SAND2012-6033C

A Materials Science Perspective on the Mechanics of Sintering

Rasmus Bjørk
DTU Risö
Roskilde, Denmark
and
Veena Tikare
Sandia National Laboratories
Albuquerque, NM

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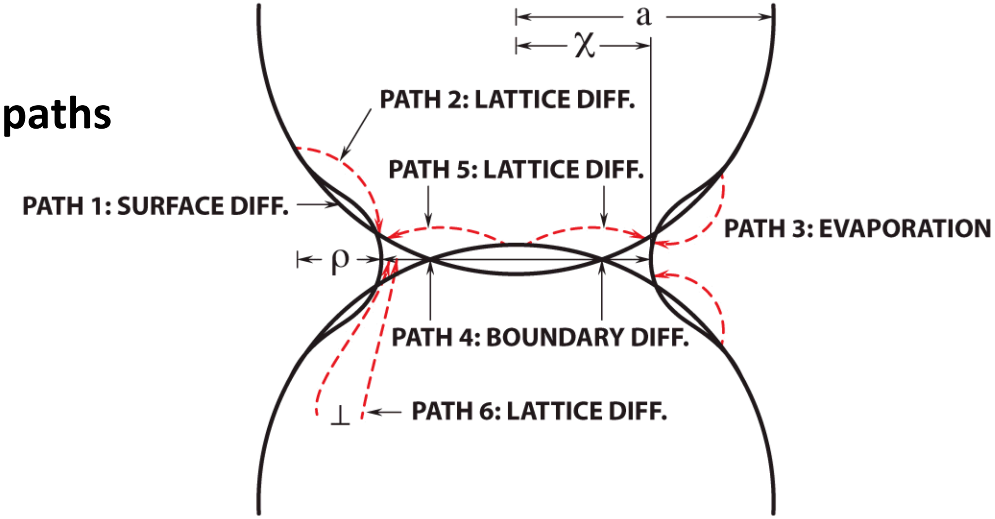
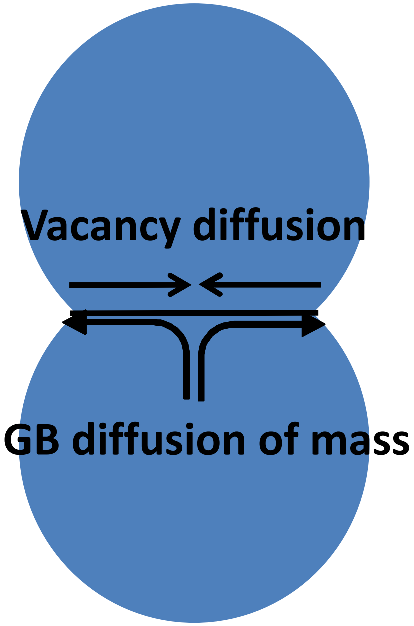
Microstructural Evolution
During Simple Solid-State Sintering

Mass transport described by
Classic Ashby model with the 6 paths

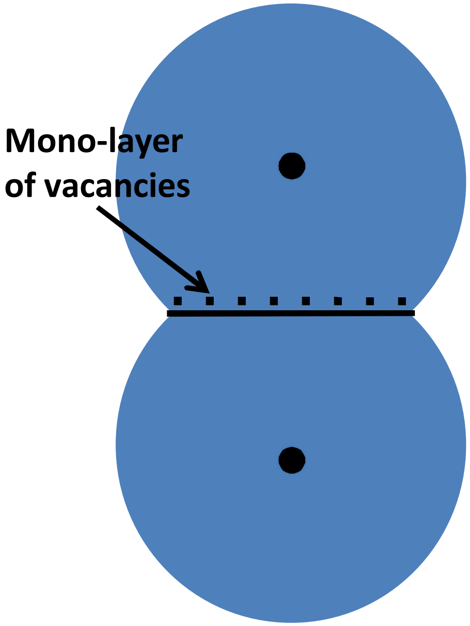
In this work:
grain boundary diffusion
surface diffusion
are active.


a
χ
PATH 2: LATTICE DIFF.
PATH 5: LATTICE DIFF.
PATH 1: SURFACE DIFF.
PATH 3: EVAPORATION
ρ
PATH 4: BOUNDARY DIFF.
⊥
PATH 6: LATTICE DIFF.


Vacancy diffusion
GB diffusion of mass

- Mass diffuses the along the grain boundary to fill the pore
- Vacancies generated at the pore surface
- Vacancies diffuse from the pore to the grain boundary
- Vacancies are annihilated at the grain boundaries

Densification in Stereological Model of Sintering*



Densification

- Vacancies diffuse along the grain boundary
- They paint the grain boundary forming a mono-layer
- The entire monolayer is annihilated
- The centers of mass of the particles move closer
- The neck grows
- The pore shrinks

Densification Rate

- Rate of vacancy annihilations $\dot{n}_A = \dfrac{\int (-D_b \nabla C)\delta dL}{A_b}$

- As the neck area grows, the time between the annihilation events increases
- τ H A_b

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*R.T DeHoff, Sci. of Sintering, 1989

Objectives

- Develop a meso-scale model to simulate microstructural evolution during solid-state sintering
  - Understand microstructural evolution details
  - Obtain engineering sintering quantities
    - Sintering stress
    - Bulk and shear viscosities

- End goal: simulate constrained sintering with the accompanying shape distortion
  - Variations in density
  - Multi-layered materials
  - Functionally graded materials
  - Powder packing defects

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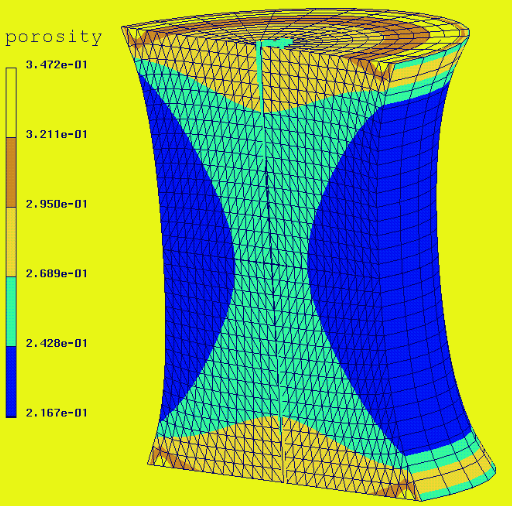
porosity
3.472e-01
3.211e-01
2.950e-01
2.689e-01
2.428e-01
2.167e-01

Objectives

- **Develop a meso-scale model to simulate microstructural evolution during solid-state sintering**
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    - **Sintering stress**
    - **Bulk and shear viscosities**

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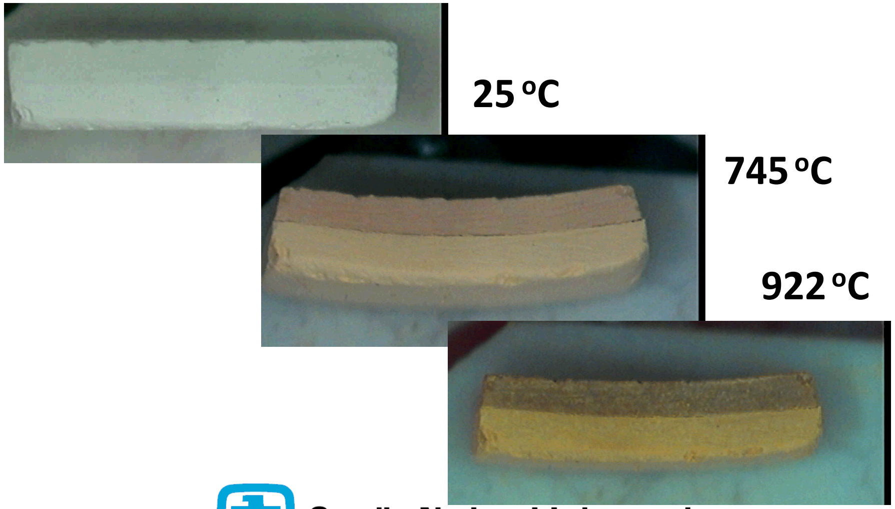
  - **Variations in density**
  - **Multi-layered materials**
  - **Functionally graded materials**
  - **Powder packing defects**



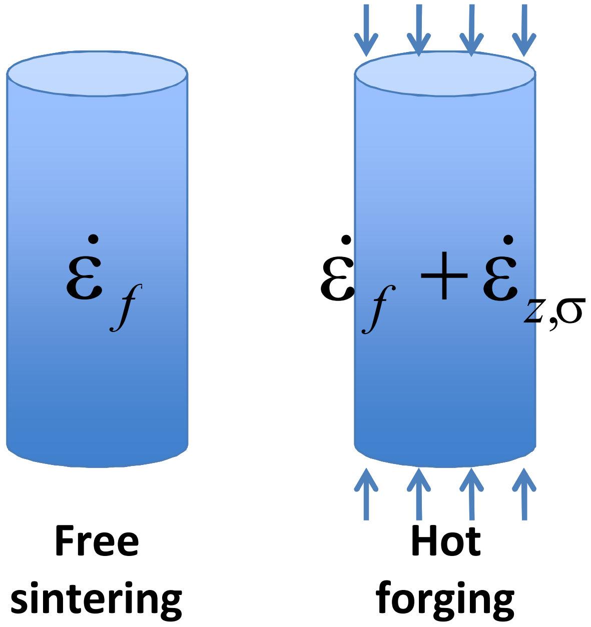
T. Garino, SNL

Experimental Measurement of Sintering Stress

- The usual method for determining sintering stress is loading dilatometry

$$\dot{\varepsilon}_f = \frac{P_L}{3K}$$

$$\dot{\varepsilon}_z = \dot{\varepsilon}_f + \frac{\sigma_z}{3(1-2\upsilon_p)}$$

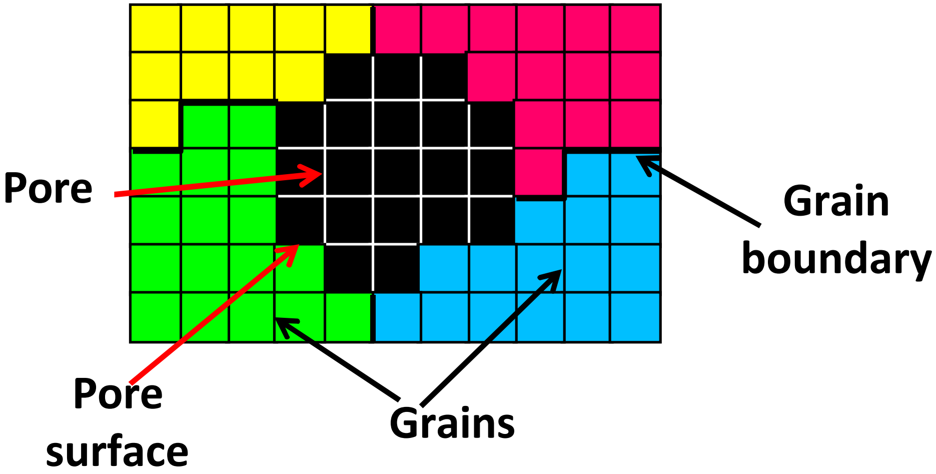

$\dot{\varepsilon}_f$
$\dot{\varepsilon}_f + \dot{\varepsilon}_{z,\sigma}$
Free sintering
Hot forging

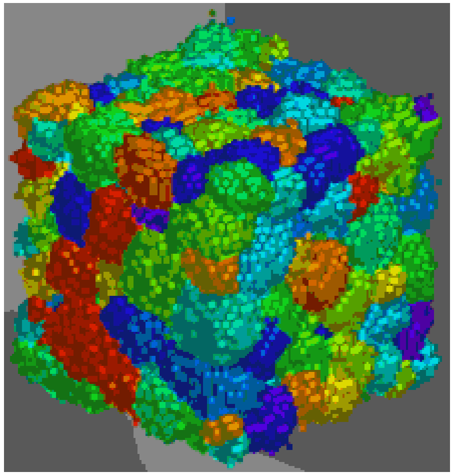
- Assumes microstructural evolution during hot forging & free sintering are the same
- Zuo et al. showed microstructural evolution is not the same for these conditions

Zuo, Aulbach & Rodel, Acta Met, 2003

Potts kMC Model

- Microstructure is represented by digitizing on a cubic lattice:


Pore
Grain boundary
Pore surface
Grains

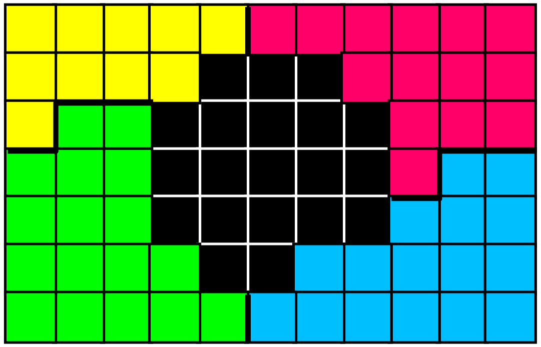


- Each voxel is a unit of matter

Potts kMC Model
Equation of State

- Driving force for sintering is the reduction in total interfacial energy

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{26} J_{ij}\left(1-\delta\left(q_i,q_j\right)\right)$$



- Dihedral angle can be changed by adjusting J_{ij}

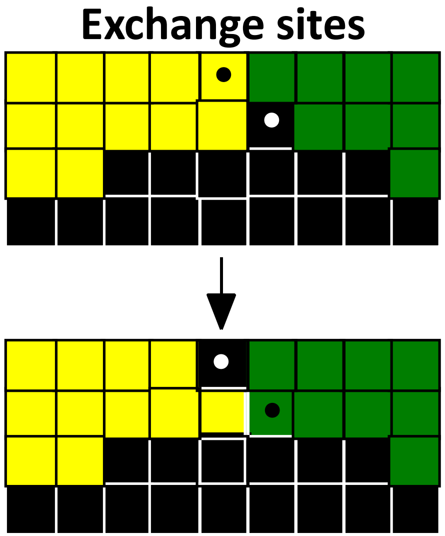
Potts kMC Model
Vacancy Generation

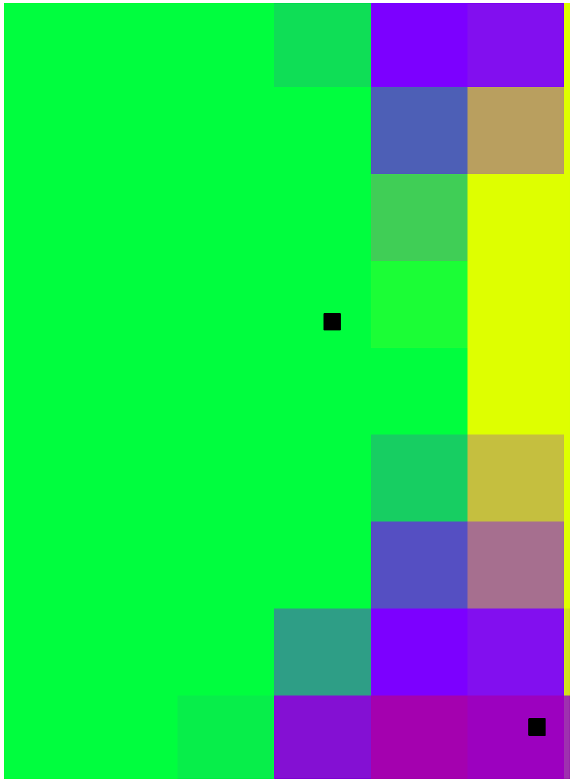
- Vacancies are generated by the exchange mechanisms as shown.
- There is an equilibrium concentration of vacancies

$$P = \exp\left(\frac{-\Delta E}{k_B T}\right) \quad \Delta E > 0$$

- Concentration of vacancies is proportional to the surface curvature

$$C_v \propto \frac{\gamma}{r}$$

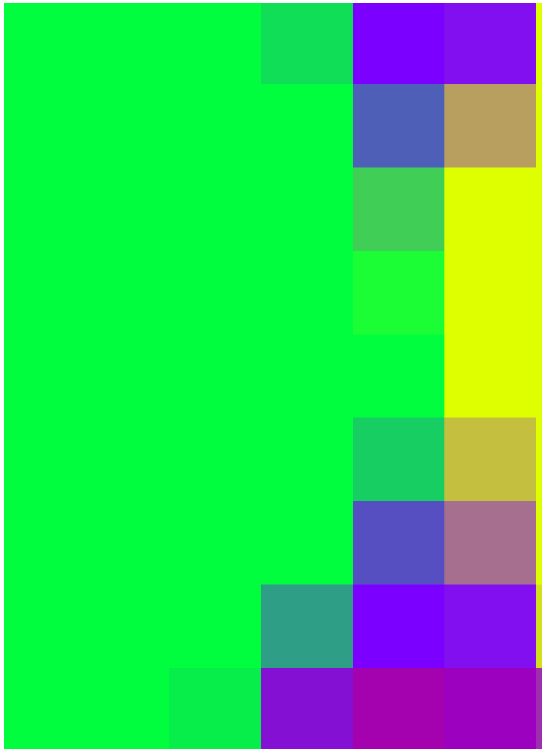




Potts kMC Model
Vacancy Diffusion and Annihilation

- Stereological model
  - Paint a layer of vacancies on the neck and annihilate them.
  - Centroids of grains move closer to give densification.

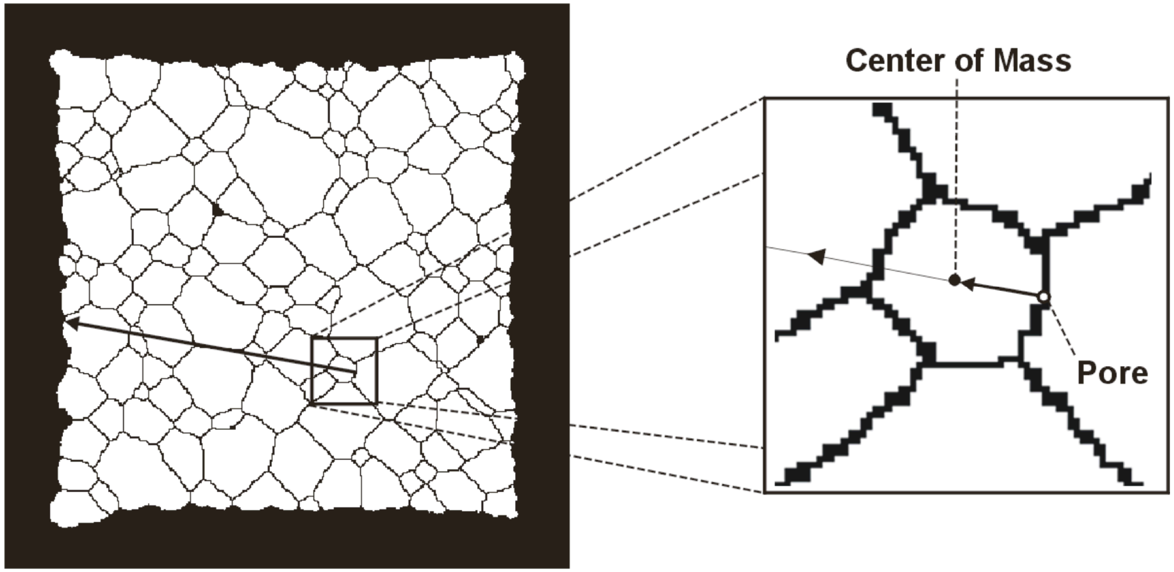
- Potts model
  - Annihilation mono-layer is not possible.
  - Annihilate one vacancy with equal probability of being anywhere in the neck.
  - Annihilation frequency is $\tau \mathrm{H} A_b$.
  - Annihilation is simulated by collapsing a column of sites.
  - Centroid of grains approach each other.
  - Powder compact densifies.



Potts kMC Model
Simulation of Annihilation

Annihilation of a vacancy on a grain boundary

- Draw a line from the vacancy through the COM to the external surface of the powder compact
- Collapse all the sites along the line by one pixel to fill the vacancy



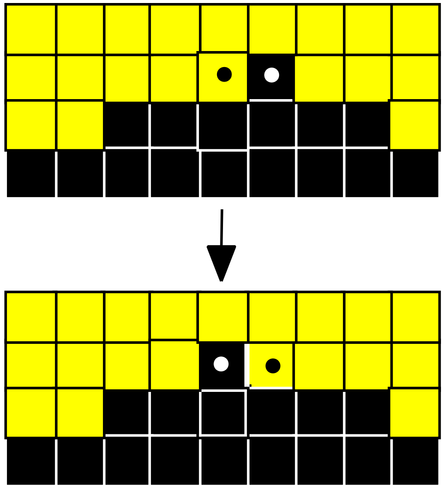
Potts kMC Model
Pore Surface Diffusion

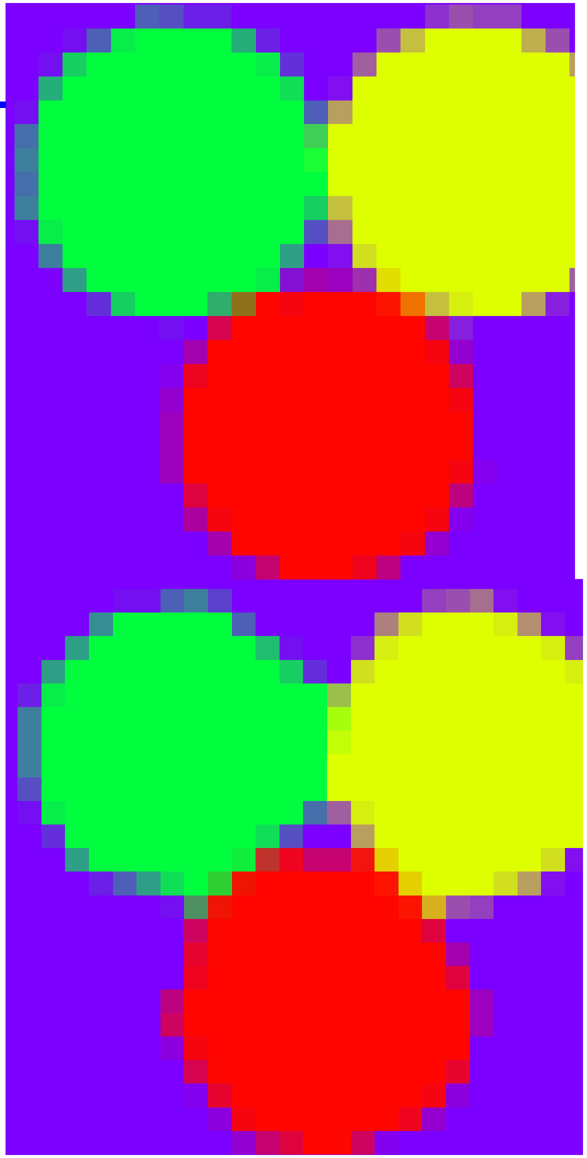
- Pore sites and grain sites at pore surface exchange places to simulate surface diffusion
- Minimize surface energy by Metropolis algorithm
- Calculate ΔE
- Probability of exchange is

$$P = 1 \qquad \Delta E \leq 0$$

$$P = \exp\left(\frac{-\Delta E}{k_B T}\right) \qquad \Delta E > 0$$

Exchange sites





Potts kMC Model
Grain Growth

Coarsening of grains during sintering

- Is a significant contributor
- Affects densification and distortions

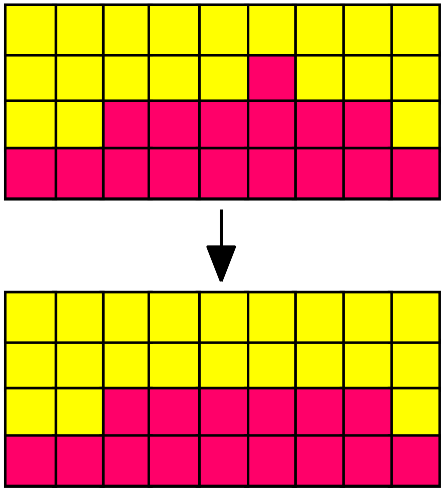
Curvature-driven grain growth is simulated by grain boundary motion

- Grain sites can change from one grain to another
- Calculate ΔE $E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{26} J_{ij}\left(1-\delta\left(q_i,q_j\right)\right)$
- Probability of change

$$P = 1 \qquad \Delta E \le 0$$

$$P = \exp\left(\frac{-\Delta E}{k_B T}\right) \qquad \Delta E > 0$$

grain growth
change pixel color



Application and Validation of Potts kMC Sintering Model

Potts kMC Sintering model was tested by simulating

- **Many simple geometries with analytic results.**

Comparing to sintering Cu-powder compact

- **Imaged with high-energy X-rays in synchrotron**
- **Cu-particles 30 – 50 μm**
- **Shows the mass and pore distribution in-situ**

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D. Bouvard

Validation by Comparing to Cu-Compact Sintering
Potts kMC Sintering Model

Grain structure extrapolated into the initial 3D image obtained from the synchrotron

- Using the Potts grain growth algorithm

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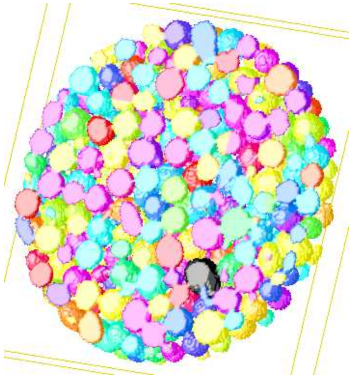
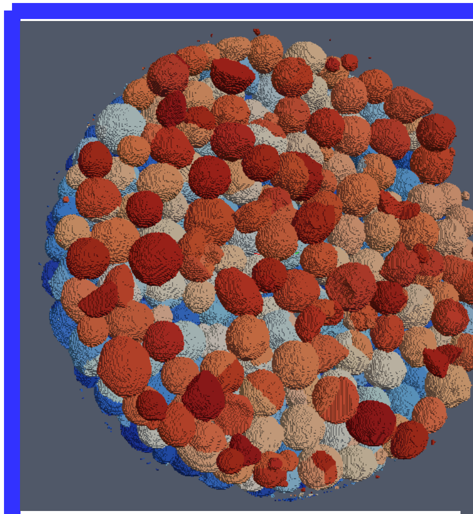
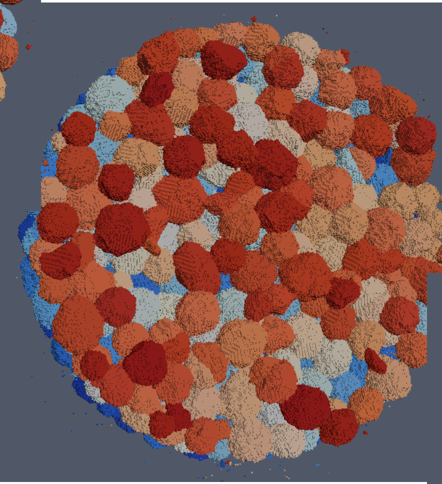


- Microstructural evolution during sintering from this image was compared to later experimentally obtained images.

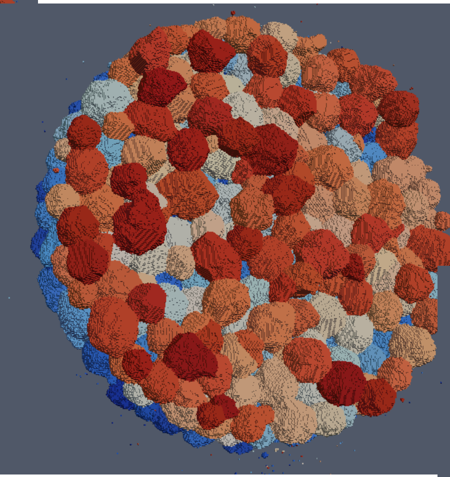
Potts kMC Model
Simulation of Cu-Particles Compact



$\rho = 72\%$

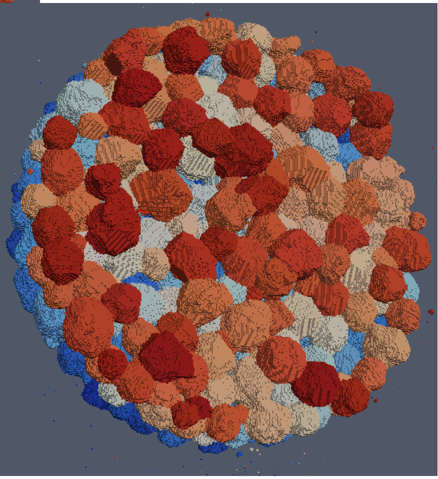


$\rho = 82\%$

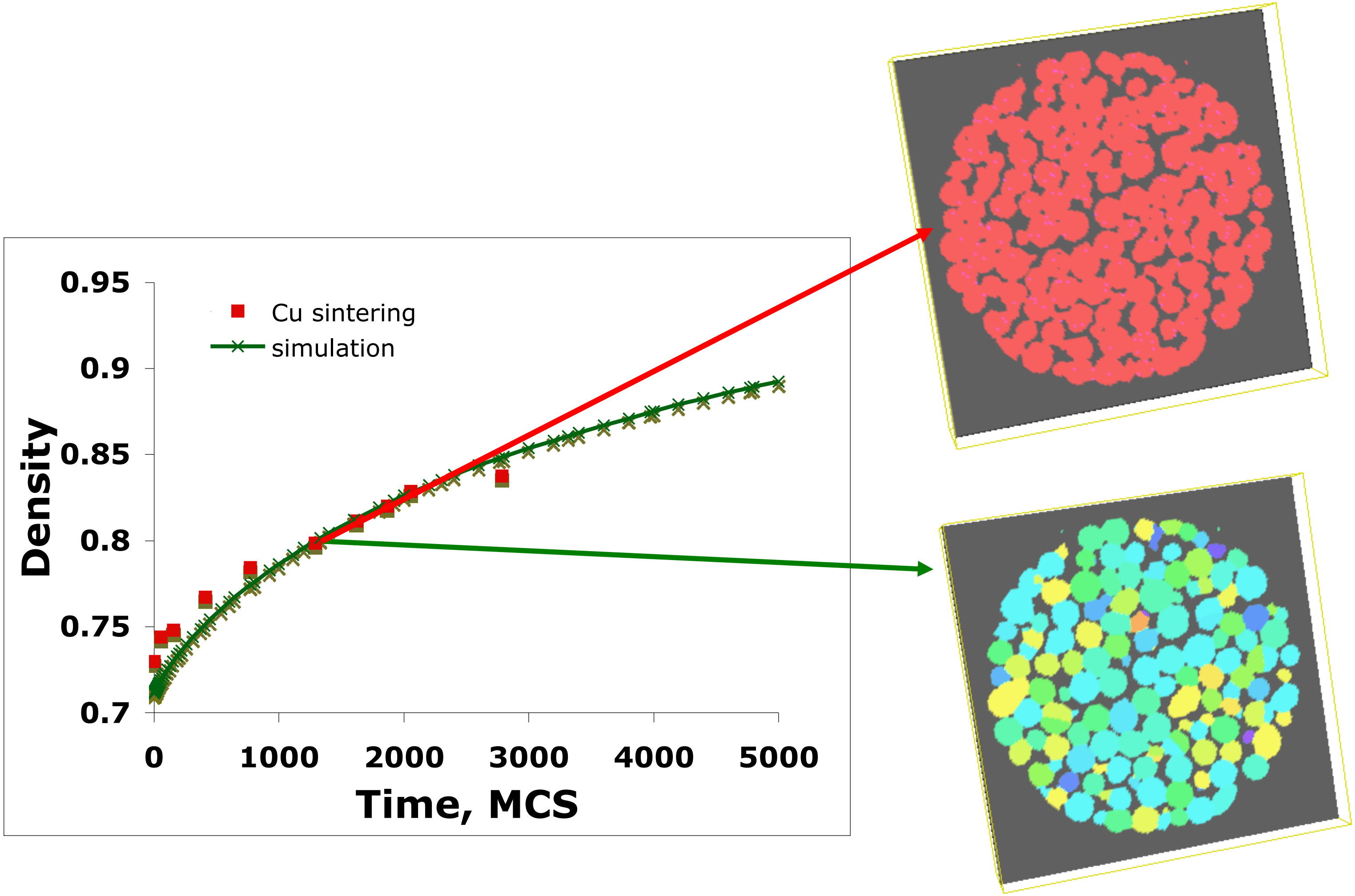


$\rho = 85\%$

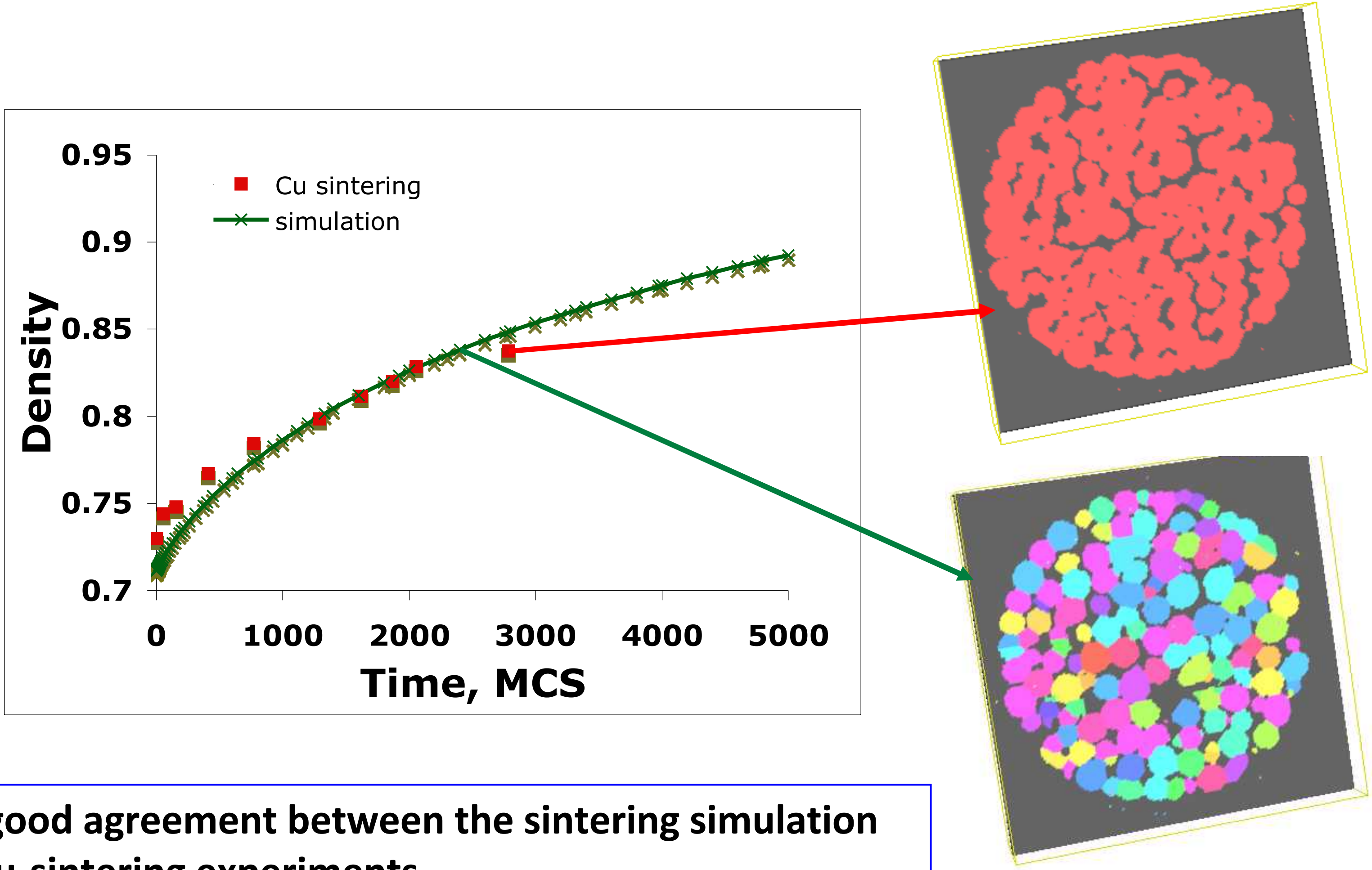
$\rho = 87\%$



Comparison of Potts Simulation and Cu-Experiments
Microstructure & Densification



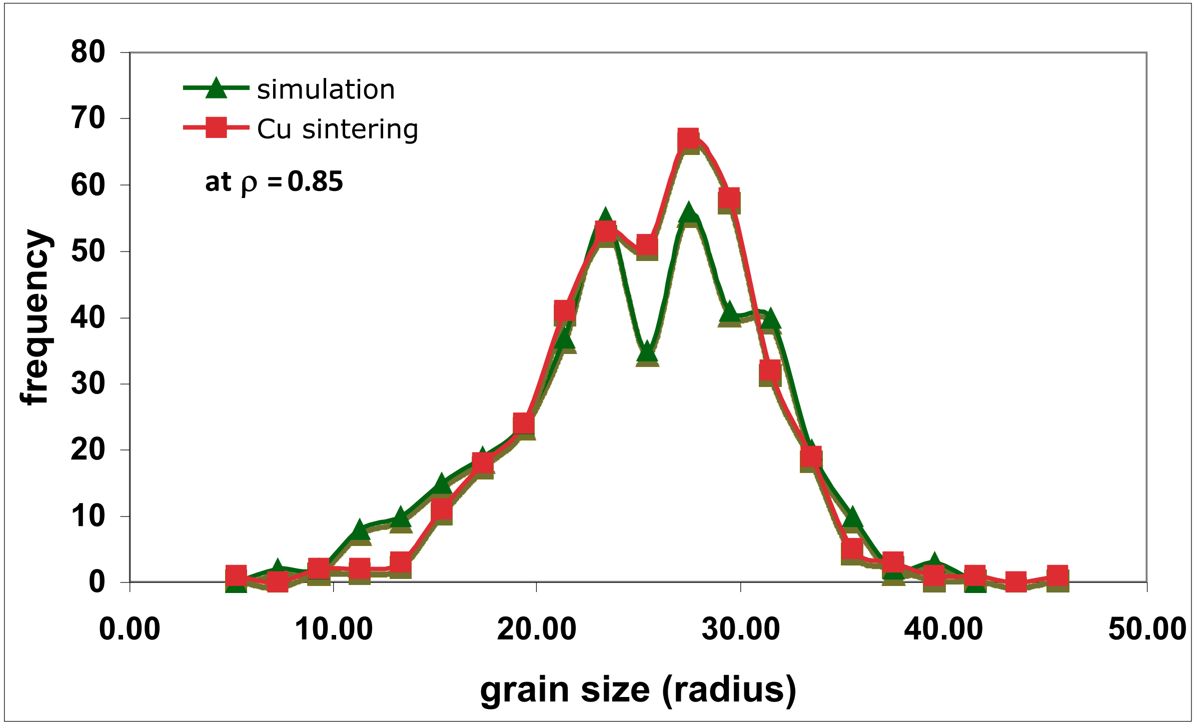
Comparison of Densification Microstructure & Densification

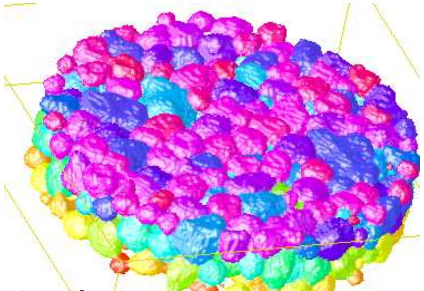


Very good agreement between the sintering simulation and Cu-sintering experiments.

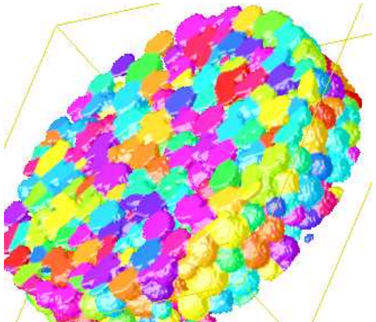
Comparison of Grain Size Distributions

- The overall GSD's have very similar sizes and distribution shape.
- There are 15 (out of 380) more grains in Cu sintering compacts because grains in the simulation are truncated at the edges.





simulation



Cu sintering

The GSD from simulated sintering is very similar to the 3D image of Cu sintering. Differences are due primarily to edge effects.

Sintering Stress

- **Driving force for sintering, ΔG, is the total change in free energy during sintering**
  - **Potts kMC model simulates the entire microstructural evolution**
  - **In response to grain boundary energy γ_{gb} and pore surface energy γ_s contributions**

$$E = A_{gb}\gamma_{gb} + A_s\gamma_s$$

- **Sintering stress, P_L, is the inherent sintering stress due to capillarity for densification.**

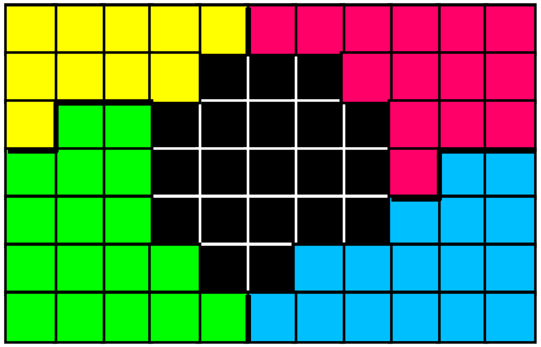
- **Energy Method**

$$P_L = \frac{E_s(V_o + \Delta V) - E_s(V_o)}{\Delta V} = \frac{\partial E_s}{\partial V}$$

- **Curvature Method**

$$P_L = \gamma_s \overline{H} = \gamma_s \frac{\frac{1}{2}\iint\limits_S \left(\frac{1}{r_1} + \frac{1}{r_2}\right) dS}{\iint\limits_S dS}$$

Sintering Stress
Measuring from Simulations



Energy Method

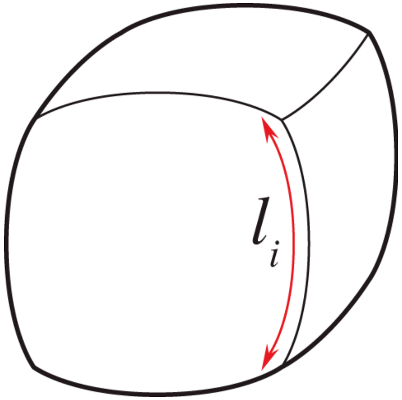
$$E = \frac{1}{2}\sum_{i=1}^{P}\sum_{j=1}^{26} J_S\left(1-\delta\left(q_i, q_j\right)\right)$$ **For all pore sites q_i**

Curvature Method

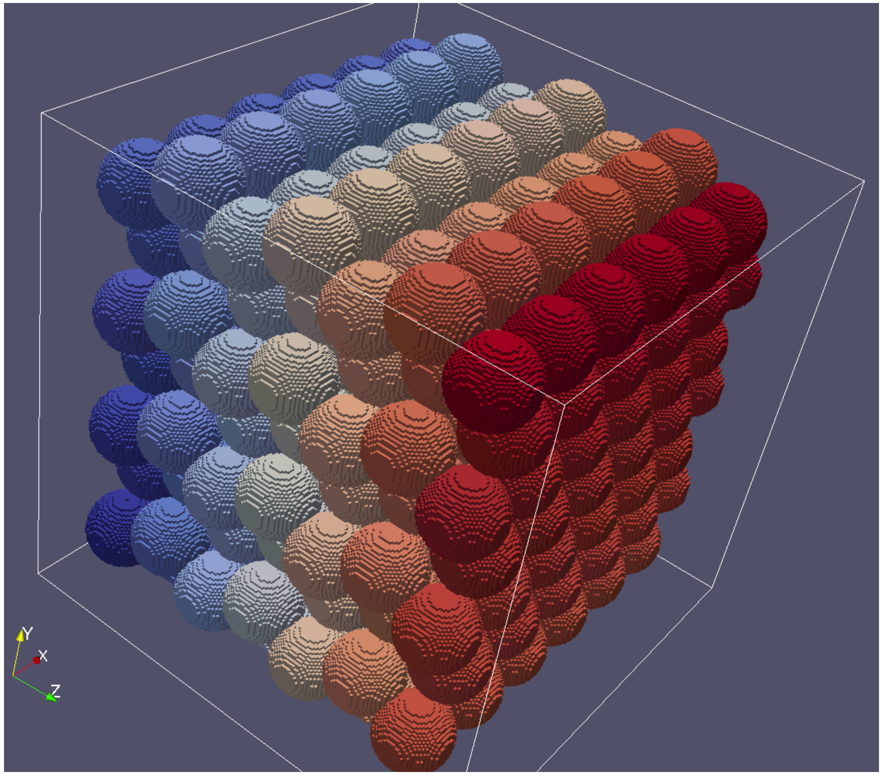
- For a polyhedron
  - Integral mean curvature

$$M_v = \underbrace{\iint_S \frac{1}{2}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) dS}_{\text{Faces} = 0} + \underbrace{\frac{1}{2\pi}\sum_{i=1}^{E} l_i \beta_i}_{\text{Edges}}$$

  - Digitized microstructure

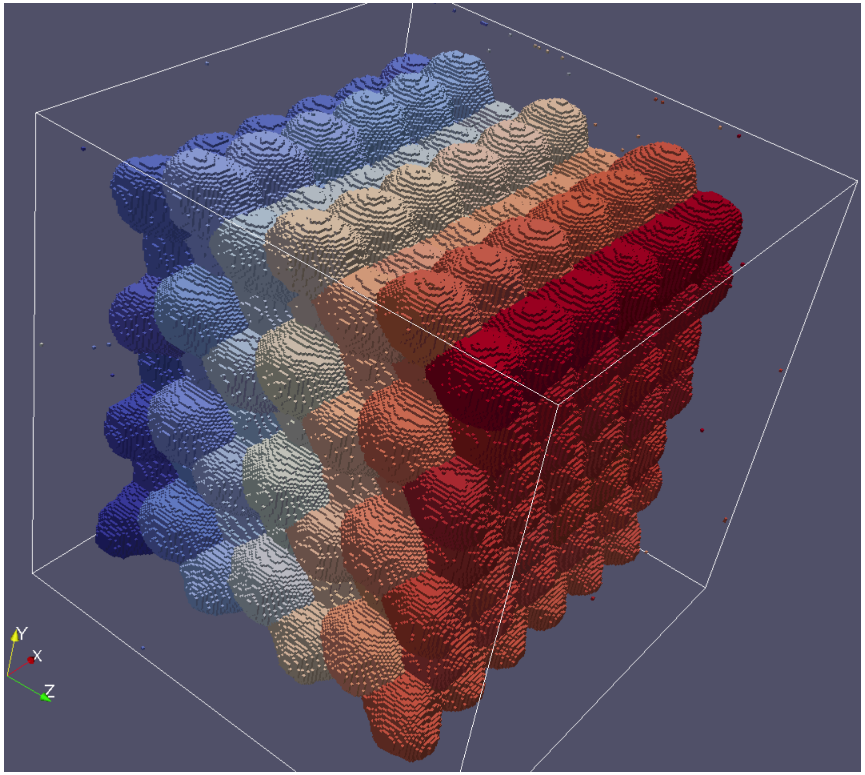


Potts kMC Model
Simulation of Close-Packed Spheres Sintering

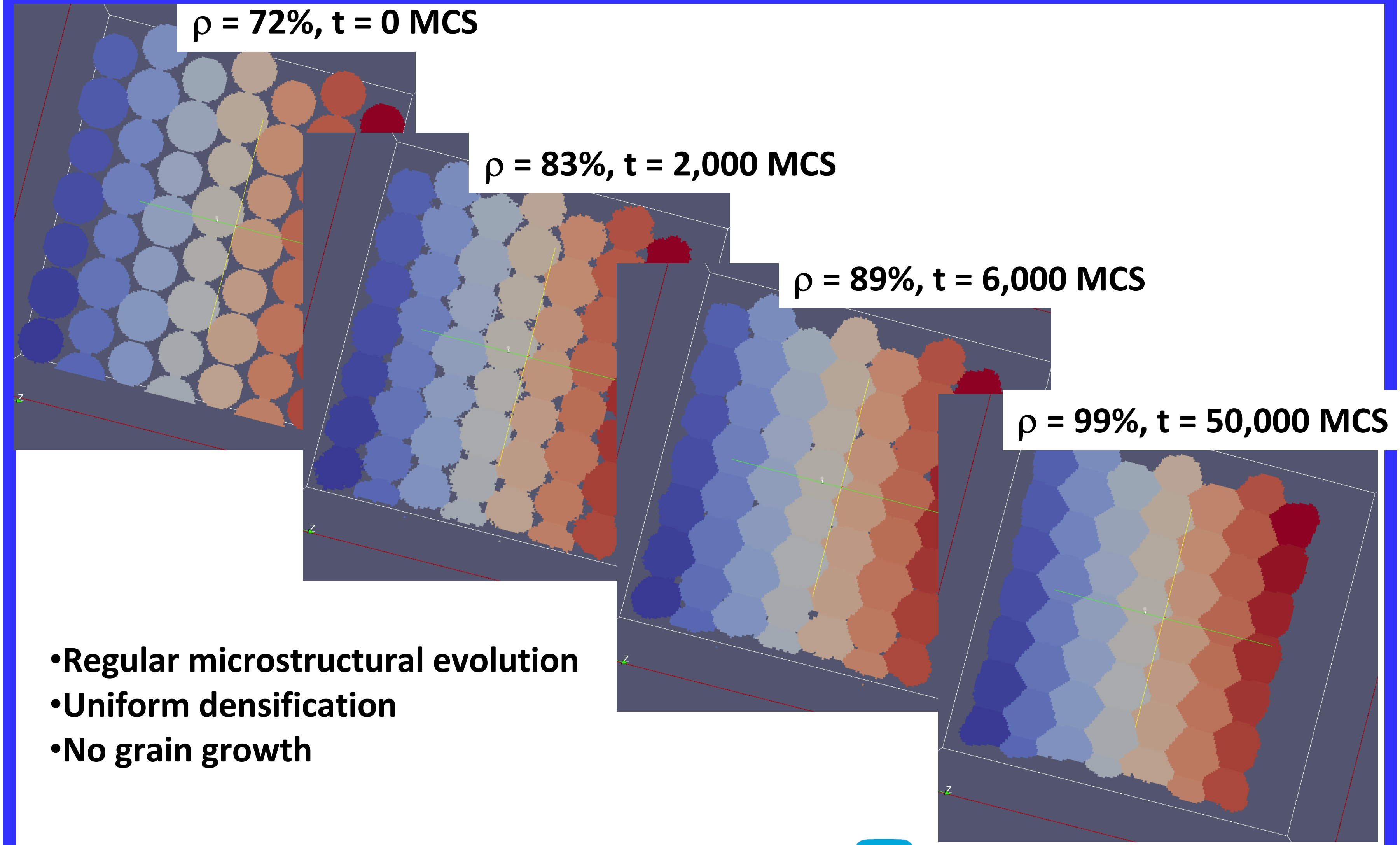


Density = 72% at t = 0 MCS

Density = 100% at t = 60,000 MCS



Potts kMC Model
Simulation of Close-Packed Spheres Sintering



ρ = 72%, t = 0 MCS

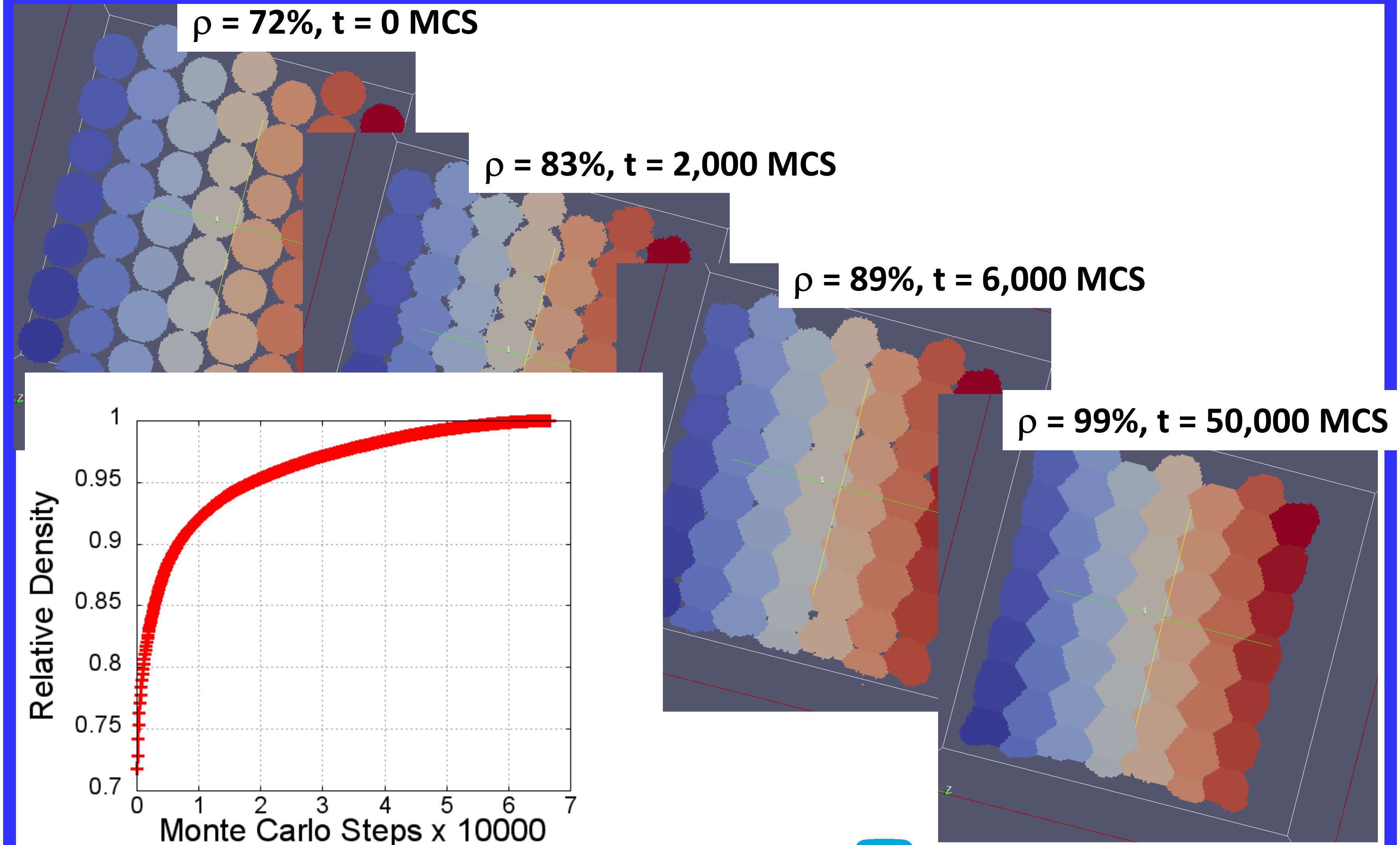
ρ = 83%, t = 2,000 MCS

ρ = 89%, t = 6,000 MCS

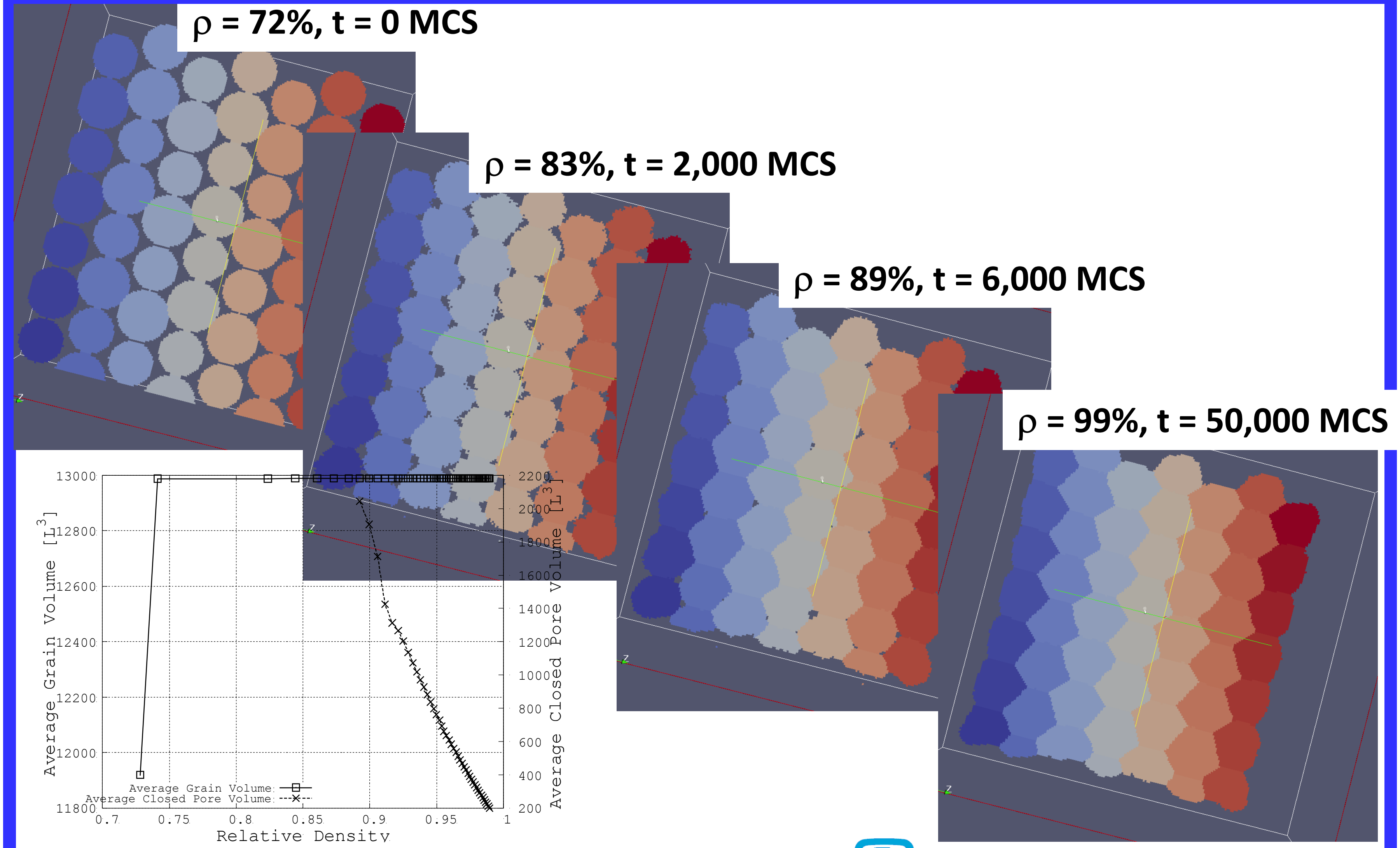
ρ = 99%, t = 50,000 MCS

- Regular microstructural evolution
- Uniform densification
- No grain growth

Potts kMC Model
Simulation of Close-Packed Spheres Sintering


ρ = 72%, t = 0 MCS
ρ = 83%, t = 2,000 MCS
ρ = 89%, t = 6,000 MCS
ρ = 99%, t = 50,000 MCS
Relative Density
1
0.95
0.9
0.85
0.8
0.75
0.7
0
1
2
3
4
5
6
7
Monte Carlo Steps x 10000

Potts kMC Model
Simulation of Close-Packed Spheres Sintering



ρ = 72%, t = 0 MCS

ρ = 83%, t = 2,000 MCS

ρ = 89%, t = 6,000 MCS

ρ = 99%, t = 50,000 MCS

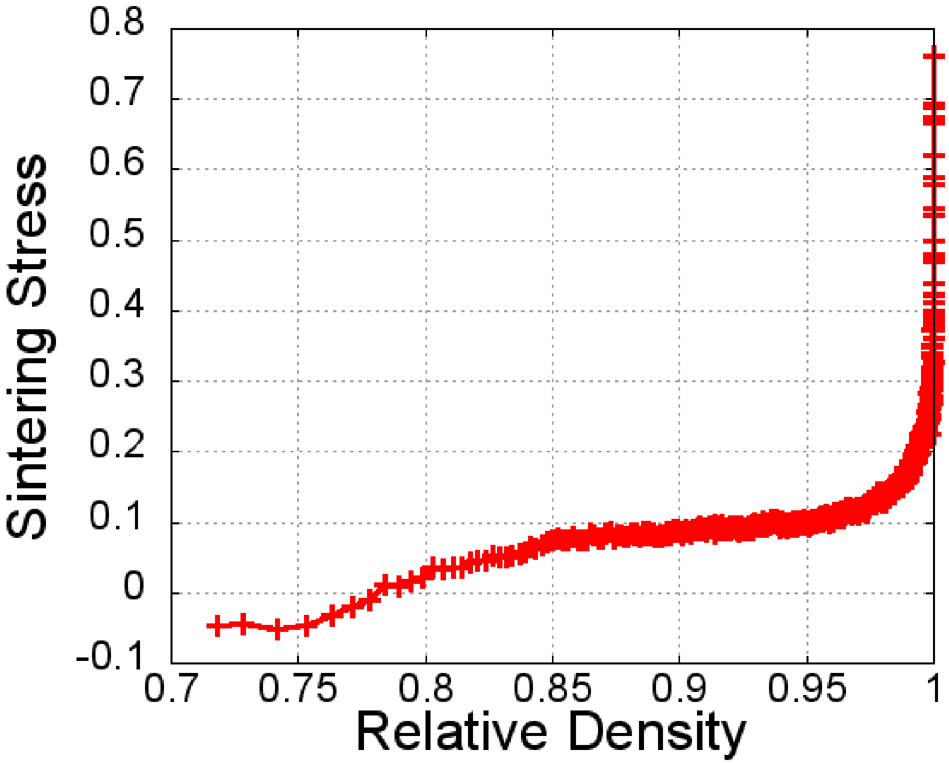
Average Grain Volume [L^3]
13000
12800
12600
12400
12200
12000
11800
Average Closed Pore Volume [L^3]
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0.7
0.75
0.8
0.85
0.9
0.95
1
Relative Density
Average Grain Volume
Average Closed Pore Volume
Z

Sintering Stress, Curvature Method
Simulation of Close-Packed Spheres Sintering

- Curvature method $P_L = \gamma_s \overline{H} = \gamma_s \dfrac{M_v}{S_v}$

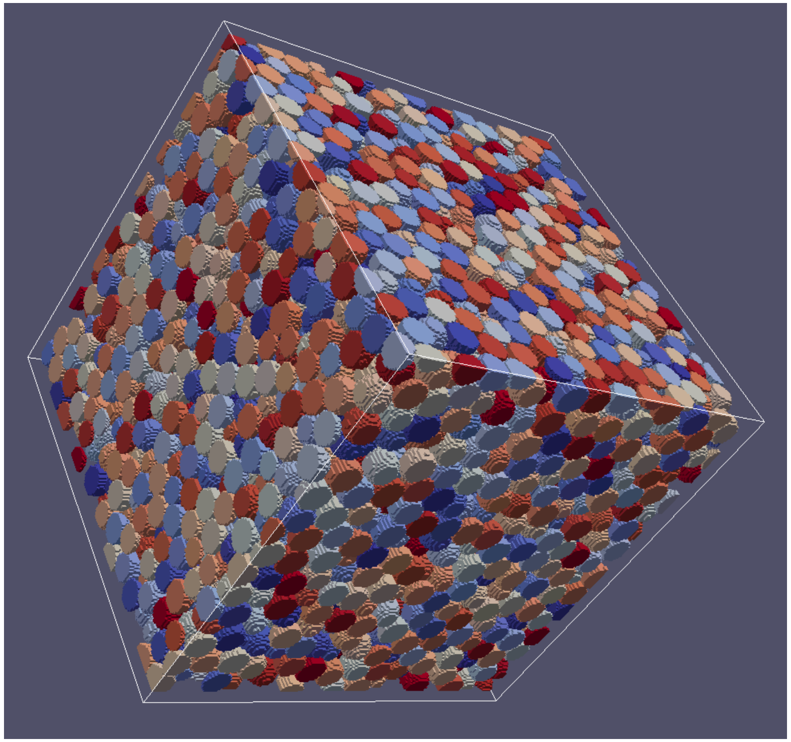
- Directly measure from the simulated microstructures
- Is an instantaneous measure and does not depend on the microstructural evolution path

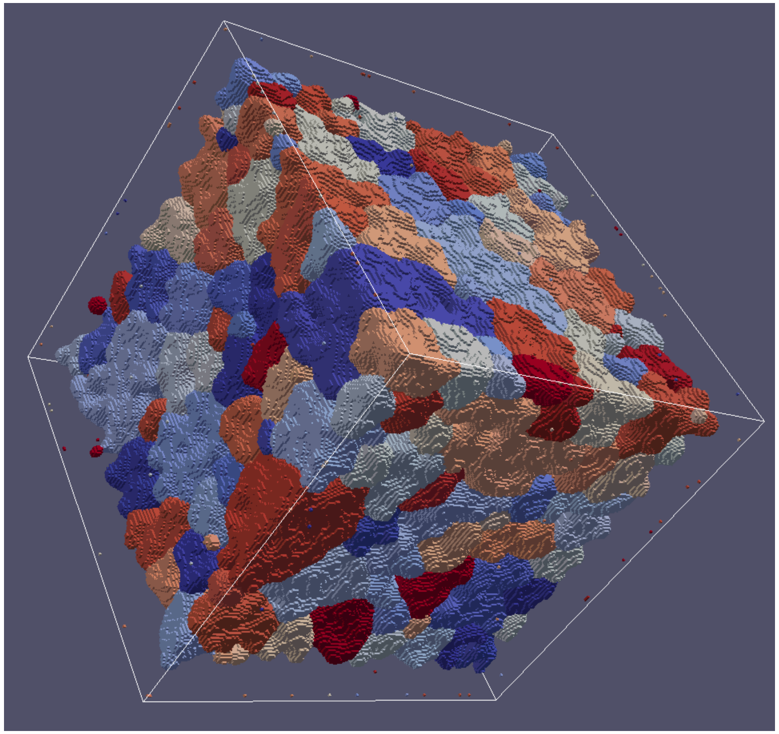
- P_L initially negative
- P_L increase with increasing pore curvature.



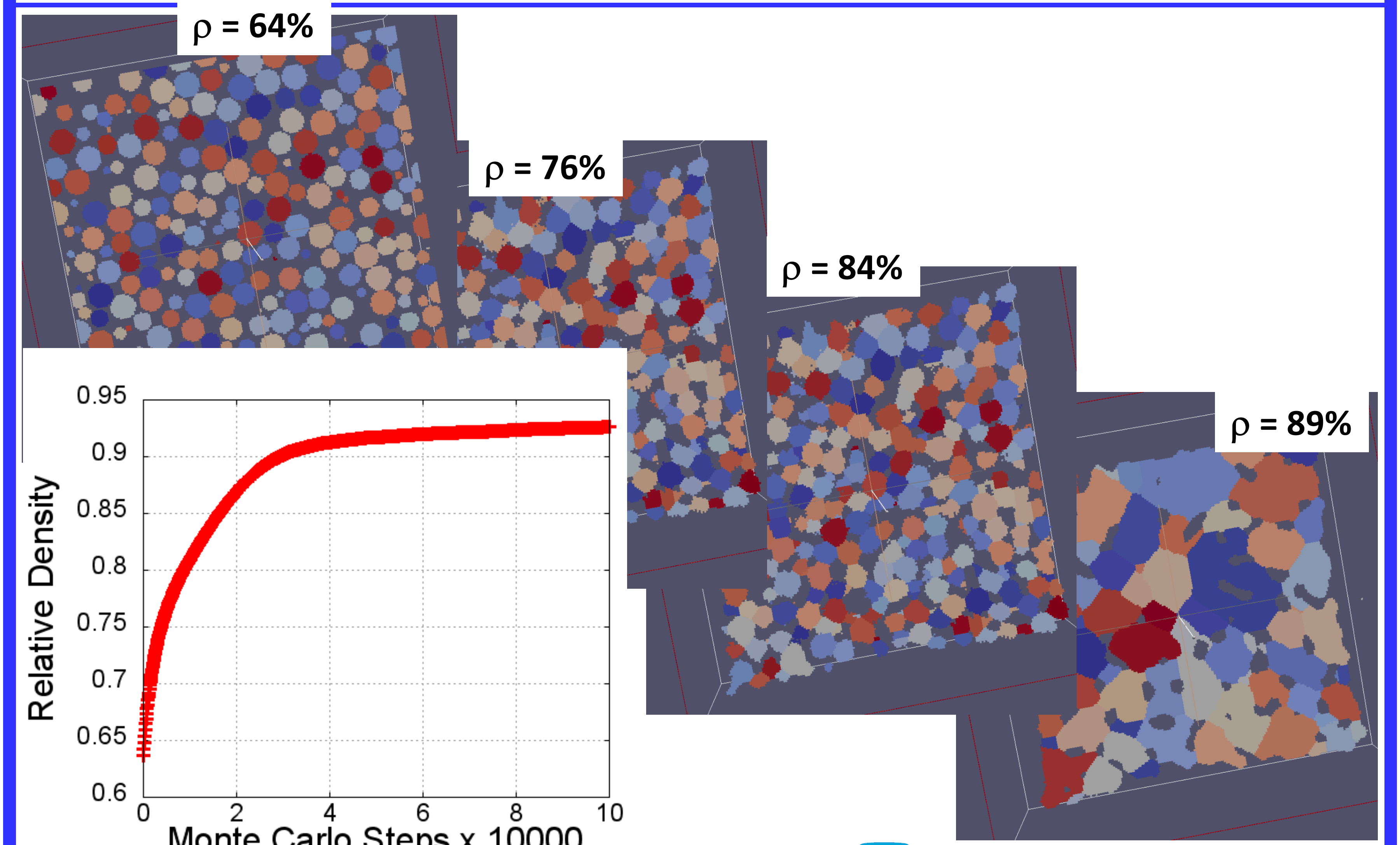
Curvature method will be used for the remainder of this work

Potts kMC Model
Simulation of Randomly-Packed Mono-Sized Spheres Sintering

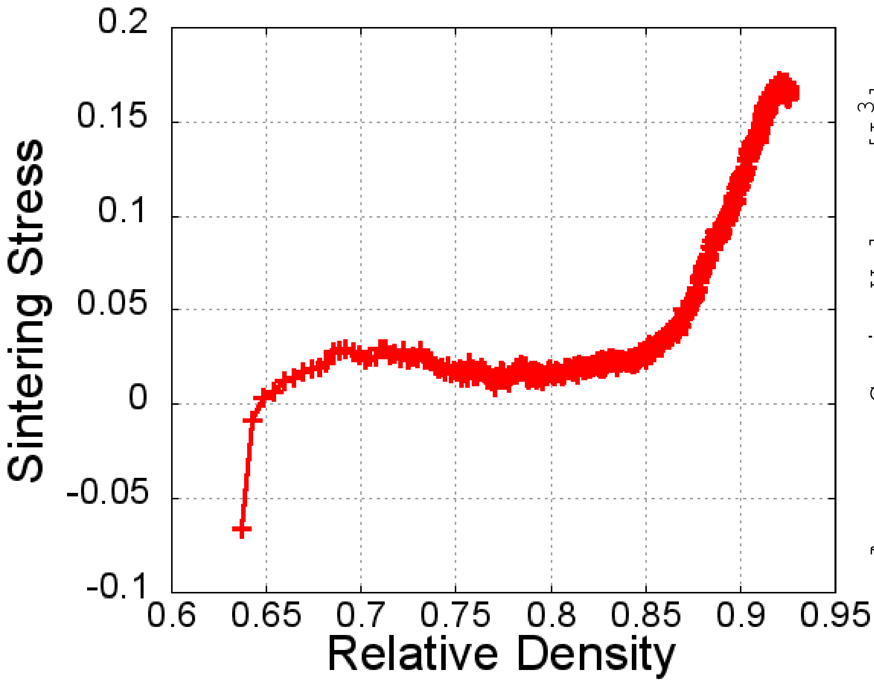


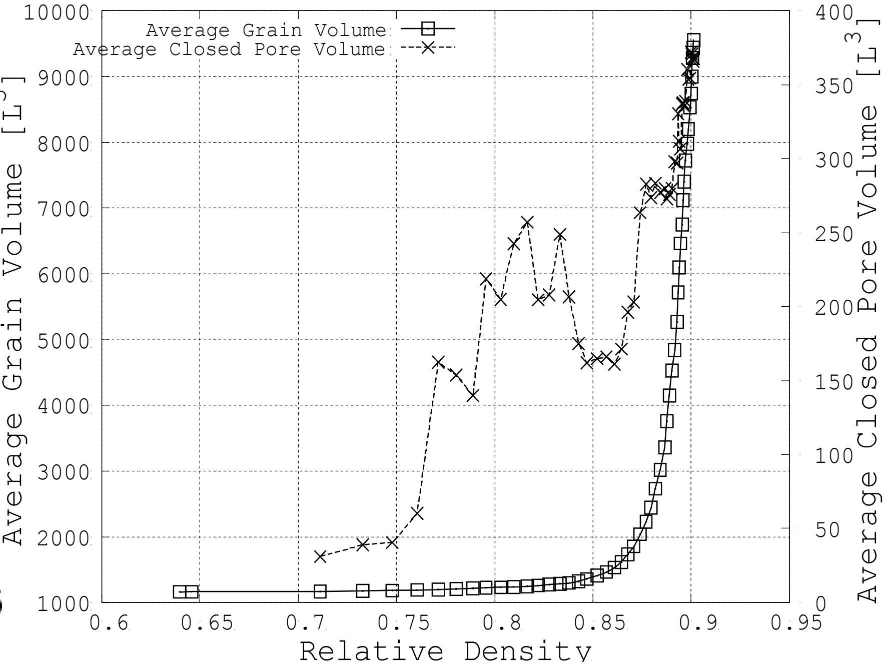


Potts kMC Model
Simulation of Randomly-Packed Mono-Sized Spheres Sintering



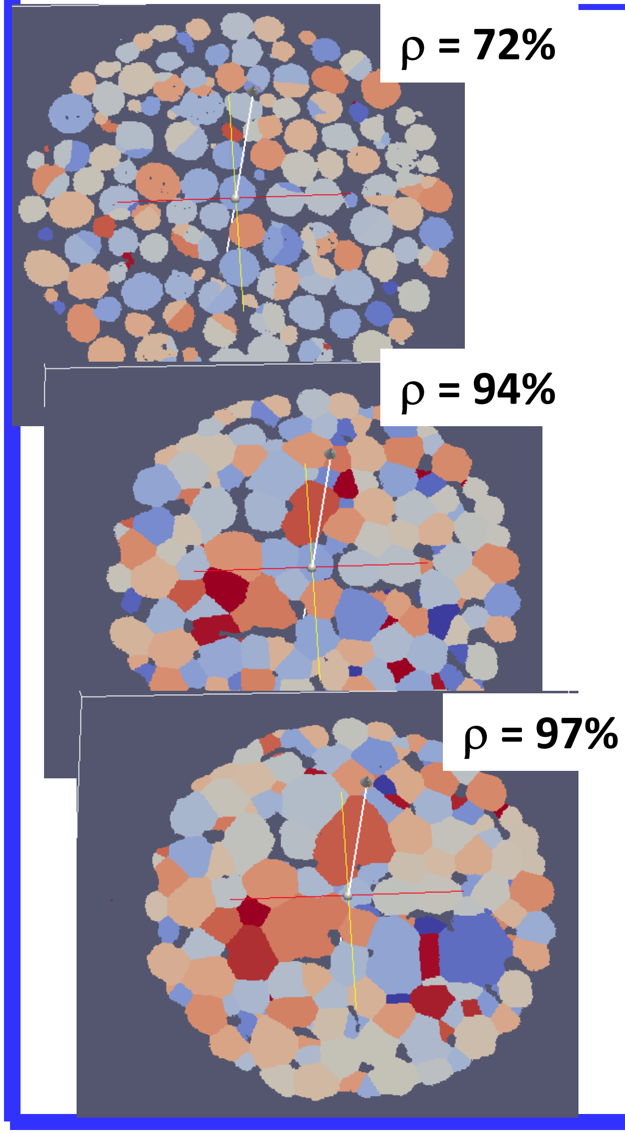
Sintering Stress
Simulation of Randomly-Packed Mono-Sized Spheres Sintering





As grains grow and pore curvature decreases at density ~90%, sintering stress also decreases.

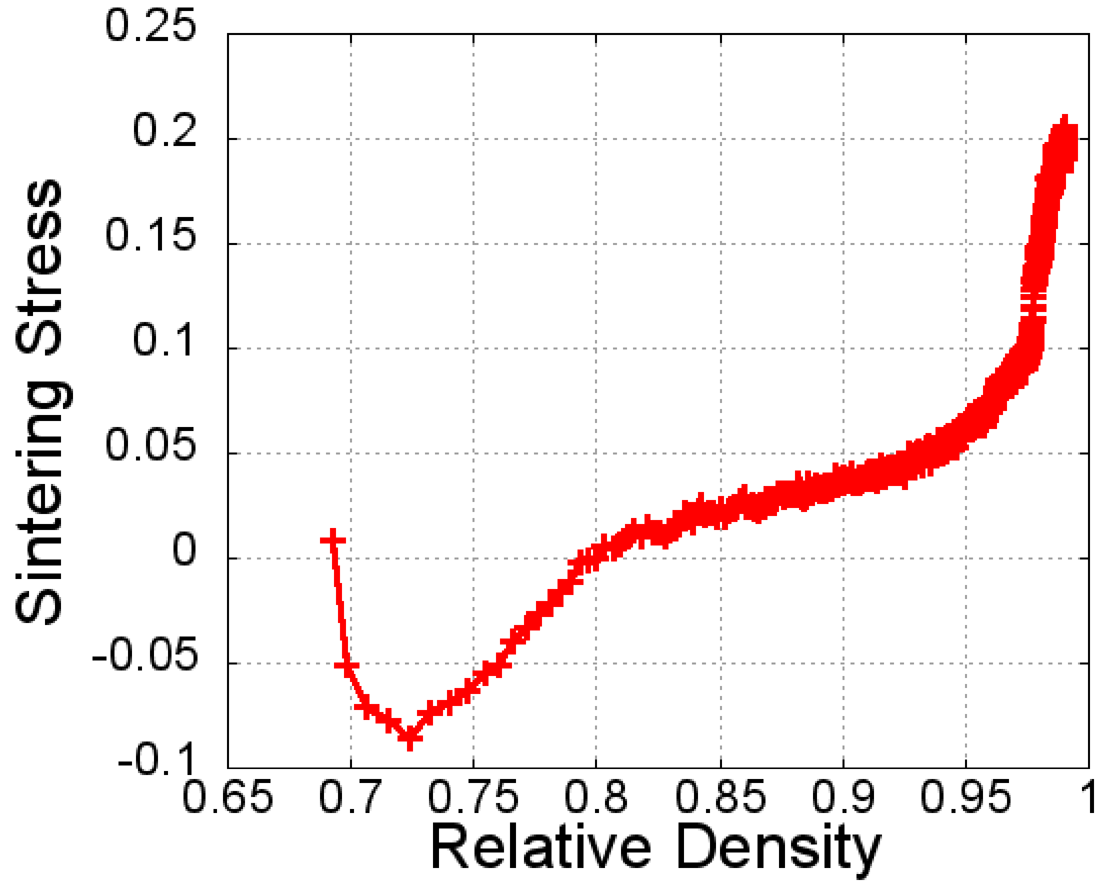
Sintering Stress
Simulation of Cu-Particle Compact Sintering



ρ = 72%

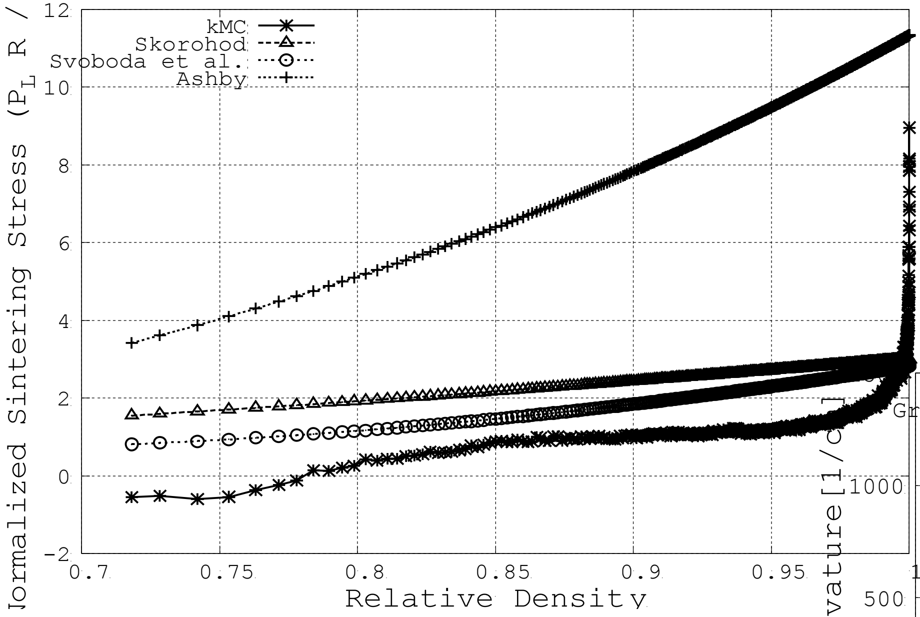
ρ = 94%

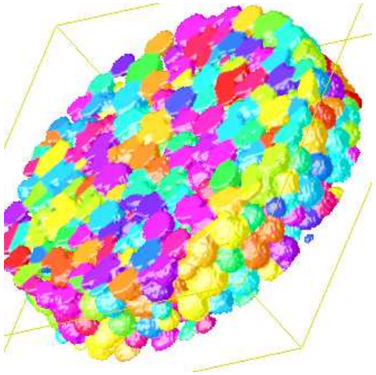
ρ = 97%

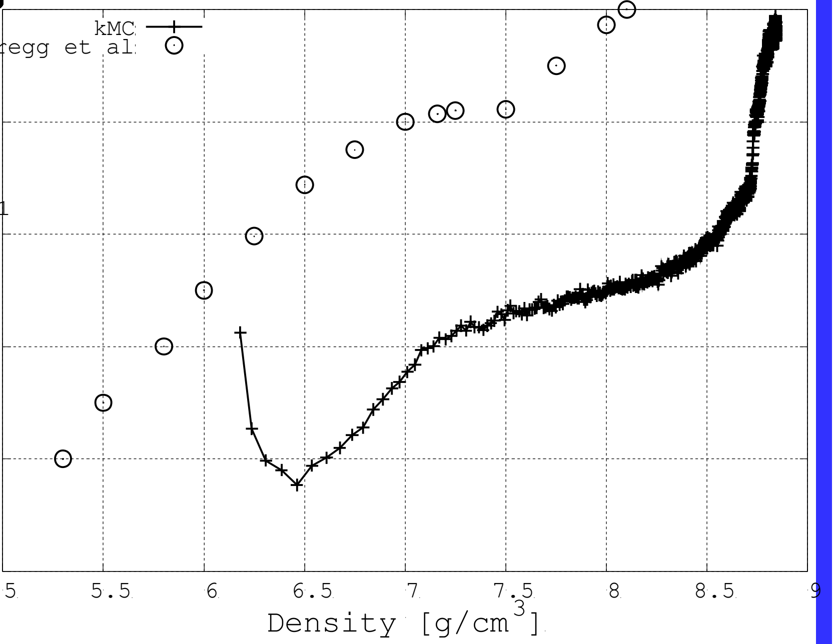


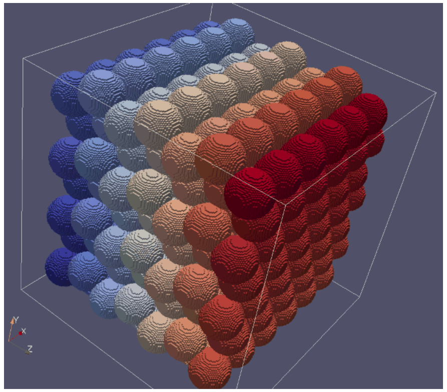
Sandia National Laboratories

Comparison of simulation results to calculations and experiment









Sandia National Laboratories

Sintering Stress
In Heterogeneous Powder Compacts

- A combination of inherent sintering stress and far-field stresses will lead to unique microstructural evolution.

- We are developing models to generate detailed microstructural evolution
  - Direct coupling between FEM – Potts. The distortions introduced in the coupling are of the same magnitude as shrinkage
  - Material Point Method. Enjoying some success, but development of coupling between microstructure and mechanics is demanding
  - Potts – DEM coupling. Just beginning. Early stages of sintering are possible, later stages remain challenging

- Actively seeking collaborations to bring other methods to develop these models.

Summary and Conclusions

- A model that is capable of simulating simple, solid-state sintering has been presented.
  - True meso-scale with hundred or thousands of particles
  - Arbitrarily complex powder particles of different geometries
- It can incorporate all the mechanisms necessary for simulation of microstructural evolution during sintering
  - Generation, diffusion and annihilations of vacancies
  - Surface diffusion at pore surface
  - Curvature-driven grain growth
- Has sufficient detail to characterize detailed topological features and their influence kinetics
- Can be extended to include more mechanisms and vary thermodynamics and kinetic characteristics.

Potts kMC Model
Available as open source code in October 2012

SPPARKS is a Monte Carlo simulation code

- **with kinetic Monte Carlo (kMC), rejection MC and Metropolis MC**
- **2- or 3D simulations**
- **on- and off-lattice, with several lattice choices**
- **serial and parallel, supports MPI**
- **C++**
- **open source, download from**
  http://www.cs.sandia.gov/~sjplimp/spparks.html
- **designed to modify and extend to many materials processes**

SPPARKS has been adapted to 3D simulate sintering

- **the serial algorithm was parallelized**
- **can run much larger simulations in more detail**

SPPARKS Developer: Steve Plimpton, SNL

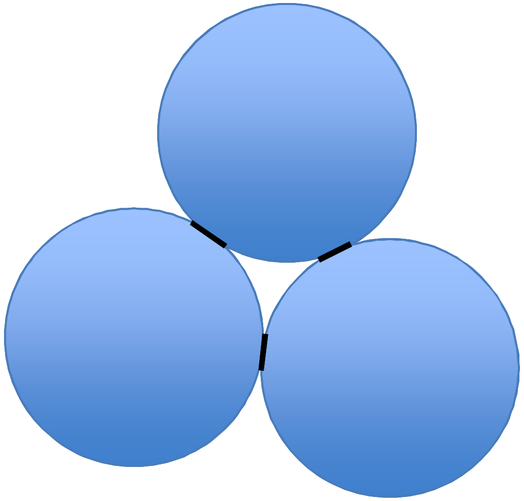
Sintering/SPPARKS Developer: Cristina Garcia C., SNL / SDSU

Surface Diffusion at Pore Surfaces in Stereological Model of Sintering*

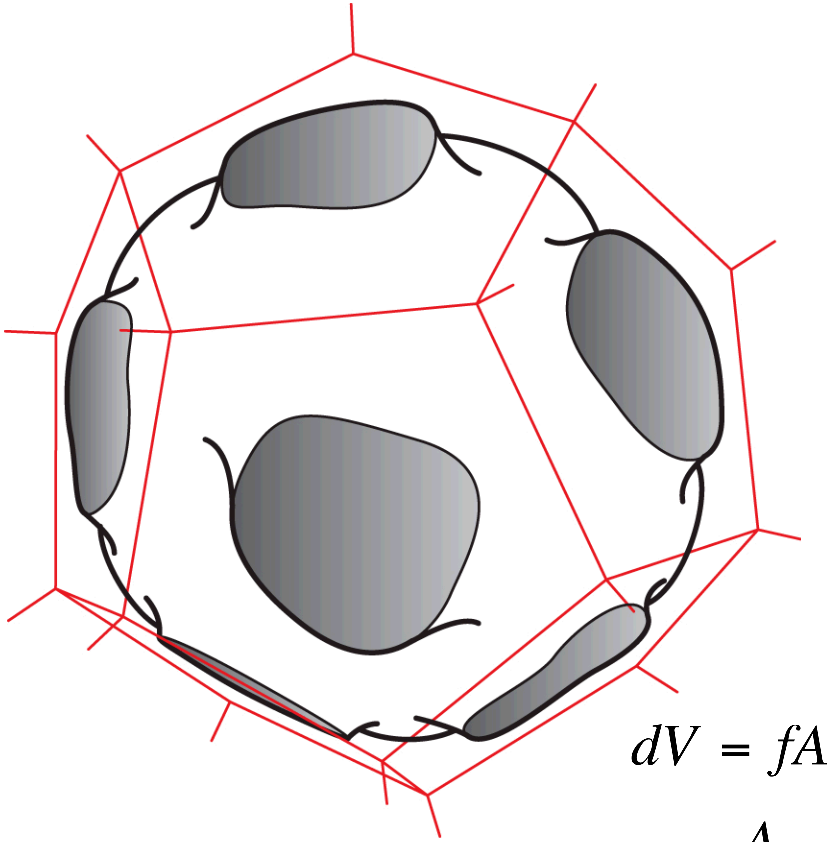
- Pores continually reshape themselves to lower their surface free energy
- Material is transported from areas of high curvature to lower curvature

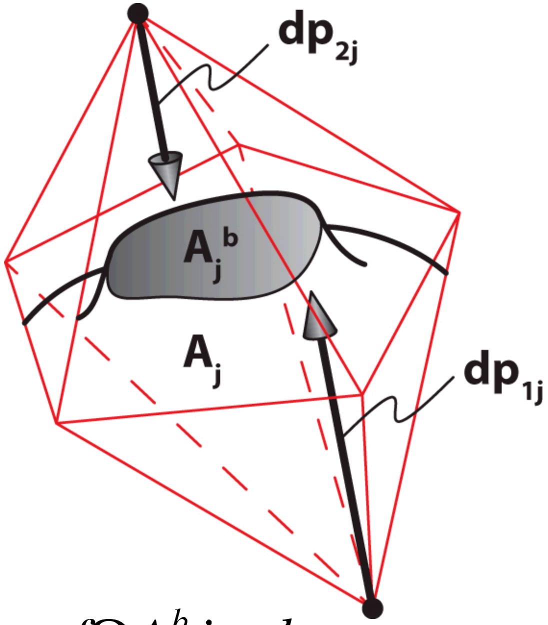
- Velocity of pore surface

$$v_s = -\Omega\delta\nabla \bullet J_s$$



Bi-Crystal View
Stereological Model of Sintering*




dp2j
Aj b
Aj
dp1j

$$dV = fA_j^b dp_j = -f\Omega A_j^b \dot{n}_{Aj} dt$$

$$f = \frac{A_j}{A_j^b}$$