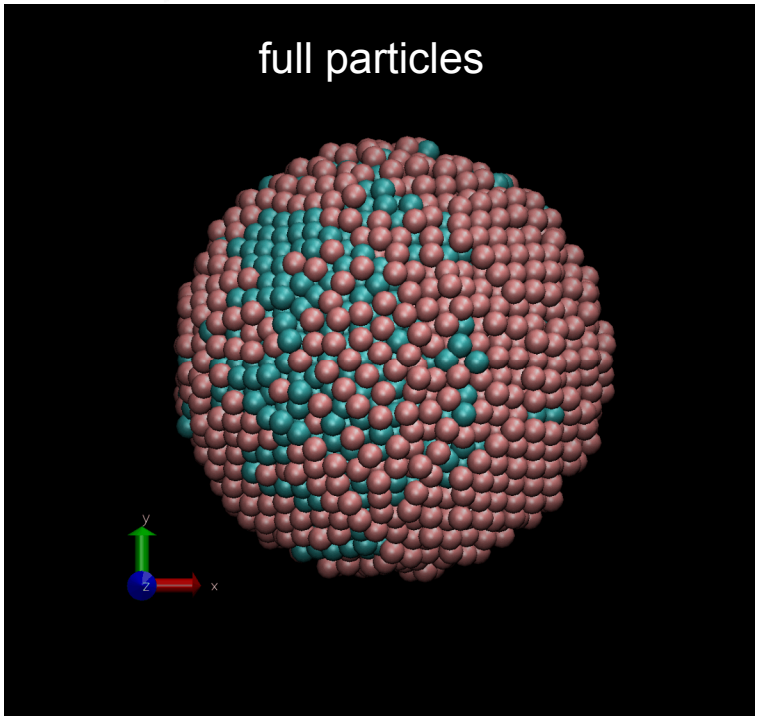
- 10nm Janus nanoparticles (left half Cu, right half Ag)
- At 800K (below eutectic) for < 1 ns
- Shows opposite behavior

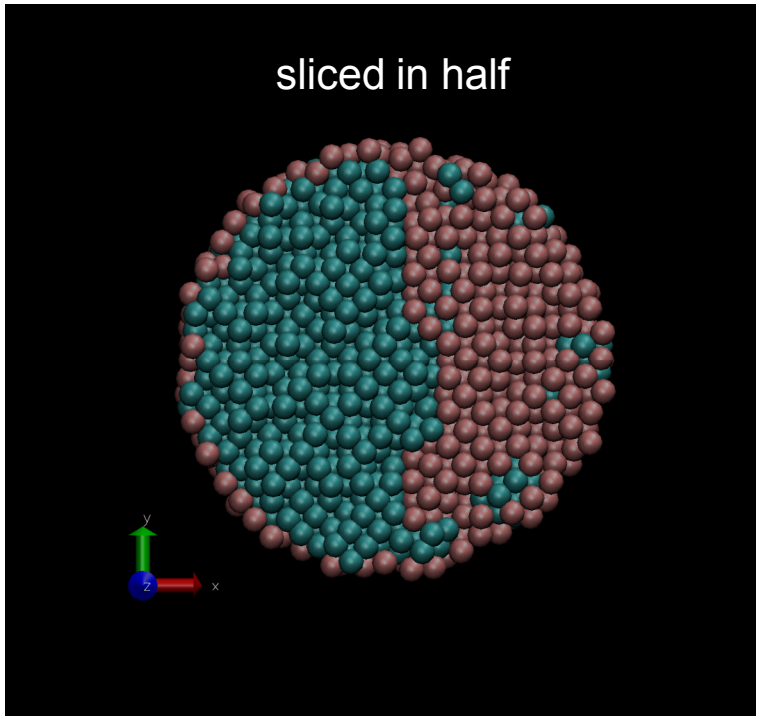
Smaller Particles



- 800K for 12.5 ns
- Particle cut in half for detail
- Complete silver shell formed

Monte Carlo Simulations





- Simulation is not real time, but can be slow
- Randomly pick two particles to swap (with small translation)
- Accept move if energy is lower, or according to Boltzmann
- 5nm particle after 20M steps

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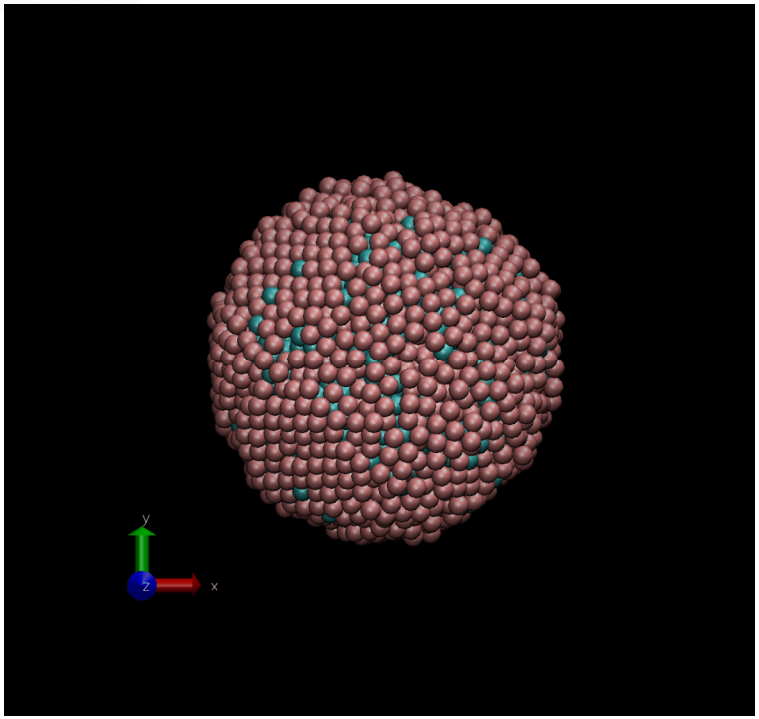
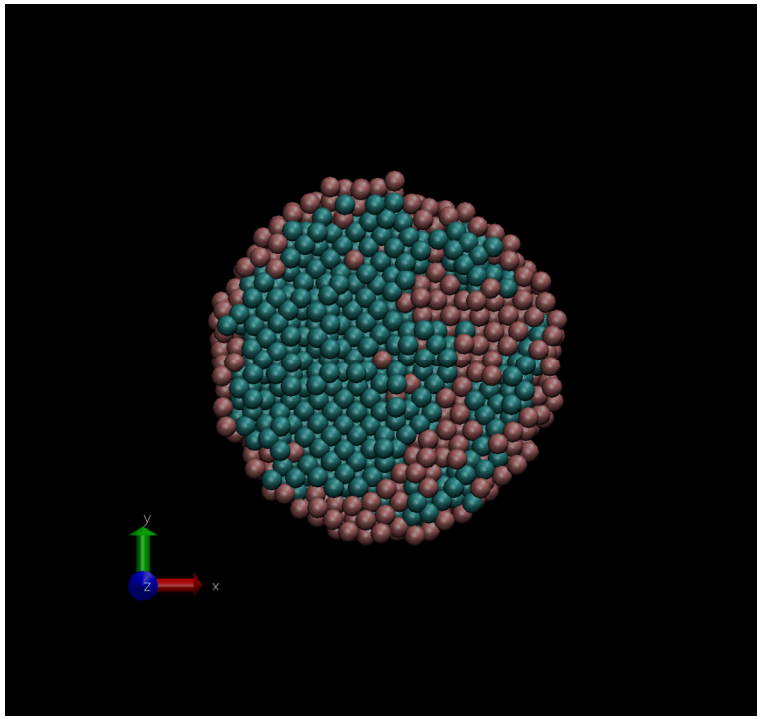
Longer Time Results

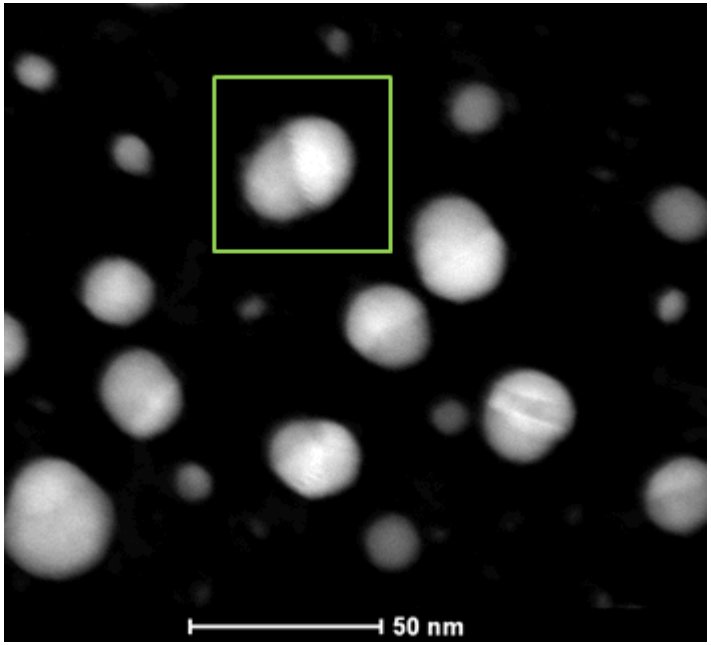


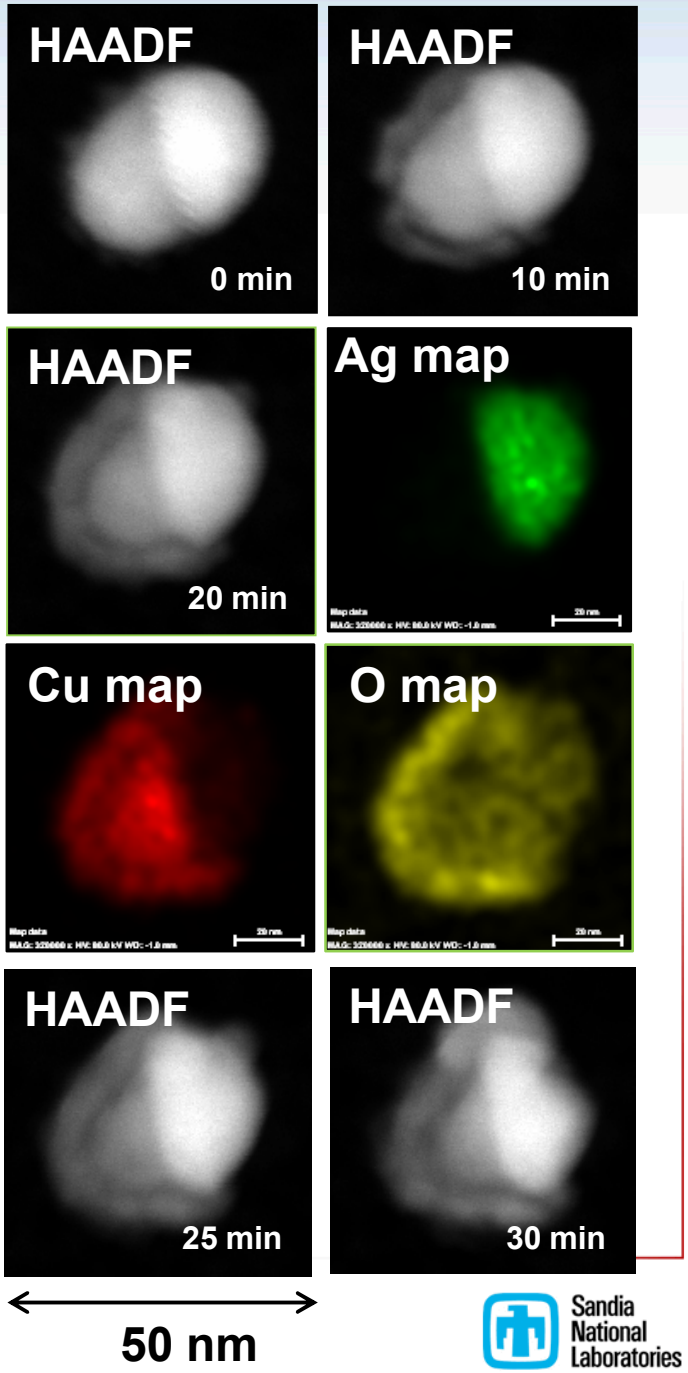


- 5nm, after 60M steps
- Shell is clearly favored at 800K

In-Situ TEM Challenges

- Electron beam induced effect
  - Electron beam exposure, even at 80 kV, during the EDS mapping leads to oxidation of Cu NPs
- Sample drift during heating and cooling





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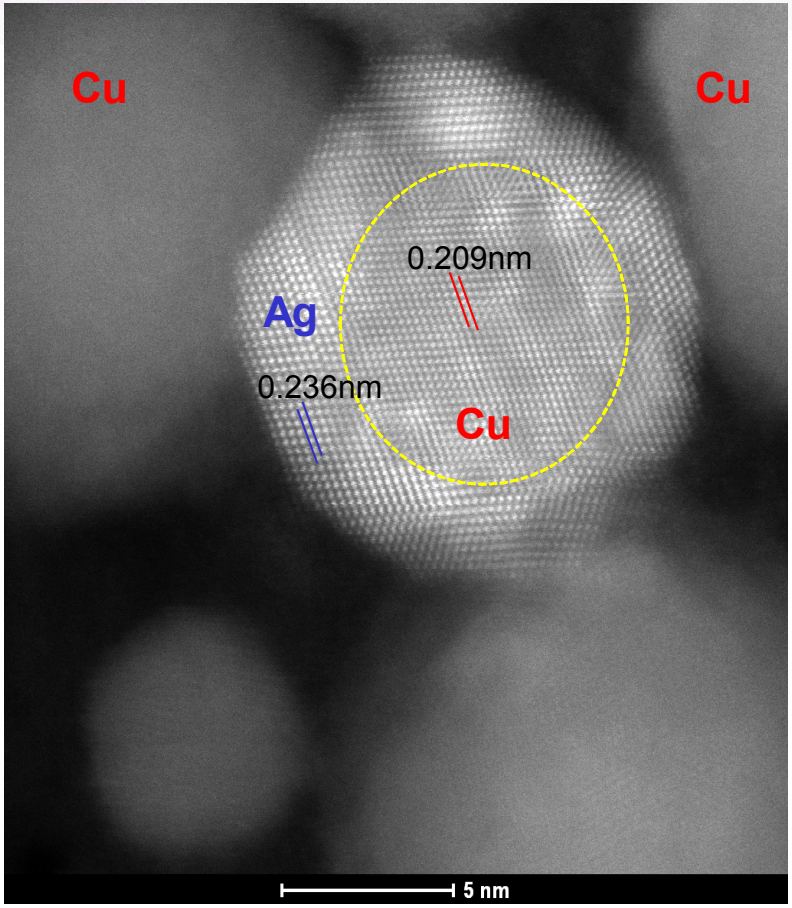
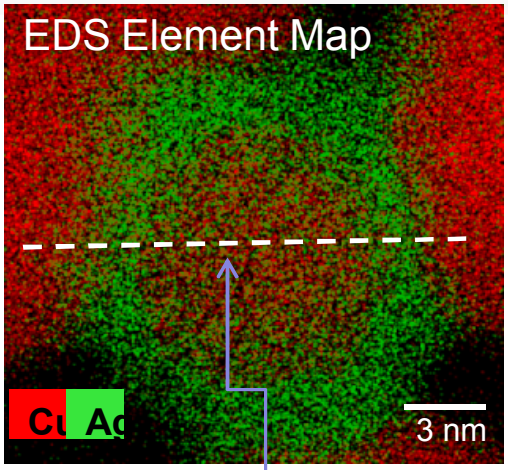
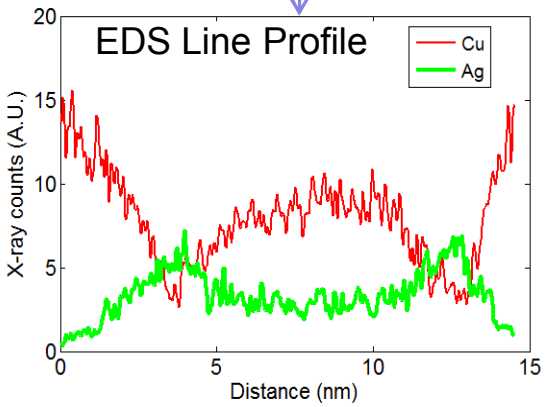
New Experimental Results







- Results from heating to 150°C
- Carefully avoid electron beam heating
- Now agrees with prediction from simulations
- ~9nm Cu core with ~2.5nm Ag-shell, preference for {111}

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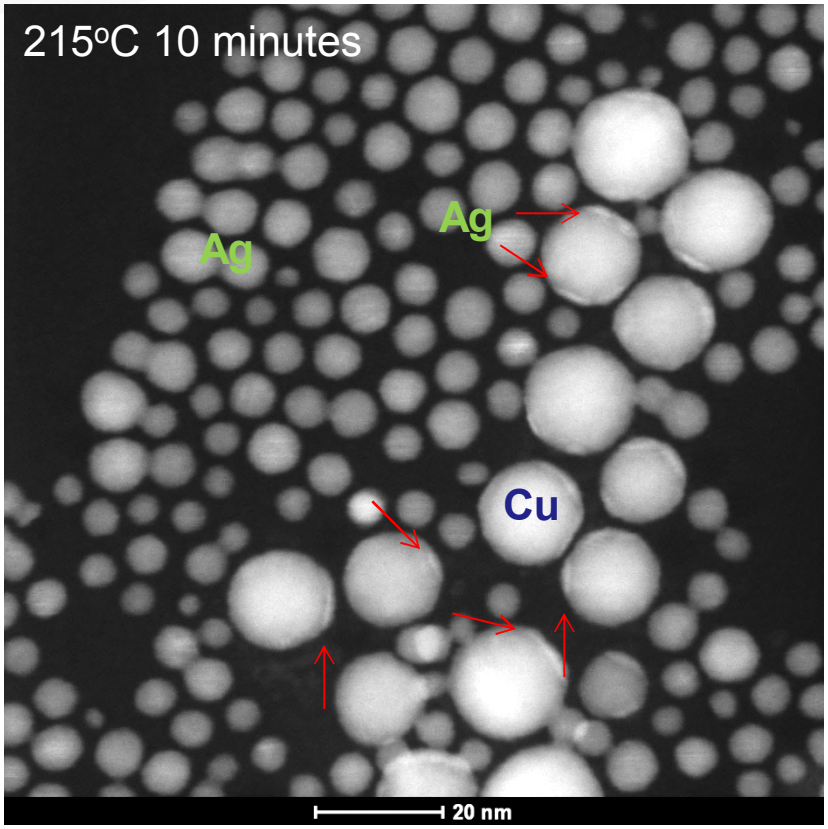
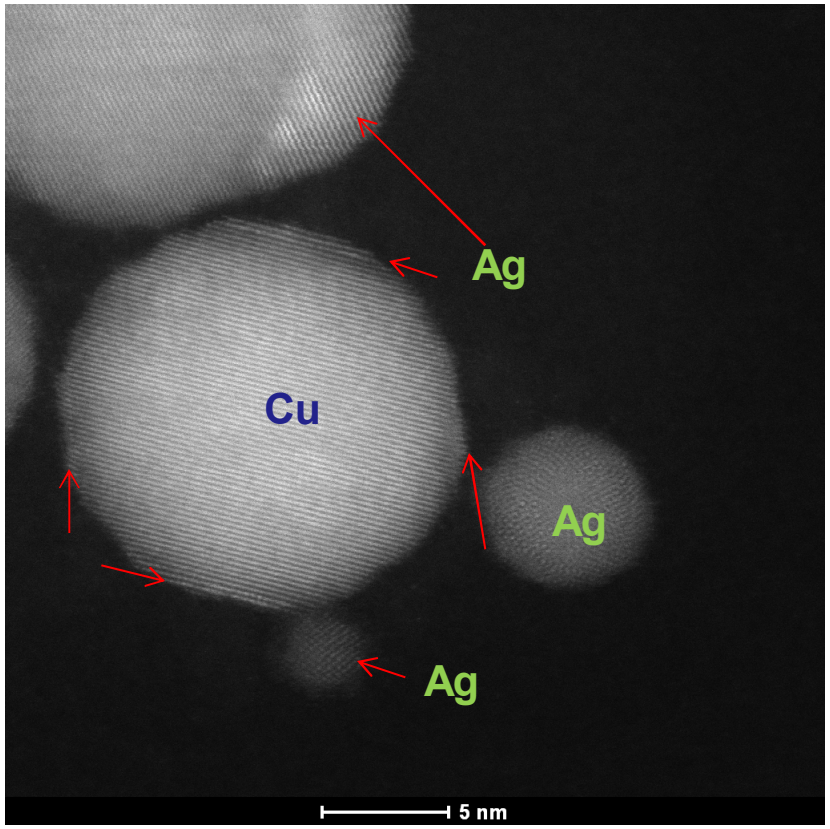
Further Demonstration of {111}





- Slightly higher temperature
- Ag shell caught in the act of formation
- Demonstrates preference for {111} formation

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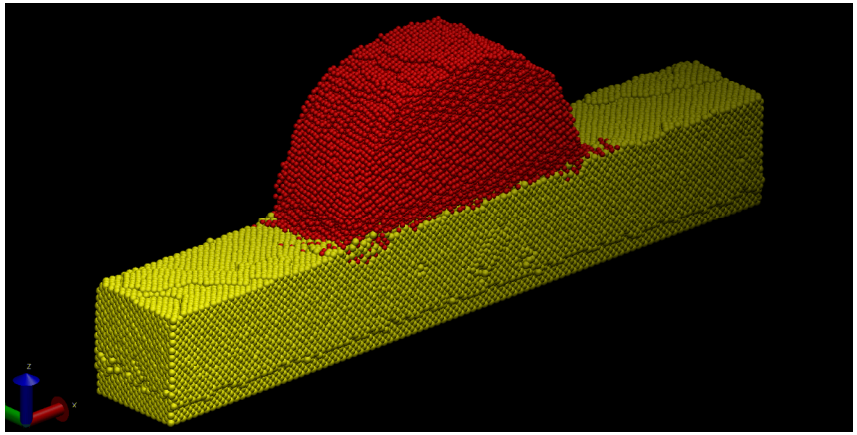
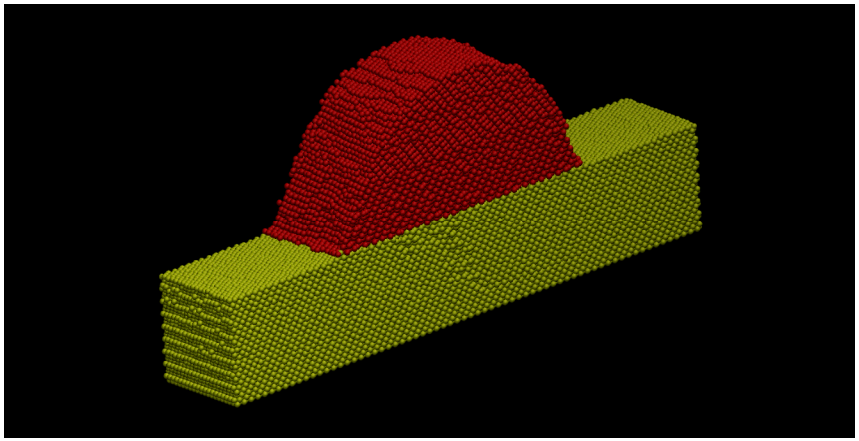
Why {111}?



Ag on Cu{100}
~ 10 ns

Ag on Cu{111}
~ 20 ns



- Simulations of sessile drop spreading
- Run with MD at 500°C
- Infinite half-cylinder on infinite substrate
  - psuedo-2D version of drop
  - Same spreading dynamics
- Not much spreading on {100} or {111}

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Why {111}?

Interfacial Energies

	Ag(100)	Ag(111)
Cu(100)	5.2 J/m^2	4.3 J/m^2
Cu(111)	4.5 J/m^2	**2.0 J/m^2**

- Calculate interfacial energies
- Need several simulations
  - Cu(100), Ag(100), Cu(111), Ag(111)
  - All separately, and all combinations
- Model gets surface energies correct (within 20%)
- Indicates strong preference for Cu{111}/Ag{111}

Conclusions

- Nanoparticles will bond
  - Bulk phase diagram indicates differently
  - Low temperature bonding is possible
- Preference is for Ag{111} on Cu{111}
  - Predicted by models
  - Verified by experiments
- Interfacial energy is likely explanation