Lecture 6

Growth of Nucleus Under Supercooling

In Lecture 5 we discussed the thermodynamics of nucleation under supercooling. From the classical nucleation theory, we know that the nucleus growth is a kinetic process with an activation energy of ΔG_c, and crystals grow faster when ΔG_c decreases. So far we have ignored other kinetic processes including heat and mass transfer. In reality the temperature and concentration profiles are not uniform during nucleation, and the nucleus growth can be controlled by heat / mass transfer when such processes are much slower than adding molecules to the nucleus. In this lecture we will model the growth of a nucleus during supercooling, based on interfacial transport theory we learned so far. Depending on the governing process, the growth can be controlled by either kinetics, heat transfer or mass transfer.

6.1 Kinetic-controlled growth

Within the regime of kinetic-controlled growth, the time scale for the molecule to transfer from liquid to solid phase, is much longer than the time scale of diffusion and heat transfer (e.g. slow reaction and perfect mixing). We assume that everywhere in the system, the temperature $T\,(<T_m)$ is uniform. The molecule vibrates at a frequency of ν at T, and creates an oscillating energy landscape near the nucleus (XL) / solution (L) interface, as shown in Figure 6.1.

The activation energy from solution (L) to crystal (XL) is $E_{L\to XL}$, and *vice versa*. In the case of supercooling, we have $E_{L\to XL} < E_{XL\to L}$. Using Boltzmann distribution for the molecules, the flux in and out of the crystal phase are:

$$J_{L\to XL} = N\nu \exp\left(-\frac{E_{L\to XL}}{k_B T}\right) \tag{6.1}$$

$$J_{XL\to L} = N\nu \exp\left(-\frac{E_{XL\to L}}{k_B T}\right) \tag{6.2}$$

where J is the molar flux (number of molecules per unit area per unit time), N is the number of molecules per unit area on the crystal surface. The growth rate of a spherical cluster with

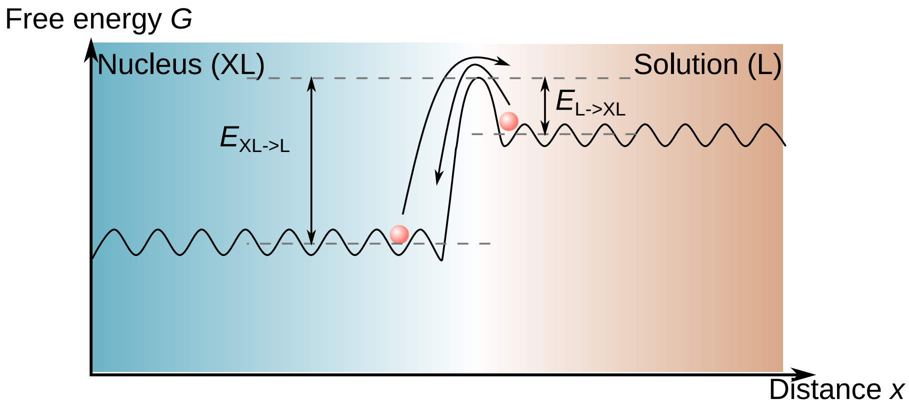

Figure 6.1: Free energy of a molecule near the nucleus (XL) / solution (L) interface as a function of the distance x. In both phases, the free energy has an oscillating landscape due to the vibration of molecules. The average free energy is higher in the solution than nucleus, and an energy barrier exists across the interface.

radius R is $\mathrm{d}R/\mathrm{d}t$ and calculated by:

$$\begin{aligned}\frac{\mathrm{d}R}{\mathrm{d}t} &= \Omega(J_{\mathrm{L}\to\mathrm{XL}} - J_{\mathrm{XL}\to\mathrm{L}}) \\ &= N\nu\Omega\exp(-\frac{E_{\mathrm{L}\to\mathrm{XL}}}{k_\mathrm{B}T})\left[1-\exp(\frac{\Delta G}{k_\mathrm{B}T})\right] \\ &\approx -\left[\frac{N\nu\Omega}{k_\mathrm{B}T}\exp(-\frac{E_{\mathrm{L}\to\mathrm{XL}}}{k_\mathrm{B}T})\right]\Delta G \\ &\approx \underbrace{-\left[\frac{N\nu\Omega}{k_\mathrm{B}T}\exp(-\frac{E_{\mathrm{L}\to\mathrm{XL}}}{k_\mathrm{B}T})\right]\frac{\Delta H}{T_\mathrm{m}}}_{\text{constant}}\Delta T\end{aligned} \tag{6.3}$$

where Ω is the volume of molecule and $\Delta G = E_{\mathrm{L}\to\mathrm{XL}} - E_{\mathrm{XL}\to\mathrm{L}}$. Here we assume that $\Delta G \ll k_\mathrm{B}T$. If the crystal size is much larger than the molecular dimension, N can be regarded as constant. Therefore Equation 6.1 indicates the growth rate of the nucleus is proportional to the degree of supercooling ΔT, and is a constant when T does not change. In other words, within the regime of kinetic-controlled growth, the crystalline size can be controlled easily by time. In fact, this has been used in seeded growth of colloidal particles in which nanoparticles with narrow size distribution can be obtained.[1]

6.2 Heat and mass transfer at interface

We shall note that the kinetic-controlled growth is a rather simplified assumption, since in reality neither the temperature nor concentration profiles are uniform. In reality, the transport phenomena across the interface also need to be considered. The general equation for the conservation of heat/mass at the interface between phases A and B is:[2]

$$[(F - bv_\mathrm{I})|_\mathrm{B} - (F - bv_\mathrm{I})|_\mathrm{A}]\cdot n = B_\mathrm{s} \tag{6.4}$$

where F is the total heat / mass flux such that $F = bv_\mathrm{I} + f$, v_I is the interfacial moving speed, bv_I is the convective flux, f is the diffusive flux, n is the surface norm vector pointing from A to B, and B_s is the rate of formation per unit area. The variables b, f and B_s depend on the type of flux:

- Conservation of mass

  We have $b = \rho; f = 0; B_\mathrm{s} = 0$ where ρ is the density. The conservation of mass reads:

$$[\rho_\mathrm{A}(v - v_\mathrm{I}) \cdot n]_\mathrm{A} = [\rho_\mathrm{B}(v - v_\mathrm{I}) \cdot n]_\mathrm{B} \tag{6.5}$$

- Conservation of heat

  We have $b = \rho\hat{H}; f = -k\nabla T = q; B_\mathrm{s} = 0$, where $\hat{H}$ is the enthalpy per unit mass, and k is the thermal conductivity. The conservation of heat reads:

$$[\rho_\mathrm{A}\hat{H}_\mathrm{A}(v - v_\mathrm{I}) + q]_\mathrm{A} \cdot n = [\rho_\mathrm{B}(v - v_\mathrm{I}) + q]_\mathrm{B} \cdot n \tag{6.6}$$

Combine Equations 6.5 and 6.6, we get:

$$\begin{aligned} (q_\mathrm{A} - q_\mathrm{B}) \cdot n &= \hat{\lambda}\rho_\mathrm{A}(v - v_\mathbf{I})_\mathrm{A} \cdot n \\ &= \hat{\lambda}\rho_\mathrm{B}(v - v_\mathbf{I})_\mathrm{B} \cdot n \end{aligned} \tag{6.7}$$

where $\hat{\lambda} = \hat{H}_\mathrm{B} - \hat{H}_\mathrm{A}$ is the latent heat per unit mass. Use Equations 6.5, 6.6 and 6.7, we can model the heat and mass transfer through the system.

6.3 Heat transfer-controlled growth

The heat transfer-controlled growth assumes that diffusivity $\mathcal{D}$ of the molecules are fast enough that within the time scale of nucleus growth the concentration distribution is constant. For simplicity we model the growth of a small spherical nucleus with radius R in supercooled liquid. We assume (i) liquid and solid has same density, i.e. $\rho_\mathrm{S} = \rho_\mathrm{L} = \rho$ and (ii) the temperature at interface is the melting point $T_\mathrm{I} = T_\mathrm{m}$. Far from the nucleus the temperature is T_∞ ($T_\infty < T_\mathrm{m}$). The geometry of the system is shown in Figure 6.2.

Use the conservation of mass in Equation 6.5, since the velocity in solid $v_\mathrm{S} = 0$, the liquid phase is also still, i.e. $v_\mathrm{L} = 0$. In other words, no fluid flow is present and the growth of nucleus is solely due to phase transition. Now let's solve the heat transfer problem in solid and liquid phases. The problem can be reduced to a 1D problem since the system is spherically symmetric. Here pseudo-steady state assumption (PSSA) applies, since the time to reach heat balance is much faster than the moving of interface. In both phases (not counting the interface), there are no sources of heat and temperature follows the Laplace equation:

$$\nabla^2 T = \frac{\partial}{\partial r}(r^2 \frac{\partial T}{\partial r}) = 0 \tag{6.8}$$

which can be solved in each phase with different boundary conditions:

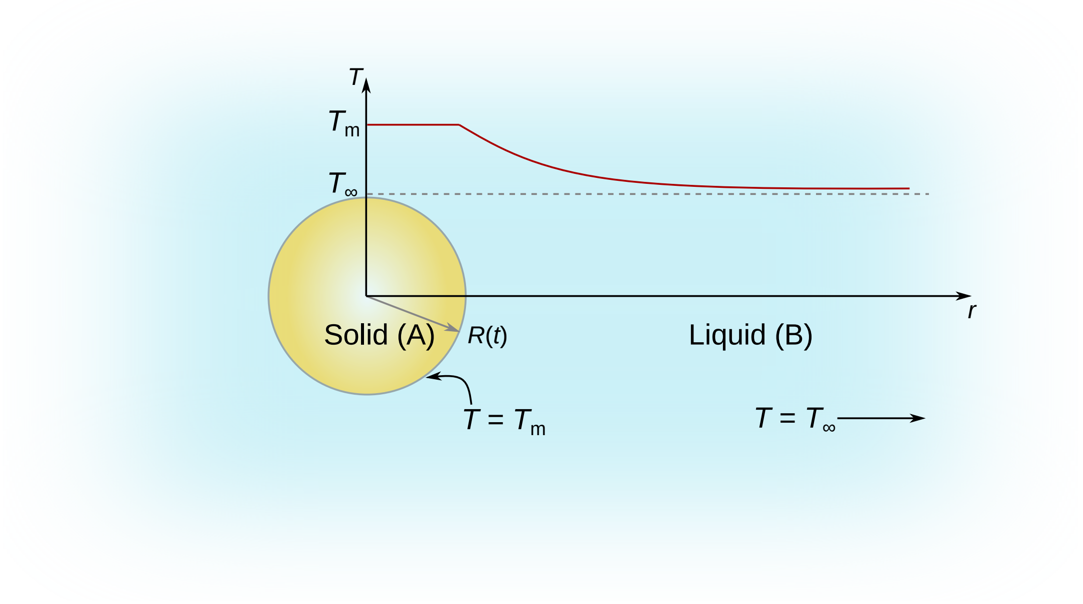

Figure 6.2: Temperature profile of a small nucleus in a supercooled liquid, studied in a spherical coordinate system. The temperature profile is superimposed with the geometry of the system.

- Solid phase

  The boundary conditions are $\frac{\partial T}{\partial r}(r = 0) = 0$ due to symmetry and $T(r = R) = T_{\mathrm{m}}$, which gives $T = T_{\mathrm{m}}$ everywhere in the solid phase.

- Liquid phase

  The boundary conditions are $T(r = R) = T_{\mathrm{m}}$, $T(r \to \infty) = T_\infty$ and $\frac{\partial T}{\partial r}(r \to \infty) = 0$. The solution is:

  $$T(r, t) = T_\infty + (T_{\mathrm{m}} - T_\infty)\frac{R(t)}{r} \quad r \geq R(t) \tag{6.9}$$

  Note T is dependent on t since the radius R increases over time. However using PSSA we can take "snapshots" of $T(r, t)$ and $R(t)$ and solve Equation 6.9 for each time frame. A typical temperature profile can be found in Figure 6.2, superimposed with the geometry of nucleus.

At the interface ($r = R(t)$), the conservation of heat follows:

$$k_{\mathrm{L}}\frac{\mathrm{d}T}{\mathrm{d}r}|_{r=R(t)} = -\hat{\lambda}\rho\frac{\mathrm{d}R}{\mathrm{d}t} = -\hat{\lambda}\rho(v_{\mathrm{I}} \cdot e_{\mathrm{r}}) \tag{6.10}$$

where $\mathrm{d}R/\mathrm{d}t$ equals the interfacial moving speed $v_{\mathrm{I}} \cdot e_r$. The contribution from heat conduction in solid is $q_{\mathrm{s}} = k_{\mathrm{s}}\mathrm{d}T/\mathrm{d}r = 0$ since T is constant. Combine with Equation 6.9 we know $\mathrm{d}R/\mathrm{d}t = \frac{k_\mathrm{L}}{\hat{\lambda}\rho}\frac{\Delta T}{R}$, where $\Delta T = T_\mathrm{m} - T_\infty$, and the size of the nucleus is given by:

$$R(t) = \sqrt{R_0^2 + \frac{2k_\mathrm{L}\Delta T}{\hat{\lambda}\rho}t} \tag{6.11}$$

where R_0 is the radius of nucleus at $t = 0$. As expected, the growth rate become faster when ΔT increases (more supercooling). However unlike kinetic-controlled process where $\mathrm{d}R/\mathrm{d}t$ is constant, the growth rate in heat transfer-controlled process decreases with larger R.

6.4 Mass transfer-controlled growth

In the heat transfer-controlled growth, we assume the interfacial temperature is the melting point, i.e. $T_\mathrm{I} = T_\mathrm{m}$, this holds for a pure liquid or azeotrope mixture. However it is usually not the case for nucleation in a solution, due to the different solubility in liquid and solid phases. As shown in Figure 6.3, the $T - c$ profiles for solid and liquid phases are different. Using the level rule of binary phase diagram,[3] we can see that when the interfacial temperature $T_\mathrm{S/L} < T_\mathrm{m}$, the concentration in solid and liquid phases c_S and c_L are different.

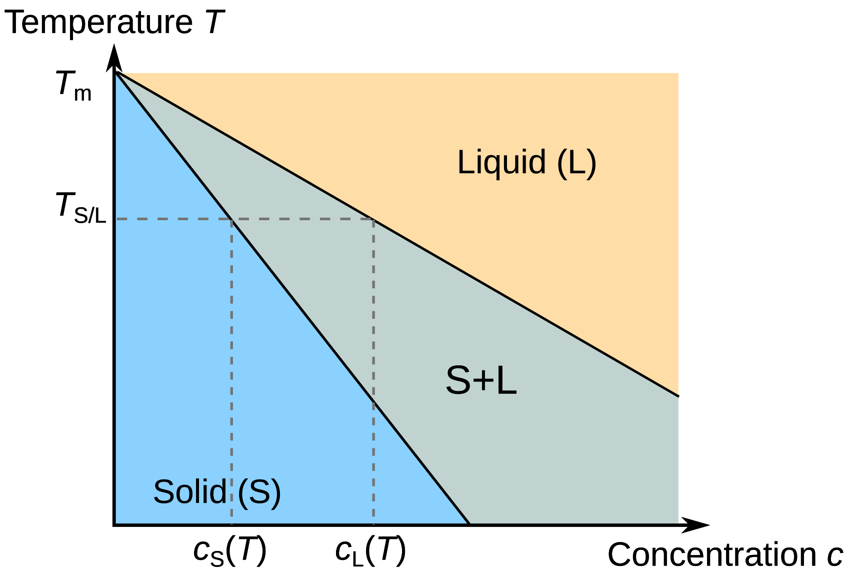

Figure 6.3: Phase diagram (temperature-concentration profile) of a solid-liquid system near $c = 0$. When the interfacial temperature $T_\mathrm{S/L}$ is smaller than T_m, the concentration in solid and liquid phases are different.

As a result the interfacial temperature changes with time, and the problem is more complicated than the heat transfer-controlled growth. Here we will briefly discuss how such problem can be solved self-consistently. Under the PSSA assumption, neglecting fluid velocities v_S and v_L, the conservation of species at the interface gives:

$$-\mathcal{D}_L(\frac{\partial c}{\partial r})|_{r=R(t)} + \mathcal{D}_s(\frac{\partial c}{\partial r})|_{r=R(t)} = [c_L - c_s](\frac{dR(t)}{dt}) \tag{6.12}$$

where $\mathcal{D}_L$ and $\mathcal{D}_S$ are the mass diffusivities of liquid and solid phases, respectively. The conservation of heat is the same as in the heat transfer-controlled growth:

$$-k_L\frac{\partial T_L}{\partial r}|_{r=R} + k_S\frac{\partial T_S}{\partial r}|_{r=R} = \hat{\lambda}R\frac{dR}{dt} \tag{6.13}$$

In total we have 4 variables that are dependent on both r and t: c_L, c_s, T_L, T_s, and 1 variable dependent on t: R. Starting from the initial concentration profile at $t = 0$, we can solve the time-dependent differential equations numerically. In fact, mass and heat transfer-controlled growth models can be described in a same manner. Similar to the idea of mass diffusivity $\mathcal{D}$, we can define a heat diffusivity $\alpha = k/(\rho c_p)$, where c_p is the heat capacity of the material, which also has unit of [length^2]/[time]. At same length scale L, mass diffusion has time scale of $L^2/\mathcal{D}$ and heat diffusion has time scale of L^2/α. Therefore we can distinguish which transport phenomenon is dominating by:

- $\alpha \gg \mathcal{D}$: growth is controlled by mass transfer
- $\mathcal{D} \gg \alpha$: growth is controlled by heat transfer

References

(1) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. *Chem. Rev.* **2014**, *114*, 7610–7630.

(2) Deen, W. M., *Analysis of transport phenomena*, 2nd ed; Topics in chemical engineering; Oxford University Press: New York, 2012.

(3) Atkins, P.; Paula, J. d.; Keeler, J., *Atkins' Physical Chemistry*, Eleventh Edition; Oxford University Press: Oxford, New York, 2017.