Particle Adhesion and Removal
Adhesion and Adhesives: Fundamental and Applied Aspects

The topics to be covered include, but not limited to, basic and theoretical aspects of adhesion; modeling of adhesion phenomena; mechanisms of adhesion; surface and interfacial analysis and characterization; unraveling of events at interfaces; characterization of interphases; adhesion of thin films and coatings; adhesion aspects in reinforced composites; formation, characterization and durability of adhesive joints; surface preparation methods; polymer surface modification; biological adhesion; particle adhesion; adhesion of metallized plastics; adhesion of diamond-like films; adhesion promoters; contact angle, wettability and adhesion; superhydrophobicity and superhydrophilicity. With regards to adhesives, the Series will include, but not limited to, green adhesives; novel and high-performance adhesives; and medical adhesive applications.

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Particle Adhesion and Removal

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Preface

The importance of particle adhesion and removal is quite manifest in many areas of human endeavor (ranging from microelectronics to optics, and space to biomedical). A complete catalog of modern precision and sophisticated technologies where removal of particles from surfaces is of cardinal importance will be prohibitively long, but the following eclectic examples should suffice to underscore the concern about particles on a variety of surfaces where particulate contamination is a bête noire. In the semiconductor world of ever-shrinking dimensions, particles which, just a few years ago, were cosmetically undesirable but functionally innocuous, are now “killer” defects. As device sizes get smaller, there will be more and more concern about smaller and smaller particles. In the information storage technology, the gap between the head and the disk is very narrow, and if a particle is trapped in the gap this can have very grave consequences. The implications of particulate contamination on sensitive optical surfaces are all too manifest. So the particulate contamination on surfaces is an anathema from functional, yield, and reliability points of view. With the burgeoning interest in nanotechnologies, the need to remove nano and sub-nano particles will be more and more intense. Apropos, it should be mentioned that in some situations, particle adhesion is a desideratum. For example, in photocopying the toner particles must adhere well to obtain photocopies, but these should not adhere to wrong places otherwise the result will be a dirty photocopy. Here also one can see the importance of particle removal.

One of us (KLM) has edited a series of books called “Particles on Surfaces: Detection, Adhesion and Removal” but the last volume (Volume 9) was published in 2006. Since 2006 there has been an enormous level of research activity, particularly in removing nanosize particles, and thus it was obvious that recent developments needed consolidation and this provided the vindication for the present book. This book was conceived with the core purpose of providing a comprehensive and easily accessible
reference source covering important aspects/ramifications of particle adhesion and removal, with emphasis on recent developments in understanding nanoparticle adhesion mechanism(s) and their removal. All signals indicate that R&D activity in the arena of removal of nanometer size particles will continue unabated.

Now coming to this book (containing 14 chapters), it is divided into two parts: Part 1: Particle Adhesion: Fundamentals, and Part 2: Particle Removal Techniques. The topics covered include: Fundamental forces in particle adhesion; mechanics of particle adhesion and removal; microscopic particle adhesion models and surface modified particles; characterization of single particle adhesion; high intensity ultrasonic removal of particles; megasonic cleaning for particle removal; high speed air jet removal of particles; droplet spray technique for particle removal; laser-induced high-pressure micro-spray technique for particle removal; wiper-based cleaning of particles; application of strippable coatings for removal of particulate contaminants; cryogenic cleaning of particles; supercritical carbon dioxide cleaning: relevance to particle removal; and use of surfactants to enhance particle removal.

This book represents the cumulative contribution of many internationally renowned subject matter experts in the domain of particle adhesion and removal. The book reflects the state-of-the-art with special attention to recent and novel developments.

The book containing bountiful information on the fundamental and applied aspects of particle adhesion and removal provides a unified and comprehensive source. It should serve as a portal for the neophyte and a commentary on the recent developments for the veteran. The book should be of interest to researchers in academia and R&D, manufacturing, and quality control personnel in microelectronics, aerospace, automotive, optics, solar panels, pharmaceutical, biomedical, equipment cleaning and wafer reclaiming industries. Essentially, anyone involved in or concerned with removal of particles should find this book of immense value. Also, we hope that this book will serve as a fountainhead for new ideas pertaining to particle removal.

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Part 1

PARTICLE ADHESION: FUNDAMENTALS
1

Fundamental Forces in Particle Adhesion

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Abstract
van der Waals, capillary, and electrostatic forces acting at the interface between a particle and a surface drive the adhesion behavior of the particles. If one can describe the nature and the strength of these forces as a function of the properties of the two interacting solids and the intervening medium, it is possible to predict and, in many cases, to control particle adhesion. This chapter focuses on the factors that influence the nature and strength of the forces, the fundamental theories that describe them, and the relevant mathematical expressions required to quantify them, with a caveat that the analysis presented is limited to systems with ideal geometry. Specifically, more advanced analysis, which may account for aspects such as roughness, non-uniform shape, deformation, and other complicating aspects, is not treated.

Keywords: Particle adhesion, van der Waals force, Hamaker constant, electrostatic force, double layer, capillary force, surface tension, surface energy.

1.1 Introduction

Particle adhesion influences many areas of science and engineering, including semiconductor fabrication, pharmaceuticals, cosmetics, mining, separations, petroleum production, surface coating, and food processing, to name a few. In the context of this chapter, adhesion is an interfacial...
phenomenon which appears when two solid bodies, one of which is of colloidal dimensions, approach each other closely. As the two surfaces approach, a complex interplay of van der Waals, electrostatic, and capillary forces drives the resulting behavior. Thorough knowledge of these surface forces is essential to understanding particle adhesion.

1.2 Various Forces in Particle Adhesion

In most applications of practical interest, the forces that control the adhesion between solid particles and solid surfaces are van der Waals (dipole) forces, electrostatic forces, and forces resulting from any liquid bridges due to capillaries or adsorbed molecular water between the two solids. Depending on the composition of the particle, the solid, and the ambient medium (air of varying relative humidity or aqueous solution are of interest here), the relative importance of these may change. This chapter provides an overview of these varying forces.

1.2.1 Capillary Forces

When a solid particle of characteristic dimension on the order of 100 micrometers or smaller is in contact with a solid surface in a gaseous medium (air), the relative humidity (RH) of the air is a critical factor in the relative importance of the forces that will influence the adhesion between the particle and surface [1, 2]. Specifically, water molecules in humid air will minimize their free energy by adsorbing on surfaces at low humidity and by condensing onto surfaces at higher humidity, if the surfaces of interest are sufficiently hydrophilic [3–8]. If condensed moisture forms liquid bridges between a particle and a surface, the capillary forces resulting from these liquid bridges will generally be the controlling forces in the particle adhesion [9]. The behavior of adsorbed water molecules has been studied using gravimetric methods, ellipsometry, nuclear magnetic resonance (NMR), atomic force microscopy (AFM) and the surface force apparatus (SFA), among others [3–8, 10–19].

1.2.1.1 Forces Across a Curved Liquid Interface

When a solid surface comes in contact with a liquid medium, the difference in the magnitude of the net cohesive forces between the liquid molecules \( (i.e., F_{l-l}) \), and the net adhesion force between the liquid and the solid molecules \( (i.e., F_{s-l}) \) initiates the formation of a liquid meniscus at the solid/liquid interface. The nature of the curvature of the liquid meniscus
(concave or convex) depends on which force, $F_{s-l}$ (concave) or $F_{l-l}$ (convex) is dominant. This leads to the phenomenon of wetting or de-wetting of the surface. Figure 1.1 shows an example of a liquid climbing on a solid plate. In this case, $F_{s-l} > F_{l-l}$. Solid surfaces which have $F_{s-l} > F_{l-l}$ are known as high energy surfaces. If the liquid is an aqueous solution, these are known as hydrophilic surfaces. If the liquid is non-aqueous, they are known as lyophilic surfaces. Such surfaces facilitate wetting. Mica, silicon dioxide, metals, and oxidized surfaces in general are typically hydrophilic. Solid surfaces in which $F_{s-l} < F_{l-l}$ are known as low energy surfaces. If the liquid is an aqueous solution, these are the hydrophobic surfaces. If the liquid is non-aqueous, they are the lyophobic surfaces. They facilitate de-wetting. Most organic surfaces, including most polymers, are hydrophobic. The surface energy of such materials can be increased by surface modifications (e.g., surface oxidation achieved via ultraviolet radiation, plasma discharge, laser irradiation, etc.) to enhance their hydrophilicity [20].

1.2.1.1.1 Surface Tension Force Acting at a Solid/Liquid Interface

The origin of surface tension is the unbalanced intermolecular force acting on the liquid molecules at the surface. The molecules present in the bulk of the liquid experience no net intermolecular force as they are surrounded by molecules of similar properties and hence are in a low energy state. However, the liquid molecules present at a liquid/solid or liquid/air interface are in an unbalanced or high energy state as they experience a net intermolecular force resulting from the difference in properties of the molecules in the different media. This leads to the development of the surface tension force. The surface tension ($\gamma$) is quantified as the net surface tension force acting on a unit length of the liquid/solid or liquid/air interface. Figure 1.2 is a schematic of a spherical particle in contact with a solid
surface through a liquid medium. The surface tension force, \( F_{st} \), acting on the solid/liquid boundary (the dotted line) can be obtained as

\[
F_{st} = \int \gamma dl = \gamma (\cos(\alpha)) l_{wetted}
\]  

(1.1)

where \( \alpha \) is the angle of inclination of the liquid meniscus from the vertical, and \( l_{wetted} \) is the perimeter of the meniscus boundary on the solid surface.

### 1.2.1.1.2 Capillary Pressure Force Acting Across a Curved Liquid Interface

The micro-/nano-contacts between two solid surfaces act as active sites for condensation in a humid environment if the RH is above a critical value. When condensed moisture comes in contact with the solid surfaces, a liquid meniscus is formed in the contact region bridging the two solid surfaces, as shown in Figure 1.3.

Menisci form through two methods on solid surfaces: the spontaneous condensation of a vapor in a confined space (otherwise known as capillary condensation) and, for non-volatile liquids, the combination of adsorbed layers (on the two adhering surfaces) merged into a meniscus. A meniscus induces a pressure difference across the liquid-vapor interface, as shown in Figure 1.4, where the pressure on the liquid side of the meniscus is lower than that in the surrounding vapor. This pressure difference is described by the Young-Laplace equation

\[
\Delta P = \gamma_l \left( \frac{1}{r_n} + \frac{1}{r_p} \right)
\]  

(1.2)

where \( \Delta P \) is the pressure difference across the meniscus (the Laplace pressure), \( \gamma_l \) is the surface tension of the liquid condensate, and \( r_n \) and \( r_p \) are the two principal radii of curvature (ROC) of the liquid bridge between the surfaces [21]. The Laplace pressure acts over an area, \( A \), and induces a force that pulls the two surfaces together increasing the total adhesion.
The normal surface tension force around the circumference of the meniscus (Equation 1.1) also contributes to the force, but it is usually small compared to the pressure-induced force and is often not considered for micro-scale particles [9].

The following relations can be obtained for the geometry shown:

\[
D + d = r_p (\cos(\varphi + \theta_1) + \cos(\theta_2)) \quad (1.3)
\]

\[
r_p = \frac{D + d}{\cos(\varphi + \theta_1) + \cos(\theta_2)} \quad (1.4)
\]

where \(d\) is the height of the particle inside the liquid bridge, and \(D\) is the separation distance, as shown in Figure 1.4, \(\theta_1\) and \(\theta_2\) are the contact angles of the liquid with the sphere (1) and the flat substrate (2), and \(\varphi\) is the half angle subtended at the center of the sphere by the wetted area of the sphere (this is also known as the ‘embracing’ or ‘filling’ angle).

The ROC, \(r_n\), can also be obtained from the geometry shown in Figure 1.4:
\[ r_n = R \sin(\varphi) - \left( r_p - r_p \sin(\varphi + \theta_1) \right) \]
\[ = R \left( \sin(\varphi) - \left( \frac{D + d}{R} \right) \left( \frac{1 - \sin(\varphi + \theta_1)}{\cos(\varphi + \theta_1) + \cos(\theta_2)} \right) \right) \]  \hspace{1cm} (1.5)

where \( R \) is the particle radius. The equilibrium capillary pressure force, \( F_{cp} \), is found by multiplying the Laplace pressure by the interaction area using the Young-Laplace equation \[22\]
\[ F_{cp} = A_{xy} \gamma_l \left( \frac{1}{r_p} + \frac{1}{r_n} \right) = \pi r_c^2 \gamma_l \left( \frac{\cos(\varphi + \theta_1) + \cos(\theta_2)}{D + d} + \frac{1}{r_n} \right) \]  \hspace{1cm} (1.6)

where \( r_c \) is the radius of the contact circle at the solid particle/liquid/air interface, and is given by:
\[ r_c = R \sin(\varphi) \]  \hspace{1cm} (1.7)

For a large sphere \((R \gg D \text{ and } R \gg d)\), the following approximations can be made:

I. The embracing angle, \( \varphi \), will be very small in comparison to the contact angle, \( \theta_1 \)

II. \[ \varphi = \cos^{-1}\left( \frac{R - d}{R} \right) = \cos^{-1}\left( 1 - \frac{d}{R} \right) \] will be very small,

hence \( \varphi + \theta_1 \approx \theta_1 \)

III. \( r_c \) can be obtained using the geometry shown in Figure 1.4,
\[ r_c = R \sin(\varphi) = \sqrt{R^2 - (R - d)^2} \approx \sqrt{2Rd} \]  \hspace{1cm} (1.8)

IV. \( r_n \gg r_p \) from Equations 1.4 and 1.5, therefore \( 1/r_n \) in Equation 1.6 can be neglected.

The final expression for the capillary pressure force between a large spherical particle and a planar surface, using the above approximations, can be obtained as:
\[ F_{cp}^{R \gg D, R \gg d} = 2\pi R \gamma_l \left( \frac{\cos(\theta_1) + \cos(\theta_2)}{1 + \frac{D}{d}} \right) \]  \hspace{1cm} (1.9)
When the spherical particle and the substrate are in contact \((D = 0)\), the capillary force will attain a maximum:

\[
F_{R \gg D, R \gg d}^{\max} = 2\pi R\gamma_i \left(\cos(\theta_1) + \cos(\theta_2)\right) = 4\pi R\gamma_i \cos(\theta)
\]

\[(\text{if } \theta_1 = \theta_2 = \theta) \tag{1.10} \]

It is apparent from Equation 1.10 that the capillary force for the case of a large spherical particle in contact with a flat substrate is humidity independent (as \(d\), a humidity-dependent parameter which quantifies the height of the liquid bridge, gets canceled out); and hence the capillary force in this case is a function of only the particle size and the surface tension. This has also been shown experimentally [22]. However, the capillary forces for small particles have strong humidity dependence [6, 23].

Most parameters, except \(d\), in Equation 1.9 are usually available to calculate the capillary force between a sphere and a flat plate. The estimation of \(d\) requires knowledge of the embracing angle \((\varphi)\) or the volume of the liquid bridge \((V)\).

\(d\) and \(\varphi\)

It is apparent from the geometry shown in Figure 1.4 that

\[
d = R \left(1 - \cos(\varphi)\right) = 2R\sin^2 \left(\frac{\varphi}{2}\right) \approx \frac{R\varphi^2}{2} \text{ for small } \varphi \tag{1.11} \]

The embracing angle \(\varphi\) will be very small for large spheres or for small liquid bridge volume.

\(d\) and \(V\)

The following relation exists between \(d\) and the liquid bridge volume \(V\)[24]

\[
d = \sqrt{D^2 + \frac{V}{\pi R}} - D \tag{1.12} \]

For the case of small separation distance \(D\), \(d \approx \sqrt{V / (\pi R)}\).

For the case of large separation distance \(D\),

\[
d = D \left[1 + \frac{V}{\pi RD^2}\right]^{1/2} - 1 \approx \frac{V}{2\pi RD} \]

The total capillary force acting between a sphere and a flat plate can be determined by combining the capillary pressure force (Equation 1.9) with the surface tension force (Equation 1.1) [25]

\[
F_{st} = 2\pi c_\gamma \cos(\alpha) = 2\pi R\gamma_i \sin(\varphi)\sin(\varphi + \theta) \tag{1.13} \]
where \( \alpha = \frac{\pi}{2} - (\phi + \theta_1) \) is the angle of the liquid meniscus (at the particle/liquid/air interface) from the vertical as shown in Figure 1.4. Finally,

\[
F_{\text{tot}}^{\text{sphere-plate}} = 2\pi R \gamma_1 \left( \cos(\theta_1) + \cos(\theta_2) \right) \frac{D}{1 + \frac{D}{d}} + 2\pi R \gamma_1 \sin(\phi) \sin(\phi + \theta_1)
\]  

(1.14)

The filling angle \( \phi \) is still unknown, but can be estimated by the Kelvin equation, which relates the equilibrium ROC of the meniscus to the ambient relative humidity (RH) \([26, 27]\)

\[
\left( \frac{1}{r_n} + \frac{1}{r_p} \right) = \frac{R g T \ln(\text{RH})}{\gamma_1 V_m} \quad \text{or} \quad \left( \frac{1}{r_n} + \frac{1}{r_p} \right)^{-1} = r_k = \frac{\gamma_1 V_m}{R g T \ln(\text{RH})}
\]  

(1.15)

where \( r_k \) is the so-called ‘Kelvin radius’. Specifically, by substituting Equations 1.4 and 1.5 into Equation 1.15, one may determine \( \phi \) numerically based on Equation 1.16, and then solve Equations 1.6 and 1.14 to determine \( F_{cp} \) and \( F_{tot} \)

\[
\frac{R g T \ln(p / p_0)}{\gamma_1 V} = \frac{\cos(\theta_1 + \alpha) + \cos(\theta_2)}{D + R(1 - \cos(\alpha))} - \frac{1}{R \sin(\alpha)}
\]  

(1.16)

where \( p \) = the partial pressure of water at the system conditions and \( p_0 \) = the vapor pressure of water at these conditions The magnitude of \( 2r_k \) gives the maximum separation distance between two adhering bodies over which capillary condensation can take place (i.e., the range of the capillary forces). For instance, the value of \( 2r_k \) for water (\( \gamma_1 = 74 \text{mN/m} \)) at room temperature (\( T = 298\text{K} \)) is \([1.08/\ln(\text{RH})]\) nm. Figure 1.5 shows the maximum separation distance for capillary condensation as a function of RH at this temperature. If the RH is below 50%, the maximum separation distance (\( 2r_k \)) for capillary condensation is roughly \( \sim 2 \text{ nm} \). Virtually all substrates generally have root-mean-squared (RMS) surface roughness greater than 2 nm. For this reason, unless there is substantial complementarity between the roughness on the particle and surface such that the peaks on one surface fit into the valleys on the opposing surface, capillary condensation (and correspondingly capillary forces) between particles and solid surfaces are generally negligible when the RH is below 50%.