

Lecture 9: Particle Coarsening: Ostwald Ripening

Today's topics

- The thermodynamics and kinetics behind the particle coarsening.
- Ostwald ripening is driven by the concentration gradient (kinetics factor for the diffusion) around the particle in comparison to the bulk matrix or medium (e.g., solvent or the solid substance). How such a concentration gradient depends on the particle size is the main topic of today.

About Ostwald ripening

- Ostwald ripening is an observed phenomenon in solid (or liquid) solutions which describes the evolution of an inhomogenous 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.
- This [thermodynamically](#)-driven spontaneous process occurs because larger particles are more energetically stable than smaller particles (**Lecture 8: internal pressure reversely proportional to the radius of the 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 --- **Lecture 9**.
- As Lecture 9 tells us, **Ostwald ripening** is also a typical **Kinetic** process controlled by diffusion: concentration of the molecules around the interface of smaller particle 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.**
- Ostwald ripening is also observed in liquid-liquid systems. For example, in an oil-in-water [emulsion polymerization](#), Ostwald ripening causes the [diffusion](#) of [monomers](#) from smaller to larger droplets due to greater solubility of the single monomer molecules in the larger monomer droplets. The rate of this diffusion process is linked to the solubility of the monomer in the continuous (water) phase of the emulsion. This can lead to the destabilization of emulsions (for example, by creaming and sedimentation).

Background:

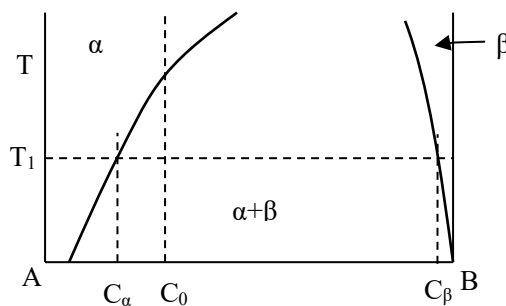
Lecture 8: $\Delta P = 2\gamma/r$ --- pressure inside a sphere particle, → small particles, droplets or protrudes are not stable. So, what usually happen for these small particles or protrudes on surface during the phase transformation? Two ways:

1. 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.
2. 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.

The rate of Ostwald ripening is determined by concentration gradient around the particles, the latter is in turn depends on the particles size.

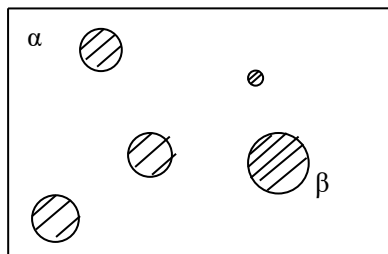
- Basically, $\Delta P = 2\gamma / r$ (Lecture 8) tells if a particle coarsening is *thermodynamically favorable* or not?
- The concentration gradient to be deduced in this Lecture will tell us how fast (Kinetics) the particle coarsening can take place?

Consider a two-component, two-phase alloy of A and B that is A-rich. For simplicity, assume A has negligible solubility in B. Shown below is a binary phase diagram of the system, where α phase is assumed to be dilute (solid) solution containing small fractions of β phase. Initially, the sample is a homogeneous, single phase α of composition with the concentration of B as C_0 . The alloy solution is then cooled to a temperature T_1 , at which the equilibrium concentration of B in α and β are respectively C_α and C_β , where $C_\alpha < C_0$.



Two assumptions to make:

1. The interfacial energy, $\gamma_{\alpha\beta}$ is isotropic so that precipitates are spherical β particles of various radius.
2. The local equilibrium is established across the α/β interface. That is, the chemical potential of A and B in both α and β are about the same in the vicinity of α/β interface. $\mu_B^\alpha = \mu_B^\beta$, $\mu_A^\alpha = \mu_A^\beta$ (They can't be exactly same, otherwise no transport can occur across the interface.) Look at the case of oil-water two phase system, where the chemical potential of oil at both sides of the interface is approximately the same, or the difference is so slight that the cross-diffusion of oil is negligible.



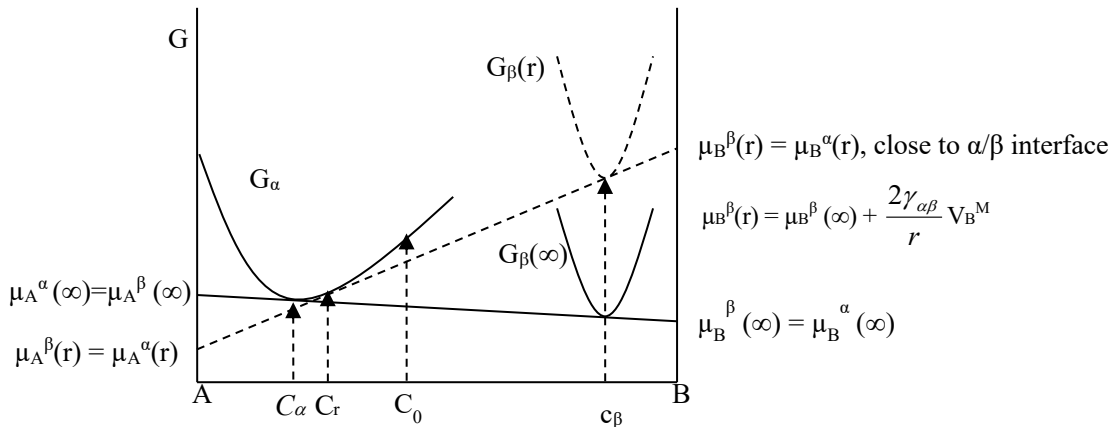
r — radius of the β particle

In the diagram above, each particle is under pressure,

$$\Delta P(r) = \frac{2\gamma_{\alpha\beta}}{r}$$

The free energy (G) vs. composition diagram at T_1 can be drawn as below.

--- Please refer to the basics of thermodynamics that you learned before for how to draw a molar free energy curve (G vs. concentration) for a binary phase system α/β , and its relationship with phase diagram, as well as how to get chemical potential μ of each of the two component A and B in the α and β phase.



From this diagram, the common tangent construction and the intercepts give the chemical potential of A and B in the coexisting phases. When the β particle grows to be large, the surface energy contribution ($\frac{2\gamma_{\alpha\beta}V_B^M}{r}$) becomes negligible, and the curve of $G_\beta(r)$ lowers down, approaching $G_\beta(\infty)$ --- as a result, *the tangent point at the G_α curve (C_r , determined by the common tangent line between the G_α and $G_\beta(r)$ curves) moves to the left to approach the value of C_α .* Apparently, when the particle size is small, the concentration of B in α next to the β -particle is greater than that next to a large β -particle (flat α/β interface), $C_r > C_\alpha$

Next we determine the relationship between C_r and C_α :

As the β particle is a small sphere of radius “ r ”, its chemical free energy per mole is

$$\mu_B^\beta(r) = \mu_B^\beta(\infty) + \frac{2\gamma_{\alpha\beta}}{r} V_B^M \quad (1) \quad \text{--- from last Lecture}$$

where $\gamma_{\alpha\beta}$ is the interface energy of α/β phase, V_B^M is the molar volume of B, r is the radius of β particle, and $\mu_B^\beta(\infty)$ is the chemical potential of β particle of infinite radius (i.e., under a flat surface).

As the concentration of B in α is small, we treat α as a dilute solution of B in A. Thus, for a flat interface ($r=\infty$),

$$\begin{aligned} \mu_B^\alpha(\infty) &= \mu_B^0 + RT \ln a_B^\alpha \\ &= \mu_B^0 + RT \ln \left\{ \gamma_B^\alpha(H) \cdot \frac{C_\alpha}{C_\alpha + C_A} \right\} \end{aligned}$$

where $\gamma_B^\alpha(H)$ is the Henrian activity coefficient and c_A is the concentration of A in α .

For a dilute solution of B in α phase, $C_A \gg C_\alpha$, so

$$\mu_B^\alpha(\infty) = \mu_B^0 + RT \ln \left\{ \frac{\gamma_B^\alpha(H) c_\alpha}{C_A} \right\}$$

Considering the local equilibrium at the α/β interface as discussed above, $\mu_B^\beta(\infty) = \mu_B^\alpha(\infty)$, then we have

$$\mu_B^\beta(\infty) = \mu_B^\alpha(\infty) = \mu_B^0 + RT \ln \left\{ \frac{\gamma_B^\alpha(H) c_\alpha}{C_A} \right\} \quad (2)$$

(chemical potential of B in β re-written as the one in α phase.)

Similarly, for a β -particle of radius r , we have

$$\mu_B^\alpha(r) = \mu_B^0 + RT \ln \left[\gamma_B^\alpha(H) \cdot \frac{c_r}{c_r + c_A} \right] = \mu_B^0 + RT \ln \left[\frac{\gamma_B^\alpha(H) c_r}{C_A} \right] \quad (3)$$

(where, again, for a dilute solution of B in α phase, $C_A \gg C_r$)

For the β -particle of radius r , at the α/β interface, a local equilibrium is assumed, $\mu_B^\beta(r) = \mu_B^\alpha(r)$

Then Eq. (1) = Eq. (3) \rightarrow

$$\mu_B^\beta(\infty) + \frac{2\gamma_{\alpha\beta} V_B^M}{r} = \mu_B^0 + RT \ln \left[\frac{\gamma_B^\alpha(H) c_r}{C_A} \right] \quad (4)$$

Replacing Eq. (2) into Eq. (4), we have,

$$\mu_B^0 + RT \ln \left\{ \frac{\gamma_B^\alpha(H) c_\alpha}{C_A} \right\} + \frac{2\gamma_{\alpha\beta} V_B^M}{r} = \mu_B^0 + RT \ln \left[\frac{\gamma_B^\alpha(H) c_r}{C_A} \right]$$

then we have:

$$C_r = C_\alpha \exp \left[\frac{2\gamma_{\alpha\beta} V_B^M}{rRT} \right]$$

The concentration of B in α next to a β particle of radius r is higher than that close to a β particle of a larger or an infinite radius (flat interface). This leads to a diffusion along concentration gradient, resulting in coarsening of particles. When r approaches ∞ , C_r approaches C_α .

Let us consider some typical values:

$$\gamma_{\alpha\beta} = 0.5 \text{ J/m}^2, \quad V_B^M = 2.5 \times 10^{-5} \text{ m}^3/\text{mole} \quad T=1000\text{K}$$

$$\text{If, } r = 1 \text{ } \mu\text{m} = 10^{-6} \text{ m, then } \frac{2\gamma_{\alpha\beta} V_B^M}{rRT} \approx 3 \times 10^{-3} \ll 1, \quad \exp \left[\frac{2\gamma_{\alpha\beta} V_B^M}{rRT} \right] \approx 1.003$$

$$\text{If, } r = 0.01 \text{ } \mu\text{m (or 10 nm), } \frac{2\gamma_{\alpha\beta} V_B^M}{rRT} \approx 0.3, \quad \exp \left[\frac{2\gamma_{\alpha\beta} V_B^M}{rRT} \right] \approx 1.35$$

Therefore, C_r is 35% larger when r is reduced from $1 \mu\text{m}$ to $0.01 \mu\text{m}$ (10 nm).

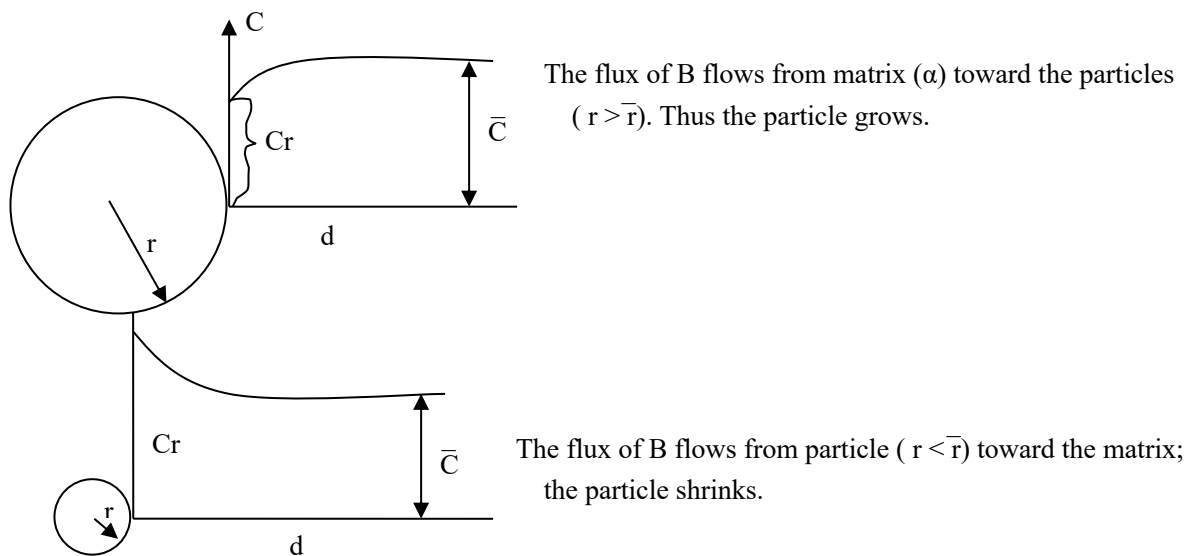
In general, we may use the following approximate expression:

$$C_r = C_\alpha \exp\left[\frac{2\gamma_{\alpha\beta}V_B^M}{rRT}\right] \approx C_\alpha \left[1 + \frac{2\gamma_{\alpha\beta}V_B^M}{rRT}\right], \text{ as } r \text{ is in the } \mu\text{m range}$$

Let \bar{r} be the average radius of β particle, the average concentration of B in the α -matrix is

$$\bar{C} = C(\bar{r}) = C_\alpha \left[1 + \frac{2\gamma_{\alpha\beta}V_B^M}{\bar{r}RT}\right]$$

The concentration next to particles smaller than \bar{r} is greater than \bar{C} , and vice versa. The following show the variation of c from the surface of a particle into the matrix α . For $r > \bar{r}$ and $r < \bar{r}$, respectively.



Ostwald ripening: Larger particles grows at the expenses of smaller particles

A case for further thinking:

Assuming all the particles are initially formed at approximately the same size, how Ostwald ripening can play for such a case?

--- this is the limiting case for Ostwald ripening, where people can make uniform size of nanoparticles and nanotubes.