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Adhesion: Solids and Liquid mediated contacts

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ADHESION: SOLID AND LIQUID MEDIATED CONTACTS

By

Manoj Kukkapalli

B.Tech Jawaharlal Nehru Technological University, 2014

A Research Paper

Submitted in Partial Fulfillment of the Requirements for the
Master of Science

Department of Mechanical Engineering and Energy Processes
in the Graduate School
Southern Illinois University Carbondale
May 2016

RESEARCH PAPER APPROVAL

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In the field of Mechanical Engineering and Energy Processes

Approved by:

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TITLE: ADHESION: SOLID AND LIQUID MEDIATED CONTACT

MAJOR PROFESSOR: Dr. Peter Filip

Adhesion is a phenomenon that arises due to interatomic forces that exist when the interfaces are in contact with each other. The study of adhesive forces is very important in determining the material that is used mainly in sliding or rolling interfaces to reduce wear and increase its reliability. This work helps in understanding the fundamental mechanisms of adhesion in both wet and dry conditions. Accordingly, this study focuses on reviewing the various techniques that are employed currently in calculating the adhesive forces in both solid and liquid mediated contact conditions. Based on the study parameters required to calculate the adhesive forces and parameters affecting adhesion are summarized.

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CHAPTER 1

INTRODUCTION

Materials in nature have a complicated structure and exhibits complex properties. Adhesion occurs when two surfaces are in contact with each other. This phenomenon increases in the presence of normal loads and is much more elevated if we combine shear or tangential forces to the normal forces. Material interfaces have capability to form bonds when they are in contact with each other and needs a force greater than the applied force called the adhesive force to separate the surfaces. Cohesion is the force that exist within the material bonding one atom to another. If we break material in bulk to two new surfaces, then we say cohesive bonds are fractured. When two different material interfaces are brought into physical contact with each other, the bonds that are formed are referred as adhesive bonds. A normal tensile force greater than the applied load is required to part the surfaces, Figure 1.

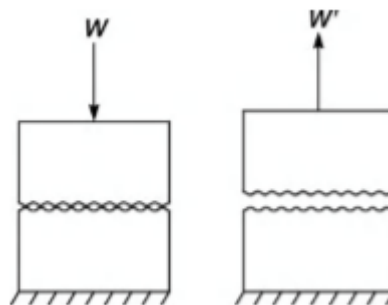


Figure 1: An Illustration of the Adhesive force between two material, W is the normal compressive force utilized and W' is the tensile force or adhesive force needed to segregate the two different surfaces [2].

The ratio of the forces W' to W , is referred as the coefficient of adhesion.

$$\mu = \frac{W'}{W}.$$

μ Depends upon duration of static contact and also separation rate [36].

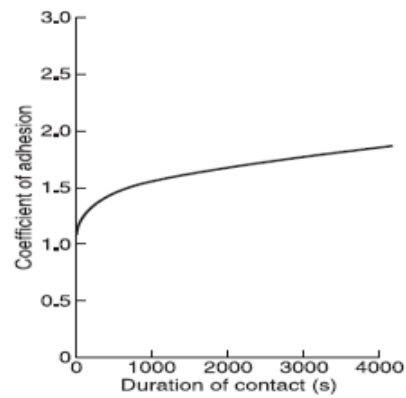


Figure 2: Experiments on Coefficient of adhesion w.r.t duration of contact in seconds for a clean steel sphere on indium [36]

Adhesion can occur when two or more solids are in contact or interposed with liquids. Adhesion is very much related to cleanliness. If solid surfaces are free from adsorbed layers, oxides, strong adhesion among the surfaces of solids occurs or vice versa [2, 4, and 11].

CHAPTER 2

SOLID-SOLID CONTACTS

Interaction of surface asperities result in an adhesion phenomenon primarily because of interatomic attractions. The proximity of asperities causes adhesion which is either physical or chemical interactions of surfaces [5, 11, 14, 21, 24, 25, 33 and 53]. A chemical interaction among asperities involves covalent, ionic, electrostatic bonds ('Triboelectricity') and metallic bonds whereas the physical interaction involves Secondary bonds like hydrogen bonds along with Vander Waals bonds [3].

The interfacial bond among solids could be greater than the cohesive bond; if it is, then separating the solid's interfaces would transfer material from the cohesively poor to that of the stronger material. Consider an example shown in Figure 3, Proximity of gold and silicon interface results in the transfer of cohesively weaker gold to that of the cohesively stronger silicon due to interfacial bonding [14].

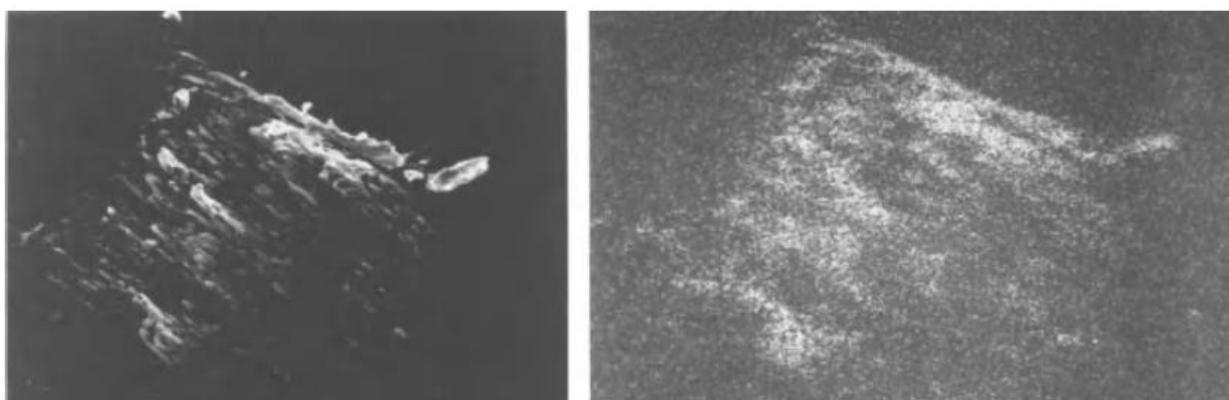


Figure 3: Silicon (111) surface after adhesive contact with gold (300 mN, 23°C, 10⁻⁸ Pa) showing (a) SEM micrograph of the transfer and (b) X-ray map for transferred gold [14].

Adhesion is a function of surface effects such as crystal structure, crystallographic

orientation, normal load, temperature, duration of contact, the solubility of one material into another and separation rate [47, 14]. Contaminants in the environment like corrosion, Physisorbed or chemisorbed layers decreases adhesion [13, 14, 18 and 25].

In corrosive environments, even Noble metals, adsorb, water vapor or oxygen on their surfaces (only up to a few molecules thick). For metals, solubility increases with temperature and results in stronger adhesion. With Polymers interdiffusion of material occurs as temperature increases which strengthen the contact.

The real area of contact is only One-Thousandth of the total geometric area due to the surface roughness. Adhesion increases with enlargement in the real area. The contact area is a function of type of the load applied (Pure normal, or combined normal and shear loads), contact duration, and mechanical properties like Poisson's ratio, or hardness of material. Adhesion force increases with an increase in the normal load and also the duration of contact, Figure 4. Visco-elastic or Visco-plastic deformation would increase the real area resulting in an increase in adhesive strength [36, 41].

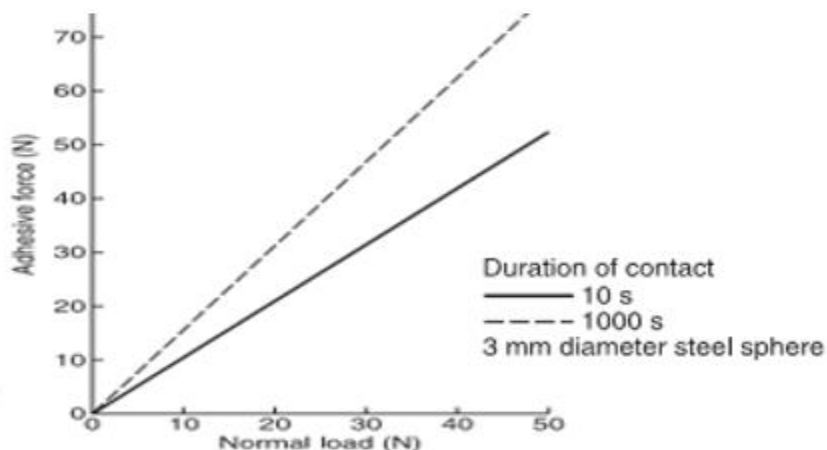


Figure 4: Adhesive force as a function of the normal load for a clean steel sphere on indium [36]

When an applied force is withdrawn from surfaces in contact, the surfaces lose their

proximity because of elastic forces, and this property is popular as elastic recovery, Figure 5 [13]. A low modulus of elasticity or Young's modulus results in a smaller amount of elastic recovery and vice versa. Mechanical property, ductility is opposite to elastic recovery. Elastic recovery is accountable for the lower adhesion of surfaces than assumed or calculated estimates. Adhesive forces appreciably rises if a tangential or shear force is supplemented to a normal force since sliding and twisting tends to penetrate the surface layers and enhance the real area of contact [47, 13].

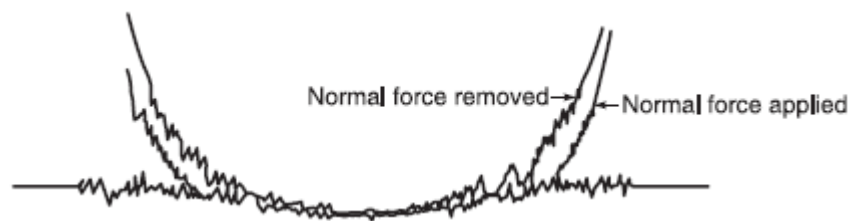


Figure 5: Schematic of the effect of elastic recovery when a normal force is withdrawn [2].

2.1 Covalent bond

Sharing electrons of polar magnetic spins between two or more atoms to form an electro-stable structural gives a covalent bond. Solids that can form a covalent bond have a high Young's modulus and are immensely rigid. It is hard to get extensive real areas of contact at high temperatures or high normal loads.

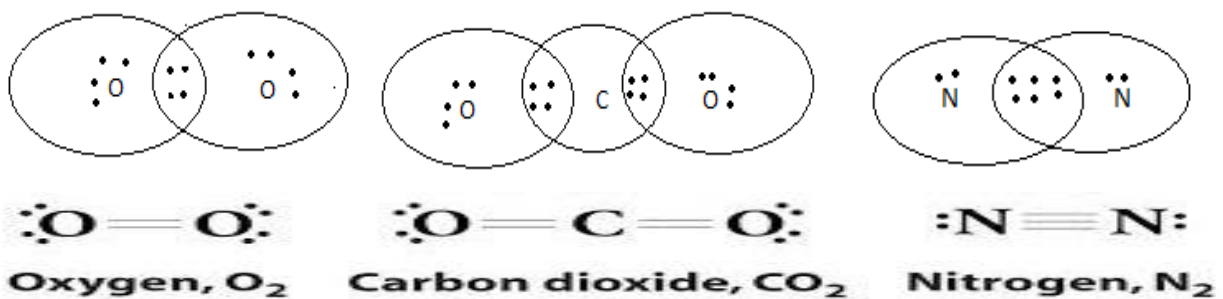


Figure 6: Illustrating the covalent bonds of Oxygen (Molecule), Carbon-di-oxide (Compound) and Nitrogen (Molecule).

2.2 Ionic or Electrostatic Bond

Transfer of electrons among two or more atoms forms an electro-neutral structure called as the ionic bond. Elements that have capability to lose their valence electrons or electropositive, form these type of bonds when they counter with elements that have capability to accept electrons or high electronegativity (usually nonmetals).

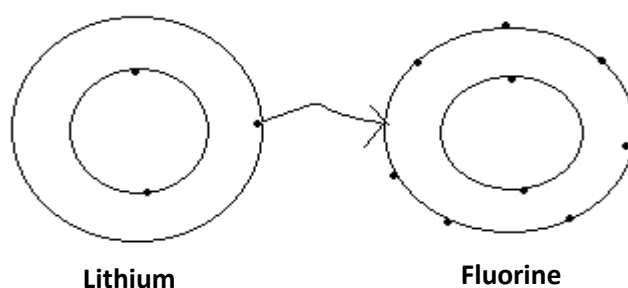


Figure 7: Schematic showing the formation of ionic bonds between Lithium and Fluorine.

If an insulator or a non-conducting element is chafed against a conductor, there is a significant segregation of charge producing an electrostatic attraction between the bodies [2, 26, 48, 19, 52, and 21].

Certain materials, usually insulators, become electrically charged when being rubbed against one another. This effect is termed as Static electricity. These electrostatic charges are not in equilibrium and perish with time.

2.3 Metallic Bond

In Metals, the valence electrons or electrons in the outermost shell do not belong to any distinct atom. The electrons have a large space to move throughout the whole lattice and are usually mentioned as delocalized electrons. The non-valence electrons and atomic nuclei have a

net positive charge, equivalent to the overall valence electron which shields them from escaping the metal lattice

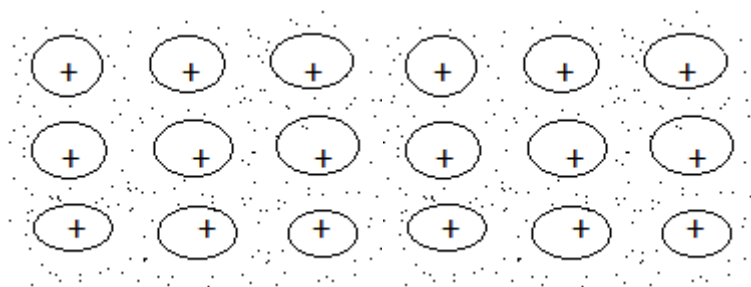


Figure 8: Figure illustrating the metallic bond

At large separations say, a few micrometers, the materials are attracted by van der Waals forces or London forces and inter atomic forces. They increase continuously with the proximity of asperities until it attains equilibrium. As the interfaces come close (few nanometers apart), a metallic bond is developed, and repulsive forces form across the atoms providing final equilibrium. Self-Adhesion is also dependent on structure. Say, hexagonal metals like cobalt create a poorly adhering group.

Table 1: *Experimental values of Adhesive forces of various metals against (011) iron. Applied normal force=200 μN , a diameter of contacting flat=3 mm, temperature=20°C, ambient pressure=10⁻⁸ Pa, contact duration=10 s [14].*

Metals	Cohesive energy (kJ/g atom)	Free surface energy (mJ/m ²)	Atomic size (nm)	Solubility in iron (at %)	Adhesive force to iron (μN^*)
<i>Clean</i>					
Iron	405	1800	0.286	100	>4000
Cobalt	426	1800	0.250	35	1200
Gold	366	1200	0.288	<1.5	500
Copper	338	1300	0.255	<0.25	1300
Aluminum	323	1000	0.280	22	2500
Lead	197	500	0.349	Insoluble	1400
<i>With H₂S Adsorption</i>					
Iron	–	–	–	–	100

*10 μN = 1 dyne

Cohesion is stronger than adhesion. Similar metal pairs that are non-hexagonal, form a congruent pair and exhibit prominent adhesion [14]. Same planes in contact exhibit greater adhesion than dissimilar planes. The polycrystalline metals exhibit greater adhesive forces when compared to a single crystal of the same metal. In the case of different metals and if they are mutually insoluble, then they would generally have low adhesion [14, 30, 31, 46].

Adhesion of the clean iron surface chafed against itself would be the more than any other metal chafed against iron because of cohesion. Adsorption of H₂S on an iron surface dwindles the adhesive force substantially. Cohesion or bonding of similar type atoms gives stronger adhesion than with any other metal. Solubility of metals, cohesive energy and free surface energy are the three major factors that decide the strength of an adhesive bond. Predominantly, adhesion increases with an increase in solubility. Lead being insoluble, but being ductile results in high adhesion.

2.4 Hydrogen Bond

Hydrogen, the lightest element is an interesting element and can prevail as a proton (positively charged) or an electron (negatively charged). A positively charged proton is formed by the removal of the electron. A negatively charged ion is formed due to the imperfect shielding, of the electron. Due to this imperfect shielding there is a constant shift in dipole that doesn't have the capacity to acquire another electron and hence forms a weaker bonds of electrostatic attraction known as hydrogen bonds [5].

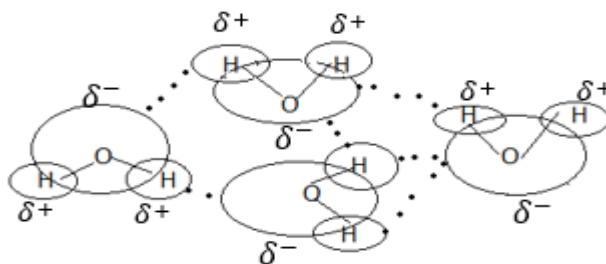


Figure 9: Schematic showing the hydrogen bonds in a water molecule.

2.5 Vander Waals Bond

Weaker bonds, which are caused due to inter-atomic attractions at large separations are Vander Waals bonds. In nonpolar molecules, they arise due to dipoles that waver in the typical atoms [25] and with dipole interactions in the case of polar molecules. Surface roughness increases with an increase in van der Waals force [39].

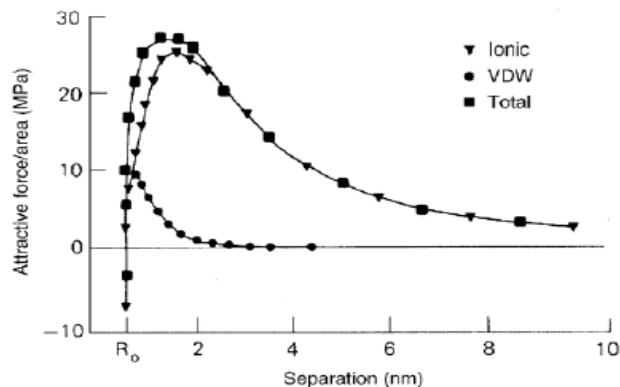


Figure 10: Contribution of Ionic and VDW forces to the total electrostatic force as a function of separation between two planes for mica sheets that are parallel [4].

Vander Waals forces are remarkable at a short range and in the zone of true contact, for separation between planes of 0.59 nm to 20 nm. Table 2 gives the bond energy ranges for various bonds.

Table 2: Bond energies of different bonds [44]

Type	Bond energy (kJ mol ⁻¹)
Primary bonds	
Ionic	600–1100
Covalent	60–700
Metallic, coordination	110–350
Donor–acceptor bonds	
Brønsted acid–base interactions (i.e., up to a primary ionic bond)	Up to 1000
Lewis acid–base interactions	Up to 80
Secondary bonds	
Hydrogen bonds (excluding fluorine)	1–25
Van der Waals bonds	
Permanent dipole–dipole interactions	4–20
Dipole-induced dipole interactions	Less than 2
Dispersion (London) forces	0.08–40

2.6 Polymer Adhesion

Polymeric Solids exhibit inherently low adhesion. Polymeric Solids mainly form van der Waals bonds [29, 14]. Still they can possess high adhesion due to the following reasons: these materials are easily deformed. Interdiffusion of polymeric chains across interface forms valence

bonds different from van der Waals bonds, [51]. For heterogeneous materials, sine insulators interaction of interfaces, may lead to turbo electricity [26, 48, 19, 52, and 21].

2.7 Free Surface Energy

The least amount of energy needed to create a new surface or energy that should be supplied to fissure a surface is the free surface energy. When elements having free surface energies γ_1 and γ_2 are interacting with each other, and the energy in their interface is γ_{12} . Bradley [12] and Bailey [3], showed that the work done by adhesion is defined as:

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

$\Delta\gamma$ Or work done by adhesion is the energy that has to be smeared to create a new surface. γ , free surface energy or surface tension depending on phase of the material. The use of lubricants or impurities reduces the surface energy of material.

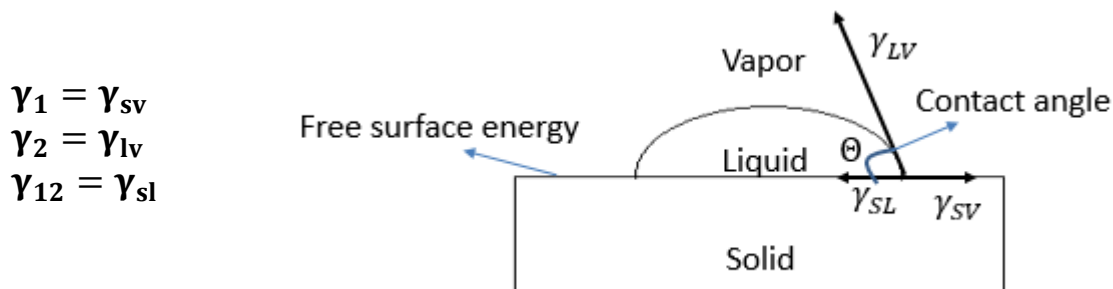


Figure 11: Figure illustrating the free surface energy of a surface for a liquid drop on solid

2.8 Contact Analyses

Contact is assumed to be a sphere or flat depending on the roughness of the interfaces. Consider a sphere (assumed to be elastic) as shown in Figure 12, interacting with a geometrically flat surface under no applied load condition. For any contact, the free surface

energy of interfaces decreases and converts into an attractive force that create a contact radius (a) so that the surface energy and the stored elastic energy are in equilibrium with each other,

Figure 12 [3]. The free surface energy

$$E_s = -\pi a^2 \Delta\gamma$$

The force F_s due to this energy change is $F_s = -dE_s/d\delta$

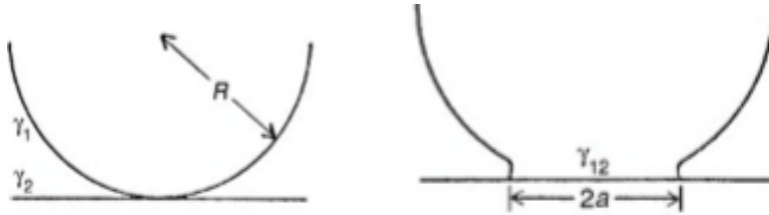


Figure 12: For no load condition, Contact between an elastic spheres on a flat surface is analyzed in hertz analyses, (a) absence of free surface energy, (b) presence of free surface energy [3].

The standard movement of the bodies, $\delta = a^2/R$.

The force and contact radius are as follows

$$F_s = \pi R \Delta r \text{ and contact radius } a = \left(\frac{3F_s R}{4E^*} \right)^{1/3}$$

R is the composite radius; a is the contact radius, and E^* is the composite modulus of elasticity.

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}, \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

Contact stresses do not follow the Hertz hypothesis, hence the theory is not suitable for all asperities. The stresses are tensile at the edge of the contact area and remain compressive in the center [28], Figure 13. The total adhesive energy is computed as a function of the contact radius (a) [28]. In JKR analysis, the assertion for a tensile force F_s used to create joint between two surfaces and the contact radius a, are $F_s = \frac{3}{2} \pi R \Delta\gamma$ and $a = \left(\frac{6\pi R \Delta\gamma^2}{E^*} \right)^{1/3}$. Accordingly at zero

load, the contact area should be finite across two interfaces, and they reduce with a reduction in the applied force to a negative value until surfaces separation starts to occur.

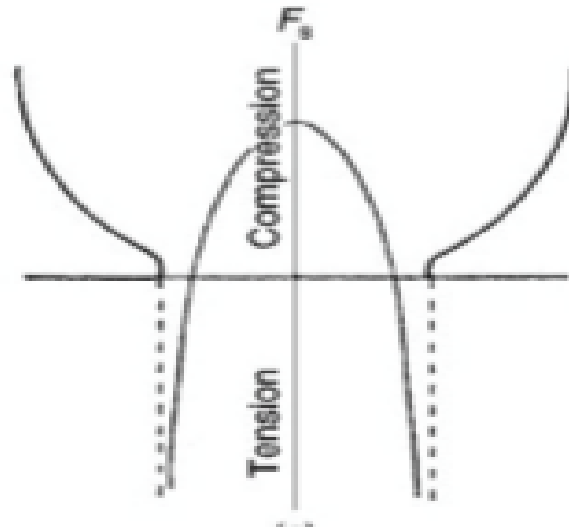


Figure 13: Pressure distribution of a sphere in contact with a level surface [2].

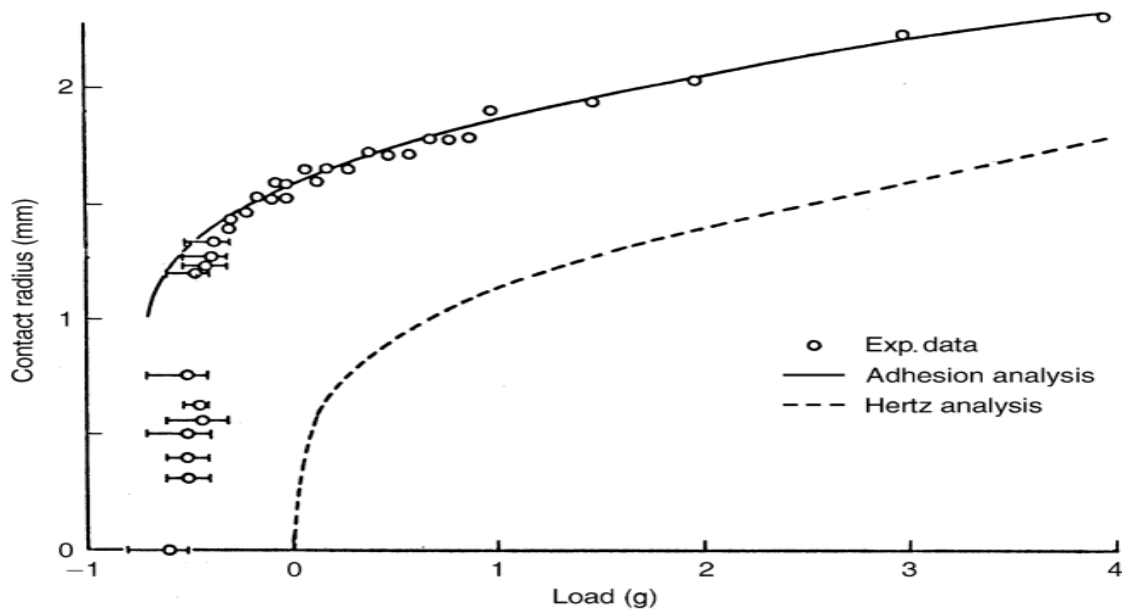


Figure 14: The Contact radius of a rubber sphere (22 mm radius) in contact with a rubber flat as the load (4grams) is reduced gradually [28].

The effect of a contact radius with reducing the load from 4g to negative is shown in Figure 13. The negative load depicts the load that we require to break the joint. The contact

radius remains determinate or fixed until at a load, $-0.74g$ is utilized then it instantly drops to zero as the interfaces are separated. Hertz analysis is nowhere near the anticipated behavior, Figure 14.

DMT analyses by Derjaguin, Muller, and Toporov [20] developed another analysis for a sphere with high Young's modulus in contact with a flat rigid surface. The contact region is only under compression if we have high elastic modulus. For trivial elastic impair of the sphere on a flat surface, $F_s = 2\pi R\Delta\gamma$. This equation is also derived by Muller [42]. The asperities of surfaces was presumed to be determined by a Leonard-Jones potential [42, 43] by Muller according to which attractive force is regulated by the distance between the two surfaces and energy of adhesion ($\Delta\gamma$). A non-dimensional parameter [49]: $\theta = \left[\frac{R(\Delta\gamma)^2}{E^*z_0^3} \right]^{1/3}$ is defined by Tabor.

Consider an elastic sphere chafed against a rough surface. When rigid solids are in contact, elastic energy is stored at surfaces which buckle to generate contact between asperities. When the elastic energy is appreciable in comparison to the free surface energy (" $\Delta\gamma$ "), the surfaces cannot come into contact, and the adhesion is also small or if surface energy is greater than the elastic energy the asperities deform and the real area of contact increases increasing adhesion.

Fuller and Tabor [22] using Greenwood and Williamson's approach modeled a parameter, known as the adhesion parameter α , to explain the adhesive behavior of the surfaces

$$\alpha = \left(\frac{4\sigma_p}{3} \right) \left[\frac{E^*}{\pi R_p^2 \Delta\gamma} \right]^{2/3}$$

Where σ_p is the composite standard deviation of summit heights, and R_p is the composite mean

radii of the summits.

Numerator in the above equation represents the elastic force necessary to press spheres. The denominator of Equation measures the adhesive force experienced by the field. The relative pull-off (adhesive) force is not dependent on the smeared force on the body and is only related to adhesion parameter, Figure 15 [22]. If the adhesion parameter (α) is low, (say < 1.5) the adhesion is high in that range since the adhesive factor dominates the elastic forces, and the adhesion parameter is large if the elastic force is greater than the adhesive force.

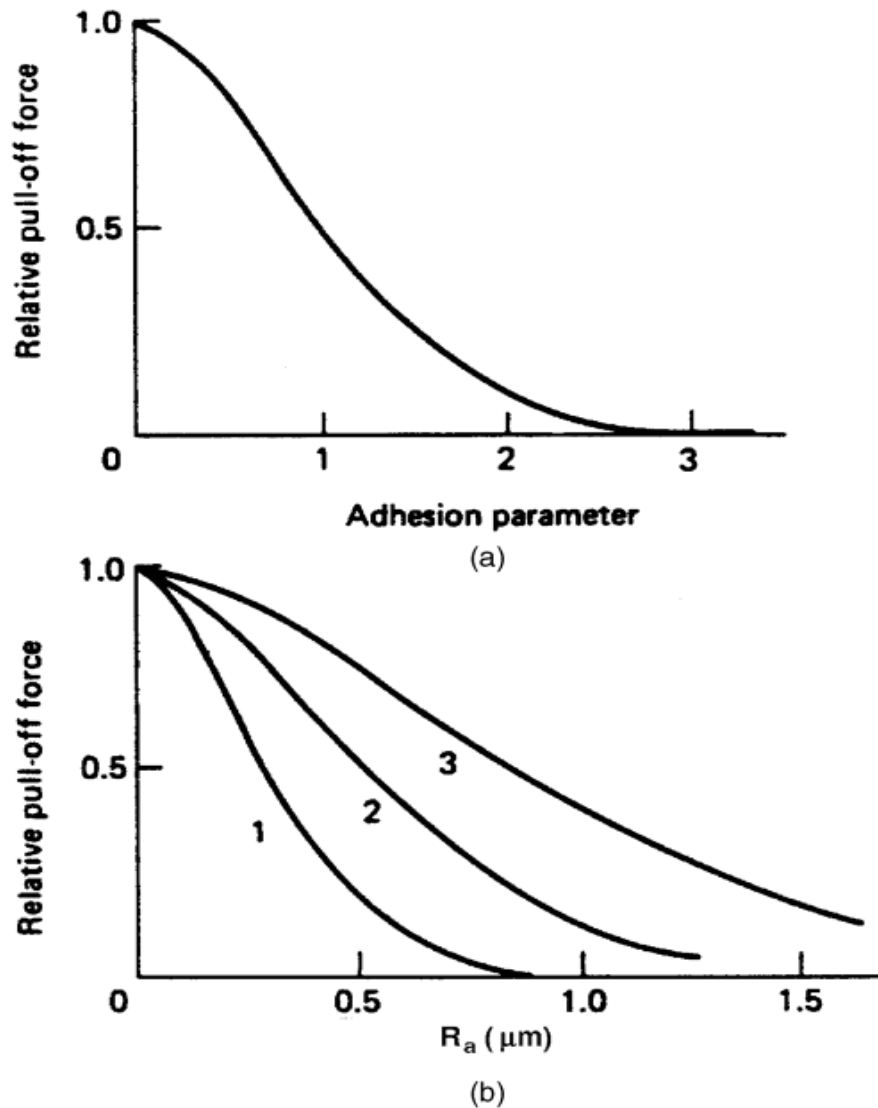


Figure 15: (a) The effect of Adhesive or the relative pull-off force with the adhesion parameter(α), (b) Adhesive or the relative pull-off force for rubber spheres of different moduli in contact with a flat surface for surfaces having various roughness; curve 1, 2.4 MPa; curve 2, 0.68 MPa; curve 3, 0.22 MPa [22].

Adhesive forces calibrated between smooth rubber spheres of different Young's moduli and a smooth interface of different roughness are shown in Figure 15 b. An increase in the modulus also decreases the adhesion.

2.9 Engineering Parameters:

Cohesive forces are generally stronger than the adhesive forces for non-hexagonal structures like Iron and is lower for similar metal pairs of hexagonal structures like cobalt. Metals with high solubility has higher adhesive force. As Temperature increases materials become soft and becomes more ductile, real area of contact and duration of contact increases adhesion whereas elastic recovery reduces adhesion. Increase load and cleanliness to increase adhesion.

In order to calculate the adhesive forces using JKR or DMT analyses we need to know the Composite Radius R

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \text{ And Composite Modulus } \frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}, \nu \text{ is the poisons ratio}$$

Composite radius can be relaxed as the depth of the material and can be measured using a Vernier calipers or the screw gauge. Modulus of elasticity can be measured using a strain gauge.

Adhesive forces increases with increase in surface energy and also composite radius. Contact radius increases with increase in surface energy, radius of sphere or decrease in the composite modulus of elasticity

Adhesion parameter is more accurate and can be calculated if we know the standard deviation of summit heights which is measured using Profilometer or perthometer, Surface energy, Composite modulus and composite radius. Adhesion parameter is inversely related to adhesive force

Adhesive forces decreases with increasing peak heights hence machining, coating or finishing reduces the peak height .Adhesive forces decrease with increasing composite modulus because of elastic recovery. Adhesion force increases with increasing surface energy and Radius

of peaks. Radius of peaks increases and standard deviation of Summit height decreases with reduction in the roughness.

CHAPTER 3

LIQUID MEDIATED CONTACTS

Meniscus develops near asperities that are touching a liquid due to surface energy. The existence of the fluid films can appreciably elevate the adhesion [16] because of an increase in the contact area (real) when liquid is present. Thus, adhesive forces (F_{ad}) is the sum of: the meniscus force, (F_m) arising due to surface effects of the liquid like surface tension and Viscous force (F_v) due to the viscosity of a liquid.

$$F_{ad} = F_m + F_v$$

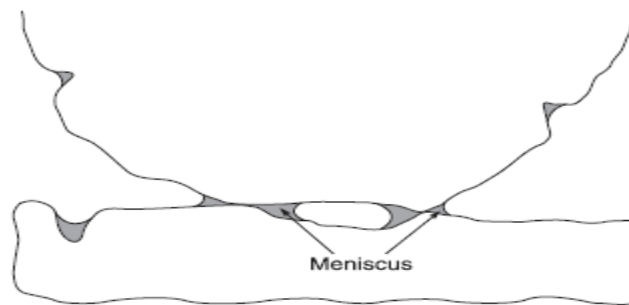


Figure 16: The figure illustrating formation of Meniscus for a liquid between two solids [3]

The meniscus curvature decreases with separation distance, Figure 17.a. since there is a decline in the meniscus area [15]. Viscous force on the other hand increases with the separation distance, Figure 17.b. [15].

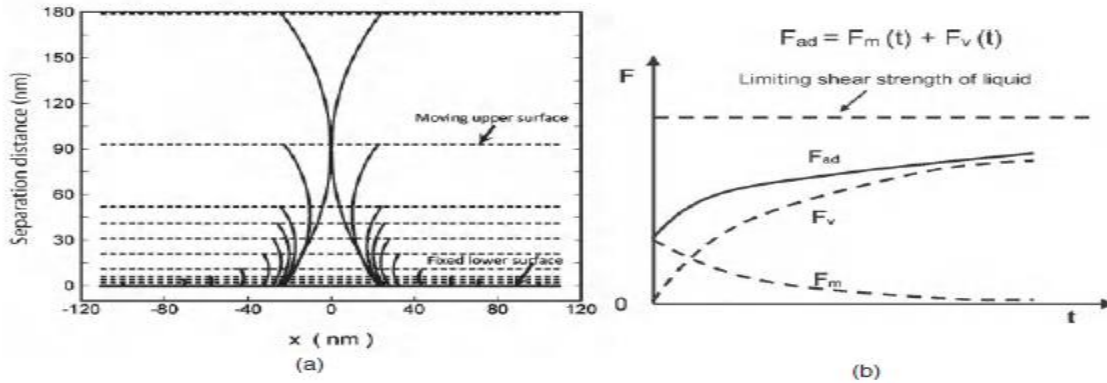


Figure 17: (a) Shape of Meniscus curvature with varying separation distance in nm when segregating surfaces parallel in the nominal direction for a hydrophilic surface, and (b) The total adhesive force due to the meniscus around the asperities [15].

Limiting shear strength is a maximum above which the shear stress viscosity of a liquid drop and liquid becomes plastic [3]. This property of a liquid like viscosity would decide the magnitude of viscous force. Cai and Bhushan, carried out a separation analysis of both hydrophilic and hydrophobic surfaces for both the symmetric (60°) and asymmetric contact angles (0 and 60°) in the normal direction [15], Figure 17. Meniscus forces increases if we use decrease the contact angle of the liquid which is a property of the liquid and also the material.

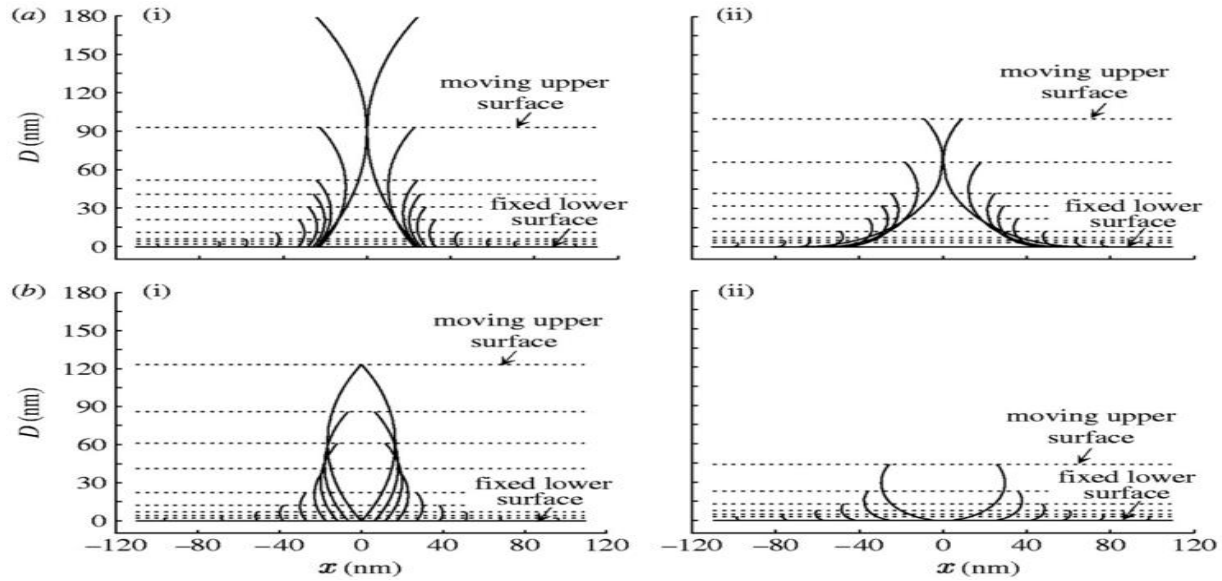


Figure 18: Meniscus curvatures as a function of separation distance between two parallel surfaces with initial meniscus contact angles (a (I)) $\theta_1=\theta_2=60^\circ$ and (ii) $\theta_1=0^\circ$, $\theta_2=60^\circ$ and (b (I)) $\theta_1=\theta_2=120^\circ$ and (ii) $\theta_1=180^\circ$, $\theta_2=120^\circ$ in the nominal direction [15].

3.1 Kelvins Equations

For a liquid in equilibrium with its vapor, the meniscus curvature ($1/r_1 + 1/r_2$) is directly proportional to relative vapor pressure (p/p_s) given by Kelvin equation [1]

$$r_k = \left(\frac{1}{r_1} + \frac{1}{r_2} \right)^{-\frac{1}{2}} = \gamma V / RT \ln \left(\frac{p}{p_s} \right),$$

Where r_k is the Kelvin radius, $1/r_1$ and $1/r_2$ are the meniscus curvatures, V is the molar volume of the liquid, R is the universal gas constant, T is the temperature, and p/p_s is the relative vapor pressure or relative humidity (RH) of water in fraction

3.2 Laplace-Young Equations

Young and Laplace stated that pressure difference over any meniscus area arises due to Surface tension (γ). The Laplace pressure in the liquid is given by the Laplace–Young equation provided the system is at Mechanical equilibrium [1].

$$\Delta p = p_l = \gamma/r_k$$

The Laplace force F_l calculated by integrating the Laplace pressure over the area of the meniscus

$$F_l = \int \int_{\Omega} \Delta p d\Omega$$

γ , the surface tension (Liquid), ΔP is the Laplace pressure and can be negative or positive based on surface nature. If a liquid is hydrophilic in nature with the surface, then, $\theta < 90^\circ$, (here θ represents the contact angle between liquid and a solid) as shown in figure 19. The hydrophilic surfaces form a concave meniscus with Kelvin radius, $r_k < 0$. The Laplace pressure inside of liquid bridges is less than that outside the liquid, developing attractive forces [1]. If a liquid is hydrophobic in nature with the surface, then, $90^\circ < \theta \leq 180^\circ$, the interfaces form convex meniscus. The hydrophobic surfaces form a meniscus radius, $r_k < 0$. The Laplace pressure near the liquid bridges is greater than exterior of the fluid, developing a repulsive force [1].

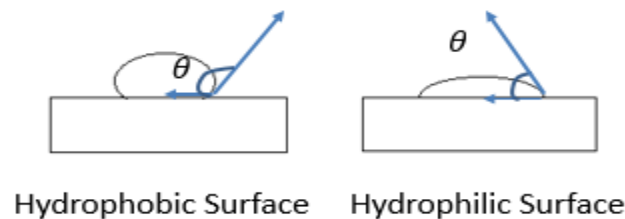


Figure 19: Water spreading over a) hydrophobic surface and b) hydrophilic surface

3.3 Meniscus Forces

The Adhesive force is calculated with Laplace force (F_l), the surface tension (γ) and the projected area of contact at the interface. Cai and Bhushan estimated the meniscus forces for both sphere in contact with a flat and flat in contact with a flat. They modified the equations modified by Mathewson [25, 15] considering the following cases. A thin fluid layer present between an elastic sphere and a hard surface as shown in Figure 20 a. A thick fluid layer with a

separation D in between sphere and hard surface as illustrated in Figure 20 b. At a separation D with a continuous film and meniscus formed on the sides of the spheres as shown in Figure 20 c.

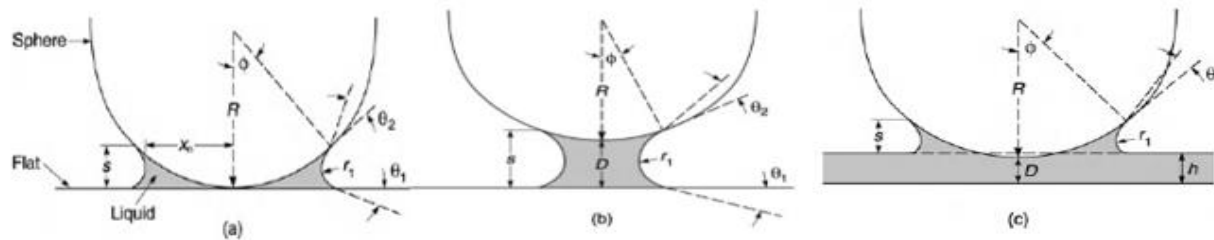


Figure 20: Meniscus formation of liquid between a sphere and a hard flat surface (a) Thin liquid film, (b) Thick liquid film, and (c) Continuous liquid film [3].

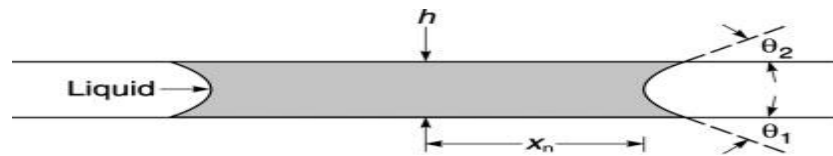


Figure 21: Meniscus formation of liquid between two parallel surfaces [3]

3.3.1 Flat on Flat:

$$F_m = \frac{\pi x_n^2 \gamma (\cos\theta_1 + \cos\theta_2)}{h} + 2\pi \gamma x_n \sin\theta_{1,2}$$

where x_n is the radius of the solid-liquid exterior's interface, Meniscus heights $s = \gamma(\cos\theta_1 + \cos\theta_2)$, ϕ is the filling angle, D is the separation, h is the film thickness.

3.3.2 Sphere in contact with Flat:

$$F_m = \pi x_n^2 R \gamma (\cos\theta_1 + \cos\theta_2) + 2\pi R \gamma \sin\phi \sin(\phi + \theta_2)$$

$$\sim 2\pi R \gamma (\cos\theta_1 + \cos\theta_2) \quad (\text{Thin liquid Film})$$

$$\sim \frac{2\pi R \gamma (\cos\theta_1 + \cos\theta_2)}{1 + \frac{D}{s-D}} \quad (\text{Thick liquid Film})$$

$$\sim 2\pi R \gamma (1 + \cos\theta) \quad (\text{Continuous liquid film})$$

Parameters required for estimating and affecting Meniscus forces

For a sphere in contact with a flat :

We require the following to calculate the Meniscus forces: Radius of sphere which can be relaxed as the depth of the material , Surface tension of liquid, Separation between sphere and flat could be measured by inducing liquid of known thickness, Meniscus curvature or meniscus radius and contact angles that liquid makes with sphere and flat.

For a flat on flat :

Projected meniscus area can be measured using a computer generated maps where we need the roughness of the material and thickness of the liquid, surface tension of the liquid, liquid film thickness and contact angles that liquid makes in contacting and near contacting asperities.

3.3.4 Viscous Forces

The viscous force (rate dependent force) for a liquid that has a motion is given by the following equation [36]

$$F_v = \frac{\beta\eta l}{t_s}$$

Where η is the dynamic viscosity, β is a proportionality constant, and t_s is the rate of separation of two surfaces. The Normal separation of two material occur if they are separated perpendicular to their direction of contact. Tangential or divergent separation occurs if two surfaces are slided parallel to the direction of their contact. Many scientists [35,5,7] bestowed that viscous force is a factor depending on impulse. Recent study submitted by Cai and Bhushan, based on Reynolds' lubrication theory, viscous forces are accurately estimated.

3.3.5 Flat on Flat surface:

Normal separation: $F_v \sim \frac{3\pi\eta x_{n0}^4}{4t_s h_0^2 (\text{for } h_s \sim \infty)}$

Tangential separation: $F_v = \frac{8\eta x_n'^3}{3t_s h_0}$

3.3.6 Sphere on Flat surface:

Normal separation: $F_v \sim 6\pi\eta R^2/t_s \ln\left[\frac{(4RD_0+x_{n0}^2)^2}{8RD_0(x_{n0}^2+2RD_0)}\right]$ (for $D_s \sim \infty$)

Tangential separation: $F_v = \frac{8\eta[2R(s-D_0)]^{3/2}}{3t_{ss}}$. Where x_n is the radius of the solid-liquid exterior,

η is the kinematic viscosity, t_s is the rate of separation of two surfaces, h_0 is the initial depth, h_s is separation at the break point and $h_s = \infty$ where the separation starts, D_0 is the initial meniscus gap, $D_s \sim \infty$ is distance where separation occurs.

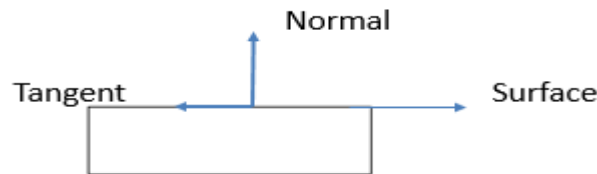


Figure 22: Schematic of Tangential and Normal separation of surfaces

Flat on Flat:

In order to calculate the viscous forces we need the dynamic viscosity of the liquid introduced, Meniscus area that can be measured by computer maps if we introduce liquid of known thickness and properties, and Separation time or time required to separate the two surfaces and film thickness.

Sphere on Flat:

In order to calculate the Viscous forces we need the dynamic viscosity of the liquid, Radius of sphere that can be relaxed as the depth of the sphere, Projected Meniscus area that can be estimated using computer plots, Meniscus height can be measured by introducing liquid of known properties and measuring the surface roughnesses, Separation time and film thickness.

3.4 Effect of Water vapour

Water vapor has a prominent effect on the adhesive force. Its effect on adhesive force is shown for a Nickel-Zinc ferrite against itself in Figure 22. The adhesive force increased slowly below 65% RH, and it elevates considerably with the rise in relative humidity above it. Adhesive force was reversible on dehumidifying.

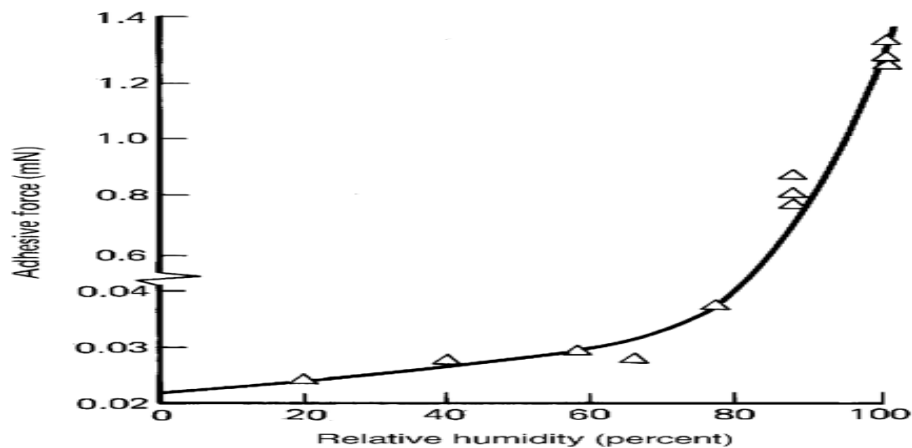


Figure 23: The effect of Relative humidity on adhesion of a hemispherical pin of 2 mm radius of Nickel-Zinc ferrite against a flat Nickel-Zinc ferrite in the nitrogen atmosphere [40].

3.4.1 Kinetic Meniscus Analyses

When two surfaces are in contact and a liquid is interposed between them, then the interfaces is never in an equilibrium because of the surface tension of the fluid. Fluid flow increases the area of meniscus because of an increase in the Laplace pressure continuously and this process breaks when the bodies attain equilibrium [17]. Adhesive force is proportional to the span of contact [9].

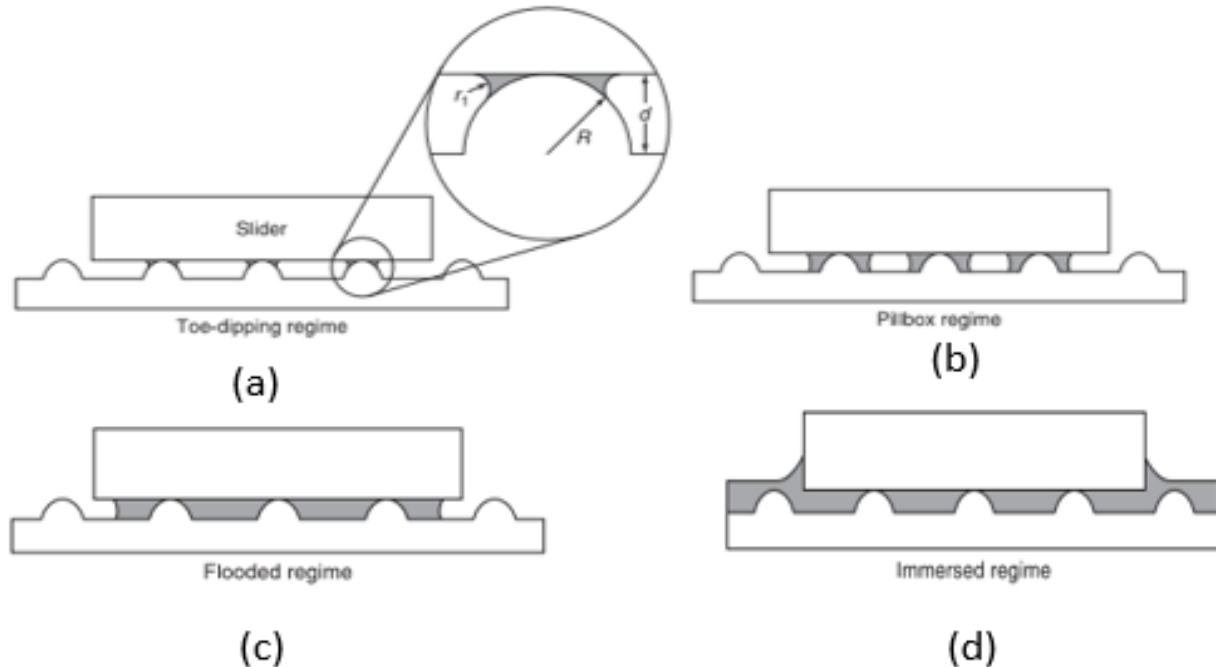


Figure 24: Regimes based on liquid levels at the interfaces [2]

Figure 23 shows a Kinetic Meniscus model of the flat and rough surface contact region with various levels of liquid. Four different types of regimes based on Kevin's radius and interplanar separation are explained considering an asperity touching a flat [10, 34, and 5]. The first (Toe-dipping regime) the liquid is in feeble quantity, and is just sufficient to occupy a small area around the sphere and in the second (pillbox regime), the liquid occupies the area around a few spheres. In the flooded regime liquid is sufficient to occupy a greater number of spheres. The adhesive forces increases drastically from a pill box to the flooded regime since the former is unstable and reaches stability by absorbing water. For the immersed regime or the fourth regime the whole entire region is submerged in liquid and has a meniscus to the sides of the interfaces.

Based on inter planar distance for a thin liquid film so that the Kevin's radius is greater than the inter planar separation (d), $r_1 < d/2$, the interfaces are said to be in the first or toe-dipping regime. Contrary to the above situation if we have a adequately dense film such that

the Kelvin radius is significant than half the interplanar separation d and the capillary radius $r_l > d/2$ around the asperities forming the pill box regime or second regime. The pillbox regime is thermodynamically volatile and any change in liquid quantities will aggravate the adhesion. The pillboxes because of surface tension effects have a very high laplace pressure and will pull fluid around the spheres upto a point where the interface becomes flooded or even immersed. This unstability continues until an apt and symmetrical meniscus radius forms along the sides of the body.

3.5 Statistical Analysis of Contacts

A non-gaussian asperity in correspondence with a smooth interface, interposed a fluid in between them is shown in Figure 25 a. In general, given the mean peak radius (R_p), the thickness of liquid film (h), the contact angle (θ), the total meniscus force (F_m), the surface tension of the liquid (γ_l), the height distribution function of peaks $p(z)$. Meniscus force is defined by Gao, Tian and Bhushan as the integration of all the meniscus forces at every interface (contacting or non contacting), Figure 25 b [23]:

$$F_m = \int_{d-h}^{\infty} (F_m)_i NP(z) dz = 2\pi R_p \gamma_l (1 + \cos\theta) N \int_{d-h}^{\infty} P(z) dz$$

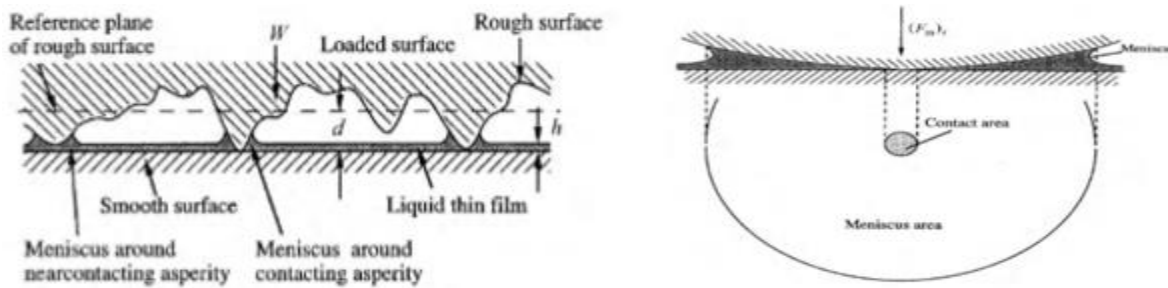


Figure 25: (a) Illustration of a non-Gaussian asperity in touch with a hard interface interposed with a liquid film, and (b) Contact and Meniscus areas of the non-Gaussian surface [2].

The meniscus force is analogous to the film thickness (h). The relative meniscus force is

inversely proportional to the standard deviation of peak heights (σ_p) for a constant radius of peaks, the number of peaks, load. It also increases with an increase in radii of peaks (R_p) and number of peaks (N) for a constant peak heights, Figure 26

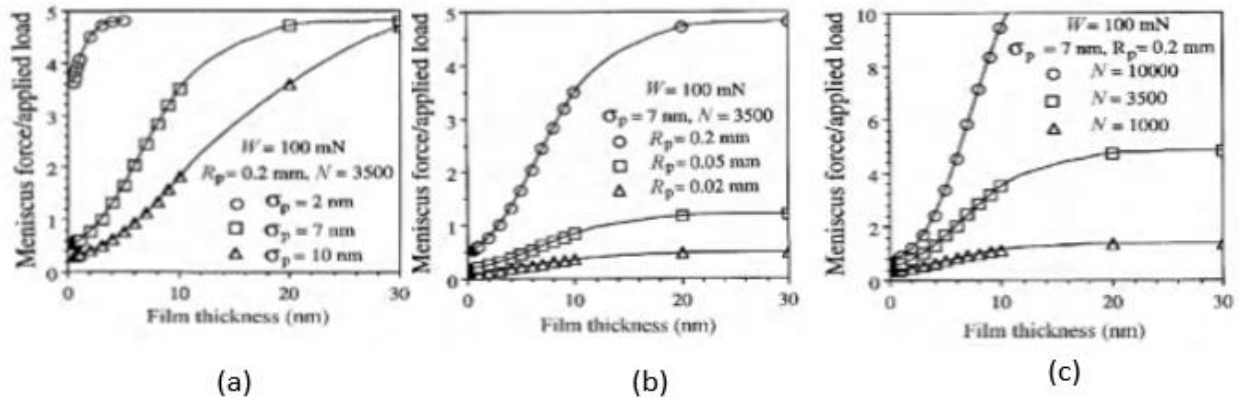


Figure 26: Relative Meniscus force as a function of film thickness (nm) at different σ_p , R_p , and N for a Gaussian surface [23].

Meniscus force is a function of Radius of Peaks which can be measured by a tunneling microscope, Surface tension of the liquid, Contact angle and peak distribution of summit heights which is measured by a profilometer

$$F_m = 2\pi R_p \gamma (1 + \cos\theta) N \int_{d-h}^{\infty} p(z) dz$$

3.6 Numerical Three-dimensional contact models

To analyze two rough interfaces or non gaussian surface a numerical model is developed to calculate the meniscus forces at multiple interfacial contacts with a prevailing liquid. The meniscus force F_m is

$$F_m = \int \int_{\Omega} P_1(x, y) d\Omega = \gamma \int \int_{\Omega} \frac{1}{r_1} d\Omega \quad [50]$$

Where γ is the surface tension of the liquid, r_1 is the meniscus radius and Ω is the projected area of meniscus. For multiple menisci it is the sum of the areas of individual meniscus. Meniscus radius and Projected areas are a function of the shape and the size of the meniscus [50].

Bhushan [50, 45] explained an experimental procedure in calculating meniscus forces for rough surfaces and liquid interposed between them. The contact of the dry, rough surfaces was first analyzed without any liquid in their interfaces. Now a liquid of known properties and thickness was interposed between the interfaces. The meniscus area was obtained using a computer generated model and we must choose those areas where both solids are in contact and liquid forms meniscus around the asperities. Figure 26 shows the computer-generated surfaces.

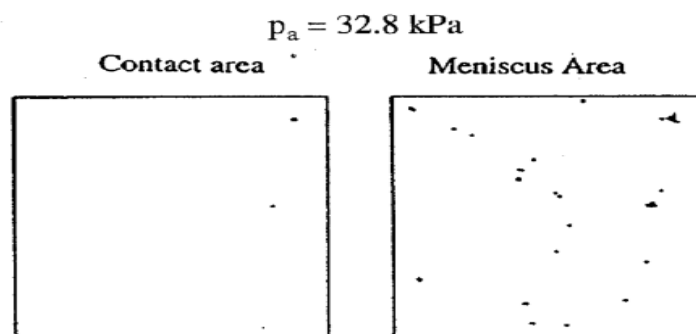


Figure 27: Schematic of computer generated Non-Gaussian surface in contact with a smooth surface with a composite elastic modulus of 100 GPa and a nominal pressure(P_a) of 32.8kPa, in the presence of water film thickness of 1 nm and meniscus height of 1nm [45].

The dry contact area is very much smaller than the area in contact or near contact with the asperities, as shown in figure 26. The Relative humidity response on adhesive strength over the projected area on a glass ceramic disk of elastic modulus 100Gpa, nominal pressure 32.8 kPa in contact with a smooth surface is provided in Figure 27. The effect of relative meniscus force to that of the relative humidity and roughness are shown in figure 28. As roughness increases the relative meniscus force decreases. Critical film thickness is the point for a surface above which the meniscus force rises abruptly with an expansion in surface roughness [5].

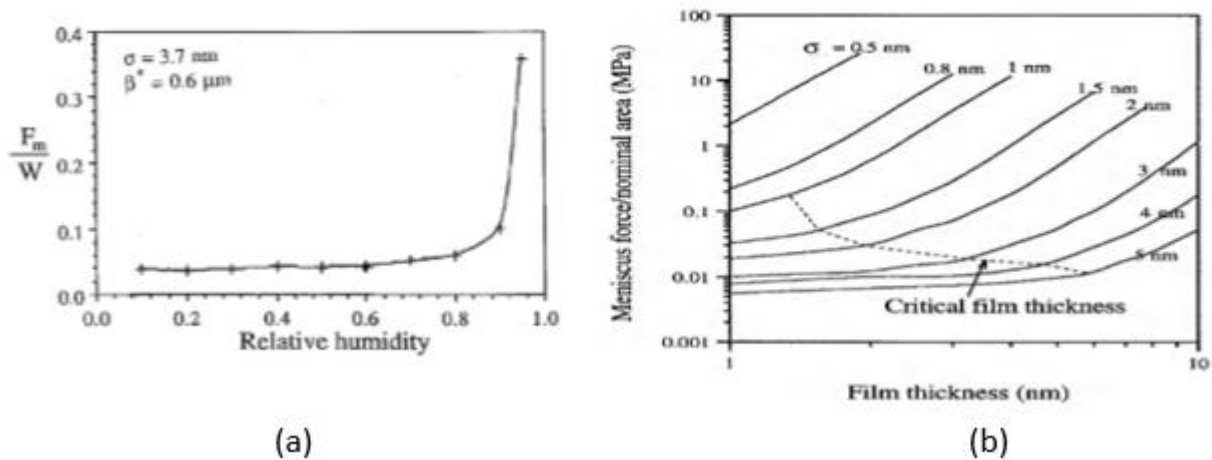


Figure 28: (a) Relative meniscus force as a function of Relative humidity b) The relative meniscus force for various roughness values in the presence of a liquid film [45].

Irregular or Non-Gaussian asperities display very little contact area(real). Three-dimensional contact analyses of surfaces are studied to predict the significance of skewness and kurtosis on a Fractional real area of contact and Relative meniscus forces[6,7,16]. Figure 30 a reveal the skewness effects on the fractional area of contact for different pressures at constant kurtosis and relative meniscus force at constant kurtosis and sensitivity. Figure also depicts the effect of kurtosis on fractional area and relative meniscus force for a constant skewness and sensitivity. A negative skewness exhibits high fractional areas and high adhesive strengths. Positive skewness around 0.19 for higher pressures and 0-0.18 for low pressures results on the contrary behaviour like small real area and relative meniscus force. Fractional Contact area and meniscus force are greater with a decrease in the kurtosis. Figure 30 b. Shows the meniscus force variations with the h/σ ratio for different skewness at constant kurtosis and kurtosis at constant skewness at a nominal pressure. The Sensitivity of h/σ to meniscus force shows the same pattern and decreases at a positive skewness(low or high pressure) and kurtosis values of about five or larger are optimum.

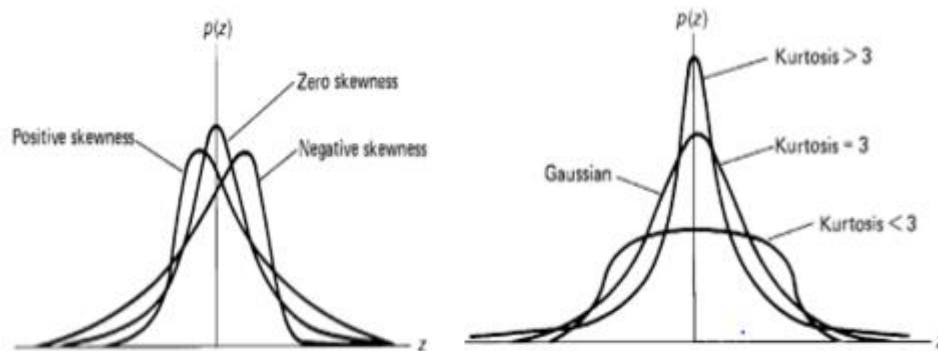
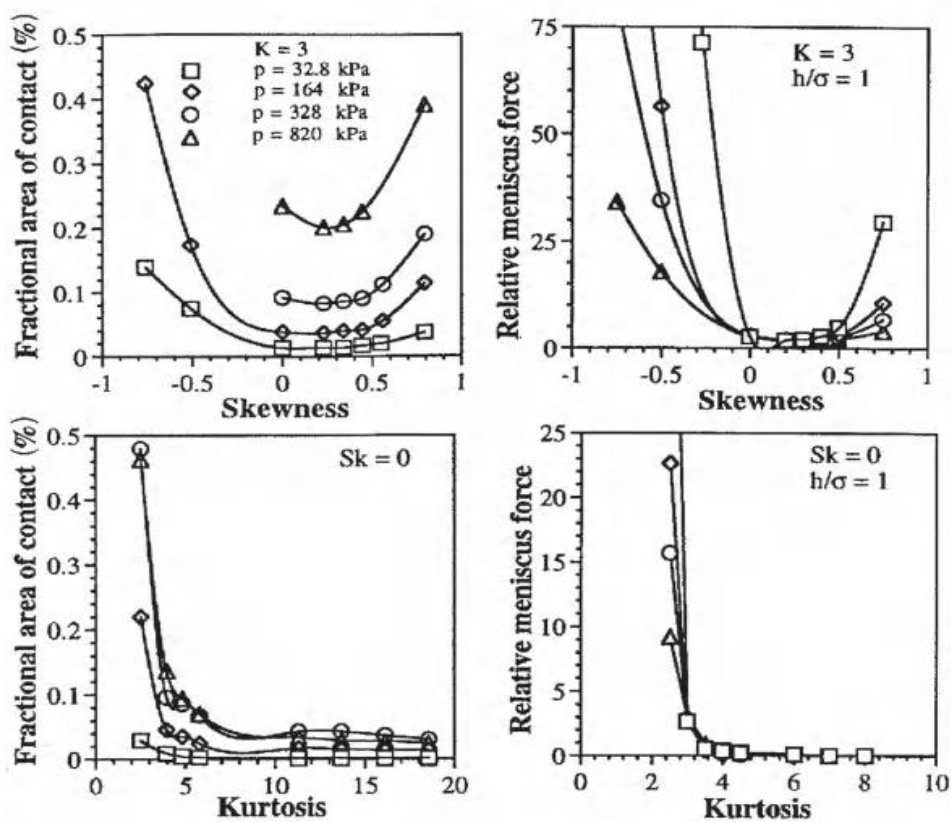


Figure 29: Probability distribution for heights with different Skewness and symmetrical distribution with various kurtosis [2].

$$\sigma = 1 \text{ nm}, \beta^* = 0.5 \mu\text{m}$$



(a)

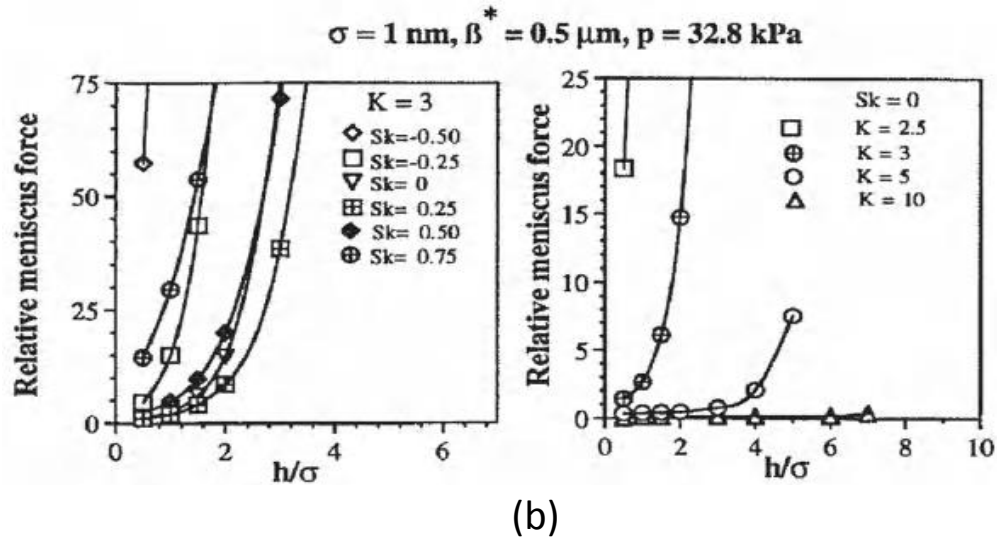


Figure 30: (a) Fractional real area of contact in percentages and relative meniscus force as a function of Skewness and kurtosis at various pressures and constant roughness, and (b) Corresponding meniscus force as a function of h/σ in the presence of liquid for different Skewness and kurtosis values [16].

3.7 Engineering Parameters

Viscous forces increase with viscosity of the liquid since dynamic viscosity increases with viscosity. Lower Contact angle results in higher adhesion and this can be achieved more easily if we use non polar liquids. Above certain Relative humidity the meniscus forces increases drastically but with increase in thickness the adhesive forces decreases. After immersed regime the meniscus forces will not increase with the increase in the relative humidity.

Meniscus forces increase with decrease in contact angles since the affinity to the surface increases thus increasing the surface tension of the liquid, increase in the Radius of sphere which is also relaxed as the depth of the material, increase in surface tension of the liquid, increase in the Meniscus height which is increased by increasing the quantity of the liquid and increase in projected meniscus area. Adhesive forces decreases with increase in liquid thickness.

Viscous forces increases with increase in the viscosity of the liquid since the

dynamic viscosity of the liquid increases, projected area of menisci by increasing the quantity of liquid, Radius of the sphere which is the depth of the material and meniscus height. Viscous forces decrease with increase in the liquid thickness and separation time.

Meniscus forces increases with decrease in the standard deviation of Peak heights or increase in the peak height distribution. This can be measured using profilometer and controlled by machining the surfaces. If we decrease roughness radius of peak increases which increases the Meniscus forces. Increase in number of peaks increases meniscus forces since more meniscus areas are obtained. Meniscus forces are dependent on Radius of peaks, standard deviation of mean summit heights which can be measured using a profilometer, and Number of peaks.

Increasing the roughness decreases the meniscus forces. Increase in the fluid thickness or relative humidity increases the meniscus forces considerably but if meniscus height is greater than interplanar distance the adhesive forces decreases. Non Gaussian contacts have least effect on the amount of the liquid.

CHAPTER 4

CONCLUSION

Adhesion is strictly a surface phenomenon that arises due to atomic forces and many scientists argue that it is electrostatic in nature. Sharing of electrons gives covalent bonds that provide surface forces. Transfer of electrons gives ionic surfaces provide high adhesive forces. Sliding or rotating on surfaces will give an electrostatic layer that increases adhesion when surfaces are in contact and dissipate when surfaces lose contacts. When metals are in contact, due to their valence electrons, Metallic bonds are formed. Hydrogen has the ability to be a positive or negative ion and hence it is very likely to form hydrogen bonds in the presence of Hydrogen. Bonds are formed between all solids when they are at any separations referred as Vander Waal forces.

Adhesion is calculated concerning free surface energy for both solid and liquid mediated contacts. Lower the free surface energy the adhesion will also be little. Surface cleanliness is an important factor for adhesive strength. The cleaner the surface stronger the bonds its form. The real area of contact and surface roughness are important factors on which the adhesion depends on. Temperature, Surface Properties and Mechanical properties all influence the adhesion of Surfaces.

The Liquid in between surfaces will increase adhesion. Forces in the presence of liquid include both Meniscus and viscous forces. As humidity increases meniscus force increases considerably. Meniscus force depends on the surface tension of the liquid. Viscous forces depend on the velocity of separation and direction of segregation. As Surface roughness increases the meniscus force decreases and Non-Gaussian distribution of peak heights will also

exhibit poor adhesion. Estimation of adhesive forces helps in predicting the surface energy, Radius of peak, Standard deviation of peak heights, and Number of peaks.

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Major Professor: Dr.Peter Filip