PennState College of Engineering

*NucE 497: Reactor Fuel Performance*

# Lecture 20: Grain Growth in $UO_2$

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# Today we will discuss grain growth in $UO_2$

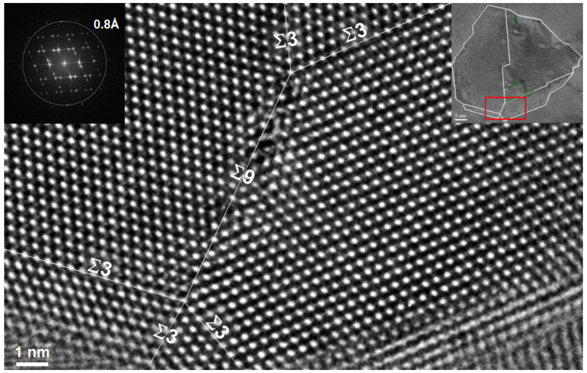
- Module 1: Fuel basics
- Module 2: Heat transport
- Module 3: Mechanical behavior
- Module 4: Materials issues in the fuel
  - Property evolution and Intro to materials science
  - Chemistry
  - **Grain growth**
  - Fission products and fission gas
  - Densification, swelling, and creep
  - HBS
  - Fracture
  - Thermal conductivity
- Module 5: Materials issues in the cladding
- Module 6: Accidents, used fuel, and fuel cycle

# Here is some review from last time

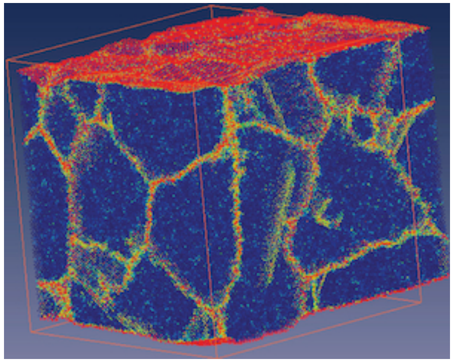
- What is the O/M ratio in the fuel?
  a) The orientation to matrix ratio, defining the grain orientation
  b) The oxygen to Mo ratio, controlling the oxygen potential
  c) The orange to magenta ratio, controlling the color of the fuel
  d) The oxygen to metal ratio, defining the stoichiometry
- Why are fresh fuel pellets fabricated to have an O/M ratio of 2?
  a) Stoichiometric $UO_2$ has the highest melting temperature
  b) Stoichiometric $UO_2$ has the most stable structure
  c) Stoichiometric $UO_2$ has the highest thermal conductivity

# Grain boundaries are planes where misoriented crystal lattices meet (two dimensional)

- Materials are typically composed of various regions where the crystal lattice is oriented differently. These regions are called **grains**.
- When two grains meet, there is a plane of atoms that do not follow the crystal lattice called a **grain boundary**.




High-res transmission eleectron microscopy can also show individual atoms (palladium) *www.knmf.kit.edu/TEM.php*

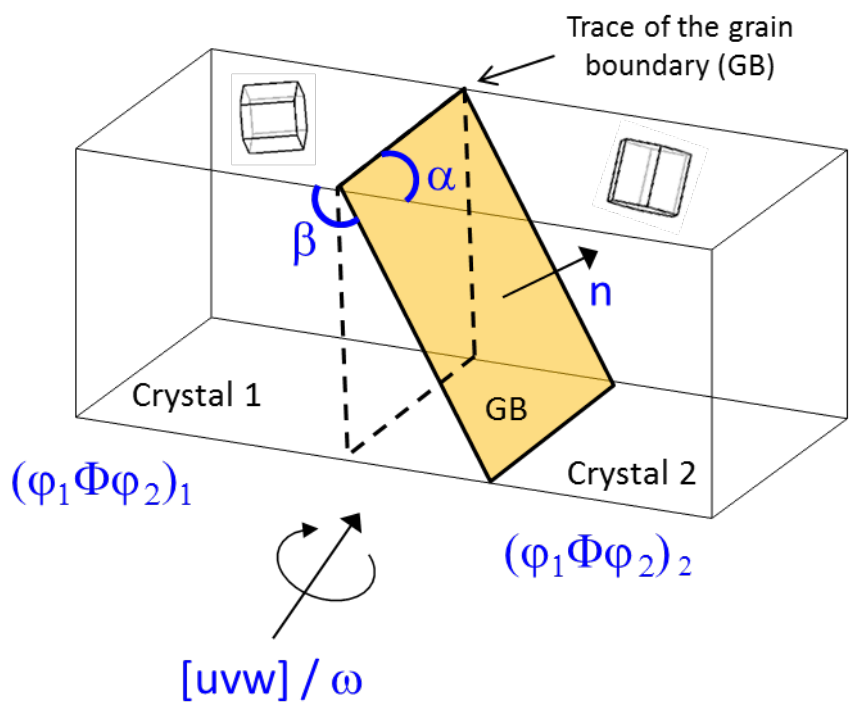


Atomistic simulation of grain boundaries in 3D

- Most crystalline materials are polycrystalline, not single crystal

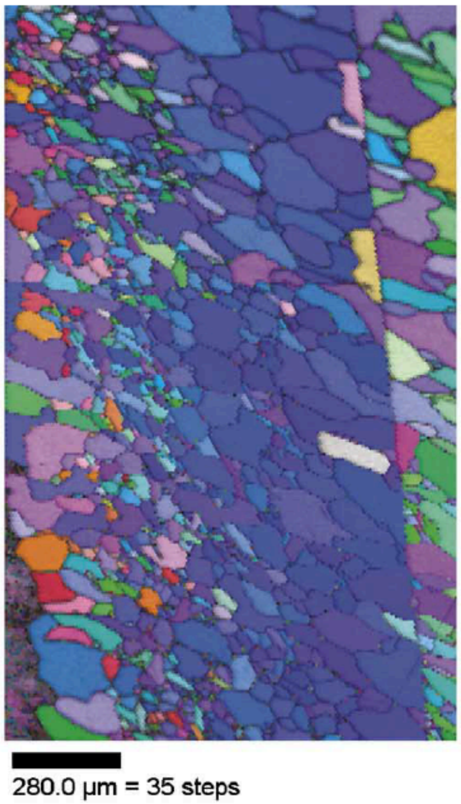
# Grain boundaries add energy to the material that is a function of their structure

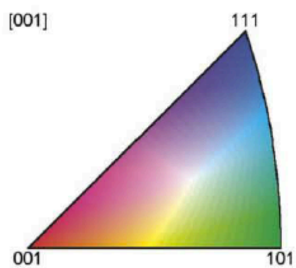
- A grain boundary's energy is determined by its:
  - **Inclination** – the orientation of the 2D grain boundary plane (2 degrees of freedom)
  - **misorientation** – the rotation required to align one grain with the other (3 degrees of freedom)



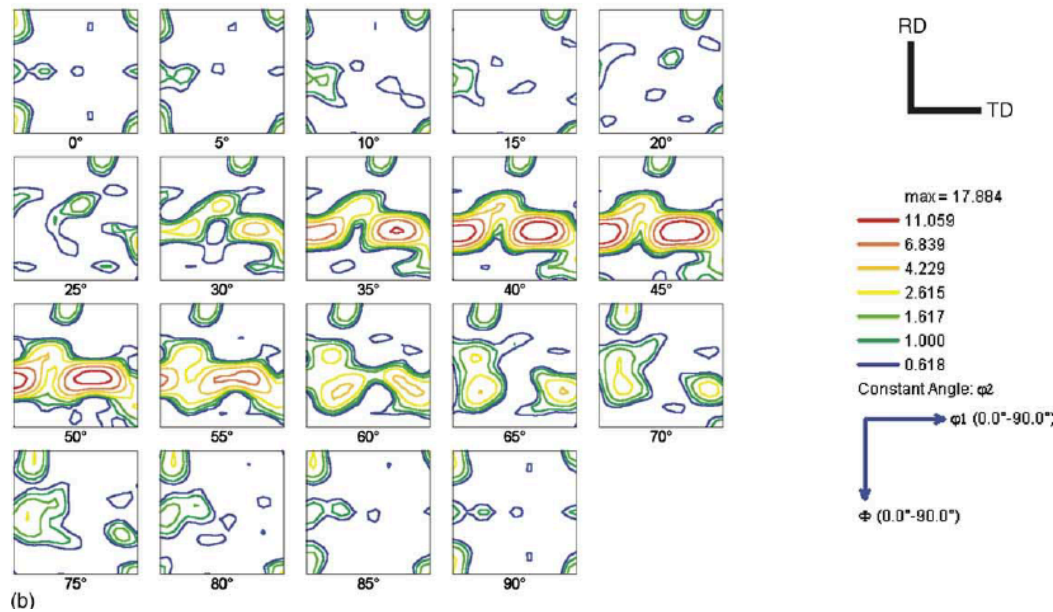
# The orientation of all the grains in a material is called the texture

Electron back scatter diffraction map
for cubic crystal structure



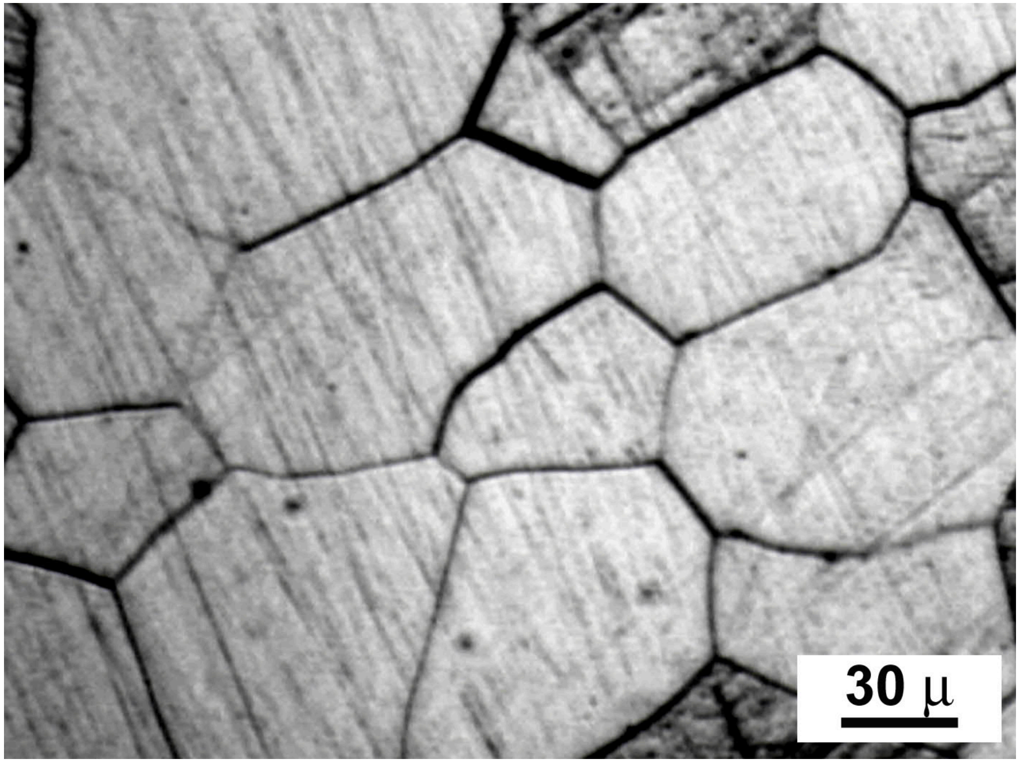



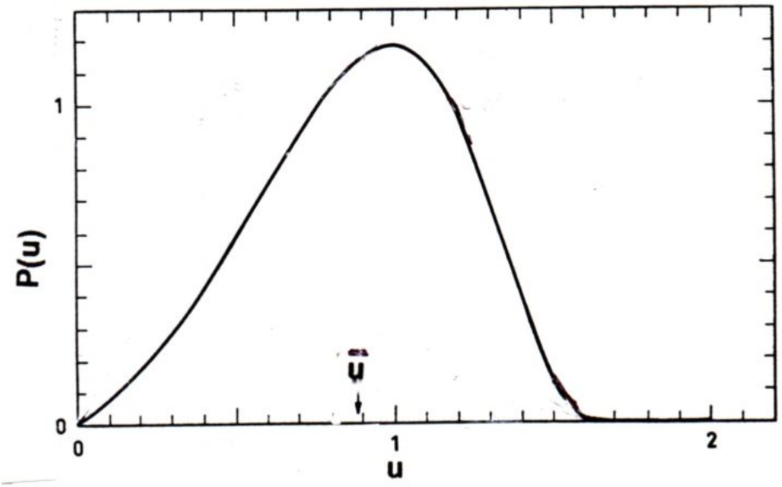

Orientation distribution function



# In a polycrystal, there is also a distribution of grain sizes

- Not every grain is the same size
- Therefore, we commonly refer to the **grain size distribution** and the **average grain size**

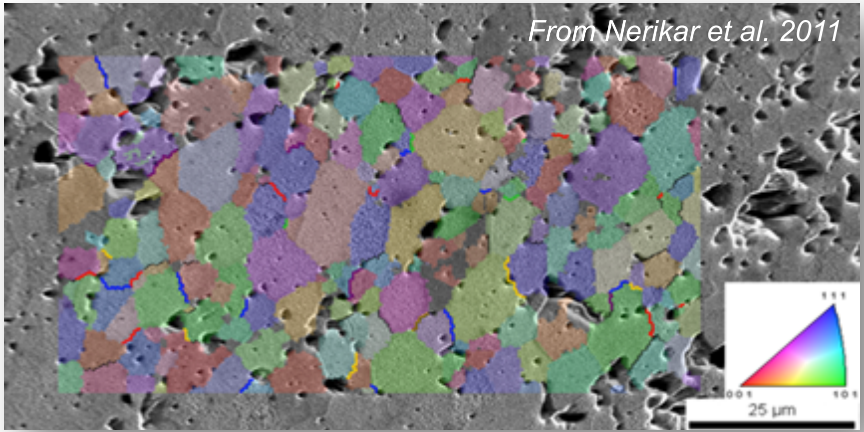


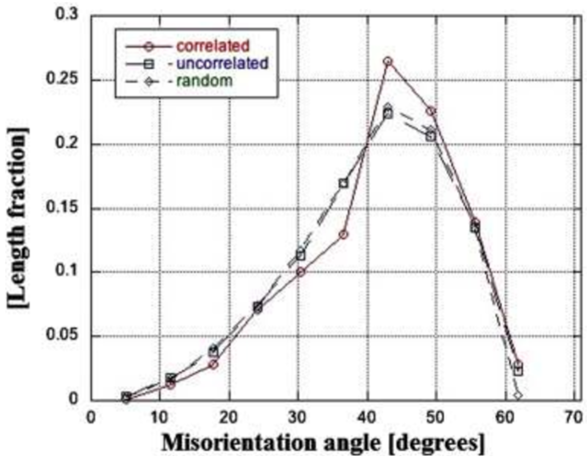




The Hillert distribution is an analytical distribution for grain size. Real materials often vary from this behavior

# The average grain size of the fuel has a significant impact on its behavior

- Typical LWR fuel as an initial average grain size of about 10 microns

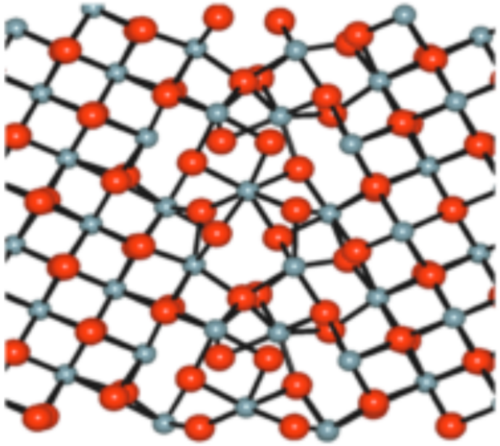



- The average grain size impacts
  - Fission gas release
  - Swelling
  - Thermal conductivity
  - Creep

# Diffusion often occurs faster along grain boundaries than in the perfect crystal

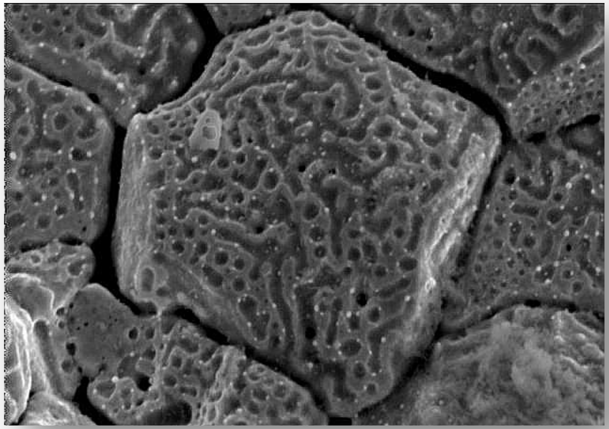
- Grain boundaries have more space than the perfect lattice
- So, atoms diffuse faster along grain boundaries than through the perfect lattice
- This means that grain boundary, or intergranular, diffusion increasingly dominates volume, or intragranular, diffusion as the temperature is reduced.
- Grain boundary vacancy diffusion has a large impact on creep



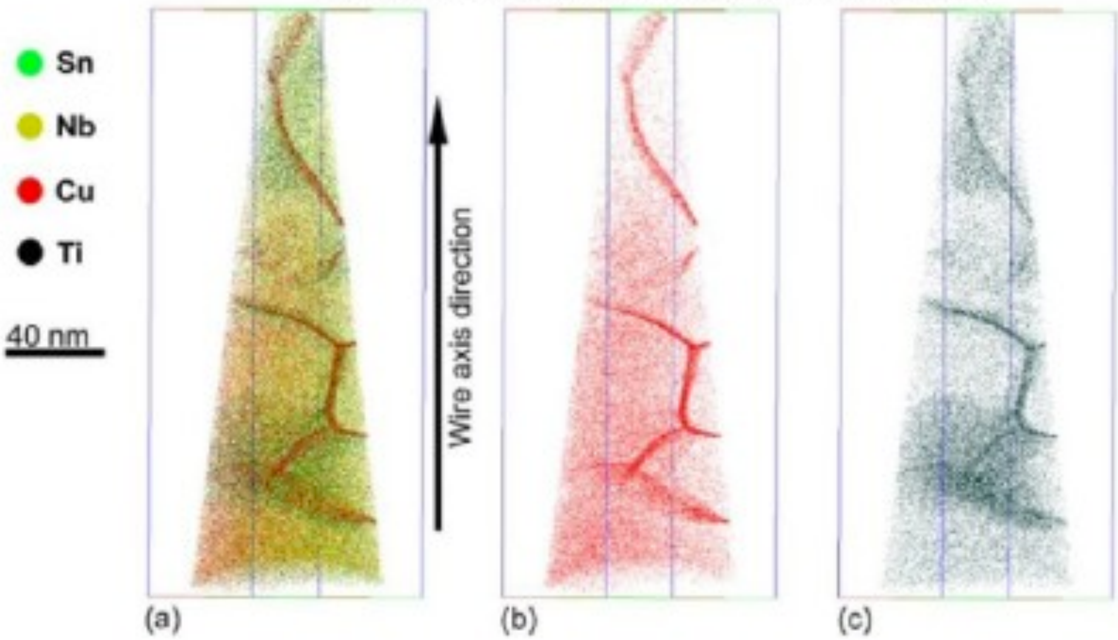
# Impurity atoms (such as fission gas) and other defects move to grain boundaries

- Due to grain boundaries having more open space, impurity atoms have a lower energy when they are on grain boundaries.
- This is called **grain boundary segregation**

Brohan 2000



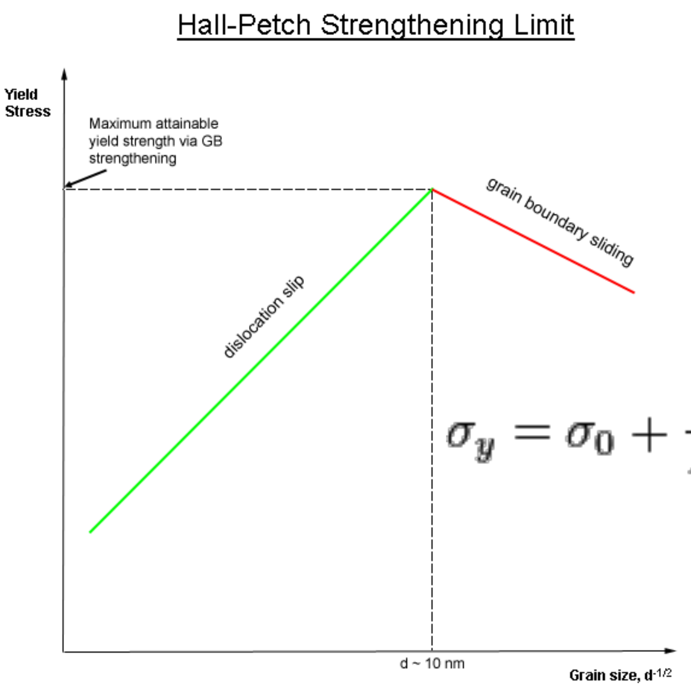
M J R Sandim Supercond. Sci. Technol. 26 (2013) 055008



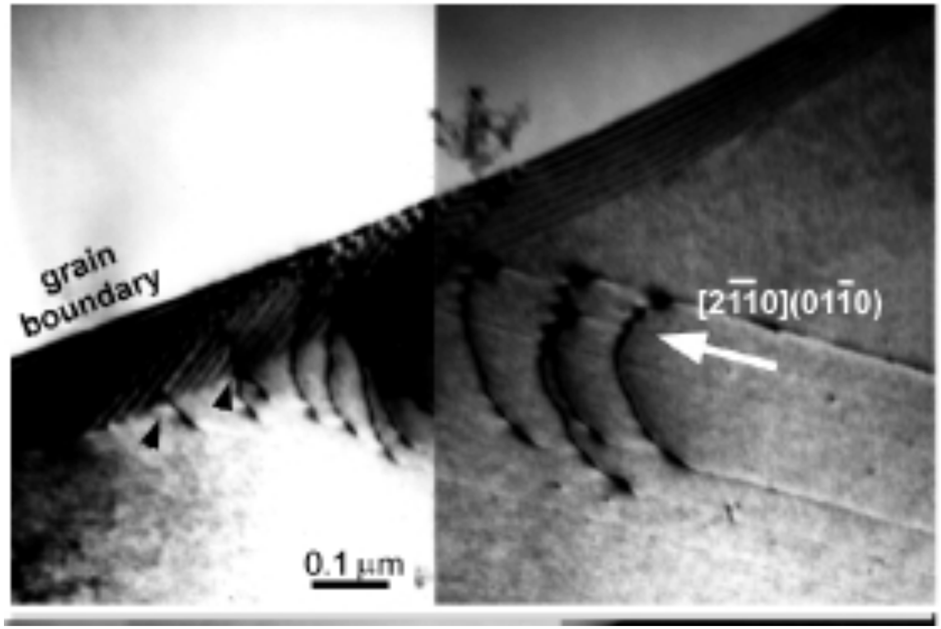

APT reconstruction : (a) elements mapped in the sample and (b) and (c) show only Cu and Ti

# Grain boundaries impede dislocation motion

- The number of dislocations within a grain impact how easily dislocations can traverse grain boundaries and travel from grain to grain.
- So, by changing grain size one can influence dislocation movement and yield strength.
- This is called the Hall-Petch effect

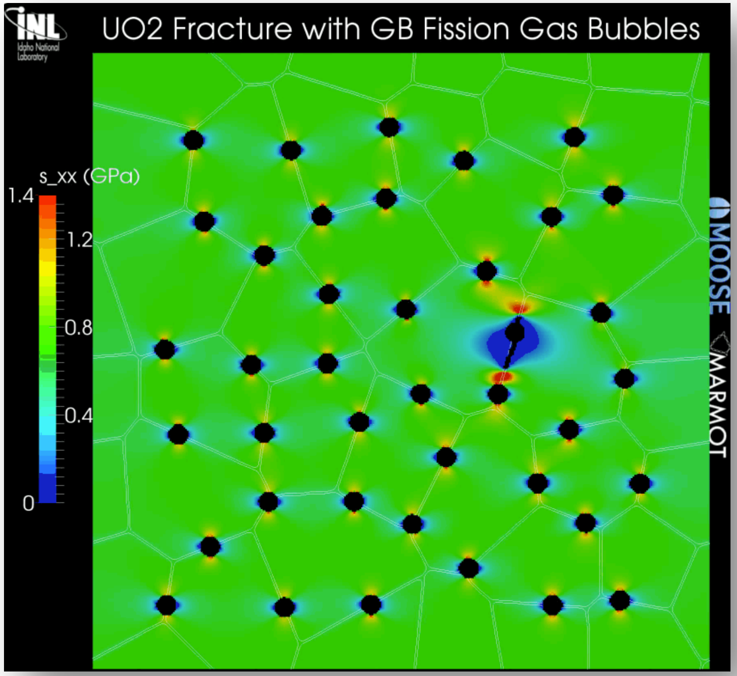



$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$



# Materials often crack along grain boundaries

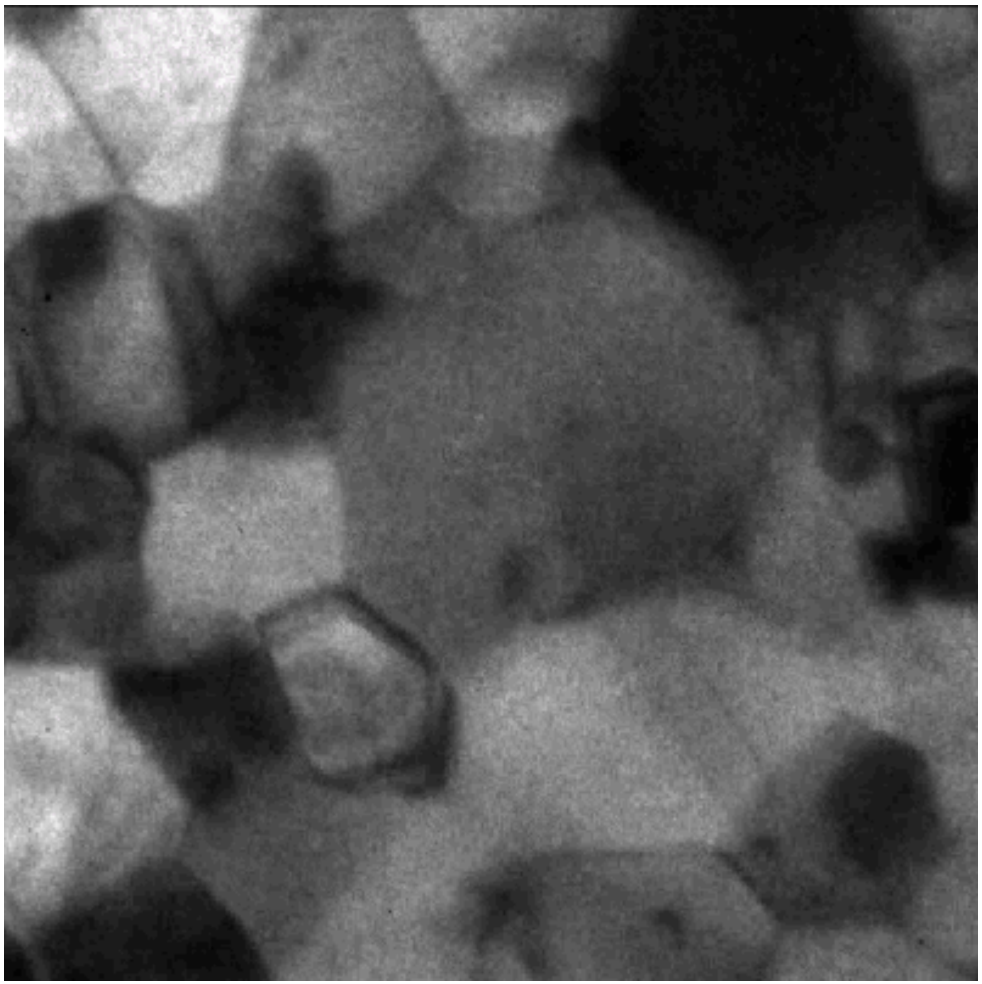
- Grain boundaries can be weaker than the perfect lattice.
- Thus, fracture will often occur along grain boundaries (intergranular fracture)




# However, the grain size doesn't remain constant. It increases with time

- A single crystal has a lower energy state than a polycrystal, due to the grain boundary energy.
- So, grain boundaries migrate to reduce the energy
- $v_{GB} = M_{GB}\,(P_d - P_r)$
  - $M_{GB}$ is the grain boundary mobility
  - $P_d$ is the driving force (pressure) for grain growth
  - $P_r$ is the pressure resisting grain growth

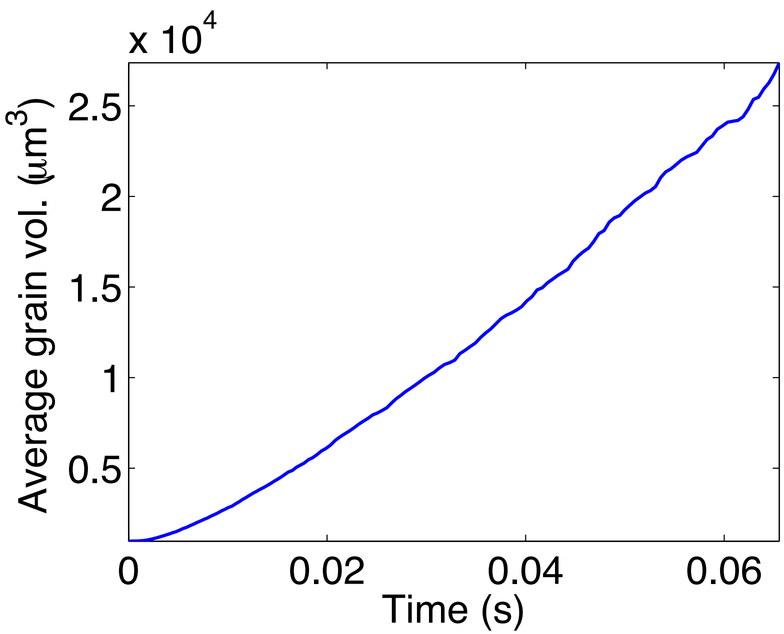
# In Situ TEM movie of grain growth in iron

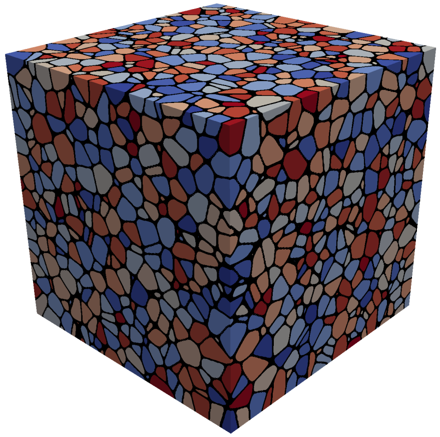


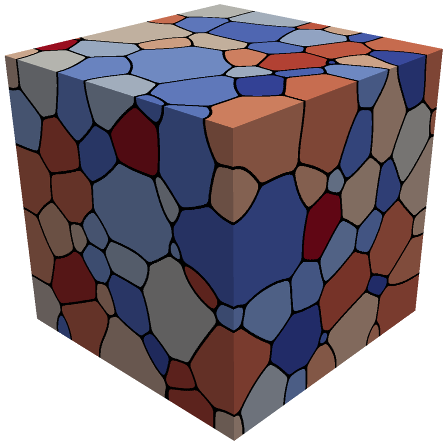
TEM video of in-situ annealing of a Fe nanocrystalline thin film sample (10x speed) from Professor Mitra Taheri's group at Drexel University. Experiment performed by grad student Greg Vetterick.

# Due to grain boundary migration, the average grain size goes up with time

- As grain boundaries migrate, some grains grow and some shrink
- Shrinking grains eventually disappear
- The average grain volume $\bar{V}_{gr} = V_{mat}/N_{grains}$
- Therefore, as $N_{grains}$ decreases due to grain disappearance, the average grain volume goes up.





# The grain boundary mobility is a function of temperature and GB type

- The grain boundary mobility is determined according to
  - $M_{GB} = M_0 e^{-\frac{Q}{k_b T}}$ m$^4$/(J s)
  - $k_b$ = 8.6173303e-5 ev/K is the Boltzmann constant
- Both the prefactor $M_0$ and the activation energy Q change as a function of the grain boundary misorientation
- We often use an average grain boundary for a material, taken from polycrystal measurements.

| Material | $M_0$ (m$^4$ /(J s)) | Q (eV) |
|---|---|---|
| $UO_2$ | 4.6e-09 | 2.77 |

- What is the mobility of $UO_2$ at 1600 K?

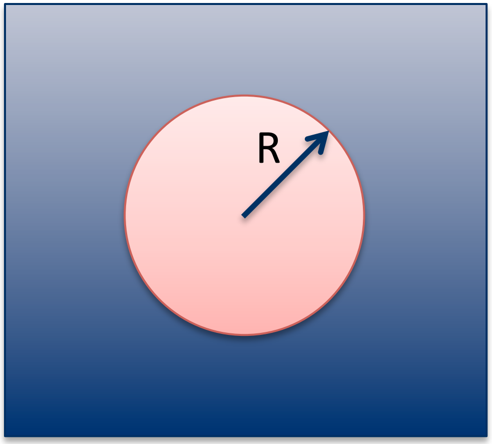
- $M_{GB} = M_0 \exp(-Q/(k_b T))$
- $M_{GB}$ = 4.6e-9*exp(-2.77/(1600*8.6173303e-5)
- $M_{GB}$ = 8.7e-18 m$^4$/(J s)

# There are various driving forces for grain growth

- The most common driving force is the reduction of grain boundary energy
  - $P_d = \frac{\gamma_{GB}}{R}$, where $\gamma_{GB}$ is the GB energy and R is the radius of curvature
  - It is often called the curvature driving force, because it drives grain boundaries to be straight.
  - It also causes larger grains to grow at the expense of smaller ones
- Other driving forces include
  - Temperature gradients
  - Elastic energy gradients
  - Dislocation energy gradients
  - Magnetic free energy density gradients

# In class problem: Grain boundary migration of a circular grain

- Consider a cylindrical grain imbedded in a larger grain, with only the curvature driving force present.
- Will the grain shrink or grow?
- Derive an expression for the rate of change of the volume of the circular grain




$$v_{GB} = M\frac{\gamma_{GB}}{R}$$

**Solution:**

$$V = \pi R^2 h$$

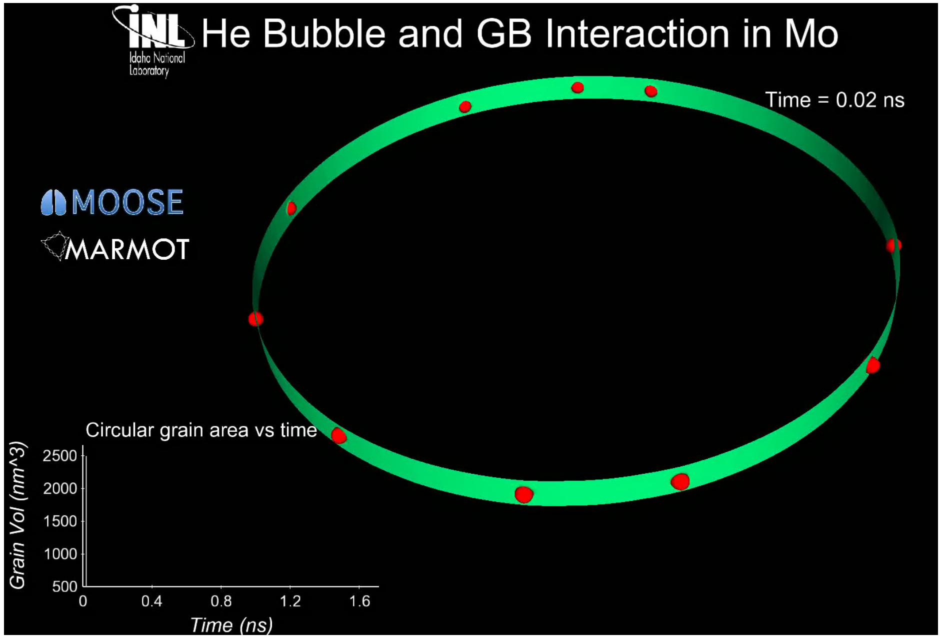
$$\dot{V} = 2\pi R h \dot{R}$$

$$\dot{R} = v_{GB} = M\frac{\gamma_{GB}}{R}$$

$$\dot{V} = 2\pi h M \gamma_{GB}$$

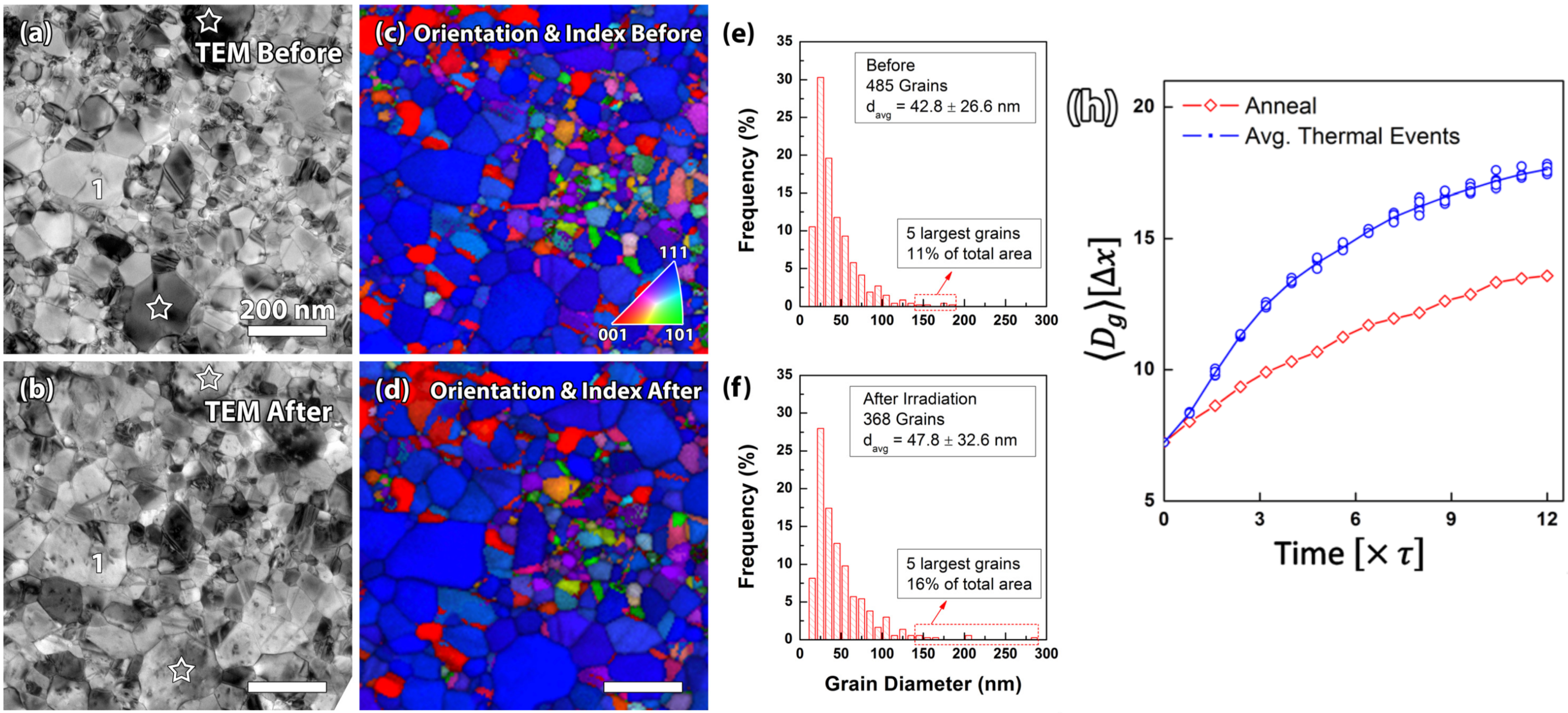
# Grain boundary motion is inhibited by pores, precipitates, solute atoms, etc

- Solute atoms (whether in interstitial sites or vacancies) can decrease the grain boundary mobility.
  - This is called **Solute Drag**
  - Even a small concentration of impurities can decrease the mobility by 3 to 4 orders of magnitude
- Particles and pores resist grain boundary motion



# Irradiation can accelerate grain growth, but it is only significant with small grains and low temperature

Grain growth with in situ ion irradiation




Bufford et al. 2016

# A more pragmatic approach to grain growth is to set a max grain size where growth will stop

- Why would grain growth every stop?
- Consider a material with an average grain size D
- The change in D can be written as

$$\frac{dD}{dt} = k\left(\frac{1}{D} - \frac{1}{D_m}\right)$$

  - $k = 2\, M_{GB}\, \gamma_{GB}$ is a rate constant that can be determined from experiments
  - $D_m$ is the grain size at which the driving force equals the resistive pressure
- For $UO_2$ (taken from Ainscough et al., 1973)

| Material | $M_0$ ($m^4$ J/s) | Q (eV) | $\gamma_{GB}$ (J/$m^2$) |
|---|---|---|---|
| $UO_2$ | 4.6e-09 | 2.77 | 1.58 |

- $D_m$ is a function of temperature $D_m = 2.23 \cdot 10^3\ \exp(-7620/T)$ microns

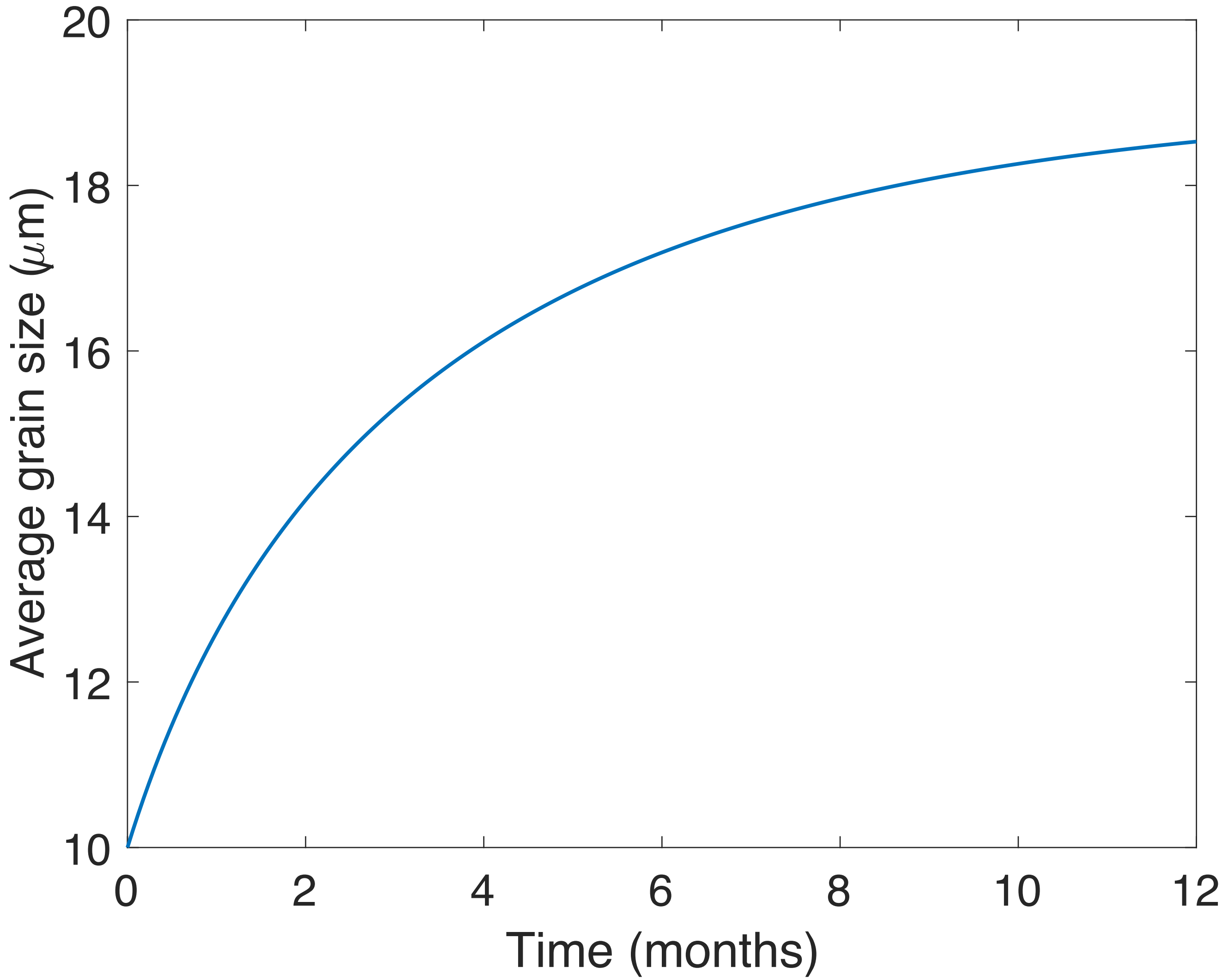
# What is the average grain size of the fuel in the center of the fuel rod after 1 year?

- A fuel pellet has an initial grain size of 10 microns and the centerline temperature is 1600 K.
- We need to solve our ODE:

$$\frac{dD}{dt} = k\left(\frac{1}{D} - \frac{1}{D_m}\right)$$

- With $M_{GB}$ = 8.7e-18 $m^4/(J\ s)$
- $k = 2\ M_{GB}\ \gamma_{GB}$ = 2*8.7e-18*1.58 = 2.75e-17 $m^2/s$
- $D_m$ = 2.23e3*exp(-7620/T) = 2.23e3*exp(-7620/1600) = 19.05 microns
- We can't solve the ODE analytically, so we need to solve it numerically using backward Euler's method
  - $D(t+dt) = D(t) + dt\ k(1/D(t) - 1/D_m)$
- So, the first step would be
  - D(t + dt) = 10e-6 + dt 5.47e-17 (1/10e-6 – 1/19.05e-6)

# After one year, the average grain size has neared its maximum value



# Summary

- The average grain size in $UO_2$ impacts
  - Fission gas release
  - Swelling
  - Thermal conductivity
  - Creep
- The material wants to reduce its energy by having large grains grow at the expense of small grains
- Grain growth eventually stops due to other defects reducing the grain boundary migration