Chap.6 Surface Energy

(1) Background:

Consider the atoms in the bulk and surface regions of a crystal:
Surface: atoms possess higher energy since they are less tightly bound.
Bulk: atoms possess lower energy since they are much tightly bound.

→ The sum of all the excess energies of the surface atoms is the surface energy.

→ Surface energy is of the essence of “energy”, and can be defined in term of Gibbs free energy:

\[
dG \equiv -SdT + VdP + \gamma dA
\]

\[
\Rightarrow \gamma \equiv \left( \frac{\partial G}{\partial A} \right)_{T,P}
\]

(2) Criterion at equilibrium:

System tends to reduce its free energy as it is reaching the equilibrium state. In some cases, this stable state can be achieved by the reduction of the surface energy of system.

E.g. a. Smaller drops aggregate into larger ones.
   b. Sintering of small metal or ceramic particles under high temperature.

(3) Surface energy for liquid: surface tension

1. Definition: Consider the attractive forces that molecules in a liquid exert on one another at the bulk and surface regions:
At surface, this net attractive force (內聚力) causes the liquid surface to contract toward the interior until other repulsive external force are exerted. This force is termed the surface tension, and is defined as the force unit length (dyne/cm or N/m).

2. Experimental approaches:

a. Stretching film: 表面拉膜法

b. Capillary tube: 毛細管法

When inserting a capillary tube into the liquid, adhesive of the liquid to the tube wall, pointing in upward, will cause a rise of the liquid along the tube. Once the adhesive force equals to the weight of liquid in capillary, equilibrium is reached.

\[ f \cos \theta = mg \]
\[ r \ast 2r \ast \cos \theta = \rho V g = \rho (\pi r^2 h) g \]

\[ \Rightarrow r = \frac{\rho \pi h g}{2 \cos \theta} \]

※ If cohesive force < adhesive force

\[ 0^\circ < \theta < 90^\circ \]

tube wall is partially wet, e.g. H_2O, most of the liquid
If cohesive force > adhesive force

(4) Surface energy for solid:

Consider the atoms in the surface regions of a crystal:
Surface energy ~ sublimation energy
~ The breaking of bonds of atoms of surface.
~ The energy of one bond for atoms.

→ We could then define the energy of one bond for atoms in crystal through the concept of sublimation energy.

For one-mole crystal, there are \( N_A \) atoms and at least \( 0.5N_A \) bonds will form among them. Take the coordination number into account, there will be \( (0.5N_A*Z) \) bonds in one-mole crystal.

The energy of one bond can thus be written as:
\[
\varepsilon = \frac{\Delta H_s}{0.5N_A Z}, \text{ where } \Delta H_s \text{ is the molar enthalpy of sublimation.}
\]

For the (111) plane in FCC crystal, atoms at the surface possess a CN of 9, which means that 3 bonds per atoms are broken at the surface of (111).

As a result, the energy required to form one (111) surface in FCC can be given as:
\[
E_{(111)} = (\text{energy of one bond})*(\text{number of bonds broken / atom})
= \varepsilon * 3 \equiv \frac{\Delta H_s}{2N_A} (Z=12 \text{ for FCC}) \ldots \text{energy required per surface atom}
\]
The surface energy $\gamma$ is then defined as follows:

$$\gamma \equiv \text{(Energy required per surface atom)} \times \left( \frac{\text{number of surface atoms}}{\text{surface area}} \right)$$

For (111) plane in FCC crystal:

$$\gamma_{(111)} = \frac{\Delta H_s}{2N_A} \left( \frac{N}{A} \right)_\text{(111)} = \frac{2}{\sqrt{3} \frac{\sqrt{2}a_0}{2}} = \frac{4}{\sqrt{3}a_0^2}$$

For (111) plane in FCC crystal:

Atom at the surface process a CN of 8, meaning 4 bonds per atom are broken at the surface (100).

$$\rightarrow E_{(100)} = \varepsilon \times 4 = \frac{2\Delta H_s}{3N_A} \ldots \text{energy required per surface atom}$$

$$\gamma_{(100)} = E_{(100)} \left( \frac{N}{A} \right)_{(100)} = \frac{2\Delta H_s}{3N_A} \left( \frac{2}{a_0^2} \right) = \frac{4\Delta H_s}{3N_Aa_0^2}$$

The ratio of the two surface energy is about:

$$\frac{\gamma_{(111)}}{\gamma_{(100)}} = \frac{2\sqrt{3}}{4/3} \approx 0.87$$
* For FCC crystal: $\gamma_{(110)} > \gamma_{(100)} > \gamma_{(111)}$

* For BCC crystal: $\gamma_{(111)} > \gamma_{(100)} > \gamma_{(110)}$

(5) Relative surface energy:

1. Definition:
   An excess of energy at the interface between two different phases in solid can be referred as: $\gamma_{\alpha\beta}$
   $\to$ due to the difference in atomic vibration mode $\to$ cohesive force

2. Phase separation at equilibrium: (solid-solid interface)
   Consider three phases different in composition/orientation are allowed to equilibrate to form:

   $\gamma_{23}\sin\theta_3 = \gamma_{12}\sin\theta_1$ (perpendicular to $\gamma_3$)
   $\gamma_{23}\sin\theta_2 = \gamma_{13}\sin\theta_1$ (perpendicular to $\gamma_2$)

$\Rightarrow \frac{\gamma_{23}}{\sin\theta_1} = \frac{\gamma_{12}}{\sin\theta_3} = \frac{\gamma_{31}}{\sin\theta_2}$, one can determine the relative surface energy by measuring the angles among those phases.
3. Wettability & contact angle at equilibrium: (liquid-solid-vapor interface)

Consider a drop of liquid on the solid surface at the ambient atmosphere:

“The equilibrium” is reached by the force balance at P among these three interfaces: $\gamma_{s,v} = \gamma_{l,s} + \gamma_{l,v} \cos \theta_c$, where $\theta_c$ = contact angle, which can be measured experimentally.

$10^\circ < \theta_c < 30^\circ$, the surface is of high wettability or called “hydrophilic”.

$70^\circ < \theta_c < 90^\circ$, the surface is of low wettability or called “hydrophobic”.

Note: $\gamma_{s,v} = \gamma_{l,s} + \gamma_{l,v} \cos \theta_c$, to enhance the wettability of the surface (to lower $\theta_c$), we could perform a proper surface modification on surface to increase $\gamma_{s,v}$. 

Edited by Prof. Yung-Jung Hsu
(6) Equilibrium shape of a crystal

1. Anisotropic tendency

* For a solid, the surface energy is anisotropic, i.e., different crystal planes possess variable surface energies.
* At equilibrium, planes with lower surface energies will be favored and exposed. Thus, the exterior shape of a crystal is determined by considering the relative surface energies among crystal planes (to minimize the total surface free energy of the crystal).

2. The shape of a crystal

To determine the shape of the crystal at equilibrium, we have to evaluate the total surface free energy of the crystal.

\[
E_{\text{tot}} = E_{\text{edge}} + E_{\text{top-surf}}
\]

\[
E_{\text{edge}} = E_{(100)} + E_{(110)} = \gamma_{(100)} \cdot A_{(100)} + 2 \cdot \gamma_{(110)} \cdot A_{(110)}
\]

For simplicity, we set the height of the crystal to be unit.

\[
A_{(100)} = (a - \frac{c}{\sqrt{2}}) \cdot A_{(110)} = c \quad \therefore E_{\text{edge}} = 2(a - \frac{c}{\sqrt{2}}) \cdot \gamma_{(100)} + c \cdot \gamma_{(110)}
\]

\[
E_{\text{top-surf}} = E_{(001)} = \gamma_{(001)} \cdot A_{(001)} \cdot 2 (\text{上下之面})
\]

\[
A_{(001)} = a^2 - \frac{c^2}{4} \quad \therefore E_{\text{top-surf}} = (a^2 - \frac{c^2}{4}) \cdot \gamma_{(001)} \cdot 2
\]
For the crystal at equilibrium, its total surface free energy is minimized.

→ $E_{edge}$ is minimized & $E_{top-surf}$ is minimized.

$$\frac{dE_{edge}}{dc} = (2a \frac{da}{dc} - \sqrt{2}) \gamma_{(100)} + \gamma_{(110)} = 0 \quad \therefore \frac{da}{dc} = \frac{1}{2} \left( \frac{\sqrt{2} - \gamma_{(110)}}{\gamma_{(100)}} \right)$$

$$\frac{dE_{top-surf}}{dc} = (2a \frac{da}{dc} - \frac{c}{2}) \gamma_{(001)} = 0 \quad \therefore \frac{da}{dc} = \frac{1}{4} \frac{c}{a}$$

$$\therefore \frac{c}{a} = 2 \left( \frac{\gamma_{(110)}}{\gamma_{(100)}} \right)$$

a. The size of (100) is proportional to $\left( a - \frac{c}{\sqrt{2}} \right)$.

The size of (110) is proportional to $c$.

b. If $\gamma_{(110)}$ is equal to or greater than $\left( \sqrt{2} \gamma_{(110)} \right)$, $c$ will be zero

→ (110) will not be exposed at surface at equilibrium.

c. If $\gamma_{(100)} = \gamma_{(110)}$, $c = 2a(\sqrt{2} - 1)$

The ratio of the sizes in (100) to (110) will be:

$$\frac{2(a - \frac{c}{\sqrt{2}})}{c} = \frac{2(a - 2a(\sqrt{2} - 1))}{2a(\sqrt{2} - 1)} = 1$$

At equilibrium:

$$\Rightarrow \frac{\gamma_{(110)}}{\gamma_{(100)}} = \frac{\sqrt{2} - \frac{c}{2a}}{h_{(110)}}$$

$$\therefore \text{for crystal growth at equilibrium}$$

$$\Rightarrow \frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = \frac{\gamma_3}{h_3} = \ldots = \text{Constant}$$

, where 1, 2, 3, … represent the planes exposed at surface at equilibrium.
(7) Relevant phenomena of surface energy:

2. Nanosize particle: high solubility, high vapor pressure, lower melting point.
4. Non-spheric shape of solid crystal at equilibrium.