Chapter 4

Adhesion between Contacting Surfaces

1 Introduction

As the free surfaces of two solid materials come in close proximity of each other, atoms in one material begin to experience the electronic environment of the other material. The result is often adhesive interaction. Adhesion is somewhat analogous to internal cohesion of atoms in the bulk, except that it is the result of interatomic interactions between atoms at or near the free surfaces of separate materials. Adhesion phenomena can result in the absence of intervening medium (e.g. solid surfaces in a vacuum environment) or through the agency of an intervening fluid phase (e.g. liquid mediated adhesion).

2 Capillarity Phenomena

As mentioned before, the electronic state of atoms on material surfaces is drastically different from that of atoms in the bulk. An atom on a surface has fewer nearest neighbors and excess unsaturated bonding compared to one in the bulk. The net result is free surface energy. The effect of this free surface energy is readily observed at liquid-gas interfaces as a broad collection of capillary phenomena. Specifically, atoms at the surface experience a pull towards the interior and this creates a tendency for the interface to contract. Atoms in fluids have relatively high mobilities. Hence when such an interface is stretched, atoms from the bulk move to the surface and when the interface contracts, atoms move from the surface into the bulk. This process takes place rather quickly such that a state of mechanical equilibrium is reached practically instantly. L-G interfaces spontaneously contract until they contain the maximum volume of bulk material possible per unit area of interface. Work must be done in order to extend a L-G interface. The work done per unit area of new interface is the free surface energy.

The free surface energy in L-G interfaces is also known as the surface tension. The reason for this is readily understood from the results of a few simple experiments. Consider a thin layer of fluid (e.g. a soap film) in the shape of a square membrane of side L surrounded by a gas. If a force F is applied normal to one edge of the square membrane in order to stretch it by an amount dx, the energy spent in stretching the L-G interface is given by

$$dG = \gamma dA = \gamma = Ldx$$

where $\gamma = G^s = dG/dA$ is the work done in stretching the interface a unit area (units J/m^2). The quantity γ can also be interpreted as the force per unit length that must be applied to stretch the L-G interface, i.e.

$$\gamma = \frac{F}{L}$$

in units of N/m.

As a second example, consider now the thin liquid film has the shape of a closed surface (e.g. a soap bubble). The equilibrium radius r of the bubble is the result of a balance between surface tension and the pressure drop across the film. The total free energy of the surface ($G = 4\pi r^2\gamma$) would be reduced by the amount $dG = 8\pi r\gamma dr$ if the bubble radius were to decrease by dr. However, this would require the performance of work against the pressure difference across the film ΔP in the amount $\Delta P dV = \Delta P 4\pi r^2 dr$, therefore

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

This important result is known as the Young-Laplace formula and it indicates that rather large pressure differences can be expected at equilibrium across films in tiny soap bubbles.

A simple method for the approximate determination of the value of γ consists in measuring the weight of a drop ejected from a capillary tube. If the radius of the tube is r and the measured mass of one drop is m, the surface tension is approximately given by

$$\gamma = \frac{mg}{2\pi r}$$

The phenomenon of adhesion is intimately connected to surface energy. Consider two different liquids 1 and 2 exposed to a gas phase. The corresponding surface tensions of the L-G interfaces are γ_1 and γ_2, respectively. Imagine now that the free surfaces of the two liquids are brought in contact so as to form a liquid-liquid interface with surface tension γ_{12} (and thus replacing the interfaces formed between the individual liquids and the gas phase). If one were then to separate the two liquids, the amount of energy involved would be given by

$$W = \gamma_1 + \gamma_2 - \gamma_{12}$$

This is known as the work of adhesion and is known as Dupre's formula. Note that if the value of γ_{12} is relatively small (i.e. atoms at the $1-2$ interface experience only a weak inward pull into the bulk phases 1 and 2), W_{12} would be positive, i.e. work will have to be spent in separating the phases since they adhere to each other. On the other hand, if the value of γ_{12} is relatively large, the liquid phases repel and useful work could be obtained from the system as they do so.

3 Surface Energy in Solids and Solid-Liquid Interfaces

As is the case with liquids, atoms at the surface of a solid have fewer neighbors than those in the interior. As a result, there is an excess energy at the surface, namely, the *surface energy* γ . Surface energies of solids in contact with their vapor are of the order of 0.5 to 2 J/m^2 while those of liquids range between 0.05 and 0.2 J/m^2.

In solids, the mobilities of atoms are significantly less. As a result, when an interface is pulled in the tangential direction, is more difficult for atoms from the bulk to move rapidly to the surface. As a result, the interatomic bonds of the surface atoms are stretched and the surface energy of a solid surface will vary with the amount of deformation of the surface and will be given by

$$G^s = \gamma + (\frac{\partial G}{\partial A})$$

An important situation is what happens at the line where a liquid, a gas, and a solid phase meet. Such is the case obtained when a liquid droplet is deposited onto a solid surface exposed to air. Depending on the materials involved, the droplet will spread for some distance until it acquires an equilibrium shape determined by the angle of contact θ (sessile drop). Denoting vapor, liquid and solid by V, L and S, and regarding the corresponding interfacial free energies as surface tensions acting tangentially to the corresponding interfaces, a balance of force along the horizontal direction yields

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

If this is combined with Dupre's equation expressing the solid-liquid work of adhesion W_{SL} one obtains

$$W_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta)$$

This indicates that the contact angle is directly related to the strength of the adhesion between liquid and solid and suggests that contact angle measurements can be used to estimate adhesion energies.

4 Adhesion Coefficient

When two solids are pushed together by a force F_p often they tend to remain attached to each other when the load is removed and a separating force, the *adhesive force* F_a, is required to pull them apart despite elastic recovery. The *coefficient of adhesion* f_a between the two bodies is defined as

$$f_a = \frac{F_a}{F_p}$$

Factors affecting the strength of the adhesive bond include

- the chemical compatibility of the materials
- the presence of intervening film(s) between the two solids
- the crystallographic orientation of the surfaces
- the temperature of the system
- the roughness of the surfaces

5 Material Compatibilities and Energy of Adhesion

If two materials, 1 and 2 with surface energies γ_1 and γ_2, respectively, are pushed together to form an interface $1-2$ with interfacial energy γ_{12}, the *work of adhesion* W_{ad} is defined as

$$W_{ad} = \Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$$

Note that if the value of γ_{12} is relatively small (i.e. atoms at the $1-2$ interface experience only a weak inward pull into the bulk phases 1 and 2), W_{12} would be positive.

Since interfacial energies γ_{12} are often difficult to estimate or measure it is convenient to write the adhesion energy as

$$W_{ad} = c_m(\gamma_1 + \gamma_2)$$

where c_m is the *compatibility parameter* describing the extent of the affinity between the two materials.

Values of the compatibility parameter depend on the extent of the affinity between the two materials involved. Specifically, in the case of metals, greater compatibility is associated with increased solubility as indicated by the phase diagram. A semiquantitative classification is given in the following table

Contact	Compatibility Parameter c_m
Identical Metals	1.0
Identical Nonmetals	1.0
Compatible Metals	0.5
Compatible Nonmetals	0.6
Partially Compatible Metals	0.32
Partially Incompatible Metals	0.20
Incompatible Metals	0.12
Incompatible Nonmetals	0.36
Other Solids	0.22

Compatibility coefficients are often found to be directly proportional to the ratio of the adhesion energy over the hardness of the softer material W_{ad}/H.

6 Adhesion and Solid-Solid Contact

Adhesion forces influence the geometry of contacts leading to non-Hertzian behavior even in the elastic case. Consider a smooth sphere of with radius R (material 1) which is brought into elastic contact with a smooth, flat, rigid surface (material 2) under the action of a load L. If there were no adhesion, the sphere would initially touch the flat surface at a single point. However, adhesion forces pull the surface atoms of the sphere that are in close proximity to the contact point towards the flat surface and a contact area (radius a) is established even if the applied normal load is zero.

Johnson-Kendall-Roberts developed a model of contact with adhesion (JKR model). They first assumed that the contact pressure p was expressible as the sum of a pressure distribution producing uniform displacement and the Hertzian distribution, i.e.

$$p = p_{0,1}(1 - \frac{r^2}{a^2})^{1/2} + p_{0,2}(1 - \frac{r^2}{a^2})^{-1/2}$$

Assuming linear elastic behavior, the principle of superposition yields the resulting displacement due to p as

$$u_z = \frac{\pi a}{E^*}[p_{0,1} + \frac{1}{2}p_{0,2}(1 - \frac{r^2}{2a^2})]$$

The surface displacement is also related to the far field displacement (or penetration distance) δ by

$$u_z = \delta - \frac{r^2}{2R}$$

Solving the above for p_0 and p_1 yields

$$p_{0,1} = \frac{2aE^*}{\pi R}$$
$$p_{0,2} = \frac{E^*}{\pi}(\frac{\delta}{a} - \frac{a}{R}) = 2\sqrt{\frac{\gamma E^*}{\pi a}}$$

where γ is the energy of the contact interface and, as before

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

is the contact modulus and

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

is the relative or reduced radius

Now, the total energy of the system U_T, consists of an elastic and an adhesive component, i.e.

$$U_T = U_{el} + U_{ad} = \frac{1}{2}\int\int p u_z dx dy + \gamma\pi a^2$$

The equilibrium contact radius is the one that minimizes the total energy, i.e. $\partial U_t/\partial a = 0$. This yields the following relationship between δ and a:

$$\delta = \frac{a^2}{R} \pm \sqrt{\frac{2\gamma\pi a}{E^*}}$$

Furthermore, the force on the sphere is given as

$$F = -\frac{dU_T}{d\delta} = -\frac{\partial U_T}{\partial\delta} = E^*[2\delta a - \frac{2}{3}\frac{a^3}{R}]$$

since $\partial U_T/\partial a = 0$. Introducing the expression obtained above for δ finally yields

$$F = \frac{4E^*a^3}{3R} - \sqrt{8\gamma\pi E^* a^3}$$

Note that this reduces to the Hertz formula when $\gamma = 0$. This force has a minimum for the critical contact radius a_c, given by

$$a_c = (\frac{9}{8}\frac{\gamma\pi R^2}{E^*})^{1/3}$$

and the minimum value is

$$F_{min} = -\frac{3}{2}\pi R\gamma$$

This is called the adhesive force since it is the force required to pull the sphere apart from the flat surface.

Alternatively, in the Deryagin-Muller-Toporov (DMT) model the contact is assumed to remain Hertzian and that the adhesive forces act just outside the contact area. According to the DMT model the force of interaction of the non-deformed sphere which is making contact at the surface just at one point is

$$F_0 = 2\pi R\psi_a$$

where ψ_a is the *specific energy of adhesion*, obtained when the sphere is replaced by a half space of the same material and is then allowed to come to equilibrium with the flat surface at an equilibrium separation ϵ of a fraction of a nanometer. Under load, a contact area forms with radius

$$a = \sqrt{\alpha R}$$

where α is the approach from the center of the sphere to the surface under loading. The resulting pressing force F_h is the sum of the externally applied load L and the molecular interaction of the particles of the sphere with the substrate, the *adhesion force of molecular interaction* F_a which is in turn given by

$$F_a = \frac{dW}{d\alpha} = \pi R\psi_a + 2\pi\int_0^\infty \frac{d\psi}{dH}\frac{\partial H(x,\alpha)}{\partial\alpha}xdx$$

where W is the total energy of molecular interaction, $x = (r^2 - \alpha^2)^{1/2}$, and H is the distance between elements of the surfaces of the sphere and the substrate, i.e.

$$H(r,\alpha) = \frac{1}{\pi R}[r_a\sqrt{r^2 - r_a^2} - (2r_a^2 - r^2)\tan^{-1}(\sqrt{\frac{r^2}{r_a^2} - 1})] + \epsilon$$

Moreover,

$$\frac{d\psi}{dH} = \frac{8}{3}\frac{\psi_a}{\epsilon}[(\frac{\epsilon}{H})^3 - (\frac{\epsilon}{H})^9]$$

inspired on the well known Lennard-Jones interaction potential. With the above one can then calculate the adhesion force.

The DMT is most appropriate when dealing with hard solids (small deformations) while the JKR model is best for soft solids.

7 Liquid Mediated Adhesion

Thin intervening liquid films often increase adhesion of solids because of the effect of capillary forces. The basis for this behavior lies on Laplace's equation which gives the pressure difference ΔP across a curved liquid-vapor interface as

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

where γ is the surface tension of the liquid and r is the radius of curvature of the interface.

Consider now two large solid cylinders of materials 1 and 2 and radii R. The cylinders are joined at their bases with an intervening liquid phase of thickness h and surface energy γ_l. The liquid film forms a *meniscus* at the outer rim of the gap between the cylinders. Let the radius of the meniscus be r and the contact angles of the liquid film with solids 1 and 2 be α and β, respectively. The resulting adhesive (meniscus) force is

$$F_a \approx \frac{\pi R^2 \gamma}{r} = \frac{\pi R^2 \gamma}{h/(\cos(\alpha) + \cos(\beta))}$$

The term *stiction* is sometimes used to describe the adhesive effect associated with thin intervening liquid films. A common example is the interaction between head and disk in magnetic recording systems. At high ambient humidities thin water films (up to 50 nm in thickness) form on the surface of magnetic media. If the film is discontinuous, it will form localized islands (toe-dipping or pillbox regimes) and the stiction will be low. When the gap is immersed in liquid, the radius of curvature of the meniscus is low and the stiction is low again. The stiction is maximum when the gap is just entirely filled with a liquid film having a small radius of curvature at the rim.

When one of the contacting surfaces is rough and there are N peaks of mean radius R_p in the nominal contact area with an average gap d and a liquid film of thickness $h < d$, surface tension γ and contact angle θ the meniscus force F_a is given by

$$F_a = 2\pi R_p \gamma (1 + \cos\theta) N$$