Particle Coarsening: a process also called 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 <u>Wilhelm Ostwald</u> in 1896. When a phase <u>precipitates</u> out of a solid, energetic factors will cause large precipitates to grow, drawing material from the smaller precipitates, which shrink.
- This <u>thermodynamically</u>-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 <u>surface energy</u>). As the <u>system</u> 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.
- Lecture 9 tells us: 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 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 <u>emulsion</u> <u>polymerization</u>, Ostwald ripening causes the <u>diffusion</u> of <u>monomers</u> 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).

Real-world examples of Ostwald ripening

- An everyday example of Ostwald ripening is the re-crystallization of water within ice cream which gives old ice cream a gritty, crunchy texture. Larger ice crystals grow at the expense of smaller ones within the ice cream, thereby creating a coarser texture.
- Another gastronomical example is in the <u>ouzo effect</u>, where the droplets in the cloudy microemulsion grow by Ostwald ripening.
- In chemistry, Ostwald ripening refers to the growth of larger crystals from those of smaller size which have a higher solubility than the larger ones. In the process, many small crystals formed initially slowly disappear, except for a few that grow larger, at the expense of the small crystals. The smaller crystals act as fuel for the growth of bigger crystals. Limiting Ostwald ripening is fundamental in modern technology for the solution synthesis of <u>quantum dots</u> (the nanoparticles).
- A movie slip showing crystals growth through Ostwald ripening under constant temperature: <u>http://www.eng.utah.edu/~lzang/images/ostwald-ripening.avi</u> where you can clearly see 1) smaller particles (crystals) disappear with larger crystals growing, and 2) the irregular sharp protrudes (small crystals) disappear (are polished away) --- leading to formation of larger regular crystals with smooth surface. *Lecture 8: as indicated by Young-Laplace equation, small protrudes have small positive radius (and thus huge internal pressure), representing a thermodynamically unstable state.*