Monte Carlo Simulations
III. MC Examples in Materials Simulation

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Course Structure

- Part A: Introduction to Modelling
- Part B: Monte Carlo Simulations
  - Basic Concepts
  - Metropolis Monte Carlo Simulations
  - **Examples of MC in Materials Simulation**
- Part C: Density Functional Theory (DFT) Calculations

Previously on …

- Metropolis MC simulation: general derivation and its application on finding the minimum energy state
- Computational tricks used for effectively simulating large scale systems.

A Glimpse Into Practical Monte Carlo Simulations

- We will cover two examples:

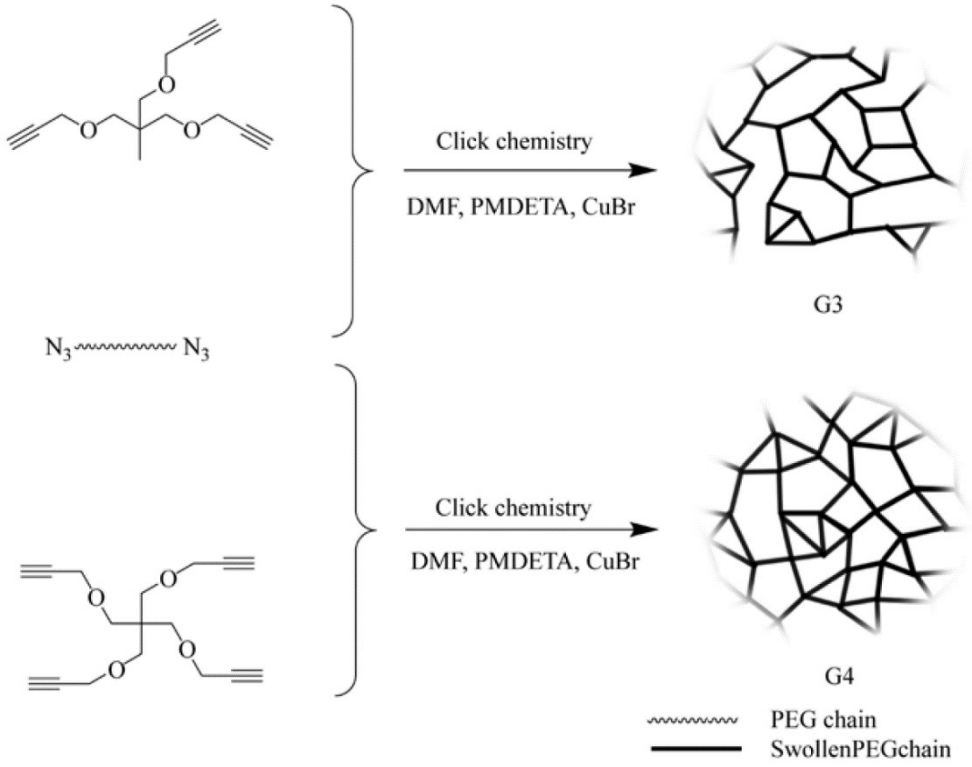
- Structural Properties of Hydrogels
- *Strongly linked with last lecture*

- Potts Model for Grain Growth
- *Brief Introduction to Ising Model*

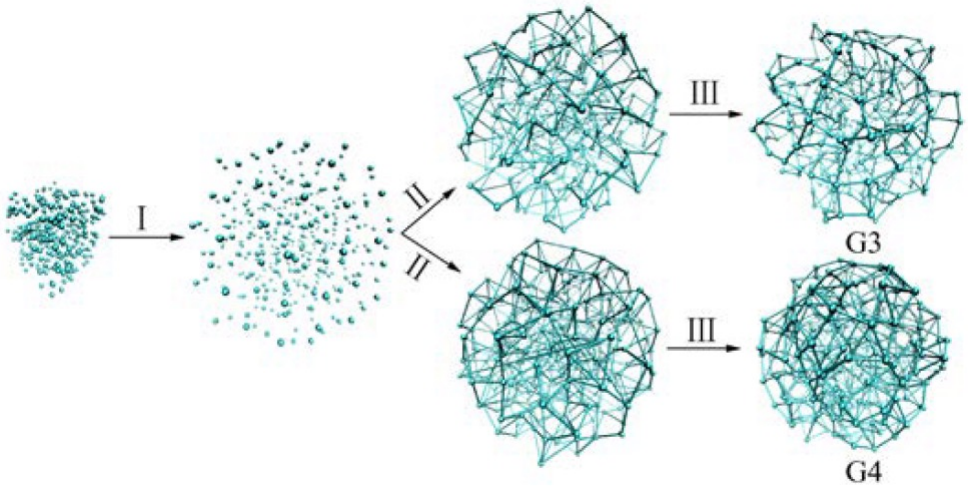
Three-dimensional Molecular Geometry of PEG Hydrogels by an "Expansion-Contraction" Method through Monte Carlo Simulations

Three-dimensional hydrogel networks based on poly(ethylene glycol)s (PEGs) swell readily in water. Because of their excellent biocompatibility, PEG hydrogels are promising candidate ranging from tissue scaffolds[1] to drug carriers[2]. Hence the study on the typical 3-dimensional topology of hydrogels is an important objective[3, 4]. For instance, the physical and mechanical properties of hydrogels mediate their applications through the structure and conformation at the molecular scale. It is obvious that the pores of freeze-dried hydrogels at the micron scale observed under scanning electron microscope (SEM) do not represent that of the actual swollen structures that plausibly should be at nm scale. Due to experimental limitations in the characterization at the molecular level[5], computer simulations including Monte Carlo (MC) simulations[6, 7] and molecular dynamics of hydrogels[8, 9] provide a reasonable alternative approach to explore structure-property relationships.

Background


Click chemistry
DMF, PMDETA, CuBr
G3
N_3 N_3
Click chemistry
DMF, PMDETA, CuBr
G4
PEG chain
SwollenPEGchain

Simulating the Ideal Hydrogel Network



Diffusion -> Crosslinking -> Relaxation

Difficulties in this simulation

- Different interatomic potential for different steps
- How to determine the “trial move” (we will use a weighted approach)
- How do we judge the configuration after “trial move” can be accepted?
- How to stop the “indefinite loop”?

Cracking the algorithm

- Different interatomic potential for different steps
- How to determine the “trial move” (we will use a weighted approach)
- How do we judge the configuration after “trial move” can be accepted?
- How to stop the “indefinite loop”?
- How do we do the crosslinking?

Calculate system energy (denoted as E_0)(based on Hookean theory)
while *step* < 1,000,000 do
    randomly select a node (denoted as A)
    compute the resultant force(denoted as $\boldsymbol{F}$) on A
    move A with $C^* \boldsymbol{F}$
    compute system energy after move (denoted as E)
    $\Delta E \leftarrow E - E_0$
    if $\Delta E < 0$ then
        accept the move
        $E_0 \leftarrow E$
    else
        generate a random number between 0 and 1 (denoted as R)
        if $\exp(-\Delta E/k_B T) > R$ then
            accept the move
            $E_0 \leftarrow E$
        else
            reject the move
        end if
    end if
    if *step* % 100 == 0 then
        output E
    step ++
end while
}

Simulating the Ideal Hydrogel Network

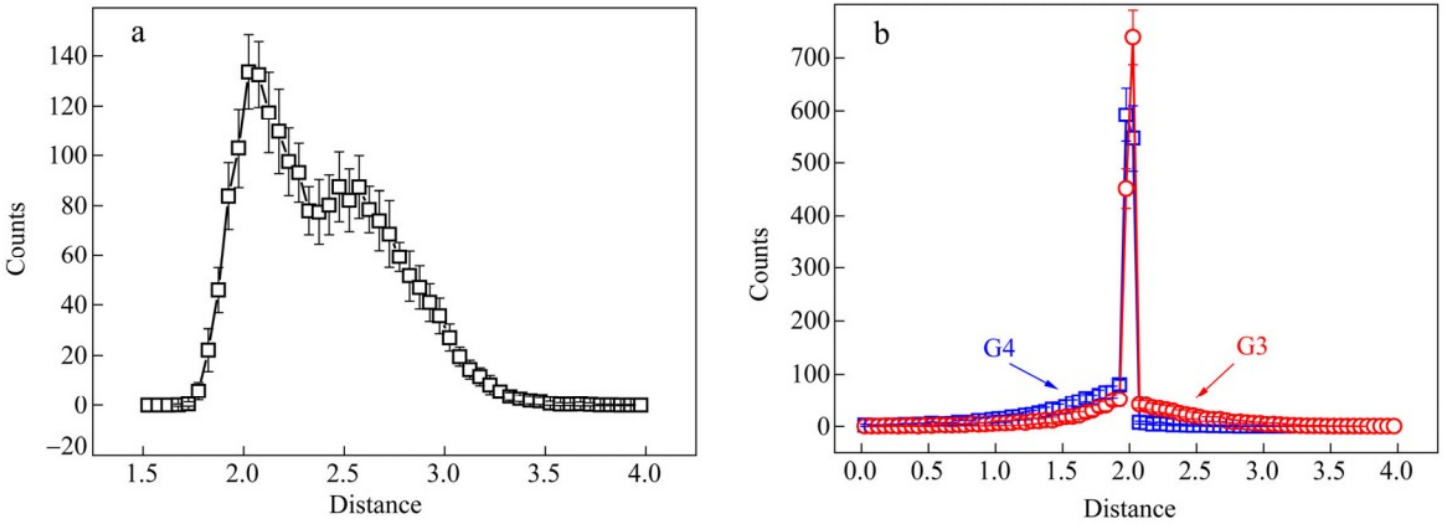


Fig. S1 Statistic data of the 5 nearest distance among nodes after diffusion (a) and relaxation (b) averaged over 20 independent runs

Simulating the Ideal Hydrogel Network

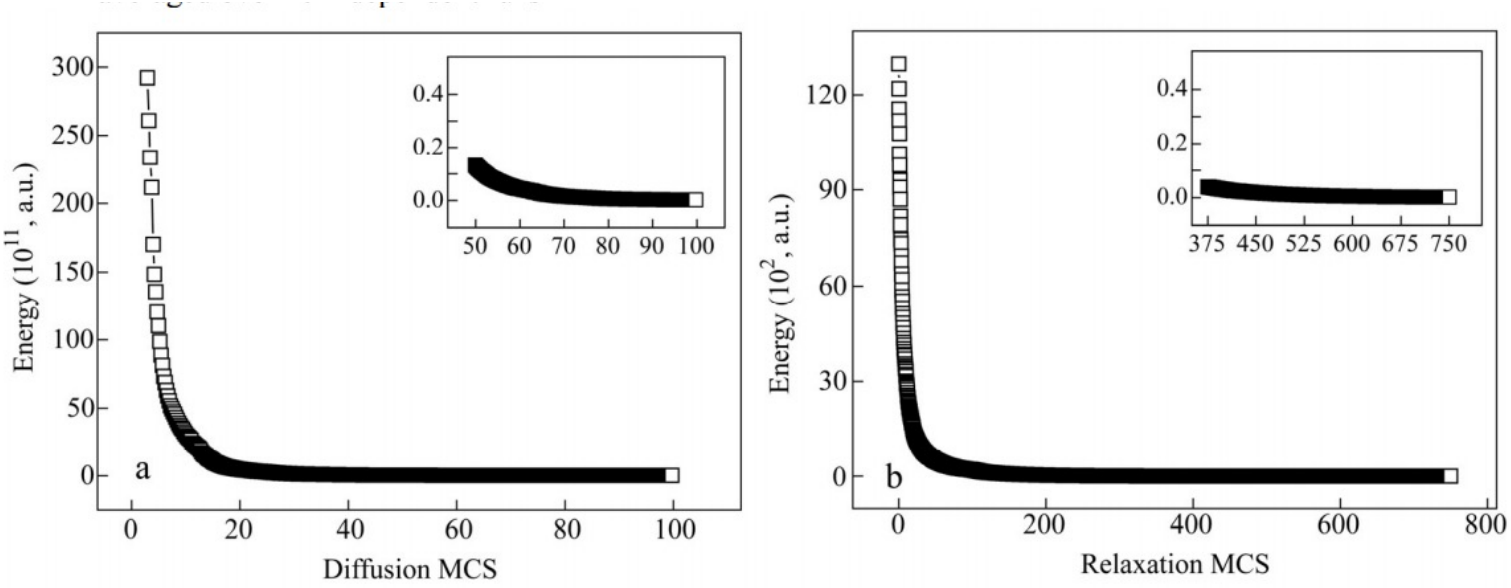


Fig. S2 Typical energy profile in the diffusion (a) and relaxation (b) steps

Simulating the Ideal Hydrogel Network

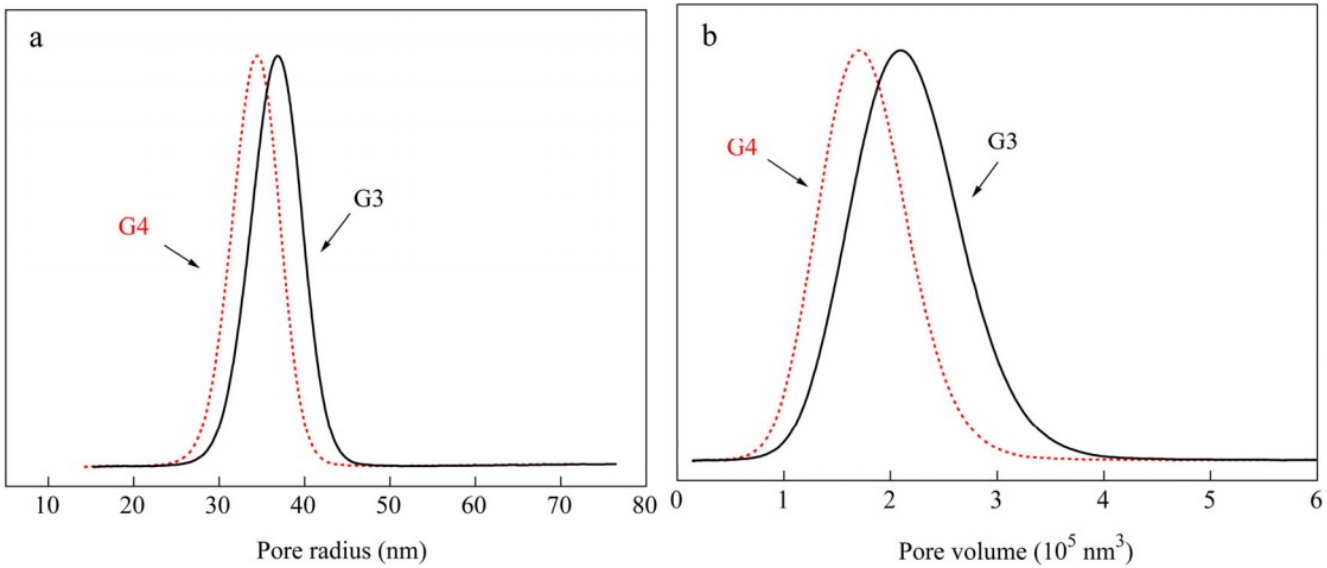
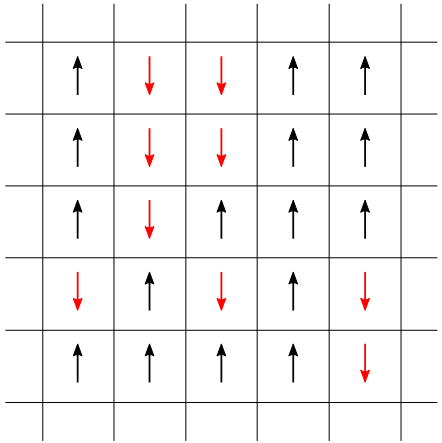


Fig. S5 Experimental pore radius and pore volume calculated based on molar mass distribution of DAP

The Ising model

Theoretical model of ferromagnetism in statistical physics (1925)



Magnetic dipole moments are represented in a regular array. They have two possible states (spins): +1 (up) or -1 (down)

- Interaction energy of the system:

$$E_{\text{Ising}} = \frac{J}{2}\sum_{i}^{N}\sum_{j}^{Z}\left(1-\delta_{S_iS_j}\right)$$

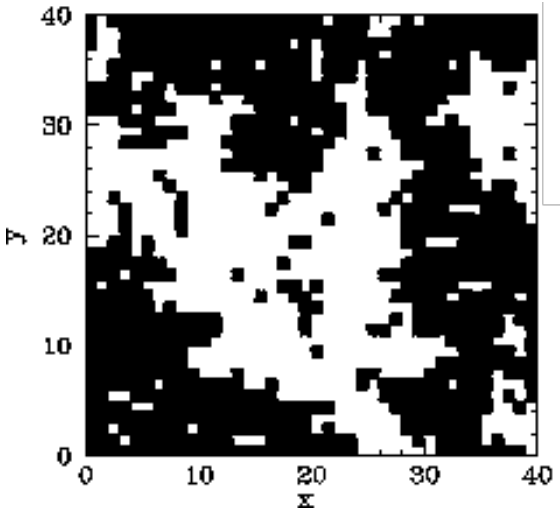
- Monte Carlo approach:
  - pick a site at random
  - calculate the change in energy by switching the state, ΔE
  - Accept the switch with probability $P(\Delta E)$

$$P(\Delta E) = 1 \qquad \text{If} \quad \Delta E < 0$$

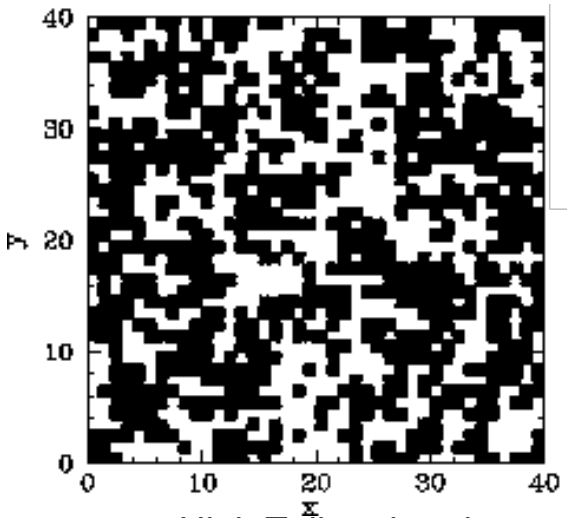
$$P(\Delta E) = \exp\left(-\frac{\Delta E}{kT}\right) \qquad \text{If} \quad \Delta E > 0$$

Metropolis criterion

- The algorithm generates random samples sequentially
- Low energy samples are more probable, unless there is high thermal fluctuations
- The Ising model predicts a phase transition at a critical temperature



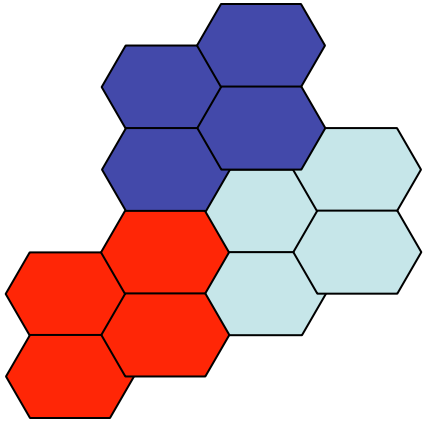
Low T: ordered



High T: disordered

Potts model

Generalisation of the Ising model for **multiple states** in a crystalline structures

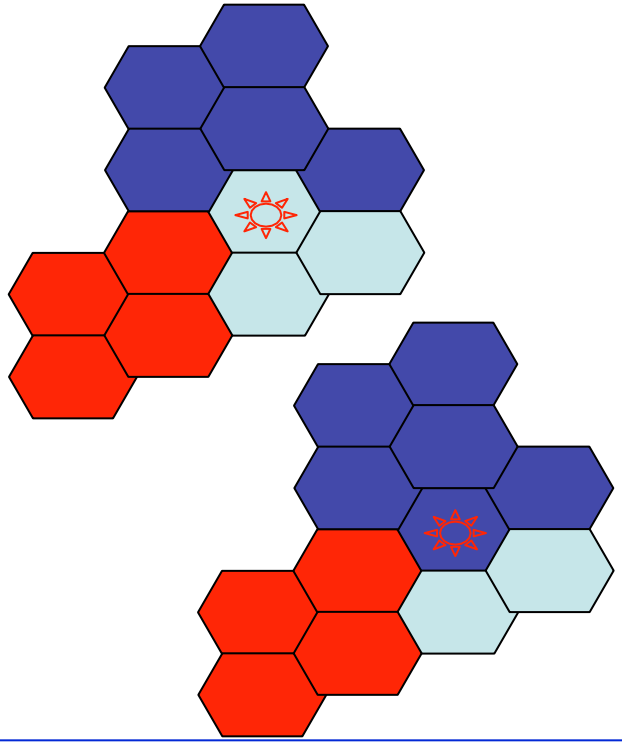


Here ‘states’ are crystalline orientations (represented by different colors)

- Energy is attributed to grain boundaries between grains with different orientation
- Total energy of the system:

$$E_{\text{Potts}} = \frac{J}{2}\sum_{i}^{N}\sum_{j}^{Z}\left(1-\delta_{s_i s_j}\right)$$

Potts model implementation



$$E_{\text{Potts}} = \frac{J}{2}\sum_{i}^{N}\sum_{j}^{Z}\left(1-\delta_{s_i s_j}\right)$$

- Consider only the energy associated with the site highlighted in the current state:

  (0+0+1+1+1+1) = 4J units of boundary energy

- If the cell is flipped to join the blue grain, the energy becomes

  (0+0+0+1+1+1) = 3J units of boundary

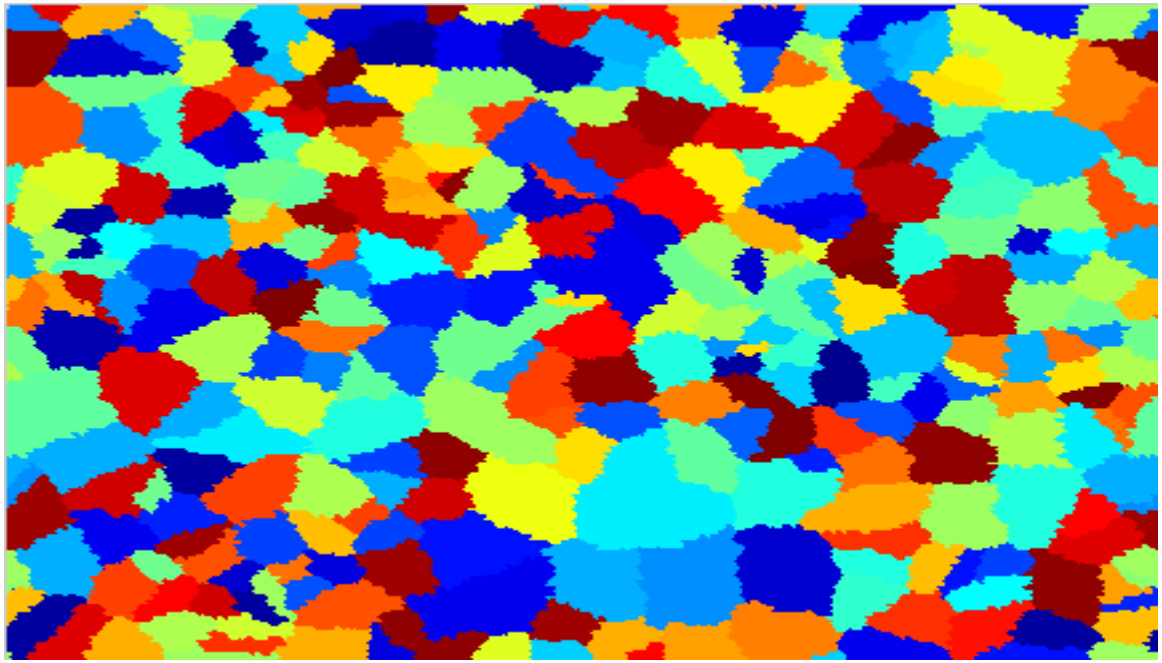
energy The change in energy is 3J-4J= -1J

Monte Carlo Potts algorithm

- Sites are chosen at random (the Monte Carlo component)
- The change in energy associated with a change in spin is calculated (the Potts component)
- This is converted to a probability that the spin will actually occur
- A random number is compared to the probability and the flip is made (or not) based on this probability. (A similar Metroploiis criteria)

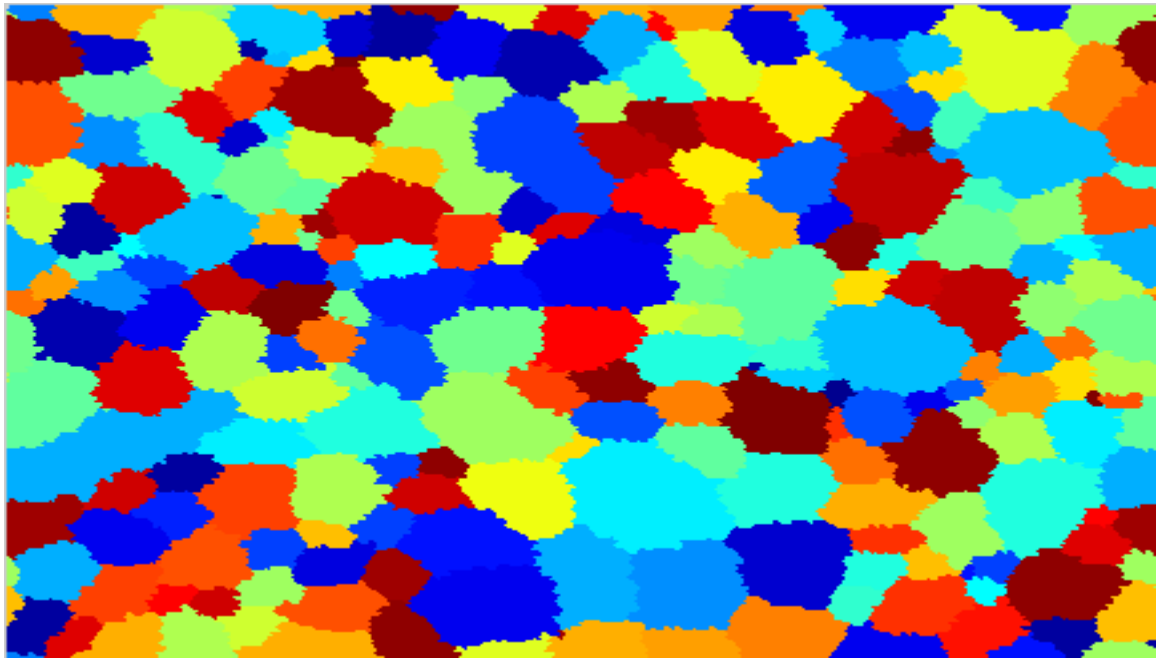
Monte Carlo simulation of grain growth

Initialised with 300 grains



MCS=0

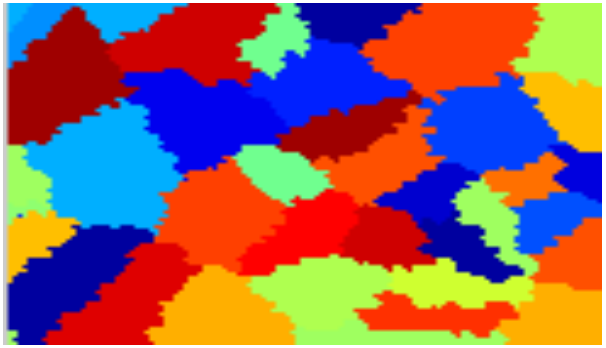
Monte Carlo simulation of grain growth

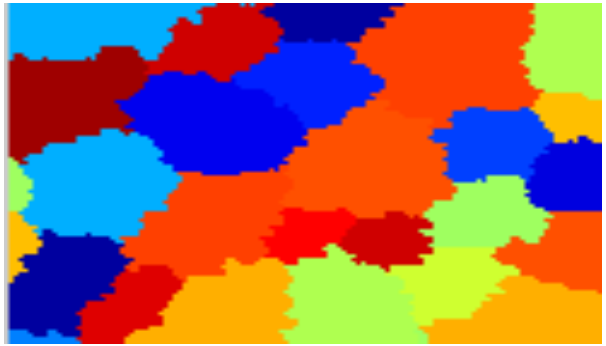


MCS=2000

We will do this in the tutorial!

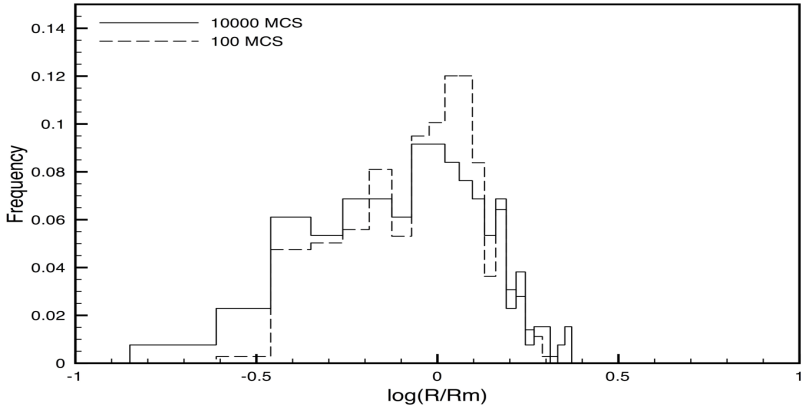
Validation of the simulation





Small grains shrink; large grains grow

Distribution remains *approximately* log-normal



Next Lecture

- Exercise on MC calculations
- Bring your computer (Excel / MATLAB installed)