a) For a spherical nucleus, derive the following expression, the energy change during nucleation as a function of number of atoms n in cluster (v is atomic volume).

$$\Delta G = -n\ \Delta G_a + (36\pi)^{\frac{1}{3}}\ n^{\frac{2}{3}}\ v^{\frac{2}{3}}\ \gamma$$

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

$\frac{4}{3}\pi r^3 = n\cdot v$ 이므로. ($r = (3nv/4\pi)^{\frac{1}{3}}$)

$$\Delta G = -n\cdot v\Delta G_v + 4\pi\left(\frac{3nv}{4\pi}\right)^{\frac{2}{3}}\cdot\gamma$$

$$= -nv\Delta G_v + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v^{\frac{2}{3}}\cdot\gamma$$

b) Using the result of (a), derive the expression for the critical number of atoms and energy barrier.

$$\left.\frac{\partial\Delta G}{\partial n}\right|_{n=n^*} = -v\Delta G_v + \frac{2}{3}(36\pi)^{\frac{1}{3}}\cdot n^{-\frac{1}{3}}\cdot v^{\frac{2}{3}}\gamma\Big|_{n=n^*}$$

$$= -v\Delta G_v + \frac{2}{3}(36\pi)^{\frac{1}{3}}(n^*)^{-\frac{1}{3}}v^{\frac{2}{3}}\gamma = 0$$

$$(n^*)^{\frac{1}{3}} = \frac{\frac{2}{3}(36\pi)^{\frac{1}{3}}v^{\frac{2}{3}}\gamma}{v\Delta G_v}$$

$$\therefore n^* = \frac{32}{3}\frac{\pi\cdot\gamma^3}{v(\Delta G_v)^3}$$

$$\Delta G^* = -\frac{32\pi\gamma^3}{3\cancel{v}(\Delta G_v)^{2}}\cancel{v\Delta G_v} + (36\pi)^{\frac{1}{3}}\left(\frac{32\pi\gamma^3}{3\cancel{v}(\Delta G_v)^3}\right)^{\frac{2}{3}}\cdot\cancel{v^{\frac{2}{3}}}\gamma$$

$$= \frac{1}{3\Delta G_v}\left\{-32\pi\gamma^3 + \left(\frac{4\cdot 32^2}{\cancel{3^2}}\right)^{\frac{1}{3}}\cdot\pi\cdot\gamma^3\right\}$$

$$= \frac{16}{3}\pi\cdot\frac{\gamma^3}{(\Delta G_v)^2}$$

c) Assuming isotropic and constant surface energy for both of graphite and diamond, and using the data : $\gamma_{gr} = 3.1\ Jm^{-2}$, $\gamma_{dia} = 3.6, 3.65$ and $3.7\ Jm^{-2}$, respectively $v_{gr} = 8$ Å^3/atom, $v_{dia} = 6$ Å^3/atom, ${}^oG_{dia} - {}^oG_{gr} = 0.02$ eV/atom

For the three slightly different values of surface energy of diamond, compute the number of atoms in clusters where the stability of diamond becomes the same as that of graphite.

$$\Delta G_{gr} = -n({}^oG_v - {}^oG_{gr}) + (36\pi)^{\frac{1}{3}}\ n^{\frac{2}{3}}v_{gr}^{\frac{2}{3}}\gamma_{gr}$$

$$\Delta G_{dia} = -n({}^oG_v - {}^oG_{dia}) + (36\pi)^{\frac{1}{3}}\ n^{\frac{2}{3}}v_{dia}^{\frac{2}{3}}\gamma_{dia}$$

When $\Delta G_{gr} = \Delta G_{dia}$

$$-n({}^oG_{dia} - {}^oG_{gr}) = (36\pi)^{\frac{1}{3}}\ n^{\frac{2}{3}}\left(v_{dia}^{\frac{2}{3}}\gamma_{dia} - v_{gr}^{\frac{2}{3}}\gamma_{gr}\right)$$

$${}^oG_{dia} - {}^oG_{gr} = (36\pi)^{\frac{1}{3}}\ n^{-\frac{1}{3}}\left(v_{gr}^{\frac{2}{3}}\gamma_{gr} - v_{dia}^{\frac{2}{3}}\gamma_{dia}\right)$$

$$\therefore n = \frac{36\pi\left(v_{gr}^{\frac{2}{3}}\gamma_{gr} - v_{dia}^{\frac{2}{3}}\gamma_{dia}\right)^3}{{}^oG_{dia} - {}^oG_{gr}}$$

i) $\gamma_{dia} = 3.6$

$$n = \frac{36\pi\left[(8Å^3/atom)^{\frac{2}{3}}\cdot 3.1\ J/m^2 - (6Å^3/atom)^{\frac{2}{3}}\cdot 3.6\ J/m^2\right]^3}{(0.02\ eV/atom)^3}$$

$\cong 466125\ [10^{-3}\cdot atom] = 466$개.

$$\left(\because \frac{(10^{-30}\cancel{m^3}/atom)^2\cdot(J/\cancel{m^2})^3}{(eV/atom)^3} = 10^{-60}\left(\frac{J}{eV}\right)^3\cdot atom\right.$$

$$\left.= 10^{-60}\cdot(10^{19})^3\cdot atom = 10^{-3}\cdot atom\right)$$

ii) $\gamma_{dia} = 3.65\ J/m^2$ → $n = 145$개

iii) $\gamma_{dia} = 3.7\ J/m^2$ → $n = 24$개

d) What is the necessary condition for a diamond cluster of any size to be more stable than graphite ?

$\Delta G_{dia} < \Delta G_{gr}$ 이면.

$$\underbrace{{}^{o}G_{dia} - {}^{o}G_{gr}}_{<0} = (36\pi)^{\frac{1}{3}} n^{-\frac{1}{3}} \underbrace{\left(V_{gr}^{\frac{2}{3}}\sigma_{gr} - V_{dia}^{\frac{2}{3}}\gamma_{dia}\right)}_{>0}$$ 이며.

$$V_{gr}^{\frac{2}{3}}\sigma_{gr} - V_{dia}^{\frac{2}{3}}\gamma_{dia} > 0$$

$$\therefore \left(\frac{V_{gr}}{V_{dia}}\right)^{\frac{2}{3}} > \frac{\gamma_{dia}}{\gamma_{gr}}$$

e) Assuming that the critical number of atoms for graphite nucleation is 100, estimate the driving force for graphite nucleation.

$$n_{gr}^{*} = \frac{32}{3} \cdot \frac{\pi \cdot \sigma_{gr}^{3}}{V_{gr}(\Delta G_{gr})^{3}} = 100$$

$$\Delta G_{gr} = \left(\frac{32}{300} \cdot \frac{\pi \sigma_{gr}^{3}}{V_{gr}}\right)^{\frac{1}{3}}$$

$$= \left(\frac{32}{300} \cdot \frac{\pi \cdot (3.1\,J/m^2)^3}{8\times10^{-30}\,m^3/atom^3}\right)^{\frac{1}{3}} = 1.25\times10^{-10}\,(J/m^3)$$

f) For the three values of surface energy of diamond, compute the ratio of nucleation rate between graphite and diamond, I_{gra}/I_{dia}.
For the nucleation rate, use the expression: $I = A\cdot\exp(-\Delta G^*/kT)$, and assume that A is the same constant for both of graphite and diamond and T = 300 K.

$$\frac{I_{gra}}{I_{dia}} = \frac{\cancel{A_{gra}} \exp(-\Delta G^{*}_{gra}/kT)}{\cancel{A_{dia}} \exp(-\Delta G^{*}_{dia}/kT)} = \exp\left(\frac{\Delta G^{*}_{dia} - \Delta G^{*}_{gra}}{kT}\right)$$

$$\Delta G_{v,gr} V_{gr} - \Delta G_{v,dia} V_{dia} = {}^{o}G_{dia} - {}^{o}G_{gr} = 0.02\,eV/atom$$

$$\Delta G_{v,dia} = \frac{\Delta G_{v,dia} V_{dia} - 0.02\,eV/atom}{V_{dia}} = 1.39\times10^{10}\,J/m^3$$

$$\Delta G^{*}_{dia} = \frac{16}{3}\pi \frac{\sigma_{dia}^{3}}{\Delta G_{v,dia}^{2}}$$

i) $\gamma_{dia} = 3.6\,J/m^2$

$$\Delta G_{dia} = \frac{16}{3}\pi \cdot \frac{3.6^3}{(1.39\times10^{10})^2} = 4.04\times10^{-18}\,J$$

ii) $\gamma_{dia} = 3.65\,J/m^2$

$$\Delta G_{dia} = 4.22\times10^{-18}\,J$$

iii) $\sigma_{dia} = 3.7\,J/m^2$

$$\Delta G_{dia} = 4.39\times10^{-18}\,J$$

$$\Rightarrow \frac{I_{gra}}{I_{dia}} = \exp\left(\frac{\Delta G^{*}_{dia} - \Delta G^{*}_{gra}}{kT}\right) = \exp\left(\frac{\Delta G^{*}_{dia} - 4.28\times10^{-18}}{kT}\right)$$

i) $\gamma_{dia} = 3.65\,J/m^2$

$$\frac{I_{gra}}{I_{dia}} = \exp\left(\frac{4.04 - 4.28}{1.38\times10^{-23}\times300}\times10^{-18}\right) = 6.6\times10^{-26}$$

ii) $\gamma_{dia} = 3.65\,J/m^2$

$$\frac{I_{gra}}{I_{dia}} = 5.08\times10^{-7}$$

iii) $\gamma_{dia} = 3.7\,J/m^2$

$$\frac{I_{gra}}{I_{dia}} = 3.46\times10^{11}$$

g) What is your conclusion on this problem?

CVD를 통해 다이아몬드가 만들어질 수 있는 것은 surface를 일 때 nucleation rate 차이가 크기 때문이다. 하지만 특정 surface E (3.65~3.7 J/m²) 이상부터는 다이아몬드 형성이 보인다.