

Chapter 6

Solidification

Almost all processing of technologically important metals includes a step where liquid material is cooled to form a solid. It is very common, for example, for the components of metallurgical alloys to be mixed in the liquid state so that, upon solidification, an alloy with the desired composition is formed. In order to form a solid from an undercooled melt we need formation of crystalline nuclei and growth of these nuclei to form a solid. Transformations which occur by these two processes, nucleation and growth, are examples of first order phase transitions. Before beginning our discussion of nucleation and growth of pure materials, we make some general comments about phase transitions.

The condition of thermodynamic equilibrium implies minimization of some free energy. For processes at constant pressure P , we minimize the Gibbs free energy, $G = H - TS$, while for processes at constant volume V we minimize the Helmholtz free energy $F = U - TS$, where H and U are the enthalpy and internal energy respectively and are related by $H = U + PV$, and S is the entropy and T the temperature. For most solid-liquid or solid-solid transitions it is usually more practical to work at constant pressure, so G is the appropriate thermodynamic potential. However, at atmospheric pressure, the changes in the PV term for condensed phase reactions are usually small compared to changes in the other terms, so either F or G can be used.

A first order phase transition involves two distinct phases which are physically separated by a sharp¹ interface, across which there is usually a sym-

¹It is often impossible to distinguish the phase of the atoms right at the interface, so

metry change. Each phase is represented by a free energy which is a function of temperature, pressure (or volume), and composition. In equilibrium, the system will configure itself in the phase which has the lower free energy. Points where the free energies of the two phases cross are transition points. For example, consider the free energy as a function of temperature for solid and liquid phases shown in Fig. 6.1. The free energies of the liquid and solid cross at the melting temperature T_m . In equilibrium, the free energy of the system is a continuous curve following the free energy of the liquid above T_m and that of the solid below T_m . There is a slope change in the free energy at the T_m , so entropy given by:

$$S = - \left. \frac{\partial G}{\partial T} \right|_P = - \left. \frac{\partial F}{\partial T} \right|_V$$

will have a discontinuity at the transition point:

$$\Delta S_F = \left(S^{\text{liquid}} - S^{\text{solid}} \right) \Big|_{T=T_m} = \left(\left. \frac{\partial G^{\text{solid}}}{\partial T} \right|_P - \left. \frac{\partial G^{\text{liquid}}}{\partial T} \right|_P \right) \Big|_{T=T_m}$$

A liquid which is cooled infinitely slowly will transform to the solid phase at the melting temperature. However real transitions occur at finite rates, and thus involve excursions from equilibrium which provide the driving force for the transition. A liquid cooled below T_m will have a free energy higher than that of the solid by an amount:

$$\Delta G = G^{\text{liquid}} - G^{\text{solid}}$$

Since solidification will decrease the free energy of the system, ΔG is said to be the driving force for the transformation. This is exactly analogous to the driving force for diffusion being provided by gradients in external potentials or gradients in the non-ideal part of the chemical potential (Sec. 4.3).

We can estimate this driving force with a very simple expression if we are willing to assume that there is no difference in the heat capacities of the two phases. Since $G = H - TS$ we find for the temperature derivatives:

$$\left. \frac{\partial G}{\partial T} \right|_P = -S = \left. \frac{\partial H}{\partial T} \right|_P - T \left. \frac{\partial S}{\partial T} \right|_P - S$$

even sharp interfaces may be spread out over a few atomic distances.

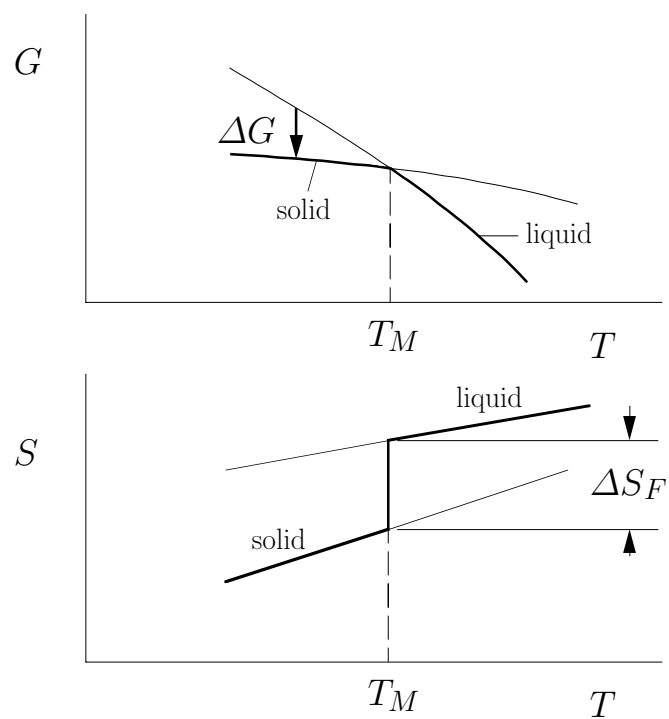


Figure 6.1: Schematic of free energy versus temperature for solid and liquid phases.

So that:

$$C_P \equiv \left. \frac{\partial H}{\partial T} \right|_P = T \left. \frac{\partial S}{\partial T} \right|_P = -T \left. \frac{\partial^2 G}{\partial T^2} \right|_P$$

where C_P is the heat capacity at constant pressure, which is the change in enthalpy per change in temperature. We can then find the difference in enthalpy between the liquid and solid states by integrating from the transition temperature:

$$\Delta H = H^{\text{liquid}} - H^{\text{solid}} = \Delta H_F + \int_{T_m}^T \Delta C_P dT$$

where ΔH_F is the heat of fusion which is the heat released by solidification given by:

$$\Delta H_F = \left(H^{\text{liquid}} - H^{\text{solid}} \right) \Big|_{T=T_m}$$

and $\Delta C_P = C_P^{\text{liquid}} - C_P^{\text{solid}}$. Similarly we can find the entropy difference:

$$\Delta S = S^{\text{liquid}} - S^{\text{solid}} = \Delta S_F + \int_{T_m}^T \frac{\Delta C_P}{T} dT$$

Since $\Delta G = \Delta H - T\Delta S$, and at $T = T_m$ $\Delta G = 0$ we see that:

$$\Delta H_F = T_m \Delta S_F \quad (6.1)$$

If we now assume that $\Delta C_P = 0$, that is the curvature of the free energies of the two phases are zero or equal, then we see that:

$$\Delta G = \Delta H_F - T \Delta S_F$$

Inserting Eqn. 6.1 we find:

$$\begin{aligned} \Delta G &= \Delta H_F - T \frac{\Delta H_F}{T_m} \\ &= \Delta H_F \left(\frac{T_m - T}{T_m} \right) \end{aligned} \quad (6.2)$$

Equation 6.2 is known as the Turnbull extrapolation. It is valid for most practical solidification situations, except in cases of extremely rapid cooling where large undercoolings can be present.

In contrast to the behavior of a first order phase transition, a second order phase transition has both a continuous free energy and a continuous

entropy (free energy slope). The transition usually occurs over a temperature range of several degrees rather than at one point. The free energy is usually represented as a single continuous curve, while the entropy has separate curves for the two phases. There is a discontinuity in slope of S , which results in a discontinuity in heat capacity, as shown in Fig. 6.2.

Some structural transitions are second order phase transitions, for example the FCC to FCT transition in BaTiO_3 . Order-disorder transitions, for example the β to β' transition in CuZn , can also be second order phase transitions.

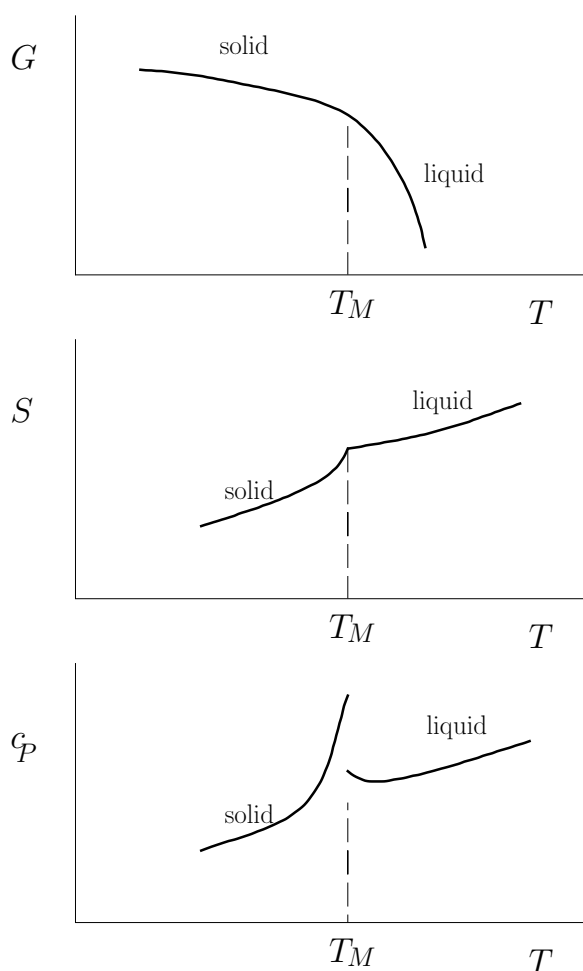


Figure 6.2: Schematic of free energy, entropy and heat capacity as a function of temperature for a second order phase transition.

6.1 Nucleation

We now return to solidification of a pure undercooled melt, which, of course, is an example of a first order phase transition. The thermodynamic driving force provided by the undercooling, must accomplish two processes; nucleation and growth. In considering nucleation, we first establish that the surface or interface energy will result in an energy barrier which destabilizes nuclei under a certain critical size. We then examine the population of nuclei and the rate at which critical nuclei form to find the nucleation rate.

6.1.1 Nucleation Barrier

We consider the free energy change associated with formation of a solid particle from an undercooled liquid, as shown schematically in Fig. 6.3. There are two terms, the first is the negative, volume term associated with the bulk condensation energy, and the second is the positive, surface term associated with formation of the new interfacial area between the solid and the liquid. Thus, if ΔG_T is the total free energy change associated with formation of a solid particle, we can write:

$$\Delta G_T = -\frac{V}{V_A}\Delta g_A + A\gamma_{SL}$$

where V is the volume of the solid particle, A is the solid particle surface area, V_A is the atomic volume, Δg_A is the free energy change per atom associated with the liquid-solid transformation, and γ_{SL} is the surface energy. The free energy change per atom Δg_A is related to the free energy change per volume ΔG_V through:

$$\Delta g_A = \Delta G_V V_A$$

If we take N to be the number of atoms in the solid particle, we can write:

$$\Delta G_T = -N\Delta g_A + \eta N^{2/3}\gamma_{SL} \quad (6.3)$$

where η is a shape factor defined by:

$$\eta = \frac{A}{N^{2/3}}$$

Since the negative, volume term of Eqn. 6.3 is linear in n while the positive, surface term varies as $N^{2/3}$, the sum of the two terms will exhibit a

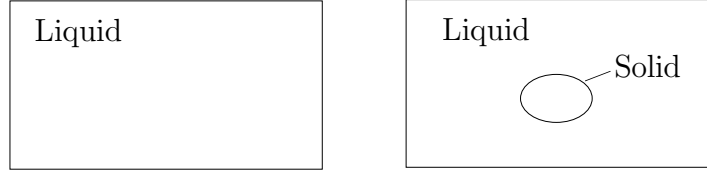


Figure 6.3: Schematic of undercooled liquid and an undercooled liquid with a solid particle.

peak, as shown in Fig. 6.4. The critical number of atoms, N^* , corresponding to this can be found by setting:

$$\left. \frac{\partial \Delta G_T}{\partial N} \right|_{N=N^*} = 0$$

and solving for N^* , we find:

$$N^* = \left(\frac{2\eta\gamma_{SL}}{3\Delta g_A} \right)^3 \quad (6.4)$$

This expression for the critical number of atoms in a solid particle is valid for arbitrarily-shaped particles.

The free energy, ΔG^* , of a critical size solid particle can be found by inserting N^* from Eqn. 6.4 into the expression for the free energy change as a function of number of atoms Eqn. 6.3. We find:

$$\begin{aligned} \Delta G^* &= -N^* \Delta g_A + \eta \gamma_{SL} (N^*)^{2/3} \\ &= \frac{4}{27} \frac{\eta^3 \gamma_{SL}^3}{\Delta g_A^2} \\ &= \frac{\gamma_{SL} \eta (N^*)^{2/3}}{3} \end{aligned} \quad (6.5)$$

If our solid particles are spherical in shape, the number of atoms in a particle with radius r is:

$$N = \frac{4}{3V_A} \pi r^3$$

and the shape factor becomes:

$$\eta = \frac{A}{N^{2/3}} = \frac{4\pi r^2}{[4\pi r^3/(3V_A)]^{2/3}} = (36\pi)^{1/3} V_A^{2/3}$$

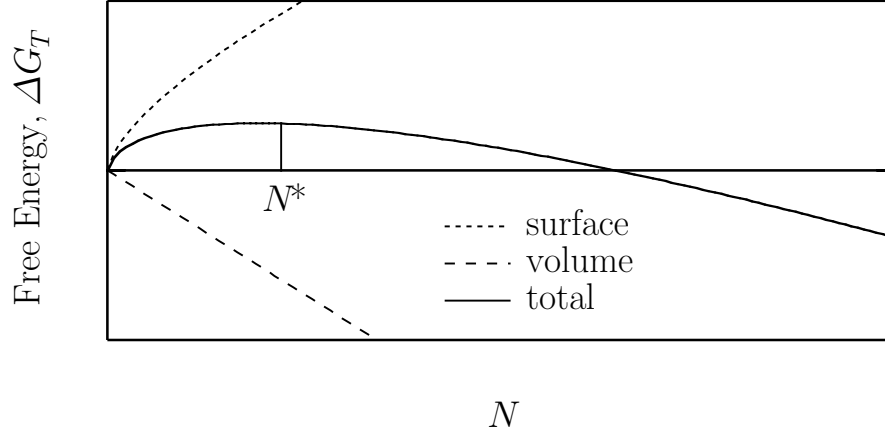


Figure 6.4: ΔG_T versus N showing volume and surface contributions resulting in a peak at $N = N^*$.

so that the free energy change associated with forming a particle of radius r is:

$$\Delta G_T = -\frac{4}{3}\pi r^3 \frac{\Delta g_A}{V_A} + 4\pi r^2 \gamma_{SL} = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

We can find the critical radius r^* by differentiating this directly or by substituting the above expressions for η and n into Eqn. 6.4:

$$r^* = \frac{2\gamma_{SL}V_A}{\Delta g_A} = \frac{2\gamma_{SL}}{\Delta G_V}$$

The energy change associated with formation of a particle of this radius is:

$$\Delta G^* = \frac{16\pi V_A^2 \gamma_{SL}^3}{3\Delta g_A^2} = \frac{16\pi \gamma_{SL}^3}{3\Delta G_V^2} \quad (6.6)$$

If we consider the process of adding an one additional atom to a solid particle of a given size, we see that for solid particles with $N < N^*$ the addition of one more atom will increase the free energy, while for solid particles with $N > N^*$, addition of an atom will decrease the free energy. Hence, solid particles with $N < N^*$ tend to shrink and disappear. These solid particles are known as embryos. Solid particles with $N > N^*$ will grow, since this

decreases the free energy. The process of adding one additional atom to a solid particle with $N = N^*$ is the nucleation process, since this results in a nuclei, the growth of which will decrease the free energy.

6.1.2 Distribution of Solid Particle Sizes

The equilibrium distribution of solid particles is described by x_N which is the number fraction of solid particles with a given size. The concentration of a particle of a given size can be found in a manner exactly analogous to that used in finding the equilibrium concentration of vacancies. The formation of clusters in the collection of atoms increases the number of ways the system can arrange itself, and hence increases the entropy. Thus, even though the enthalpy will increase if a sub-critical cluster is formed, there will be some concentration of clusters of a given size which will minimize the free energy. Thus x_N is given by:

$$x_N = \exp\left(-\frac{\Delta G_T}{k_B T}\right)$$

where ΔG_T is given by Eqn. 6.3. The actual number fraction of solid particles of a given size will be different from the equilibrium distribution since solid particles with $N > N^*$ will grow and will be removed from the distribution. The Volmer-Webber theory of nucleation assumes that the actual number fraction of solid particles with N atoms, Z_N , is given by:

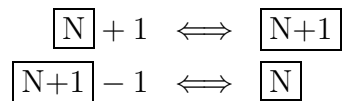
$$Z_N = \begin{cases} x_N & \text{if } N < N^* \\ 0 & \text{if } N > N^* \end{cases} \quad (6.7)$$

In this theory, the number of critically sized nuclei is given by:

$$Z^* = \exp\left(-\frac{\Delta G^*}{k_B T}\right) = x_{N^*}$$

with ΔG^* given by Eqn. 6.5 or 6.6.

The Becker-Döring theory of nucleation goes beyond the unrealistic assumptions of Eqn. 6.7 and considers the effect of the nucleation process on the population of particles. By considering the evolution of the population distribution via the reactions:



they find (after some mathematical shenanigans which are beyond the scope of this course) the number of critical sized nuclei:

$$\begin{aligned} Z^* &= \frac{1}{N^*} \left(\frac{\Delta G^*}{3\pi k_B T} \right)^{1/2} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \\ &= \frac{1}{N^*} \left(\frac{\Delta G^*}{3\pi k_B T} \right)^{1/2} x_{N^*} \end{aligned}$$

The factor:

$$\frac{1}{N^*} \left(\frac{\Delta G^*}{3\pi k_B T} \right)^{1/2} \equiv \Gamma_z$$

is known as the Zeldovich factor and was first derived by Farkas. A comparison of the population of particles predicted by the Volmer-Webber and Becker-Döring theories is shown in Fig. 6.5.

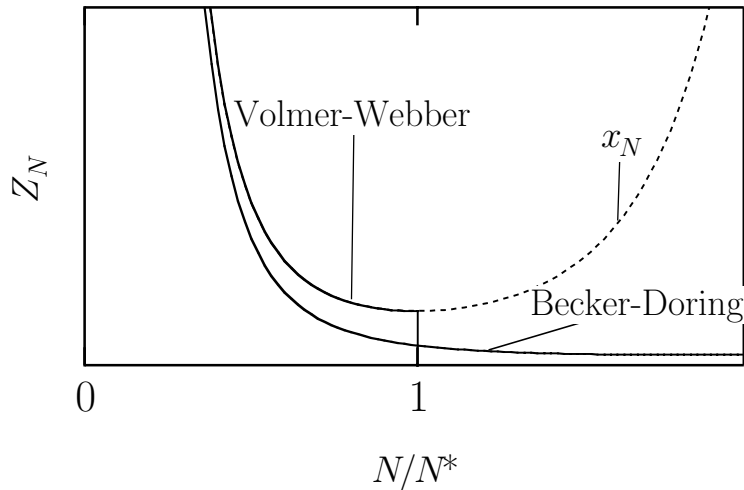


Figure 6.5: Schematic of number of nuclei as a function of number of atoms for Volmer-Webber and Becker-Döring nucleation theories. Dotted line is the equilibrium number assuming no depletion due to growth.

6.1.3 Nucleation Rate

A nuclei will be formed each time an atom sticks to a critical sized particle. Hence the nucleation rate, I , per volume is given by:

$$I = R\sigma A^* \frac{Z^*}{V_A}$$

where R is the sticking rate per site, σ is the sites per area on the critical nucleus, and A^* is the area of a critical nucleus, and V_A is the atomic volume.

In the case of a liquid-solid transformation, the attachment rate is exactly analogous to the exchange frequency in the diffusion process, and can be expressed as:

$$R = \nu_0 \exp\left(-\frac{\Delta G'_M}{k_B T}\right)$$

where ν_0 is some vibration frequency, and $\Delta G'_M$ is the activation energy for the jump process. Thus we have for the nucleation rate:

$$I = \frac{\sigma A^* \nu_0}{V_A N^*} \left(\frac{\Delta G^*}{3\pi k_B T}\right)^{1/2} \exp\left[-\left(\frac{\Delta G^* + \Delta G'_M}{k_B T}\right)\right]$$

The temperature dependence is dominated by ΔG^* which is given by Eqn. 6.5 or for a sphere, Eqn. 6.6. We can use the Turnbull extrapolation to find Δg_A for the liquid-solid case:

$$\Delta g_A = \Delta h_F \frac{\Delta T}{T_m}$$

where $\Delta h_F = h_L - h_S$ is the difference in enthalpy per atom between the liquid and solid states. For spherical nuclei we find:

$$\begin{aligned} \Delta G^* &= \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \\ &= \frac{16\pi V_A^2 \gamma_{SL}^3 T_m^2}{3\Delta h_F^2 (\Delta T)^2} \end{aligned}$$

Relative to this $1/(\Delta T)^2$ dependence in the exponent the other terms are nearly constant, and Turnbull has suggested that homogeneous nucleation of the solid from an undercooled liquid can be approximated by:

$$I \left(\frac{1}{\text{m}^3\text{s}}\right) \approx 10^{39} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \quad (6.8)$$

6.1.4 Heterogeneous Nucleation

In practice, nucleation of the solid phase rarely takes place homogeneously in the bulk of the liquid. In most situations, nucleation initiates on the walls of the containment vessel or on particles of high melting point oxides inadvertently dispersed in the melt. These inhomogeneous nucleation sites reduce the nucleation barrier by lowering the surface energy cost of forming a nucleus. In fact, only by dispersing the liquid into droplets small enough so that there is an appreciable chance of not having any nucleation sites in a droplet, can homogeneous nucleation be achieved.

To examine how heterogeneities effect the energy of forming a solid phase particle in an undercooled liquid, we consider formation of a spherical solid cap of radius r and contact angle θ on a mold wall, as shown in Fig. 6.6. Here we have three different interfacial energies to consider: γ_{SL} is the surface energy between the solid and liquid, γ_{SM} is that between the solid and the mold, and γ_{LM} is that between the liquid and the mold. The contact angle θ is determined by the surface energy balance:

$$\gamma_{LM} = \gamma_{SM} + \gamma_{SL} \cos \theta$$

This expression, derived in Appendix C can be viewed as a force balance considering each of the surface energies as a surface stress, although strictly speaking γ is the surface energy and not the surface stress. It is straightforward geometry to show that the volume V_S of the spherical cap is:

$$V_S = \frac{\pi r^3}{3} (2 - 3 \cos \theta + \cos^3 \theta)$$

and the area A_{SL} of the solid liquid contact is:

$$A_{SL} = 2\pi r^2(1 - \cos \theta)$$

and the area A_{SM} of solid mold contact is:

$$A_{SM} = \pi(r \sin \theta)^2$$

The formation of this spherical cap involves: changing the liquid to the solid, creating new interface area A_{SL} and changing the interface energy from γ_{LM} to γ_{SM} in the contact area A_{SM} . Hence the free energy of formation is:

$$\Delta G_T = -V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{SM} (\gamma_{SM} - \gamma_{LM})$$

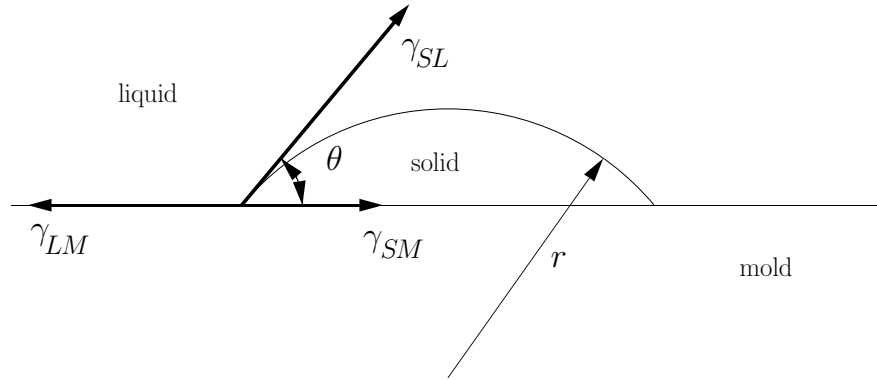


Figure 6.6: Schematic of a solid spherical cap with radius r and contact angle θ forming on a mold wall.

which can be shown to be given by:

$$\Delta G_T = \left[-\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \right] S(\theta)$$

where $S(\theta)$ is a contact angle dependent function:

$$S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4$$

which is shown plotted in Fig. 6.7.

Apart from the factor of $S(\theta)$, this is the same expression we obtained for homogeneous nucleation. The energy of formation will again have a peak at a the critical radius r^* given by:

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$

but the energy barrier will be reduced by a factor of $S(\theta)$:

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} S(\theta)$$

This is shown schematically in Fig. 6.8.

Since ΔG_{het}^* is much less than ΔG_{homo}^* , nucleation can occur at much smaller undercoolings. This is a result of the increased ratio of volume to surface energy for the spherical cap compared to a sphere.

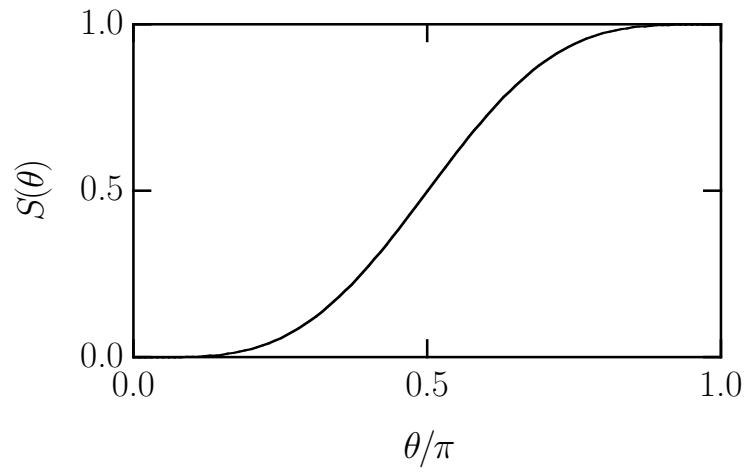


Figure 6.7: Plot of the reduction factor $S(\theta)$ for nucleation barrier for heterogeneous nucleation.

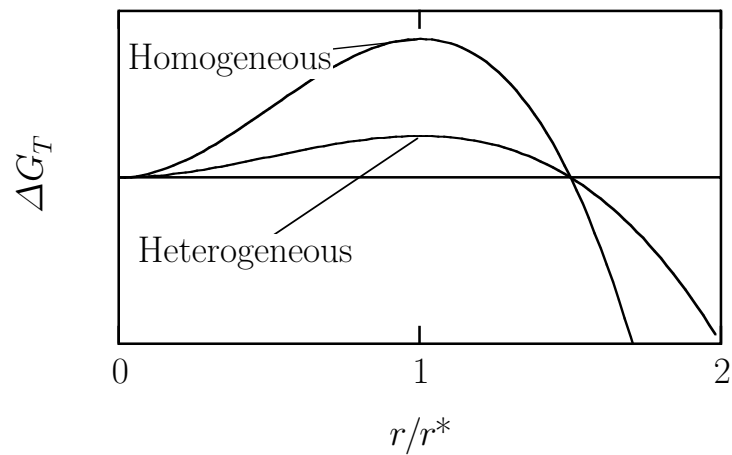


Figure 6.8: Formation free energy as a function of particle radius both homogeneous and heterogeneous nucleation of a solid particle in an undercooled liquid.

Recall that the probability of a critical nucleus occurring on a site is:

$$\exp\left(-\frac{\Delta G^*}{kT}\right)$$

so that even though the number of possible sites for nucleation is much smaller for heterogeneous nucleation, the probability of it happening on a given site is so much higher that heterogeneous nucleation usually dominates.

6.1.5 Numerical Estimation of Nucleation Rates

So far we have discussed nucleation with only passing reference to any real numbers. We can make some good headway toward estimating nucleation rates by using a couple of simple assumptions which are in the spirit of those often made this course. The result of this simple analysis is a good starting point for estimations of nucleation rates and helps to solidify our understanding of the underlying materials science.

We first consider the critical radius r^* , given by

$$r^* = \frac{2\gamma}{\Delta G_V}$$

where γ is the interface energy, in this case between liquid and solid, and ΔG_V is the volume driving force for the transition, given by

$$\Delta G_V \approx \Delta H_F \frac{\Delta T}{T_m} = \frac{\Delta h_F}{V_A} \frac{\Delta T}{T_m}$$

where V_A is the atomic volume, ΔH_F and Δh_F are the enthalpy of fusion per volume and per atom respectively, and ΔT and T_m are the undercooling and melting temperature respectively. The interface energy γ can be estimated as

$$\gamma \approx \mathcal{F}_{BB} \Delta h_F \sigma$$

where \mathcal{F}_{BB} is the fraction of broken bonds at the interface and σ is the atom surface density. Using $\Delta h_F = \Delta H_F V_A$ and

$$\sigma \approx (1/V_A)^{2/3}$$

and taking $\mathcal{F}_{BB} \approx 1/2$ as found for liquid/solid interfaces in our chapter on surfaces, we can find

$$r^* \approx V_A^{1/3} \frac{T_m}{\Delta T}$$