INTERPARTICLE FORCE BASED METHODOLOGY FOR PREDICTION OF COHESIVE POWDER FLOW PROPERTIES

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2005
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by

Madhavan S. Esayanur
This study is dedicated to my mother and father, who taught me the importance of patience and perseverance, and encouraged me to pursue my dreams.
ACKNOWLEDGMENTS

I would like to acknowledge my advisor, Dr. Brij Moudgil, for his invaluable guidance and support. His deep insight into the fundamentals of particle science encouraged me to seek excellence in my research. Dr. Yakov Rabinovich additionally deserves acknowledgment for introducing me to and guiding me through the finer points of the interaction of surfaces and surface force measurements. Many of the achievements during my graduate school career would not have been possible without his assistance. Thanks are also due to all the other faculty members who helped me with discussions and suggestions. Those who deserve special recognition include Dr. Hassan El-Shall, Dr. Dinesh Shah, Dr. Wolfgang Sigmund, Dr. Rajiv Singh, Dr. Kerry Johanson, Dr. Brian Scarlett, Dr. Jan Miller and Dr. Abbas Zaman. I would also like to thank the National Science Foundation, Particle Engineering Research Center for Particle Science and Technology and our industrial partners for financially supporting this research.

I would like to gratefully acknowledge my group members including Dr. Joshua Adler, Dr. Bahar Basim, Dr. Pankaj Singh, Dr. Ivan Vakarelski, Scott Brown, Suresh Yeruva, Vijay Krishna, Kyoung-Ho Bu, and Rhye Hamey, for their help in experimentation, and also for their support and encouragement. Thanks go out to all my friends: Sunil Bharadwaj, Babu Sivaraman, Subramanian Arcot, Sivakumar Ariyakula, Rajeshwari Srinivasan, Amol Patil, Ajay Kale, Karthik Ramani, Seemanth Rawal, Karthik Subramanian, Dauntel Specht, Milorad Djomlija, Maria Palazuelos, Marco
Verwijs, Steven Tedeschi, Yunmi Kim and Elanor Pinto, for making my stay in Gainesville enjoyable.

I would also like to thank the administration and staff of the Particle Engineering Research Center including Rhonda Blair, Cheryl Bradley, Noeleen Brophy, Gill Brubaker, Shelley Burleson, Dawn Byrd, Dr. Richard Chapas, Dr. Anne Donnelly, John Henderson, Donna Jackson, Victor Jackson, Sophie Leone, Dr. Kevin Powers, Gary Scheiffele, Nancy Sorkin and Jo-Anne Standridge for their assistance during the course of this study.
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The transport and handling of powders are key areas in the process industry that have a direct impact on the efficiency and/or the quality of the finished product. A lack of fundamental understanding of powder flow properties as a function of operating variables such as relative humidity, and particle size, leading to problems such as arching, rat-holing and segregation, is one the main causes for unscheduled down times in plant operation and loss of billions of dollars in revenues. Most of the current design strategies and characterization techniques for industrial powders are based on a continuum approach similar to the field of soil mechanics. Due to an increase in complexity of the synthesis process and reduction in size of powders to the nanoscale, the surface properties and inter particle forces play a significant role in determining the flow characteristics. The use of ensemble techniques such as direct shear testing to characterize powders are no longer adequate due to lack of understanding of the changes in the property of powders as a function of the major operating variables such as relative humidity,
temperature etc. New instrumentation or techniques need to be developed to reliably characterize powder flow behavior. Simultaneously, scalability of the current models to predict powder flow needs to be revisited.

Specifically, this study focuses on the development of an inter particle force based model for predicting the unconfined yield strength of cohesive powders. To understand the role of interparticle forces in determining the strength of cohesive powders, the particle scale interactions were characterized using Atomic Force Microscopy (AFM), contact angle, surface tension, and coefficient of friction. The bulk scale properties such as unconfined yield strength, packing structure, and size of the shear zone were also investigated. It was determined that an interparticle force based model incorporating the effect of particle size and packing structure leads to a reasonable prediction of the bulk strength of cohesive powders. Additionally, the role of particle size distribution and liquid distribution in the powder was considered. The findings of this research should be helpful to the practitioners in providing reliable input for the design of cohesive powder flow and handling equipment.
CHAPTER 1
INTRODUCTION

Traditional and emerging technologies such as electronic and advanced structural ceramics, particulate coatings, drug tableting, and nanocomposite materials rely on transport and handling of bulk powders as raw materials or finished products. Most industrial processes are designed for handling powders based on a certain application, and changing the powder characteristics leads to problems with flow.

Scientific and Technological Barriers Encountered during Powder Transport and Handling Processes

The most common problems encountered during powder transport and handling are the following:

• Formation of a stable arch in the storage bin or silo referred to as arching, as shown in Figure 1-1. The powder at the exit of the storage bin is unconfined (unrestricted by any physical boundary) and yet the powder exhibits sufficient strength to form a stable arch. The strength of a powder in such an unconfined state is defined as the unconfined yield strength.

• Non-uniform flow of powder leading to faster discharge through the middle and no flow at the walls leading to a stable hole in the center called a rat hole, also illustrated in Figures 1-1 and 1-2. The ideal flow situation would be the mass flow regime where all the contents of the storage bin flow out at the same time.

• Separation of coarse and fine particles in a powder due to differences in their relative densities and composition known as segregation. Figures 1-3 and 1-4 show two cases of segregation in typical powder processes.

All powder flow problems deal with either one or more and sometimes a combination of the above mentioned phenomena. All powders can be classified into two categories, non-cohesive powders and cohesive powders. Cohesive powders exhibit more flow problems, due to the inherent force of attraction between the particles and the
adsorption of moisture and addition of liquid binders (used to avoid segregation) leading to capillary forces in the system.

The first attempt at theoretical prediction and design of bins and hoppers for powders was done by Jenike [1,2]. Most of the existing design tools rely on bulk testing of powders to measure and study the flow properties and bulk behavior of powders. The lack of more sophisticated equipment and the absence of nanosize powders, thereby necessitating a systematic study of the particle scale interactions, played a role in employing that protocol. Today, with increased focus on nanoscale materials, the problems are more challenging, requiring numerous tests and better models for scalability. Powders at the nanoscale behave very differently from those at the micron to millimeter sizes. Surface forces become more dominant with reducing particle size and need to be thoroughly understood to gain better understanding of the macroscopic phenomena. The perennial need of high throughput and most reliable systems has necessitated more focused research in this area.

One of the great difficulties of researching the extensive literature relevant to powder mechanics is in correlating the information obtained from the numerous materials studied. The powder properties presented by one researcher are rarely comparable with others. Most of the studies deal with general trends in the bulk properties of the powder such as the angle of internal friction and cohesion and provide empirical correlations for a particular system. Therefore, a systematic study is needed for quantifying the changes in the properties and developing a correlation between the operating variables and the bulk flow behavior of the powder.
Figure 1-1. A schematic showing the two most common problems encountered in powder flow. Arching, as shown on the left, is the formation of a stable arch at the outlet of a bin, and rat holing, as shown on the right, is drainage of the powder through the middle of the bin or hopper.

Figure 1-2. Schematic representation of two kinds of flow in a bin or hopper. Mass flow as shown on the left leads to uniform discharge of the powder throughout the container, versus, funnel flow as shown on the right leading to flow from the center to the edges developing undesirable dead zones in the container.
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Figure 1-4. A picture showing segregation of a powder during tumbling in a cylindrical mixer.

Outline of Dissertation

To achieve desired results in applications involving powder transport and handling, the mechanical properties of the powder must be controlled and manipulated. In addition, understanding the contribution of surface forces on the bulk properties in applications such as caking, powder mixing, tableting, and segregation necessitates the development of a reliable model to predict the change in flow behavior based on
fundamental properties of the system such as particle size, binder content etc. The most common flow and hang-up problems discussed in the previous section are due to the cohesive strength of the powder defined as the unconfined yield strength. The cohesiveness of a powder, as manifested by the unconfined yield strength, is the parameter used as input to design flow and handling equipment. The present work is focused on developing an interparticle force based framework to predict the strength of cohesive powders.

A brief overview of powder mechanics and the different classification of powders is presented in chapter 2. Chapter 3 reviews the fundamentals of inter particle forces with emphasis on capillary forces. Theoretical formulae for calculating the capillary force as a function of separation distance, for a sphere/plate geometry, are developed for a constant volume and a constant radius liquid bridge. Chapter 4 extends the theoretical formulae developed in the preceding chapter for the interaction of two spheres and discusses the application of the Derjaguin approximation to the capillary force interaction between two unequal size spheres. Based on the theoretical developments for capillary forces, a model is proposed for predicting the unconfined yield strength of cohesive powders in Chapter 5. The unconfined yield strength of a system of mono disperse smooth glass beads is determined first, followed by incorporation of other effects such as surface roughness, friction forces and bi modality of particle size. The model predictions of the unconfined yield strength are compared with experimental data from direct shear testing using the Schulze cell. Finally, chapter 6 summarizes the findings of this investigation and proposes possible avenues for further research.
A powder is an assembly of particles. Its properties are determined partly by its individual components, and their interaction with each other, and partly by the properties of the fluid filling the interstices between the particles. The current technologies still use traditional methods of testing based on direct shear measurements using the Jenike shear cell [2], the Johanson indicizer [3], the Schulze cell [4] and the Peschl cell [5] and various other modifications of these equipments. The complete analysis and design of powder handling equipment are currently done via the soil mechanics (continuum) approach. The ensemble of particles is considered as a continuum and a Mohr circle (Figure 2-1) characterizes the state of stress of the powder.

![Mohr circle diagram](image)

**Figure 2-1. Mohr circle diagram**

The Mohr circle is a two dimensional representation of all the equivalent states of stress in terms of a shear stress ($\tau$) and a normal stress ($\sigma$) that correspond to the major
principal stresses ($\sigma_1, \sigma_3$) acting on the system. A typical direct shear test of a powder involves consolidation of the sample at a given normal load followed by lowering of the normal load and determination of the shear stress required to initiate flow (fail) in the sample. The largest Mohr circle to the right represents the consolidation state of a powder and the subsequent Mohr circles to the left represent the (failure) stress states of the powder at lower normal loads that lead to incipient flow in the system, as shown in Figure 2-1. The yield locus is the line tangent to the failure Mohr circles, and the slope of the yield locus is called the angle of internal friction of the powder. According to the Jenike approach, the unconfined yield strength of the powder ($f_c$) is the key parameter for evaluating the flow characteristics of the powder. The unconfined yield strength is defined as the yield stress of a bulk sample at a given consolidation load with one of the major principal stresses equal to zero. A zero stress on one of the axes represents a powder not confined in that direction of the stress, which is the case during flow of powder out of a bin or a hopper. Apart from the unconfined yield strength, the Mohr circle also enables the determination of the cohesion (C) and the angle of internal friction (angle of repose, $\phi$) that are bulk parameters characterizing the flow properties of the powder. This approach is reasonable for a system involving contact forces, friction and shear. For cohesive systems with decreasing particle size, surface forces are comparable in magnitude with other macroscopic forces (shear, consolidation and gravity). Applying a continuum approach in such cases would not provide any further understanding of the intrinsic behavior of the system. The two parameters (C, $\phi$) do not represent the force of adhesion and friction as experienced at the particle scale. Consequently, this approach
would only provide qualitative predictions for the effect of surface forces on ensemble behavior.

**Non-cohesive Systems**

The handling of non-cohesive powders is relatively easier than cohesive powders, primarily due to their free flow characteristics. However there are important challenges in understanding the physical properties of such systems [6]. Depending on the type of particles, the system is modeled as either completely elastic or completely plastic or visco-plastic. The development of constitutive equations for such systems is the focus of current researchers in this field. Engineering mechanics and computer modeling are the key tools utilized in developing a fundamental understanding of the bulk behavior of non-cohesive systems [7-9].

The current advances in the field of nanotechnology lead to the processing of finer size and function specific particles. Reduction in particle size and production of multifunctional particles demand a fundamental understanding of the particle scale forces and surface phenomena for better modeling the flow behavior of these systems.

**Cohesive Systems**

The area of cohesive powders adds another complexity into the system in the form of cohesion. The most common cause of cohesion between particles is van der Waals force of attraction. Additionally, under humid conditions, the adsorption of water vapor leads to formation of liquid bridges, yielding much stronger adhesion between particles. Most of the recent studies relating bulk behavior to interparticle forces [10] have used the first works by Molerus [11,12] as the platform. Molerus developed analytical expressions for the force of adhesion between particles under consolidation due to van der Waals forces. The loading history of the powder sample was taken into account to
calculate the resulting plastic deformation at the contact points. The analysis was based on a balance of the sum of applied normal load (N) and van der Waals interaction ($F_{vdW}$) forces, to the resistance (elastic or plastic) force of the material ($F_w$). An expression relating the contact force to the stresses experienced by the particle was developed for a randomly packed mono size spherical particle system. The calculated value of the van der Waals force as a function of consolidation load was incorporated in the normal and radial components of stress to calculate the unconfined yield strength of the powder. This theory was shown to reasonably predict the cohesion between limestone particles of less than 15 micron size using material constants values from the literature.

Cohesion (C) on the bulk scale is defined as the shear stress acting on the bulk powder sample causing it to yield at a condition where the normal pressure equals zero. Cohesion depends on the pre-consolidation state of the material. Higher consolidation pressure leads to higher cohesion due to increase in the contact area. As shown in Figure 2-1, there is a unique value of cohesion for a given family of yield loci, which describes the failure behavior of the bulk powder. A measure of cohesion in powders as measured by powder mechanics engineers is the unconfined yield strength ($f_c$) which is a related property to describe the flow or no-flow conditions of the bulk. The unconfined yield strength is the major principal stress acting on the bulk material causing it to yield in shear. It is related to cohesion through Eq. (2-1).

$$f_c = \frac{2\cos(\phi)}{1-\sin(\phi)} C$$  \hspace{1cm} (2-1)

where $\phi$ is the internal angle of friction, $C$ is the cohesive stress and $f_c$ is the unconfined yield strength. Since there is a unique value of cohesion for each consolidation pressure, there also exists a unique value of unconfined yield strength. The stress state describing
this unconfined yield condition is given by the Mohr circle. It is the smallest stress state that will produce compressive stresses acting on the material. The tangent point between this Mohr circle and the yield locus describes the stress state \((\sigma, \tau)\) acting along the shear plane, which forms as the material yields or fails under compressive stress, and can be expressed in terms of the unconfined yield strength [3] by Eq. (2-2).

\[
\tau = \frac{f_c}{2} \cos(\phi)
\]  

(2-2)

**Direct Shear Testers**

There are a number of different types of direct shear testers used to characterize powder flow properties. The testers listed below differ in the cell geometry and the shearing action applied to the powder:

- Jenike Shear Tester
- Peschl Ring Shear Tester
- Schulze Tester
- Johanson Indicizer

In the current study the Schulze tester was used for characterizing the strength of the cohesive powders. The Schulze cell has an annular geometry; the powder sample is filled inside the cell and a top lid held in place by two lever arms is placed on the base as shown in Figure 2-2. A consolidation load is applied, pulling the lid down on to the powder sample. The base is rotated and the torque generated on the lid is recorded through load cells connected to the two lever arms supporting the lid. One set of experiments is carried out at a given consolidation load, failing the sample at various fail loads (less than the consolidation load). A typical set of load parameters for a consolidation load of 2000 gm is listed in Table 2-1.
Table 2-1. Consolidation and Fail Loads used for Characterization of Powder Sample on the Schulze Cell.

<table>
<thead>
<tr>
<th>Consolidation Load (gm)</th>
<th>Failure Load (gm)</th>
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<tr>
<td>2000</td>
<td>1500</td>
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<td>2000</td>
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<tr>
<td>2000</td>
<td>200</td>
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Figure 2-2. A schematic of the Schulze cell. The annular region of the cell is filled with powder with the two load arms connected to the stationary top. The bottom of the cell is rotated to shear the sample consolidated by applying different normal loads.

Each set of experiments are carried out at a given consolidation load and the powder is failed at loads lower than the consolidation load. The set of failure points for a consolidation load defines the yield locus as shown in Figure 2-3. The unconfined yield strength, $f_c$, is extrapolated by drawing a Mohr circle tangent to the yield locus and passing through the origin. A complete set of points for the unconfined yield locus is generated at different consolidation loads and hence generating the flow function. The flow function defines the change in the strength of a powder ($f_c$) as a function of the applied consolidation load.
Continual Deformation

Failure

Yield Locus

Figure 2-3. A typical result from consolidation and fail of a powder sample. The corresponding points on the Mohr circle are shown to illustrate the procedure of generating the Yield Locus.

The use of direct shear testers enables characterization of the ensemble properties of the powder such as the cohesion, unconfined yield strength and the internal angle of friction. The interactions between particles at the microscopic level are discussed in the next chapters, leading to a correlation between the two scales of measurement.
CHAPTER 3
INTER PARTICLE FORCES IN POWDERS

Introduction

Packing of powders has a direct impact on the strength of the system and its resistance to flow. The unconfined yield strength of powders is found to increase with increased consolidation of the sample. This is a direct consequence of re-arrangement of particles, thereby increasing interparticle interactions that result in higher strength. In the case of coarse (non-cohesive) particles, particle packing is controlled mainly by two factors, particle size distribution and shape. The introduction of cohesive forces (van der Waals force, capillary force) leads to restrictive motion of the particle hence altering the packed bed density. Due to the complexity of factors involved, most of the latest studies in this field still remain to be empirical relationships derived between porosity, liquid content and particle size [13].

An illustration of the forces acting between particles in a powder is shown in Figure 3-1, where $F_{ad}$ is the force of adhesion due to van der Waals and capillary bridge forces, $F_F$ and $F_S$ are the friction and shear forces respectively acting at the particle level, and $F$ and $S$ are the overall normal and shear forces acting on the ensemble of particles.

Basic formulae for the determination of these forces are briefly reviewed in the following sections and the expressions developed for prediction of these forces are verified experimentally.
Figure 3-1. An illustration of the key forces acting between particles in a powder.

**van der Waals Forces**

Although van der Waals forces are commonly considered for the interaction of colloidal particles, the forces were originally developed for interaction between gas molecules. To explain the behavior of gases and their deviation from ideality, J. D. van der Waals [14] first suggested that the interactions could be expressed as a modification of the ideal gas law, \( PV = nRT \),

\[
(P + \frac{n^2 a}{V})(V - nb) = nRT
\]  

(3-1)

where \( P \) is pressure, \( n \) is the number of moles of gas, \( V \) is the volume, \( R \) is the gas constant, \( T \) is temperature, and ‘\( a \)’ and ‘\( b \)’ are constants specific to a particular gas. The constant ‘\( b \)’ describes the finite volume of the molecules comprising the gas, and the constant ‘\( a \)’ takes into account the attractive forces between the molecules. This modification significantly improved the model for predicting the behavior of gases. The various types of attractive forces between molecules are now collectively termed van der Waals forces. The concept of an attractive force is also used to describe the properties of condensed matter. The commonly used Lennard–Jones potential [15]
\[ W_{\text{atom/atom}} = -\frac{C}{r^6} + \frac{B}{r^{12}} \]  

(3-2)

where the net potential energy between atoms, \( W_{\text{atom/atom}} \), at distance, \( r \), can be described by the competition of an attractive London dispersion force [16], characterized by constant \( C \) and a Born repulsion term (arising from the overlap of electron clouds) characterized by constant \( B \). The London constant, \( C \), is primarily related to the synchronization of instantaneous dipoles created when the energy fields of neighboring atoms overlap.

**Microscopic Approach**

In the microscopic approach, the summation of pair wise interactions between the atoms in one body and the atoms in another body is used to derive an expression for the energy of attraction between them. Using this approach, the interaction energy, \( W \), between two spherical particles may be expressed in the following manner

\[
W_{\text{sph/sph}} = \frac{A}{6} \left[ \frac{2R^2}{H(4R + H)} + \frac{2R^2}{(2R + H)^2} + \ln \left( 1 - \frac{4R^2}{(2R + H)^2} \right) \right] 
\]

(3-3)

where \( A \) is Hamaker’s constant, \( R \) is the particle radius, and \( H \) is the separation distance between the particle surfaces. This relation is valid for all particle sizes. However, if the radius of the two particles is much greater than the separation distance, the expression may be reduced to the more commonly used form represented by Eq. (3-4) [17].

\[
W_{\text{sph/sph}} = \frac{AR}{12H} 
\]

(3-4)

Derjaguin [17], de Boer [18], and Hamaker [19] all contributed significantly to the understanding of the van der Waals interactions between macroscopic bodies based on the individual interactions of London dispersion forces between atoms. Energies of
interaction based on different geometries, assuming the extent of the van der Waals attraction to be small compared to the radius of curvature, are given in Table 3-1.

However, the more important outcome of these initial approaches was the separation of the fundamental nature of the interaction of materials from their geometry. In this manner the force or energy between two bodies was expressed as a factor that may be changed depending on shape and a constant resulting from the material’s fundamental composition.

Table 3-1. van der Waals Attraction between Different Geometries. Theoretical formulae for the prediction of the energy or force of attraction between bodies of differing geometries where $A$ is the Hamaker constant, $H$ is the surface separation distance, $R_1$ and $R_2$ are the particle/cylinder radii, and $L$ is the cylinder length. Note that these were derived for conditions in which the extent of significant van der Waals attraction is far less than the radius of the particles or cylinders and that force is the negative differential of energy.

<table>
<thead>
<tr>
<th>Geometry of Interaction</th>
<th>Energy of Interaction ($J$)</th>
<th>Force of Interaction ($N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two Plates</td>
<td>$\frac{A}{12\pi H^2}$</td>
<td>$\frac{A}{6\pi H^3}$</td>
</tr>
<tr>
<td>Sphere/Plate</td>
<td>$\frac{A R}{6H}$</td>
<td>$\frac{A R}{6H^2}$</td>
</tr>
<tr>
<td>Sphere/Sphere</td>
<td>$\frac{A}{6H (R_1 + R_2)}$</td>
<td>$\frac{A}{6H^2 (R_1 + R_2)}$</td>
</tr>
<tr>
<td>Crossed Cylinders</td>
<td>$\frac{A \sqrt{R_1 R_2}}{6H}$</td>
<td>$\frac{A \sqrt{R_1 R_2}}{6H^2}$</td>
</tr>
<tr>
<td>Parallel Cylinders</td>
<td>$\frac{AL}{12\sqrt{2}H^{3/2} \sqrt{R_1 R_2}}$</td>
<td>$\frac{AL}{8\sqrt{2}H^{5/2} \sqrt{R_1 R_2}}$</td>
</tr>
</tbody>
</table>

Macroscopic Approach

In the microscopic approach, the interaction between atoms or dipoles is calculated, assuming that a vacuum exists between the interacting atoms. However, for an atom at the core of a solid particle interacting with an atom in the core of another particle, the intervening media consists of other atoms of the solids, and hence the approach is not
correct, since the intervening atoms can have a significant impact on the interaction. Additionally, in real materials several other interactions may exist that can contribute to the total interaction force. Hence, another method to determine and predict the attraction between solids that takes into account the different types of interactions was required. On the other hand, accounting for the different types of interactions among various species in a solid is difficult. In 1956 an alternative approach was proposed by Lifshitz [20], which is based on the assumption that both the static and oscillatory fields produced by the atomic components of solids should directly affect the absorption of electromagnetic energy by the material. He derived a method to calculate the attraction between materials based on the differences in their dielectric spectra. This was the first attempt to calculate van der Waals forces based on the continuum or macroscopic approach. Although this approach clearly accounts for the different types of bonding and screening in a body, it is still a very difficult function to measure due to the wide range of frequencies and types of experiments needed to determine the entire function.

To simplify this approach, Ninham and Parsegian [21] proposed that major contributions to the overall attraction come from regions of dielectric relaxation, or regions where a specific atomic or molecular mechanism creates a resonant vibration. The characteristic absorption frequencies of some materials are relatively well characterized; for example the spectra of water have been characterized in the ultraviolet, infrared, microwave, and static frequency regimes [22,23]. However, it is still difficult to extract information for a wide variety of materials.
Hough and White [24] suggested that most contributions to the overall Hamaker constant come from dielectric relaxations in the UV and infrared regions, and hence dielectric spectra in this wavelength region could be used for the calculations.

Considering a single UV relaxation frequency, an approximation for the Hamaker constant, \( A_{131} \), of material 1 interacting with similar material through medium 3 may be written solely as a function of the differences in the static dielectric constants, \( \varepsilon (0) \), and indices of refraction in the visible range, \( n \). The result is the Tabor-Winterton [25] approximation

\[
A_{131} = \frac{3kT}{4} \left( \frac{\varepsilon_1(0) - \varepsilon_3(0)}{\varepsilon_1(0) + \varepsilon_3(0)} \right)^2 + \frac{3ho\omega_{\nu}}{32\pi\sqrt{2}} \left( \frac{n_i^2 - n_j^2}{n_i^2 + n_j^2} \right)^{3/2} \tag{3-5}
\]

where \( kT \) is the product of Boltzmann’s constant and temperature and \( h \) is Planck’s constant.

**The Derjaguin Approximation**

In the previous section, a methodology to determine the interaction between solid bodies was discussed. Using the microscopic approach, Hamaker was able to separate the critical interaction components into a material constant and a factor dependent on the geometry of the interacting surfaces [19]. While the macroscopic approach delineated more clearly the value of the Hamaker constant, changes in the geometry of the interacting bodies still require difficult multidimensional integration processes.

An approach to overcome this problem was proposed by Derjaguin in 1934 [17]. He proposed that the energy of interaction between two bodies could be calculated based on the summation of the interaction force as separation distance, \( H' \), goes from \( H \) to infinity for infinitesimally thin concentric rings of radius \( x \) and thickness \( dx \) interacting
with the projection of that ring on the opposing body as if it were two plates of area $2\pi dx$ separated by $H'$, as shown in Figure 3-2. If the assumption is then made that the range of the force between the interacting bodies is small compared to their radii and that at large separation distances the magnitude of the interaction approaches zero, relatively simple relations for the energy of interaction between flat plates and the force of interaction between bodies of differing shapes may be extracted.

![Figure 3-2. Calculation of the Derjaguin approximation. Integration of the force between the flat surface created by a ring of thickness $dx$ and radius $x$ with its projection on the sphere as separation distance goes from $H$ to $\infty$ yields the equivalent energy between flat surfaces.](image)

This approximation is extremely important for the measurement of surface forces because it simplifies the derivation of analytical formulae and allows calculation of interaction forces between bodies of different geometries. Although van der Waals attractive force has a relatively simple form, other forces are considerably more complicated and derivation or integration may not always yield analytical solutions. Additionally, many computations, such as the distribution of ions from a charged
interface, are simplified if the interface is flat. As illustrated in Table 3-2, multiplying the interaction energy between flat surfaces by a factor, the force between different geometry bodies may be calculated.

Table 3-2. Results of the Derjaguin Approximation. The interaction force, $F$, between surfaces of different geometries, according to the Derjaguin approximation, is the energy of interaction between flat plates, $W_{plt/plt}$, multiplied by a simple prefactor.

<table>
<thead>
<tr>
<th>Geometry of Interaction</th>
<th>Force</th>
<th>Derjaguin Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere/Plate</td>
<td>$F_{sph/plt}$</td>
<td>$(2\pi R)W_{plt/plt}$</td>
</tr>
<tr>
<td>Sphere/Sphere</td>
<td>$F_{sph/sph}$</td>
<td>$(\pi R)W_{plt/plt}$</td>
</tr>
<tr>
<td>Crossed Cylinders</td>
<td>$F_{cyl/cyl}$</td>
<td>$(2\pi R)W_{plt/plt}$</td>
</tr>
</tbody>
</table>

An even more important result of this approximation is that all of the forces or energies of interaction between curved bodies are seen to be directly proportional to the radius or mean radius. Hence, forces measured between spheres, cylinders, and plates may be directly related to each other. Moreover, experimentally measured values between surfaces of differing radii may also be compared to a single theoretical prediction. Surface forces for this reason are often presented normalized by the radius of the interacting bodies. Note that in this form, force divided by radius is equivalent to energy per unit area.

In spite of the simplicity of determination of interaction between spheres and other well defined geometries, the applicability of the Derjaguin approximation to forces other than van der Waals and electrostatic, such as capillary force is yet to be verified. A systematic study of the applicability of the Derjaguin approximation in the case of capillary forces is presented in Chapter 4.

**Capillary Force**

Apart from van der Waals forces, the other key interaction between particles in a powder is the capillary force. Haines and Fisher [26,27] made the first attempt at
understanding cohesion in soil due to the presence of moisture. Cohesion due to moisture was identified to be due to the formation of pendular liquid bridges. An expression for the force of cohesion due to the formation of liquid bridges of water was developed. The shape of the meniscus was given by the circular approximation resulting in a simple analytical expression for a symmetric bridge. The force of attraction due to the presence of such a capillary bridge between particles was calculated using the Kelvin and the Laplace equations. The overall strength of such system depends on the type of packing. For a close packed structure, an increased number of contact points would lead to a higher cohesion force. And on the other extreme, an open packed structure would lead to fewer contacts, representing the lower limit of cohesion for such systems. Experimental results from silt were found to be in the range of the theoretical values for the close packed and the open packed structure. This result claimed to validate the general trend observed in the cohesive strength of such systems. However, the effects of liquid bridge induced cohesion on the flow properties of powders were not discussed.

Most of the reported studies on the effect of cohesion were focused on only one part of the problem, such as the effect of meniscus shape on capillary force [28], effect of liquid bridge volume on rupture energy [29] and the effect of interparticle force on the packing of spherical granular material [30]. Other studies on the effect of particle size or liquid composition or gravity on the force of adhesion due to a liquid bridge have also been done. However, none of the past researchers considered the whole system.

The four major factors that play a role in determining the equilibrium of a liquid bridge between two surfaces are the differential pressure across the liquid given by Laplace equation, the surface tension component of the liquid, the buoyancy force and
the force of gravity. Usually, the latter two forces are considered to be negligible and for typical particle sizes (of cohesive powders) it is indeed the case [31]. The effect of relative humidity on the formation of the liquid bridge and hence the onset of the capillary force has been well understood. Rabinovich et al [32], have investigated the effect of nanoscale surface roughness on the critical humidity required for the onset of capillary forces in such systems. The presence of nanoscale roughness on surfaces has been shown to have a profound effect on the critical humidity required to induce capillary adhesion. Their study also validates a simple analytical expression developed to predict the force of adhesion as a function of particle size, humidity and roughness, which is most relevant for practical systems.

With the advent of faster computing power, simulations have provided modest inputs to understanding the flow of powders. Simulations of cohesive powders have been done using Discrete Element Modeling (DEM) to yield qualitative results. Mei et al [33] used the DEM code of Dr. Otis Walton to show the validity of particle coating on improving the flowability of cohesive powders. A surface energy approach was used to account for the van der Waals force in the system and an extended JKR theory was employed for defining the force-distance relationships in the simulation. Their simulation could only provide macroscopic velocity profiles, which showed a similar trend as the experimental results on the angle of repose and the flow rate in a funnel of coated and uncoated powders.

Simulation of cohesive powder flow with liquid bridges has been done using DEM [34,35]. The limitation on computing speed and time scales, have confined these simulations to particles of millimeter size ranges. These approaches can still provide a
qualitative picture of the overall flow field of the particles and the formation of shear zones in the system.

The incorporation of all the above findings into a single model for predicting the bulk powder strength of cohesive systems is the final goal of the present study. Development of such a tool is vital for powders, specifically in the areas of nanotechnology and pharmaceutics, where extensive evaluations on currently available powder testers are not a viable option. Moreover, the availability of adequate quantity of material, such as pharmaceutical drugs and speciality chemicals that are highly cost restrictive, for testing according to the current protocols is another limitation necessitating the development of a reliable, scalable and predictive methodology.

**Liquid Binder Addition**

The addition of liquid binders to bulk solids has been employed to increase the cohesive properties of the bulk material. This technique is often used to decrease the dustiness of a bulk material, enhance agglomeration processes, increase green strength during tablet and mold production and prevent segregation tendencies [36]. For example, roofing tile production companies may occasionally add oil to the roofing granules to prevent segregation of fine and coarse granules as they are deposited on the asphalt shingle. Food industries, chemical producers, and even wood manufactures add liquid binders to their briquetted or extruded products to produce a more robust particulate ensemble. Conversely, the presence of liquid in bulk powder materials can increase the unconfined yield strength of the bulk and create significant arching and rat hole tendencies in process equipment. These flow problems are responsible for billions of dollars in lost revenue, additional operator involvement, and high maintenance cost to manufactures. The mechanism underlying increased cohesiveness through the addition of
liquid binders is not completely understood. However, it is believed that it arises from the capillary forces between the individual particles. The different regimes of liquid distribution in a powder sample are as shown in Figure 3-3. Most industrial processes operate in the pendular regime and the current study focuses on that regime. Understanding capillary forces will help in more reliable prediction of the cohesive properties acting within a bulk material.

![Figure 3-3. Regimes of liquid distribution in a powder sample. A – Pendular state, where individual liquid bridges exist between particles; B – Funicular state, two or more liquid bridges on adjacent particles start to coalesce with each other; C – Capillary state, all the interstices between the particles is completely filled with liquid [37].](image)

The bulk property of a particulate ensemble system that characterizes segregation tendencies, agglomerate production, and tablet integrity is the unconfined yield strength. This term is defined as the major principal stress acting on an unconfined sample of material, which causes shear failure. The actual failure of the bulk sample occurs at some angle relative to the major principal stress direction. At the failure surface, an individual particle must rise past the peak of an adjacent particle during shear, resulting in an expansion (dilation) of the bulk material. This expanding shear motion causes separation and re-forming of liquid bridges between particles in the bulk assembly. Consequently,
the force required to shear bulk particulate material depends on the sum of all the individual forces acting at the contact points between particles in the bulk. This implies that adhesion forces due to local interparticle capillary forces should play an important role in increasing the unconfined yield strength of a bulk assembly of particles.

Figure 3-4 shows the increase in unconfined yield strength as measured by the Schulze Cell technique for fine quartz powder (Novacite from Malvern Mineral Co., Hot Springs, AR) as a function of increasing oil content. White mineral oil (Norton Co., Littleton, NH) was added to the powder as a fine mist and mixed thoroughly before measurement. An increase in bulk strength of up to 150% was found to occur with the addition of only 1 to 2% oil by weight. The objective of this investigation was to develop a model that predicted capillary force as a function of separation distance between particles in order to estimate the unconfined yield strength of bulk powder.

There is a significant body of literature concerning the adhesion of films and particulates to surfaces in absence of capillary forces [38-40]. Direct measurements of adhesion have been performed with most modern instrumentation including the surface force apparatus [41], atomic force microscope [42,43], and interfacial gauge [44,45]. There have also been a number of theoretical and experimental descriptions of the force of adhesion due to liquid in a capillary. That the amount of liquid (meniscus radius) condensed from such a system may be adequately described by the Kelvin equation has been confirmed by a number of authors [46-50]. An early discussion of capillary phenomena related to particle adhesion was presented by Coelho and Harnby [51,52]. Through Kelvin’s description of the lesser radius of curvature of the meniscus [53], the Laplace prediction of the pressure inside the meniscus [53], and inclusion of the adhesion
component produced by the surface tension, a description of capillary adhesion was developed.

Figure 3-4. The dependence of unconfined yield strength on major principal stress for quartz. The experiments were conducted in the Schulze cell as a function of the amount of oil added.

More recently, Marmur [54] and de Lazzer et al. [55] have extended these basic theories for other geometries, environmental conditions, and separation distances while more accurately describing the meniscus and its effect on adhesion. de Lazzer et al. [55]
have also incorporated surface tension in their model, and have discussed capillary adhesion for a variety of probe geometries.

A direct measurement of capillary forces has been performed in systems where liquid in a capillary is in thermodynamic equilibrium with the environment. Fisher and Israelachvili [56] investigated adhesion between smooth mica surfaces in the presence of water and cyclohexane vapors and directly measured the relative contributions of solid-solid interactions and the capillary effect to the total adhesion force. Rabinovich et al. [57] further explored this area through direct measurement of the force of adhesion between fused quartz filaments in various semi-miscible liquids. Forces have also been measured in gaseous atmospheres saturated to various levels with water or organic solvent [32,47,58,59]. Capillary forces have also been measured between two oil droplets as they consolidate using the micropipette technique developed by Masliyah and coworkers [60].

As described above, the formation of capillary bonds between particles is known to have a significant effect on the mechanical properties and transport of powders [36]. In a previous investigation [32], the role of nanoscale surface roughness in the capillary adhesion forces between silica and other systems in both dry and humid atmospheres was explored. Corresponding to Figure 3-5 and based on the equations of Marmur [54] and de Lazzer et al. [55], a simplified formula was developed for capillary adhesion force, \( F_{ad} \), between a smooth spherical particle and a flat substrate with nanoscale roughness.

\[
F_{ad} = -4\pi\gamma R \cos \theta \left( 1 - \frac{H_{asp}}{2r \cos \theta} \right) \tag{3-6}
\]

In this relationship, \( \gamma \) is the surface tension of the liquid, \( R \) is the radius of the adhering particle, \( H_{asp} \) is the maximum height of the asperities above the average surface
plane, $r$ is the lesser radius of meniscus, and $\cos \theta = (\cos \theta_P + \cos \theta_S)/2$, where $\theta_P$ and $\theta_S$ are contact angles of the liquid on the adhering particle and substrate, respectively. It should be noted that Eq. (3-6) is applicable only when the meniscus is large enough to span the distance between the adhering particle and the average surface plane, i.e., $H_{asp} < 2r \cos \theta$, and when the radius of the meniscus is small compared to the adhering particle.

Figure 3-5. Illustration of the geometry of a liquid bridge between a smooth spherical particle and a rough substrate.

Although derived for rough surfaces, Eq. (3-6) is also valid for the capillary adhesion of a smooth particle and a smooth substrate separated by a distance $H$ [56]. However, the radius of the meniscus in the above formula is fixed because $r$ is determined solely by the relative humidity through Kelvin’s equation. Once the surfaces begin to separate, the liquid annulus rapidly decreases in size (evaporates) in order to maintain this radius [61]. Hence, in cases such as condensed gases in thermodynamic equilibrium with vapors in surrounding media, the capillary adhesion should rapidly decrease as the surfaces separate due to a decrease in volume (and the contact area with the surface) of the liquid bridge. In the AFM measurement of capillary force magnitude,
due to the jump-out of sphere attached to the cantilever observed during the retraction of
the tip, equilibrium is not maintained and the measured force corresponds to just the
maximum adhesion force. Similarly, during powder transport the actual
attachment/detachment process may occur rapidly and may not allow the radius of the
capillary to reach equilibrium. Additionally, for the case of an oil annulus or other non-
volatile liquid, the volume of the liquid would actually be conserved. In this case, the
magnitude of the adhesion force is expected to decrease as a function of separation
distance but remain measurable.

The present investigation demonstrates the significance of capillary forces in the
mechanical properties of bulk powders and presents direct measurements of the capillary
adhesion force acting between surfaces separated by oil droplets of various sizes.
However, theoretical formulae first need to be developed, to correlate experimental and
predicted values.

**Theoretical Force of Capillary Adhesion for Annuli of Constant Volume or Radius**

As mentioned above, Eq. (3-6) is expected to be valid for smooth surfaces,
assuming H as the shortest distance between the adhering particle and the flat substrate.
For detachment rates faster than evaporation time or for non-volatile liquids, such as oil,
the radius of meniscus will be dependent on the initial volume of the liquid annulus rather
than on the partial pressure of vapor around the annulus. Figure 3-6 schematically shows
the liquid annulus formed between a particle and a flat surface separated by a distance H
and Figure 3-7 shows the same system at contact. Corresponding to Figures 3-6 and 3-7
and according to Marmur [54] and de Lazzer et al. [55], the adhesion force, $F_{\text{ads}}$, between
a spherical particle of radius $R$ and a flat substrate, connected by a liquid annulus, is the
sum of two forces. The classical DLVO forces are not considered, as they would be much smaller compared to capillary forces that act at much larger distances.

Figure 3-6. A schematic of a liquid bridge between a spherical particle and a planar substrate.

Figure 3-7. Illustration of the geometry of a liquid bridge between a smooth spherical particle and a smooth substrate at the point of contact.

The first force, $F_{AP}$, is the result of the pressure difference, $\Delta P$, across the meniscus due to its curvature and the second force, $F_\gamma$, is the vertical component of the surface tension acting tangentially to the liquid/air interface, given as
where $x$ is the horizontal distance from the center of the annulus to its intersection with
the adhering particle, $\gamma$ is the surface tension of the liquid, $\theta_p$ is the contact angle between
the liquid and the particle, and $\alpha$ is the angle formed between the axis of interaction and
the line of intersection between the meniscus and the particle. If $r$ is the smaller radius of
curvature of the capillary, $\Delta P$ may be substituted from the Laplace equation [53]

$$\Delta P = \gamma(1/x - 1/r) \quad (3-8)$$

yielding

$$\frac{F_{ad}}{R} = \pi \gamma x' \left\{ 1 - \frac{x' \left[ \cos(\theta_p + \alpha) + \cos \theta_s \right]}{H' + 1 - \sqrt{1 - x'^2}} - 2 \sin(\theta_p + \alpha) \right\} \quad (3-9)$$

where $R$ is the radius of the adhering particle, $\theta_s$ is the contact angle between the liquid
and the substrate, $x'$ is the scaled annulus size ($x' = x/R$), $H'$ is the scaled separation
distance ($H' = H/R$) and $H$ is the separation distance between the adhering particle and
the flat substrate. The angle $\alpha$ may be calculated by,

$$\alpha = \arctan \left( \frac{x'}{\sqrt{1 - x'^2}} \right) \quad (3-10)$$

It should be noted that de Lazzer et al. [55] graphically present the theoretical
dependence of adhesion force as a function of $x'$, based on semi-emperical correlations,
but do not develop the analytical expression for this dependence.

Israelachvili [61] also suggested a simple formula for capillary force as a function
of distance, which should be valid for a small and constant volume of liquid annulus.
However, this formula includes the value of $d$, shown in Figure 3-6, which, in turn,
depends on the distance $H$. Thus, the formula given by him requires knowing the
relationship between d and H. In the limit of a small liquid annulus compared to adhered particle radius ($x' \ll 1$) and contact between the particle and substrate, it is possible to obtain the classic approximate equation of capillary adhesion force

$$\frac{F_{ad}}{R} = -4\pi \gamma \cos(\theta) - 2\pi \gamma x' \sin(\theta + \alpha)$$  \hspace{1cm} (3-11)

Using the above approximation, for non-zero separation distances (and neglecting the second term, the force due to surface tension, which is relatively small for small contact angle) Eq. (3-6) is obtained. Usually in the case of binders added to avoid segregation, the contact angle of the liquid with the particle (powder) is small to ensure good wetting. In the current study, the contact angle of the oil with the glass and silica particles used was 0-10°.

The principal difficulty in using Eq. (3-9) or (3-11) to predict adhesion force is that the experimental scaled size of the annulus, $x'$, is often unknown. Furthermore, de Lazzer et al. [55] suggest that variables $x'$ and the scaled separation distance, $H'$, are independent of each other. For many systems this is not the case. The relationship between $x'$ and $H'$ in reality will depend on boundary conditions necessitated by a particular experimental system. As mentioned previously, if the detachment process is much faster than evaporation, then the volume of liquid in the annulus will remain relatively constant as the two surfaces are separated. This limiting case should be applicable also to non-volatile systems such as oil droplets. The alternative limiting case, related to thermodynamic equilibrium between the annulus and media, is more common for systems of volatile liquids (such as water) when detachment rates are slower. For these systems the maximum stable radius of the meniscus is determined by the Kelvin equation and a boundary condition of a constant radius should be employed. Note, that the
constant volume or constant radius boundary conditions are not only possible in gaseous atmospheres but should also be valid in semi-miscible liquid mixtures [57]. The next two sections describe methodologies to implement these different boundary conditions.

**Relationship between $x'$ and $H'$ for constant volume annulus**

According to Figure 3-6, the volume, $V$, of a non-volatile liquid annulus may be approximately calculated through geometrical methods [62] as:

$$V = \pi x^2 y - (1/3)\pi(y-H)(3R-y+H) \tag{3-12}$$

where $y$ is the vertical distance from the flat substrate to the intersection of the meniscus with the particle, $x$ is the horizontal distance between the interaction axis $y$ and the intersection of the meniscus with the particle, $H$ is the minimum vertical distance between the sphere and flat substrate, and $R$ is the radius of the adhering particle. For a spherical particle, $x$ and $y$ can be related as:

$$\frac{y}{R} = \frac{H}{R} + 1 - \sqrt{1 - \left(\frac{x}{R}\right)^2} \tag{3-13}$$

Substituting Eq. (3-13) in Eq. (3-12) and assuming that $x' = x/R << 1$ (in order to limit the series expansion), the following bi-quadratic equation is obtained:

$$x'^4 + 4H'x'^2 - \frac{4V}{\pi R^3} = 0 \tag{3-14}$$

whose solution relative to $x'$ is:

$$x' = \sqrt{-2H' + 2\sqrt{H'^2 + \frac{V}{\pi R^3}}} \tag{3-15}$$

With this relationship the dependence of the capillary force of adhesion, $F_{ad}$, on the scaled separation distance, $H'$, given by Eq. (3-9) can be solved, using $\alpha$ calculated by Eq. (3-10) and $x'$ from Eq. (3-15).
**Relationship between \(x'\) and \(H'\) for constant radius annulus**

According to Figures 3-6 and 3-7, the following relation is obtained

\[
\frac{y}{R} = \frac{r}{R} \left[ \cos(\theta_s) + \cos(\theta_p + \alpha) \right] \tag{3-16}
\]

where \(y\) is the vertical distance from the flat substrate to the intersection of the meniscus with the particle, \(R\) is the radius of the adhering particle, \(r\) is the smaller radius of curvature of the meniscus, \(\theta_s\) is the contact angle between the liquid and substrate, \(\theta_p\) is the contact angle between the liquid and particle, and \(\alpha\) is the angle formed between the axis of interaction and the line of intersection between the meniscus and the particle.

Using Eq. (3-13) for small values of the scaled capillary size, \(x'\), and Eq. (3-16), the capillary radius is derived as

\[
\frac{r}{R} = \frac{H' + 0.5x'^2}{\cos(\theta_s) + \cos(\theta_p + \alpha)} \tag{3-17}
\]

For contact between the surfaces, Figure 3-7, \((H = 0\) and hence \(H' = 0\)), it follows from Eq. (3-15) that

\[
x'_0 = 4 \sqrt[4]{\frac{4V_0}{\pi R^3}} \tag{3-18}
\]

where the subscript 0 indicates zero separation distance. Substituting Eq. (3-18) in Eq. (3-17), the following expression for the capillary radius at zero separation distance, \(r_0\), is obtained

\[
\frac{r_0}{R} = \sqrt[4]{\frac{V_0 / \pi R^3}{\cos(\theta_s) + \cos(\theta_p + \alpha)}} \tag{3-19}
\]

where
\[ \alpha_0 = \arctan \left( \frac{x'_0}{\sqrt{1 - x'^2_0}} \right) \tag{3-20} \]

and \( V_0 \) is original volume of the annulus at contact. Note that for this boundary condition radius is constant so for all separation distances \( r = r_0 \). Therefore, Eq. (3-19) is equivalent to Eq. (3-17) and the relationship between \( x' \) and \( H' \) becomes

\[
x' = \sqrt{\frac{2\sqrt{V_0 / \pi R^3} \left[ \cos(\theta_s) + \cos(\theta_p + \alpha) \right]}{\cos(\theta_s) + \cos(\theta_p + \alpha)}} - 2H'^2 \tag{3-21}
\]

Hence, as for the constant volume annulus boundary condition, the adhesion force for an annulus of constant radius can be predicted from Eqs. (3-9) and (3-10) but with the value of \( x' \) from Eq. (3-21) instead of Eq. (3-15). Note that the capillary force of adhesion as a function of separation distance can also be calculated for a constant meniscus radius boundary condition using Eq. (3-6) in combination with Eq. (3-19) for the radius. It should be noted that this equation does not account for the surface tension component of the capillary force, as it was neglected for small contact angle. An experimental comparison between these two approaches for a fixed radius of meniscus is presented below.

**Experimental**

**Materials**

Adhesion force was measured between 20-50 \( \mu m \) glass microspheres from Duke Scientific Corp. and silica substrates. The spheres were found to have a Root Mean Square (RMS) roughness of less than 0.2 nm. Silica substrates were provided by Dr. Arwin (Linköping University, Sweden) and were fabricated from 180 nm thick oxidized
silicon wafers of 0.2 nm RMS roughness. All silica surfaces were cleaned by rinsing in acetone, methanol, and DI water. Cleaning was performed immediately prior to experimentation. Also before each experiment, particles were glued to tapping mode TESP rectangular atomic force microscopy (AFM) cantilevers, supplied by Digital Instruments Inc. using a low melting temperature resin, Epon R 1004f from Shell Chemical Company. White mineral oil of “Sharpening Stone” grade was obtained from Norton Co., Littleton, NH, and was used to form the liquid interlayer between the particle and substrate. The viscosity of the oil was 25x10⁻³ Pa.sec as measured by capillary viscometer. The contact angle of oil on the silica surfaces ranged from 0º to 10º. These very low contact angles suggest that the oil may be partially hydrophilic.

Methods

Surface forces were measured on a Digital Instruments Nanoscope IIIa AFM according to the methods described by Ducker et al. [63]. The spring constant ‘k’ for each cantilever was calibrated by the frequency method, suggested by Cleveland et al. [64]. The average value of ‘k’ was near 27 mN/m, however, individual values of ‘k’ were used for each cantilever. The sphere, attached to a cantilever of known spring constant, was positioned close to the flat substrate. Then, as the substrate was moved towards and away from the particle by a piezoelectric scanner, the deflection of the cantilever was monitored by a laser that reflected from the top of the cantilever onto a position sensitive photodiode. In this manner, the force between the two surfaces as a function of separation distance was obtained. The force/distance profiles were normalized by dividing the measured force by the radius of the sphere. In other words, the data are presented in terms of energy per unit area of flat surfaces. This enables determination of the force for
different geometries and sizes of particles as long as the range of the forces is much less than the radius of curvature of the particles.

To create the oil droplets, several larger drops on the order of a few millimeters were placed on the flat silica substrate. These drops were then disrupted by a gas jet that left many small droplets of a few micrometers in size. In order to predict the adhesion force for either boundary condition described above, the initial volume of the capillary must be known. For the case of condensation of vapor or a semi-miscible liquid in a capillary this can be derived from the geometry of the capillary and Kelvin’s equation. For non-volatile liquids (oil) the volume is dependent on the size of the oil droplets present on the surface and cannot be predicted from theory.

Fortunately, in the present experimental system, the oil volume can be estimated from the experimentally observed distance at which the oil drops present on the substrate and the particle first touch. At this separation distance, \( H_c \), there is a sudden jump in the force-distance profile as the two oil drops begin to coalesce. The geometry of the liquid drop on a flat surface is shown in Figure 3-8. Based on this geometry, the volume of the drop, \( V_d \), can be calculated as

\[
V_d = \frac{\pi H_d^3}{3} \left( 1 + \frac{1}{1 - \cos \theta} \right)
\]

(3-22)

where \( H_d \) is the height of an oil droplet on each of the surfaces and \( \theta \) is the contact angle. Note that in this approach the thickness of any wetting film is considered to be significantly smaller than \( H_d \). However, spreading of the oil film and its thickness is described, for example, in Ref. [65].
Assuming that the radius of the liquid annulus is small compared to the radius of the particle and that the size of the droplets on the substrate and the particle is equal, the annulus volume $V$ can be calculated using the experimental value of $H_c$, where $H_c$ is twice the individual droplet size.

$$V = 2V_d = \frac{\pi H_c^3}{12} \left(1 + \frac{1}{1 - \cos \theta}\right)$$  \hspace{1cm} (3-23)

**Results and Discussion**

Force/distance profiles were obtained upon approach and retraction of the two surfaces. If the viscosity of the oil is too high, then a hydrodynamic term should be included in the force/distance profile. To make sure that this is not the case, the detachment of the surfaces was measured at different rates (0.1, 0.75, 1.9, and 10 Hz). The detachment velocity can be calculated from twice the scan size ($2.5 \mu m$) multiplied by rate of detachment, which yields speeds of 0.500, 3.75, 9.5 and 50 $\mu m/s$ respectively for the four scanning rates. These results are presented in Figure 3-9. The differences between the measurements are small compared to the inherent noise in the system. This conclusion is also supported by theoretical calculation. For example, for a sphere in oil (with a dynamic viscosity $25 \times 10^{-3} \text{ Pa.sec}$) at a maximal velocity $50 \mu m/s$, Stokes’ formula yields a normalized viscous resistance force equal to 0.024 mN/m, which is
much less than the experimentally measured value (tens to hundreds of mN/m). Hence it can be concluded that the hydrodynamic force is significantly smaller than the capillary force, and can be ignored under present experimental conditions. If the binder used was viscous enough to provide a significant contribution due to hydrodynamic forces, the analytical expression developed for predicting the adhesion force can be modified to include the viscous force. A detailed description on quantification of viscous forces can be found in a recent study by Rabinovich et al. [66].

Force curves were obtained for different samples, drop sizes, cantilevers, and even using two different AFM instruments. The force/distance profiles presented in Figures 3-10, 3-11 and 3-12 were measured at a rate of 0.75-1 Hz. Each curve was measured on a different day with fresh samples. Note also that the particle size (14 to 25 µm radius) and the oil droplet volume (approximately 7x10^8 to 180x10^8 nm^3) are significantly different for various measurements.

The example in Figure 3-12 was obtained from a second AFM. In Figure 3-10, both the approaching and retracting curves are shown. As can be clearly seen in Figure 3-10, at some separation distance, corresponding to H_c, there is a jump in the approaching force/distance profile. This jump corresponds to the formation of a stable liquid annulus between the particle on the AFM tip and the substrate. After the jump, the approaching curve follows an equilibrium path until contact. Upon retraction of the two surfaces the adhesion force is observed to have the same form as the approaching curve. This suggests that the forces being measured are indeed primarily due to a capillary force at a near mechanical equilibrium state for a given separation distance.
Figure 3-9. Retracting (detaching) interaction force profiles normalized by particle radius as a function of separation distance for a particle radius of 14 µm. The four detachment rates shown (0.1; 0.75; 1.9 and 10 Hz) correspond to speeds of 0.500, 3.75, 9.5 and 50 µm/s, respectively, and are identical within the resolution of the technique. This indicates that effects from the viscosity of the oil (25x10^{-3} Pa.sec) are small compared to the equilibrium capillary forces.

The jump indicates that the process, whereby the capillary first forms, is much faster than the approach rate. It should also be noted that upon retraction the annulus does not break at $H_c$; rather the liquid continued to stretch to larger separation distances.

Usually the force at which the meniscus broke in the retracting curve was too small to be observed as compared to the background noise. However, in some cases a distinct jump
back to zero interaction force was observed. The distance at which these breaks occurred was not always consistent.

![Figure 3-10. Comparison of theoretical and experimental capillary force/distance profiles. Thick profiles are the approaching and retracting interaction forces normalized by particle radius as a function of separation distance for a particle radius of 14 µm. Curve 1 is the predicted capillary adhesion force profile derived under a constant annulus volume boundary condition from Eqs. (3-9), (3-10) and (3-15). Line 2 is derived from Eqs. (3-6) and (3-19) for a constant meniscus radius boundary condition where the surface tension component is neglected. Line 3 is derived from Eqs. (3-9), (3-10) and (3-21) for a constant meniscus radius boundary condition where the surface tension component is taken into account. The fitting value of the volume of the liquid annulus is equal to 80x10⁸ nm³ and surface tension to 27.5 mN/m. Contact angle θₘ = θₚ = 10°.](image-url)
Figure 3-11. Comparison of the theoretical and experimental capillary force profiles of a 25 µm particle. Thick profile is the retracting interaction force normalized by particle radius as a function of separation distance for a particle radius 25 µm. Curve 1 is the predicted capillary adhesion force profile derived from Eqs. (3-9), (3-10) and (3-15) under a constant annulus volume boundary condition. Line 2 is derived from Eqs. (3-6) and (3-19) under a constant meniscus radius boundary condition where the surface tension component is neglected. Line 3 is derived from Eqs. (3-9), (3-10) and (3-21) under a constant meniscus radius boundary condition where the surface tension component is taken into account. The fitting value of the volume of the liquid annulus is equal to 170x10^8 nm^3 and surface tension to 25.5 mN/m. Contact angle \( \theta_s = \theta_p = 10^\circ \).
Figure 3-12. Capillary force measurement between a 14 µm particle and a substrate, theoretical and experimental results. Thick profile is the experimental retracting interaction force normalized by particle radius as a function of separation distance for a 14 µm particle. Curve 1 is the predicted capillary adhesion force profile derived under a constant annulus volume boundary condition from Eqs. (3-9), (3-10) and (3-15). Line 2 is derived from Eqs. (3-6) and (3-19) under a constant meniscus radius boundary condition where the surface tension component is neglected. Line 3 is derived from Eqs. (3-9), (3-10) and (3-21) under a constant meniscus radius boundary condition where the surface tension component is taken into account. The fitting value of the volume of the liquid annulus is equal to $7 \times 10^8$ nm$^3$ and surface tension to 26.0 mN/m. Contact angle $\theta_S = \theta_P = 0^\circ$. 
Practically, the jump back distance indicates the maximum distance of operation of the capillary force, and the larger the distance the greater the work done in separating the two surfaces.

Also shown in Figures 3-10, 3-11 and 3-12 are the theoretical predictions suggesting an annulus with a constant volume boundary condition (based on Eqs. (3-9), (3-10) and (3-15): curves #1 in Figures 3-10, 3-11 and 3-12), a line suggesting a constant capillary radius without the surface tension component (from Eqs. (3-6) and (3-19): curves #2 in Figures 3-10, 3-11 and 3-12), and a line suggesting a constant capillary radius with the surface tension component (from Eqs. (3-9), (3-10) and (3-21): curves #3 in Figures 3-10, 3-11 and 3-12). As expected for the case of an oil droplet, although the lines representing the constant annulus radius condition (lines #2 and #3) adequately predict the maximum adhesion force (at contact), they do not describe the adhesion force profile as a function of separation distance well. Furthermore, a significantly lower energy of adhesion (integral of the force profile) would be predicted for this case than from the theory for constant annulus volume. The relatively small difference between these two curves #2 and #3 should be related to different approximations made in Eqs. (3-6) and (3-9) and to the surface tension component of the capillary adhesion force. As shown in Figure 3-12, this difference disappears for contact angle $\theta_S = \theta_P = 0^\circ$. Though the relationships presented differentiate the contact angle for the surface ($\theta_S$) and the particle ($\theta_P$), in practice the two surfaces would be the same (in a powder) and hence $\theta_S = \theta_P$. Usually, the binder added would wet the particles and the contact angle is expected to be low (0-10°).
In Figures 3-10, 3-11 and 3-12, the theoretical predictions arising from the constant annulus volume boundary conditions (curve #1) seem to better fit the experimental data. This indicates that the approximations made in the above derivations are appropriate for this system and that the principal origin of the adhesion is the annulus formed between the two surfaces by the oil. Furthermore, it seems that the rate of detachment is slow enough that at non-zero separation distances the liquid annulus is able to form a meniscus defined by the geometry of the capillary, the volume of the oil, and its surface tension. It is also noted that calculation on the basis of the formula suggested by Israelachvili [61] is in good agreement for constant volume case as shown by curve #1.

As observed in the presented graphs, there is a large difference in behavior for the constant volume (curve #1) or constant radius (curve #2 or #3) boundary conditions as a function of separation distance. This difference may be especially important in the modeling of powder flow. For powder flow it should be the energy (integral of the force profile) of adhesion during the detachment process that controls the bulk behavior. For example, if a water filled capillary and an oil filled capillary were to provide a similar maximum adhesion force, the energy needed to separate the two would be quite different, leading to dramatic differences in handling characteristics such as flow of powders. Also to initiate powder flow or remove particles from a surface, different forces would have to be applied. For example, a mechanical oscillation would have to be applied which is not only enough to overcome the capillary adhesion, but also its duration must be long enough (or amplitude large enough) to allow the liquid annulus between the two surfaces to be broken. These concepts as they relate to powder flow in the presence of capillary forces will be discussed in the chapters 4 and 5.
The theoretical predictions described above depend on two variables, the volume of the liquid annulus and the surface tension of the liquid; and the former is not known experimentally. Each measured capillary adhesion profile and the ones presented in Figures 3-10, 3-11 and 3-12 was fitted using the various values of these two variables. For all the measured adhesion profiles, the fitting value of surface tension used was 26.5 ± 2 mN/m. However, using the Wilhelmy plate technique [53] with a platinum blade, the surface tension was found to be 30 ± 0.5 mN/m. Although these values are close, the difference may represent a systematic error associated with the calibration of the AFM cantilever.

The volume of the liquid annulus was also used as a fitting parameter in the prediction of the adhesion force curves. However, as described earlier, Eq. (3-23), this volume can also be calculated based on the distance upon which the liquid droplets on the two surfaces first make contact, H_c. A comparison of the fitted annulus volume and H_c using Eq. (3-23), should show a cubic dependence and can be used to extract a value for the contact angle. Figure 3-13 shows this correlation (on a log/log scale) for a number of experimentally measured force profiles. The straight line has a slope of 3 indicating cubic dependence and adequate correlation. Moreover, the intersection of the correlation line with the ordinate axis can be used to calculate the contact angle from Eq. (3-23).

The calculated value of 3.7°, fits well with the measured values which fell between 0 and 10° for oil on the silica surface. Hence, it appears that the approximations developed in this investigation are reasonable for modeling capillary adhesion forces between surfaces mediated with oil.
Figure 3-13. Fitting value of the volume of liquid annulus (for a constant volume liquid bridge, boundary condition) as a function of the critical separation distance \( H_c \). The point of first contact, \( H_c \), is determined from the approaching interaction force profiles. Symbols are experimental values and line is a best fit with a slope of 3 on the log scale. That \( H_c \) and the fitting annulus volume have cubic dependence indicates that Eq. (18) is valid. Furthermore, from the line’s intercept at the ordinate axis and Eq. (18) the contact angle of the oil on glass is found to be 3.7° which correlates well with the measured values which ranged from 0-10°.

**Conclusions**

In the above discussion, the role of the capillary force produced by an oil annulus between surfaces and its influence on adhesion and powder mechanics was explored. Although the maximum adhesion force has been investigated in the literature for a number of systems, the distant dependent nature of the capillary force has not been verified experimentally. In order to interpret this behavior, a simplified theoretical model of the capillary force of adhesion as a function of separation distance was developed with
boundary conditions for a constant volume and constant radius liquid bridge. For surfaces
with intervening oil droplets, the boundary condition of a constant volume liquid bridge
was found to correspond to the experimental data. The approach for theoretical
estimation of capillary force based on the calculation of the energy of interaction (by
Israelachvili) assumes thermodynamic and mechanical equilibrium between the two
surfaces during detachment. The agreement between the approach based on the pressure
difference across the liquid bridge, as discussed in the current study, and the Israelachvili
approach shows that for the current system the oil droplets during the detachment process
approximated the mechanical equilibrium state for surfaces separated by a specific
distance.

Based on the analytical expression developed for prediction of capillary force, the
effect of variables such as the binder polarity (wettability), surface tension and viscosity
on the adhesion force is well understood. The general guidelines to choose a binder for a
particular system would be: to ensure good wetting of the particles by the oil (polar or
non-polar depending on the type of powder), tailor the surface tension based on the
strength of adhesion required (higher surface tension leading to greater adhesion). The
calculation of the distance dependent capillary force of adhesion is expected to be
important in the prediction of adhesion energy required to significantly control the flow
behavior of powder systems. The incorporation of the analytical expression developed for
prediction of capillary force towards calculating the work done in shearing a powder
sample will be discussed in Chapter 5.
CHAPTER 4
CAPILLARY FORCES BETWEEN TWO SPHERES WITH A FIXED VOLUME LIQUID BRIDGE

Introduction

One of the most common and simple geometry for estimation of the capillary force is the sphere / plate interaction. The extrapolation of the theoretical expressions, for estimation of the capillary force, from the sphere / plate geometry to the sphere / sphere geometry is not straightforward. The formulae for interaction of two spheres separated by a liquid bridge are also developed in the present study and their predictions are compared against experimentally measured values using the AFM. The results of the calculations based on the sphere / sphere interaction formulae are discussed from the point of view of the Derjaguin approximation [67].

Experimental

Materials

Capillary forces between glass spheres of 20-50 µm diameter glass (from Duke Scientific Corp.) and silica substrates were measured using a Digital Instruments AFM as described in Chapter 3. Glass spheres were also glued to a silica substrate using a two-part epoxy adhesive.

Methods

The force (given by the cantilever deflection times the spring constant) between the two surfaces was measured as a function of the separation distance. The force/distance profiles were normalized with respect to the radius of the sphere. In other words, the data
is presented in terms of energy per unit area of the flat surface. This enables
determination of the force for different geometries and size of particles, as long as the
range of the forces is less than the radius of curvature of the particles.

**Theoretical Calculation of Capillary Adhesion Force between Sphere and Plate for a
Liquid Bridge of Fixed Volume**

As discussed in the previous chapter (# 3), an expression for calculation of the
capillary force between a sphere and a plate separated by a liquid bridge of small fixed
volume, \( V \), is given by

\[
F_{\text{sp/pl}} = -\frac{4\pi \gamma R \cos \theta}{1 + H / d_{\text{sp/pl}}} - 2\pi \gamma R \sin \alpha \sin(\theta + \alpha)
\]

where \( \gamma \) is the liquid surface tension, \( \theta \) is contact angle, \( \alpha \) is “embracing angle”, \( H \) is the
shortest distance between the sphere and the plate (see Figure 3-6). The above expression
is similar to the derivation by Israelachvili [61] except that the second term on the right
hand side of Eq. (4-1) was not included. This term is the force due to vertical component
of the surface tension of the liquid bridge [54,55]. This force does not play a significant
role in the case of a small volume liquid bridge, i.e., \( \alpha < < 1 \).

Rabinovich et al. [68] derived an expression for determining \( d_{\text{sp/pl}} \), as

\[
d_{\text{sp/pl}} = -H + \sqrt{H^2 + V / (\pi R)}
\]

On the other hand, it follows from the geometry as shown in Figure 3-6, that

\[
d_{\text{sp/pl}} = R \alpha^2 / 2
\]

Comparing Eqs. (4-2) and (4-3), we obtain the following relationship between the
embracing angle, \( \alpha \), and the liquid bridge volume, \( V \),

\[
\alpha_{\text{sp/pl}}^2 = \frac{2H}{R} \left( -1 + \sqrt{1 + \frac{V}{\pi RH^2}} \right)
\]
Equation (4-1) can be further simplified for the cases of short and long separation distances. Namely, for short H, when

\[ \frac{V}{\pi RH^2} >> 1, \]

Eqs. (4-1) and (4-2) combined, result in

\[
F_{sp/pl}^{\text{tot}} = -\frac{4\pi\gamma R \cos \theta}{1 + H\sqrt{\pi R/V}} - 2\pi\gamma R \sin \alpha \sin(\theta + \alpha) \tag{4-5}
\]

For long separation distance H, the expression is modified as,

\[
F_{sp/pl}^{\text{tot}} = -\frac{2\gamma V \cos \theta}{H^2} - 2\pi\gamma R \sin \alpha \sin(\theta + \alpha) \tag{4-6}
\]

Note, that in Eq. (4-6) the first term on the right hand side is independent of the radius of the sphere, R. Depending on the packing structure and the distance of displacement of the particles in a powder, the use of the appropriate expression for the force would lead to a reliable prediction of the adhesion force. For example, in a powder with large particles (larger than 300 µm) with very low binder content (less than 0.1 wt%), Eq. (4-6) for large separation distance would be applicable.

The derivation by Israelachvili was based on the total energy of the liquid bridge, given by

\[
W_{\text{tot,sp/pl}} = -2\pi\gamma R^2 \alpha^2 \cos \theta \tag{4-7}
\]

In this equation, only the energy of the solid surface under the liquid bridge is taken into account and the energy of the surface of the meniscus itself is ignored. As a result, Israelachvili [61] obtained Eq. (4-1) for \( F_{sp/pl} \) with only the first term on the right hand side of the equation.

However, to check the validity of Eq. (4-1) for a thermodynamically non-equilibrium process as the separation of a fixed volume bridge, Rabinovich et al. [32]
developed the following formulae based on the pressure difference inside and outside the liquid bridge

\[
F_{p/p_l}/R = \pi \gamma x' \left[ 1 - \frac{x \left[ \cos(\theta_p + \alpha) + \cos \theta_f \right]}{H' + 1 - \sqrt{1 - x'^2}} \right] - 2 \sin(\theta_p + \alpha)
\]  \tag{4-8}

\[
\alpha = \arctan \left[ x'/(1 - x'^2) \right]
\]  \tag{4-9}

\[
x' = \sqrt{-2H' + 2\sqrt{H'^2 + V/\pi R^3}}
\]  \tag{4-10}

where \(\theta_p\) and \(\theta_f\) is the contact angle of liquid on the particle and the flat surface, respectively, \(x' = x/R\), where \(x\) is one of the liquid bridge radii (as shown in Figure 3-6), and \(H' = H/R\).

The theoretical capillary force calculated using Eqs. (4-1), (4-2) and (4-4), and Eqs. (4-8)-(4-10), is compared in Figure 4-1. The two pairs of curves relate to two different liquid bridge volumes. The two curves in each set are in good agreement, suggesting that either of the two approaches (Israelachvili or Rabinovich et al.) is applicable for prediction of the capillary force.

The curves shown in Figure 4-1 were plotted using the radius of the particle as measured by optical microscopy. The other variables such as the surface tension assumed as 26 mN/m was independently measured to be 30 ± 0.5 mN/m, contact angle assumed as 10° and the measured values ranged from 0-10°, thereby validating the values used as fitting parameters for the two sets of curves.
Figure 4-1. Theoretical capillary force/distance profiles of sphere/plane interaction. The two sets of curves (1 and 3) and (2 and 4) are theoretical estimates based on [Eqs. (4-8), (4-9) and (4-10)] and [Eqs. (4-1), (4-2) and (4-4)] respectively. The following parameters are used: for curves 1 and 2, radius of sphere, R, is 12 µm, volume of the liquid bridge, V = 7x10^8 nm^3, and the contact angle θ = 0°; for curves 3 and 4, the radius R=25 µm, V = 170x10^8 nm^3 and θ =10°. Surface tension of oil γ = 26 mN/m. The agreement of the two sets of curves confirms the validity of either approach (total energy and the pressure difference across the bridge) for estimation of the capillary force.

However, at zero separation distance, H = 0, the difference ΔF (H) between the forces calculated using the two sets of equations is given by

\[ ΔF(H = 0) = -πγRα(1 + 2\sin θ + \alpha \cos θ) \] (4-11)

where (for H = 0)

\[ \alpha^2 = 2\sqrt{V/(πR^3)} << 1 \]

For small α and low contact angle θ, the force difference given by Eq. (4-11) is small as compared with the total capillary force. However, for θ > 90° (which is the case for mixture of hydrophobic particles) the total capillary force is small, as a result, the magnitude of ΔF can be comparable to the total force. In our opinion, the difference
between the forces calculated using the two sets of formulae is a result of the inherent assumptions made in the development of the equations (4-1) and (4-8), rather than due to a difference in the approaches of Rabinovich [32] and Israelachvili [61]. Reasonable agreement between these equations (as shown in Figure 4-1) proves that Eq. (4-7) for total energy of annulus is correct for process of separation of sphere/plane with annulus of fixed volume.

**Theoretical Calculation of Capillary Force between Two Spheres**

The Derjaguin approximation [67] can be used to calculate the force of adhesion between two spheres (as shown in Figure 4-2) or the sphere / plane geometry (Figure 3-6), as given by

\[ F(H) = kRU(H) \]  \hspace{1cm} (4-12)

where \( k = \pi \) or \( 2\pi \) for interaction of two spheres or sphere / plane, respectively; \( U(H) \) is specific energy (per unit area) of interaction of two flat surfaces at a separation distance of \( H \). However, the application of the Derjaguin approximation for the case of two different surface energies, the energy of interaction through inside of the liquid bridge and the dry interaction outside, is not clear.

Taking into account the specific energy, \( U \), acting through a liquid layer at the point of contact,

\[ U = -2\gamma \cos \theta \]  \hspace{1cm} (4-13)

The force for the sphere/plate interaction based on Eq. (4-12) is given by

\[ F_{sp/pl}(H = 0) = -4\pi \gamma R \cos \theta \]  \hspace{1cm} (4-14)

which corresponds to the first term of Eq. (4-1) at \( H = 0 \).
However, at $H \neq 0$, the Derjaguin approximation for capillary force is invalid, as it follows directly from a comparison of Eqs. (4-12) and (4-1). In distinction from Eq. (4-12), Eq. (4-1) shows that $F_{sp/pl}$ is not proportional to the sphere radius $R$, because the value of $d_{sp/pl}$ depends on the sphere radius. Moreover, for the limiting case of large separation distance (given by Eq. (4-6)), it follows that the first term of the total capillary force is independent of the radius of the sphere.

The validity of the Derjaguin approximation for capillary force was also studied by Willett et al. [69], concluding that the approximation is valid for $H = 0$ and for very large distances and inapplicable at intermediate distances. This conclusion (at least for $H = 0$) has been on the basis of the proportionality of the capillary force to the sphere radius.
However, as is clear from the above discussion, the proportionality of the capillary force to the radius is a necessary, but not a sufficient condition for the validity of the Derjaguin approximation. Moreover, at large separation distances (Eq. (4-6)), the force is not proportional to the radius. Therefore, we believe that the Derjaguin approximation for capillary force is valid only at $H = 0$ and invalid for any finite separation distance. One of the possible reasons for the invalidity is that the capillary force acts in a restricted area under the liquid bridge and this area changes with the separation distance, $H$. As a result the integral method used in the Derjaguin approximation is not applicable for the capillary liquid bridge.

An alternative method to derive the formula for capillary force between two spherical particles is discussed as follows: According to Israelachvili [61], for two spheres, of radius $R$ and contact angle $\theta$, the total energy of the liquid bridge is given by Eq. (4-7). The force between the two spheres with a liquid bridge derived from the total energy is

$$ F_{sp/sp}(H,V) = -\frac{dW}{dH} = 4\pi R^2 \alpha \gamma \cos \theta \frac{d\alpha}{dH} \tag{4-15} $$

The volume of the liquid bridge between the two spheres is given by

$$ V_{sp/sp} = \pi R^2 \alpha^2 H + 0.5 \pi R^3 \alpha^4 \tag{4-16} $$

For a fixed volume of the liquid bridge, $dV/dH = 0$ and from Eq. (4-16)

$$ \frac{d\alpha}{dH} = \frac{-1}{(2H/\alpha) + 2R\alpha} \tag{4-17} $$

Combining Eqs. (4-15) and (4-17), the following equation for the force between the two spheres is obtained
Accounting for the attraction force due to the vertical component of the liquid bridge, the complete formula for the capillary force is given by

\[ F_{sp/sp}(H,V) = -\frac{2\pi R \gamma \cos \theta}{1 + (H / 2d_{sp/sp}(H,V))} - 2\pi \gamma \sin \alpha \sin(\theta + \alpha) \]  

(4-19)

The value of \(d_{sp/sp}(H, V)\) for the interaction of two spheres can be obtained from Eq. (4-16) as,

\[ d_{sp/sp}(H, V) = (H / 2) \times [-1 + \sqrt{1 + 2V / (\pi RH^2)}] \]  

(4-20)

Validity of this approach is evaluated by comparing experimental data and the theoretical force values calculated using Eq. (4-19), as discussed in the following section.

**Experimental Results for Sphere/Sphere Capillary Force**

A comparison of experimentally measured capillary force between two spheres and theoretically calculated force values is shown in Figure 4-3. The experimental force/distance curves were obtained using the AFM for spherical particles of radius 19 - 35 \(\mu\)m. Theoretical curves plotted in Figure 4-3 are based on Eqs. (4-19) and (4-20) with the volume of the liquid bridge, \(V\), as a fitting parameter. Due to lack of theoretical formulae for capillary force between two unequal size spherical particles, an effective particle radius was used [67]

\[ R_{\text{eff}} = \frac{2R_1R_2}{R_1 + R_2} \]  

(4-21)

Although the effective particle radius is based on the Derjaguin approximation, it is used as a first approximation for estimating the capillary force between two unequal sized spheres.
Figure 4-3. Experimental (points) and theoretical (solid curves) for the capillary force between two silica spheres. The radius of the spheres are $R_1 = 19 \, \mu m$ and $R_2 = 35 \, \mu m$ (curve 1), $32.5 \, \mu m$ (curve 2) and $27.5 \, \mu m$ (curve 3). Theoretical curves are estimates based on Eqs. (4-19) and (4-20) with surface tension, $\gamma = 27$, 24 and 28 mN/m and volume of the liquid bridge, $V = 2$, 12 and $36 \times 10^8 \, nm^3$ (for curves 1, 2 and 3, respectively). The contact angle between the oil and the spheres was, $\theta = 10^\circ$. A good agreement between theoretical and experimental data proves validity of developed equations (4-19) and (4-20) for sphere/sphere capillary interaction.

To account for the variation in the experimentally measured forces, due to the use of different set of cantilevers and particles, the surface tension $\gamma$ was also used as a fitting parameter. The experimentally measured value of surface tension was 27.5 mN/m. As seen from Figure 4-3, for three different liquid bridge volumes, the theoretical (solid line) and experimental (data points) force curves are in good agreement, hence validating Eqs. (4-19) and (4-20). On the other hand, this verification is semi-quantitative, because of the use of a fitting value for the liquid bridge volume. However, the values for the volume of the liquid bridge used as fitting parameters were found to be in the expected range ($10^8 \, nm^3$) as shown in Figure 3-13, leading to a realistic estimate ($3.7^\circ$) for the contact angle.
of oil on glass. An independent estimation of the volume of the bridge can be obtained from either the point contact of the liquid film on the two interacting surfaces or the point of rupture of the liquid bridge, on the experimental force/distance curves [32].

**Conclusions**

In this chapter, theoretical formulae reported in the literature for the estimation of capillary force due to a liquid bridge were compared. The distance dependence of capillary force can be derived theoretically based on two approaches: the total liquid bridge energy, and the pressure difference across the liquid bridge (Laplace equation). In order to corroborate the application of the two different approaches, experimental measurements of capillary force using an AFM were compared with the theoretical estimates. The experimental and theoretical results are found to be in good agreement.

Most of the theoretical expressions, for capillary forces, reported in literature are based on the sphere/plate geometry for the interaction of the two surfaces. The extension of these expressions to predict the force between two spheres is based on the Derjaguin approximation. The validity of the Derjaguin approximation for estimation of capillary force was studied and it was shown to be applicable only at zero separation distance. An alternative framework for theoretical estimation of capillary force between two spheres was developed, and validated with experimental data. The calculation of the distance dependent capillary force of adhesion is expected to be important in the prediction of the total adhesion energy required to control and modify the flow behavior of powder systems, or in avoiding segregation (enhance binding) in key industrial processes such as mixing.
CHAPTER 5
DEVELOPMENT OF A PREDICTIVE INTERPARTICLE FORCE BASED MODEL

The discussions and results from Chapters 3 and 4 lead to a framework for developing an inter particle force based model to predict the unconfined yield strength of cohesive powders, as described below.

PERC Model

The bulk properties of a powder, such as the unconfined yield strength, $f_c$, and the shear stress, $\tau$, determine the flow behavior of powder. Oil additives, which are used often to avoid segregation of powder, significantly affect the mechanical properties and flowability of the powder. The Particle Engineering Research Center (PERC) model was developed for a system of mono disperse randomly packed, smooth spherical particles. Further refinement of the model in terms of accounting for a polydisperse size distribution and surface roughness were also attempted and are discussed later in this chapter.

The energy of a liquid bridge can be calculated as given by Israelachvili [6],

$$E_i = 2\pi \gamma R^2 \cos \theta \alpha^2$$  \hspace{1cm} (5-1)

where $\gamma$ is the liquid surface tension, $\theta$ is the contact angle and $\alpha$ is the half-embrace angle as shown in Figure 4-7. The correlation between the energy of the liquid bridge and the powder shear stress (or the powder yield strength) is discussed below.

The mechanical properties of the powder were measured using the Schulze cell as discussed in Chapter 2. The calculation of the liquid bridge energy using Eq. 5-1 requires
the value of the embracing angle, $\alpha$, of the bridge which is connected with the bridge volume, $V_1$. In a given sample, the volume $V_1$ can be determined from the concentration of oil in powder, $C$, as follows,

$$V_1 = \frac{8\pi R^3 C \rho_{sol}}{3n \rho_{oil}} \quad (5-2)$$

where $C$ is weight concentration of oil, g/g, $\rho_{oil}$ is the density of oil which is equal to 0.95 g/cm$^3$ and $\rho_{sol}$ is the solid density ($\rho_{quartz}=2.65$ g/cm$^3$ or $\rho_{silica}=2.2$ g/cm$^3$) and $n=6$ is assumed for the number of liquid bridges per particle, i.e., the coordination number. In Eq. 5-2 each liquid bridge is assumed to belong to a pair of particles.

The bridge volume is related to the embracing angle, $\alpha$, as

$$\alpha^2 = \sqrt{2V_1 / \pi R^3} \quad (5-3)$$

The total number of liquid bridges, $N$, in one layer of particles is given by

$$N = A^3 k_r^2 \pi n / (2\pi R^3) \quad (5-4)$$

where $A$ is the area of one layer (i.e., cross sectional area of the Schulze cell) and $k_r=0.64$ is the random volume packing coefficient [70]. Eq. 5-4 takes into account that each bridge belongs to two particles.

Figure 5-1. Schematic of the formation of a shear zone in a powder. The particles in the powder sample are colored to show the formation of a distinctive S-shaped shear zone in the sample.
The initiation of flow in a powder system occurs in a band (zone) of particles, as shown in Figure 5-1, and the bed of particles does not fail at just one layer. The width of the (shear) zone defines the number of layers of particles participating in the flow initiation process [71]. The total energy, $E$, is defined as the energy required for breakage of the liquid bridges during movement of $n_l$-layers (width of the shear zone) of powder by one elementary (unit) step. In the shear zone, $p$, denotes the probability of breakage of liquid bridges in one layer. A value of $p = 1$, would represent the breakage of all liquid bridges in each layer of the shear zone. Then, using Eqs.5-1 through 5-4, the following formula for $E$ is obtained,

$$E = 4A\gamma \cos \theta n_p \sqrt{k_r^2 \frac{Cn\rho_{sol}}{3\rho_{liq}}}$$

The energy $E$ is spent during the movement of $n_l$-layers by an elementary step. The elementary step distance in a randomly packed powder is calculated as the distance between two particles in a hexagonal close packed (which is equal to 2R) powder multiplied by the ratio of the cube root of the corresponding volume packing coefficients ($k_h$ and $k_r$). This elementary step (distance) $l$ is approximately equal to

$$l = 2R \sqrt[k_r]{k_h / k_r}$$

where $k_h = 0.74$ and $k_r = 0.64$ are the hexagonal and random volume packing coefficients [72], respectively.

On the other hand, the mechanical work, $W$, done by the application of the shear stress, $\tau$, in moving $n_l$ layers of particles by one elementary step was calculated as follows

$$W = Al\tau = 2AR\tau \sqrt[k_r]{k_h / k_r}$$

The shear stress, $\tau$, is related to the unconfined yield strength, $f_c$, by Eqn. 2-2.
\[ f_c = \frac{2\tau}{\cos \varphi} \quad (2-2) \]

where \( \varphi \) is the angle between the yield locus and abscissa.

Assuming that the mechanical work \( W \) is equal to the energy \( E \) of breakage of the liquid bridges and using Eqs.5-5, 5-7 and 2-2, the formula for the shear strength was derived as follows

\[ f_c = \frac{4\gamma \cos \theta k_n p}{R^2 k \cos \varphi} \sqrt{\frac{C n \rho_{sol}}{3 \rho_{liq}}} \quad (5-8) \]

As a first approximation, the above formula is valid only for small volume of the liquid bridges, as compared with the particle volume; no friction forces were taken into account; the powder was assumed to be monosize; the volume of each liquid bridge was assumed to be the same; all particle contacts were considered to contain liquid bridges (i.e., there are no dry contacts); and all the liquid exists in the capillary bridges and there is no other liquid film on the particle surface.

The experimentally measured unconfined yield strength was found to be directly proportional to the square root of the liquid binder concentration \( (C^{1/2}) \) and inversely proportional to the particle radius \( (R) \) for a monosize powder system, as shown in Figures 5-2 and 5-3 respectively [73-75]. The validity of the above expression, for a system of monosize smooth glass beads, was established assuming random close packing (coordination number, \( n_c = 6 \)) and the number of shear layers was calculated to be ten, which is in agreement with values reported in literature [71,76-80].
Figure 5-2. Unconfined yield strength, $f_c$, of smooth glass beads as a function of oil concentration, $C^{1/2}$.

Figure 5-3. Unconfined yield strength of glass beads measured using a Schulze cell (triangles) as a function of the inverse of particle diameter. A comparison with a theoretically predicted straight-line correlation between the two axes provides the number of shear layers in the system to be 8-10.
The comparison of experimental data with the theoretical prediction based on Eq. (5-8) as shown in Figure 5-3, shows some deviations indicating that the capillary force considered in the model is one of the major components acting towards the strength of the powder, but is not the only component. For better prediction and application to real systems, the effect of van der Waals and friction forces and surface roughness need to be incorporated. The following section discusses incorporation of these forces into the model.

**PERC Model Extension**

The PERC model was extended to include the effect of surface roughness (K) and friction force (μ), which are first order contributions to the unconfined yield strength. The expressions for determining the van der Waals force were as discussed in Chapter 2. Earlier studies have shown that the van der Waals force of adhesion between surfaces is significantly lower in the presence of surface roughness [42,43]. The roughness factor, K, accounts for the height and width of the asperities on the surface and is incorporated in the expression to account for the reduction in the adhesion force. The surface roughness was measured directly by topographical scanning using the Atomic Force Microscope.

The friction force between particles plays a major role in determining the angle of repose and the strength in non-cohesive powders [81]. In cohesive system with the addition of liquid binder, the coefficient of friction is reduced due to the lubrication effect of the binder. The friction force was determined by Amontons law where the frictional force is directly proportional to the normal loading force [82]. The constant of proportionality is the coefficient of friction, μ, measured directly by Lateral Force Microscopy [82].
With the incorporation of the friction coefficient, surface roughness and the force of adhesion due to van der Waals forces, the following expression was developed:

\[
f_c = \frac{4\gamma \cos \theta k_r n_i p (C n_r P_{\text{oil}})^{\frac{1}{2}}}{(k_h^2) R \cos \phi (3P_{\text{liq}})^{\frac{3}{2}}} + \frac{(k_r^2) \mu n i p}{R \cos \phi} \left( \frac{A_H}{12\pi H^2 K} + 2\gamma \cos \theta \right) \tag{5-9}
\]

where the additional variables are: \(A_H\) - the Hamaker constant, \(H\) - the distance of closest approach, \(K\) - the roughness factor and \(\mu\) - the friction coefficient.

The two terms on the right hand side of Eq. (5-9) represent, the contribution of the liquid bridge (capillary) forces (first term on the right), and the adhesion force in the dry state (second term). Spherical silica particles were used to compare the experimental data with the theoretical estimates based on Eq. (5-9). The coefficient of friction between particles in the dry state and in the presence of the liquid binder (oil) was determined using Lateral Force Microscopy and was determined to be \(\mu_{\text{dry}} = 0.2\) and \(\mu_{\text{oil}} = 0.05\) respectively, indicating that the presence of oil acts as a lubricant, thereby reducing the friction force between the particles. The surface roughness on the particles as determined by AFM imaging was found to be 0.5 nm, and the roughness factor (K) corresponding to that RMS roughness was determined to be 17 [42,43]. The effect of surface roughness on the adhesion force has been incorporated into the proposed model, based on earlier studies done at the PERC [42,43].

For a dry powder system, the unconfined yield strength was measured and compared with the theoretical estimate based on Eq. (5-9), as shown in Figure 5-4. The open diamonds are the experimental points and the squares represent the theoretical estimates.
For a dry powder system, the first term in Eq. (5-9) would be zero as the liquid binder concentration, C = 0, in the system. The agreement between experimental and theoretical data shows the contribution of friction and surface roughness to the unconfined yield strength of the powder.

Similarly in the presence of the liquid binder (oil), the comparison of the experimental data points with theoretical estimates including the effect of friction and surface roughness (Eq. 5-9) on the unconfined yield strength for a cohesive powder system is plotted in Figure 5-5. The friction coefficient in this case goes down to 0.05 in the presence of oil.
The agreement between the theoretical and experimental results is good. Both the results discussed above have inherent assumptions (based on literature and past experience) for some variables (such as \( n_l \) and \( n_c \)). To verify and validate the judiciousness of these assumptions, an independent determination of these variables was attempted. As a first step, the technique of Discrete Element Modeling (DEM) based computer simulation was used to obtain values of the coordination number (\( n_c \)) in the given powder system.

**DEM Simulation**

The Discrete Element Method is used to simulate the current system of particles in the Schulze shear cell. The exact geometry of the shear cell was used and the particles were allowed to rain down into the cell. After deposition of the particles in this fashion, the system was equilibrated (by simulating shaking of the cell) until the incremental contact forces between particles were negligible. The contact number for each particle...
(coordination number) in the equilibrated state was determined and the distribution of the coordination number in the system is plotted in Figure 5-6. To determine the effect of the packing density, the simulations were carried out at packing densities of 0.3 and 0.4, and the average coordination number of the particle was found to remain (in the range of 5-7) unchanged. The value for another parameter – the coordination number \( n_c \) in the PERC model was 6, which is in the range of the simulation results (5-7).

![Figure 5-6. DEM simulation of coordination number in a mono size powder at different packing densities.](image)

To check the statistical significance of the number of particles simulated in the system, the DEM simulations were carried out at different particle populations as shown in Figure 5-7. These results indicate that the sample population chosen is statistically significant and there is no change in the average coordination (~ 6) between two systems with total number of particles of 10000 and 80000 respectively.

**X-Ray Tomography**

The rheological behavior of cohesive particles depends significantly on the packing arrangement and the structure of the particulate assembly as discussed above. Liquid distribution between particles, relative motion of particles and the width of the shear zone
are a few parameters impacting the analysis of the flow behavior of particle beds. X-Ray Microtomography has emerged as a powerful technique for direct three-dimensional imaging of powder samples [83,84]. This technique, in collaboration with J.D. Miller and C.L. Lin at the University of Utah, was employed to gain additional information with regard to the formation of the shear zones within a shearing powder sample.

![Graph](image)

Figure 5-7. DEM simulation of coordination number in a monosize powder with different particle population.

The application of the principles of cone-beam computed tomography (CT) at the microscale level (microtomography) allows for the quantitative examination of objects in three dimensions. Practical microtomography systems have only recently been developed. Spatial resolution on the order of 10 µm can be achieved with the use of microfocus X-ray generators. For cone-beam CT, a complete 3D data set is acquired with only one rotation of the sample. In a cone-beam design, each projection of the object is similar to a radiograph. Attenuation measurements are simultaneously made for the entire sample rather than for a single slice.
A unique cone-beam X-ray micro-CT system has been designed, assembled, and installed at the University of Utah [85]. The cone-beam Xray micro-CT system at the University of Utah was designed based on a system geometry optimized to obtain high resolution 2D and 3D CT images of small samples but with the flexibility to examine larger objects as required and a detector with the resolution, efficiency and dynamic range required to obtain high quality data from a broad spectrum of samples. A schematic of the system is shown in Figure 5-8.

Figure 5-8. A schematic of the cone beam X-ray microtomography system [84].

A specially designed micro ring shear tester, similar in construction to the Schulze cell discussed in Chapter 2, was used for imaging using X-Ray Tomography. The X-Ray attenuation signal is proportional to the density of the particles. For better tracking, iron ore particles were added as markers. The relative movement of the marker particles as a function of height of the shear cell is illustrated in Figure 5-9. The results shown in Figure 5-9 were taken for a sample of fine silica (Novacite from Malvern Mineral Co., Hot Springs, AR) particles with an average diameter of 10 µm. The shear zone is in the region marked as the partial vane zone that corresponded to 100 layers. The top (solid
line) boundary of the shear zone corresponds to just below the vanes of the Schulze cell and the shear zone is created in that region [4]. The lower solid line is chosen at the point of maximum change in slope of the curve and that point is taken to be the lower boundary of the shear zone. The value currently used in the model for the 50 µm spherical particles is 30 layers. This value was considered reasonable in comparison to the experimentally measured value, as fine powders (used for X-ray tomography) tend to aggregate leading to shearing of agglomerates instead of individual particles.

![Graph](image)

**Figure 5-9.** Mean angular movement of particles along the height of micro-ring shear tester.

**Bimodal Distribution**

Real systems do not always involve a mono-size distribution of particles. The effect of a particle size distribution on the bulk powder behavior is evident from the parameters used in the model in terms of the packing (co-ordination number and fraction of type of particle contact) structure. Before establishing the validity of the model with an industrial relevant system, the applicability of the current model to a mixture of two sizes (bimodal distribution) was tested as the first level of complexity (towards a completely random
particle size distribution). Using a system of spherical glass beads, two samples of different sizes (45 µm - particle A and 130 µm - particle B) were mixed (by wt%) in different proportions to generate a binary mixture. The fraction of contact between the two sizes of particles was determined using DEM and the results are given in Table 5-1. Based on the fraction of contact, the model for mono size distribution is used to calculate the theoretical unconfined yield strength as a weighted average of the particle sizes. This is done as a first order approximation to check the applicability of the model to bimodal systems.

Table 5-1. DEM Results for Contact Fraction of Particles in a Bimodal Distribution.

<table>
<thead>
<tr>
<th>Percentage of Fine Particles (A)</th>
<th>Fraction of two fine particle contact (A-A)</th>
<th>Fraction of a fine and a coarse particle contact (A-B)</th>
<th>Fraction of two coarse particle contact (B-B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.46</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td>40</td>
<td>0.678</td>
<td>0.151</td>
<td>0.171</td>
</tr>
<tr>
<td>60</td>
<td>0.831</td>
<td>0.071</td>
<td>0.098</td>
</tr>
<tr>
<td>80</td>
<td>0.905</td>
<td>0.038</td>
<td>0.057</td>
</tr>
</tbody>
</table>

As shown in Figure 5-10, the experimental values of the unconfined yield strength of the bimodal mixtures of particles go through a maximum at about 60% to 80% fines in the binary mixture. The theoretical estimates do not match the experimental points. This deviation is attributed primarily to the assumption of similar conditions of packing (coordination number) and the width of the shear zone in all cases. A more reliable model would require independent determination of the packing, the coordination number, fraction of contacts and packing density (using DEM), and quantification of the shear zone inside a shearing powder sample (using X-Ray CT).
Figure 5-10. Comparison of the theoretical (open circles) and experimental (black diamonds) values of the unconfined yield strength of a bimodal powder mixture as a function of percentage of fines in the sample.

In summary, identification and quantification of the primary inter-particle forces acting in a powder system can provide the necessary input to estimate the cohesive powder properties of a bulk sample. Incorporation of friction and surface roughness has been shown to improve the predictive capability of the PERC model for a monosize powder.

The current PERC model is reliable in predicting the unconfined yield strength as a function of particle size and binder content for a monosize powder. Though not many industrial systems are monosize, the PERC model provides a handle on prediction of powder strength that could serve as a reliable input to design powder handling equipment. In comparison to the current state-of-the art, the PERC model would be the first to provide a scalable predictive quantitative estimate of the unconfined yield strength of cohesive monosize powders. The PERC model eliminates the need for extensive shear
testing of powders to determine changes in strength of powders with change in the operating conditions.
CHAPTER 6
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Conclusions

The field of powder mechanics has traditionally dealt with flow behavior of powders based on experience and empirical measurements. Solutions to most engineering problems due to powder flow have been handled on a macro scale, focusing on the quickest solution to resume the function of a piece of equipment or process. The strategies currently used to overcome the limitations of scalability are based on measurement of ensemble properties of powders. The drive towards production of multi functional and high value added powders has lead to the need for understanding the particle scale interactions in powders as related especially to cohesive powder flow behavior.

The forces acting in cohesive powders in the presence of liquid bridges have been shown to be dependent on the geometry of interaction (sphere/plate and sphere/sphere) and most importantly on the dynamics of the transport process such as the consolidation load, and rate of flow (translating to the rate of approach/retraction between two particles). The nature of the liquid also plays a key role in determining the boundary condition for defining the process of shearing of a cohesive powder as the flow initiates. In the presence of a volatile liquid like water in the pendular bridges, the liquid-vapor equilibrium is reached quickly and the shearing process would involve a constant capillary radius condition. On the other hand, non-volatile liquids such as oil are characterized by a constant volume condition.
In the present study, theoretical formulae have been developed for estimating the capillary force in the presence of a non-volatile liquid bridge for the sphere/plate and the sphere/sphere geometry. The theoretical estimates were validated by direct AFM measurement of the force/distance profiles between surfaces in the presence of an oil liquid bridge. These expressions for capillary forces were used to develop a PERC model to predict the unconfined yield strength of cohesive powders.

The key parameters identified for input into the model are:

- Particle properties such as Particle Size (distribution), Wettability (Contact angle with liquid, $\theta$), Surface Roughness, $K$.
- Binder properties such as Surface Tension, $\gamma$, and Viscosity, $\eta$.
- Packing parameters such as Coordination number, $n_c$, Width of the shear zone, $n_i$, and fraction of contacts between different sets of particles
- Binder homogeneity in the powder based on the distribution of liquid in the sample.

Among the parameters identified as input to the model, the key parameters that dictate the outcome of the predicted results are determined to be particle size, binder content, surface roughness, and friction force. The comparison of model based predictions and experimental data for smooth glass spheres exhibited direct proportionality of the strength of the powder to the square root of the binder content and inverse particle radius. Incorporating the effects of friction and surface roughness further improved the model prediction. The packing parameters assumed for a mono size distribution of particles were verified by Discrete Element Modeling. The improvement in the model predictions shows that friction force and surface roughness have a direct influence on the bulk strength of the powders. The friction force, depending on the particle size, could contribute up to 40% of the strength of the powder, based on the
comparison of data in Figures 5-3 and 5-2 (with and without oil). At lower particle sizes (below 50 microns) the relative contribution of the friction force in comparison to the surface forces such as van der Waals and capillary force could be limited to 10%. The effect of surface roughness on the reduction in the van der Waals has been shown to be 50% for a surface with nanoscale roughness. Hence, these two important factors need to be taken into account for a reliable prediction of cohesive powder flow behavior.

Extending the model to an industrial system would require incorporation of a particle size distribution term and modeling of the liquid distribution within the sample. The bimodal mixture of particle sizes was simulated and showed a maximum in the unconfined yield strength at 60% of fines. The DEM simulations provided input in regards to the fraction of contacts between each set of particles (two coarse particles, versus two fine or a coarse-fine particle).

The maximum in the strength of the bimodal powder shows the effect of the coordination number. The increase in coordination number due to an increase in the percentage of fine particles leads to a greater number of liquid bridges resulting in higher strength of the powder. The model predictions for a bimodal particle size distribution could not predicted the maximum as observed by the experimental data. However, the theoretical predictions for a real powder system (poly disperse particle size distribution) based on the PERC model would lead to an overestimation of the strength. The current model determines the strength of a poly disperse size distribution as a weighted sum of the fraction (as given by the particle size distribution) of a given size of particle times the strength of a mono size powder of that size as predicted by the model.
Suggestions for Future Work

The PERC model developed in this investigation clearly identifies the important variables contributing towards the strength of the powder. These include the particle size distribution, coordination number, width of the shear zone, probability of rupture, volume of the liquid bridge and homogeniety of the liquid distribution in the powder. The extrapolation of the current model to industrial powder systems would require independent measurement of the width of the shear zone and the probability of rupture.

The width of the shear zone could be measured using X-Ray Tomography in the presence of marker particles in the powder sample. The probability of rupture of individual liquid bridges would require doping the liquid with a high atomic number element such as Iodide (or as Iodine) to provide higher X-Ray attenuation and contrast. One of the most common additives, to improve resolution (by increased X-Ray attenuation), for aqueous liquids is Potassium Idoide (KI). But for very low concentration of binder and fine powders, the limited resolution in X-Ray Tomography may not be sufficient to reliably measure the probability of breakage of the liquid bridges. Two other promising techniques for measurement being explored currently in the field of moisture migration and caking are Magnetic Resonance Imaging (MRI) and Nuclear Magnetic Resonance (NMR) Imaging [86,87].

The resolution of an MRI scan is better than X-Ray Tomography, but requires doping the liquid with an isotope such as deuterium (D$_2$O) in the case of water or other magnetically responsive agent. The NMR stems from the fact that the nuclei of specific isotopes (e.g. of the hydrogen isotope 1H) posses a magnetic moment (spin) and are precessing under a specific angle with respect to an external magnetic field. Successful use of an NMR to quantify the amount of free versus bound water on the surface of silica
particles has been demonstrated by Gotz et al. [87]. Similarly, the MRI was used to image moisture distributions across a cross section of grains at 100°C [86].

The other task would be to systematically study the effects of liquid distribution and surface roughness in determining the regime of liquid bridges as shown schematically in Figures 6-1 and 6-2. Though the effect of surface roughness has been considered in the current study, the contributions have been accessed from the perspective of reduction in the adhesion force and change in the friction coefficient of the inter particle interaction only.

Figure 6-1. Effect of surface roughness on the formation of liquid bridges. Depending on the relative humidity (a) multiple liquid bridges could form at the contact points, or, (b) at high relative humidity one single liquid bridge would form encompassing the contact zone between the sphere and the substrate [61].

Figure 6-2. Regimes of capillary adhesive force as a function of liquid volume for rough particles. I: Asperity regime, II: Roughness regime, III: Spherical regime [88].
The presence of surface roughness could lead to multiple contact points between two surfaces and the regimes of liquid defined traditionally [37] to identify the pendular region, would now be modified due to the increased number of liquid bridges accommodated in the contact zone of the two surfaces. The presence of liquid in between the asperities and determination of the regimes of liquid distribution could be achieved using an Environmental Scanning Electron Microscope (ESEM) or a Variable Pressure Scanning Electron Microscope (VP-SEM). Some preliminary studies were carried out for a system of 50 µm silica particles with white mineral oil (Norton Co., Littleton, NH) added as a binder. Using a Toshiba VP-SEM, the presence of liquid between two particles was imaged as shown in Figure 6-3. Both these techniques can be used to image a powder sample to identify the presence of liquid. Hence, the identification of the liquid regimes in the presence of roughness could be done by direct imaging of the different powder samples using these techniques.

Figure 6-3. Variable Pressure Scanning Electron Microscopy (VP-SEM) image of oil bridges between silica particles

One of the possible extrapolations of the current model would be in the field of powder caking for prediction of strength. The major forces acting in the caking process involve capillary and van der Waals forces, in addition to the chemical forces between
the particles. A direct study of the moisture adsorption isotherm, in the case of moisture induced caking, would determine the dynamics of formation of the liquid bridges. The basic framework developed in the current investigation could provide guidelines for predicting the strength of powder cakes formed between two components with different affinities for moisture adsorption.

After the establishment of the reliability and robustness of the model in predicting the strength of powders, it could be used as an industrial tool to determine the optimum amount of liquid binder to be added for avoiding segregation and minimizing the increase in strength of the powder sample. Moreover, a robust model would eliminate empirical measurements and provide reliable extrapolations for design, from one powder system to another, without starting all over again. The PERC model could emerge as a powerful tool not only for design of powder handling equipment, but to generate quantitative estimates to validate powder testing equipment for their precision and reliability in characterizing powder strength.
APPENDIX A
ADDITIONAL FORMULAE FOR CALCULATION OF CAPILLARY FORCES

This section provides some additional formulae for the calculation of capillary forces for the sphere/plate and the sphere/sphere geometries. Comparison of Eq. (4-2) for \( d_{sp/pl} \) with Eq. (4-20) yields two relationships between \( d_{sp/pl} \) and \( d_{sp/sp} \), as follows

\[
\frac{d_{sp/pl}}{d_{sp/sp}} = \frac{2H}{V} \quad (A-1)
\]

\[
\frac{d_{sp/pl}}{d_{sp/sp}} = \frac{H}{V} \quad (A-2)
\]

Comparing Eqs. (4-3) and (4-20), the following equation for \( \alpha_{sp/sp} \) is obtained

\[
\alpha_{sp/sp}^2 = \frac{HR}{\pi} \left( -1 + \sqrt{1 + \frac{2V}{\pi RH^2}} \right) \quad (A-3)
\]

Note, that the same, as Eq. (4-18), force/ distance dependence for two spheres, can be obtained by another simple method. Introducing the symmetry plane between two interaction spheres (Figure 4-2) and comparing the annular geometry in Figures 3-5 and 4-2, results in

\[
F_{sp/sp}(H,V,\theta_p) = F_{sp/pl}(H/2,V/2,\theta_p,\theta_f = \pi/2) \quad (A-4)
\]

Now, the first term of Eq. (4-1) can be modified for different contact angles \( \theta_p \) and \( \theta_f \) as follows

\[
F_{sp/pl}(H,V,\theta_p,\theta_f) = -\frac{2\pi \gamma R (\cos \theta_p + \cos \theta_f)}{1 + H/d_{sp/pl}(H,V)} \quad (A-5)
\]

Replacing \( F_{sp/pl} \) in Eq. (A-5) for Eq. (A-4) and accounting Eqs. (4-2) and (4-20), the same Eq. (4-18) will be obtained. Using this method for Eqs. (4-8)-(4-10) (without
contribution of vertical component of surface tension), equations for force between two spheres was obtained, which gives practically the same numeric results as Eq. (4-18).
APPENDIX B
CAPILLARY FORCE AT LARGE AND SMALL SEPARATION DISTANCES FOR SPHERE/PLATE AND SPHERE/SPHERE GEOMETRIES

This section provides simplified version of the formulae for adhesion between sphere/plate and sphere/sphere geometries at the two limiting cases of large and small separation (H) distances.

At large separation distances,

\[ V \ll \pi R H^2 \]

Both Eqs. (4-2) and (4-20) for \( d_{sp/pl} \) and \( d_{sp/sp} \) give

\[ d_{sp/pl} = d_{sp/sp} = V / (2\pi R H) \]  

(B-1)

As a result, both the first terms of Eq. (4-1) and Eq. (4-18) yield

\[ F_{sp/pl} = F_{sp/sp} = -2\gamma V \cos \theta / H^2 \]  

(B-2)

At small separation distances,

\[ V \gg \pi R H^2 \]

In this case, the following formulae are valid,

\[ d_{sp/pl} = \sqrt{V / (\pi R)} \]  

(B-3)

\[ d_{sp/sp} = \sqrt{V / (2\pi R)} \]  

(B-4)

\[ F_{sp/pl} = -4\pi \gamma R \cos \theta (1 - H \sqrt{\pi R / V}) \]  

(B-5)

\[ F_{sp/sp} = -2\pi \gamma R \cos \theta [1 - H \sqrt{\pi R / (2V)}] \]  

(B-6)
Note that Eqs. (B-5) and (B-6) account only for the contribution of the pressure difference across the liquid bridge and do not account for the vertical component of the surface tension.

Comparison of the approximate expressions \{Eqs. (B-2), (B-5) and (B-6)\} with the more precise \{Eqs. (4-1) and (4-18)\} set of formulae is shown in Figure B-1. It appears that the set of approximate formulae are valid in the corresponding range of distances that is 0-200 nm for the short-range force and above 1 µm for the long-range force.

![Figure B-1](image)

Figure B-1. Comparison of the simplified set of formulae for capillary force between the sphere/plate and sphere/sphere geometries. Curves 1 and 3 show the capillary force for the sphere/sphere geometry based on Eq. (4-18) and Eq. (B-6) respectively. Curves 2, 4 and 5 for the sphere/plate geometry are based on Eq. (4-1), Eq. (B-5) and Eq. (B-2) respectively. The value of the parameters in the experiment are \(\theta = 6^\circ\), \(V = 10^{10}\) nm\(^3\), \(R = 20\) µm, \(\gamma = 28\) mN/m.

Using the simplified expressions for the force, another test of the applicability of the Derjaguin approximation for capillary force can be done based on Eq. (B-2) and Figure B-1. One of the consequences of Derjaguin approximation (Eq. (4-12)) is

\[
F_{sp/ pl} = 2F_{sp/sp}
\]  
(B-7)
However, from Eq. (B-2) it follows that this condition is not fulfilled, which confirms the conclusion made in Chapter 4 about the inapplicability of the Derjaguin approximation for capillary force.
LIST OF REFERENCES


47. Fisher, L. R.; Israelachvili, J. N. "Experimental studies on the applicability of the Kelvin equation to highly curved concave menisci," *Journal of Colloid and Interface Science* 1981, 80, 528.


BIOGRAPHICAL SKETCH

Madhavan was born in Chennai, India, on November 5, 1975. He finished his high school education from St. Joseph’s English School, India. In August 1993 he was admitted into the physics program at the Birla Institute of Technology and Science (BITS), Pilani. He earned a Bachelor of Engineering degree along with a Master of Science in physics from BITS in May 1998. In August 1999, he came to the United States of America in pursuit of graduate education, and joined the Department of Materials Science and Engineering at the University of Florida (UF). While at UF, he obtained a master’s degree in the Summer of 2002, and expects to obtain a Doctor of Philosophy degree in the Spring of 2005. After graduation he plans to join MEMC, St. Louis, Missouri.