

## 나노기술과 재료

### Homework No 3;

1. During the lecture, I introduced several models of how the melting temperature is changed with respect to the feature size. The models that I introduced are based on several papers published on this topic. The models might be different depending on how, thermodynamically, they approached.

In the following I will introduce one simple model. Study this and read the models proposed by others and compare each model.

One of the simplest models is as follow;

- (a) Take a particle of solid in equilibrium with its liquid.

At equilibrium,  $T_s = T_l$  and  $\mu_s = \mu_l$ .

The pressure in solid and liquid are related by:  $P_s - P_l = \frac{2\gamma_{l \rightarrow s}}{r}$

$$d\mu_l = -S_l dT + V_l dP_l$$

$$d\mu_s = -S_s dT + V_s dP_s = -S_s dT + V_s d\left(P_l + \frac{2\gamma_{l \rightarrow s}}{r}\right)$$

- (b) At equilibrium, the chemical potential of solid and liquid are equal, and they remain equal as the temperature and pressure change. Thus their differentials are equal.

$$-S_l dT + V_l dP_l = -S_s dT + V_s d\left(P_l + \frac{2\gamma_{l \rightarrow s}}{r}\right)$$

$$(S_l - S_s)dT - (V_l - V_s)dP_l - 2V_s\gamma_{l \rightarrow s} \frac{dr}{r^2} = 0$$

Assuming that we are not concerned with overall pressure changes on the liquid ( $dP_l=0$ ), and noting that  $(S_l - S_s) = \Delta S_m$ , the entropy of melting, we have,

$$\Delta S_m dT = 2V_s \gamma_{l \rightarrow s} \frac{dr}{r^2}$$

- (c) Integrating from the melting temperature of a large particle (with infinite radius of curvature) to the melting temperature of a particle with radius  $r$  assuming that the entropy of mixing is constant over a small temperature range, we have,

$$\begin{aligned} \Delta S_m \int_{T_\infty}^{T_r} dT &= 2V_s \gamma_{l \rightarrow s} \int_{r=\infty}^r \frac{dr}{r^2} \\ \Delta S_m (T_r - T_\infty) &= \Delta S_m \Delta T = -2V_s \frac{\gamma_{l \rightarrow s}}{r} \\ \Delta T &= -\frac{2V_s \gamma_{l \rightarrow s}}{\Delta S_m} \frac{1}{r} \end{aligned}$$

The entropy of melting is the enthalpy of melting divided by the equilibrium melting temperature, i.e. the melting temperature of the large particles, thus;

$$\Delta T = -\frac{2V_s \gamma_{l \rightarrow s} T_m}{\Delta H_m} \frac{1}{r}$$

The change in melting temperature of a small, spherical particle is inversely proportional to its radius. The same conclusion applies to surfaces. The melting temperature is inversely proportional to the radius of curvature (or the sum of the inverse principal radii of curvature).

2. One of the factors which I think is important is to find out the analogy in between the vacuum process and liquid process. For instance, in the lecture, I mentioned that the nucleation rate is expressed as

$$\begin{aligned} \dot{N} &= n^* (\# \text{ of stable nuclei}) \times \nu_d (\text{collision frequency}) \\ &= K_1 \exp\left(-\frac{\Delta G^*}{kT}\right) K_2 \exp\left(-\frac{Q_d}{kT}\right) \end{aligned}$$

But, in the textbook, you will notice that the nucleation rate in liquid is different

in the sense of finding out the jump frequency. In equation (3.9), it expressed as,

$$R_N = nP\Gamma = \left\{ \frac{C_0 kT}{3\pi\lambda^3 \eta} \right\} \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Please explain why the nucleation rate in the liquid expressed as shown above.

3. During the lecture, I mentioned that I can not derive the equation of (3. 10) in the textbook which describes the growth rate of nanoparticle in the solution. The equation looks as follow.

$$\frac{dr}{dt} = D(C - C_s) \frac{V_m}{r} \quad (3.10 \text{ in textbook})$$

Will you guys please help me and let me know how this equation is derived.