a) For a spherical nucleus,

$\Delta G = -\frac{4}{3}\pi r^3 \cdot \Delta G_v + 4\pi r^2 \gamma$ (여기서 $\Delta G_v = \Delta G_{vaporization}$) ……㉠

spherical nucleus는 atomic volume v를 가진 n개의 atom이 모여 형성되었으므로,

$$V = \frac{4}{3}\pi r^3 = n\cdot v \longrightarrow r = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}} v^{\frac{1}{3}} \quad \text{……㉡}$$

㉡을 ㉠에 대입하면

$$\begin{aligned}
\Delta G &= -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \\
&= -\frac{4}{3}\pi \cdot \frac{3}{4\pi} n\cdot v \cdot \Delta G_v + 4\pi \cdot \left(\frac{3}{4\pi}\right)^{\frac{2}{3}} n^{\frac{2}{3}} v^{\frac{2}{3}} \gamma \\
&= -nv\Delta G_v + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma \\
&= -n\Delta G_a + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot v^{\frac{2}{3}} \gamma
\end{aligned}$$

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

b) Critical number of atoms를 n^*, critical energy barrier를 ΔG^*라 하자. a)를 이용하여, $\frac{\partial \Delta G}{\partial n}$를 구하면

$$\left.\frac{\partial \Delta G}{\partial n}\right|_{n=n^*} = -\Delta G_a + (36\pi)^{\frac{1}{3}} \cdot \frac{2}{3} n^{-\frac{1}{3}} v^{\frac{2}{3}} \gamma = 0$$

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

$$\begin{aligned}
\therefore n^* &= \left(\frac{3\Delta G_a}{2(36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} \gamma}\right)^{-3} \\
&= \frac{8}{27} \cdot \frac{36\pi \cdot v^2 \gamma^3}{(\Delta G_a)^3} \\
&= \frac{32\pi}{3} \cdot \frac{v^2\gamma^3}{(\Delta G_a)^3} \\
&= \frac{32\pi}{3} \cdot \frac{v^2\gamma^3}{(v\Delta G_v)^3} \\
&= \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_v}\right)^3
\end{aligned}$$

$$\begin{aligned}
\Delta G^* = \Delta G|_{n=n^*} &= -n^*\Delta G_a + (36\pi)^{\frac{1}{3}} n^{*\frac{2}{3}} v^{\frac{2}{3}} \gamma \\
&= -\frac{32}{3}\pi \cdot \frac{v^2\gamma^3}{(\Delta G_a)^3} \cdot \Delta G_a + (36\pi)^{\frac{1}{3}} \cdot \left(\frac{32\pi}{3} \cdot \frac{v^2\gamma^3}{(\Delta G_a)^3}\right)^{\frac{2}{3}} v^{\frac{2}{3}} \gamma \\
&= -\frac{32\pi}{3} \cdot \frac{v^2\gamma^3}{(\Delta G_a)^2} + 16\pi \cdot \frac{\gamma^3 v^2}{(\Delta G_a)^2} \\
&= \frac{16}{3}\pi \cdot \frac{v^2\gamma^3}{(\Delta G_a)^2} \\
&= \frac{16}{3}\pi \frac{\gamma^3}{(\Delta G_v)^2} \longleftarrow \Delta G_a = v \cdot \Delta G_v
\end{aligned}$$

$2^2 \cdot 3^2$ $\quad 2^{\frac{2}{3}} \cdot \cancel{3^{\frac{2}{3}}} \cdot \frac{2^{\frac{10}{3}}}{\cancel{3^{2}}}$ $\quad 2^5$

$$\boxed{\begin{aligned}
\therefore n^* &= \frac{32}{3}\pi \frac{v^2\gamma^3}{(\Delta G_a)^3} = \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_v}\right)^3 \\
\Delta G^* &= \frac{16}{3}\pi \frac{v^2\gamma^3}{(\Delta G_a)^2} = \frac{16\pi}{3} \cdot \frac{\gamma^3}{(\Delta G_v)^2}
\end{aligned}}$$

c) 주어진 조건에서 $V_{gr} = 8\,\mathring{A}^3/atom = 8\times10^{-30}\,m^3/atom$, $V_{dia} = 6\,\mathring{A}^3/atom = 6\times10^{-30}\,m^3/atom$ 이고,

$^\circ G_{dia} - {}^\circ G_{gr} = -({}^\circ G_{gr} - {}^\circ G_{dia}) = -\Delta G_a = 0.02\,eV/atom = 0.032\times10^{-19}\,J/atom$ 이다.

$$\Delta G_{gr} = -n({}^\circ G_v - {}^\circ G_{gr}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gr}^{\frac{2}{3}} \gamma_{gr}$$

$$\Delta G_{dia} = -n({}^\circ G_v - {}^\circ G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$$

문제의 조건에서 $\Delta G_{gr} = \Delta G_{dia}$ 이므로,

$$-n({}^\circ G_v - {}^\circ G_{gr}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gr}^{\frac{2}{3}} \gamma_{gr} = -n({}^\circ G_v - {}^\circ G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$$

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

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

ⓘ $\gamma_{dia} = 3.6\,J/m^2$ 일 때,

$$n = 36\pi \times \left(\frac{(6\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.6\,J/m^2 - (8\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.1\,J/m^2}{-0.032\times10^{-19}\,J/atom} \right)^3 = 466.13\ atoms \simeq 466\ atoms$$

ⓘⓘ $\gamma_{dia} = 3.65\,J/m^2$ 일 때,

$$n = 36\pi \times \left(\frac{(6\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.65/m^2 - (8\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.1\,J/m^2}{-0.032\times10^{-19}\,J/atom} \right)^3 = 145.41\ atoms \simeq 145\ atoms$$

ⓘⓘⓘ $\gamma_{dia} = 3.7\,J/m^2$ 일 때,

$$n = 36\pi \times \left(\frac{(6\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.7\,J/m^2 - (8\times10^{-30}\,m^3/atom)^{\frac{2}{3}} \times 3.1\,J/m^2}{-0.032\times10^{-19}\,J/atom} \right)^3 = 21.11\ atoms \simeq 21\ atoms$$

$\therefore\ \gamma_{dia} = 3.6\,J/m^2 : n = 466\ atoms$

$\gamma_{dia} = 3.65\,J/m^2 : n = 145\ atoms$

$\gamma_{dia} = 3.7\,J/m^2 : n = 21\ atoms$

d) diamond cluster가 graphite보다 stable 하기 위한 조건은 $\Delta G_{dia} < \Delta G_{gr}$ 이다.

$\Delta G_{gr} = -n({}^\circ G_v - {}^\circ G_{gr}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gr}^{\frac{2}{3}} \gamma_{gr}$, $\Delta G_{dia} = -n({}^\circ G_v - {}^\circ G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$ 이므로

$$-n({}^\circ G_v - {}^\circ G_{gr}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gr}^{\frac{2}{3}} \gamma_{gr} > -n({}^\circ G_v - {}^\circ G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$$

$$\therefore\ n < 36\pi \left(\frac{V_{dia}^{\frac{2}{3}} \gamma_{dia} - V_{gr}^{\frac{2}{3}} \gamma_{gr}}{{}^\circ G_{gr} - {}^\circ G_{dia}} \right)^3$$

$\therefore\ n < 36\pi \left(\frac{V_{dia}^{\frac{2}{3}} \gamma_{dia} - V_{gr}^{\frac{2}{3}} \gamma_{gr}}{{}^\circ G_{gr} - {}^\circ G_{dia}} \right)^3$ 이어야 한다.

e) b)에서 구한 critical number of atoms n^*에서

$$n^* = \frac{32\pi}{3V_{gr}} \cdot \left(\frac{\gamma_{gr}}{\Delta G_v}\right)^3, \quad n^* = 100 \text{ 이므로}$$

$$\therefore \Delta G_{v,gr} = \left(\frac{32\pi}{3n^* V_{gr}}\right)^{\frac{1}{3}} \cdot \gamma_{gr}$$

$$= \left(\frac{32\pi}{3 \times 100 \times 8 \times 10^{-30}}\right)^{\frac{1}{3}} \times 3.1\ J/m^2$$

$$= 1.08 \times 10^{10}\ J/m^3$$

$$\boxed{\therefore \Delta G_{v,gr} = 1.08 \times 10^{10}\ J/m^3}$$

f) $\Delta G^* = \frac{16}{3}\pi \cdot \frac{\gamma^3}{(\Delta G_v)^2}$, e)에서 $\Delta G_{v,gr} = 1.08 \times 10^{10}\ J/m^3$

①

$\Delta G_{v,gr} V_{gr} - \Delta G_{v,dia} V_{dia} = {}^{\circ}G_{dia} - {}^{\circ}G_{gr} = 0.032 \times 10^{-19}\ J/atom$ 에서

$$\Delta G_{v,dia} = \frac{\Delta G_{v,gr} V_{gr} - 0.032 \times 10^{-19}\ J/atom}{V_{dia}}$$

$$= \frac{1.08 \times 10^{10}\ J/m^3 \times 8 \times 10^{-30}\ m^3/atom - 0.032 \times 10^{-19}\ J/atom}{6 \times 10^{-30}\ m^3/atom}$$

$$= 1.387 \times 10^{10}\ J/m^3 \qquad \therefore \Delta G_{v,dia} = 1.387 \times 10^{10}\ J/m^3$$

②

$$\Delta G^*_{gr} = \frac{16}{3}\pi \cdot \frac{\gamma_{gr}^3}{(\Delta G_{v,gr})^2}$$

$$= \frac{16\pi}{3} \times \frac{(3.1\ J/m^2)^3}{(1.08 \times 10^{10}\ J/m^3)^2}$$

$$= 4.28 \times 10^{-18}\ J$$

③ $\Delta G^*_{dia} = \frac{16}{3}\pi \cdot \frac{\gamma_{dia}^3}{(\Delta G_{v,dia})^2}$ 구하기

i) $\gamma_{dia} = 3.6\ J/m^2 \rightarrow \Delta G^*_{dia} = \frac{16\pi}{3} \times \frac{(3.6\ J/m^2)^3}{(1.387 \times 10^{10}\ J/m^3)^2} = 4.06 \times 10^{-18}\ J$

ii) $\gamma_{dia} = 3.65\ J/m^2 \rightarrow \Delta G^*_{dia} = \frac{16\pi}{3} \times \frac{(3.65\ J/m^2)^3}{(1.387 \times 10^{10}\ J/m^3)^2} = 4.24 \times 10^{-18}\ J$

iii) $\gamma_{dia} = 3.7\ J/m^2 \rightarrow \Delta G^*_{dia} = \frac{16\pi}{3} \times \frac{(3.7\ J/m^2)^3}{(1.387 \times 10^{10}\ J/m^3)^2} = 4.41 \times 10^{-18}\ J$

④ $T = 300\ K$ 일 때, $kT = 1.38 \times 10^{-23}\ J/K \times 300\ K = 4.14 \times 10^{-21}\ J$

$$\frac{I_{gr}}{I_{dia}} = \frac{A\exp\left(-\frac{\Delta G^*_{gr}}{kT}\right)}{A\exp\left(-\frac{\Delta G^*_{dia}}{kT}\right)} = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{kT}\right) \text{ 이므로}$$

i) $\gamma_{dia} = 3.6\ J/m^2$ 일 때, $\frac{I_{gr}}{I_{dia}} = \exp\left(\frac{4.06 \times 10^{-18}\ J - 4.28 \times 10^{-18}\ J}{4.14 \times 10^{-21}\ J}\right) = 8.35 \times 10^{-24}$

ii) $\gamma_{dia} = 3.65\ J/m^2$ 일 때, $\frac{I_{gr}}{I_{dia}} = \exp\left(\frac{4.24 \times 10^{-18}\ J - 4.28 \times 10^{-18}\ J}{4.14 \times 10^{-21}\ J}\right) = 6.37 \times 10^{-5}$

iii) $\gamma_{dia} = 3.7\ J/m^2$ 일 때, $\frac{I_{gr}}{I_{dia}} = \exp\left(\frac{4.41 \times 10^{-18}\ J - 4.28 \times 10^{-18}\ J}{4.14 \times 10^{-21}\ J}\right) = 4.34 \times 10^{13}$

$$\boxed{\begin{aligned} \therefore\ \gamma_{dia} = 3.6\ J/m^2 &\rightarrow \frac{I_{gr}}{I_{dia}} = 8.35 \times 10^{-24} \\ \gamma_{dia} = 3.65\ J/m^2 &\rightarrow \frac{I_{gr}}{I_{dia}} = 6.37 \times 10^{-5} \\ \gamma_{dia} = 3.7\ J/m^2 &\rightarrow \frac{I_{gr}}{I_{dia}} = 4.34 \times 10^{13} \end{aligned}}$$

g) bulk에서는 graphite가 diamond보다 stable하다. 하지만, c)에서 n이 증가하면, surface energy γ가 증가하여
γ가 증가하면, f)에서 볼 수 있듯이, nucleation rate는 $I_{dia} > I_{gr}$이 된다. 즉, surface energy가 어느 critical 값 이상 커지면,
graphite보다 nucleation이 더 잘 일어날 수 있다.