Nucleation and Growth of Domains [pln35]

Unmixing process from metastable mixed macrostate initiated by local fluctuations impeded by energy barrier.

Consider spontaneously formed, small droplets of unmixed liquids in the otherwise homogeneous mixed bulk state.

Free energy of droplets with radius r relative to mixed reference state:

$$\Delta F(r) = -\frac{4\pi}{3} r^3 \Delta f_V + 4\pi r^2 \gamma,$$

- Δf_V: bulk difference in free-energy density,
- γ: interface free-energy density.

The graph of $\Delta F(r)$ versus r first rises quadratically, reaches a smooth maximum, then goes negative as the cubic term becomes dominant.

Threshold radius: $r^* = \dfrac{2\gamma}{\Delta f_V}$ (location of energy-barrier maximum).

Activation energy: $\Delta F(r^*) = \dfrac{16\pi\gamma^3}{3\Delta f_V^2}$ (height of energy barrier).

Nucleation probability: $P \propto \exp\left(-\dfrac{\Delta F(r)}{k_\mathrm{B} T}\right)$,

- nucleated droplets of radius $r < r^*$ tend to shrink and disappear,
- nucleated droplets of radius $r > r^*$ tend to continue growing.

Distinguish *homogeneous* nucleation (in bulk) and *heterogeneous* nucleation (from walls or impurities) with significantly reduced energy barriers.

Growth of phase-separated domains driven by reduction in interfacial energy:

- initiation: via spinodal decomposition (from unstable mixed state) or via nucleation (from metastable mixed state),
- early stage of growth: domain size and interface width both grow (fluctuations slow down as their wavelengths increase),
- intermediate stage of growth: domain size grows and interface width shrinks (toward energetically optimized value),
- late stage of growth: domain size continues to grow at roughly constant interface width,
- Ostwald ripening: smaller domains are absorbed in larger domains.