

# Fundamentals of Materials Science

## Homework 21, SS 2017

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This homework assignment continues with a practice on homogenous nucleation for its thermodynamic and structural conditions. The derivation of the critical radius and activation energy for nucleation is very important with the assumption of a spherical solid as the starting nucleation piece. It is also desirable that you understand the concepts of critical undercooling and its relationship with the nuclei radius. The problem statements seem to be longer than usual, but it is a context for which each problem is posed.

1. Do it again and again for it is very important. Below  $T_m$ ,  $\Delta G_v$  is positive so that the free energy change associated with the formation of a small volume of solid has a negative contribution due to the lower free energy of a bulk solid, but there is also a positive contribution due to the creation of a solid/liquid interface. The excess free energy associated with the solid particle can be minimized by the correct choice of particle shape. If  $\gamma_{SL}$  is isotropic this is a sphere of radius  $r$ . Then we can arrive at the equation discussed in class like

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \quad (\text{Eq. 1})$$

Show that differentiation of Equation 1 leads to Equations 2 and 3 below.

$$r^* = \frac{2\gamma_{SL}}{\Delta G_v} \quad (\text{Eq. 2})$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2} \quad (\text{Eq. 3})$$

Solution

When the differentiation of Equation 1 is equal to 0, we can get  $r^*$ ,

$$\begin{aligned} \frac{d(\Delta G_r)}{dr} &= -\frac{4}{3}\pi \Delta G_v (3r^2) + 4\pi \gamma_{SL} (2r) = 0 \\ \therefore -4\pi \Delta G_v r^2 + 8\pi \gamma_{SL} r &= 0 \\ \Delta G_v r - 2\gamma_{SL} &= 0 \end{aligned}$$

Thus,

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

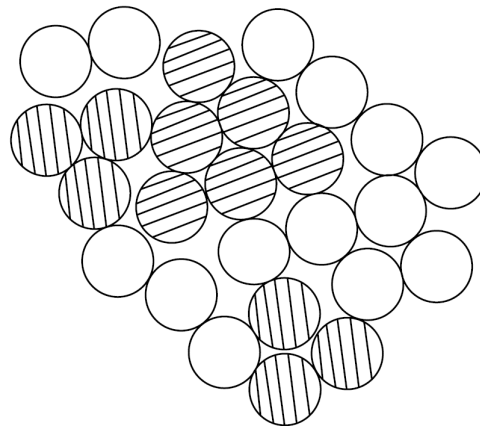
Substitute  $r^*$  into Equation 1, we can get  $\Delta G^*$ ,

$$\begin{aligned} \Delta G^* &= -\frac{4}{3}\pi \left( \frac{2\gamma_{SL}}{\Delta G_v} \right)^3 \Delta G_v + 4\pi \left( -\frac{2\gamma_{SL}}{\Delta G_v} \right)^2 \gamma_{SL} \\ &= -\frac{32\pi\gamma_{SL}^3}{3\Delta G_v^2} + \frac{16\pi\gamma_{SL}^3}{\Delta G_v^2} = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} \end{aligned}$$

2. To understand how it is possible for a stable solid nucleus to form homogeneously from the liquid it is first necessary to examine the atomic structure of the liquid phase. From dilatometric measurements it is known that at the melting point the liquid phase has a volume 2–4% greater than the solid. Therefore, there is a great deal more freedom of movement of atoms in the liquid and when averaged over a period of time the atom positions appear completely random. However, an instantaneous picture of the liquid would reveal the presence of many small close-packed clusters of atoms which are temporarily in the same crystalline array as in the solid, as shown in Fig. 1 below. On average the number of spherical clusters of radius  $r$  is given by

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right) \quad (\text{Eq. 4})$$

where  $n_0$  is the total number of atoms in the system,  $\Delta G_r$  is the excess free energy associated with the cluster, Equation 1, and  $k$  is Boltzmann's constant. For a liquid above  $T_m$  this relationship applies for all values of  $r$ . Below  $T_m$  it only applies for  $r \leq r^*$  because clusters greater than the critical size are stable nuclei of solid and no longer part of the liquid. Since  $n_r$  decreases exponentially with  $\Delta G_r$  (which itself increases rapidly with  $r$ ) the probability of finding a given cluster decreases very rapidly as the cluster size increases. For example, by combining Equations 1 and 4 it can be shown that 1 mm<sup>3</sup> of copper at its melting point ( $\sim 10^{20}$  atoms) should on average contain  $\sim 10^{14}$  clusters of 0.3 nm radius (i.e.  $\sim 10$  atoms) but only  $\sim 10$  clusters with a radius of 0.6 nm (i.e.  $\sim 60$  atoms). These numbers are of course only approximate. Such small clusters of atoms cannot be considered to be spherical, and even more important the effective value of  $\gamma$  used in calculating  $\Delta G_r$  (equation 1) is very probably a function of the cluster size. However, the above calculations do illustrate how sensitively cluster density depends on their size.



**Figure 1** A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are present.

Use Equations 1 and 4 to estimate the number of crystal-like clusters in 1 mm<sup>3</sup> of copper at its melting point for spherical clusters containing (a) 10 atoms, (b) 60 atoms. What volume of liquid copper is likely to contain one cluster of 100 atoms? The atomic volume of liquid copper is  $1.6 \times 10^{-29}$  m<sup>3</sup>,  $\gamma_{SL}$  is  $0.177$  J m<sup>-2</sup>,  $k = 1.38 \times 10^{-23}$  J K<sup>-1</sup>,  $T_m = 1356$  K.

### **Solution**

Since it is at melting point for spherical clusters,  $\Delta G_v$  is equal to 0, thus,

$$\Delta G_r = 4\pi r^2 \gamma_{SL}$$

$r$  can be calculated by

$$\begin{aligned} nV &= \frac{4}{3} \pi r^3 \\ \Rightarrow r &= \sqrt[3]{\frac{3nV}{4\pi}} \end{aligned}$$

Thus,  $\Delta G_v$  is equal to,

$$\Delta G_r = 4\pi r^2 \gamma_{SL} = 4\pi \left( \frac{3nV}{4\pi} \right)^{\frac{2}{3}} \gamma_{SL}$$

(a) When n is equal to 10,

$$\begin{aligned} \Delta G_r &= 4\pi \left( \frac{3nV}{4\pi} \right)^{\frac{2}{3}} \gamma_{SL} \\ &= 4\pi \left( \frac{30 \times 1.6 \times 10^{-29} m^3}{4\pi} \right)^{\frac{2}{3}} \times 0.177 J/m^2 \\ &= 25.22 \times 10^{-20} J \end{aligned}$$

Thus, according to the Equation 4, the number of clusters per  $mm^3$  is equal to,

$$\begin{aligned} n_r &= n_0 \exp \left( - \frac{\Delta G_r}{kT} \right) \\ &= \frac{1 \times 10^{-9} m^3}{1.6 \times 10^{-29} m^3} \exp \left( - \frac{25.22 \times 10^{-20} J}{1.38 \times 10^{-23} J/K \times 1356 K} \right) \\ &= 8.76 \times 10^{13} \end{aligned}$$

(b) When n is equal to 60,  $\Delta G_r = 4\pi \left( \frac{3nV}{4\pi} \right)^{\frac{2}{3}} \gamma_{SL}$

$$\begin{aligned} &= 4\pi \left( \frac{180 \times 1.6 \times 10^{-29} m^3}{4\pi} \right)^{\frac{2}{3}} \times 0.177 J/m^2 \\ &= 83.28 \times 10^{-20} J \end{aligned}$$

Thus, according to the Equation 4, the number of clusters per  $mm^3$  is equal to,

$$\begin{aligned} n_r &= n_0 \exp \left( - \frac{\Delta G_r}{kT} \right) \\ &= \frac{1 \times 10^{-9} m^3}{1.6 \times 10^{-29} m^3} \exp \left( - \frac{83.28 \times 10^{-20} J}{1.38 \times 10^{-23} J/K \times 1356 K} \right) \\ &= 2.94 \end{aligned}$$

(c) When n is equal to 100,  $\Delta G_r = 4\pi \left( \frac{3nV}{4\pi} \right)^{\frac{2}{3}} \gamma_{SL}$

$$\begin{aligned} &= 4\pi \left( \frac{300 \times 1.6 \times 10^{-29} m^3}{4\pi} \right)^{\frac{2}{3}} \times 0.177 J/m^2 \\ &= 117.07 \times 10^{-20} J \end{aligned}$$

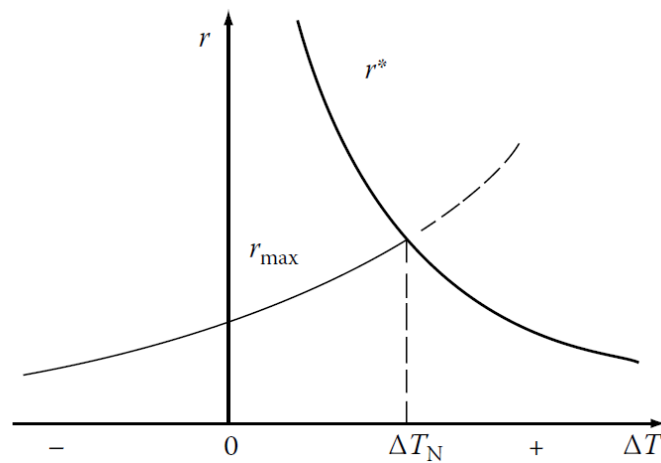
Thus, according to the Equation 4, the number of clusters per  $mm^3$  is equal to,

$$\begin{aligned} n_r &= n_0 \exp \left( - \frac{\Delta G_r}{kT} \right) \\ &= \frac{1 \times 10^{-9} m^3}{1.6 \times 10^{-29} m^3} \exp \left( - \frac{117.07 \times 10^{-20} J}{1.38 \times 10^{-23} J/K \times 1356 K} \right) \\ &= 4.22 \times 10^{-8} \end{aligned}$$

The volume of liquid copper contain one cluster of 100 atoms is,

$$V = \frac{1}{n_r} = \frac{1}{4.22 \times 10^{-8}} = 2.4 \times 10^7 mm^3$$

3. Continued from Problem 2, it can be seen that there is effectively a maximum cluster size,  $\sim 100$  atoms, which has a reasonable probability of occurring in the liquid. The same sort of calculations can be made at temperatures other than  $T_m$ . Below  $T_m$  there is an increasing contribution from  $\Delta G_v$  in Equation 1 as the solid becomes progressively more stable and this has the effect of increasing the 'maximum' cluster size somewhat. Figure 2 shows schematically how  $r_{\max}$  varies with  $\Delta T$ . Of course larger clusters than  $r_{\max}$  are possible in large enough systems or given sufficient time, but the probability of finding clusters only slightly larger than  $r_{\max}$  is extremely small. The critical nucleus size  $r^*$  is also shown in Fig. 2. It can be seen that at small undercoolings,  $r^*$  is so large that there will be virtually no chance of forming a stable nucleus. But as  $\Delta T$  increases  $r^*$  and  $\Delta G^*$  decrease, and for supercoolings of  $\Delta T_N$  or greater there is a very good chance of some clusters reaching  $r^*$  and growing into stable solid particles. In the small droplet experiment, therefore, homogeneous nucleation should occur when the liquid is undercooled by  $\sim \Delta T_N$ . The question to this problem is thus: Why does  $r_{\max}$  in Fig. 2 vary with  $\Delta T$ ?



**Figure 2** The variation of  $r^*$  and  $r_{\max}$  with undercooling  $\Delta T$ .

**(?) Solution**

$r_{\max}$  is considered as the biggest radius particle that can exist at the given temperature, the figure shows when the  $r^*$  curve is beyond the critical undercooling, the critical radii of nuclei becomes smaller than the clusters that would form because of the thermal fluctuations. Thus, the probability of these clusters turning into nuclei are large.

4. Calculate the homogeneous nucleation rate in liquid copper at undercoolings of 180, 200 and 220 K, using the following data:

$$L = 1.88 \times 10^9 \text{ J m}^{-3}, \quad T_m = 1356 \text{ K}, \quad \gamma_{SL} = 0.177 \text{ J m}^{-2},$$

$$f_0 = 10^{11} \text{ s}^{-1}, \quad C_0 = 6 \times 10^{28} \text{ atoms m}^{-3}, \quad k = 1.38 \times 10^{-23} \text{ J K}^{-1}.$$

**Solution**

The homogeneous nucleation rate  $N$  can be calculated by

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2}; \quad \Delta G_v = \frac{\Delta H_f(T_m - T)}{T_m}$$

$$\Rightarrow \Delta G^* = \left( \frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2}$$

$$\dot{N} = C_0 f_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

- (a) When the homogeneous nucleation rate in liquid copper at undercoolings of 180K,

$$\Delta G^* = \left( \frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2}$$

$$= \left( \frac{16\pi \times 0.177^3 \text{ J}^3/\text{m}^6 \times 1356^2 \text{ K}^2}{3 \times 1.88^2 \times 10^{18} \text{ J}^2/\text{m}^6} \right) \frac{1}{180^2 \text{ K}^2}$$

$$= 1.49 \times 10^{-18} \text{ J}$$

$$\dot{N} = C_0 f_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$= 6 \times 10^{28} / \text{m}^3 \times 10^{11} / \text{s} \times \exp\left(-\frac{1.49 \times 10^{-18} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} \times 1176 \text{ K}}\right) = 0.8 \text{ m}^{-3} \text{ s}^{-1}$$

- (b) When the homogeneous nucleation rate in liquid copper at undercoolings of 200K,

$$\Delta G^* = \left( \frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2}$$

$$= \left( \frac{16\pi \times 0.177^3 \text{ J}^3/\text{m}^6 \times 1356^2 \text{ K}^2}{3 \times 1.88^2 \times 10^{18} \text{ J}^2/\text{m}^6} \right) \frac{1}{200^2 \text{ K}^2}$$

$$= 1.21 \times 10^{-18} \text{ J}$$

$$\dot{N} = C_0 f_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$= 6 \times 10^{28} / \text{m}^3 \times 10^{11} / \text{s} \times \exp\left(-\frac{1.21 \times 10^{-18} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} \times 1156 \text{ K}}\right) = 6.9 \times 10^6 \text{ m}^{-3} \text{ s}^{-1}$$

- (c) When the homogeneous nucleation rate in liquid copper at undercoolings of 220K,

$$\Delta G^* = \left( \frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2} \right) \frac{1}{(T_m - T)^2}$$

$$= \left( \frac{16\pi \times 0.177^3 \text{ J}^3/\text{m}^6 \times 1356^2 \text{ K}^2}{3 \times 1.88^2 \times 10^{18} \text{ J}^2/\text{m}^6} \right) \frac{1}{220^2 \text{ K}^2}$$

$$= 1.00 \times 10^{-18} \text{ J}$$

$$\dot{N} = C_0 f_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$$

$$= 6 \times 10^{28} / \text{m}^3 \times 10^{11} / \text{s} \times \exp\left(-\frac{1.00 \times 10^{-18} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} \times 1136 \text{ K}}\right) = 1.2 \times 10^{12} \text{ m}^{-3} \text{ s}^{-1}$$