

TOPIC: GRAIN GROWTH AND PARTICLE COARSENING KINETICS

Group Number 3

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Research paper referred:

Kinetics of Normal Grain Growth Depending on
the Size Distribution of Small Grains

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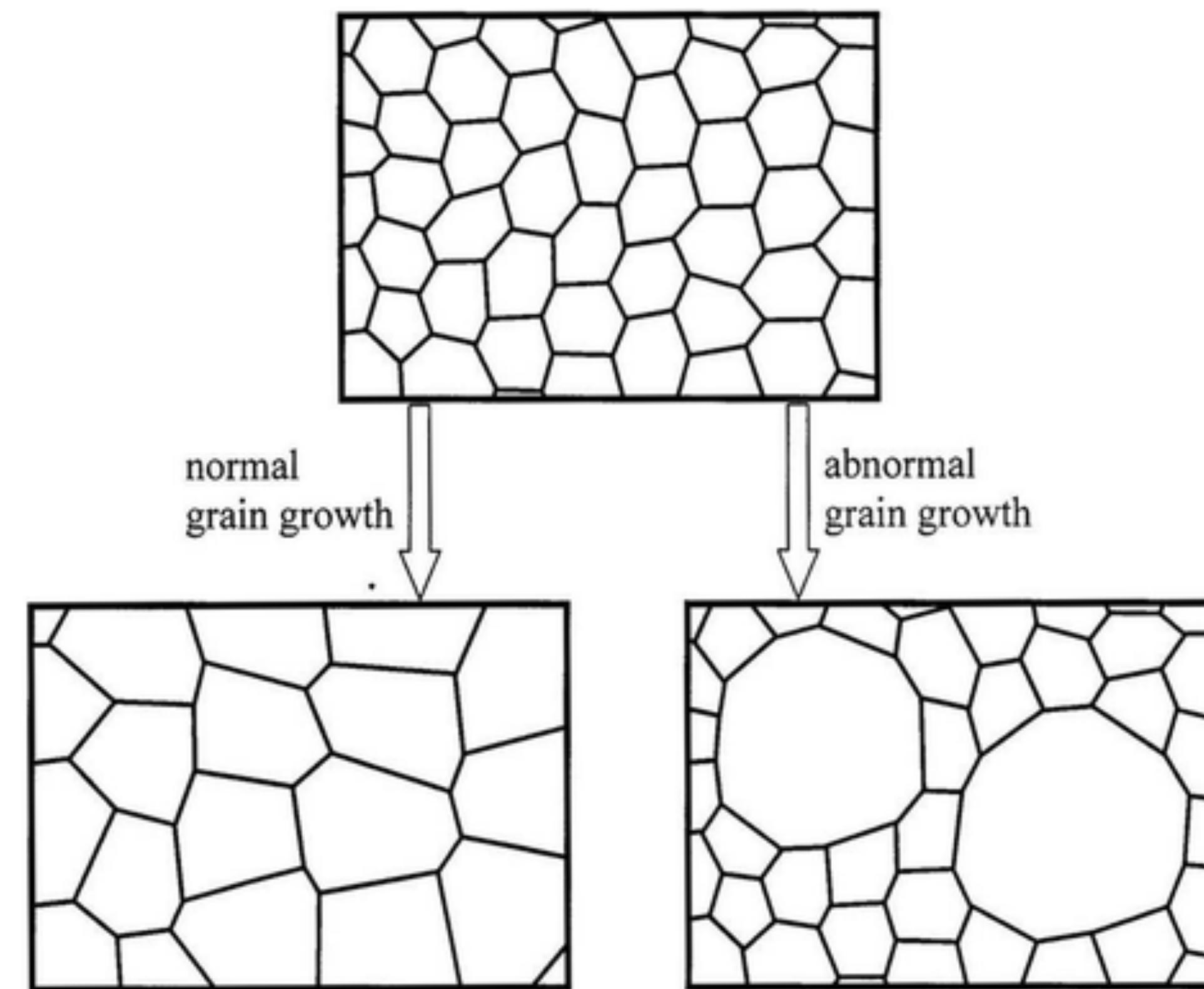


TOPICS COVERED

- Basics of Grain growth and annealing
- Growth kinetics by Grain annihilation
- Particle coarsening
- Ostwald Ripening: thermodynamical perspective
- Particle coarsening kinetics (Ostwald Ripening: kinetic perspective)
- Experimental observations
- Conclusion

INTRODUCTION

- **Normal grain growth:** In normal grain growth, the average grain size increases with time but the grain-size distribution remains self-similar (invariant in time).



- The kinetics of normal grain growth is given by this equation:

$$\langle R \rangle^n - \langle R \rangle_0^n = kt$$

where:

t = time

$\langle R \rangle$ = Average grain radius at t

$\langle R \rangle_0$ = Average grain radius at $t=0$

n = grain growth exponent

k = kinetic coefficient

- Despite a variety of analytic methods, most of the studies predict the value of n as 2.
- In the studies giving $n=2$, however, the obtained size distributions of grains in a steady state are various.
- This implies that there is NO RELATIONSHIP between grain growth exponent (n) and the size distribution. However, it is found that this is not a rigid fact.
- In this research topic, we examine the relationship between grain growth kinetics and size distribution in a steady state.

BASICS OF GRAIN GROWTH

- Grain Growth is a part of Annealing process, it's the last stage of the process.
- Annealing is a heat treatment that alters the physical and sometimes chemical properties of a material to increase its ductility and reduce its hardness, making it more workable.
- Grain growth is the term used to describe the increase in the average grain size of a polycrystalline material.
- Driving force for grain growth is the reduction of grain boundary surface energy.

Reduction in Grain Boundary Surface Energy due to Grain Growth

- Let the initial Grain size be = D_i

- Let the final Grain size be = D_f

	Initial	Final
Volume	$\pi(D_i)^3/6$	$\pi(D_f)^3/6$
Grain Boundary surface area/grain	$\pi(D_i)^2/2$	$\pi(D_f)^2/2$

► Grain boundary surface area/ Volume

$$= (\pi(D)^3/6) / (\pi(D)^2/2$$

$$= 3/D$$

► Change in GB surface energy per unit volume is given as:

$$3/D_f - 3/D_i$$

► This value is less than 0.

► Reduction in Grain boundary energy per unit volume = **Driving force for Grain Growth**

$$= \{ 3/D_f - 3/D_i \} * \gamma$$

(Where γ is GB energy per unit area)

GROWTH KINETICS BY GRAIN ANNIHILATION

- The minimum number of faces available for 3D grains is 4- a tetrahedral.
- Almost all of the grains with extremely small sizes are tetrahedra prior to annihilation.
- Normal grain growth occurs through the annihilation of small grains with 4-faces in a 3-dimensional (3D) polycrystalline structure.

- Von Neumann-Mullins law: *when a grain boundary migrates with a driving force originating from its curvature, the growth rate dR^2/dt of grains with radius R in a 2-dimensional (2D) polycrystalline structure depends solely on the number of the grain edges.*
- Mullins later extended the law to 3D, and derived an equivalent relation between the growth rate and the number of faces.
- Although the relation varies depending on the shape of the component polygonal faces, it holds for the mean value of grains with the same number of faces and was verified by a 3D simulation of grain growth.
- the growth rate dR^2/dt is regarded as a constant for tetrahedra.
- Then, the grain radius R_h , below which the tetrahedra disappear during an infinitesimal time of Δt , is obtained as $R_h^2 = c\Delta t$ where c is a constant.
- And the disappearance of the tetrahedra smaller than R_h causes eventually grain growth.

- Now let me introduce a size function: $F(r) = ar^m$, which is a normalised size function around $r=0$.

Here: $F(r)$ =probability density function

$$r = \langle R \rangle / \langle R \rangle_0$$

a, m are constants

- The grain size distribution $F(r)$ is self-similar in a steady state, the normalised distribution holds the same form throughout the grain growth process.
 - The number of tetrahedra disappearing during time Δt is given by this equation:

$$\Delta N = -\beta N \int_0^{r_h} ar^m dr = -\frac{a\beta N}{m+1} {r_h}^{m+1}$$

- Where β is the ratio of total number of tetrahedra to the number tetrahedra with radius smaller than R_h

- Comparing ΔN with the initial stage ΔN_0

- We get:

$$\frac{\Delta N}{\Delta N_0} = \frac{N}{N_0} \left(\frac{R_h/\langle R \rangle}{R_h/\langle R \rangle_0} \right)^{m+1} = \frac{N}{N_0} \left(\frac{\langle R \rangle_0}{\langle R \rangle} \right)^{m+1}.$$

.....2

- For an average grain radius, we define:

$$(4/3\pi)\langle R \rangle^3 = V_T / N$$

.....3

Where V = total grain volume

N = number of total grains

- Rearranging; we get

$$\langle R \rangle^3 = 3V_T/(4\pi N)$$

.....4

- Conservation of the total grain volume gives a relationship of

$$N/N_0 = (\langle R \rangle_0 / \langle R \rangle)^3 \dots \dots \dots \textcolor{red}{5}$$

- Substituting this value in equation 2 gives us:

$$\Delta N / \Delta N_0 = (\langle R \rangle_0 / \langle R \rangle)^{m+4}.$$

- Another relationship between ΔN and $\langle R \rangle$ can be derived by differentiating equation 3:

- Thus we finally obtain:

$$\Delta \langle R \rangle / \Delta \langle R \rangle_0 = (\langle R \rangle_0 / \langle R \rangle)^m.$$

► Recall the kinetic equation:

$$\langle R \rangle^n - \langle R \rangle_0^n = kt$$

► Differentiating this equation, we get:

$$\Delta \langle R \rangle / \Delta \langle R \rangle_0 = (\langle R \rangle_0 / \langle R \rangle)^{n-1}.$$

.....8

► Recall equation 7:

$$\Delta \langle R \rangle / \Delta \langle R \rangle_0 = (\langle R \rangle_0 / \langle R \rangle)^m.$$

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► Comparing the two we finally obtain:

$$n = m + 1.$$

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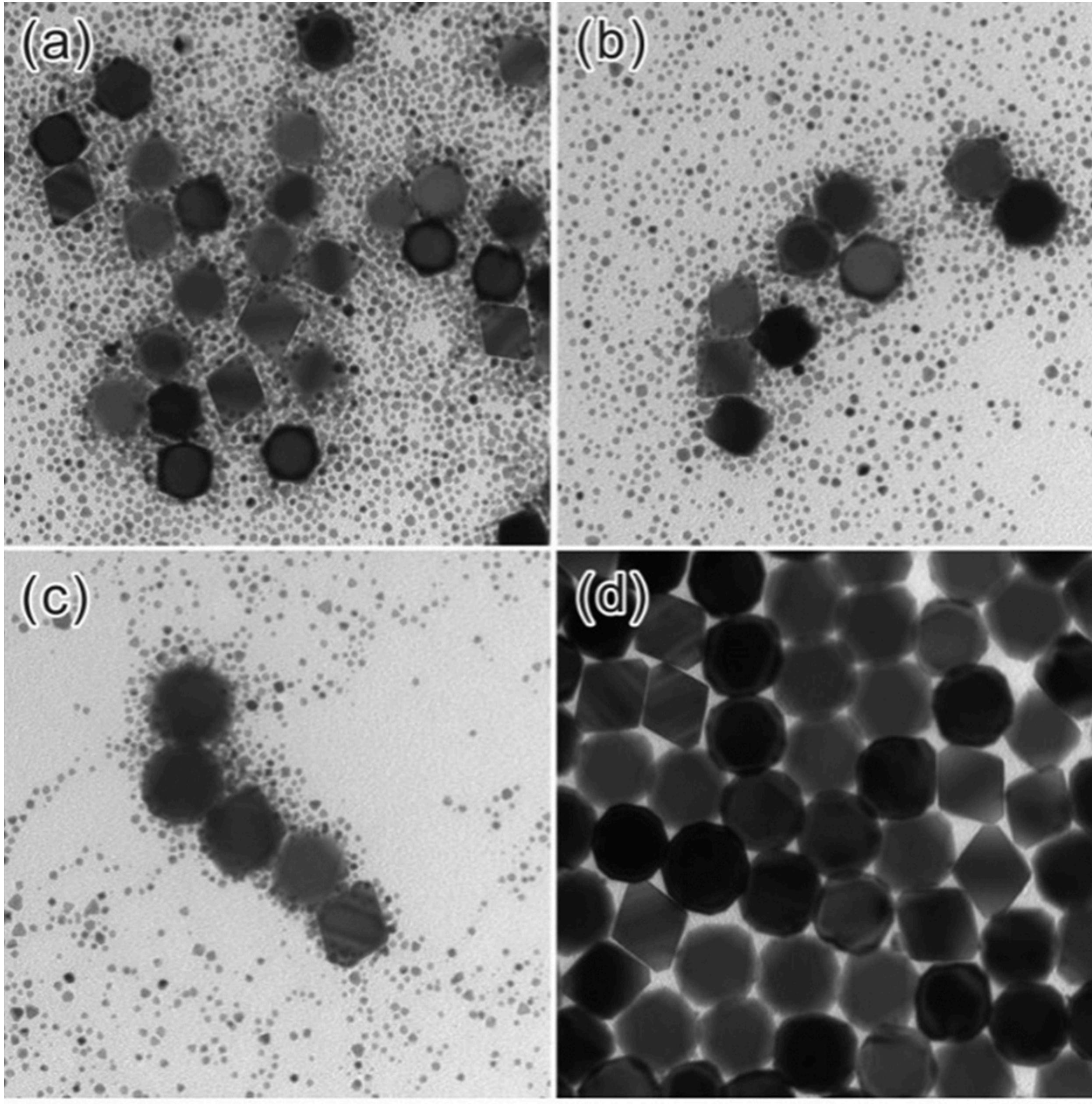
► Thus, we have related the grain growth kinetics and size distribution function.

PARTICLE COARSENING

A PROCESS ALSO CALLED OSTWALD RIPENING

INTRODUCTION

- Ostwald ripening is an observed phenomenon in solid (or liquid) solutions which describes the evolution of an in-homogenous structure over time
- The phenomenon was first described by Wilhelm Ostwald in 1896.
- When a phase precipitates out of a solid, energetic factors will cause large precipitates to grow, drawing material from the smaller precipitates, which shrink.



— 50 nm

Ostwald ripening in Pd **nanoparticles** dissolved in **formaldehyde** at 6 (a), 24 (b), 48 (c) and 72 hours (d). The small Pd particles are being consumed as the larger ones grow bigger.

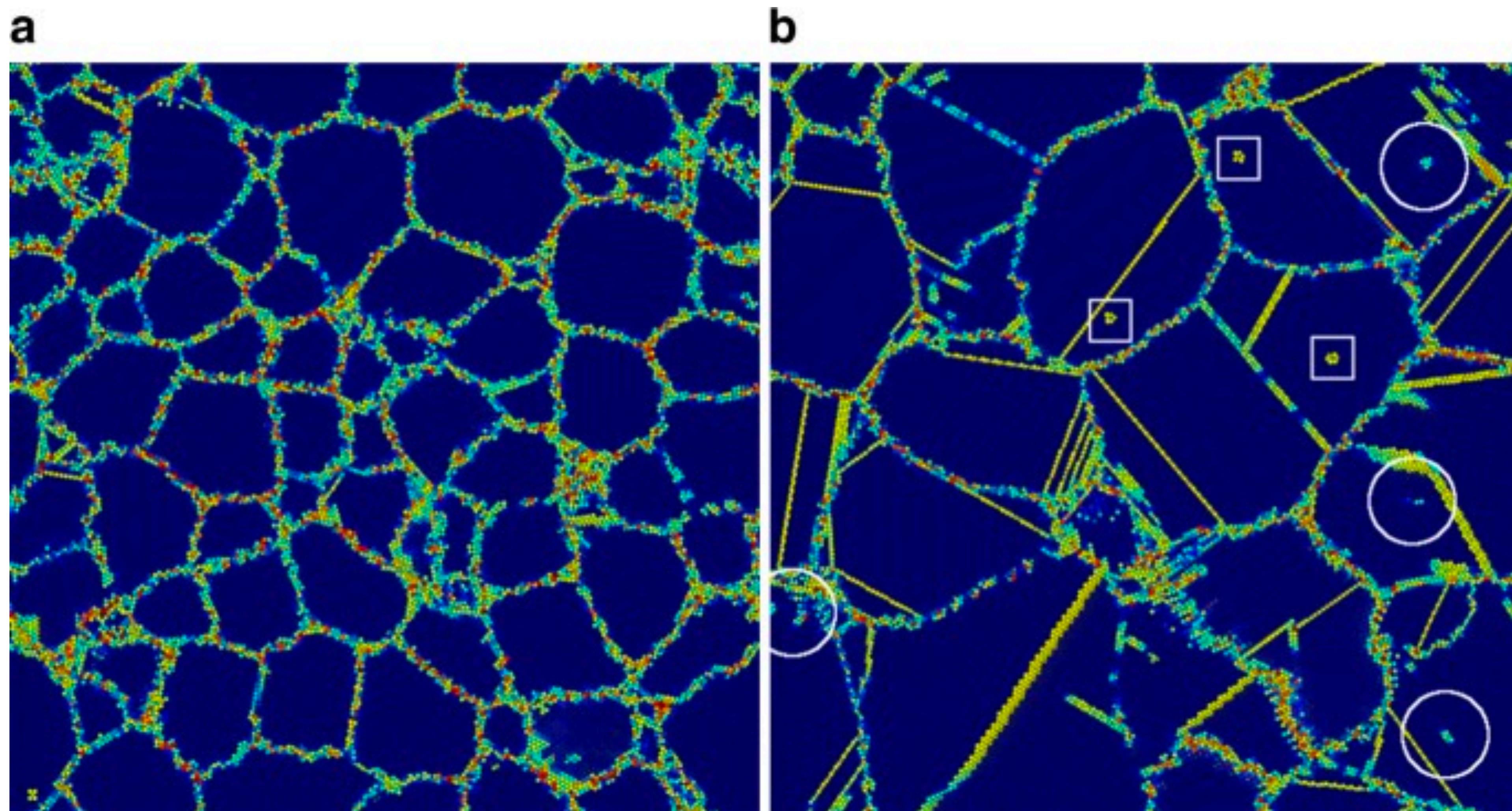
THERMODYNAMICAL PERSPECTIVE

- This **thermodynamically**-driven spontaneous process occurs because larger particles are more energetically stable than smaller particles
- This stems from the fact that molecules on the surface of a particle are energetically less stable than the ones already well ordered and packed in the interior
- Large particles, with their lower surface to volume ratio, results in a lower energy state (and have a lower **surface energy**).
- As the **system** tries to lower its overall energy, molecules on the surface of a small (energetically unfavorable) particle will tend to detach and diffuse through solution and then attach to the surface of larger particle. Therefore, the number of smaller particles continues to shrink, while larger particles continue to grow

DIFFUSION INVOLVED

- Concentration of the molecules around the interface of smaller particles is larger than the average concentration in bulk solution, resulting in net flux of molecules flowing from particle to the solution phase, leading to shrinking of the small particle.
- Reversely for the larger particle, where the local concentration around the interface is lower than average concentration in bulk solution, resulting in net flux of molecules flowing from the solution phase to the particle, thereby leading to growth of the large particle.
- Ostwald ripening: Larger particles grow at the expenses of smaller particles

DIFFUSION INVOLVED IN GRAIN GROWTH

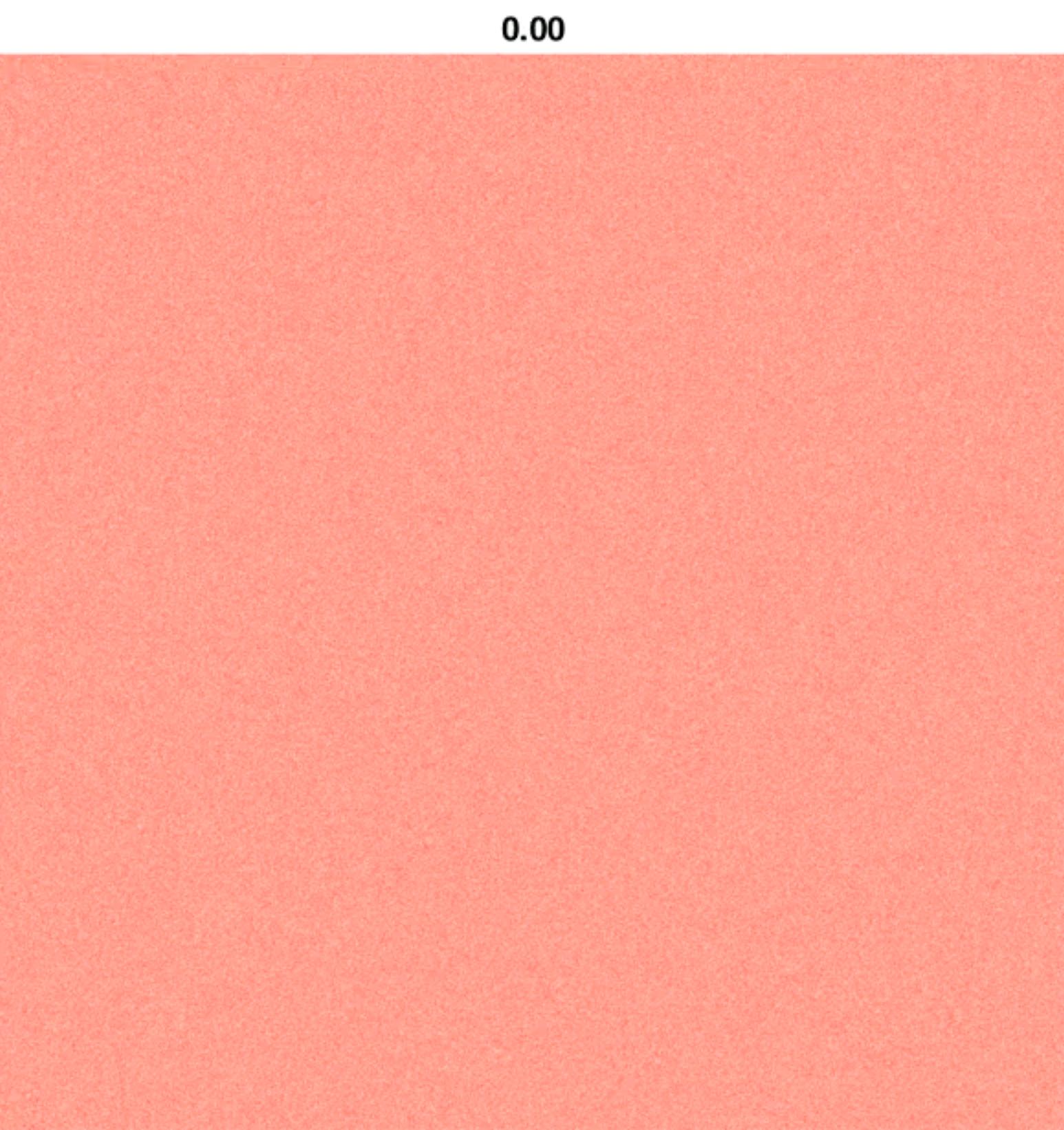


MECHANISM INVOLVED

- Small particles, droplets or protrudes are not stable. So, what usually happen for these small particles or protrudes on surface during the phase transformation? Two ways:
- fuse into other particles (or droplets) to form larger ones that possess lower energy, like you see in the case of small oil droplets in water.
- Dissolve themselves back to smaller clusters or even monomers (molecules or atoms), followed by depositing on the larger particles or flat or concave surfaces (wherever with lower surface energy). The result of such a process is smaller particles get smaller, while the larger ones get even larger. Growth of large particles at expense of small ones --- Ostwald ripening.

LIVE DEMO VIDEO

- A live video of particle coarsening.



Evolution of 2D li



OSTWALD RIPENING : PARTICLE COARSENING KINETICS

- Ostwald Ripening says that larger particles grow at the expense of smaller particles .
- The concentration gradient suggests how fast the particle coarsening can take place .
- Considering a two component, two phase alloy, A and B with phases, alpha and beta.
- Assumptions:
- The interfacial energy($\gamma_{\alpha\beta}$) is isotropic so that the precipitates are spherical particles of various radii.

We know that the chemical potential of a particle of radius a is given by

$$\mu_A = \mu_A^P + 2V\gamma/a \quad -(1)$$

Assuming A and B form an ideal solution

$$\mu_A = \mu_0 + RT\ln(x_A)a \quad -(2)$$

Equating (1) and (2)

$$\mu_A^P + 2V\gamma/a = \mu_0 + RT\ln(x_A)a$$

We get

$$\mu_A^P = \mu_0 + RT\ln(x_A)P \quad -(3)$$

Where,

$$(x_A) = (x_A)_P \exp(2VY \div RTa) \quad -(4)$$

Similarly, we also get for concentration

$$(c_A) = (c_A)_0 \exp(2VY \div RTa) \quad -(5)$$

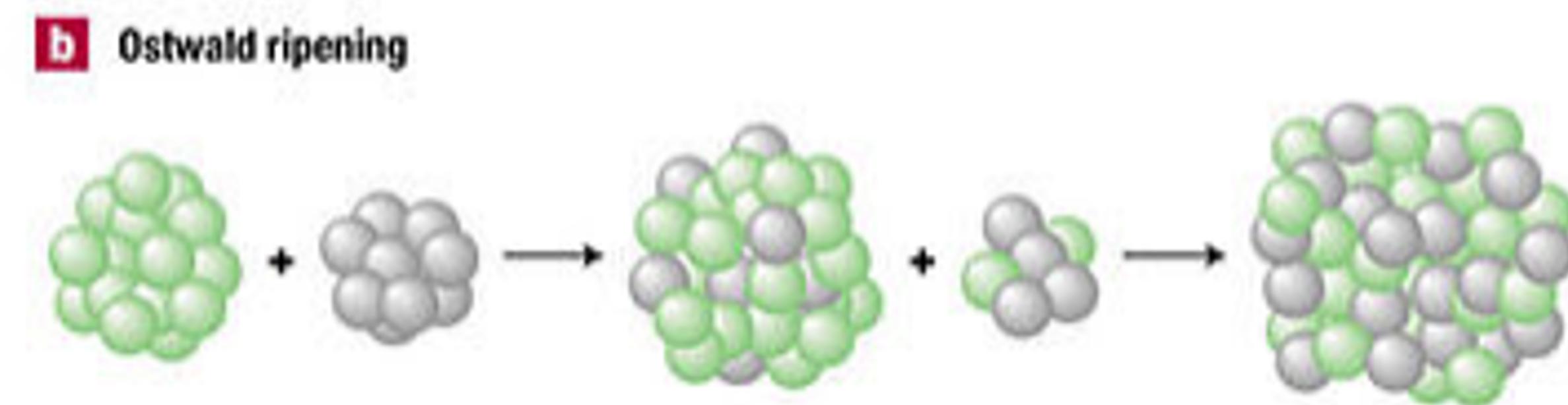
This equation clearly implies that particles that are small are surrounded by A rich phase while particles that are big are surrounded by A poor phase .

FUNDAMENTAL EQUATION OF OSTWALD RIPENING!

The particles with size smaller than the average particle size will shrink

The particles with size larger than the average particle size will grow.

$$\frac{da}{dt} = -\frac{2coD\bar{V}^2\gamma_{sl}}{RTa} \left(\frac{1}{a} - \frac{1}{\bar{a}} \right)$$



EXPERIMENTS

There were several experiments conducted to find out the relation between size distribution of grain and kinetics of grain growth.

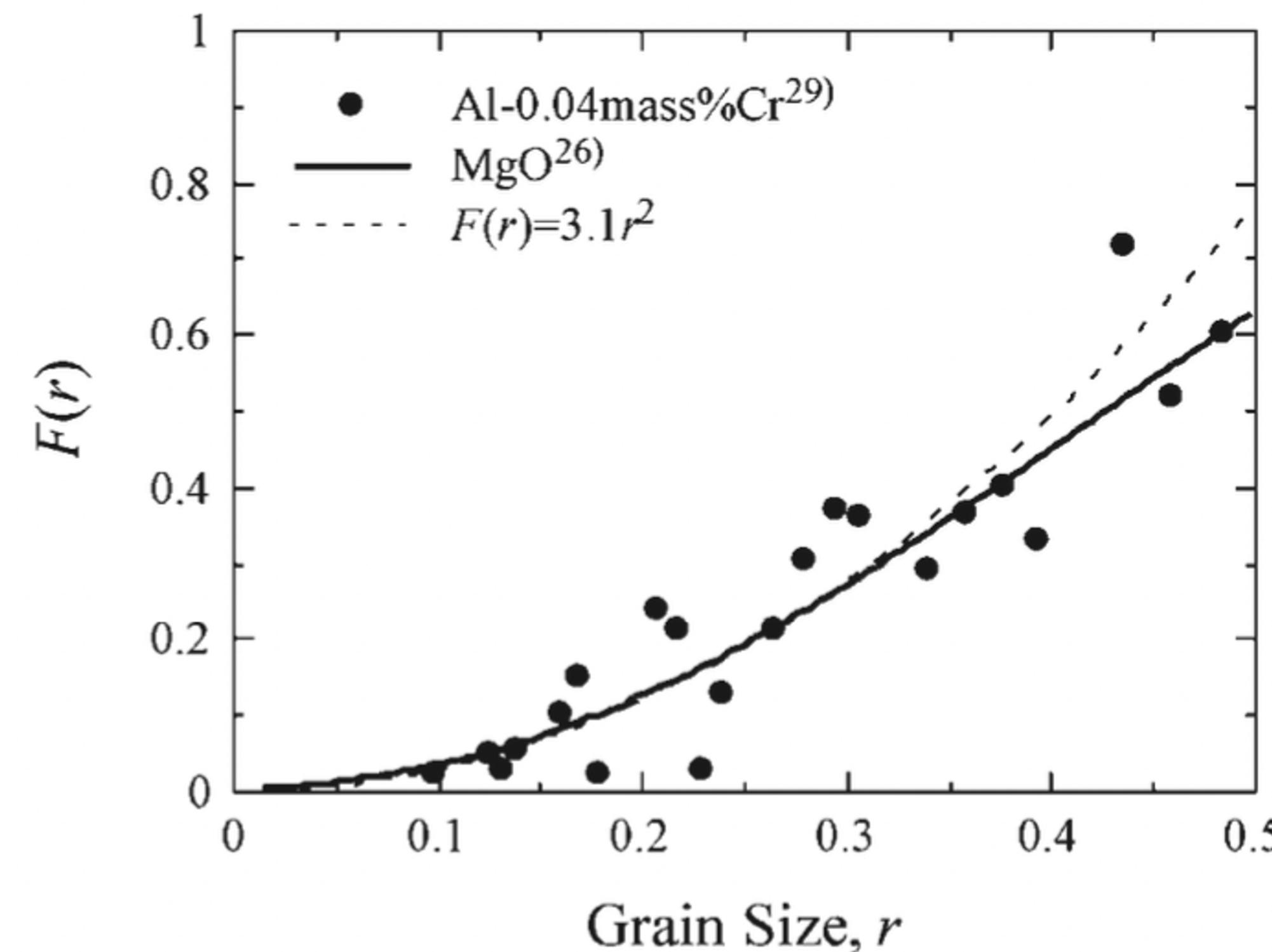


Fig. 3 Experimental size distributions of grains for MgO and Al-0.04 mass%Cr.

CONCLUSION

- The theoretical relationship between the kinetics of normal grain growth and the size distribution of small grains reveals that the grain growth exponent n is equal to $m + 1$, when the distribution of the normalized grain size r is proportional to r^m around $r = 0$.
- Although an infinite number of size distributions can exist in a steady state, the relationship $n = m + 1$ provides the criteria which should be satisfied.
- The present analysis is consistent with the size distributions which have been experimentally measured on the sectional surface of actual poly crystals.
- We also showed that the relationship, $n = m + 1$, holds for particle coarsening by Ostwald ripening.



THANK YOU