Chapter 7   Solid Surface
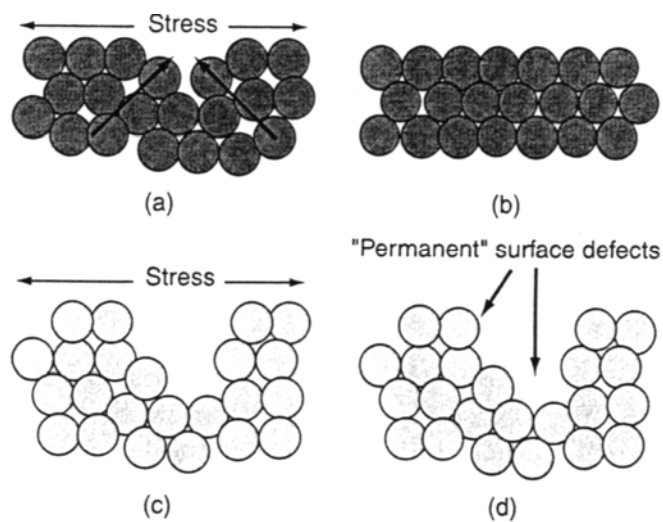
■ **Definition of solid :**
A matter that is rigid and resists stress.

■ **Difference between solid and liquid surface :**
Liquid : always <u>in equilibrium</u> and <u>equipotential.</u> (Fig 7.1a,b)
Solid : the two assumptions are not valid. (Fig 7.1c,d)

FIGURE 7.1. Schematic illustration of the responses of liquid and solid surfaces to stress: (*a*) a stressed liquid surface with "vacancies"; (*b*) molecules below the surface rapidly flow into the stressed area to "heal" the imbalance of forces; (*c*) a stressed solid surface with various defects; (*d*) due to lack of mobility, molecules cannot readily move into the stressed areas and the defects remain to produce a higher surface energy.

7.1 Surface Mobility in Solids

Consider a surface being in a dynamic state with interchange of molecules between the surface , the bulk , and the vapor phase .

The impinging rate of vapor on a surface : Z

$$Z = 0.23P\left(\frac{3}{MRT}\right)^{\frac{1}{2}} \quad [\,cm^{-2} \cdot \sec^{-1}]\ldots\ldots (7.1)$$

> P: vapor pressure of the material
> M: molecular weight

ex. for tungsten(W) , $P \approx 10^{-37}$ mmHg

$Z \approx 10\text{~}20\left(atoms\,/\,cm^2 \cdot \sec\right)$

Lifetime $\approx 10^{37}$ sec

■ **Tamman Temperature : (for bulk diffusion)**
  ● The temperature at which the atoms or molecules of the solid acquired sufficient energy for their bulk mobility and reactivity to become appreciable. (ex : sintering)
  ● Tamman temperature $\approx$ one-half of melting point (K)

  ● For example : for Cu at 725℃

    $P \approx 10^{-8}$ mmHg , $Z \approx 10^{15}$ atoms/cm^2.sec
    Surface resident time $\approx$ 1 sec
    Bulk diffusion rate $\approx$ 10nm in 0.1 sec
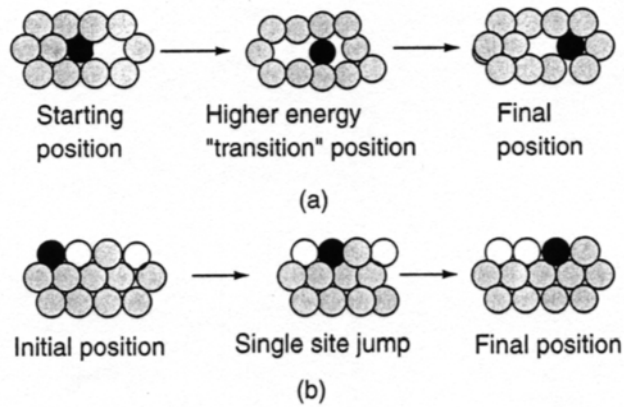   But at room temperature $\Rightarrow$ 10nm needs 10^{27} sec

■ **Surface diffusion :**
      perform below the Tamman temperature
  bulk diffusion : no change in total activation energy (Fig 7.2a)
  surface diffusion : has a much lower barrier to diffusion (Fig 7.2b) , and much greater mobility.
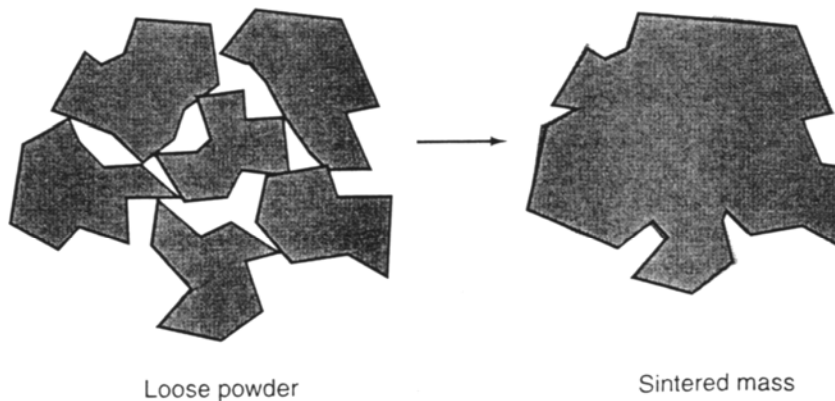
FIGURE 7.2. Schematic illustration of the comparative energetics of diffusion in bulk and in a surface: (*a*) bulk diffusion, illustrated in cross section, involves the displacement of several nearest-neighbor units, representing a relatively large energy barrier; (*b*) surface diffusion, shown in a top view, involves the displacement of fewer neighboring units, and therefore a relatively lower activation energy for the process. As a result, systems that undergo bulk diffusion with difficulty may exhibit orders of magnitude more surface diffusion under the same conditions.

■ **The history (especially thermal) of the material is important to the property (nature) of a solid surface.**

Surface changes ⇒ alterations in characteristics such as
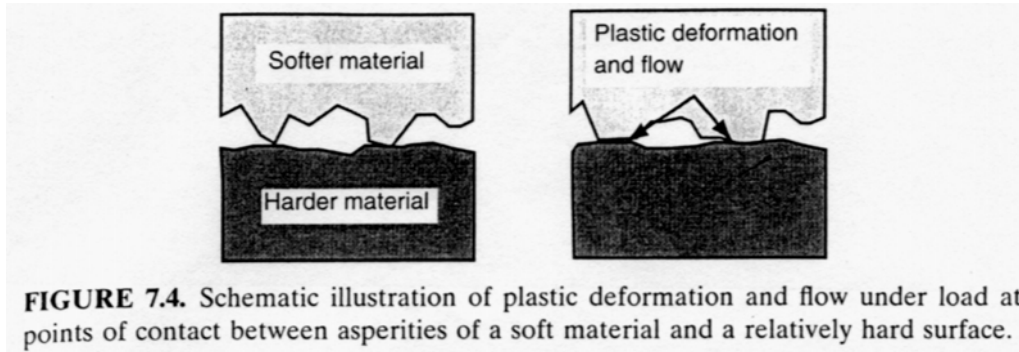adsorption , wetting , adhesion , friction , or
lubrication

7.1.1 Sintering

Definition : For solid powders , fusion of adjacent particles occur when the system is heated to some temperature below the melting point. (Fig 7.3)

Loose powder   Sintered mass

FIGURE 7.3. Schematic illustration of the stepwise process of particle sintering.

■ **The main driving force for sintering :** surface tension atoms located at sharp asperities on the surface have higher local excess surface energies , and have a greater surface tension and surface mobility.

FIGURE 7.4. Schematic illustration of plastic deformation and flow under load at points of contact between asperities of a soft material and a relatively hard surface.

7.2 "History" and the characteristics of solid surface

Surface energy and related characteristics $\Leftrightarrow$ relative immobility of atoms in the surface of a solid below its melting point

■ A clean cleaved crystal surface $\Rightarrow$ lower energy (the cleaving process occurs along the face of lowest energy)
■ Grinding and polishing $\Rightarrow$ leave small defects and increase the surface energy
■ Factors that affect the surface energy :
  ● friction , corrosive action , adsorption.
  ● history of its formation – crystal surface may contain defects , screw , spiral dislocations.
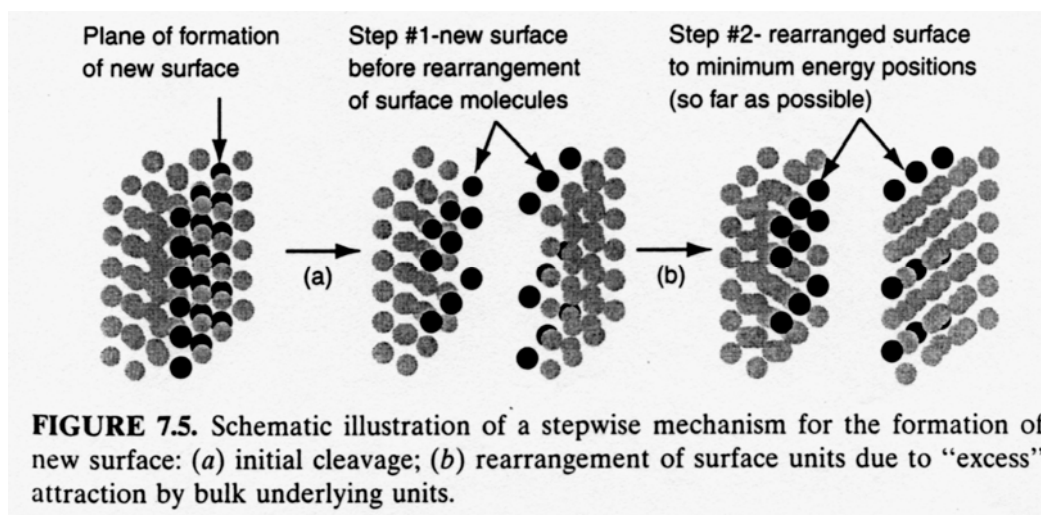
Effects of adsorption and surface contamination :
  ● low energy , or amorphous solids (ex : polymer)
    – not significant.
  ● higher energy crystalline , metallic , inorganic glassy
    – pose significant experimental problems.
    – surface energy range : $10^2 \sim 10^3$ mJ/m^2
    – "do anything" to lower surface by adsorption (O_2 , N_2 , H_2O , ….). so , it's difficult to prepare a truly clean surface.
    – surface studies (analysis) on solid are carried out in high vacuum and under ultraclean conditions.

TABLE 7.1. Reported Surface Energies of Commonly Encountered Solids

Material	Surface Energy (mJ m^{-2})	Material	Surface Energy (mJ m^{-2})
Teflon	20	Lead iodide (PbI$_2$)	130
Paraffin wax	26	Silica	462
Polypropylene	28	Lead fluoride (PbF$_2$)	900
Polyethylene	36	Iron	1360
Polystyrene	44	Gold	1500
Ice	82	Mica	4500

7.3 Solid Surface Free Energy versus Surface Tension

■ Total energy in the surface layer = "native" specific free energy + "stress energy"

■ The mechanism of surface formation can be considered as a two-step process.

   (a) the condensed phase is divided , but the molecules in the new surface are held in the exact locations they occupied in the bulk. (Fig.7.5a)

   (b) the atoms in the newly formed surface are allowed to relocate into their most stable configuration.(Fig.7.5b) – occur very slowly.

FIGURE 7.5. Schematic illustration of a stepwise mechanism for the formation of new surface: (*a*) initial cleavage; (*b*) rearrangement of surface units due to "excess" attraction by bulk underlying units.

7.4 The Formation of Solid Surfaces

7.4.1 Crystalline Surfaces

■ **Crystallization :** a process in which an ordered solid phase is precipitated from a gaseous , liquid , or solid phase.
Occurs when : the chemical potential of the solid phase is less than that of the material in solution . That is , supersaturated solution.

■ **Supersaturation methods :**
1. Cooling (or heating).
2. Evaporating the solvent by heating.
3. Adiabatic evaporation.
4. Adding another solvent – miscible with the primary solvent , but is a poorer solvent for the material being crystallized.
5. Salting out : adding a common ion with the crystallized substance , thereby reducing its solubility.
6. chemical reaction : formation an insoluble material.

■ **Small supersaturation :** metastable region
Low nucleation rate , crystal already present grow. growth of large (or single) crystal.

■ **High supersaturation :**
high nucleation rate , formation large numbers of small crystals.

Crystallization can be divides into two stages :
(1) nucleation (formation of two crystal nuclei)
(2) crystal growth
Both stages occurs simultaneously

7.4.2 Nucleation Process

■ **Primary nucleation :**
Crystals begins to form in the absence of solid particles of the crystallized substance.
● Homogeneous nucleation : without the intervention of solid surface.
● Heterogeneous nucleation : the presence of foreign surface (dust , colloid , wall) acts as a catalyst to initiate crystal formation.

The Theory of Limiting Force

- An old theory for thermodynamic approaches to explain crystal growth and habit.
- Derivation of relationship between the crystal habit and the surface energy of various crystal faces.
- When a crystal is in equilibrium with its mother liquor (or vapor phase) $\Rightarrow$ the overall surface energy is a minimum ($\Delta G=0$).

$$\Delta \sum_{i}^{n} \sigma_i A_i = 0 \qquad \text{(V,T=constant) (7.2)}$$

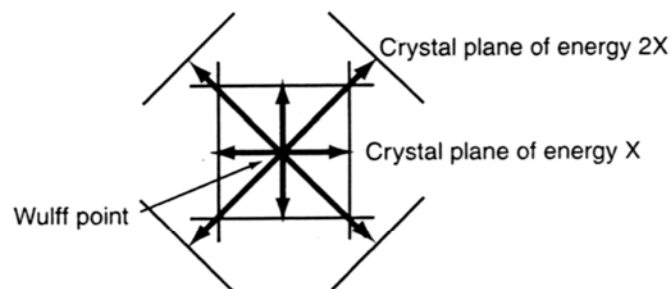σ_i : specific surface energy of the ith face

A_i : area of the ith face

Eq.(7.2) leads to Wulff theorem :

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = ... \frac{\sigma_i}{hi} = ... = \frac{\sigma_n}{h_n}$$

h_i : the distance of the ith plane from the center of the crystal

(the Wulff point)

FIGURE 7.6. A Wulff construction for a hypothetical, two-dimensional crystal with surface energies X and $2X$, from which the "ideal" geometric shape of the crystal can be predicted. The arrows emanating from the common point are proportional to the surface free energy of the intersecting crystal faces.

When equilibrium is disturbed , the system will reestablish a condition of minimum energy :

Faces with small σ $\Rightarrow$ small growth rate (h) $\Rightarrow$ larger area

Faces with high σ $\Rightarrow$ greater growth rate $\Rightarrow$ area become smaller and disappear eventually.

- **Crystal Growth Modification**
  - Example : the growth of ice crystals in ice cream , the ith crystal should be small enough.
    Crystallization is controlled by the addition of various natural gums (e.g., locust bean gum)
  - Example : Control the growth of ice crystals in biological systems.
    - The fish in cold polar seas are protected from freezing by a natural antifreeze (compounds of protein and sugar).
    - The "antifreeze" do not actually lower the freezing point significantly , but inhibit the growth of crystals by adsorption onto the preferred crystal face.

7.4.3 Amorphous Solid Surface

- The principles applied to studying and modeling ordered crystalline surfaces are not valid to amorphous polymer surfaces (plastic nature , noncrystalline).
- Surface energies of polymer : history-dependent
  Low surface energy (contamination may not be significant).
- Dynamics in Polymer Surface
  - Solid surface are always assumed to be rigid and immobile – surfaces themselves do not change or respond to the presence of a contacting liquid.
  - Glass is always considered to be inert and rigid.
    - However , surface alternation was found when contact with liquids (such as water).
  - Polymer surface can not be considered their equilibrium condition because it composes of mixture of long , anisotropic molecules of various molecular weights.
- Transition temperature from solid to liquid :
  Crystalline material : occur at sharp and well-defined temperature (melting point).
  Amorphous polymer and glasses : occur ar a temperature range. The physical properties changes from rigid , brittle to a viscous liquid.
- Relaxations and transitions of polymer molecules in or near the surface – interact with the surrounding phase , orient themselves to attain the configuration of minimum surface energy (time and
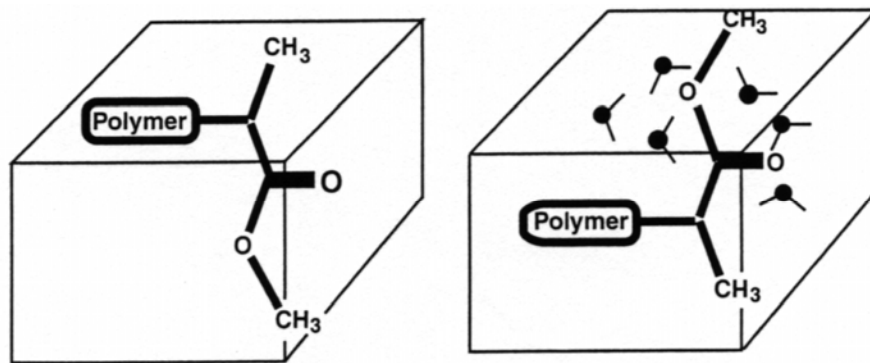
temperature dependent).
- Example : poly(methylmethacrylate)

PMMA :
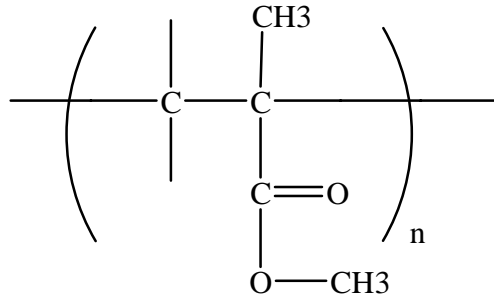
- The hydrophilic ester will , in contact with water , undergo surface molecular reorientation.

FIGURE 7.7. Rigid, hydrophobic polymers such as poly(methylmethacrylate) that contain somewhat hydrophilic ester side chains may, in prolonged contact with water, undergo surface molecular reorientation due to the interaction of water with the ester groups. The interfacial region may become plasticized or softened as a result of the water–ester interaction, liberating to some extent the side chains (or "lubricating" the interchain interaction region) and increasing their mobility.

- A practical example – polymer in biomedical applications such as an implant device.
A material that is biocompatible based on the typical surface analysis (contact angle , XPS....) may be no longer biocompatible after surface transition and relaxation.