Supercooling and Nucleation
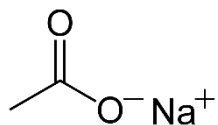

What is the stabilizing liquid water when T < 0°C ?

Supersaturation and Nucleation

What is stabilizing supersaturated sodium acetate in water ?

Lecture 5

Supercooling and Nucleation

Phase transition is the process that changes the states of matter. In reality, phase transition is more than the simply thermodynamic picture we learned from undergraduate physical chemistry, which involved both heat and mass transfer at the interfaces between two or more phases. We are able to explain several important physical phenomena by applying our knowledge of fluid mechanics in Lecture 4 to phase transition. On example is the supercooling of liquid, that crystallization does not occur even if temperature is lower than the freezing point, due to the absence of nucleation. In this lecture we will study the phenomenon of nucleation during freezing, a process that nano- to microscale crystals called nuclei forms in the liquid phase. Nucleation is the first step of crystallization and also a kinetic process. Even when crystallization is thermodynamically favorable, nucleation can be slow or even unobservable under supercooling. What is the cause of supercooling? Can we engineer the nucleation process? We will find the answers in this lecture.

5.1   Thermodynamics of freezing

For a pure liquid with melting temperature T_m, the Gibbs free energy between its solid state (S) and liquid state (L) has the relation:

- $T > T_\mathrm{m} \to G_\mathrm{L} < G_\mathrm{S} \to$ Liquid is thermodynamically favored

- $T < T_\mathrm{m} \to G_\mathrm{L} > G_\mathrm{S} \to$ Solid is thermodynamically favored

The change of free energy G as a function of temperature T of a solid-liquid phase transition can be seen in Figure 5.1. The free energy of liquid phase G_L has a steeper slope than G_S, which results in a first-order phase transition (discontinuous $\partial G/\partial T$) around T_m.

The change of Gibbs free energy is: $\Delta G = G_\mathrm{S} - G_\mathrm{L} = \Delta H - T\Delta S$. The process L$\to$S is exothermic and therefore $\Delta H < 0$. Since at $T = T_\mathrm{m}$, $\Delta G = 0$, we have: $\Delta S = \Delta H/T_\mathrm{m} < 0$. This makes sense since from liquid to solid the randomness of molecule orientation becomes smaller. If we assume that ΔH is independent of T, ΔG is related to the temperature perturbation ΔT near T_m:

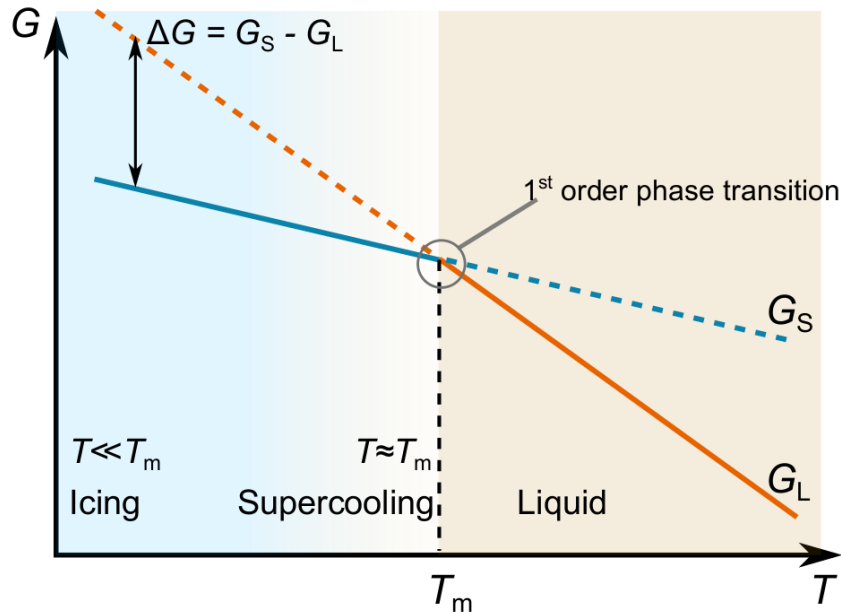$$\Delta G(T) = \frac{\Delta H \Delta T}{T_\mathrm{m}} \tag{5.1}$$

Figure 5.1: Free energy G of a solid-liquid phase transition. First order phase transition occurs at $T = T_{\mathrm{m}}$. The change of Gibbes free energy $\Delta G = G_{\mathrm{S}} - G_{\mathrm{L}}$ is a relative measure of the nucleation. When ΔG becomes more negative when T is much lower than T, and nucleation is more favored.

where $\Delta T = T_{\mathrm{m}} - T$. This means thermodynamically the process of crystallization is sponateous once $T < T_{\mathrm{m}}$. However we usually observe that water does not freeze if we cool it down just below 0 °C. On the contrary, very pure liquid water can be kinetically stable until ∼-40 °C.[12] This phenomenon is known as the supercooling of liquid.

The crystallization process is a kinetic problem, since common sense indicates the freezing is much faster when ΔT = -40 °C, compared with ΔT = -0.1 °C. To model this we can view the nucleus as cluster of molecules. For a small molecule cluster A_n with n molecules of A, it can either form a larger cluster A_{n+1} through addition of one A molecule, or be formed from dissociating one A molecule from A_{n+1}:

$$A_{\mathrm{n}} + A \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A_{\mathrm{n+1}}$$
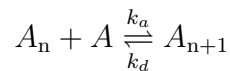
where k_a and k_d are the kinetic constants for addition and dissociation, respectively. For the nucleation to occure one must have $k_a > k_d$. What is the cause for the disassociation if the free energy for phase transition is already negative? We will answer this in the next section.

5.2   Free energy of nucleation

There are two contributions to the free energy ΔG of nucleation: the volume part (ΔG_{V}) that comes from the free energy of phase transition, and the surface part (ΔG_{A}) that comes from the creating of new interface

- Volume part ΔG_V (favorable)

  The volume part $\Delta G_V = \dfrac{\Delta H(T_m - T)}{T_m}$ is always smaller than 0, when $T < T_m$.

- Surface part ΔG_A (unfavorable)

  Phase transition increases the interfacial, which is energetically unfavorable ($\Delta G_A > 0$).

To combine both parts, we can calculate the total free energy change ΔG_n when the amount of molecules in the nucleus if n:

$$\begin{aligned}\Delta G_n &= \Delta G_V + \Delta G_A \\ &= n(G_S^m - G_L^m) + \eta n^{\frac{2}{3}}\gamma_{SL}\end{aligned} \tag{5.2}$$

where G_S^m and G_L^m are the molar free energies of solid and liquid phases, respectively, η is the shape factor which is defined as $\eta = (4\pi)^{\frac{1}{2}}(3\Omega)^{\frac{2}{3}}$ where Ω is the molecular volume, assuming spherical nucleus.[3] As shown in Figure 5.2, since $\Delta G_{V,n} \sim -n$ and $\Delta G_{A,n} \sim n^{\frac{2}{3}}$, eventually the volume part overcomes the surface part when the cluster is large enough. When n is larger than the critical cluster size n_c, $\partial\Delta G_n / \partial n < 0$ and the clusters continue to grow. The value for
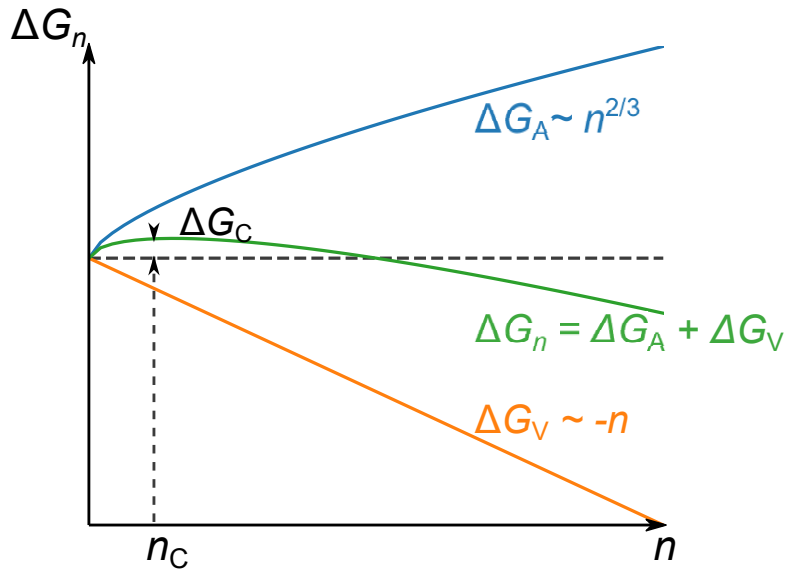

Figure 5.2: Volume and surface contributions to the free energy ΔG_n during nucleation, as a function of the cluster size n. A energy barrier of ΔG_c at $n = n_c$ exists.

n_c can be determined by solving $\partial\Delta G_n / \partial n = 0$ using Equation 5.2, which gives:

$$n_c = -\frac{8}{27}\left[\frac{\eta\gamma_{SL}}{G_S^m - G_L^m}\right]^3 \tag{5.3}$$

When $n = n_c$, there is a potential barrier ΔG_c that prevents the nucleation:

$$\Delta G_c = \frac{1}{3}\eta\gamma_{SL}n_c^{\frac{2}{3}} = \frac{4}{27}\eta^3\gamma_{SL}^3\frac{T_m^2}{(\Delta H \Delta T)^2} \tag{5.4}$$

Look again at Figure 5.1, when T is only slightly smaller than T_{m}, ΔG_{V} is not enough to overcome the surface energy ΔG_{A}. From Equation 5.4, the energy barrier $\Delta G_{\mathrm{c}} \propto \dfrac{\gamma_{\mathrm{SL}}^3}{(\Delta T)^2}$. For small ΔT below T_{m}, the potential barrier is high enough to keep the liquid phase kinetically stable. From classical nucleation theory (CNT), the probability to form a cluster with size n_{c}, p_c, is:[3] $p_{\mathrm{c}} = N_{\mathrm{tot}} \exp\left(\dfrac{-\Delta G_{\mathrm{c}}}{kT}\right)$, where N_{tot} is the total number of nuclei. When ΔG_{c} decreases, the probability of forming a nucleus with size n_{c} increases. The rate of nucleation $\dot{N}$ (how many new nuclei forms per unit time) can be estimated using:[3]

$$\dot{N} \sim k p_{\mathrm{c}} Z \tag{5.5}$$

where k the rate for a molecule in liquid to join a solid cluster and Z is the Zeldovich imbalance factor that considers the dissociation of nuclei.[4] The rate k_{n} is associated with the total number of nuclei n_{tot}, the diffusivity $\mathcal{D}_{\mathrm{AB}}$ and the critical surface area A_{c} of a cluster with $n = n_{\mathrm{c}}$:

$$k = \frac{3}{4} N_{\mathrm{tot}}^{4/3} \mathcal{D}_{\mathrm{AB}} A_{\mathrm{c}} \tag{5.6}$$

On the other hand, Z is associated with ΔG_{c}, n_{c}, and T:

$$Z = \sqrt{\frac{\Delta G_{\mathrm{c}}}{3\pi n_{\mathrm{c}}^2 k_{\mathrm{B}} T}} \tag{5.7}$$

Plug in all the parts into Equation 5.5 we have the expression for $\dot{N}$:

$$\dot{N} = \frac{3}{4} N_{\mathrm{tot}}^{\frac{7}{3}} A_{\mathrm{c}} \mathcal{D}_{\mathrm{AB}} \left(\frac{\Delta G_{\mathrm{c}}}{3\pi n_{\mathrm{c}}^2 k_{\mathrm{B}} T}\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta G_{\mathrm{c}}}{k_{\mathrm{B}} T}\right) \tag{5.8}$$

which tells us the nucleation rate can be controlled by $\mathcal{D}_{\mathrm{AB}}$, T, ΔG_{c}, etc. Note that these variables are not completely independent (e.g. both $\mathcal{D}_{\mathrm{AB}}$ and ΔG_{c} depend on T).

5.3 Crystallization of solute

The above analysis for nucleation in pure liquid can also be applied to a solution of molecule A. The only difference is that ΔG of crystallization becomes the difference of chemical potentials μ_{A} in solid and liquid phases:

$$\Delta G = \mu_{\mathrm{A}}^{\mathrm{S}} - \mu_{\mathrm{A}}^{\mathrm{L}} \tag{5.9}$$

As seen from the solubility diagram of the solution system (Figure 5.3), at temperature T, a saturated solution of A has concentration $c^\star(T)$. Crystalline can be achived by either reducing the temperature or increasing concentration. Let's consider the analog to supercooling, that crystallization is induced by decreasing solution temperature T at the same concentration. There is a metastable region when the solute concentration c is slightly smaller than $c^\star(T)$, where nucleation rate is slow, similar to the case of supercooling. The width Δc_{met} of the metastable region depends on both $\dot{N}$ and c^*. A practical estimation is $\Delta c_{\mathrm{met}} \propto 1/\dot{N}$.[5,6] In industry, larger crystals can be grown with a larger metastable width Δc_{met}. Therefore it is desirable to have smaller $\dot{N}$. Using Equation 5.8, this can be achieve by:
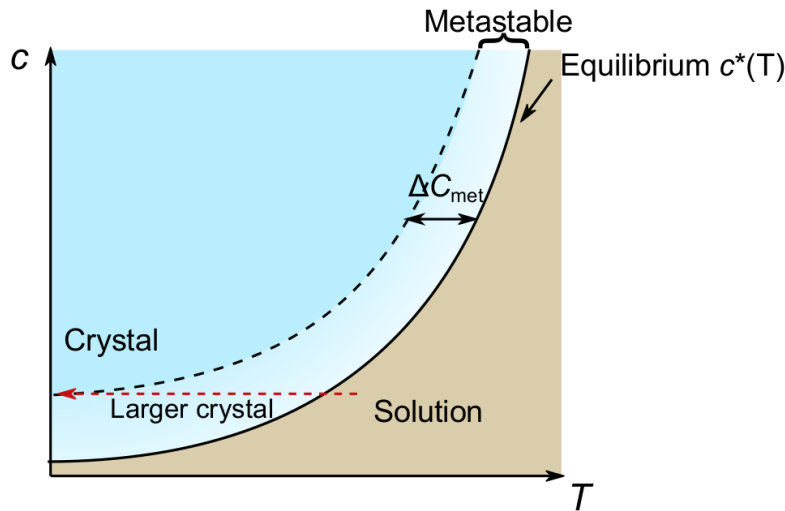
Figure 5.3: Typical solubility diagram of concentration c as a function of temperature T. The equilibrium solubility is $c^\star$. When c is slightly smaller than $c_\star$, there is a metastable region where nucleation rate is slow, analog to supercooling.

- Reducing T

- Reducing $\mathcal{D}_{\mathrm{AB}}$

From the Einstein-Stokes equation $\mathcal{D}_{\mathrm{AB}} = kT/(6\pi\eta r)$ (will be discussed in Lecture 15), where η is the viscousity of the liquid and r is the radius of the soluble molecule. Reducing T already decreases $\mathcal{D}_{\mathrm{AB}}$. We can also use a solvent with larger viscousity to achieve a smaller $\mathcal{D}_{\mathrm{AB}}$.

5.4 Heterogeneous nucleation

The above discussions are based on the assumption that nucleation forms in the bulk solution. However in experiments, we usually find the nucleation is more preferred on the wall of container (heterogeneous nucleation) instead of in the bulk solution (homogeneous nucleation). We can understand the mechanism of heterogeneous nucleation by studying the volume and surface contributions to the free energy during nucleation. If the nuclei are small enough, we can simplify them as "droplets". On the wall of container, such "nucleus droplet" (n) has contact angle θ, and a spherical shape with radius R (Figure 5.4).

The geometry of the droplet gives:

- Volume of nucleus: $V_{\mathrm{n}} = \frac{\pi R^3}{3}(2 - 3\cos\theta + \cos^3\theta)$

- Interfacial area of nucleus with solution: $A_{\mathrm{s}} = 2\pi R^2(1 - \cos\theta)$

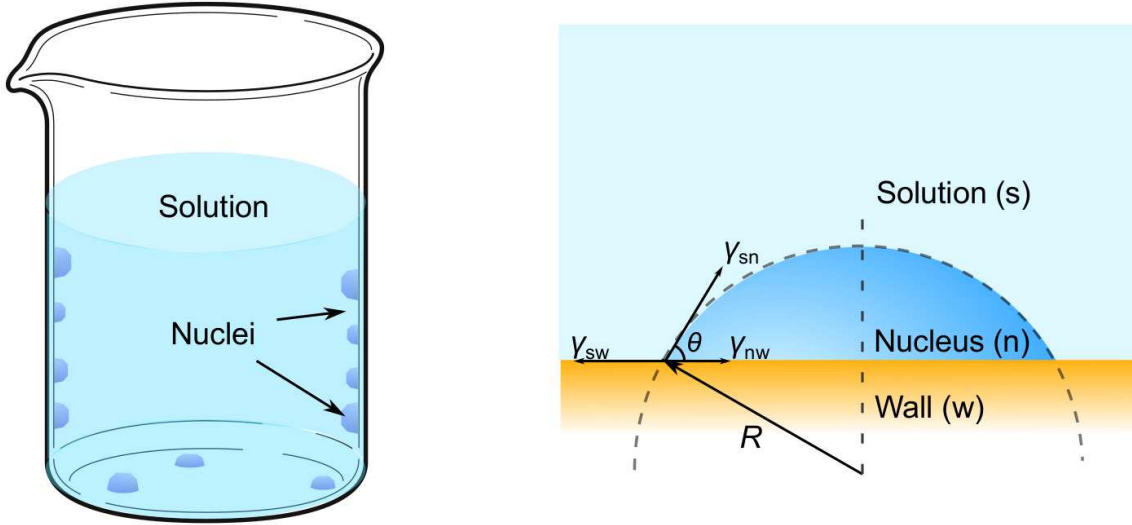- Interfacial area of nucleus with wall: $A_{\mathrm{c}} = \pi R^2 \sin^2\theta$

Figure 5.4: Heterogeneous nucleation. Left: heterogeneous nucleation occurs on the wall of container. Right: simplied geometry of a nucleus on wall. The nucleus is assumed to be a spherical droplet with contact angle θ.

The total free energy of the system considering volume and surface contributions is:

$$\Delta G = V_\mathrm{n}\Delta G_\mathrm{V} + \gamma_\mathrm{sn}A_\mathrm{s} + (\gamma_\mathrm{nw} - \gamma_\mathrm{sw})A_\mathrm{c} \tag{5.10}$$

where the index s, n and w denote the solution, nucleus and wall, respectively. The interfacial tensions are linked by the Young equation:

$$\gamma_\mathrm{sw} = \gamma_\mathrm{nw} + \gamma_\mathrm{sn}\cos\theta \tag{5.11}$$

The heterogeneous nucleation free energy is then:

$$\Delta G_\mathrm{het} = \underbrace{\left[\frac{4\pi R^3}{3}\Delta G_\mathrm{v} + 4\pi R^2\gamma_\mathrm{sn}\right]}_{\Delta G_\mathrm{homo}}\left[\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right] \tag{5.12}$$

We can see that the heterogeneous and homogeneous nucleation free energy differ only by a factor:

$$\frac{\Delta G_\mathrm{het}}{\Delta G_\mathrm{homo}} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = f \tag{5.13}$$

As seen in Figure 5.5a, the value of f monotonically increases with θ. As a consequence, the heterogeneous nucleation free energy ΔG_het decreases when θ is smaller. If $\theta \to 0$, the heterogeneous nucleation barrier $\Delta G_\mathrm{c,het} \to 0$, the nucleus completely wets the wall and the heterogeneous nucleation is spontaneous. For θ form 0° to 180°, $\Delta G_\mathrm{het} \leq \Delta G_\mathrm{homo}$, which means heterogeneous nucleation is always preferred over homogeneous nucleation, since ΔG_c for heterogeneous nucleation is lowered due to larger nucleus-wall interaction (Figure 5.5b). To suppress the heterogeneous nucleation and get large and uniform crystals grown from bulk
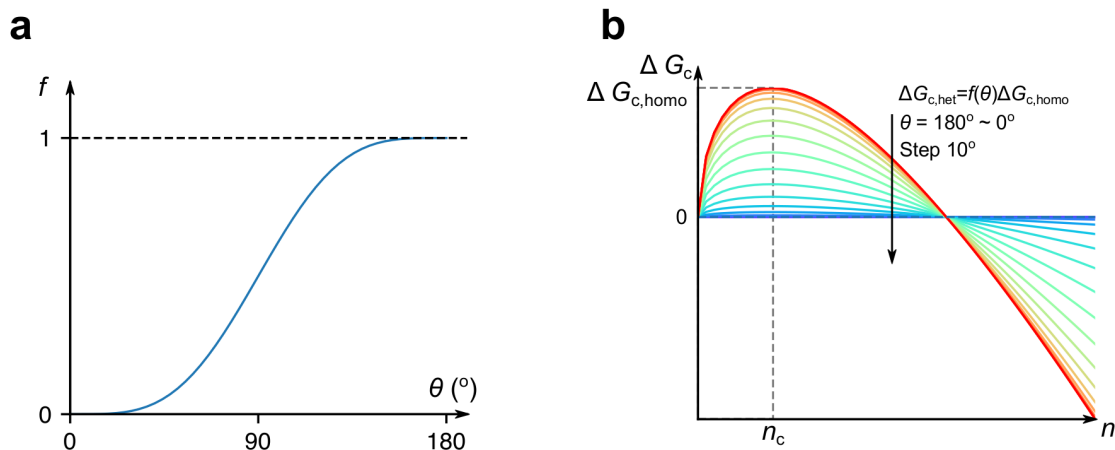
Figure 5.5: (a) Value of f (ratio between ΔG_{het} and ΔG_{homo}) as a function of contact angle θ. (b) Evolution of ΔG_{het} with θ. When θ drops the nucleation barrier decreases.

solution, we need to find a low-energy wall with larger contact angle θ, such as teflon. Since $\dot{N} \sim \exp(-\frac{\Delta G_c}{k_B T})$, increasing θ also suppress the nucleation rate. On the other hand, we can also enhance the heterogeneous nucleation, by reducing the surface contact angle. In this case rough (fractal) surfaces are usually involved due to the Wenzel-like wetting state[7] which we discussed in Lecture 2.

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