# MATE 664 Lecture 17

**Growth Phenomena: Coarsening**

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## Learning outcomes

After this lecture, you will be able to:

- **Recall** coarsening as a surface-energy-induced growth phenomenon
- **Recall** the main assumptions of coarsening theory
- **Identify** the competition between diffusion and reaction-rate control
- **Analyze** particle size distribution functions during coarsening

## Recap: continuous and discontinuous phase transformation

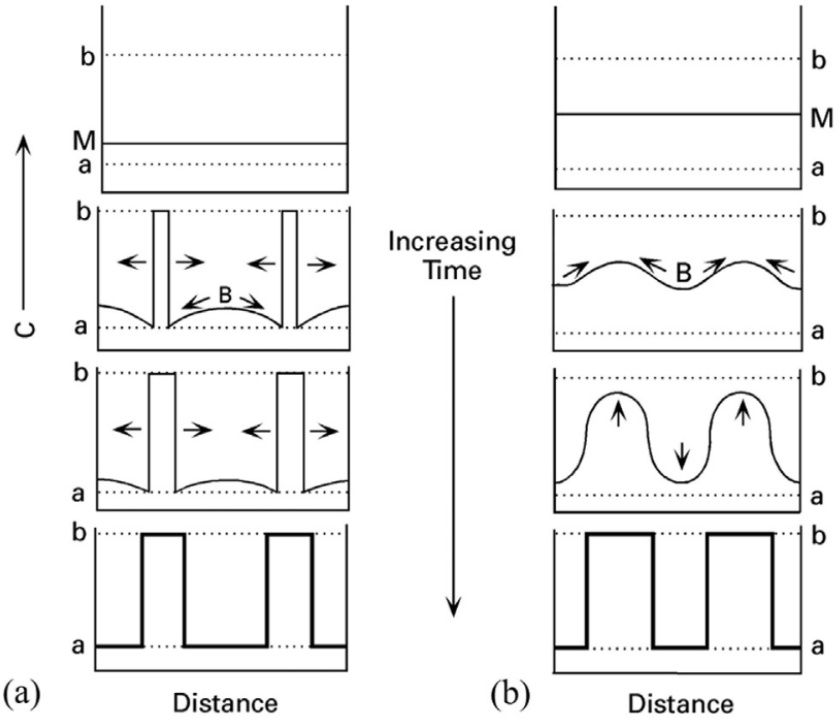
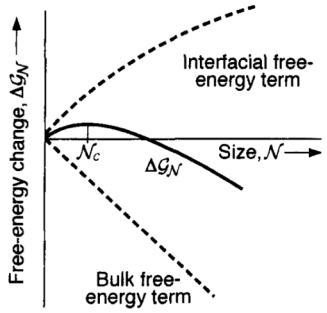



**Figure 13.6** (a) Droplet nucleation and (b) spinodal decomposition over time. *(Reproduced from Varshneya and Mauro [1]).*

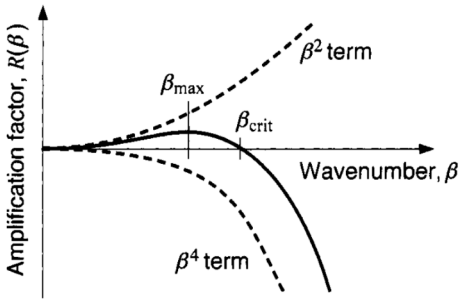
## Recap: growth barrier comparison

Nucleation




$$\Delta G_c = \frac{4}{27}\frac{(\eta\gamma)^3}{(\mu_\beta - \mu_\alpha)^2}$$

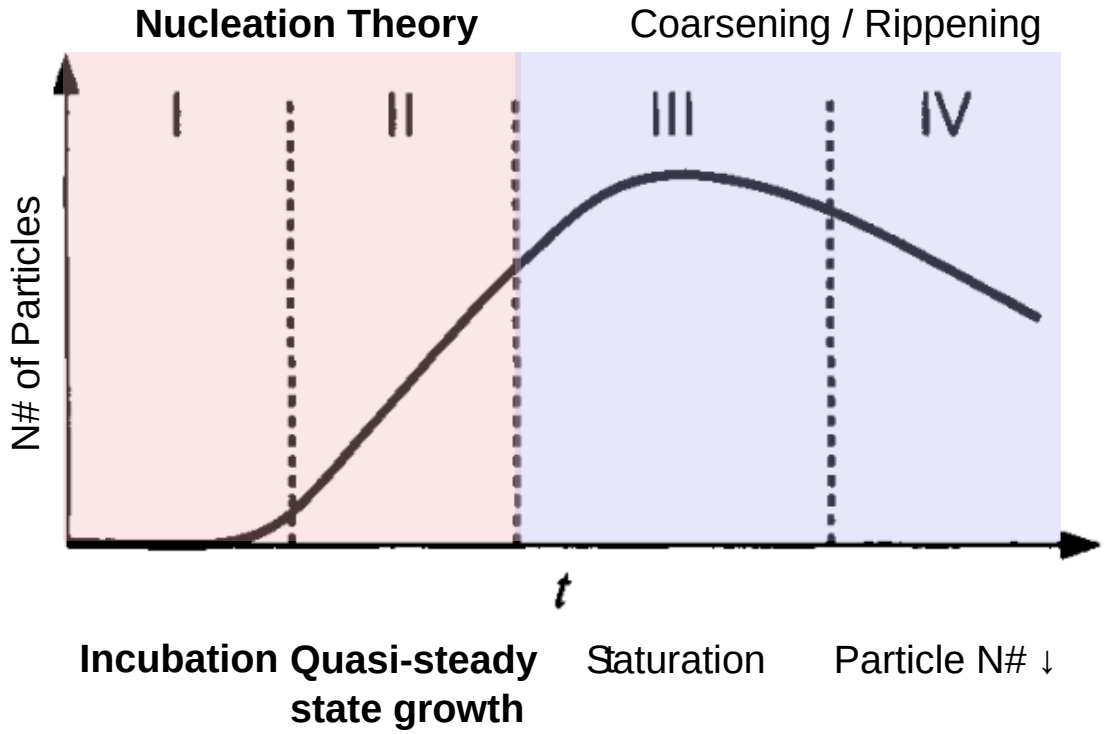
Spinodal decomposition




$$R(\beta) = -M_0\left(\frac{\partial^2 f}{\partial c_B^2}\beta^2 + 2\kappa\beta^4\right)$$

**Recap: growth stages in a nucleation process**

- What happens to stages III and IV? Coarsening process




**Coarsening: growth mechanism involving particle size distribution**

Pb-Sn alloy coarsening experiment shows that particle distribution remains almost constant (Stage III)

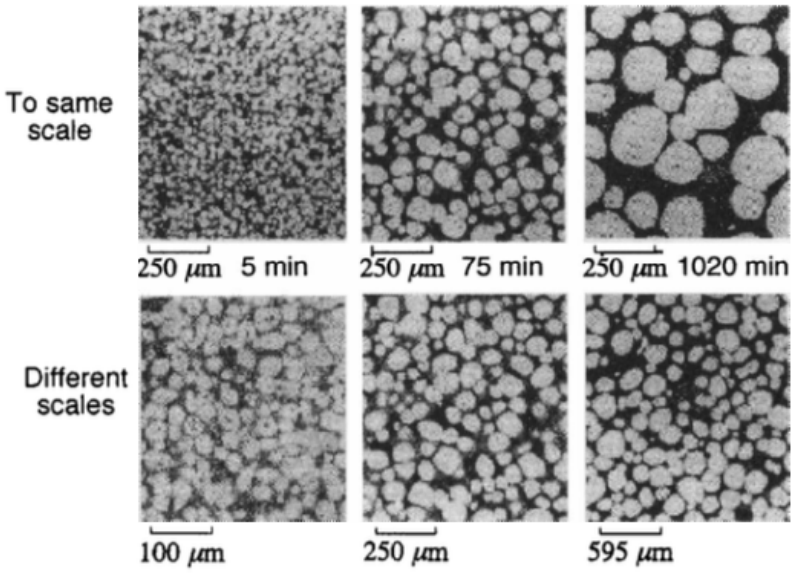



**Figure 15.6:** Particle distributions observed in coarsening experiments on semisolid Pb–Sn alloys. The volume fraction of particles is 0.64. The upper row shows a steady increase in mean particle size with aging time. The lower row is scaled so that the apparent mean particle size is invariant—demonstrating that the particle distribution remains essentially constant during coarsening. From Hardy and Voorhees [7].

Figure 1: *Metall. Trans.*, 1988, 19A, 2713-2721

## Another angle: Ostwald ripening

Experimental observation of small Pt particles are "absorbed" by the larger particles (Stage IV)

**Fig. 3. TEM images of Pd octahedra obtained after ripening for different periods of time: (a) 6 h, (b) 24 h, (c) 48 h, and (d) 72 h.**

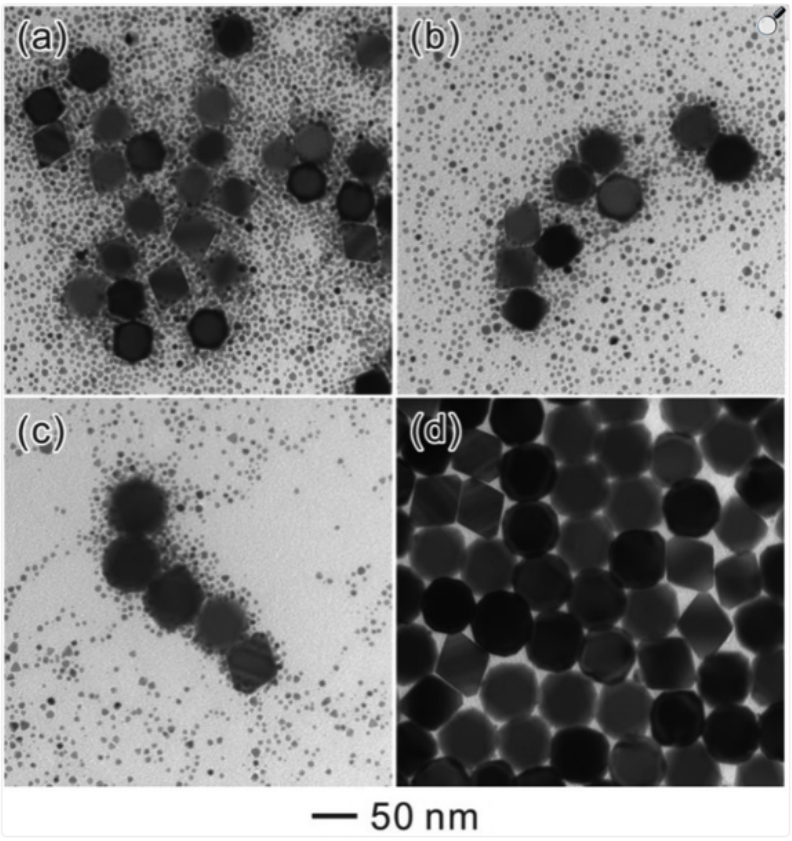



Figure 2: *Chem Sci.* 2015, 6, 5197-5203

## Analog: two-balloon experiment

- The effect of curvature on the total free energy is analogous to the two-balloon experiment
- The driving force is **capillarity**
- YT Video

## Capillarity as a driving force

The term "capillarity" refers to a broad variety of phenomena involving the interface

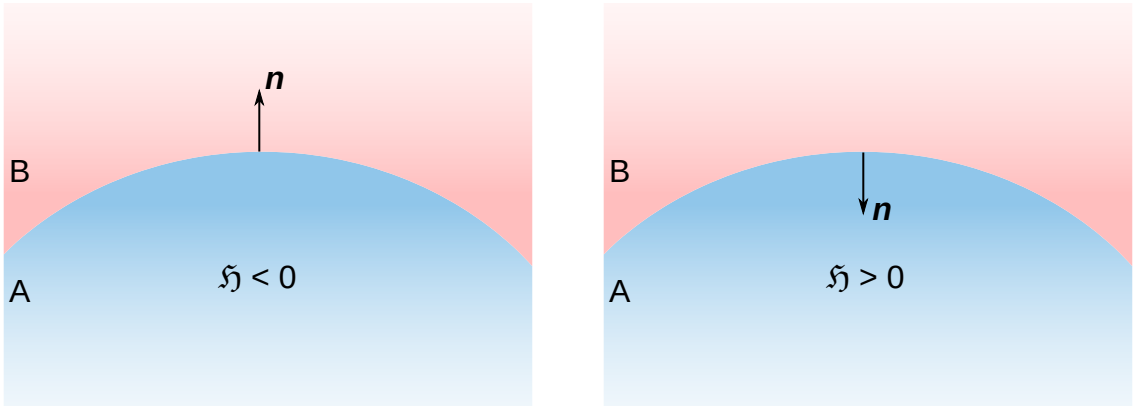
- Excess free energy caused by surface energy + curvature
- Driving force: minimizing interfacial area
- Morphology change: interfaces will move during the optimization process

– **Coarsening**: large particles "absorb" small particles; particles *do not touch*
– **Coalescence/sintering**: interface between close-contact particles disappear; particles *touch and merge*

## Crash course: interfacial coordinate system

For the interface between A and B that has no parallel movement, the curvature $H$ depends on the direction of the normal vector $\mathbf{n}$, so that

$$p_{\mathrm{A}} - p_{\mathrm{B}} + 2H\gamma = 0$$



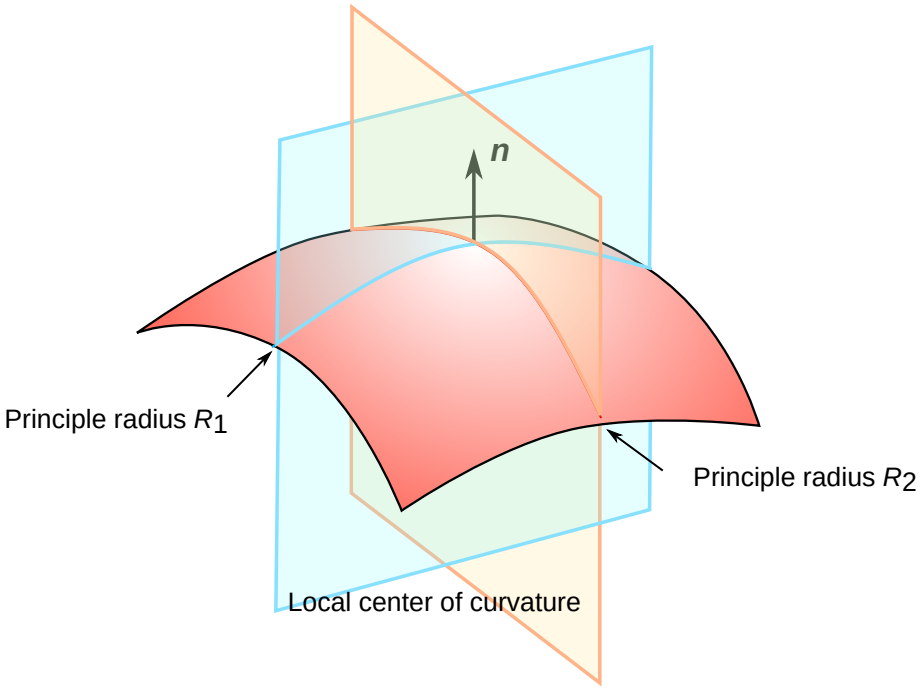

in either definition, $p_A > p_B$ (makes sense?)

## Crash course: interfacial curvature

The surface curvature (H) can be expressed using the two principle radii (R_{1}) and (R_{2}) of the surface:

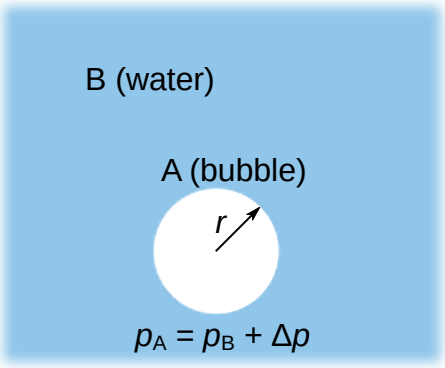
$$|H| = \frac{1}{2}(\frac{1}{R_1} + \frac{1}{R_2}) \tag{1}$$

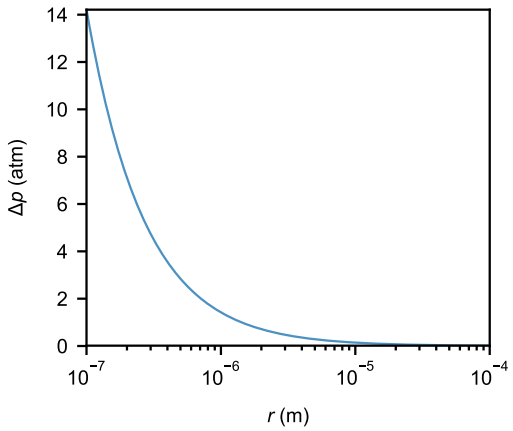
$$= \frac{1}{2}(\kappa_1 + \kappa_2) \tag{2}$$




**Capillary force: water droplet situation**

Nanoscale droplet will have excessive pressure!



## Capillarity as driving force: high level description

The driving force from capillarity $\delta f$ is generally the energy change caused by the volume swept out by the interface, so that

$$\delta f = \gamma(\kappa_1 + \kappa_2) \tag{3}$$

The driving force has 2 factors:

- non-zero surface energy $\gamma$:
- curvatures $\kappa_1$, $\kappa_2$ ($\propto 1/R$)

## Coarsening (Ostwald ripening)

The evolution of an inhomogeneous structure in a solid solution or a colloidal system (stages III and IV)

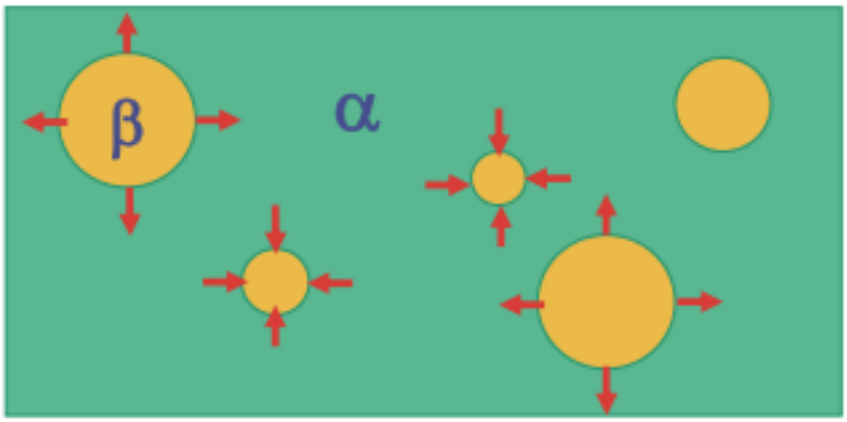
- **Feature**: small particulates dissolve, and redeposit onto large particulates.
- **Driving force**: minimization of total interfacial energy.
- **Mass transport**: driven by curvature-dependent surface potential.
- **Size** and **number** of particles change with time.

## Classical mean-field theory of coarsening

- Most prominent theory LSW theory (**L**ifshitz-**S**lyozov-**W**agner, 1961)
- Spherical $\beta$ particles embedded in $\alpha$ matrix in A-B mixture

Key take-aways:

1. Eq. concentration at interface: increase on smaller particles
2. B atoms: small particle –> matrix –> large particle
3. Smaller particles shrink; larger particles grow




### Influence of curvature on free energy: Gibbs-Thompson effect

From our balloon analog, curvature-induced pressure for an isotropic sphere is:

$$\Delta p = p_A - p_B = \gamma(\kappa_1 + \kappa_2) = 2\frac{\gamma}{R}$$

By adding an B particle in to the $\beta$ phase, the change of volume is $\Omega_B$ and there is an increase of free energy $2\frac{\gamma\Omega_B}{R}$. The interfacial concentration $c_B^{\text{eq}}(R)$ is then higher than $c_B^{\text{eq}}(\infty)$

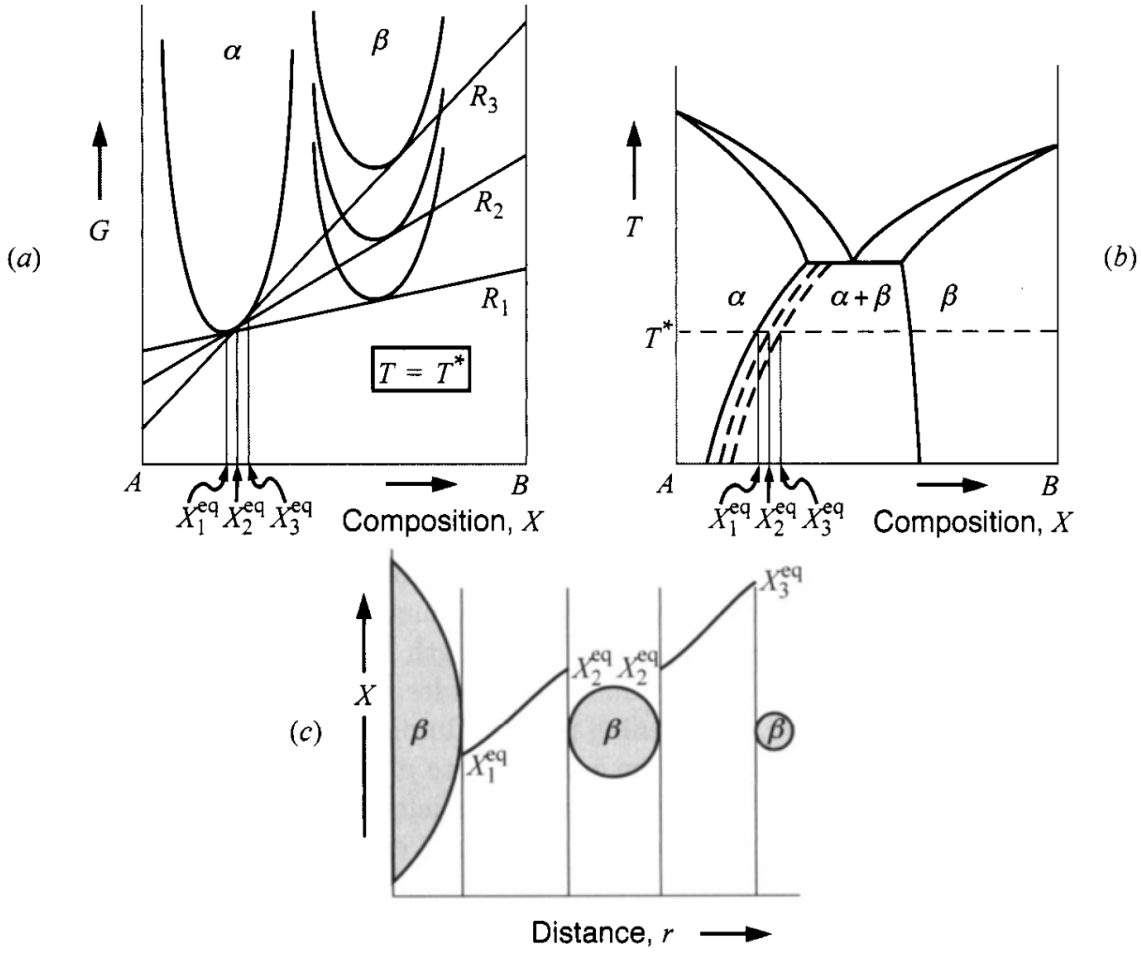
$$c_B^{\text{eq}}(R) = c_B^{\text{eq}}(\infty)\exp(\frac{2\gamma\Omega}{k_B T R}) \tag{4}$$

$$\approx c_B^{\text{eq}}(\infty)\left[\exp(\frac{2\gamma\Omega}{k_B T R})\right] \tag{5}$$

This is known as the Gibbs-Thompson effect

### Gibbs-Thompson effect in a phase diagram

- Gibbs-Thompson effect will shift $\mu_B$ to higher values when particles are smaller
- Difference between interfacial concentration creates a diffusion field!



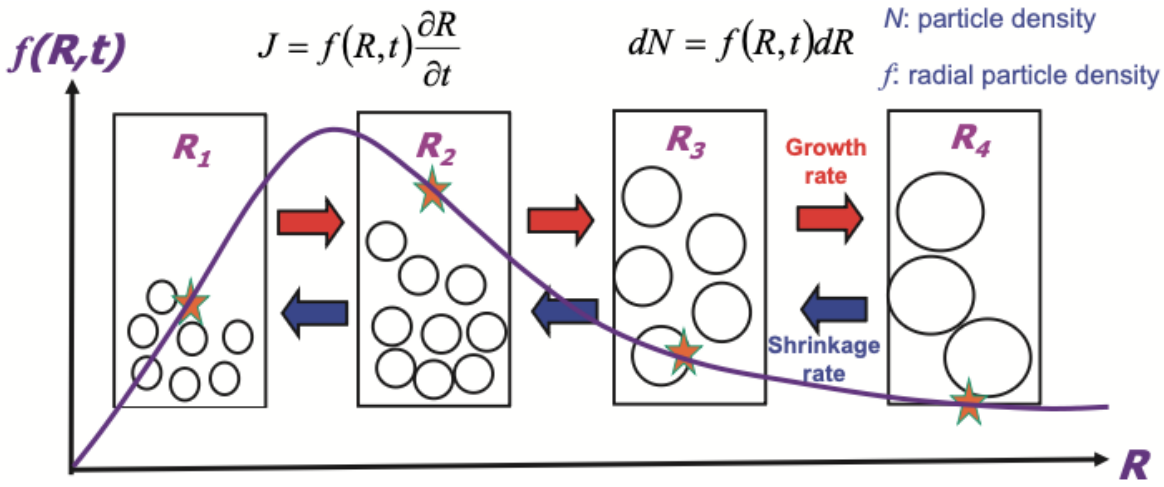

## LSW theory: the particle distribution picture

Similar to the nucleation theory where $J_n$ measures the flux of particle size distribution function $N(n,t)$, we're also interested in the particle size distribution over time, $f(R,t)$, with following components

- distribution (density) function of particle size $R$: $f(R,t)$
- radial particle density between $R \to R+dR$: $dN(R \to R+dR,t) = f(R,t)dR$
- conservation of volume: $\sum_i R_i^2 \dfrac{dR_i}{dt} = 0$

## The radial distribution function

Compare with the quasi-steady state picture of nucleation in Lecture 14. The R has no cutoff compared with the QSS treatment in constrained growth.




## Diffusion-controlled coarsening kinetics

In the diffusion-controlled regime of coarsening, the rate of growth for particles is associated with the surface flux from excess concentration to the bulk.

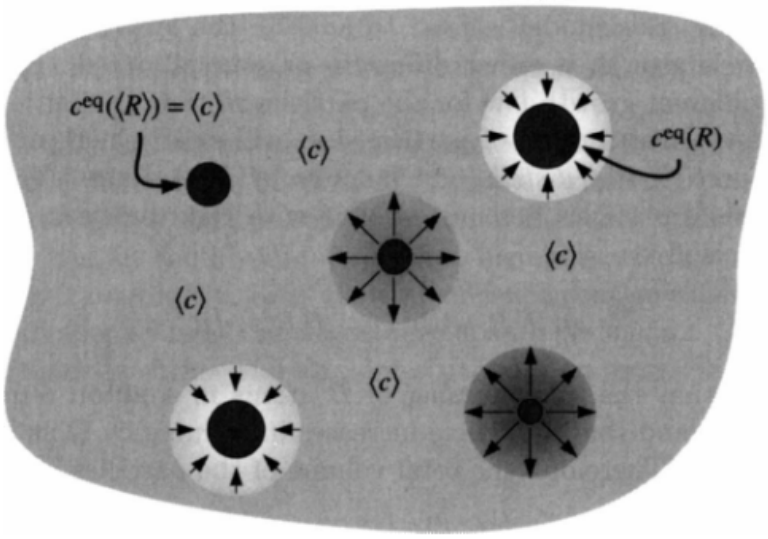



**Figure 15.2:** The mean-field approximation for diffusion-limited coarsening. Each particle is surrounded by a spherically symmetric diffusion field (fluxes are indicated by arrows). The concentration in the matrix at the interface of each particle is fixed by Eq. 15.4 and the concentration far-removed from particles is fixed at $\langle c \rangle$. The flux is zero near particles of average size, $\langle R \rangle$.

## Rate equations in diffusion-controlled regime

- Growth rate from flux onto a sphere

$$\frac{dR}{dt} = -\tilde{D}\frac{(c^{\mathrm{eq}}(R) - < c >)}{R}\omega_B$$

- Excess surface concentration:

$$c_B^{\mathrm{eq}}(R) \approx c_B^{\mathrm{eq}}(\infty)\left[\exp(\frac{2\gamma\Omega}{k_B T R})\right]$$

- Conservation

$$\sum_i R(c^{\mathrm{eq}}(R) - < c >) = 0$$

## Diffusion-controlled regime: final results

The growth rate at each $R$ is:

$$\frac{dR}{dt} = \frac{2\tilde{D}\gamma\Omega_B^2 c^{\text{eq}}(\infty)}{k_B T R}\left(\frac{1}{< R >} - \frac{1}{R}\right) \tag{6}$$

- $< R >$: average radius of particles. $f(< R >) = 0$
- $R << R >$: $dR/dt < 0$ shrink!
- $R_{\max} = 2 < R >$

## The steady-state particle size distribution

The radius distribution has a very nice feature that even if $< R >$ grows over time, at steady state, the normalized radius $R/ < R >$ has the same distribution:

- most frequent size $R \approx 1.13 < R >$
- no particle larger than $1.5 < R >$ (cutoff)

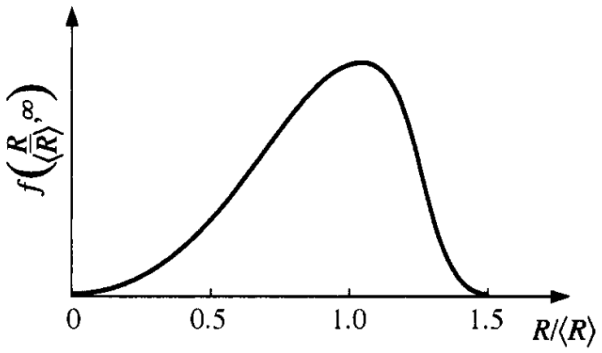



**Figure 15.5:** Final steady-state normalized particle-size distribution for diffusion-limited coarsening.

## Diffusion-controlled regime rate law

**Power-of-3** law: particle size growth rate

$$< R(t) >^3 - < R(0) >^3 = \frac{8\tilde{D}\gamma\Omega^2 c^{\text{eq}}(\infty)}{9kBT} = K_D t \tag{7}$$

In experiment the measured growth follows $\langle R\rangle \propto t^{1/3}$. See previous example of Pb-Sn alloy

## Source-limited growth regime

Another regime is the source-limited coarsening. Diffusion in matrix is very fast and rate limiting step is the source / sink at interface.

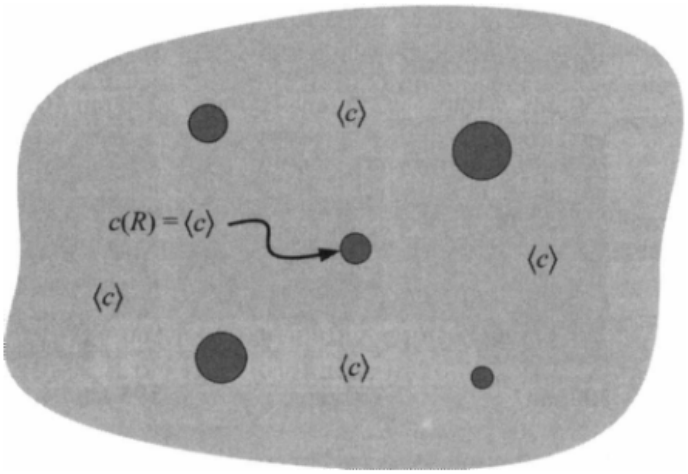



**Figure 15.7:** Solute concentration field for source-limited kinetics. The matrix concentration field is essentially uniform and $c = \langle c \rangle$ everywhere, including the regions adjacent to the particles where $c(R) = \langle c \rangle$.

## Source-limited growth: change of formula

Again, we have curvature-dependent interfacial concentration difference, but the growth rate is purely controlled by the concentration difference!

$$\frac{dR}{dt} = \frac{2Kc^{\text{eq}}(\infty)\Omega^2\gamma}{k_BT}\left(\frac{< R >}{< R^2 >} - \frac{1}{R}\right)$$

- Particle will shrink if $R << R^2 > / < R >$

## Source-limited growth: change of power law

For source-limited growth, we will have the radius grow in a **power-of-2** fashion

$$\langle R^2(t)\rangle - \langle R^2(0)\rangle = \frac{64Kc^{\text{eq}}(\infty)\Omega^2}{81k_BT} \tag{8}$$

$$= K_s t \tag{9}$$

In experiments you will measure that $\sqrt{\langle R^2(t) \rangle} \propto t^{1/2}$, a different power law than the diffusion-controlled growth!

## Summary

- Driving force for coarsening: capillarity (surface energy + curvature)
- Key take away from coarsening: particle growth kinetics & size distribution
- Diffusion and rate-limit regimes