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# On Sintering Stress in Complex Powder Compacts

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# Outline

- What are we trying to model – simple solid-state sintering
- Which processes are we trying to model

# Objectives

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

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

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  - **Functionally graded materials**
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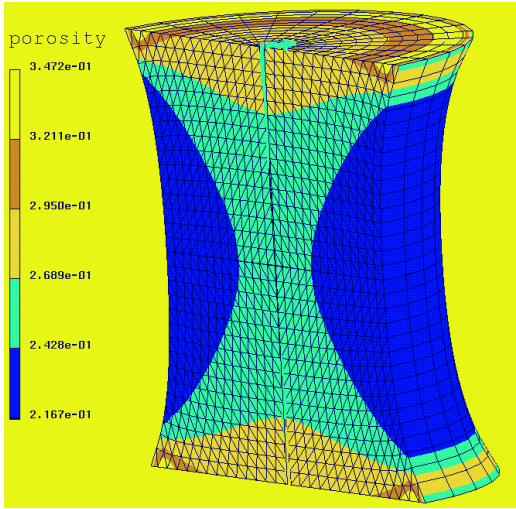

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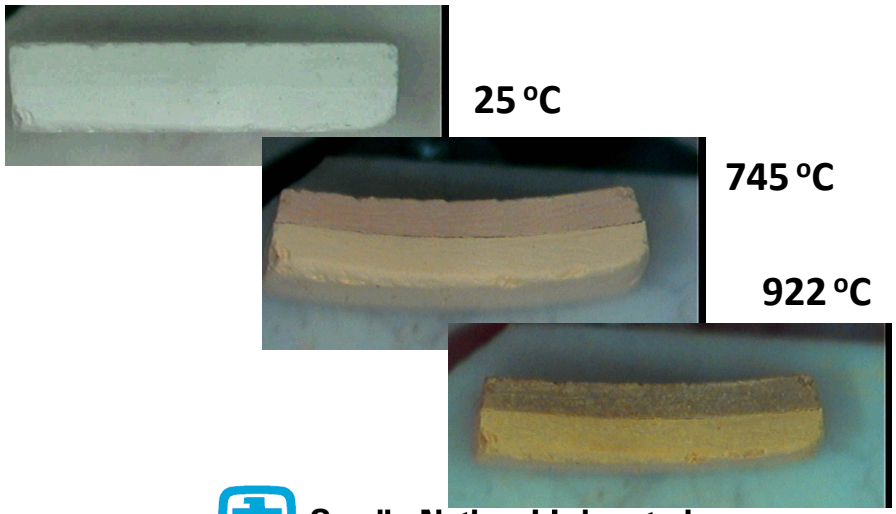



T. Garino, SNL

# During Simple Solid-State Sintering:

Mass transport described by

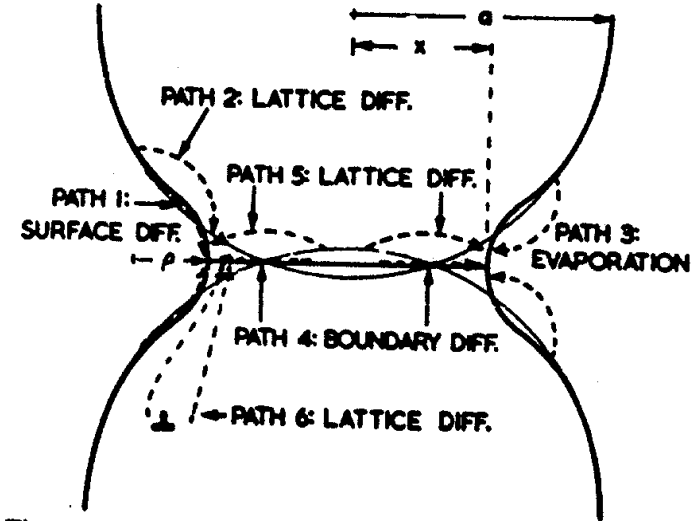
Classic Ashby model with the 6 paths

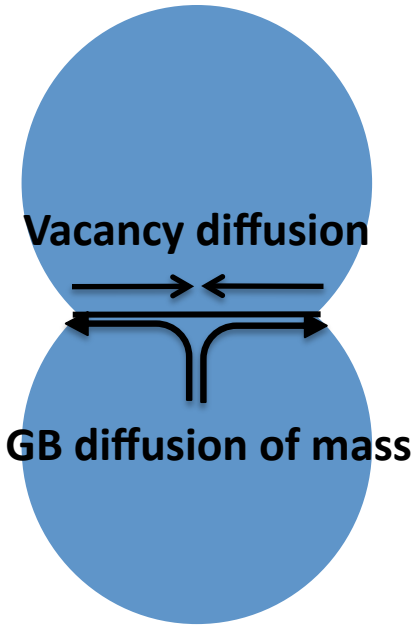
In this work:

grain boundary diffusion

surface diffusion

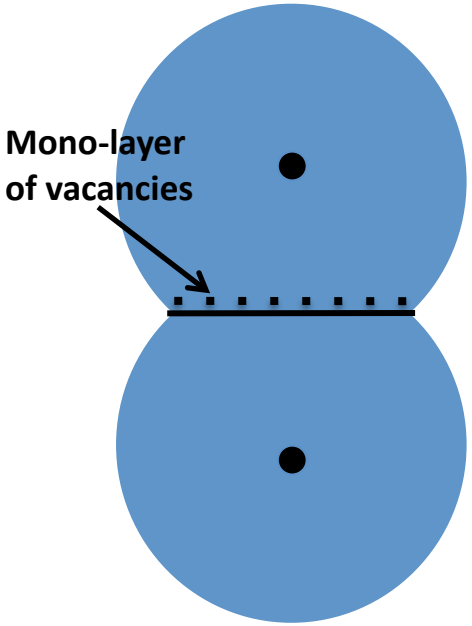
are active.




- Mass diffuses from 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
- $\tau \approx A_b$

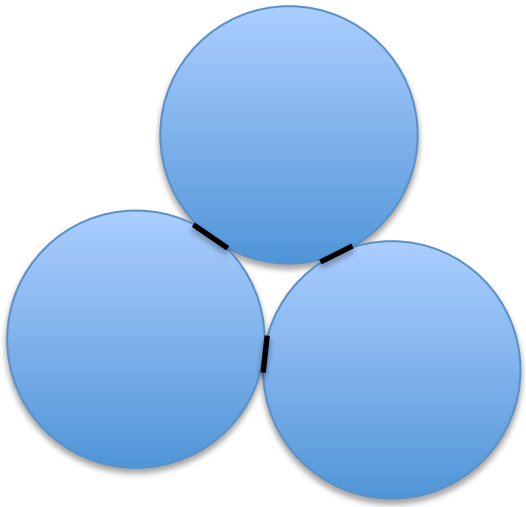
*R.T DeHoff, Sci. of Sintering, 1989

# 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

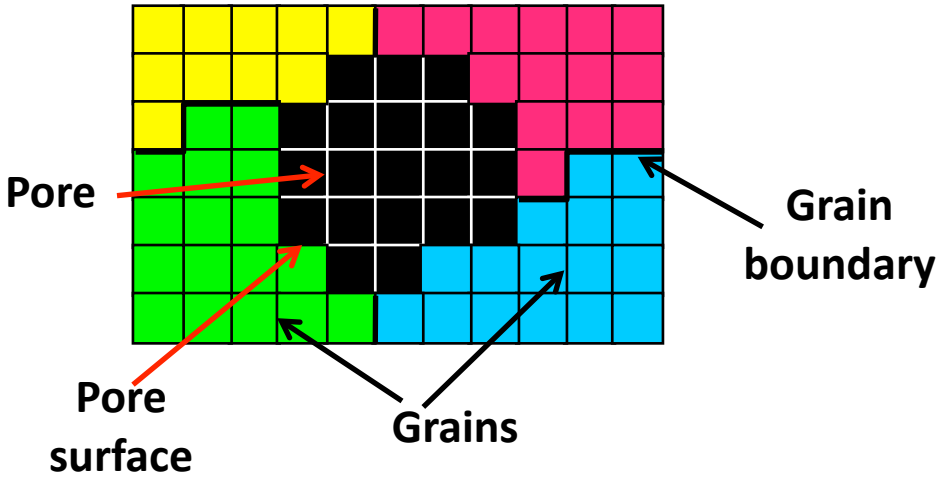
- Velocity of pore surface

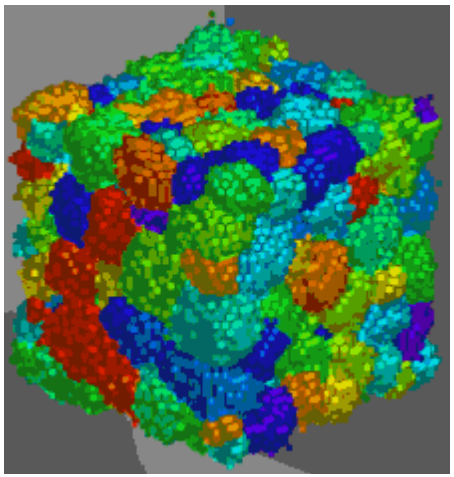
$$v_s = -\Omega \delta \nabla \bullet J_s$$



# Potts kMC Model

- **Microstructure is represented by digitizing on a cubic lattice:**



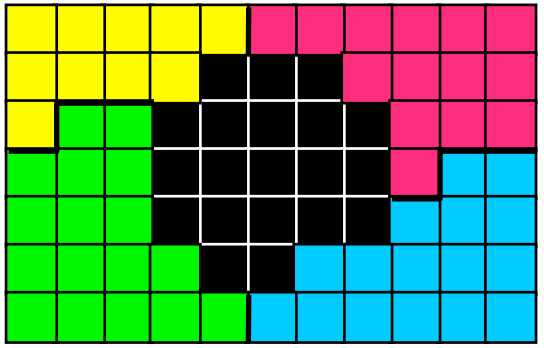



- **Each voxel is a unit of matter**

# 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 $J_{ij}$**

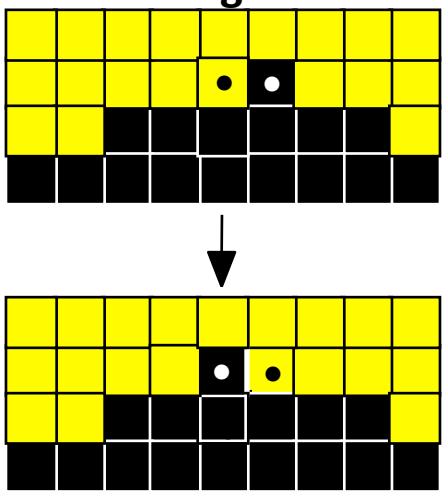
# Potts kMC Model
# Pore Surface Diffusion

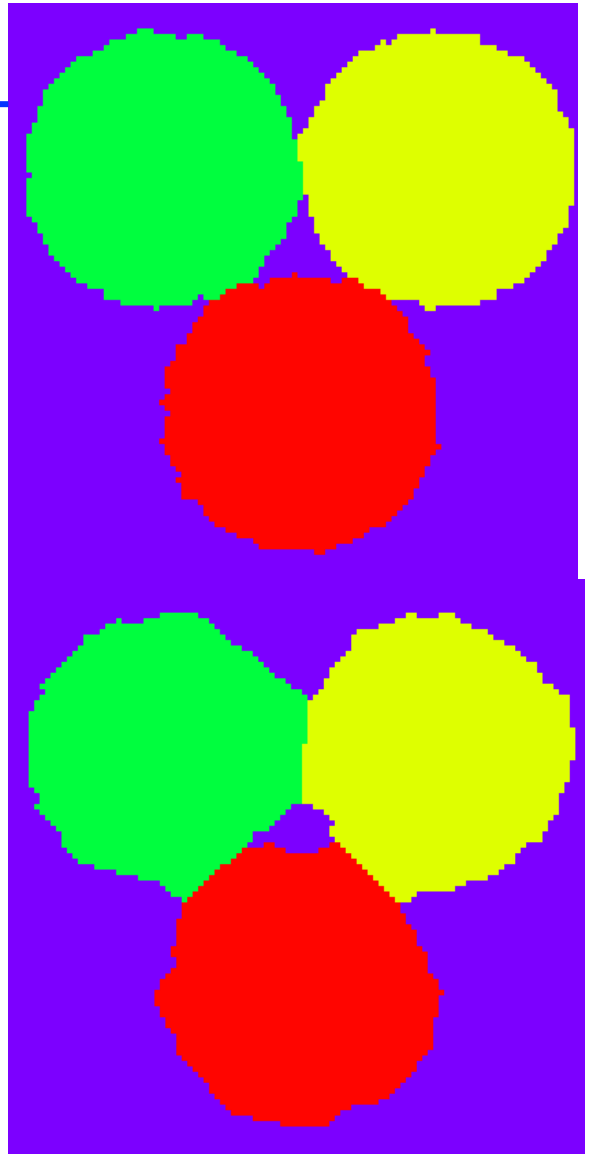
- Pore sites and grain sites at pore surface exchange places to simulate surface diffusion
- Minimize surface energy by Metropolis algorithm
- Calculate ΔE
- Probability of exchange is

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

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

Exchange sites





# Potts kMC Model
# Vacancy Generation

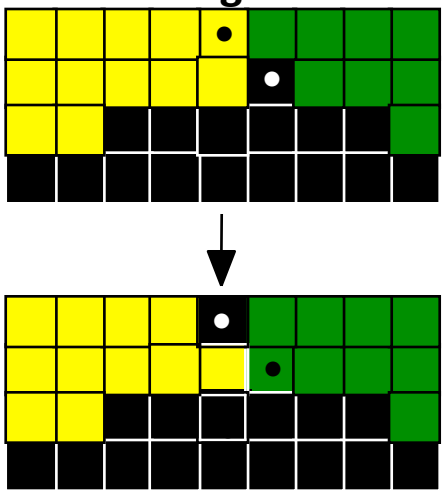
- Vacancies are generated by the exchange mechanisms as shown.
- There is an equilibrium concentration of vacancies

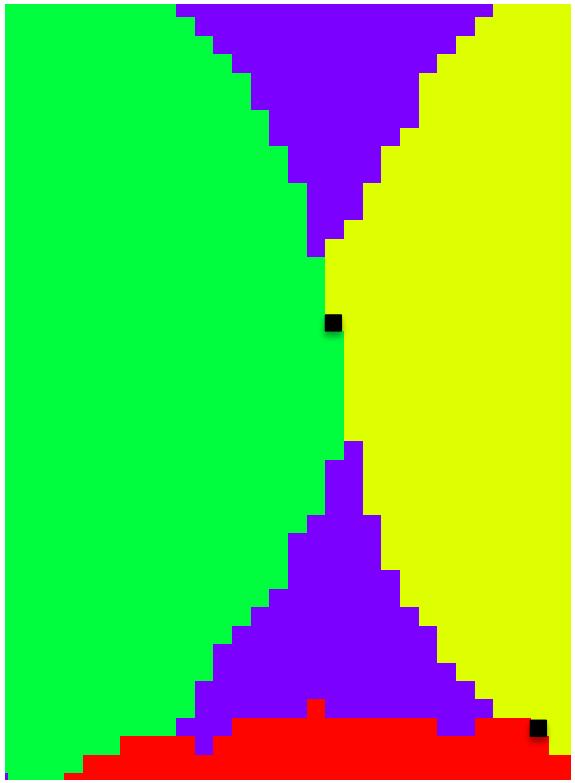
$$P = \exp\left(\frac{-\Delta E}{k_B T}\right) \quad \Delta E > 0$$

- Concentration of vacancies is proportional to the surface curvature

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

Exchange sites

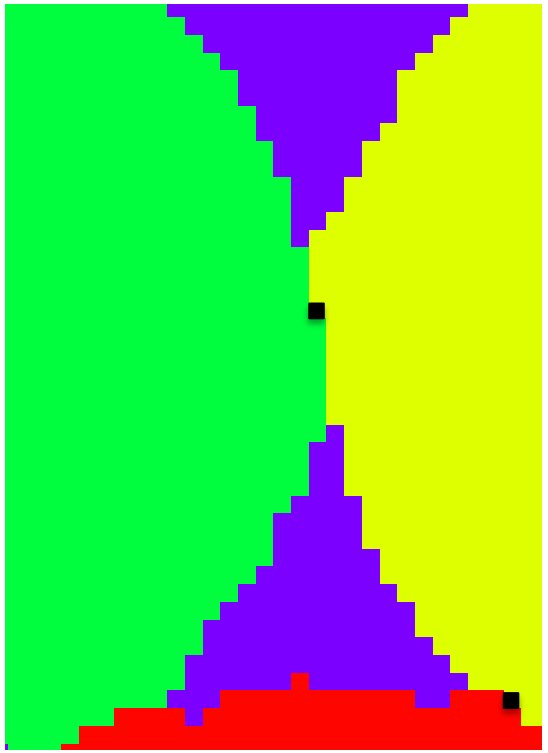




# Potts kMC Model
# Vacancy Diffusion and Annihilation

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

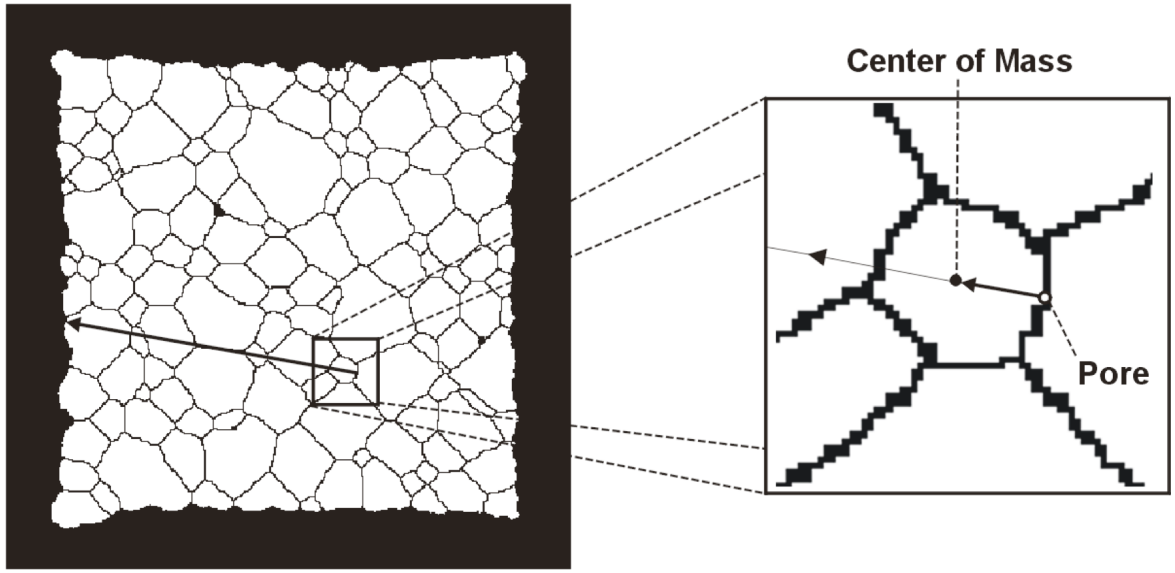
- Potts model
  - Annihilation mono-layer is not possible.
  - Annihilate one vacancy with equal probability of being anywhere in the neck.
  - Annihilation frequency is $\tau \approx A_b$.
  - Annihilation is simulated by collapsing a column of sites.
  - Centroid of grains approach each other.
  - 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
# Grain Growth

**Coarsening of grains during sintering**

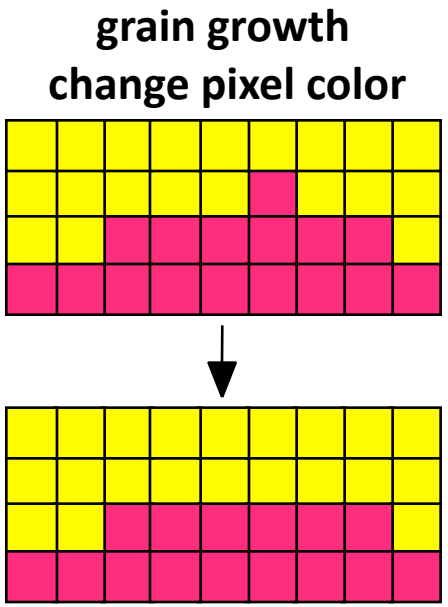
- **Is a significant contributor**
- **Effects densification and distortions**

**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**

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

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

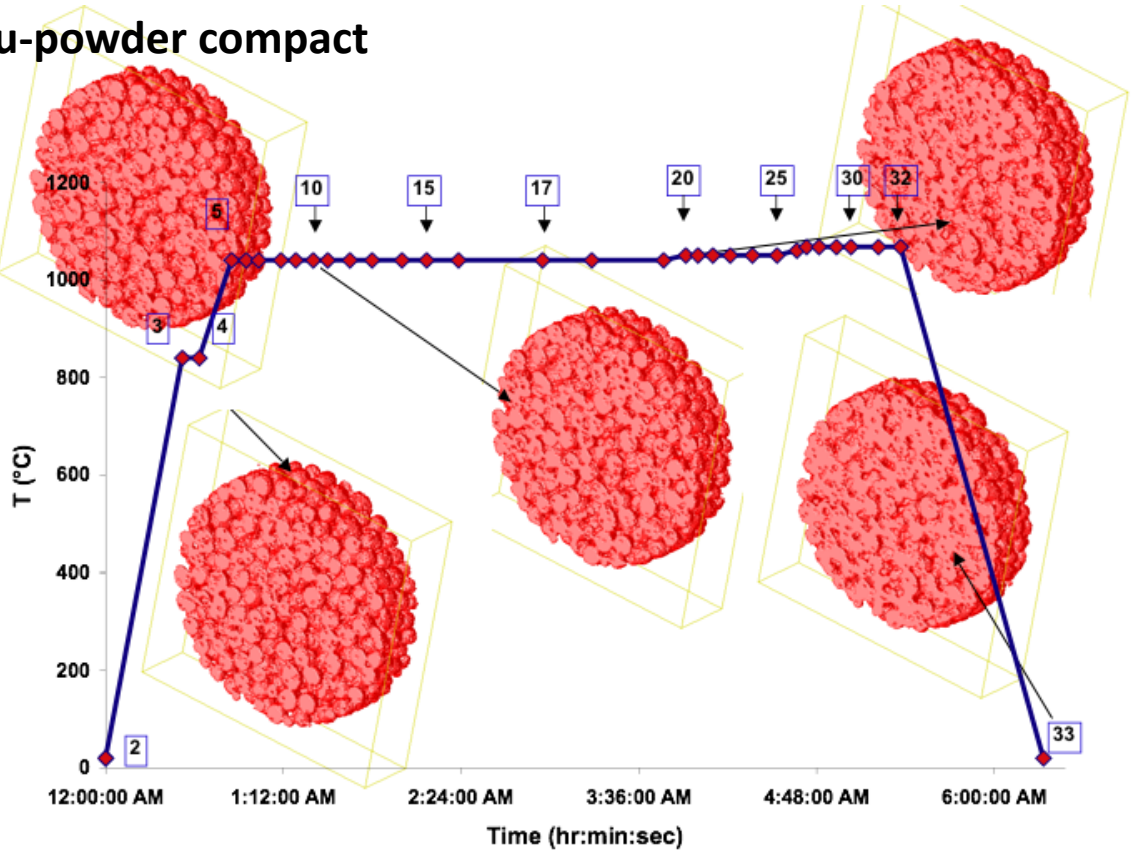


# Application and Validation of Potts kMC Sintering Model

**Potts kMC Sintering model was tested by simulating**

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

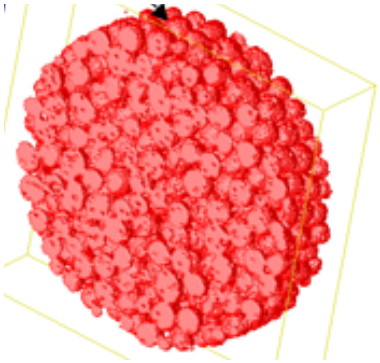
- **Comparing to sintering Cu-powder compact**
- **Imaged with high-energy X-rays in synchrotron**
- **Cu-particles 30 – 50 μm**
- **Shows the mass and pore distribution in-situ**

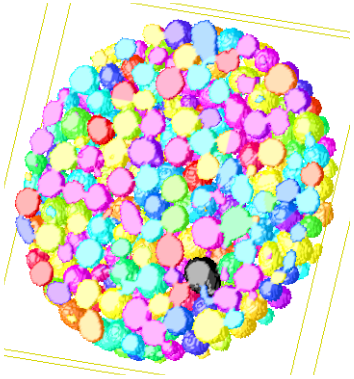


# Validation by Comparing to Cu-Compact Sintering Potts kMC Sintering Model

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

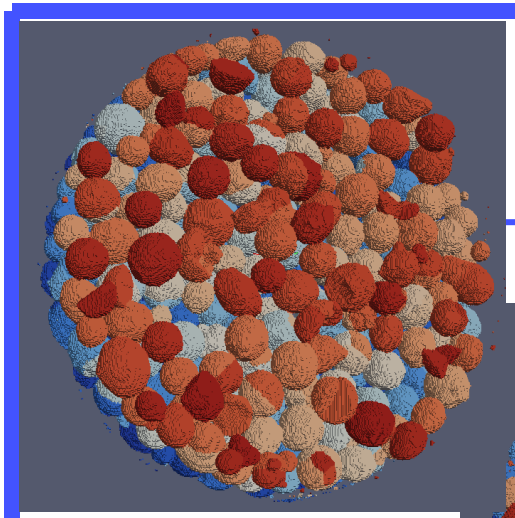
- **Using the Potts grain growth algorithm**



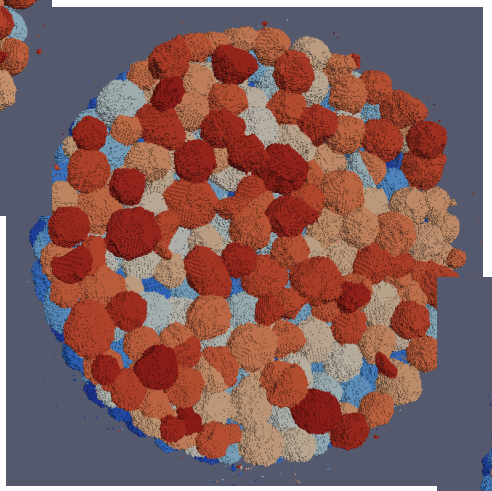


- **Microstructural evolution during sintering from this image was compared to later experimentally obtained images.**

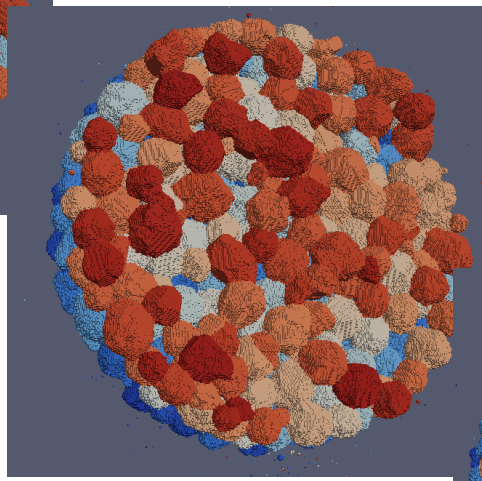
# Potts kMC Model
# Simulation of Cu-Particles Compact



$\rho$ = 72%

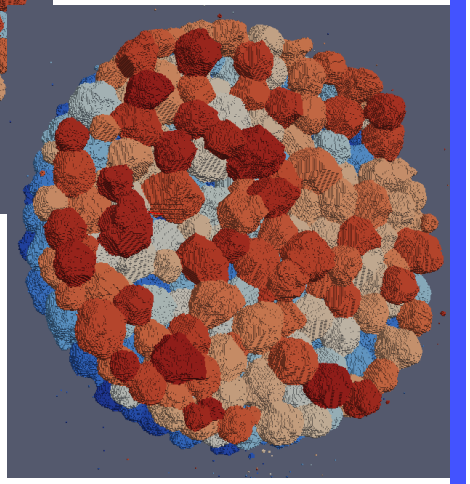


$\rho$ = 82%



$\rho$ = 85%

$\rho$ = 87%



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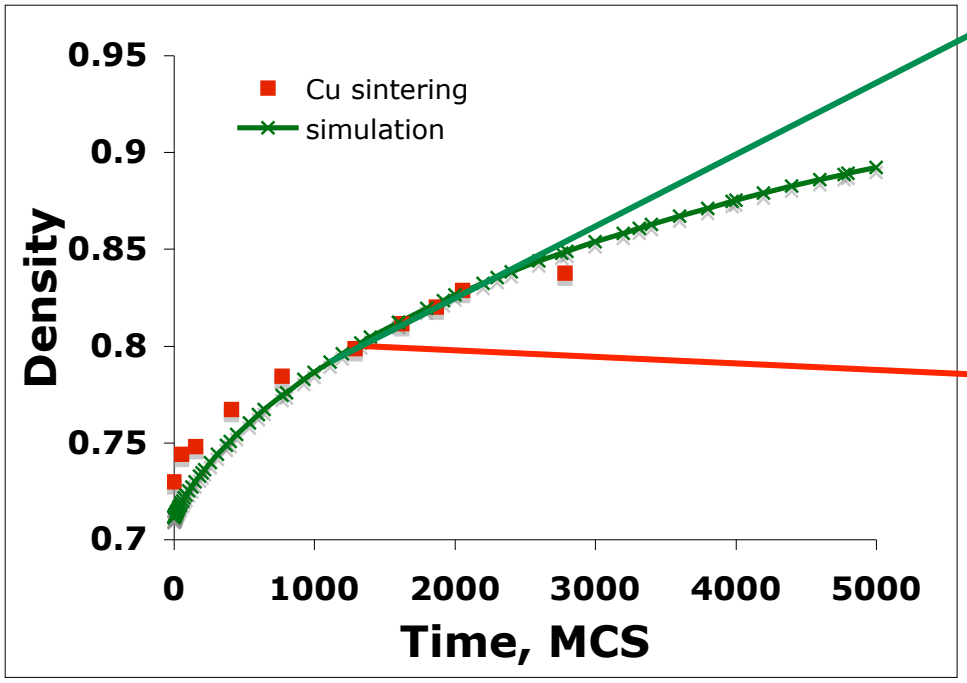
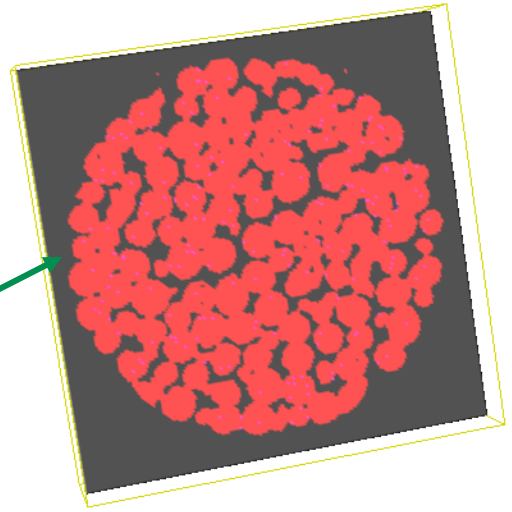
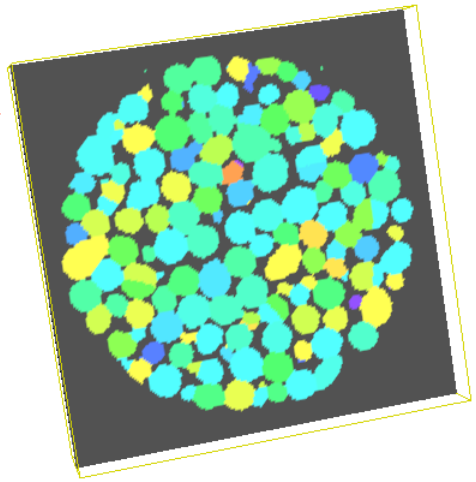
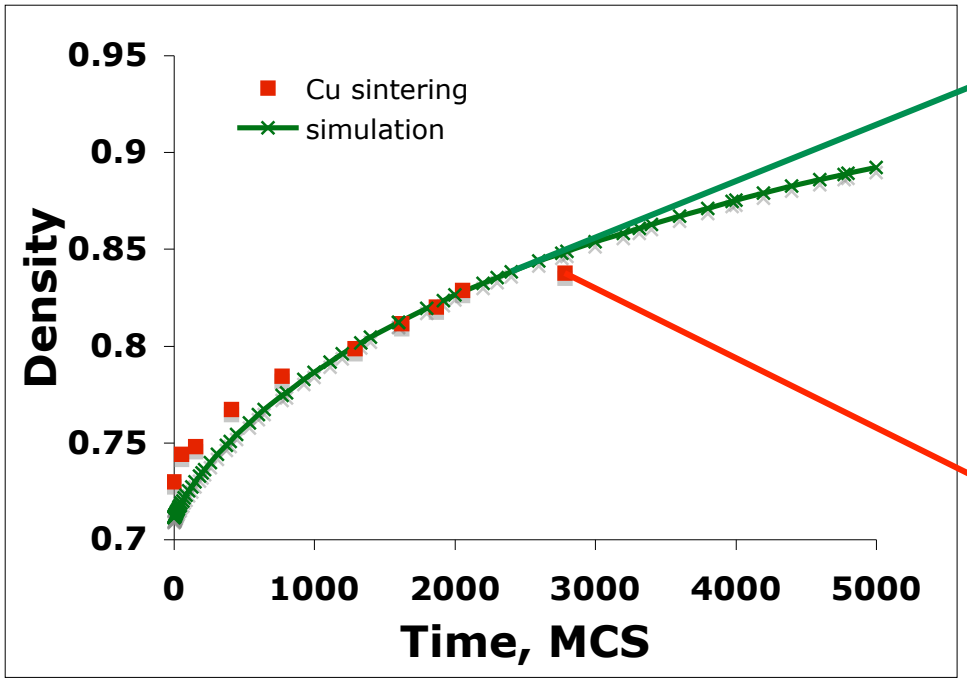
# Comparison of Potts Simulation and Cu-Experiments
# Microstructure & Densification

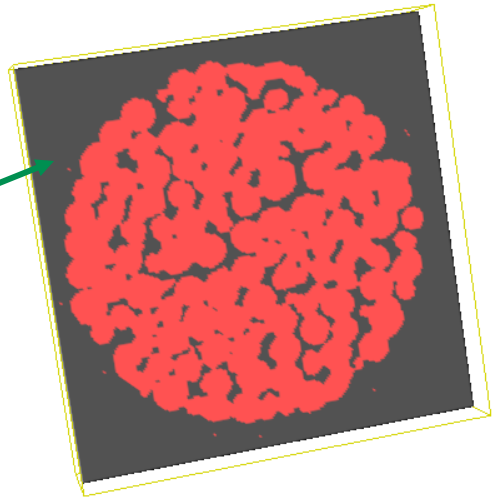


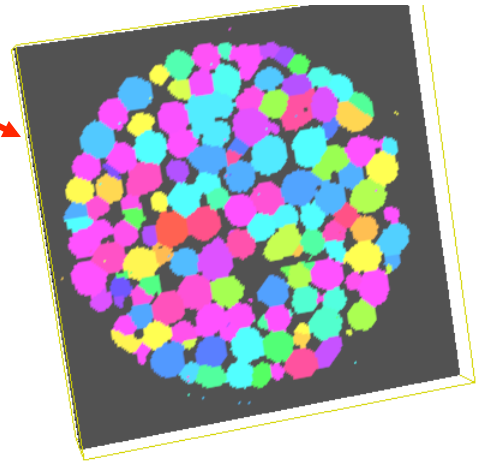





# Comparison of Densification Microstructure & Densification



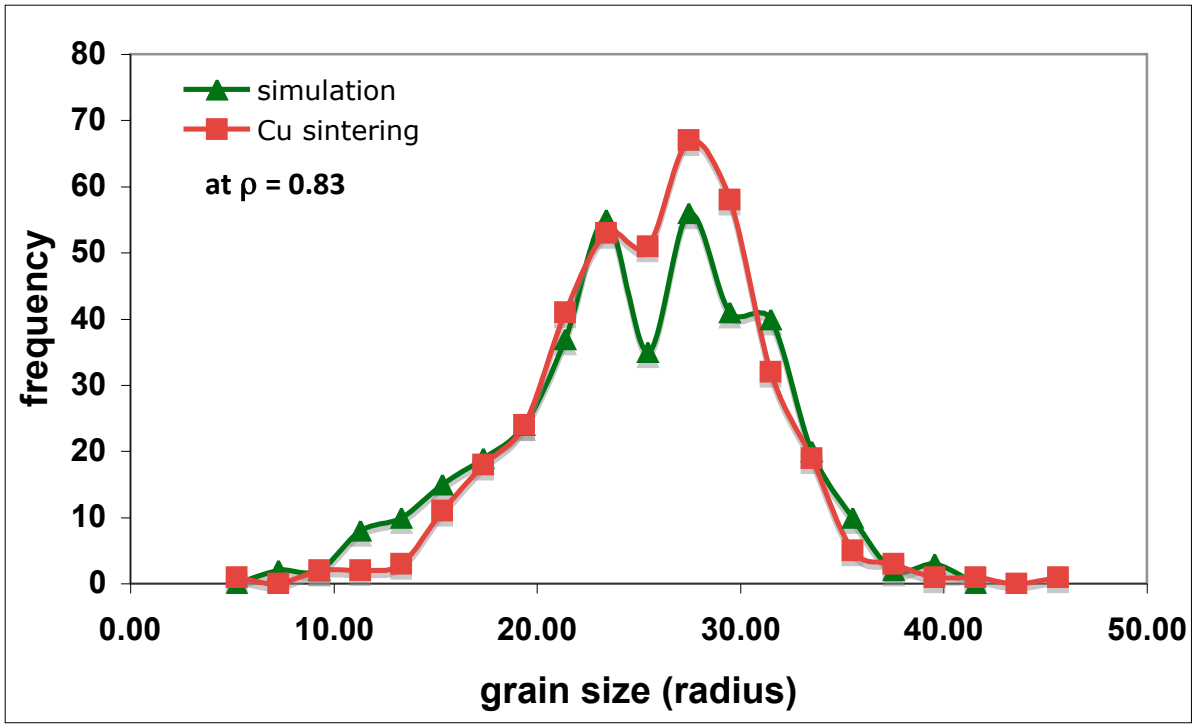



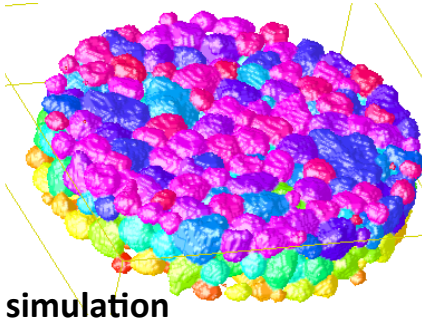


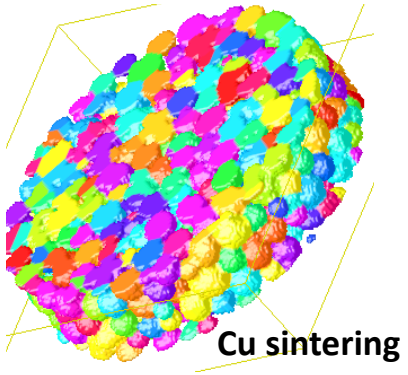
**Very good agreement between the sintering simulation and Cu-sintering experiments.**

# 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.




**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, $\Delta G$, is the total change in free energy during sintering
  - Potts kMC model simulates the entire microstructural evolution
  - In response to grain boundary energy $\gamma_{gb}$ and pore surface energy $\gamma_s$ 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

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

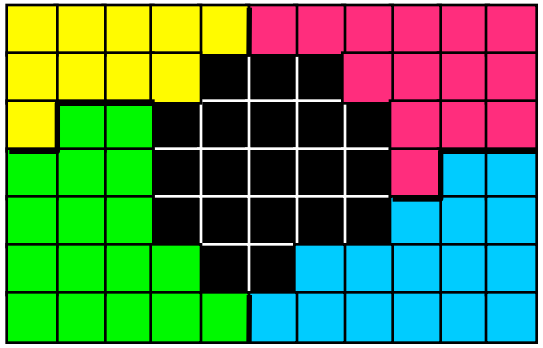
- Curvature Method

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

# 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 $q_i$**

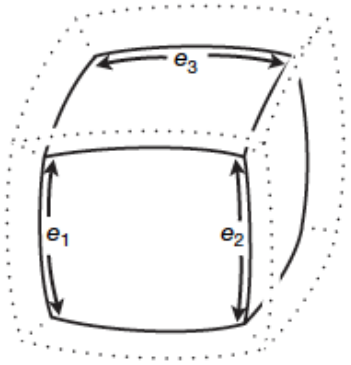


**Curvature Method**

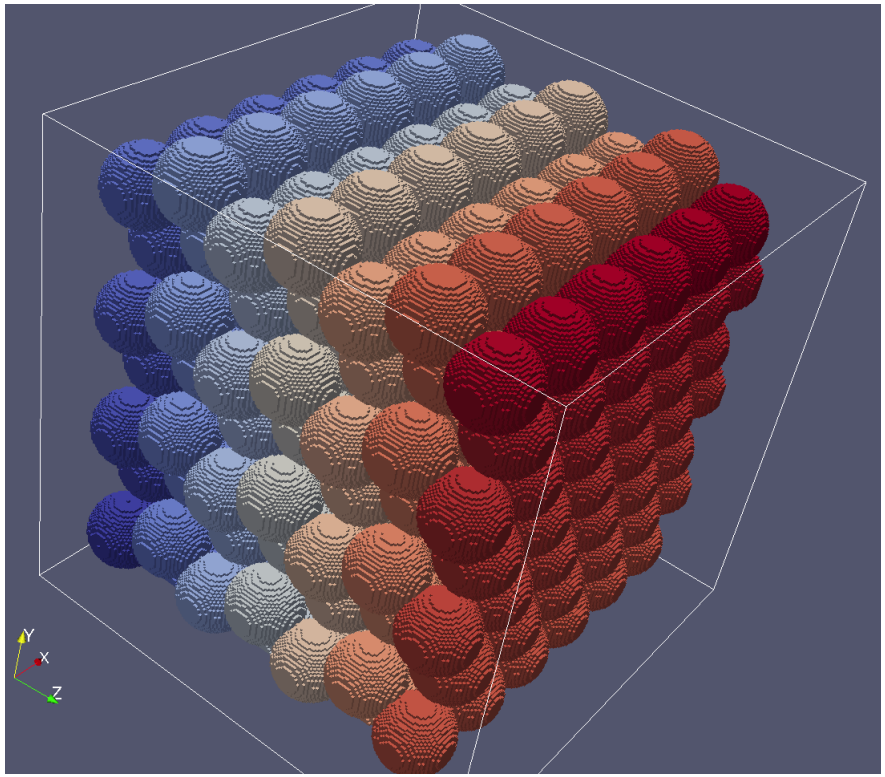
- **For a polyhedron**
  - **Integral mean curvature**

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

  - **Digitized microstructure**

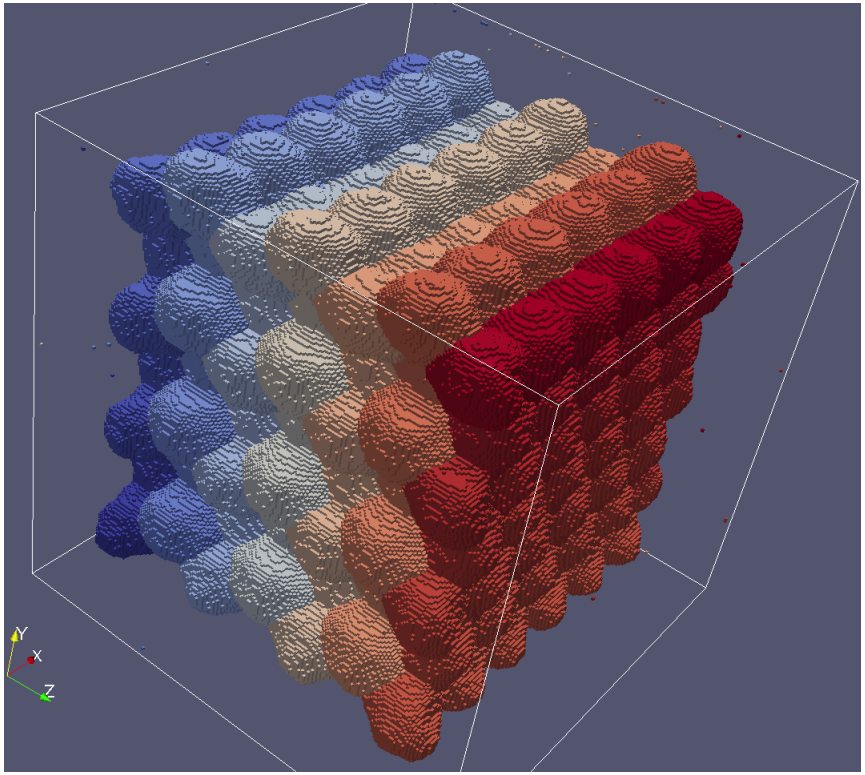


# Potts kMC Model
# Simulation of Close-Packed Spheres Sintering



Density = 72% at t = 0 MCS

Density = 100% at t = 60,000 MCS



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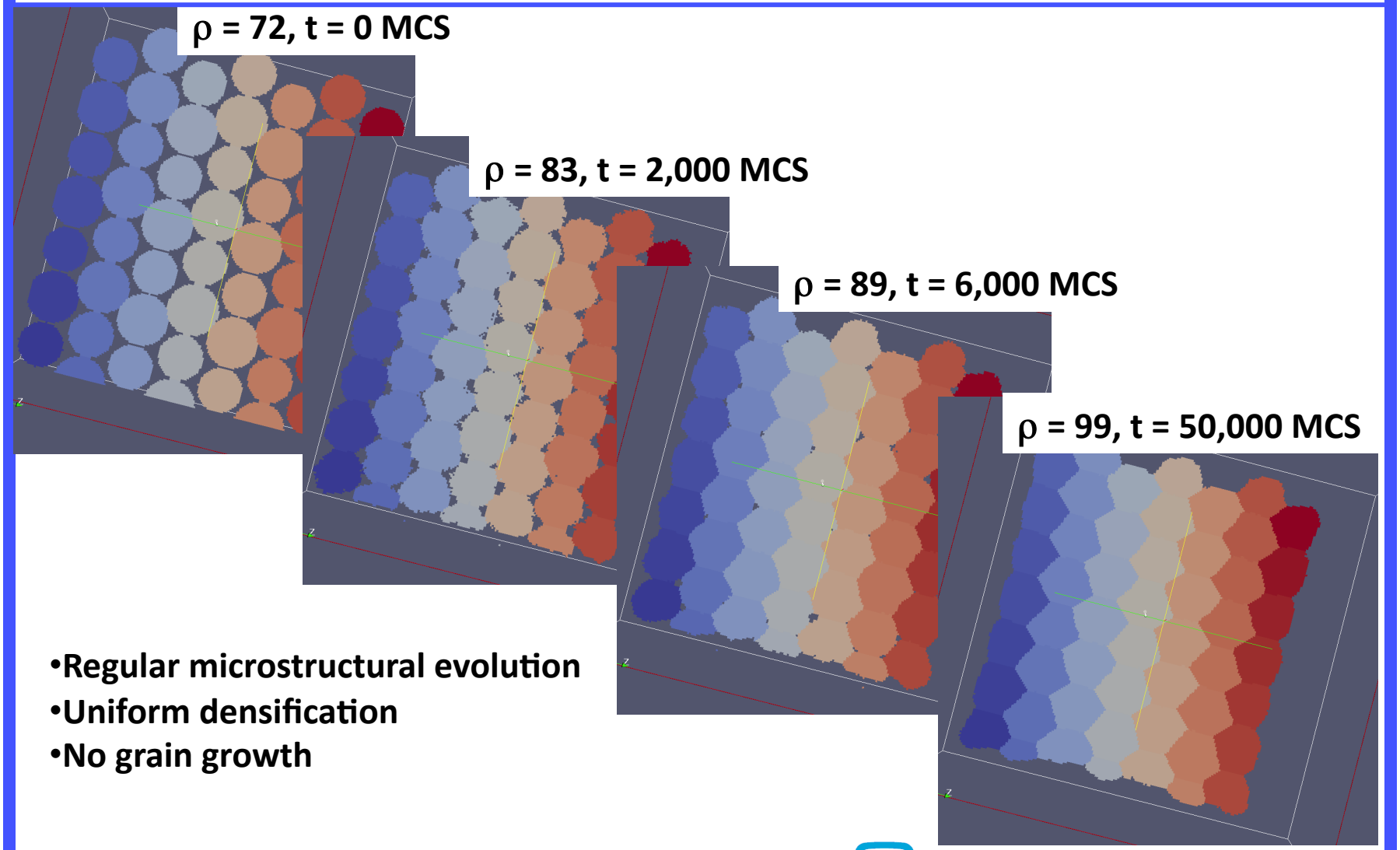


- Regular microstructural evolution
- Uniform densification
- No grain growth

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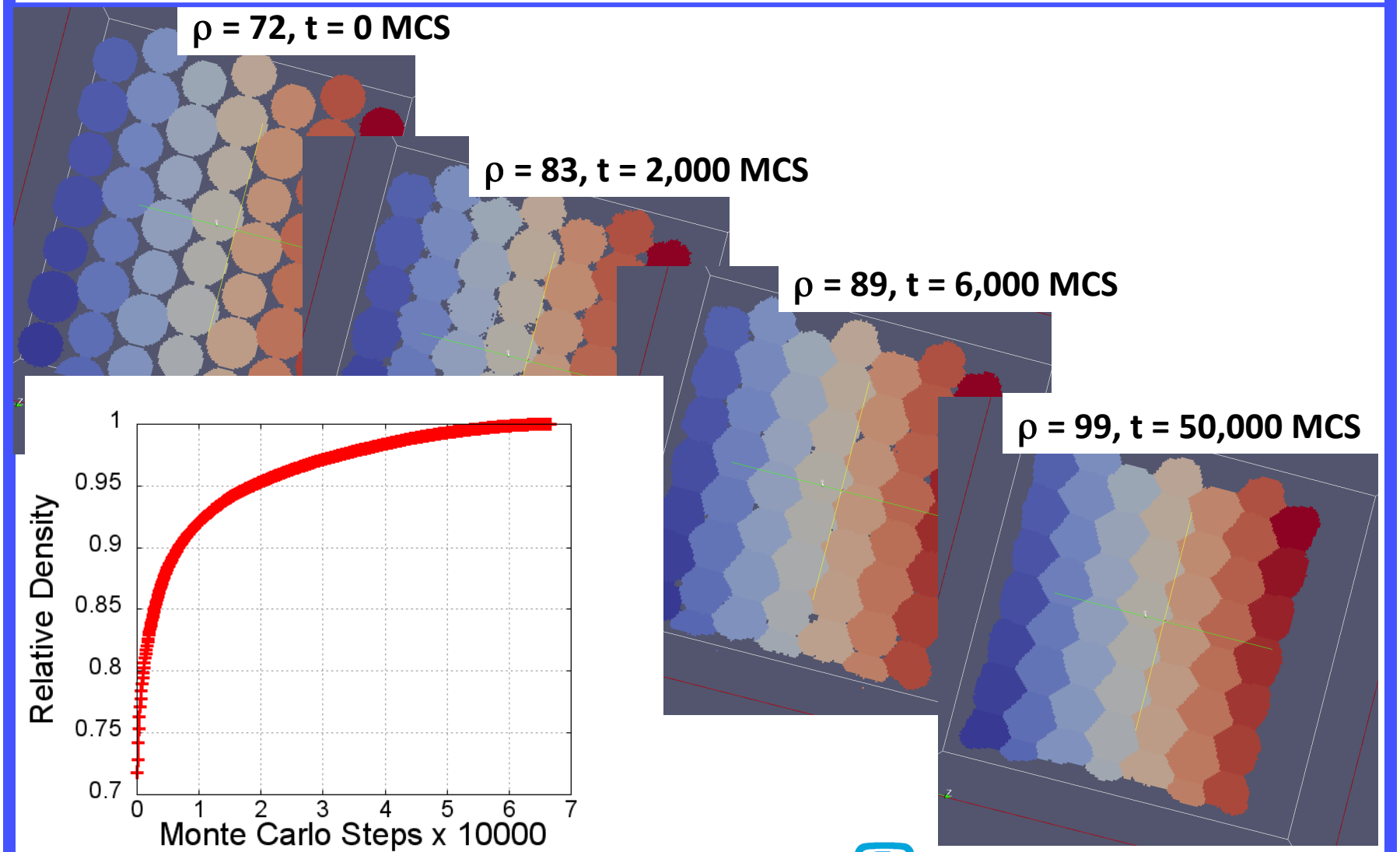
# Potts kMC Model
# Simulation of Close-Packed Spheres Sintering

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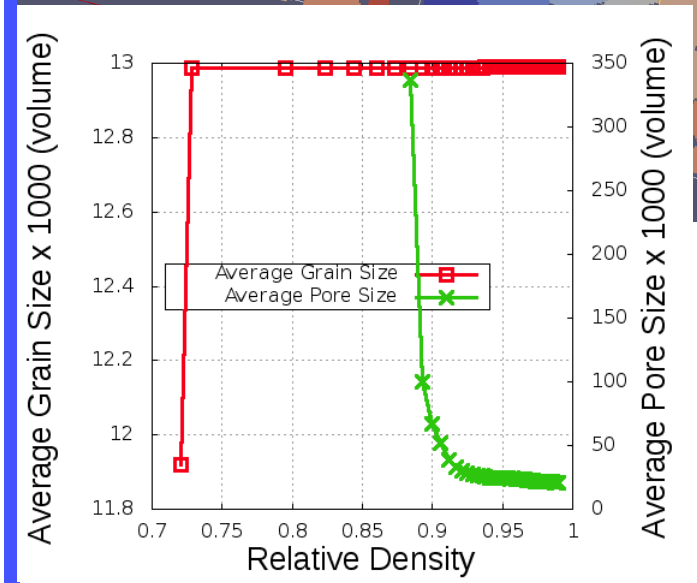
# Potts kMC Model
# Simulation of Close-Packed Spheres Sintering

ρ = 72%, t = 0 MCS

ρ = 83%, t = 2,000 MCS

ρ = 89%, t = 6,000 MCS

ρ = 99%, t = 50,000 MCS

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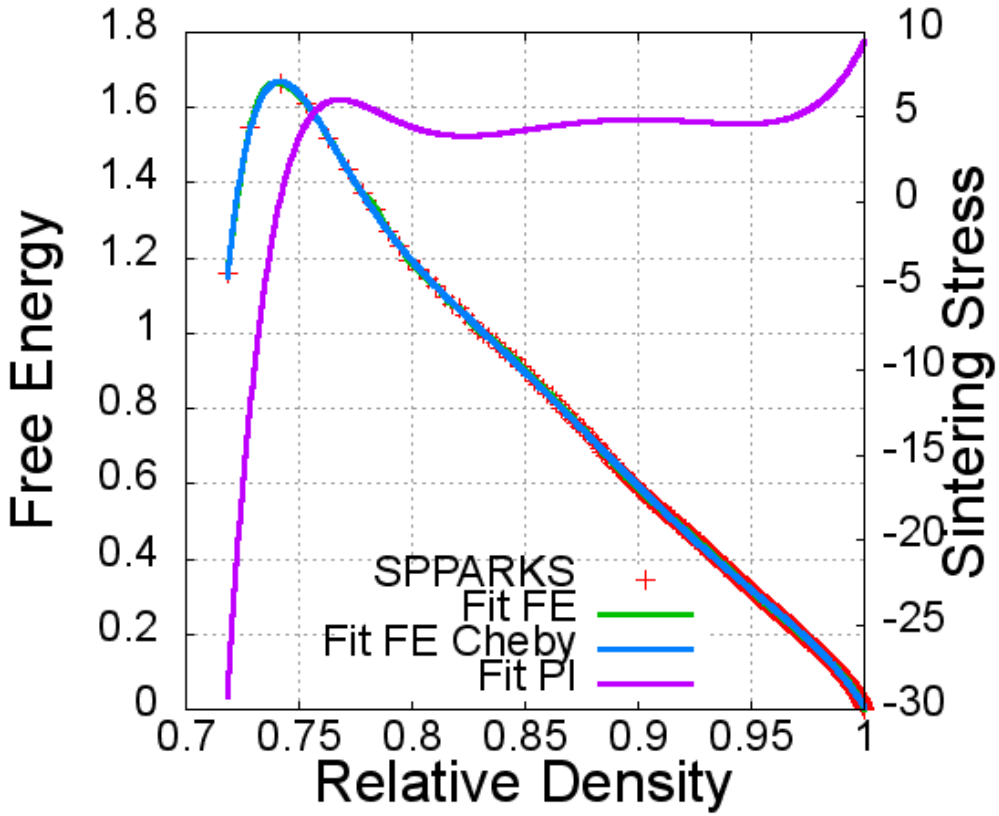
# Sintering Stress, Energy Method
# Simulation of Close-Packed Spheres Sintering

- Energy method $P_L = \frac{\partial E_s}{\partial V}$
- Data from simulations is $E_s(\rho)$
- Fit $E_s(\rho)$ with splines, results in noisy $P_L$
- Fit $E_s(\rho)$ with Chebyshev poly
- Resulting $P_L$
- $P_L$ is initially negative due to initial pore curvature.
- Becomes ~constant and then increases at pores become isolated and small.



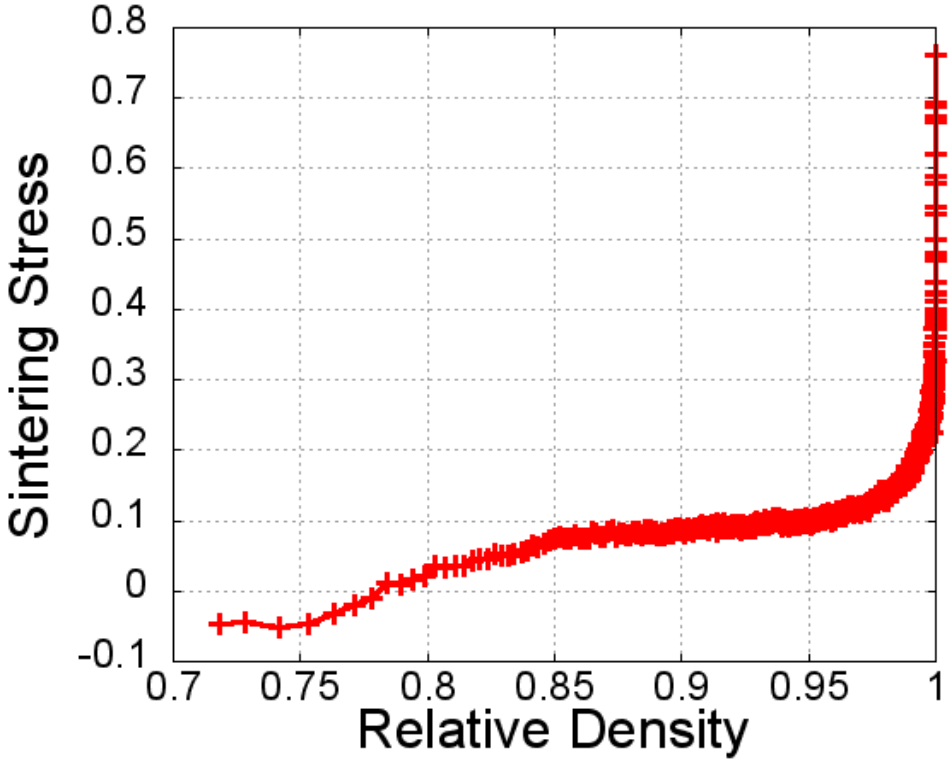

**While overall trend is accurate, $P_L$ is sensitive to the fitting technique used with the energy method**

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

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

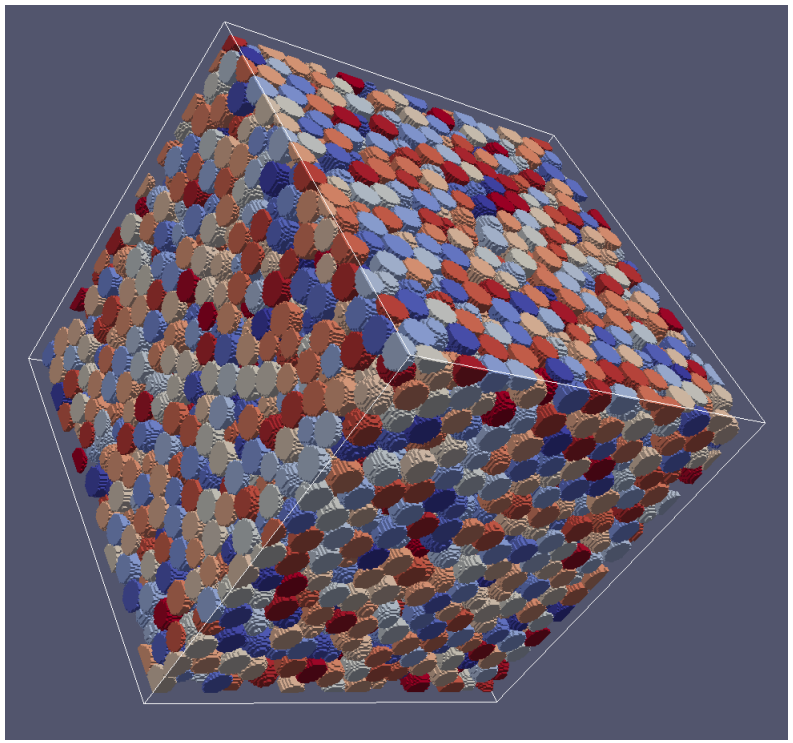
- **Directly measure from the simulated microstructures**
- **Is an instantaneous measure and does not depend on the microstructural evolution path**

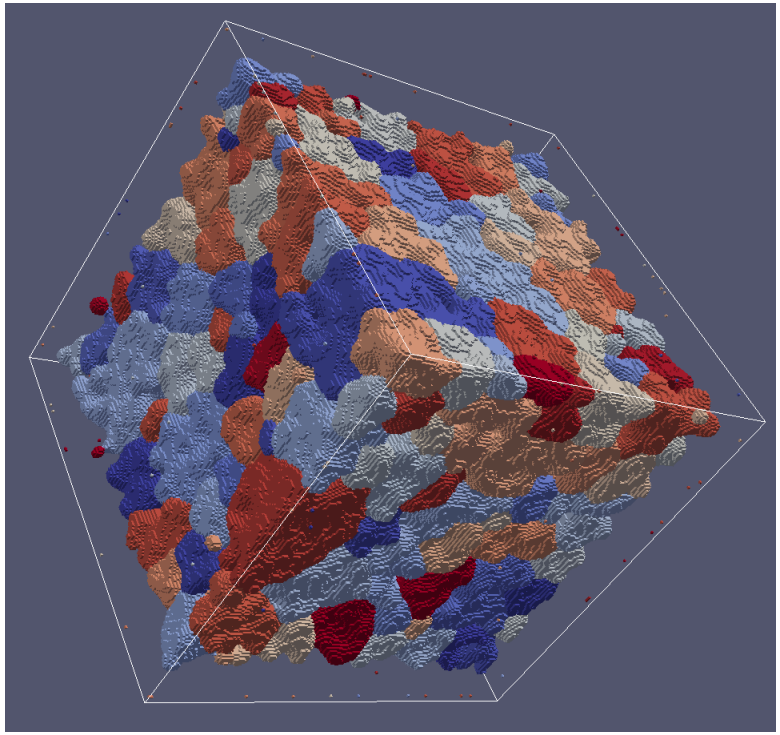
- $P_L$ **initially negative**
- $P_L$ **increase with increasing pore curvature.**



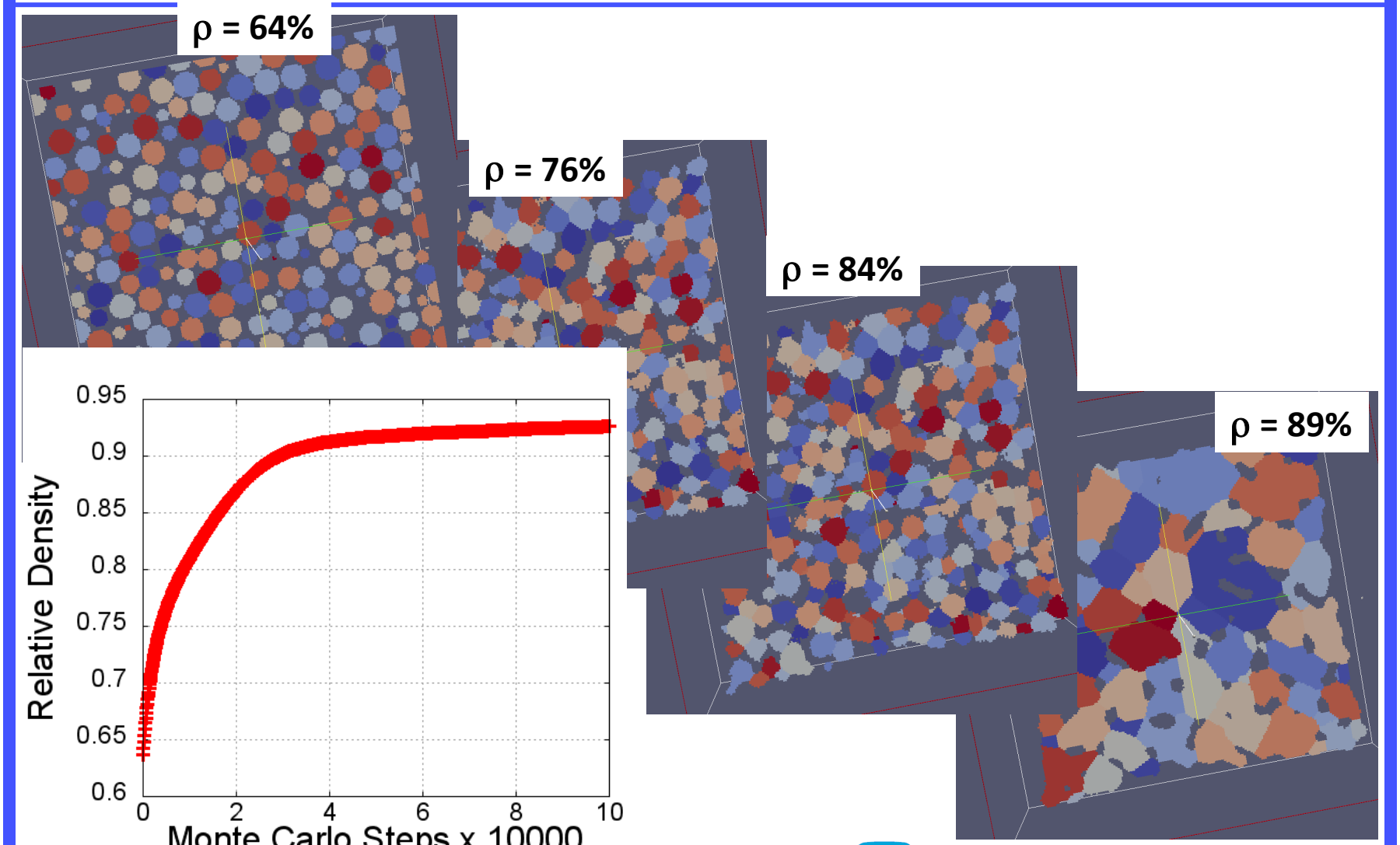

**Curvature method will be used for the remainder of this work**

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





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

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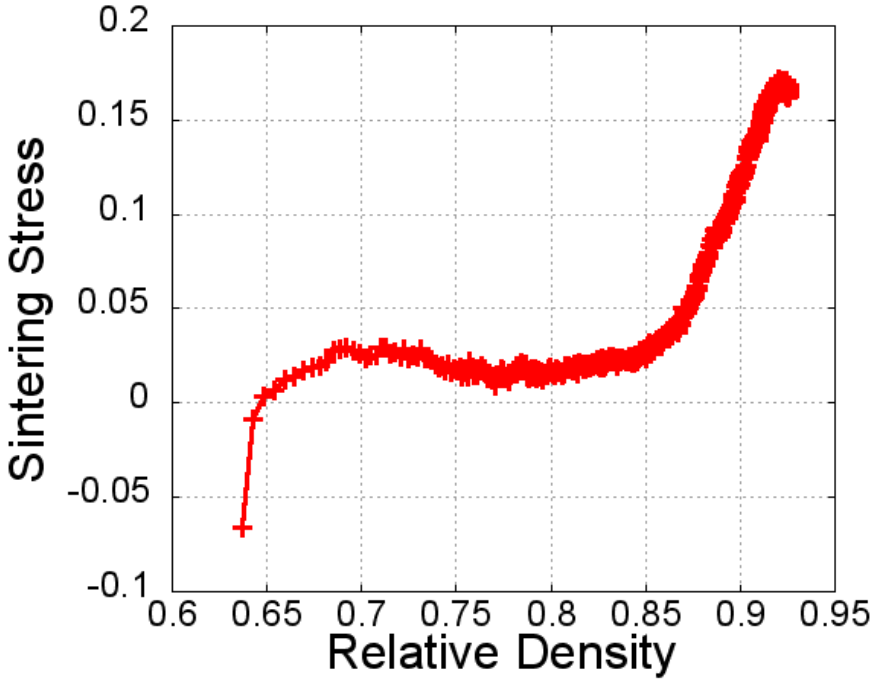
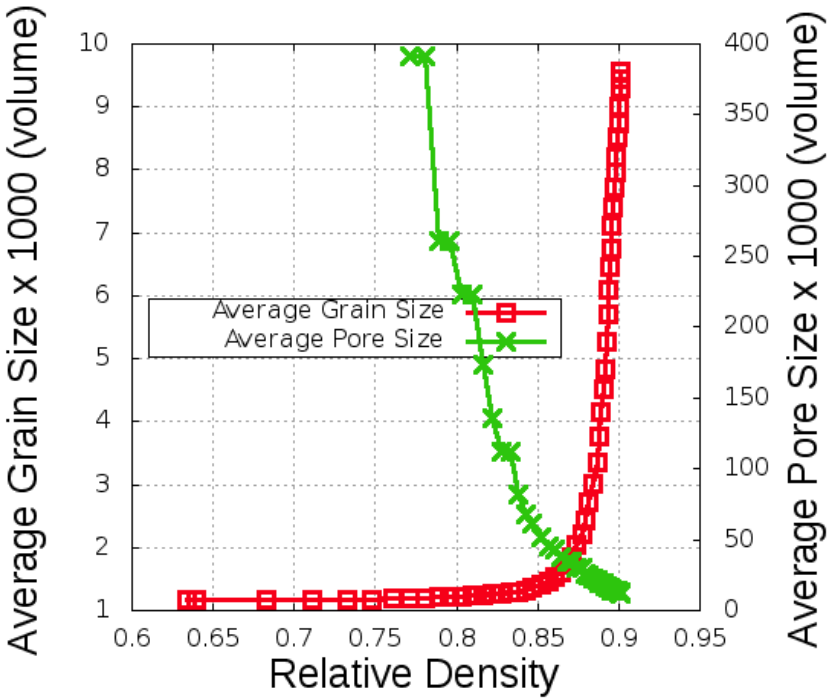
# Sintering Stress
## Simulation of Randomly-Packed Mono-Sized Spheres Sintering

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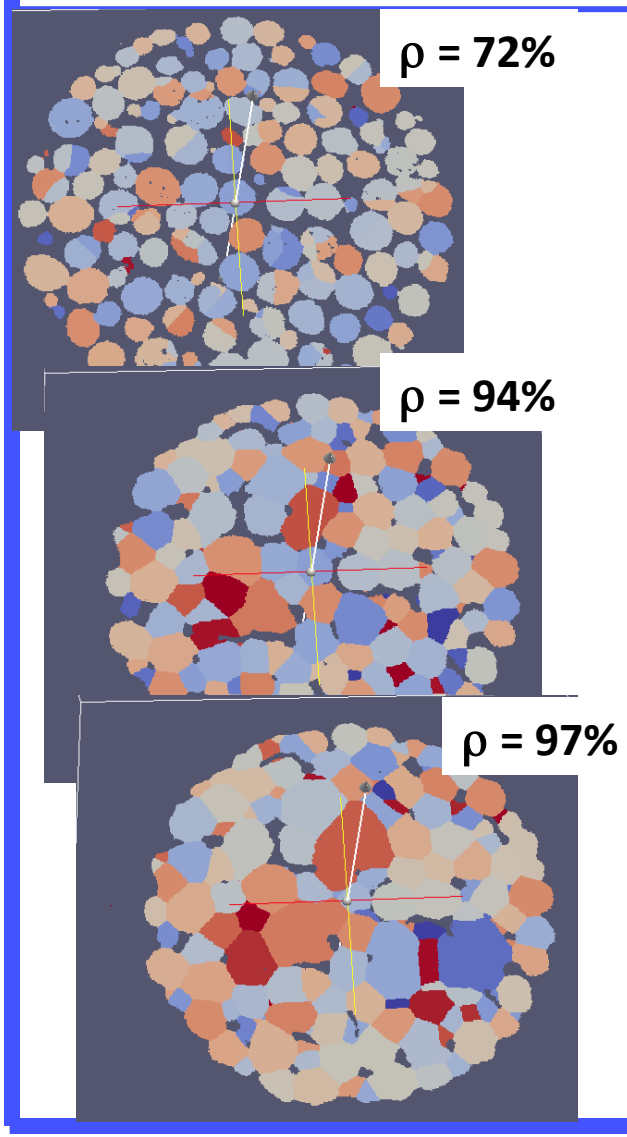
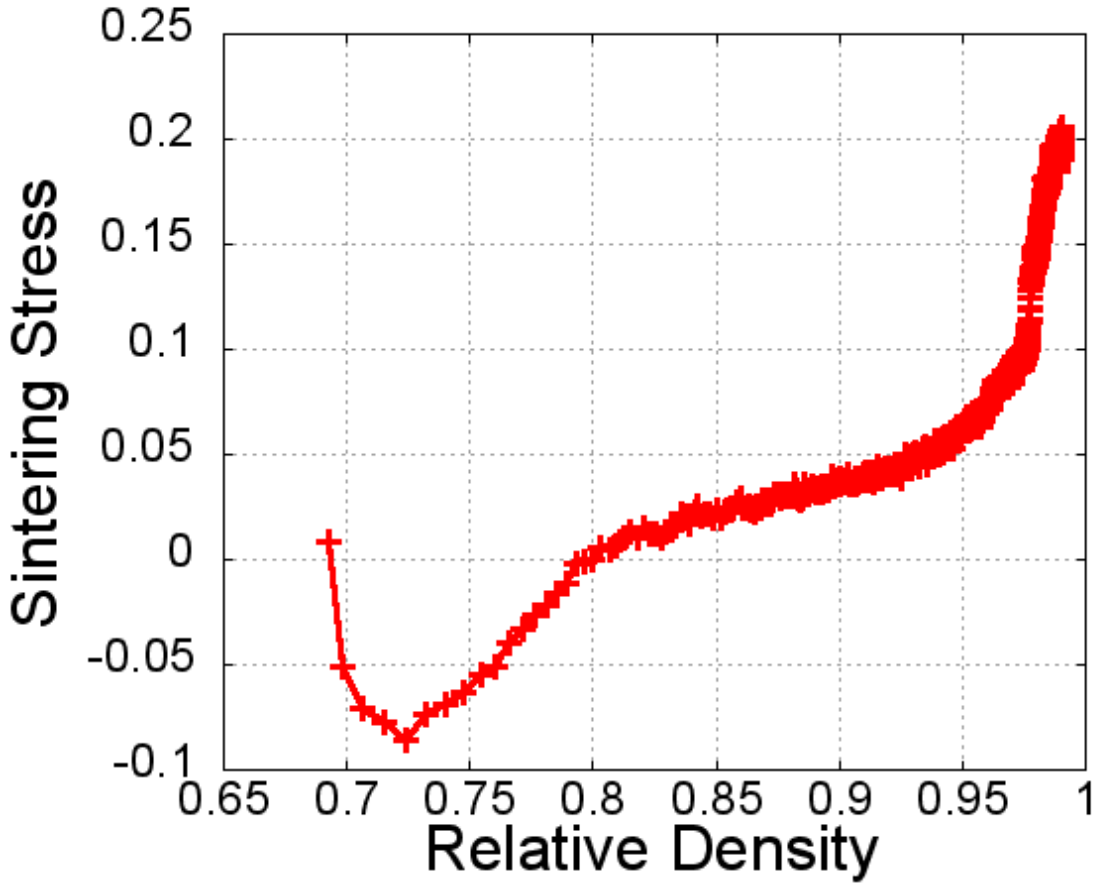
# Sintering Stress
# Simulation of Cu-Particle Compact Sintering

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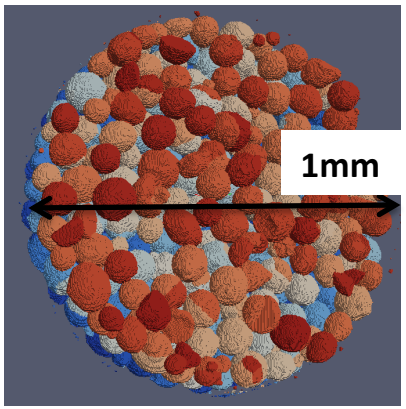
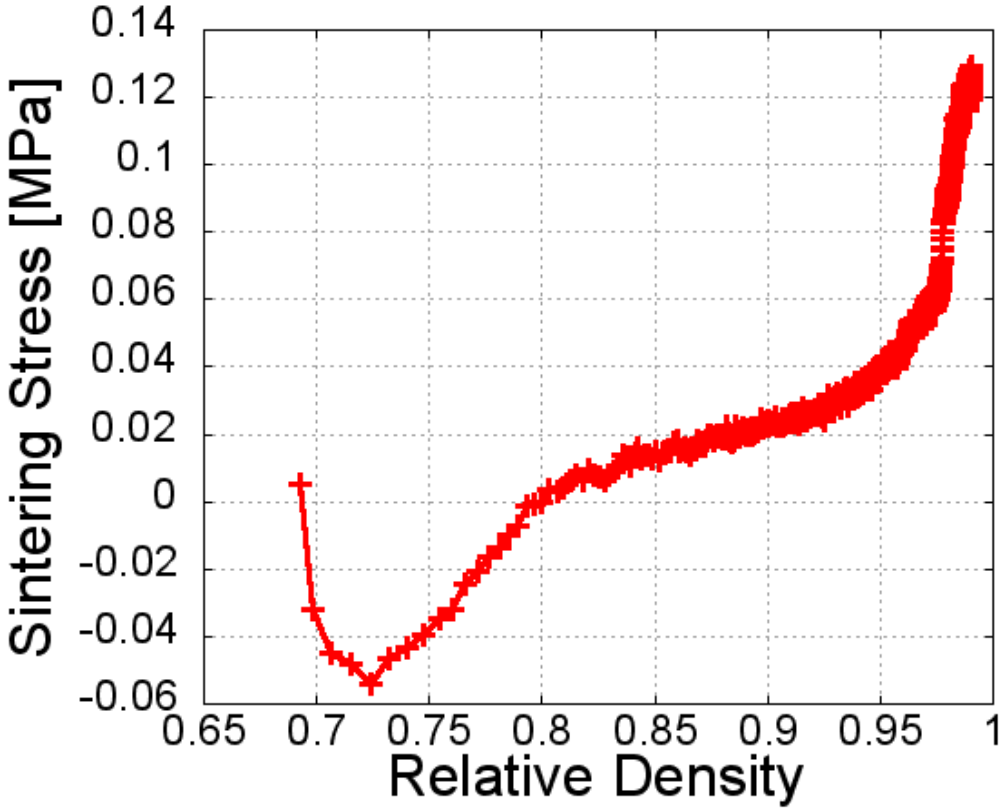
# Sintering Stress
# Simulation of Cu-Particle Compact Sintering

## Obtaining $P_L$ with units for real systems

- units of spatial dimension




- Assume $\gamma_s$ = 1 J/m$^2$ at 1050 $^o$C



# Summary and Conclusions

- A model that is capable of simulating simple, solid-state sintering has been presented.
  - True mesoscale 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 and kinetic characteristics
- Can be extended to include more mechanisms and vary thermodynamics and kinetic characteristics.