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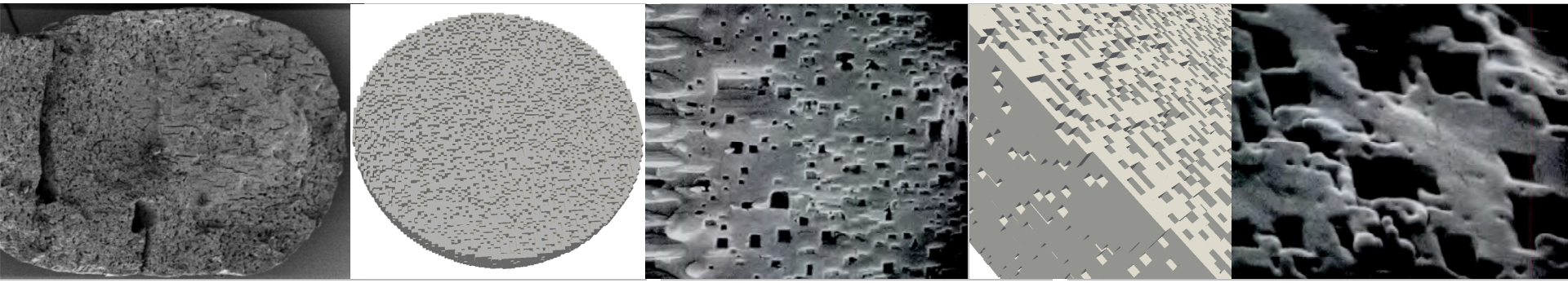

A Monte Carlo Method Applied to AP Particle Decomposition

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Sandia National Laboratories

JANNAF 61st JPM, PIB, 47th CS, 35th APS, 35th EPSS, 29th PSHS Joint Subcommittee Meeting, Newport News VA, May 16-19, 2016.

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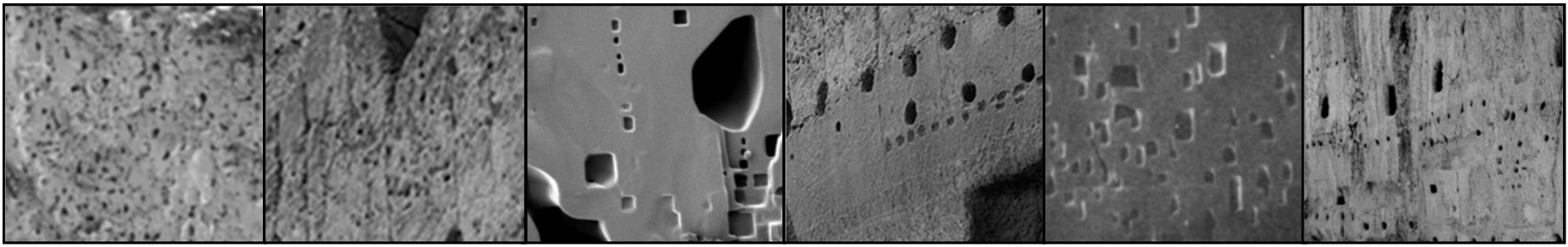
Which of these are Decomposed AP and which are Cliff Dwellings?



Which of these are Decomposed AP and which are Cliff Dwellings?

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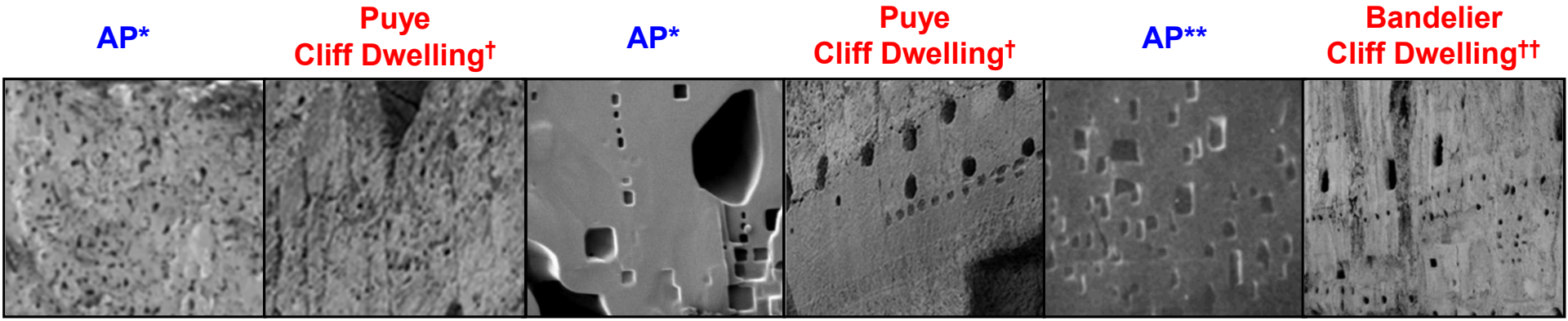


* J. J. Kay, D. Wiese-Smith, A. Highley, S. Maharrey, "Role of Internal Defects in Promoting Thermal Decomposition of Ammonium Perchlorate," JANNAF 45th CS, 33rd APS, 33rd EPSS, and 27th PSHS Joint Subcommittee Meeting, Monterey, CA, Dec. 2012.

† http://www.minamipictures.com/120709-11.puye.taos.monument-valley/120709.puye-cliff-dwellings.viga-holes.jpg

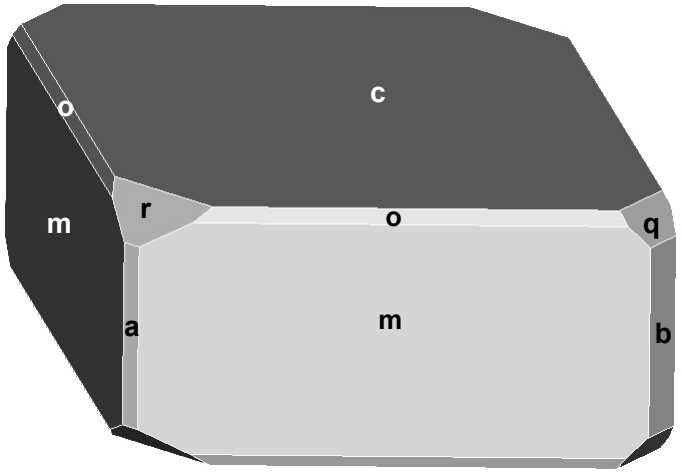
** K. J. Kraeutle, "The Thermal Decomposition of Orthorhombic Ammonium Perchlorate Single Crystals," *Journal of Physical Chemistry*, V. 74, No. 6, pp. 1350-1356, 1970.

†† http://img1.10bestmedia.com/Images/Photos/283020/Bandelier--courtesy-Bandelier-National-Monument_54_990x660.jpg

Ammonium Perchlorate (AP) NH_4ClO_4

- **AP is the principal oxidizer in most solid rocket propellants**
- **2 crystal polymorphs:**
  orthorhombic (< 240°C), ρ=1.95 g/cm^3
  cubic (> 240°C), ρ=1.76 g/cm^3
- **Two processes of AP breakdown:**
  a. **Dissociative Sublimation**
     AP → NH_3(g) + $HClO_4$(g)
     (depends on surface area, can be suppressed by increasing gas pressure)
  b. **Decomposition**
     AP → various product species
     (temperature dependent)
- **Low temperature (< 300°C)**
  - sublimation is slow, minor effect
  - **decomposition ceases** after some fraction completion
  - limit often reported at **~30% decomposition** but this **depends on particle size**
  - cessation is unrelated to phase transition
  - rates decline in cubic relative to orthorhombic
  - residue is **pure AP** (porous)
- **High temperature (> 300°C)**
  - Complete mass loss (forms all gas products)

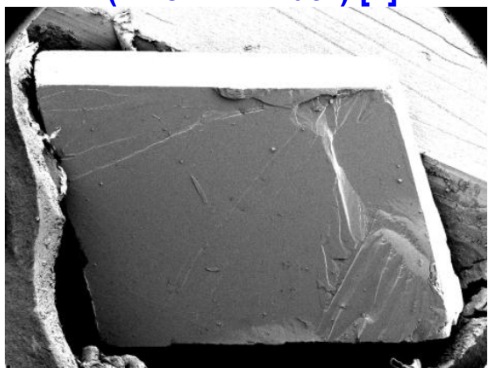
AP orthorhombic crystal with face labels



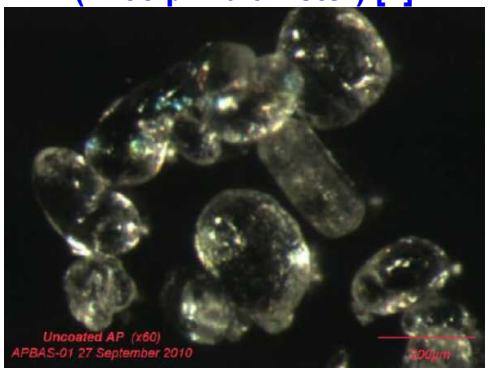
Miller Indices
a: 100
b: 010
c: 001
m: 210
o: 211
q: 011
r: 101

Unit Cell (n=4)
a=9.20 Å
b=5.82 Å
c=7.45 Å
cubic:
a=7.63 Å

Large Single AP Crystal (~2.5 mm width) [7]



Polycrystalline AP (~200 µm diameter) [7]



Low-Temperature Decomposition Observations

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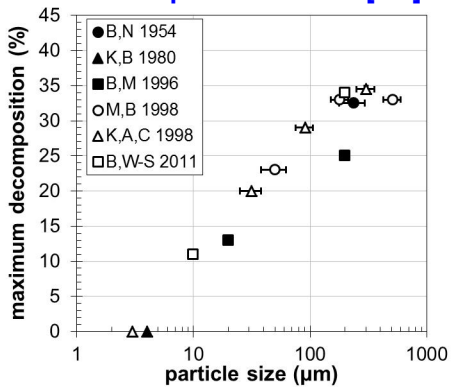
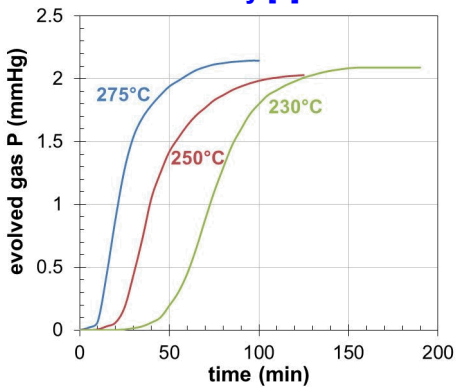
1. **Particle size dependency** (graph at right).
   - Early studies (1950's) showed ~30-35% decomposition. These were for large particles, the size effect was not fully investigated.
   - Later studies indicated a strong effect of particle size.
   - Limit varies approximately linearly with log of particle size.
   - Zero decomposition for particles < 3-4 μm.
2. **Sigmoidal time evolution** (induction, acceleration, deceleration) behavior has been observed (graph far right).
3. Decomposition **begins at or near the particle surface and progresses inward** (upper left photo).
4. **Preferential decomposition** occurs on m-faces (rectangular) vs. c-faces (rhombic).
5. **Voids often** (but not always) **resemble shape of crystal face** (lower photos). Others are more smooth (upper left photo).
6. **Pore size is limited**. Small pores of size ~0.5 μm have been observed, as well as larger pores ~3-5 μm, but growth stops.

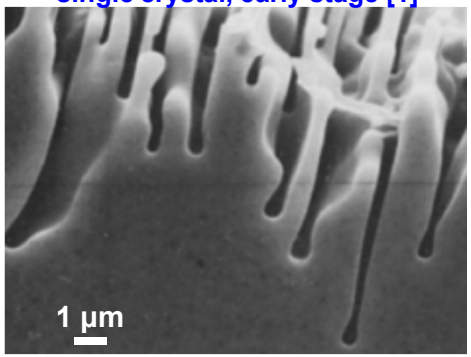
Effect of Particle Size on AP Decomposition Limits [2-8]



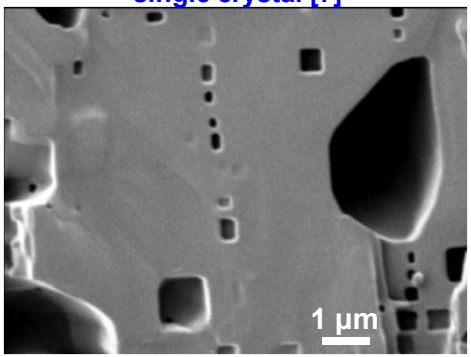
Sigmoidal Decomposition History [2]



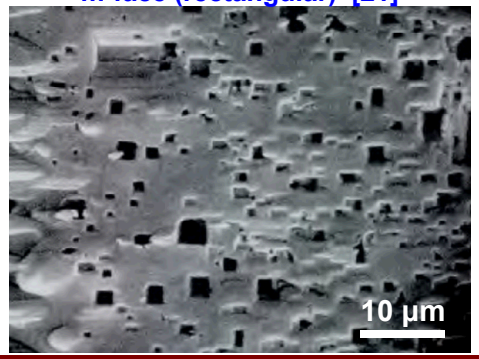
single crystal, early stage [1]



single crystal [7]



m-face (rectangular) [21]



c-face (rhomboidal) [21]

Theories for AP Decomposition Limiting

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Several ideas have been proposed for why AP decomposition results in the pore shapes it does and why it ceases. (More than one may apply?)

- **Depletion of Reactive Intermediate [1, 16]**
  - A reactive intermediate, liquid nitronium perchlorate (NO_2ClO_4, MP=135°C) catalyzes reaction at bottom of pores leading to "wormholing."
  - **Reaction stops when NO_2ClO_4 disappears.**
- **Accumulation of H_2O in Pores or Knudsen Diffusion Limits [11, 12]**
  - A proton transfers within NH_4ClO_4 molecule resulting in formation of ammonia (NH_3) and perchloric acid ($HClO_4$) gases. These gases collect in pores / dislocations within the crystal.
  - Faster Knudsen diffusion of NH_3 molecules exiting pores results in **net accumulation of $HClO_4$** molecules in pores.
  - **$HClO_4$ decomposition products attack the NH_4ClO_4 on walls of pore**, increasing the pore diameter and **products, including H_2O, accumulate**.
  - Growth of pore is self-limited by either becoming large enough that preferential Knudsen diffusion is no longer controlling or H_2O accumulation stabilizes decomposition.
  - **Reactions cease at pore sizes of 2-3 μm.**
- **Pressure / Lattice Strain Effects [4, 5, 7, 14, 15]**
  - **Reactions occur within blind pores** (defects/inclusions?) below the surface, **resulting in high gas pressure**.
  - Pressure induces stress/strain in vicinity of reaction—increasing number of defects and allowing reaction to spread.
  - **Reactions cease when gas vents to surface and pressure drops.**
- **Nucleation site depletion [8,15]**
  - Nucleation sites control reaction initiation/propagation
  - **Once nucleation sites are depleted, reactions stop.**
  - Reactions can be reinitiated for additional mass loss if AP is partially recrystallized (via water vapor dissolution, etc.)

Percolation Theory—General Concepts

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- Percolation deals with "connectedness" of a lattice or matrix.
- A network "percolates" if connected continuously from side to side.

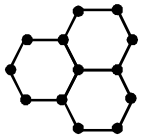
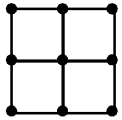
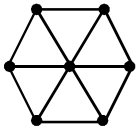
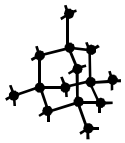
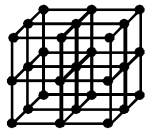
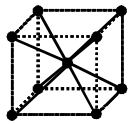
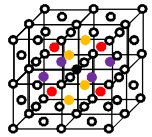
A. Bond Percolation

- Network of connecting links (e.g. the wires in a window screen)

B. Site Percolation

- Array of objects (e.g. blocks stacked)

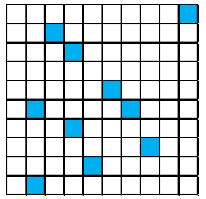
- Critical percolation threshold (p_c) is the density of bonds or sites that just barely allows connection to occur.
- Threshold depends on lattice type & dimensionality. (Table adapted from [17]

Lattice Type	Honeycomb	Square	Triangular	Diamond	Simple Cubic	BCC	FCC
Graphic							
Coordination Number, Z	3	4	6	4	6	8	12
p_c (site)	0.6962	0.5927	0.5	0.4299	0.3116	0.2464	0.199
Z_{bond}	4	6	10	6	10	14	22
p_c (bond)	1-2sin(π/18) = 0.6527	0.5	2sin(π/18) = 0.3473	0.3886	0.2488	0.1795	0.119

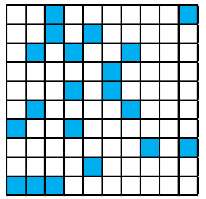
- The site percolation threshold for a cubic lattice is ~31%.
- Low temperature decomposition of AP is limited at a level of ~30-35% (less for smaller particles).
- Is there a connection between AP decomposition level and the geometry associated with a percolation network?
- Can we build models of AP particle decomposition using percolation theory and Monte Carlo techniques?

Example: Site Percolation
10x10 square lattice;
sites occupied at random.

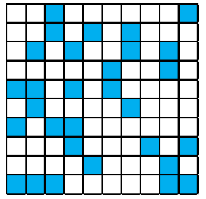
10/100 sites



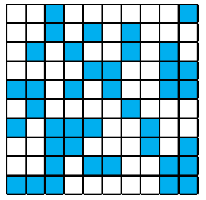
20/100 sites



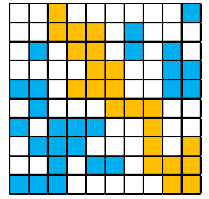
30/100 sites



40/100 sites



47/100 sites, percolation achieved



Monte Carlo/Percolation Decomposition Model

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Rules for Model:

1. The domain is divided into uniform boxes (squares in 2-D, cubes in 3-D). The domain is initially all filled. Locations within the domain are chosen at random to "decompose" (change from solid to gas, forming a void).
2. A "zone of reactivity" near but not touching the outer edge of domain (**green boxes**) is the only place where reactions can initially occur. Void insertion deep in the interior (**gray boxes**) or connected to the outside (**blue boxes**) is disallowed.
3. Insertion of a void (**yellow boxes**) induces a "stress" or "defect" in surrounding material, which extends the zone of reactivity around the void location (example extends zone of reactivity by 2 boxes).
4. (**blue boxes**) Voids cannot be inserted next to the outer edge (or to voids that are connected to the outer surface, the **white boxes**) UNLESS they are also adjacent to another unconnected void (**yellow boxes**).
5. "Adjacent" for purposes of connecting voids is only at the box faces (2-D has 4 neighbors; 3-D has 6 neighbors). Boxes that are touching only at corners are assumed to not be connected.
6. Algorithm stops when no more voids can be inserted & all connected to outside. Statistics (void fraction, # of steps, etc.) are reported.

Example: 12x12 array in 2D with 4 neighbors

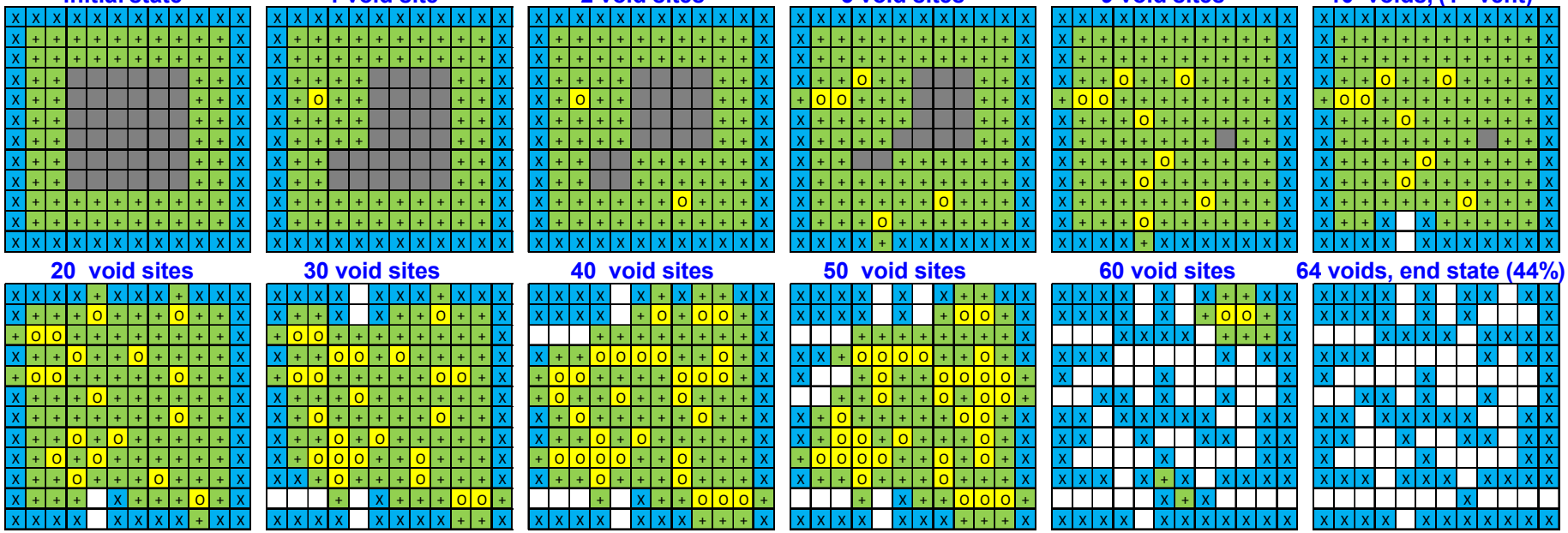
Not allowed: deep in the interior

\+ Allowed: within zone of reactivity

X Not allowed: adjacent to outside (or connected void) but NOT adjacent to unconnected void

O Voids unconnected to the outside

Voids connected to the outside



Monte Carlo/Percolation Decomposition Model

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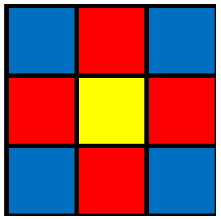
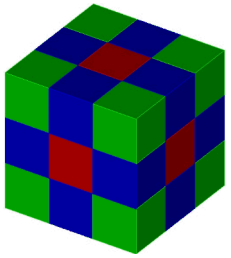
- Can also alter the rules slightly, for instance including more “neighbors” in the stencil used for determining connections to the outside
- The **more neighbors** included in stencil, the **lower** the limiting value of void fraction because locations are more likely to be adjacent to voids which are connected to the outside.
- Possible to include just some of the neighbor pairs, to mimic preferential decomposition directions (e.g. image at far right)

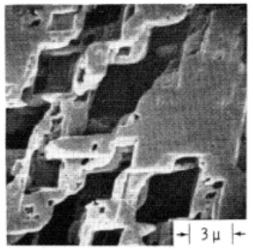
2D (8 possible)
4 face (red)
+ 4 corner (blue)



3D (26 possible)
6 face (red)
+ 12 edge (blue)
+8 corner (green)



Preferential decomposition directions?



Ref. [21]

Example: 12x12 array in 2D with 8 neighbors

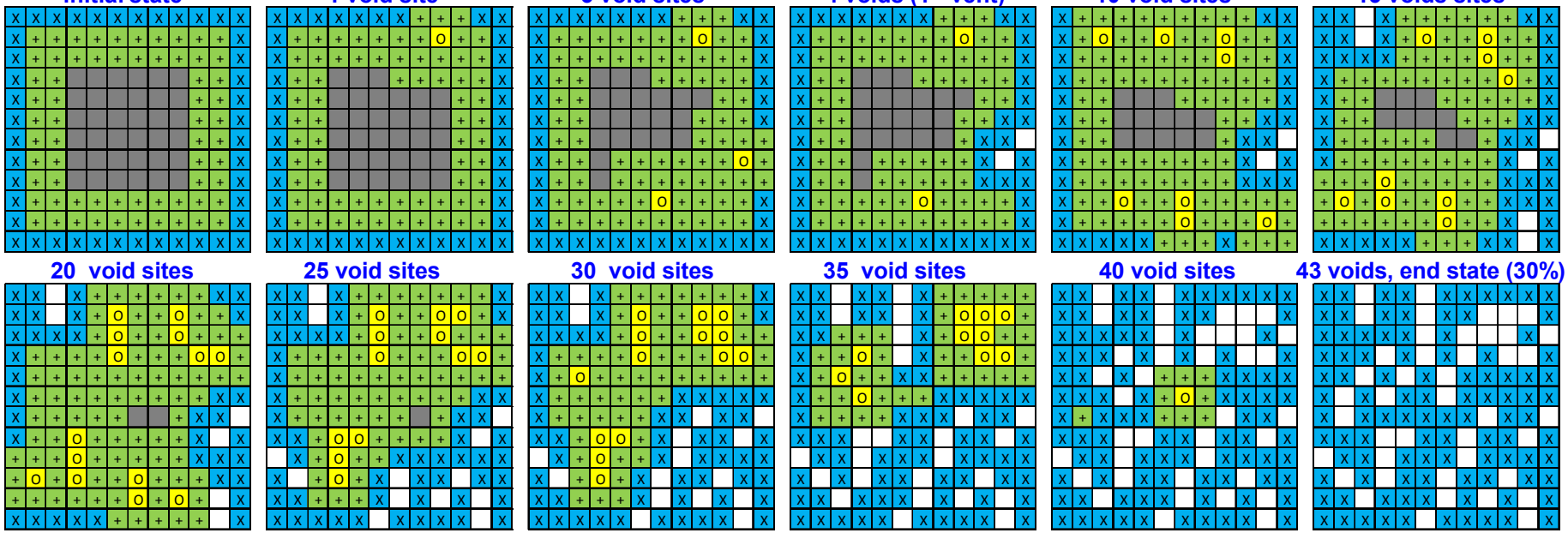
Not allowed: deep in the interior

\+ Allowed: within zone of reactivity

X Not allowed: adjacent to outside (or connected void) but NOT adjacent to unconnected void

O Voids unconnected to the outside

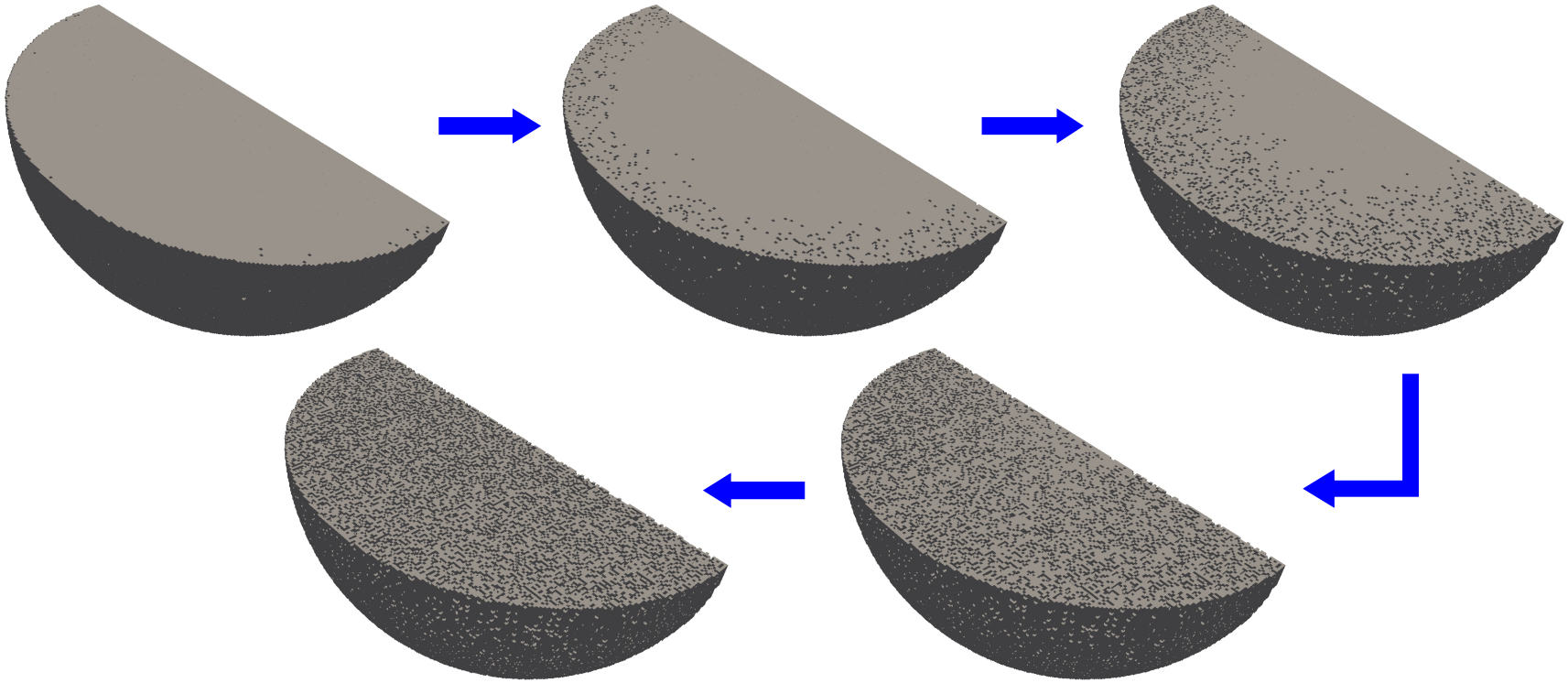
Voids connected to the outside



Overall Model

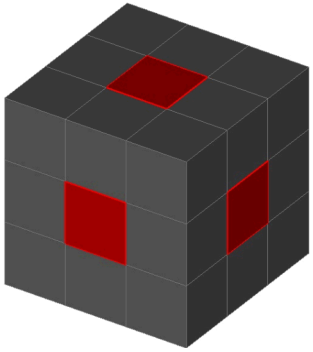
- **The Newman-Ziff [18] algorithm was employed to efficiently track cluster connection**
- **Coded in Fortran; typical runs took seconds to a few minutes depending on particle size (running on one processor); if graphics files were generated, runs took longer.**
- **Monte Carlo / percolation model was applied to various geometries including spheres, ellipsoids, and parallelepipeds of various sizes**
- **The number of neighbors was also varied**

Time Evolution of Particle Decomposition
(cutaway of sphere, radius = 100 pixels, 6 neighbor stencil)



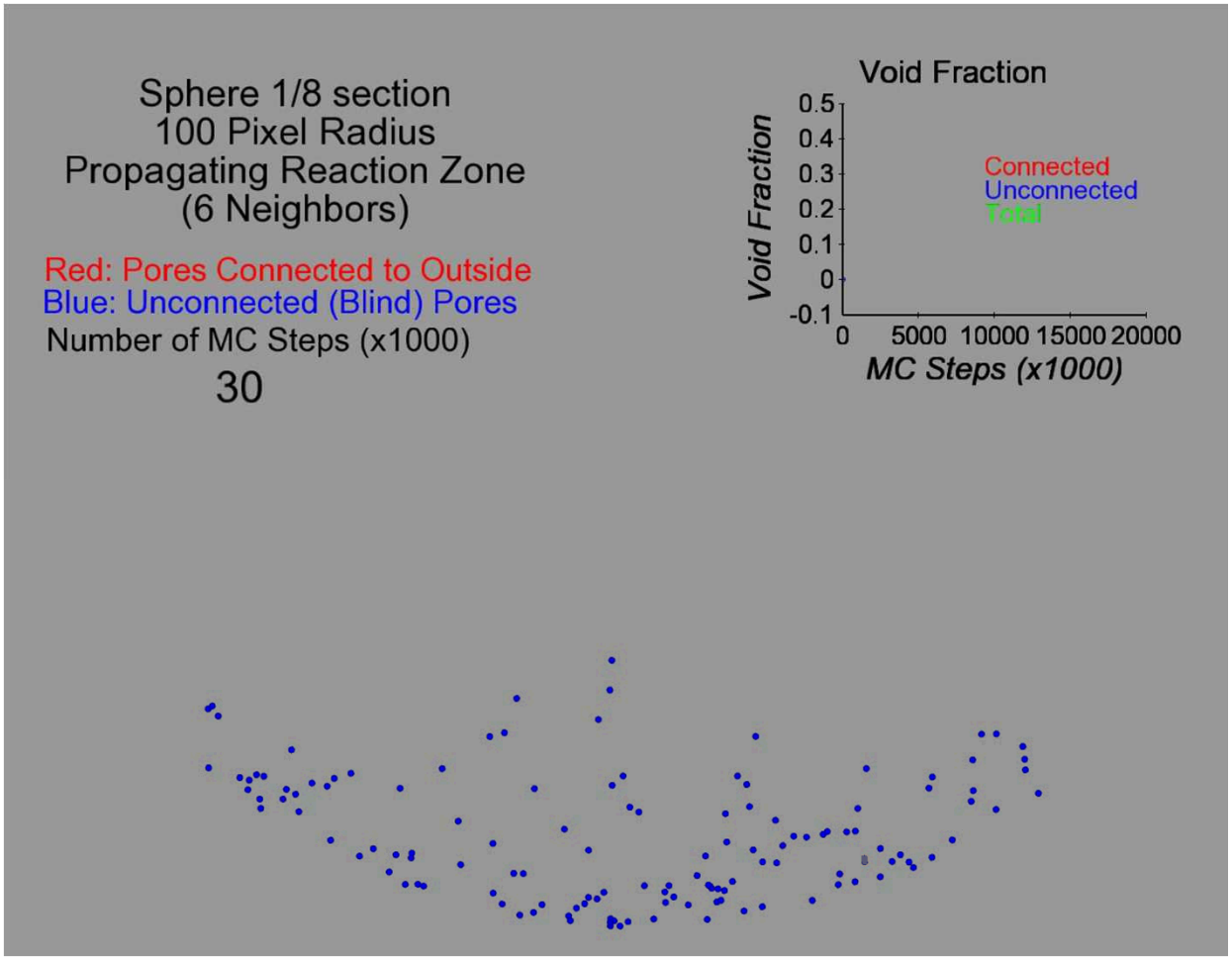
Monte Carlo/Percolation Decomposition Model

- **Sphere geometry with 100 pixel radius**
- **Stencil of 6 neighbors includes only sides**



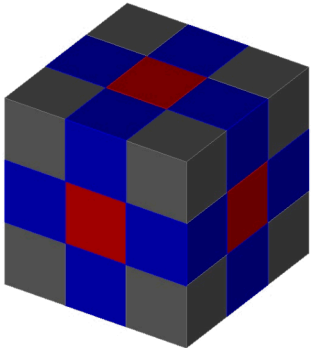
- **Initial reaction zone defined 2 pixels from surface**
- **Limiting value is void fraction of ~42%**
- **Sigmoidal shape to void development (assume # of MC steps proportional to time)**

Sample Simulation—Sphere 100 pixel radius, 6 Neighbors



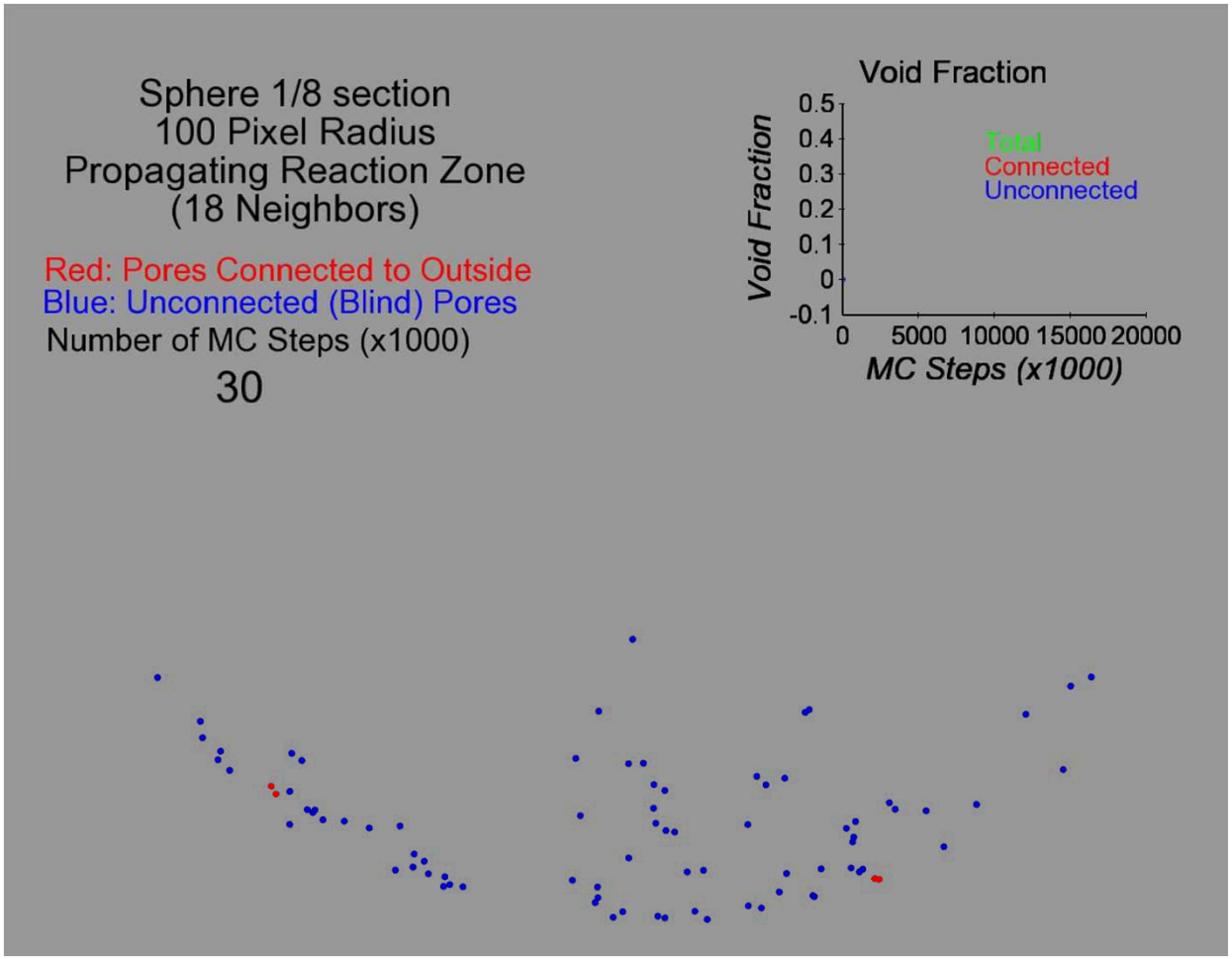
Monte Carlo/Percolation Decomposition Model

- **Sphere geometry with 100 pixel radius**
- **Stencil of 18 neighbors includes sides / edges**



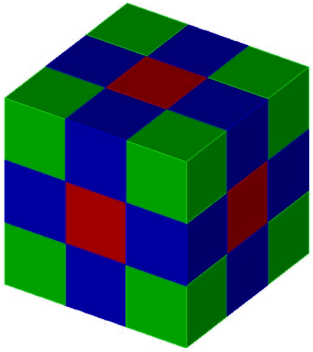
- **Initial reaction zone defined 2 pixels from surface**
- **Limiting value is void fraction of ~18.5% (more pathways for easier connection with outside)**
- **Sigmoidal shape**

Sample Simulation—Sphere 100 pixel radius, 18 Neighbors



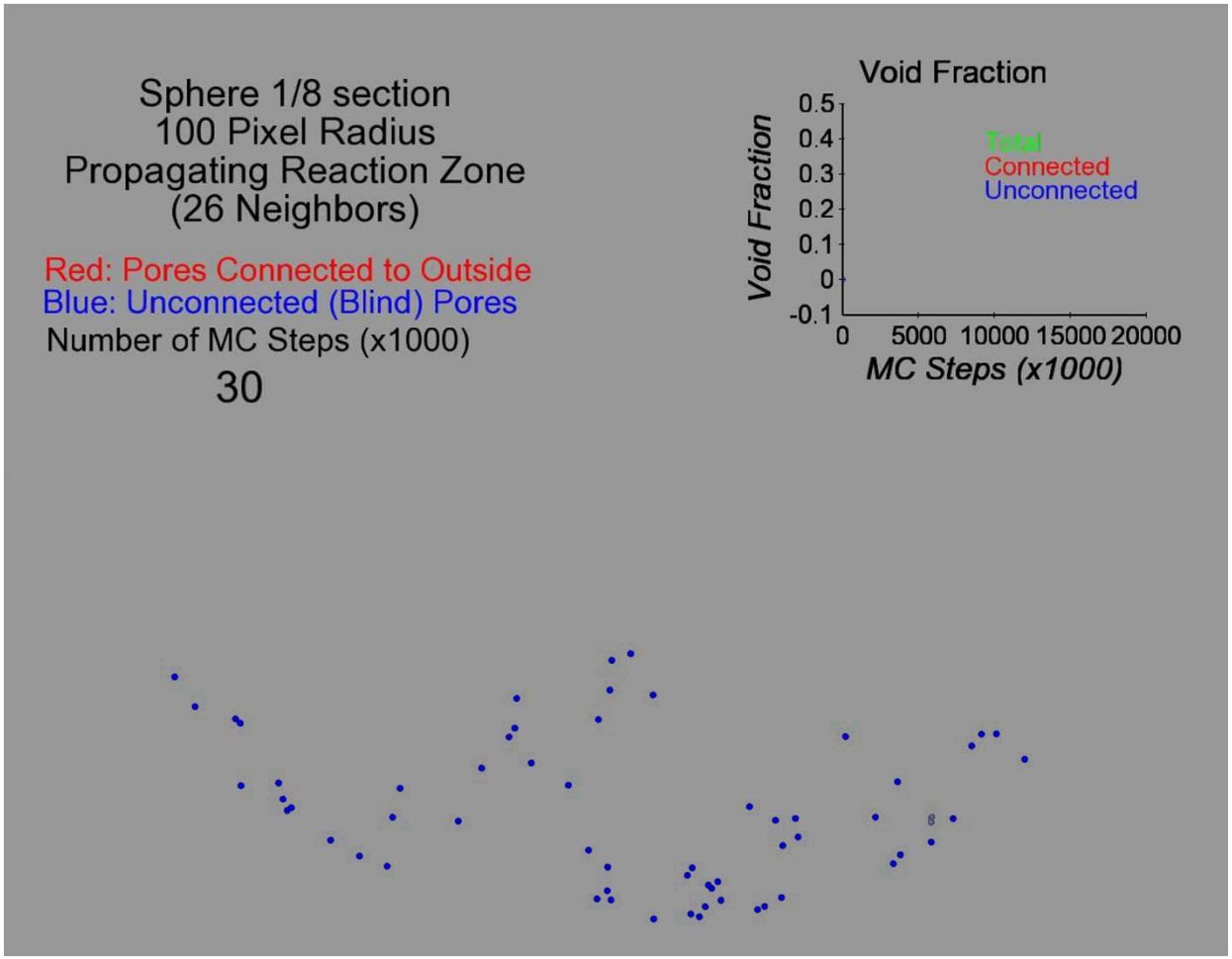
Monte Carlo/Percolation Decomposition Model

- **Sphere geometry with 100 pixel radius**
- **Stencil of 26 neighbors: sides / edges / corners**



- **Initial reaction zone defined 2 pixels from surface**
- **Limiting value is void fraction of ~13.2% (more pathways for easier connection with outside)**
- **Sigmoidal shape**

Sample Simulation—Sphere 100 pixel radius, 26 Neighbors



Monte Carlo/Percolation Decomposition Model

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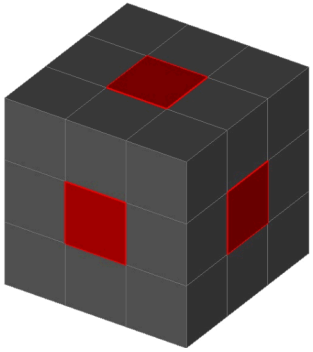
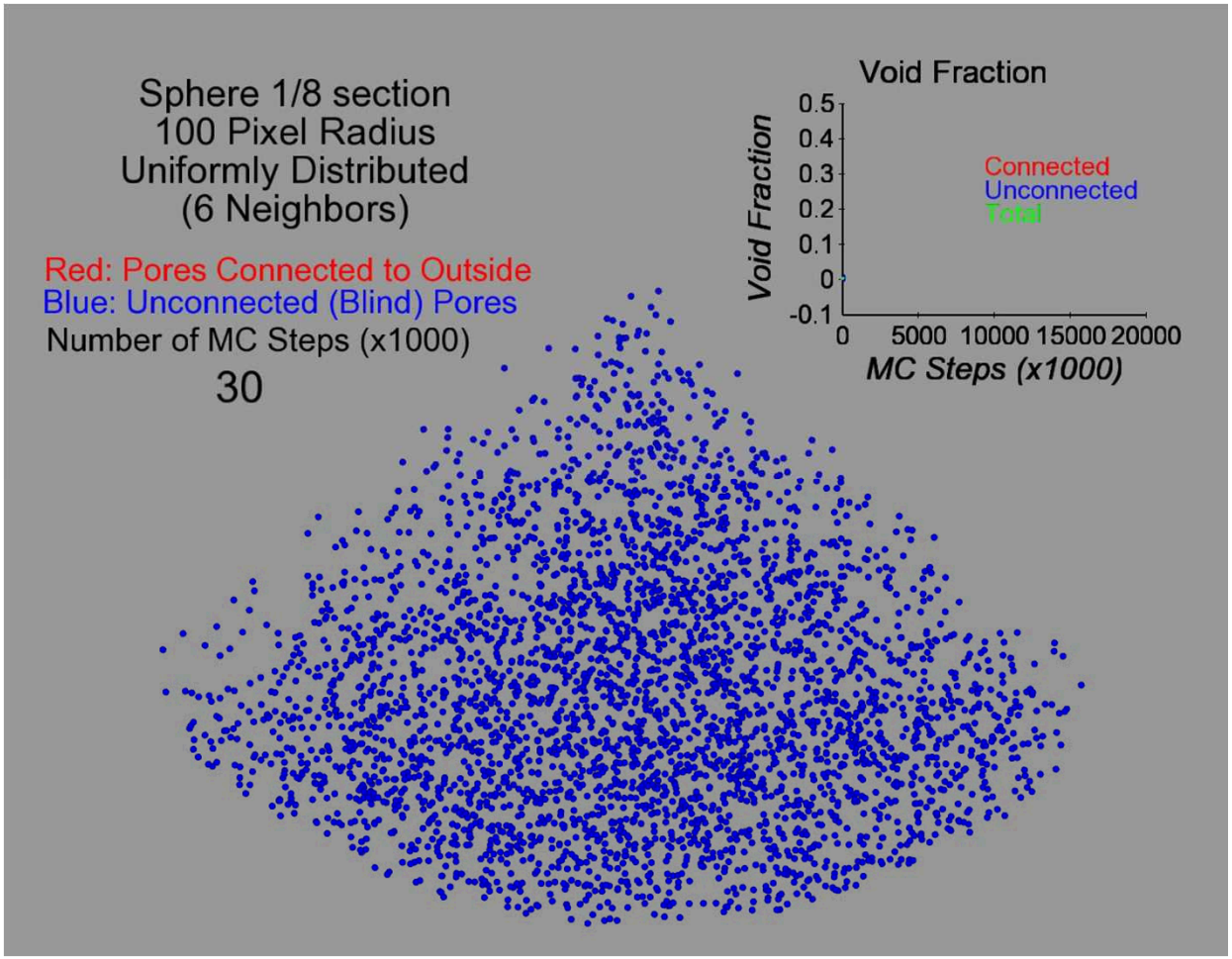
- **Sphere geometry with 100 pixel radius**
- **Stencil of 6 neighbors includes only sides**



- **Initial reaction zone covers entire volume (no preferential region)**
- **Limiting value is void fraction of ~42%**
- **No Sigmoidal Shape**
- **Sudden change in unconnected to connected at ~31% (like traditional percolation)**

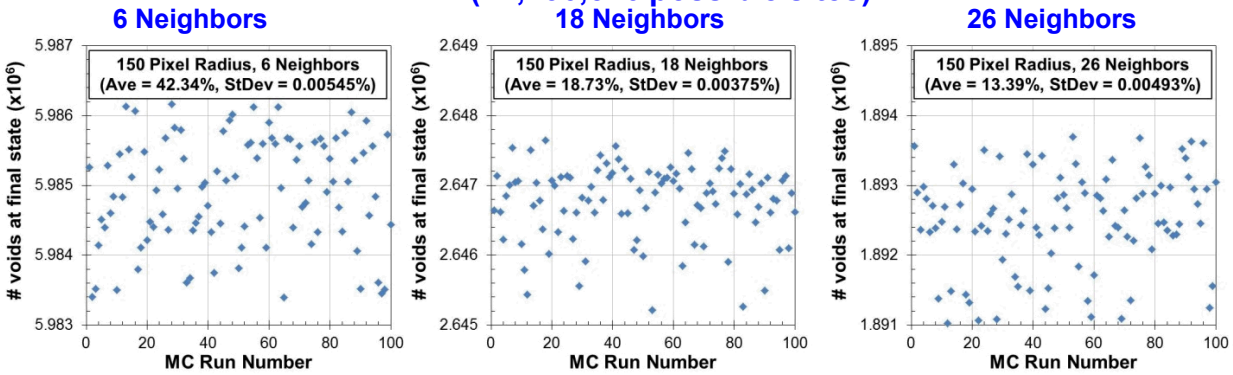
Sample Simulation—Sphere 100 pixel radius, 6 Neighbors, Equal Probability



Model Results / Statistics

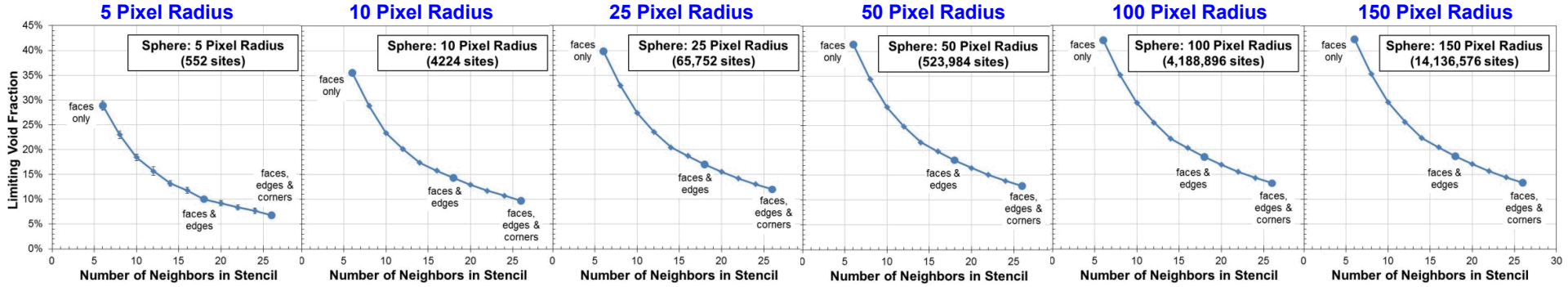
- **To check repeatability and statistics, 100 repeat runs were made at each condition.**
- **Repeatability was very good; (St. Dev. <0.01% at 150 pixel radius as in graphs here)**

Final Void Populations for Sphere of Radius 150 Pixels (14,136,576 possible sites)



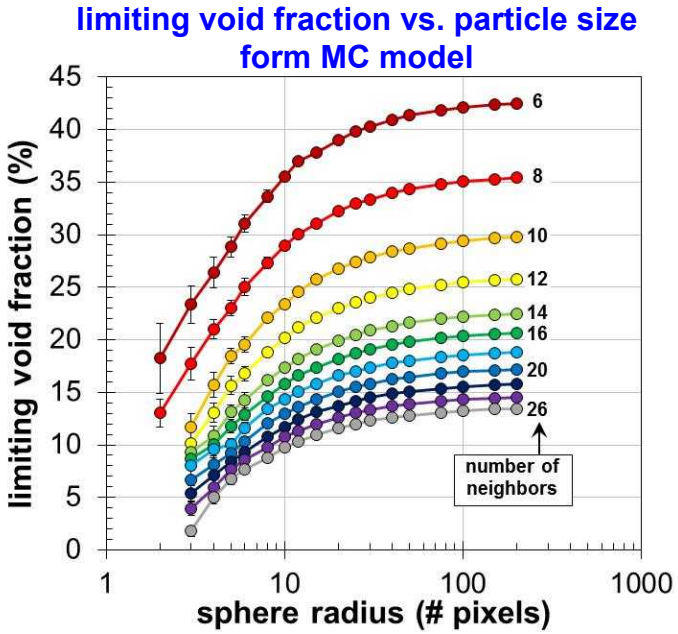
- **The effects of particle size and number of neighbors in the stencil on the limiting void fraction were determined.**
- **Particle size effects were most pronounced at small sizes; at large size not much change.**
- **Effect of neighbor stencil was consistent: lower void fractions with higher number of neighbors.**

Limiting Void Fraction



MC Model Size Effect Compared with AP Data

- **Spheres radii of 2 to 200 pixels were computed**
- **At large sizes, limiting void fraction asymptotically approach constant values**
- **At small sizes, void fraction heads towards zero.**

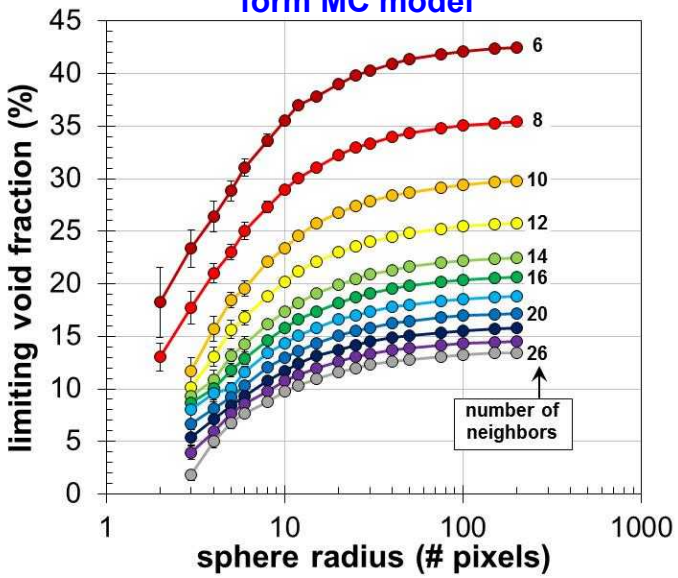


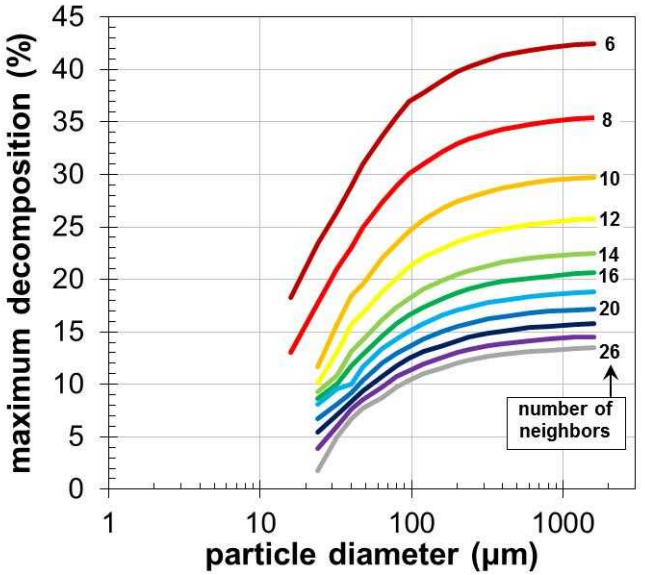
MC Model Size Effect Compared with AP Data

- **Spheres radii of 2 to 200 pixels were computed**
- **At large sizes, limiting void fraction asymptotically approach constant values**
- **At small sizes, void fraction heads towards zero.**
- **Attempt to relate dimensionless simulated quantities by assuming pixel length scale is 4 μm.**
- **Justified by:**

  "characteristic thickness of the walls of this sponge-like structure was 3-5 μm" [8]
  "new germs arise mainly in the nearest neighbour (4-6 μm)" [8].

limiting void fraction vs. particle size form MC model





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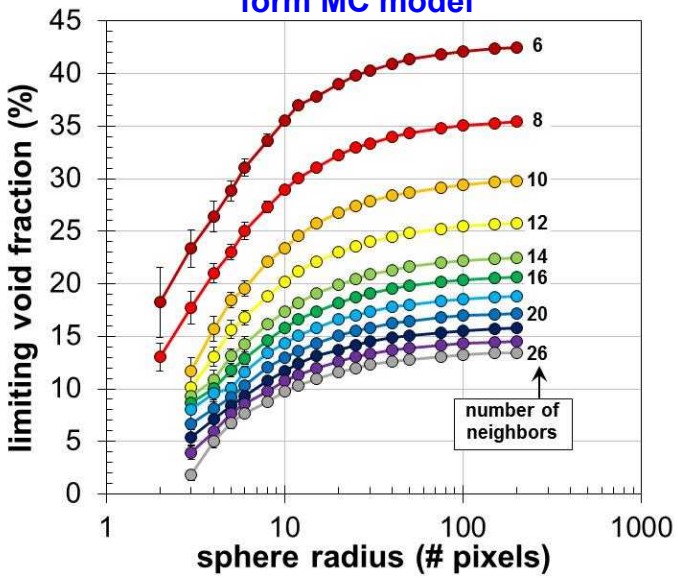
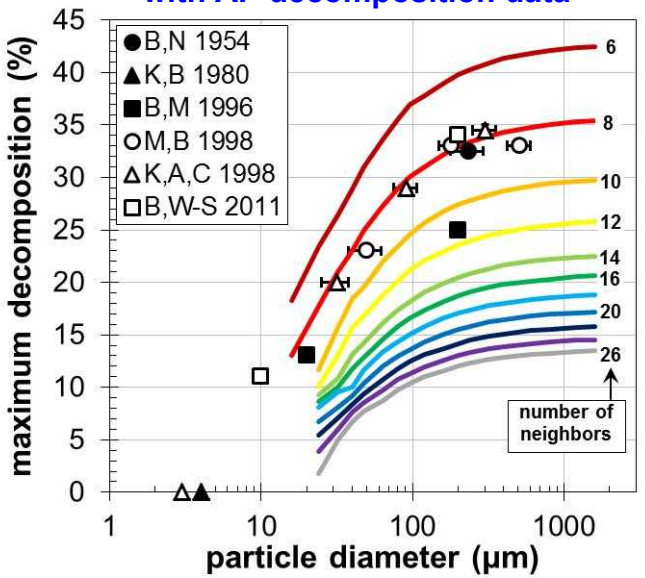
- **Justified by:**

  "characteristic thickness of the walls of this sponge-like structure was 3-5 μm" [8]
  "new germs arise mainly in the nearest neighbour (4-6 μm)" [8].
- **If this 4 μm pixel size assumption is made, data can be overlaid as in graph at lower right.**
- **Experimental trends are reproduced, with best fit appearing to be an 8-neighbor stencil.**

limiting void fraction vs. particle size form MC model



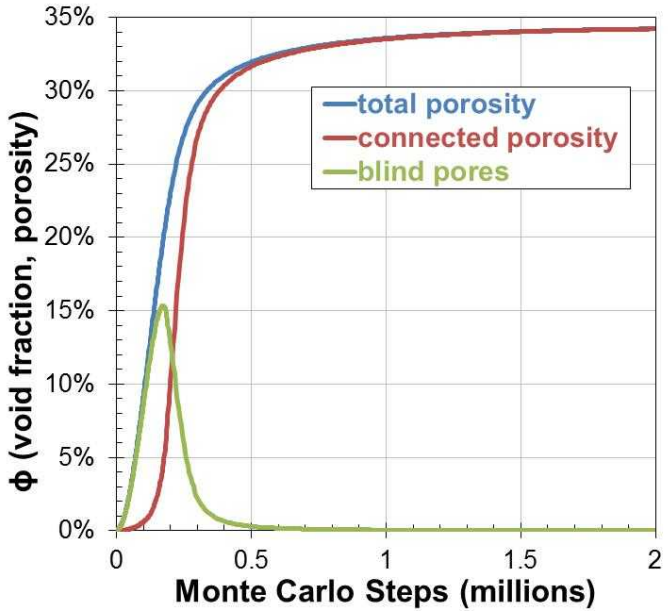
Comparison of MC model results with AP decomposition data



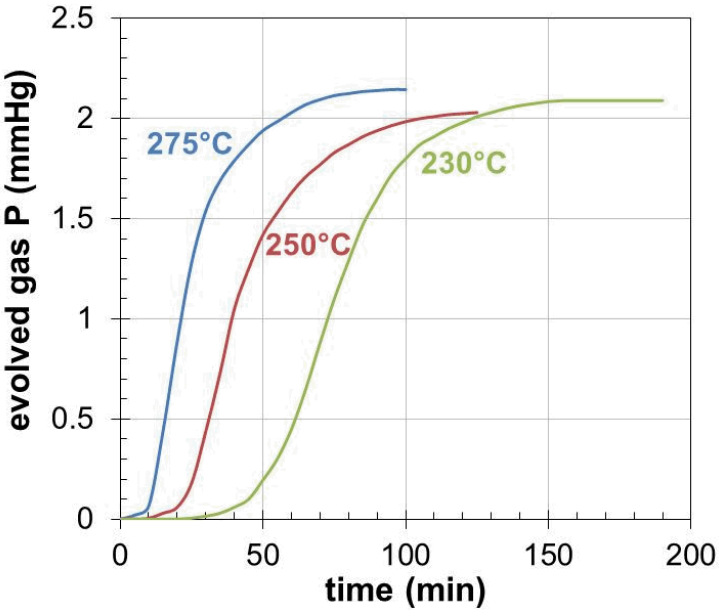
Results—Time Dependency?

- **If we make the assumption that the number of Monte Carlo steps taken (total number of steps, not just the "hits") is related to time, then we can qualitatively plot the temporal behavior.**
- **Which is more appropriate?**
  - **Total porosity might correspond with reaction rate**
  - **Porosity connected to outside might correspond with mass loss (perhaps compare with TG data?)**
- **Sigmoidal shape indicated. Qualitative agreement with experiment.**

"Temporal" Behavior of Monte Carlo Simulation (particle diameter = 100 pixels, 8 neighbors)



AP Decomposition Data [2]



Videos Showing Particle Void Evolution

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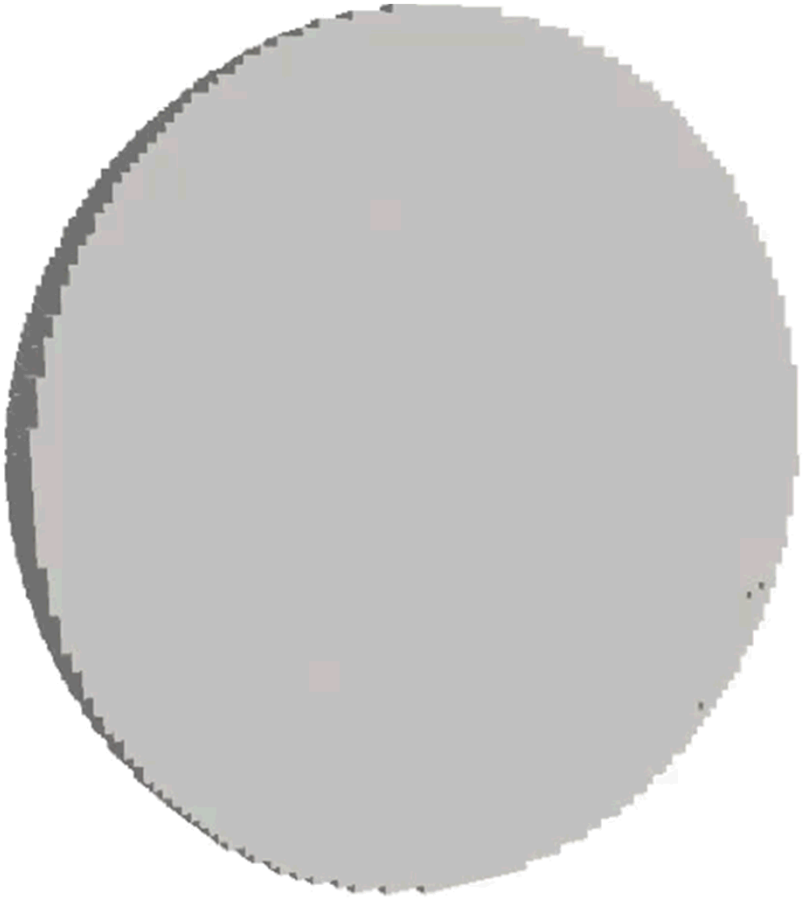
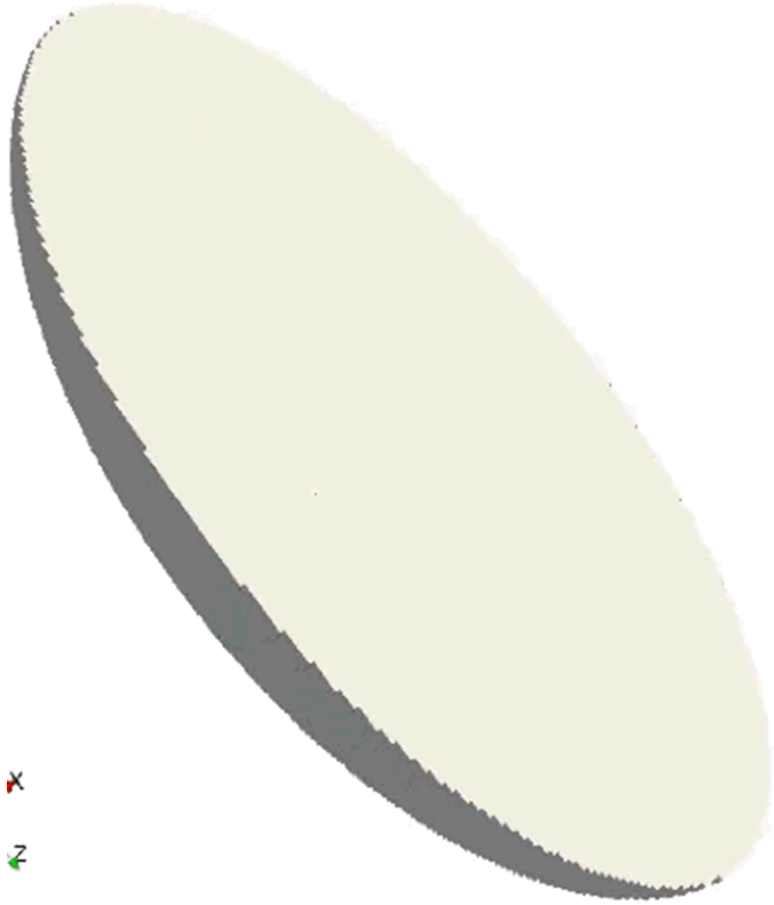
Sphere, diameter = 100 pixels
(6 neighbors, 41% void)



Ellipsoid, 100x100x200 pixels
(8 neighbors, 34.4% void)



Still Images of Final State Showing Particle

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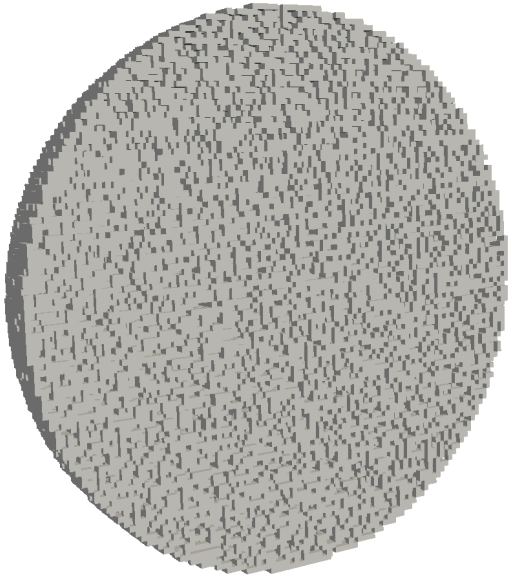
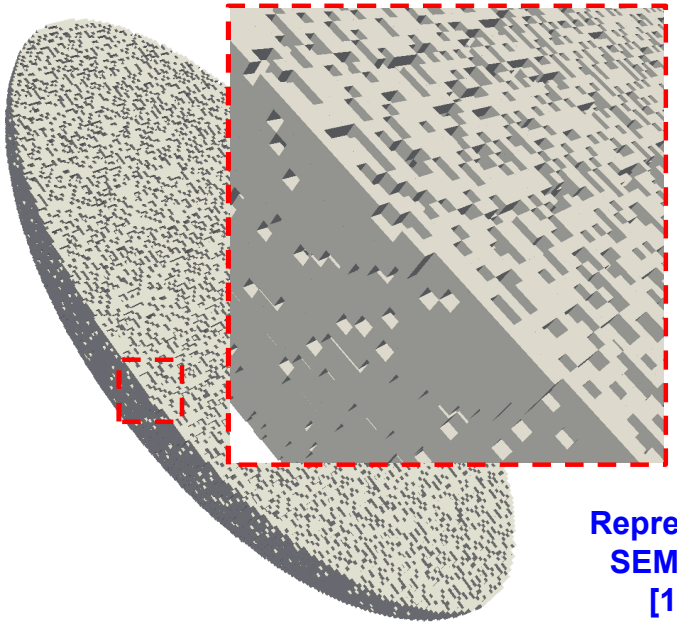
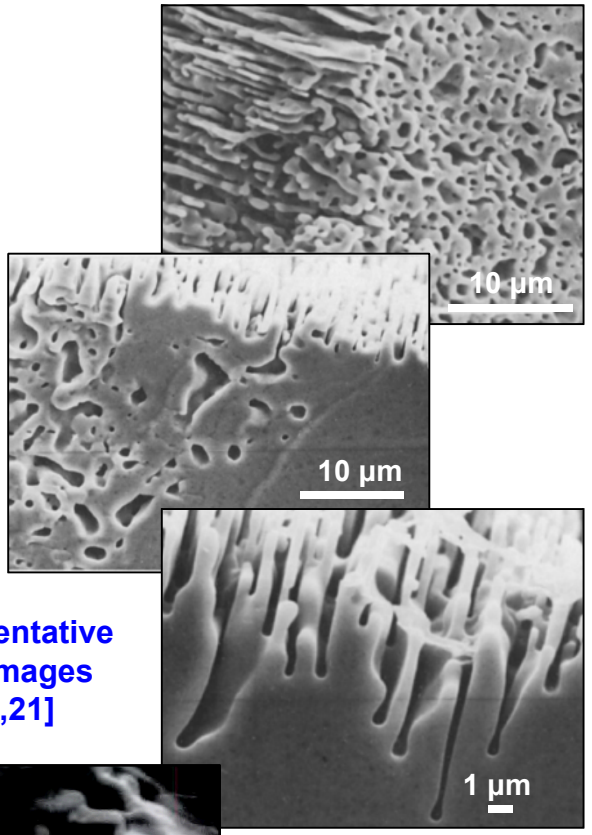
Sphere, diameter = 100 pixels (6 neighbors, 41.3% void)



Ellipsoid, 100x100x200 pixels (8 neighbors, 34.4% void)

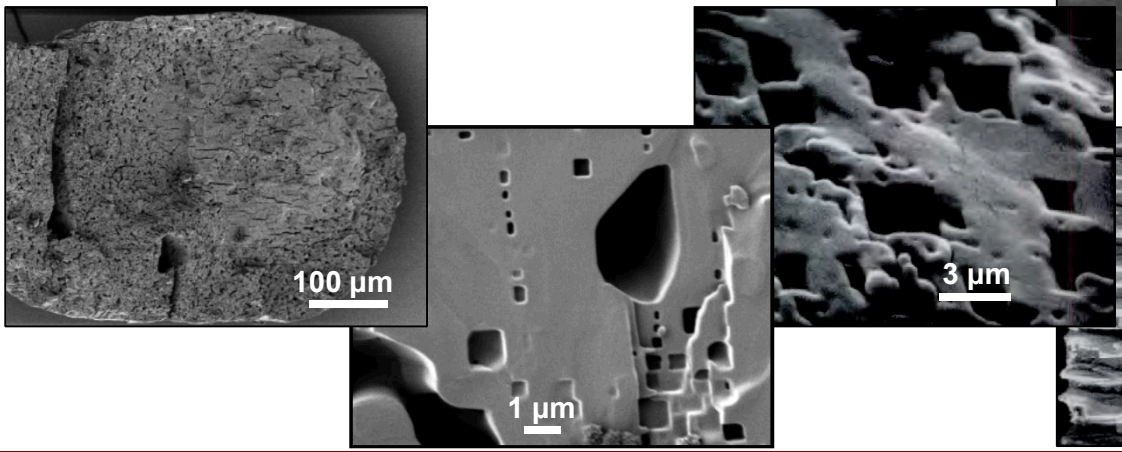


Representative SEM images [1,7,21]



Q. Do Monte Carlo model results look like AP decomposition?

A. Partially. Reality has more than one pore size.



Conclusions / Comments

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- A model for AP decomposition was developed based on a simple set of Monte Carlo rules
  - Emphasis on geometry and a few physical ideas
  - No chemistry whatsoever
- Model qualitatively replicates some of the observed behavior in AP decomposition:
  - Limit of porosity developed
  - Effect of particle size
  - Sigmoidal time response
- Other sets of "rules" could possibly be incorporated to represent some of the other observations and theories of AP decomposition (might require including more chemistry and physics).
  - Finite number of nucleation sites?
  - Maximum "tunnel" diameter?
  - Catalysis by reactive intermediate leading to "wormholing"?
  - Multiple length scales (small pores vs. large)?
  - Crystal orientation effects?
  - Polycrystalline particles?
- Study suggests the utility of clever experiments to uncover interior pore structure and other relevant quantities:
  - Micro- or nano-CT of partially decomposed single particles? With in situ heating?
  - Characterization of dislocations within crystals (type and density) via X-ray diffraction or other methods?
  - Effect of grinding or mechanical damage to crystals; can we make particles that decompose less?

Acknowledgments

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The helpful reviews / discussions by Jeff Kay and Cole Yarrington are appreciated.

Jeff Kay [SNL] and Trevor Hedman [China Lake] (from Karl Krauetle's files) supplied some of the SEM images of AP particles. SEM images from Galwey and Mohamed [1] used in the paper were by permission of the publisher/copyright owner.

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[1] A. K. Galwey and M. A. Mohamed, "The Low Temperature Thermal Decomposition of Ammonium Perchlorate: Nitryl Perchlorate as the Reaction Intermediate," *Proceedings of the Royal Society of London, A*. 396 (1984) pp. 425-440.

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Backup Material

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Newman-Ziff Monte Carlo Algorithm [18]

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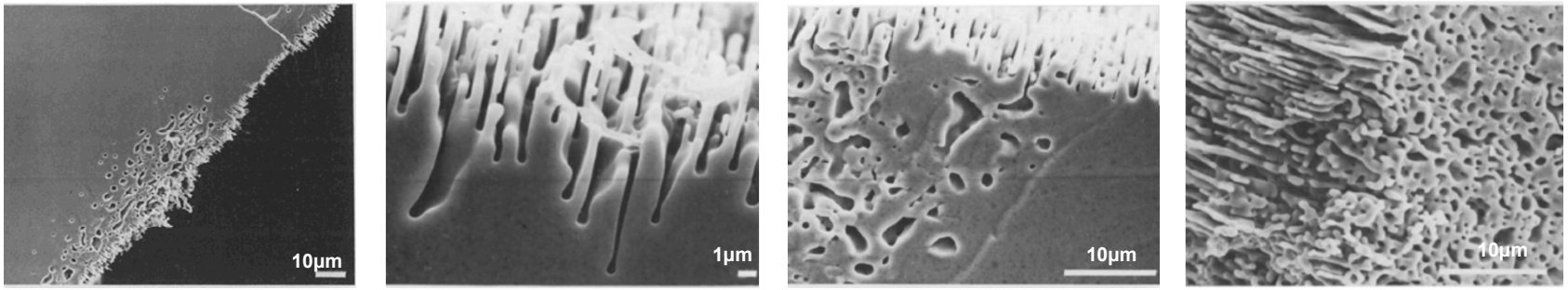
- **Summary of Newman-Ziff Algorithm:**
  - Each site in domain has an integer "pointer" variable attached. It has three possible values
    a) Empty (–[N+1], where N is the total number of sites) means site is in initial (undecomposed) state
    b) Positive means site is part of a cluster (i.e. a cluster of connected voids)
    c) Negative (but not "empty") means site is the root site of a cluster
  - Positive values of the pointer refer to the index location of another site in the connected cluster whose pointer points to another (recursively) until it reaches a "root" site (e.g. twig points to branch which points to trunk which points to root)
  - Pointer at a cluster root site contains a negative number (negative of cluster size)
  - Initially each site is set to "empty"
  - When a site is chosen to "decompose" (and is eligible based on the rules we defined earlier):
  - If all neighbors are "empty" then site's pointer is initialized with value of -1, indicating it is a root site and that the cluster size is 1.
  - If one non-empty neighbor, the site is joined to that neighbor's cluster by setting the site's pointer to the root site of neighbor (and adding 1 to that root site's cluster size)
  - If site is neighbor to 2 or more clusters (i.e. it becomes a bridge between them) then clusters are combined into a single cluster. The root of the larger of the two clusters becomes root of the total (root of the smaller cluster is changed to point to root of the larger, and overall root site has its size is adjusted to reflect the total aggregate cluster size.)
  - In determining connectivity to the outside, we define an extra site which represents the outside and assign the first interior layer of sites as having that extra "outside" site as a neighbor. Once interior sites become connected to the "outside" site, they share a common root an hence connectivity can be easily checked.
- **Some code for Newman-Ziff algorithm in Fortran or C is available on internet [18]; the remainder was coded in Fortran.**
- **Overall MC algorithm was very efficient, simulations typically took just a few minutes on one processor; longer if had to generate graphics files. Ran up to 200 pixel radius spheres (33 M sites)**

Interior Pore Structure in AP Decomposition

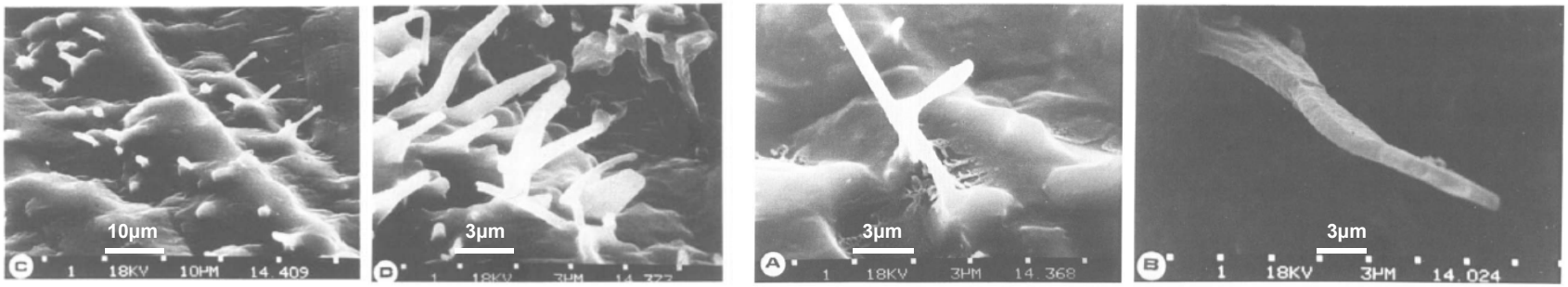
- **Channels / some evidence of blind pore formation**

Cleaved Surface of AP Particles at Various Decomposition Levels (Galwey & Mohamed, 1984*)



- **Pore replicates (Formvar resin injected into pores, cured, then AP dissolved away)**
- **Indication of some pore branching as well as rectangular cross section**
- **Blind pores would not be accessible to resin, nor would extra deep pores**

Formvar Replicates of Pore Structure (Galwey et al. 1988‡)



- **Possibility Micro CT scan of partially decomposed particles? In situ?**

* A.K. Galwey and M. A. Mohamed, "The Low Temperature Thermal Decomposition of Ammonium Perchlorate: Nitryl Perchlorate as the Reaction Intermediate," *Proceedings of the Royal Society of London, A*, 396 (1984) 425-440.

‡ A.K. Galwey, P.J. Herley, and M.A. Mohamed, "Replication Micrography of Ammonium Perchlorate Surfaces During their Initial Stages of Thermal Decomposition," *Reactivity of Solids*, 6 (1988) 205-216.