SURFACE AND INTERFACIAL PHENOMENA

1. Surface Energy

A surface is any inhomogeneous boundary between two materials or phases. The atoms at the surface are in a very different environment than those in the bulk of either phase because (1) there are not as many bonds, (2) the atoms are spaced to give a different density, (3) the atoms are adjacent to or bonded to different atoms.

When some bonds are broken, the electron orbitals are not filled completely, so the atoms are at a higher energy state. Thus the energy required to remove a surface atom to infinity is less than that for a bulk atom. In other words, to remove a surface atom, fewer bonds must be broken than a bulk atom, so less energy is required to remove it to infinity; therefore it started out at higher energy.

This excess energy of surface atoms is called surface energy. Because these atoms have higher energy, their equilibrium spacing is larger (their oscillations are larger) and the density of surface atoms is less than bulk atoms. Another model explaining the lower surface density is that there is asymmetry of the force field acting to pull atoms or molecules back into the bulk phase. Some surface atoms are pulled back into the bulk and leave fewer and more widely separated atoms on the surface.

When atoms of different phases are adjacent to each other, they may bond, but usually at a higher energy than the bulk atoms. Whether they bond or not, there is excess energy from both sides of the adjacent phases, producing an excess energy at the interface between the phases.

Since the potential energy of a surface molecule (or atom) is greater than that of a bulk molecule, work must be done to transport or transform a bulk molecule into a surface molecule. Thus when a new surface is produced, the energy is increased by the reversible work required to form the surface:

$$-dW_s = \gamma dA \qquad (1)$$

where $-dW_s$ is the work expended on the system to increase the surface area by dA, and γ is the surface energy (positive work W_s is defined as work done by the system).

If the surface is created at constant temperature and pressure the reversible work is equal to the increase in Gibbs free energy, dG_s:

$$-dW_s = dG_s = \gamma dA. \qquad (2)$$

(If the surface is created at constant volume and temperature, then the reversible work is the Helmholtz free energy.) If γ is independent of the area,

$$\Delta G_s = \gamma \Delta A \qquad (3)$$

or

$$\gamma = \Delta G_s / \Delta A. \qquad (4)$$

Example 1. Sliding wire experiment to measure surface free energy of a liquid.

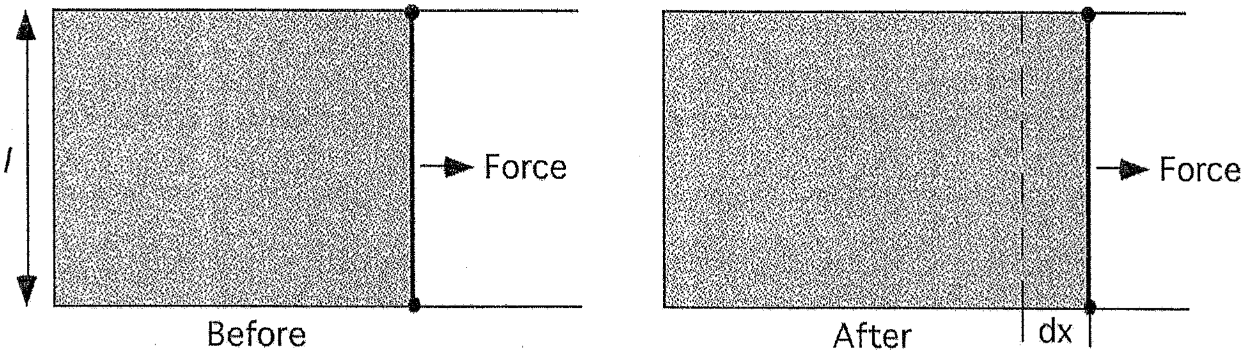


Fig. 1. A liquid film on a sliding wire illustrates the concept of surface tension and surface energy.

Assume there is a liquid film on a rectangular piece of wire, with a sliding wire bounding the 4th side of the film. We must maintain a force F on the wire to keep it from sliding to the left. If we displace the wire by dx to the right, we have put work into the system.

$$-d(work) = Fdx \tag{5}$$

This force is proportional to the length of the sliding wire, l, with proportionality constant γ.

$$F = \gamma l \tag{6}$$

$$- d(work) = \gamma l \, dx \tag{7}$$

$$- d(work) = \gamma d(Area), \tag{8}$$

where $d(Area)$ is $l \, dx$. Solving for γ,

$$\gamma = \frac{-d(work)}{dA} = \frac{dG_s}{dA} \qquad \text{(same as Equation 4)}$$

1.1 Solid Surface

1.1.1 Crystalline Solid.

When the new surface is created in a solid, the surface atoms usually cannot relax completely and the process is not reversible, so the equilibrium equations above do not apply perfectly for solids. By convention we usually say the solid surface still has surface energy, γ, but not surface free energy because equilibrium is not achieved. For liquids, the surface is usually mobile enough that surface stretching is reversible, and the surface is in equilibrium with the bulk. Thus liquids are usually said to have surface free energy, which is also called surface tension. For solids, surface energy is defined by

$$\gamma = \Delta E_s / \Delta A \tag{9}$$

and the surface energy usually varies with the crystallographic plane of the area, and sometimes with the process used to make the new area.

The abrupt termination of the crystal lattice at a solid surface causes many dangling bonds (high energy, unpaired electron orbitals) as well as many surface imperfections. These surface imperfections include holes, steps, edges, corners, dislocations, and more. Each kind of imperfection has a bit of excess surface energy associated with it, and the sum of all the imperfections produces the macroscopic surface energy. The surface energy of an imperfection can be estimated by counting the number of broken bonds associated with the imperfection. Example 2 shows how this may be calculated for a smooth surface. The surface energy of crystals is usually so high that the surface is very reactive (with oxygen) or very adsorptive.

Example 2. Cleavage of a crystal to measure the surface energy of a solid.

Estimate the surface energy of the (111) plane of gold.

Data:
Heat of vaporization is 334.4 kJ/mol
Atomic radius is 0.144 nm
Gold has FCC structure
Atomic mass is 197g/mol

Solution:

The surface energy is the energy required to break the bonds along the (111) divided by the total area created when the bonds are broken.

Steps:
1. Identify the energy per bond in gold (by calculation or by looking it up).
2. Calculate the bonds broken per atom by a cut parallel to (111).
3. Calculate the atoms/m^2 in the (111) plane.
4. Multiply these to get the energy of bonds broken in this plane.
5. Calculate how much new area is made.
6. Calculate energy per new area.

Basis: 1 m^2 of cut on the (111) plane.

1. Calculate the energy per bond in gold. The heat of sublimation is not known, but the heat of vaporization is usually only slightly less than the heat of sublimation for metals. In FCC each atom is surrounded by 12 others (CN = 12); but during sublimation, only 6 bonds per atom are broken because 2 atoms share 1 bond. Hence

$$\text{Energy/bond} = H_V/(CN/2)/N_A = 334.4\text{ kJ/mol} / 6 / 6.02\times10^{23}\text{ bond/mol} =$$
$$= 9.258\times10^{-20}\text{ J/bond}$$

2. Calculate the bonds broken per atom by a cut parallel to (111). Look at 1 atom in the plane. It is bonded to 6 atoms within the plane. A cut parallel to the plane will not cut any of these. There are 3 more bonds sticking out above the plane and 3 sticking out below the plane. A cut above the plane will cut these 3 bonds. Therefore you cut 3 bonds/atom.

3. Calculate the atoms/m^2 in the (111) plane. What is the atomic planar density in (111)?

$$\frac{2\text{ atoms}}{4\sqrt{3}r^2} \times \left(\frac{r}{0.144\times10^{-9}\text{m}}\right)^2 = 1.392\times10^{19}\text{ atoms/m}^2$$

4. Multiply these to get the energy of bonds broken in this plane.

$$1.392\times10^{19}\text{ atoms/m}^2 \times 3\text{ bonds/atom} \times 9.258\times10^{-20}\text{J/bond} = 3.87\text{ J/m}^2$$

5. Calculate how much new area is made. The cut has formed 2 surfaces, each with area 1m^2.

6. Calculate energy per new area. $\gamma = \frac{3.87\text{ J}}{2\text{m}^2} = 1.93\text{ J/m}^2 = 1933\text{ erg/cm}^2$.

This is typical for metals, which have γ from about 400 to 4,000 ergs/cm^2 or 0.4 to 4 J/m^2.

1.1.2 Amorphous Solid. Examples of amorphous solids are glasses and non-crystalline polymers. In metal oxide glasses the unbonded orbitals at the surface usually react with atmospheric oxygen to form an oxide layer. This oxide layer usually has fairly high surface energy, but not as high as the pure metal. For example, normal soda-lime glass has a surface energy of about 120 erg/cm^2. Metal oxides have γ from about 80 to 500 ergs/cm^2.

In polymers there are usually no unbroken covalent bonds. The long chains lie along the surface. The energy to form these surfaces is just the small amount to overcome the weak Van der Waals interactions holding the polymer together. Non-polar polymers usually have a surface energy around 20-30 erg/cm^2, which is low enough that the surface is fairly unreactive. Polar polymers have γ from about 30 to 90 ergs/cm^2.

1.2 Liquid Surface Energy.

Liquid surfaces are extremely dynamic. Atoms (or molecules) are continually coming to the surface from the bulk, leaving the surface to the bulk, evaporating from the surface, or condensing onto the surface. The surface atoms have lower density and higher energy than the bulk atoms. The surface can easily change shape in response to external or internal forces. Because liquid surfaces are free to move, they tend to form shapes which will lower the total free energy of the system. This usually results in rounded (not always spherical) surfaces with minimal areas. The unfilled electron orbitals of the surface atoms produce the surface energy which can range from very low for saturated hydrocarbons (no unbonded orbitals) to very high for liquid metals (mercury) or salts.

Liquid surface energies are easily measured in the laboratory by a number of different techniques such as the Wilhelmy plate, deNouy ring, pendant drop size, pendant drop shape, undulating jet, and more. Some typical surface energies (surface tensions) of some liquids are given below.

Water	72 erg/cm^2 = 72 mJ/m^2	Ethanol	22.3 mN/m
Mercury	436 erg/cm^2 = 436 mN/m	Liquid helium	0.12 mN/m (-269°C)

1.3 Interfacial Surface Energy

At a phase boundary atoms of one phase are forced against a different phase of atoms. Excess energy at this surface (called an interface) results from several sources such as unbonded orbitals, bonded orbitals with different atoms (which make a higher energy compound), misaligned grain boundaries, and more. **If** the juxtaposition of two phases produces an interface which has **lower** energy than either phase, the interface will be unstable and the two phases will diffuse into each other producing a new phase which has lower energy. A stable interface is usually only a few atoms thick, but in some cases it can be thicker if the structure of the bulk phase is perturbed by the presence of the adjacent phase. In this case one has a interfacial volume, called an interphase, which has properties different than either phase. Interfacial energies can be extremely low (water against ice) or very high (mercury against air).

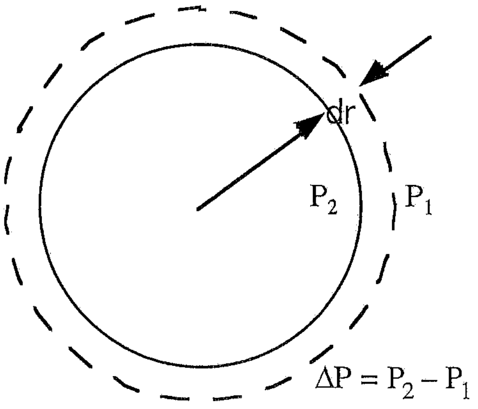
2. Interfacial Phenomena

Interfacial phenomena occur in many chemical engineering processes where there are interfaces such as liquid/liquid, liquid/gas, liquid/solid, solid/gas and solid/solid. The phenomena are governed by the excess free energy and excess pressure at curved interfaces. The most important governing equations are the LaPlace and the Young equations.

2.1 LaPlace Equation.

The surface energy of a liquid drop or bubble tends to pull the bubble into a spherical shape and slightly squeeze the fluid inside. This can be illustrated by considering a *gas bubble surrounded by liquid.* In the absence of flow, gravity, or other fields, the bubble is spherical with radius r and surface area $4\pi r^2$. If work is done on the system (bubble and liquid) to cause the radius to increase by dr, the corresponding increase in free energy is $8\pi\gamma r dr$. The increase in surface free energy due to expansion must be balanced by application to the system of pressure volume work $\Delta P 4\pi r^2 dr$, i.e. the work required for expansion is equal to the increase in surface free energy or the work to make a new surface (note that work W is positive if done by the system and ΔP the pressure across the film is P_2-P_1 or P_2-P_{amb}., since the pressure inside the bubble is higher than ambient pressure P_{amb}):

Fig. 2



work to expand = work to make new surface

$$-dW = \text{force} \times \text{distance} \qquad -dW = dG_s = d(A\gamma)$$

$$-dW = \Delta P \times \text{area} \times dr \qquad d(A\gamma) = d(4\pi\gamma r^2)$$

$$-dW = \Delta P \times 4\pi r^2 \times dr \qquad d(A\gamma) = 4\pi\gamma 2 r dr$$

$$\Delta P \times 4\pi r^2 dr = 8\pi\gamma r dr$$

$$\Delta P = \frac{2\gamma}{r}$$

where $\Delta P = P_2 - P_1$. Thus

$$\Delta P = 2\gamma/r \tag{10}$$

This is known as the LaPlace equation and gives the magnitude of the pressure drop across the film. A more general form of the LaPlace equation is:

$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{11}$$

where r_1 and r_2 are the two orthogonal radii of curvature of the surface. The pressure is always highest on the inside curvature side of the interface. If you measure the pressure drop across a soap film bubble, the pressure drop is $4\gamma/r$ because you must cross two interfaces (gas to liquid, then liquid to gas). Equations 10 and 11 account for capillary rise and other capillary phenomena.

Example 3: Derivation of Capillary Rise Equation

If a capillary is placed in a liquid reservoir, surface tension can bring about a rise in the liquid level inside this capillary relative to the reservoir height as shown in Fig. 3 below.

An approximate treatment of capillary rise is made possible in terms of the LaPlace equation. If the liquid wets the walls of the capillary, the liquid surface will lie parallel with the capillary wall and will be concave. Moreover, if the capillary is circular in cross-section and not too large in radius, the meniscus will be approximately hemispherical as illustrated in Fig. 3. Accordingly, the equation of LaPlace reduces to its simplest form:

$$\Delta P = 2\gamma/r \tag{12}$$

where r is the radius of the capillary. This equation predicts an inverse relationship between pressure drop and radius. If h denotes the height of the meniscus above the flat liquid surface, then ΔP must also equal the hydrostatic pressure in the column of the liquid in the capillary. Thus

$$\Delta P = \Delta\rho g h \tag{13}$$

where $\Delta\rho$ denotes the difference in density between the liquid and gas phase and g is the acceleration of gravity. Eliminating ΔP between Equations 10 and 12 and noting that the liquid density is generally much greater than that of the gas phase

$$\rho_l g h = 2\gamma/r \quad \text{or} \quad h = 2\gamma/\rho_l g r \tag{14}$$

Thus, the capillary rise h can be calculated from 14, given the surface tension, liquid density, and capillary radius. If wetting is incomplete, $h = 2\gamma\cos\theta/\rho_1 g r$

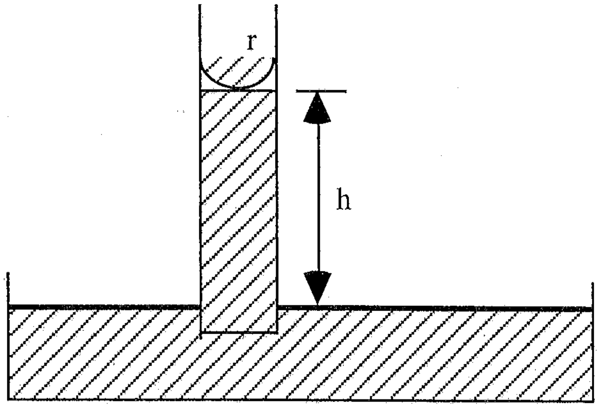


Fig. 3. Capillary rise (capillary diameter magnified greatly in relation to reservoir; capillary height not magnified).

Example 4: Calculation of Capillary Rise

What will be the capillary rise of benzene ($\gamma = 29$ dyne/cm) in a polyethylene capillary tubing of 0.2 mm inside diameter at 20°C and 1 atm? Assume benzene ($\rho = 0.88$ g/cm^3) completely wets the PE tubing. Will the rise be positive or negative?

answer: Using Equation 14 above

$$h = 2\gamma/\rho_l g r \qquad (14)$$

$$h = 2\ (29\ \text{dyne/cm})/[(0.01\ \text{cm})(0.88\text{g/cm}^3)(980\ \text{cm/s}^2)]$$

(note that a dyne is a g cm/s^2)

$h = \underline{6.7\ \text{cm}}$

2.2 Cohesion and Adhesion

Cohesion refers to how well a material is bonded to itself. We define the work of cohesion, W_C, as the work per area to separate a single phase material. Two new surfaces, each with surface energy γ are formed. Thus the work of cohesion is

$$W_c = 2\gamma_{ij} \qquad (15)$$

where the subscripts refer to the 2 new interfaces.

Adhesion refers to how well two materials adhere at their interface. We define the work of adhesion, W_a, as the work per area to separate two phases.

$$W_a = \gamma_A + \gamma_B - \gamma_{AB}. \qquad (16)$$

2.3 Wetting and Spreading of Liquids on Solids (Young's and Gibb's Equations)

2.3.1 *Complete Spreading*. When a drop of liquid contacts a solid, it can remain a spherical drop, it can partially spread out on the drop forming a spherical cap, or it can completely spread on the solid, forming a layer only a few molecules thick. To determine which is the case, let us do a thought experiment suggested by Figure 4 in which we force a small drop to spread over a large surface. Before a drop of liquid contacts the surface, the surface free energy of the system is the solid-vapor surface free energy, γ_{sv}, multiplied by the solid area (assuming the original area of the drop is much smaller than the solid area). When the liquid is spread completely on the solid, the system now consists of two interfaces (the solid-liquid and the liquid-vapor interfaces), and the surface free energy of the system is $\gamma_{lv} + \gamma_{sl}$ multiplied by the solid area. One may now ask the question, "Does the system attain the lowest free energy when the drop is spread completely on the solid?"; if so, complete spreading will occur. We can see that if the γ_{sv} is larger than the sum of $\gamma_{lv} + \gamma_{sl}$, *the reduction in free energy* will drive the drop to spread completely over the surface. Thus spreading occurs if:

$$\gamma_{sv} > \gamma_{lv} + \gamma_{sl}$$

or

$$0 < \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \tag{17}$$

Complete spreading will also occur if $\gamma_{sv} = \gamma_{lv} + \gamma_{sl}$ because the drop will flatten out until it has a contact angle of zero as will be shown in the next section.

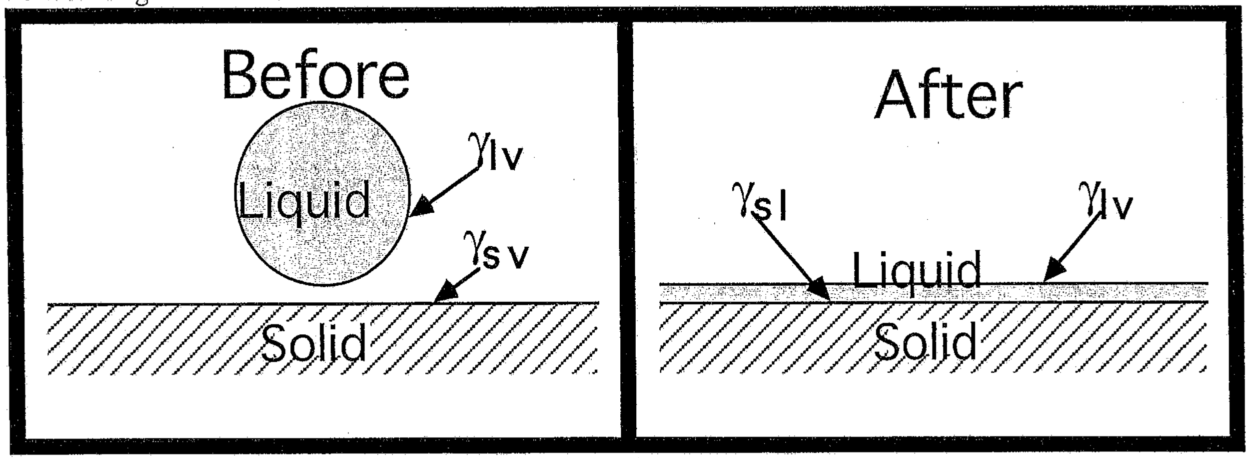


Figure 4. Complete spreading of a drop on a solid.

In the early 1920's Harkins and Feldman studied the spreading of organic liquids on a number of solid and liquid substrates. They defined a "spreading coefficient," S, as the difference between the work of adhesion, W_a, and the work of cohesion W_c. Therefore the spreading coefficient becomes

$$S = W_a - W_c \tag{18}$$

$$S = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} - 2\gamma_{lv} = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \tag{19}$$

Harkins and Feldman observed that liquids spread completely when $S \geq 0$ which is consistent with Eqs. 15, 16, and 17. In summary then, spreading is favored if (1) the surface energy of the solid (γ_{sv}) is high and (2) surface energies of the liquid and liquid-solid interface are small, since the reduction in free energy of the surface will drive the drop to spread over the surface.

2.3.2 *Partial Spreading*. Now let us examine the case in which the solid surface energy is less than $\gamma_{lv} + \gamma_{sl}$, or in which S is negative and the spreading is not complete. In this case the drop forms a sphere or spherical cap on the solid as long as the drop is small enough that gravitational distortion of the drop shape is negligible. The contact angle is defined as the angle between the solid-liquid interface and the liquid-gas interface at the edge of the drop. In 1805, Thomas Young stated (without proof) that the equilibrium among the attractive forces between particles of fluid and particles of solid will cause the fluid to form a certain angle with the solid. This angle was defined by:

$$F_s = F_{sl} + F_l \cos\theta \tag{20}$$

where the F_s, F_{sl}, and F_l refer to the forces of the solid, the common surface, and the liquid respectively. This was the genesis of Young's equation, a mechanical balance of rather ill-defined forces. There is a force balance also in the vertical direction: remember that, "when you push against an immovable wall, the wall exerts an equal force in the opposite direction." So the solid substrate exerts an equal force in the downward direction at the three phase boundary.

Unlike Young, Willard Gibbs related the contact angle to the more familiar concept of surface energy. He proposed that the 3-phase boundary line (between an insoluble solid and 2 fluids) would displace along the solid surface until it reached a point at which any further displacement of the line would create an increase in the free energy associated with the 3 phase boundary line. This condition of equilibrium reduces to

$$\gamma_{lv} (\cos \theta) = \gamma_{sv} - \gamma_{sl} \qquad (21)$$

which has the same form as Young's equation, but which employs surface energies instead of surface forces. Eqn. 21 can be rearranged to solve for the interfacial energy; if, in addition, we assume that the vapor is air and drop the v subscript the equation becomes:

$$\gamma_{sl} = \gamma_s - \gamma_l (\cos \theta) \qquad (22)$$

Thus, the interfacial energy can be calculated from Eqn. 22 if we have values for the surface energy of the solid, the surface tension of the liquid, and the contact angle.

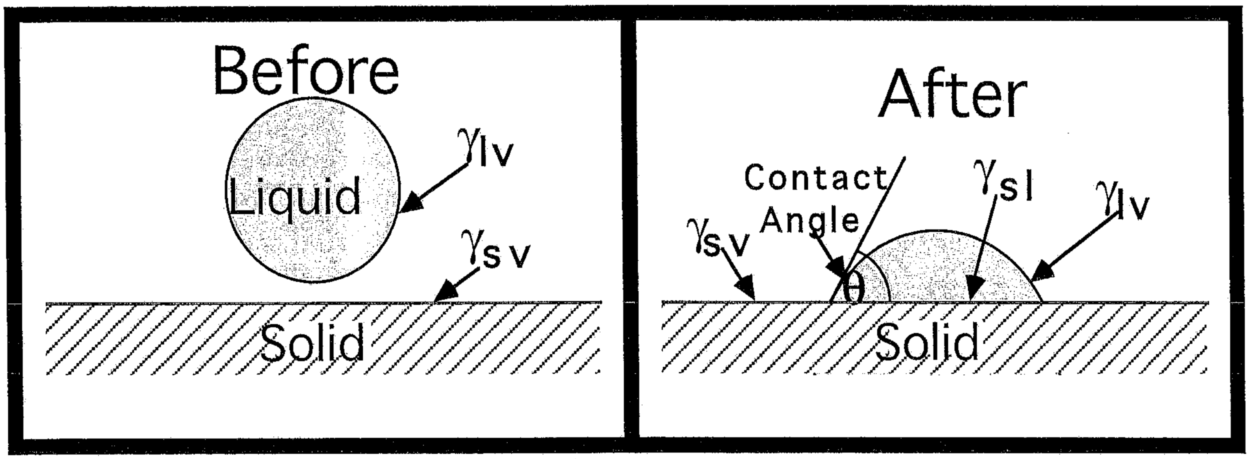


Figure 5. Partial spreading of a drop on a solid.

We can prove and illustrate this equation by combining the familiar rule that "a system moves to its state of lowest free energy" with a simple model of a liquid drop contacting a solid surface. Referring back to the discussion of the spreading coefficient, we see that if $\gamma_{sv} < \gamma_{lv} + \gamma_{sl}$, then the free energy of the system is not minimized at a state of complete spreading, and so the drop will not spread completely. The question now becomes: "How far must the drop spread to minimize the free energy of the system?" The answer is given by formulating the equation that describes the change in free energy: one simply subtracts the energy "before" from the energy "after" the drop wets the surface. The surface energy before the drop contacts the surface is:

$$\text{Total surface energy before} = S_T \gamma_{sv} + 4\pi r_d^2 \gamma_{lv} \qquad (23)$$

where S_T is the total area of the solid surface and r_d is the radius of the drop. After the drop has contacted the surface, it spreads to form a spherical cap with a contact angle θ as shown in Figure 5. The total surface energy after the wetting of the drop is:

$$\text{Total surface energy after} = (S_T - A_I)\gamma_{sv} + A_c\gamma_{lv} + A_I\gamma_{sl} \qquad (24)$$

where A_I is the area of the interface between liquid and solid, and A_c is the liquid-vapor interfacial area of the spherical cap of liquid. A_I and A_c are given by

$$A_I = \pi r_c^2(1-\cos^2\theta) \qquad (25)$$

and

$$A_c = 2\pi r_c^2(1-\cos\theta) \qquad (26)$$

where r_c is the radius of curvature of the spherical cap. The change in free energy of the system is found by subtracting Eq (23) from Eq (24):

$$\Delta G = 2\,\pi\,\gamma_{lv}\,(r_c^2(1-\cos\theta)-2\,r_d^2) + \pi\,r_c^2(1-\cos^2\theta)(\gamma_{sl} - \gamma_{sv})\,. \qquad (27)$$

The minimum in free energy is found by equating to zero the derivative of Eq (27) with respect to $\cos\theta$, and then solving for $\cos\theta$:

$$\frac{d\Delta G}{d(\cos\theta)} = 0 = \pi\left\{2\gamma_{LV}\left((1-\sigma)\frac{dr_c^2}{d\sigma} - r_c^2\right) - 2\sigma r_c^2(\gamma_{SL}-\gamma_{SV}) + (1-\sigma^2)(\gamma_{SL}-\gamma_{SV})\frac{dr_c^2}{d\sigma}\right\} \qquad (28)$$

where σ is a shorthand notation for $\cos\theta$. After much math, you can solve for σ to obtain

$$\sigma = \cos\theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \qquad (29a)$$

which is identical to Eq (21).

It is very rare to have a contact angle of 180° (absolutely no wetting). Eq. (22 or 29a) indicates that an angle of 180° would require $\gamma_s = \gamma_{sl} - \gamma_l$ (Eqn. 29b, dropping v subscripts). This is rarely the case for aqueous solutions or organic liquids on glass or solid organic solid surfaces because the interfacial free energy γ_{sl} is usually less than the liquid surface tension γ_l; hence, the requirement (Eqn. 29b) is not met—rather it predicts a negative surface energy for the solid. However, in the case of liquid metals (such as mercury) on glass or organic solids γ_l and γ_{sl} are both so high that γ_s is by comparison negligible and a contact angle of 180° is approached (see Example 4). While angles of 180° are rarely obtainable, "water-proofing" surfaces, even porous surfaces, is nevertheless possible. If the contact angle is greater than 90°, capillary pressure will resist the penetration of a liquid into a porous solid, so the rain will not penetrate unless pressure is applied.

Summary of Equations for Surface Tension:

$$S = \gamma_s - (\gamma_l + \gamma_{sl}) \qquad (19)$$

when $S \geq 0$	liquids spread completely
when $S = 0$	liquids spread completely, $\theta = 0$
when $S < 0$	droplets spread only in part with contact angle θ

for $S > 0$	$\gamma_s > \gamma_l + \gamma_{sl}$	(17)
for $S < 0$	$\gamma_{sl} = \gamma_s - \gamma_l(\cos\theta)$	(22)
$W_c = 2\gamma_{ij}$		(15)
$W_a = \gamma_s + \gamma_l - \gamma_{sl}$		(16)

Example 4: Calculation of Interfacial Energies, Work of Adhesion and Spreading Coefficient

The contact angles of mercury, water, and benzene on a solid paraffin wax are shown below. Estimate interfacial energy (γ_{sl}), work of adhesion (W_a), and spreading coefficient (S) for each liquid-paraffin pair. The surface energy (γ_s) of the solid paraffin is 50 dynes/cm.

Liquid	Surface Tension (mN/m or dyne/cm)	Contact Angle (°)
mercury	476	180
water	72.8	60
benzene	29	3

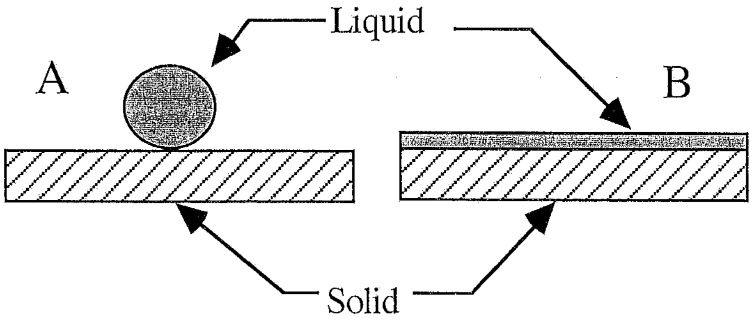
Solution: Use Equations 22, 16, and 19 in that order to calculate γ_{sl}, W_a, and S.

Liquid	γ_{sl}	W_a	S
mercury	526	0	-952
water	13.6	109	-36
benzene	21	58	0

Note: High γ_{sl} implies an unfavorable solid-liquid interface; high W_a implies good adhesion; $S < 0$ implies less than complete spreading.

Example 5: Evaluating Interfacial Free Energy

Which has the lower interfacial free energy? Liquid A or B? Assume 2 different liquids in contact with the same solid.



From Equation 22 above

for $S < 0$ $\quad \gamma_{sl} = \gamma_s - \gamma_l (\cos \theta)$ (22)

Assume an arbitrary value, such as γ_s = 100 dyne/cm. Then:

For A:

θ = 180°C (based on drawing above); γ_l is large--assume 500 dyne/cm

From Eqn. 3 $\gamma_{sl} = \gamma_s - \gamma_l (\cos\theta) = 100 - (-1)\,500 = 600$ dyne/cm

For B:

$\theta = 0°$ based on drawing; γ_l is small--assume 50 dyne/cm

From Eqn. 3 $\gamma_{sl} = \gamma_s - \gamma_l (\cos\theta) = 100 - (1)\,50 = 50$ dyne/cm

Since $\Delta G_s = \gamma\,\Delta A$, the areas are equivalent, and both systems begin with the same state, the interfacial energy is much smaller for B.

2.4 Liquid-liquid Interactions

Although the force balance concept of Young's equation does not involve free energy concepts, a force balance does exist at the corner of a drop, and the use of a force balance in the horizontal direction will help you to never forget Young's equation.

Similarly a force balance is useful to predict the relationship between fluid interfacial energies and the angles of contact. If one has 3 immiscible fluids (3 immiscible liquids or 2 immiscible liquids and a gas), a small volume of the fluid of intermediate density will form a lens between the other 2 fluids. Figure 6 shows the intersection of liquids A, B, and C with the corresponding liquid-liquid interfacial energies (tensions).

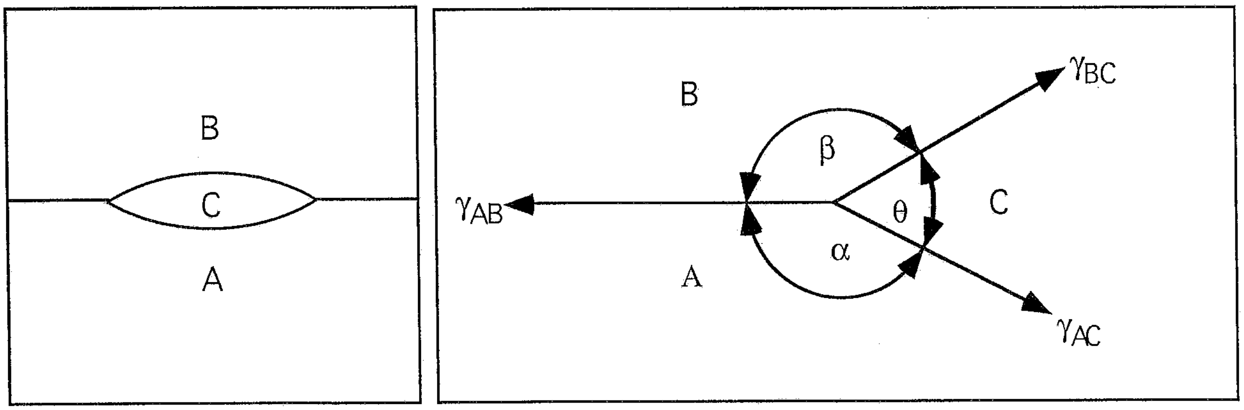


Figure 6. Three immiscible fluids (left) and the interfacial energies and angles at their intersection.

Two important relationships exist relating the angles of intersection and the interfacial energies:

$$\gamma_{AB} + \gamma_{AC}\cos\alpha + \gamma_{BC}\cos\beta = 0 \tag{30}$$

$$\frac{\gamma_{AB}}{\sin\theta} = \frac{\gamma_{AC}}{\sin\beta} = \frac{\gamma_{BC}}{\sin\alpha} \tag{31}$$

If $\gamma_{AB} = \gamma_{AC} = \gamma_{BC}$ as is the case for the junction of grain boundaries in a single phase material, then $\alpha = \beta = \theta = 120°$. Therefore equilibrium grain boundaries should meet at angles of 120°. Such a structure is called an equiaxed structure.

3. Colloidal Systems

Colloidal systems refer to two phase systems in which one of the phases is discontinuous (e.g. in the form of droplets) and has a size between 1 nm and 0.01 mm. In these finely dispersed systems the surface/volume ratio is extremely high, and the properties of the systems are dominated by surface properties such as surface energy and LaPlace pressures inside the particles. Nearly all colloidal systems are unstable because the high surface energy resulting from the high surface area can be reduced by collapsing or coagulating the system into larger particles. Major industrial effort is spent in stabilizing the colloidal system when needed, and suppressing them when not desired. The names of the various systems are:

Dispersed phase /Continuous phase	Name	Examples
Solid/Liquid	Suspension, gel, paste	Plaster, dough, jello, skim milk
Solid/Gas	Smoke	Smoke, fluidized bed, cirrus clouds
Liquid/Liquid	Emulsion	latex paint, salad dressing
Liquid/Gas	Fog	Steam, fog, clouds (cumulus)
Gas/Liquid	Foam	Shaving cream, chocolate mousse
Gas/Solid	Solid Foam	Pumice, Styrofoam, bread

3.1 Solid Suspensions, Gels and Pastes

Solid suspensions, gels and pastes are dispersions of solids in liquids. Gels are usually less concentrated (< 15 wt%) than pastes. Solid suspensions are usually not viscous (< 2 wt%). Gels usually have particles that entrain or absorb or trap large amounts of water. In some cases these solids can interlink, forming solids which can flow with application of sufficient shear stress (such as quicksand) or temperature. Pastes are usually so concentrated that solid particles are touching each other. Both gels and pastes exhibit non-Newtonian behavior.

3.2 Emulsions

An emulsion is a dispersion of 2 immiscible liquids. Usually one phase is in the form of droplets and the other is continuous. Emulsions of organic liquids in water are very important in food science, paints and chemical separation systems. Emulsion droplets about 1 micron or larger are inherently unstable and the emulsion will quickly break up unless an emulsifier is added. An emulsifier is an amphiphilic molecule with a hydrophilic and a hydrophobic end. The emulsifier adsorbs at the droplet interface and reduces the interfacial energy between the phases, thus reducing the driving force for coagulation. For droplets smaller than 0.1 micron, the electrostatic charge on the surface of the droplets often keeps the droplets separated from each other.

3.3 Foams

Foams are dispersions of large amounts of gas in a small amount of water. In true foams the bubbles are so crowded that they deform against each other and form polyhedral volumes with flat sides (polyhedral foams). These foams have equal pressure in each volume because there are no curved surfaces. In a gas emulsion foam, the volume of liquid is on the same order of magnitude as the gas volume, and the bubbles are rounded. Round bubbles with smaller diameter have higher internal pressure (LaPlace pressure), and these bubbles collapse as the gas diffuses into bubbles with lower pressure. Collapse of the small bubbles also decreases the total surface area and surface energy. Eventually only large bubbles remain. Foams can be a problem in industry when a mixing operation entrains air into a liquid containing a surfactant. Anti-foam agents usually work by reducing the liquid viscosity (so the bubbles drain) or by displacing the foaming agent (surfactant) from the air-liquid interface.

Solid foams with rigid walls are indefinitely stable.

3.4 Smokes and Fogs

Solid dispersions of very small particles in a gas (smoke) are difficult to remove from the gas. They usually do not coalesce in the gas phase because they have repulsive electrical charges on their surfaces. Smokes of combustible materials (flour, coal dust) can be very explosive because of their high surface area.

Fogs are dispersions of liquid in a gas. They can form either by condensation of a vapor or by atomizing (spraying) a liquid. They are usually unstable unless they carry some static charge.

Example 6: Stability of Colloids and Emulsions

Dr. I. M. Gud at Skruffy Peanut Butter Inc. has been charged with developing a more stable peanut oil/water emulsion for Skruffy's leading product. Dr. Gud knows his surface chemistry well and therefore he knows that he must prepare oil droplet diameters smaller than 0.1 micron so that the electrostatic charge can (at least in principle) keep the oil droplets from coming together and agglomerating. Particle size measurements on his latest preparation indicate an average oil droplet size of 0.05 micron. Measurements of surface tension with a Wilhelmy plate don't work out because the emulsion is too sticky. Fortunately, data from a titration calorimeter provide a reliable determination of ΔG_S of -47 J/liter for the formation of the emulsion.

Dr. Gud is excited with these results and asks you (his new research assistant) to determine (a) the interfacial area of the emulsion, (b) the interfacial energy, and (c) whether the emulsion is stable (he wants your opinion based on the results).

Answer:

a. Interfacial area:

Basis: 1 liter of oil phase of the emulsion; Approach: determine S/V in terms of r

$V = 4/3\pi r^3$ and $S = 4\pi r^2$

$S/V = (4\pi r^2)/(4/3\pi r^3) = 3/r$ or $S = 3V/r$

$S = 3V/r = 3(1000\ \text{cm}^3)/[(5\text{x}10^{-6}\ \text{cm})] = 6.00 \text{ x } 10^8\ \text{cm}^2 = \underline{6.00 \text{ x } 10^4\ \text{m}^2/\text{liter}}$

b. Interfacial energy:

$\gamma = \Delta G/\Delta A = (-47\ \text{J/liter})/(6.00 \text{ x } 10^4\ \text{m}^2/\text{liter}) = \underline{-7.8 \text{ x } 10^{-4}\ \text{J/m}^2}$

c Stability? Since ΔG is negative, formation of the emulsion is favored; thus the emulsion should be stable, but just barely. It should not separate like your Mom's food storage peanut butter than has an oil layer on top after 15 years in the basement.