

Introduction to Interfacial Engineering

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1.1.1 What is interfacial engineering?

Interface is the boundary between two phases where the properties or behavior of material differ from those of the adjoining phases. Interfaces play an important role in our daily life, and in the world around us. The recent developments in modern technologies involve new materials and processes in which interfaces play a crucial role. Fig. 1.1.1 illustrates the fluid–fluid and fluid–solid interfaces.

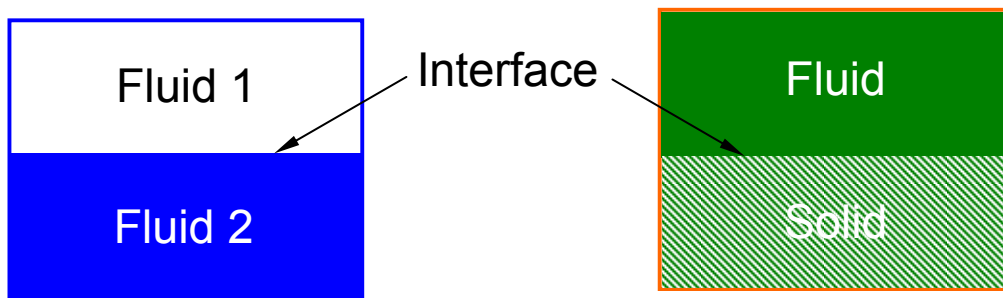


Fig. 1.1.1 Fluid–fluid and fluid–solid interfaces.

A gas–solid interface or a gas–liquid interface is often called a “surface”.

Some applications involving interfaces are:

- ◆ Adhesives and coatings
- ◆ Adsorption and ion exchange
- ◆ Alloys, cement, ceramics, fibers, plastics, and powder metallurgy
- ◆ Catalysis
- ◆ Environmental pollution control
- ◆ Food products
- ◆ Liquid crystals
- ◆ Medicines, pharmaceuticals and therapeutics
- ◆ Microelectronic fabrication and imaging processes
- ◆ Petroleum recovery and processing
- ◆ Separation processes

The engineering involved in these varied applications is termed *Interfacial Engineering*.

1.1.2 Who are involved?

- ◆ Biotechnologists
- ◆ Chemical engineers
- ◆ Chemists
- ◆ Electrical engineers
- ◆ Environmental scientists
- ◆ Materials scientists
- ◆ Mechanical engineers
- ◆ Physicists

Interfacial engineering is a cross-disciplinary subject in which the scientists and engineers from several disciplines work together using their insights for the joint development and optimization of performance of new materials and processes.

1.1.3 Some specific applications of interfacial engineering

A few specific applications of interfacial engineering are discussed here which have potentials in the future.

1.1.3.1 Microelectronic devices

- ◆ Silicon semiconductors have grown tremendously in terms of memory and logic. Every four years produce an order of magnitude improvement in the performance, keeping the cost almost constant, and sometimes lower.
- ◆ As the physical limits of the conventional silicon chips are being approached, researchers are seeking the next small thing in electronics through chemistry. By making devices from small groups of molecules, researchers may be able to pack computer chips with billions of transistors, more than 10 times as many as the current technology can achieve.
- ◆ Researchers in molecular-electronics think that it is possible to make complex circuitry by utilizing DNA's ability to recognize molecules and self-assemble.

They hope to use DNA as a template for crafting metallic wiring, or even to wire circuits with strands of DNA itself.

- ◆ Makers of computer chips are concerned with the wavelength-limits of light. As the wavelength of the light is reduced, smaller features can be printed on the chip. As a general rule of thumb, a given wavelength can make features about half its length. Typically, light of 248 nm wavelength was used in the past in optical lithography devices, and the smallest features that could be made by these devices were about 120 nm. Chipmakers are trying to build devices which use much shorter wavelengths (e.g., 157 nm). Features as small as 80 nm have already been created on silicon wafers. Researchers expect that the technology will be able to turn out features as small as 10 nm. A futuristic design of all-optical chip is shown in Fig. 1.1.2.

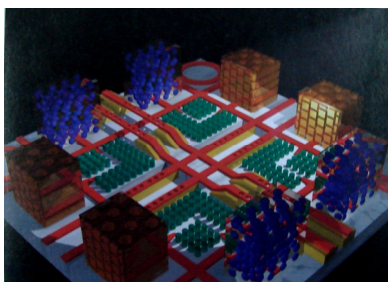


Fig. 1.1.2 Photonic crystal micropolis (source: G. A. Ozin and A. C. Arsenault, *Nanochemistry*, RSC Publishing, Cambridge, 2005; reproduced by permission from Macmillan Publishers, © 2005).

This chip is believed to be the chip of the future. It comprises of integrated microphotonic crystals with 1D, 2D, or 3D periodicity. Coupling of light from waveguide to photonic crystal may be accomplished via extrinsic defects built into the photonic lattice. Integrated photonic crystal components on all-optical chips are envisioned to function as low threshold lasers, wavelength division multiplexes, wavelength dispersion compensators, and switches.

- ◆ Very small light-emitting diodes (LED) can be made from the nanowires, as shown in Fig. 1.1.3.

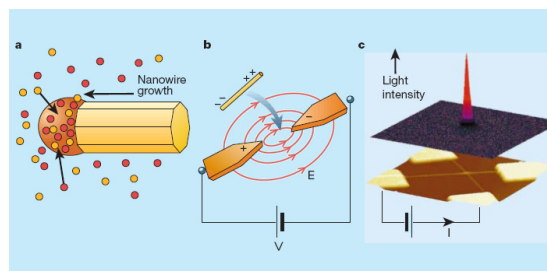


Fig. 1.1.3 World's smallest light-emitting diode (source: D. H. Cobden, *Nature*, **409**, 32, 2001; reproduced by permission from Macmillan Publishers, © 2001).

A nanowire is grown from two reagents (red and yellow dots) with the help of a metal catalyst particle (orange), as shown in Fig. 1.1.3 (a). The nanowire is assembled between two metal electrodes using an electric field gradient, as shown in Fig. 1.1.3 (b), and a *p*-doped and an *n*-doped nanowire are crossed to form a nanoscale light-emitting diode, as shown in Fig. 1.1.3 (c). When a current is passed between them, electrons and holes are injected across the junction and recombine to emit light.

1.1.3.2 Hydrogen storage

Safe storage of hydrogen for fueling motor vehicles and driving portable electronics can be made employing the metal-organic frameworks (MOFs). Lightweight and compact materials are being developed that can rapidly adsorb and desorb large amounts of hydrogen under ambient temperature and pressure conditions. For coordination framework to meet this challenge, they will need to satisfy the storage requirements and the structural integrity must be maintained on removing the template or occluded water or solvent. A candidate for this role is the MOF, $Zn_4O(BDC)_3$ where BDC is 1,4-benzene-dicarboxylate (Fig. 1.1.4). It has a sturdy cubic open-framework structure with a very large surface area (2500–3000 m^2/g), and its thermal stability is also good viz. 600–700 K.

In Fig. 1.1.4, the choice of the organic group provides control over the size of the cubic unit cell, and concomitantly the adsorption capacity of the material. The empty volume is shown by the central spheres.

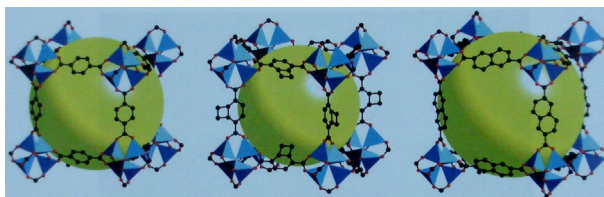


Fig. 1.1.4 Hydrogen storage MOF, $Zn_4O(RDC)_3$ (source: N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe, and O. M. Yaghi, *Science*, **300**, 1127, 2003; reproduced by permission from The American Association for the Advancement of Science, © 2003).

1.1.3.3 Catalysis

Solid catalysts are made of porous solids. As per the IUPAC classification of the porous solids, pores having diameter in the range of 2 nm and below are called *micropores*, those in the range of 2 nm to 50 nm are termed *mesopores*, and those above 50 nm are *macropores*. The distribution of size, shape and volume of the void spaces in porous materials govern their ability to perform the desired function in a particular application. The science and engineering of porous materials deal with the methodology to create uniformity in pore size, shape and volume. The first synthesis of a crystalline microporous material with uniform pores larger than 1 nm was reported in the late 1980s. A microporous material, VPI-5, is shown in the Fig. 1.1.5.

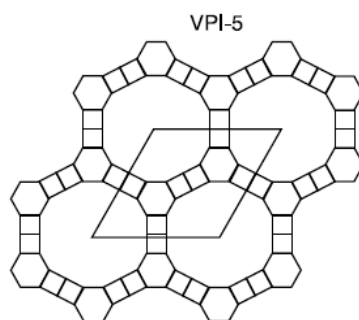


Fig. 1.1.5 Pore characteristics in VPI-5 (source: M. E. Davis, *Nature*, **417**, 813, 2002; reproduced by permission from Macmillan Publishers, © 2002).

The line segments represent oxygen atoms that bridge between two tetrahedral atoms. The aluminophosphate, VPI-5, has a pore size of 1.2 nm. The pores are uniform-diameter channels having circular cross-section. The material has 30% void fraction.

1.1.3.4 Coatings

Coating on solid surfaces has a wide variety of applications such as paints, adhesives, coated papers, automobiles, industrial equipment, domestic appliances, photographic films, and aluminum disks coated with iron oxide which make computer hard disks. A great variety of coating methods is available for the varied coating applications. The chosen method depends on the rheology of the coating liquid, type of solid surface, desired coating thickness and uniformity. Fig. 1.1.6 illustrates coating by plasma polymerization.



Fig. 1.1.6 Coating by plasma polymerization.

1.1.3.5 Enhanced petroleum recovery

Oil is produced from a reservoir when either its own pressure or an applied pressure makes it flow through permeable porous rock formations, and into a production well. The former process is termed *primary production* and the latter is termed *secondary/tertiary production*. Primary and secondary (waterflooding) production from a reservoir can only recover about 35% of the original oil-in-place. Water and other fluids can be injected to increase the oil recovery, as shown schematically in Fig. 1.1.7.

The waterflood residual oil is left in the form of oil ganglia trapped in the larger pores (in water-wet reservoirs) where the viscous forces of the driving waterflood could not completely overcome the capillary forces holding the oil in a place. Tertiary (or enhanced) oil recovery involves reducing the capillary forces restraining the oil and/or altering the viscosities in order to modify the viscous forces to drive the oil out of the

pores. The addition of a surfactant can reduce the interfacial tension and the capillary forces. It can also alter the wettability of the reservoir rock.

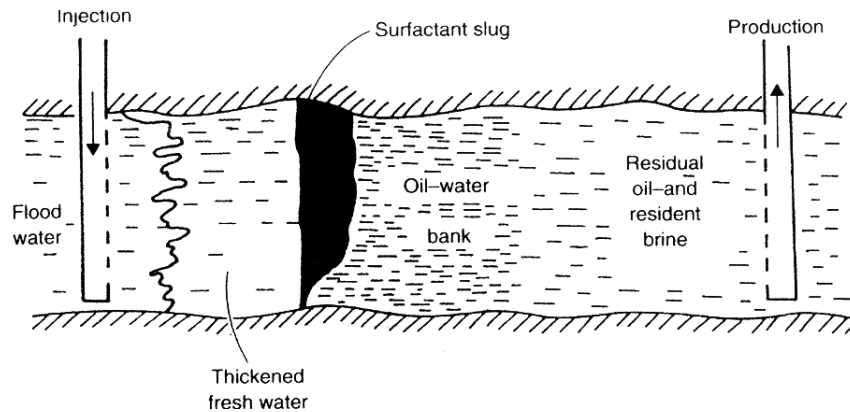


Fig. 1.1.7 Displacement of oil in a petroleum reservoir by chemical flooding using surfactants (Source: L. E. Schramm, *Emulsions, Foams, and Suspensions*, Wiley-VCH, Weinheim, 2005; reproduced by permission from Wiley-VCH, ©2005).

1.1.3.6 Microfoams

Microfoams, or colloidal gas aphanes, are dispersion of aggregates of very small spherical foam bubbles in aqueous solution (Fig. 1.1.8). The size of the bubbles is 50–100 μm . Techniques for preparation and functionalization of microfoams with surfactants, nanoparticles, pharmaceuticals and bioactive agents is under progress.

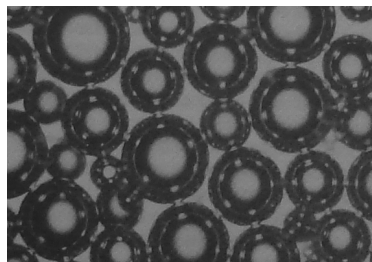


Fig. 1.1.8 Photomicrograph of a micro foam (source: L. E. Schramm, *Emulsions, Foams, and Suspensions*, Wiley-VCH, Weinheim, 2005; reproduced by permission from Wiley-VCH, ©2005).

The microfoams are useful in oil recovery, microencapsulation, materials processing, food technology, therapeutics, and imaging. They are finding extensive use in wastewater treatment.

1.1.4 Commonly observed interfacial phenomena

1.1.4.1 Capillary action

This phenomenon is responsible for the spontaneous rise of water through the trunk of the tree, or transport of water from the wet soil to the dry areas. It can be demonstrated quite easily. Suppose that a capillary is dipped in a vessel containing water. It will be observed that the liquid level inside the tube is higher than the liquid level outside. This phenomenon is known as *capillary rise* (Fig. 1.1.9). For some liquids, such as mercury, the reverse happens and *capillary depression* is observed.

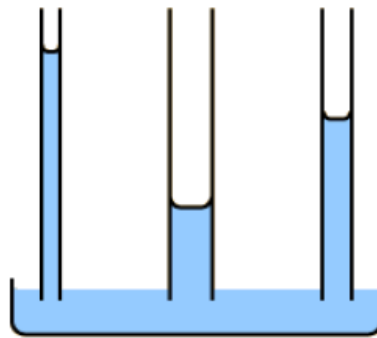


Fig. 1.1.9 Capillary action.

The reason behind capillary rise is the adhesive force between the liquid and the solid material, and the surface tension of the liquid. The upward movement of the liquid column is driven by surface tension. The liquid continues to rise until the weight of the liquid column balances the upward pull. It can be shown easily that water will rise about 30 mm above the air–water interface inside a 1 mm diameter glass tube. Water will rise higher if a smaller-diameter capillary is used. The capillary action has been used in advanced scientific analysis such as thin layer chromatography. It has also been utilized to manufacture garments used for sports and rigorous outdoor activities.

1.1.4.2 Marangoni effect

The transport of liquid due to the gradient in surface tension is known as *Marangoni effect* (named after Italian physicist Carlo Marangoni who published this effect circa 1865). A classic example of the Marangoni effect is tears-of-wine (Fig. 1.1.10). The surface tension gradient is caused by the gradient in the concentration of ethanol in this case. It is also known as *wine legs*.

This phenomenon was first scientifically interpreted by James Thomson in 1855. When a wine of high alcohol-content is taken in a glass, a ring of clear liquid is formed in the upper part of the glass. This is caused by the induced flow of liquid driven by the surface tension gradient, and capillary action.

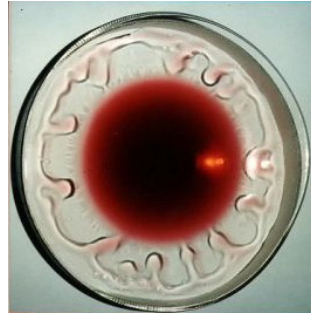


Fig. 1.1.10 Tears-of-wine.

Alcohol exhibits surface activity when it is added to water. For example, the surface tension of water is reduced to less than half its original value when a small amount of ethyl alcohol is added to it (the surface tension of water is 72.5 mN/m at 298 K whereas the same for ethyl alcohol is 23 mN/m). Capillary action forces the liquid to climb along the glass wall. Therefore, a thin liquid film is formed on the glass wall. However, alcohol has higher vapor pressure and lower boiling point than water. As a result, it evaporates faster and increases the surface tension of the liquid in the film. This creates a surface tension gradient in the film, which draws further liquid from the bulk of the wine, because the wine has lower surface tension due to its higher alcohol-content. In this process, a considerable amount of the liquid climbs up along the wall of the glass. After some time, the liquid in the film begins to fall downward due to gravity. These falling

streams manifest themselves as the ‘tears of wine’. This phenomenon is mainly related to the alcohol-content of the wine. Apparently, if evaporation is reduced, tears would subside, which is actually observed when the glass is covered.

The Marangoni effect is believed to be a very important factor in the stabilization of foams and emulsions.

1.1.5 Important role of the interfaces

In many applications where the role of interfaces are important, a large interfacial area is involved. Small particles have a high surface area per unit mass. Porous materials with very fine pores have a large internal surface area. That is the key feature of enormous importance.

Example 1.1.1: A spherical particle of 2 cm diameter is broken uniformly into a large number of tiny spheres such that the diameter of each of the new particles is 1×10^{-7} m. What is the total surface area of these particles?

Solution: The surface area of a spherical particle of 2 cm diameter is,

$$A = \pi D^2 = 1.26 \times 10^{-3} \text{ m}^2$$

The volume of the sphere is, $V = \frac{\pi D^3}{6}$

If the diameter of the new particles be d and their number be N then,

$$V = \frac{\pi D^3}{6} = N \left(\frac{\pi d^3}{6} \right)$$

Therefore, the number of particles is given by,

$$N = \left(\frac{D}{d} \right)^3 = \left(\frac{2 \times 10^{-2}}{1 \times 10^{-7}} \right)^3 = 8 \times 10^{15}$$

Therefore, the total surface area of the new particles is,

$$A_{\text{tot}} = N\pi d^2 = 8 \times 10^{15} \times \pi \times (1 \times 10^{-7})^2 = 251.2 \text{ m}^2$$

1.1.6 Specific surface area

To quantify the surface area per unit mass, a term known as *specific surface area* is used. For spherical particles, it is defined as,

$$\text{SSA} = \frac{\pi d^2}{\left(\frac{\pi d^3}{6}\right)\rho} = \frac{6}{d\rho} \quad (1.1)$$

Where d is the diameter of the particles and ρ is their density.

1.1.7 Important points to remember

- i. The work necessary to reduce the size of the droplets to the sub-micron level is quite high. Work equivalent to several hundreds of joules is necessary to generate droplets of size < 10 nm. For example, a huge amount of work is necessary to disperse water into a fog.
- ii. In many gas–liquid or liquid–liquid chemical reactions, high interfacial area is necessary for sufficient progress of the reaction leading to industrially-viable yield of the desired product. To disperse one liquid into another in the form of fine droplets, very high speed of agitation is necessary.
- iii. The effectiveness of a catalyst is greatly increased when it is in a finely-divided form, or if it is highly porous.
- iv. Removal of contaminants from water by adsorption on a suitable material, such as particulate charcoal, is effective because it has a very high surface area per unit mass.

Exercise

Exercise 1.1.1: 1 dm³ of water is atomized to form droplets of 1 μm diameter. Calculate the total surface area of the droplets. What would be the surface area if the diameter of the droplets is 10 nm?

Exercise 1.1.2: The average diameter of fine spherical particles is often expressed by the Sauter mean diameter (SMD), given by,

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where n_i is the number of particles having diameter d_i . For the data given below, compute the SMD.

No. of particles	Particle diameter (μm)	No. of particles	Particle diameter (μm)
20	3.5	20	7.9
10	9.1	10	10.8
5	11.9	5	12.5
3	14.1	4	15.4
2	16.8	1	21.4

Exercise 1.1.3: Answer the follow questions.

- i. Discuss five applications of interfacial phenomena in modern life.
- ii. Define “interface” and “surface”. Explain their difference.
- iii. Explain the application of interfacial engineering in microelectronics.
- iv. What is enhanced oil recovery?
- v. Define specific surface area.

Suggested reading

Textbooks

- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapters 1 & 11.
- ◆ R. J. Stokes and D. F. Evans, *Fundamentals of Interfacial Engineering*, Wiley-VCH, New York, 1997, Chapter 1.

Reference books

- ◆ J. Lyklema, *Fundamentals of Interface and Colloid Science, Vol. 1*, Academic Press, London, 1991, Chapter 1.
- ◆ L. E. Schramm, *Emulsions, Foams, and Suspensions*, Wiley-VCH, Weinheim, 2005, Chapter 11.

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- ◆ D. H. Cobden, *Nature*, **409**, 32 (2001).
- ◆ J. D. Joannopoulos, P. R. Villeneuve, and S. H. Fan, *Nature*, **386**, 143 (1997).
- ◆ M. E. Davis, *Nature*, **417**, 813 (2002).
- ◆ N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe, and O. M. Yaghi, *Science*, **300**, 1127 (2003).
- ◆ R. F. Service, *Science*, **293**, 782 (2001).