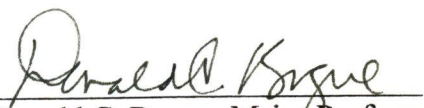
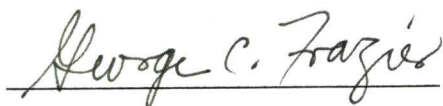


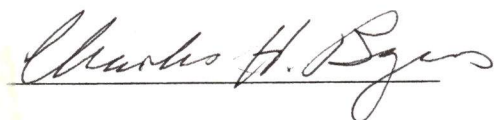
To the Graduate Council:

I am submitting herewith a thesis written by Kevin D. Heath entitled "Interaction and Adhesion Forces Between Polystyrene Spheres and Flat Mica Substrates." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

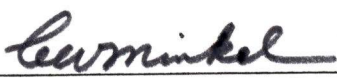

Donald C. Bogue, Major Professor

We have read this thesis
and recommend its acceptance:





Accepted for the Council:


Associate Vice Chancellor and
Dean of the Graduate School

INTERACTION AND ADHESION FORCES BETWEEN POLYSTYRENE SPHERES
AND FLAT MICA SUBSTRATES

A Thesis
Presented for the
Master of Science
Degree
at the University of Tennessee, Knoxville

Kevin D. Heath

May 1997

DEDICATION

This thesis is dedicated to my wife, Angela, whom I will always love and cherish. This thesis is also dedicated to my mother, father, and sister who have given me love and support throughout my life. And finally, this thesis is dedicated to all those who have helped me in the attainment of this work.

ACKNOWLEDGEMENT

The research work reported in this thesis was carried out in the Chemical Engineering Department at Kyoto University, Japan. The author wishes to thank Kyoto University for allowing this research work to be made available, and the Japanese government for fellowship support through the Monbusho scholarship program.

The author wishes to express special appreciation to Professor Ko Higashitani, Kazushige Ishimura, and everyone in the Surface Control Engineering section (Koza 2) for their guidance and understanding during the course of this research.

The author is deeply grateful to Professor Don Bogue for his reading of the thesis and useful comments and discussions.

The author is indebted to Professor Mike Harris for his influence and direction provided at the beginning of the program.

The author also wishes to thank Mitsubishi Rayon Co. Ltd., Hiroshima, Japan, for supplying the polystyrene samples.

ABSTRACT

An atomic force microscope has been used to measure the interaction and adhesion forces between a polystyrene particle and a mica surface in aqueous solutions. The interaction and adhesive pull-off forces, as well as particle deformation, have been measured as a function of contact force and contact time for particles with glass transition temperatures of 29°C (PS29) and 57°C (PS57). These particles (2 μm) are commercial products produced by Mitsubishi Rayon Company, Ltd., Hiroshima, Japan. These particles are copolymers made from n-butyl acrylate monomer and styrene monomer, and are currently being used as intermediates for other processes. The company's objective is to gain a better understanding of the coagulation characteristics for particles of varying softness by direct measurements via atomic force microscope.

The results from this research indicated that a noticeable particle deformation occurs during approach of the mica surface to the polystyrene particle and after contact. Various relationships were established, obtaining a more complete understanding of the interaction forces of soft particles at the microscopic level including repulsive interactions before contact and attraction forces, and particle deformation at contact.

For the particle with a transition temperature of 29°C (PS29), a study was completed that varied the approaching velocity of the mica surface to the particle in order to assess this effect on the resulting interaction forces during approach. It was found that due to particle deformation the maximum repulsive forces (at 20 nm from the mica surface) and corresponding pull-on forces were dependent on the speed at which the

surface and particle were brought together. This interpretation is supported by the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory.

At contact, the relationship of adhesive pull-off force and particle deformation with contact force and contact time was studied. The PS29 particle displayed roughly three times the attractive force of the PS57 particle at zero contact load. A linear relationship between the particle deformation and contact force was observed. This linearity is supported by the Maugis and Pollock (MP) theory, and was used to predict the yield strength and work of adhesion. The studies of adhesive pull-off force with contact time were completed by holding the contact force constant, while the approaching speed was varied. Both particles showed a marked increase in adhesive pull-off force and deformation with contact time resulting from the increase in contact area of the polystyrene particle and mica surface.

TABLE OF CONTENTS

	PAGE
1. INTRODUCTION.....	1
2. LITERATURE REVIEW.....	4
2.1 Long Range Forces Before Contact.....	5
2.1.1 Van der Waals Forces.....	5
2.1.2 Electrostatic Forces.....	11
2.1.3 The Derjaguin, Landau, Verwey and Overbeek (DLVO) Theory.....	15
2.2 Adhesion and Deformation Forces After Contact.....	17
2.3 Overview of Experimental Literature.....	22
3. EXPERIMENTAL ASPECTS.....	26
3.1 Synthesis of Polystyrene Particles.....	26
3.2 Atomic Force Microscopy.....	27
3.3 Sample Preparation.....	30
3.3.1 Description of Colloidal Probes and Cantilever Modification.....	30
3.3.2 Method of Attaching a 2 μm Particle on the Tip of a Cantilever.....	33
3.4 Force Measurement.....	34
4. RESULTS AND DISCUSSION.....	40
4.1 Typical AFM Force Curves.....	40
4.2 Repulsive Interactions at Finite Separations.....	50
4.2.1 Influence of Drag Force on Observed Repulsive Forces.....	52
4.2.2 Influence of Particle Deformation on Observed Repulsive Forces.....	54
4.3 Adhesion and Deformation Forces at Contact.....	58
4.3.1 Elastic and Inelastic Responses to Contact Load.....	58
4.3.2 Contact Force Measurements.....	61
4.3.3 Contact Time Measurements.....	68
5. CONCLUSIONS AND RECOMMENDATIONS.....	72
5.1 Conclusions.....	72
5.2 Recommendations for Further Work.....	75
REFERENCES.....	76
VITA.....	80

LIST OF FIGURES

FIGURE	PAGE
1. Models summing interaction energies of macroscopic bodies from individual molecules (1). (a) molecule and a planar surface. (b) two planar surfaces.	7
2. Model of two negatively charged surfaces with a surface charge density σ (1). (a) display of the dissociation of counterions from the surface. (b) graph of the counterion density profile ρ , and the electrostatic potential ψ	12
3. Derjaguin, Landau, Verwey, and Overbeek (DLVO) model of interaction energy versus distance (1) showing the effect of added electrolyte while defining the energy barrier and primary and secondary minimums.	16
4. Model for relating vertical particle deformation, h , with contact radius, a (14)	20
5. Atomic force microscope (AFM) apparatus (26). (a) schematic of Digital Instruments Nanoscope III, Santa Barbara, California. (b) enlargement of the AFM head unit.	29
6. SEM photos of samples used for experimental measurement. (a) repulsive interactions studied using a 0.58 N/m cantilever. (b) contact interactions studied using a 53 N/m cantilever.	32
7. Scanning electron microscope (SEM) photos of AFM cantilevers. (a) new tip before use; (b) after dulling; (c) after attachment of the polystyrene particle.	35
8. Model of ideal AFM force curve showing both the extension and retraction sections of the curve.	36
9. Force curve analysis with normalization process and variable definition.	39
10. Typical experimental AFM force curves showing both rigid and compliant contact. (a) silica particle and mica in water. (b) PS29 particle and mica in water. (c) PS57 particle and mica in water.	41
11. As-measured AFM data for the interaction of a PS57 particle and mica in water.	43

12.	As-measured AFM data for the interaction of a PS29 particle and mica in water.	44
13.	Normalization of the AFM force curve of a PS57 particle and mica in water.	46
14.	Normalization of the AFM force curve of a PS29 particle and mica in water.	47
15.	Description of the physical condition at various points along the normalized force curve for a PS29 particle and mica in water..	49
16.	Dependency of approach velocity on observed interactions for a PS29 particle with mica in water.	51
17.	Model of the motion of a viscous drop toward a fluid interface (34).	56
18.	Model of the motion of a deformable drop toward a rigid planar surface (35). ...	57
19.	Elastic and inelastic responses of the PS29 particle with mica in water.	59
20.	Elastic and inelastic responses of the PS57 particle with mica in water.	60
21.	Comparison of behavior for PS29 and PS57 particles with maximum pull-off force as a function of contact force (constant contact time).	62
22.	Comparison of behavior for PS29 and PS57 particles with particle deformation as a function of contact force (constant contact time).	63
23.	Comparison of contact radius (PS29) as calculated from adhesion force and deformation with contact force (constant contact time).	67
24.	Comparison of contact radius (PS57) as calculated from adhesion force and deformation with contact force (constant contact time).	69
25.	Comparison of behavior for PS29 and PS57 particles with maximum pull-off force and particle deformation as a function of contact time (constant contact force).	71

LIST OF TABLES

TABLE	PAGE
1. Hamaker constant notation for various media.	9
2. Summary of theoretical equations for interactions at finite separations and contact	21
3. Summary of literature on interactions studied by the atomic force microscope	25
4. Individual beaker contents for the synthesis of pure polystyrene	26
5. Polystyrene samples supplied by Mitsubishi Rayon company, Ltd.	27
6. Calculated drag forces and their effect on observed repulsive interactions.	54
7. Evaluation of the extrapolated conditions of zero applied load for the interaction between PS29 and PS57 particle and mica in water	64
8. Use of Maugis and Pollock (15) theory to determine the yield strength (Y) and work of adhesion (ω_A).	68

LIST OF SYMBOLS

Roman

A	Hamaker constant
a	contact radius
C	intermolecular interaction strength
Ca	capillary number, (function of: viscosity, surface tension, and buoyancy)
c	parameter for calculating Hamaker constant
D	distance
D_p	particle diameter
E	electric field; Young's modulus
$F(D)$	force as a function of distance
F_D	drag force
k	Boltzmann constant
H	hardness of material
h	vertical particle deformation,
P^o	applied load
R	particle radius
r	distance
T	temperature
u	velocity of particle for Stokes equation
$w(r)$	intermolecular pair potential
Y	yield strength
z	ion valency

Greek

β	parameter for the Stokes equation
$\varepsilon, \varepsilon_o$	dielectric constants of the liquid medium and free space, respectively
κ	reciprocal Debye screening length
λ	viscosity ratio
μ	viscosity
ψ_o	electrostatic surface potential
ρ	number density of molecules
ρ_o	ionic concentration
σ	surface charge density
ν	Poisson's ratio
ω_A	work of adhesion

1. INTRODUCTION

Intermolecular forces are very important in the understanding of colloidal systems. The control and prediction of these forces are involved in a variety of industrial applications such as coatings and mineral processing, paint and ink formulations, as well as processes involving adhesives, lubricants, detergents, micelles, biological molecules and membranes. It is these forces that ultimately determine the behavior and properties of such macroscopic systems. It is the purpose of the present work to develop a better understanding of polystyrene latex (PS) particles, which are important in many of these applications, including calibration of microscopes and electronic particle sizing equipment, model systems for studies in basic colloidal chemistry, and general biomedical studies. A more complete understanding of the interaction and adhesion forces of these particles on the microscopic level will provide a better foundation for predicting the interactions on the macroscopic level such as in bulk solutions. Therefore an investigation of the interactions before contact and the adhesive force and deformations after contact are fundamental to achieving an understanding of this phenomena.

At minute separations intermolecular forces control the system, and these forces can be of many forms. There are polarization forces originating from the dipole moments induced by electric fields of nearby charges and permanent dipoles; electrostatic forces arising from the coulombic force between charges; and many other forces that are in a general sense classified by Israelachvili (1) as quantum mechanical in nature. Physical van der Waals forces, which are inherently attractive, occur when two similar particles interact

✓ in a medium. When a charge is present, however, there is an electrostatic contribution. In contrast to the attractive nature of the van der Waals force, the electrostatic force is repulsive. When both forces are present simultaneously, one turns to the theory of Derjaguin, Verwey, Landau, and Overbeek (DLVO) (2,3). This theory relates these two competing forces, and predicts that a stable colloidal suspension can be achieved only when the forces balance.

✓ With the invention of the atomic force microscope (AFM) (4) in 1986, it became possible to directly measure the forces between an individual colloidal particle and a surface at minute separations. This was achieved through the attachment of a colloidal particle to a cantilever tip (colloidal probe). Many studies using an AFM have dealt with the interaction of a colloidal probe and a molecularly smooth surface. The first experiments of this type were published in 1991 by Ducker, Senden and Pashley (5,6). In this work it was found that at large separations (> 3 nm) the measured forces agreed well with classical DLVO theory. This technique has been further enhanced by a new generation of cantilevers, thereby improving the AFM's resolution and reliability. With advances made in detecting the slight deflections of the cantilever, the force between an AFM tip and a surface can now be measured with a resolution of better than 0.1 nN.

At contact, adhesion and deformation forces dominate the interaction. In addition to the interaction forces observed at minute separations, the effects at contact can be very useful to elucidate information on the adhesion forces. The adhesion and removal of particles is extremely important in many industries such as pharmaceutical, semiconductors, xerography, and certainly the coatings industries. Moreover, the

deformations, which can be the result of an elastic (flexible), a nonlinear elastic, a viscoelastic, or a plastic (malleable) response of the materials to the stresses, can significantly affect the forces needed to remove the particles from the surface.

Directly measuring the force of adhesion of particles on substrates has been of interest for some time. In the past, this has been done in a statistical way by measuring the fraction of particles removed as a function of the lift-off force. The force of removal has also been measured using techniques such as electrostatic detachment and centrifugation (8). Such techniques often require long times, which, in turn, can affect the forces of adhesion (9). While useful, these measurements allow little insight into the microscopic details which determine the force of removal.

To help clarify the interactions on the surface, direct observations of the deformations of micrometer-size particles supported on substrates due to surface forces have been previously made using scanning electron microscopy (SEM) techniques (10,11). By determining the dependence of the contact radius on such parameters as particle radius and Young's moduli (ratio of tensile strength to the resulting deformation), it was possible to distinguish elastic and plastic responses to the adhesion force.

In the present work an atomic force microscope was used to measure the interaction and adhesion forces between a polystyrene (PS) particle and a mica surface in aqueous solutions. The interaction and adhesive pull-off forces, as well as particle deformation, were measured as a function of approaching velocity, contact force, and contact time for particles with different glass transition temperatures.

2. LITERATURE REVIEW

To develop a more complete understanding of the properties of macroscopic system, one must first examine the interactions on the molecular level. In this section, the development of theories relating interactions at finite separations are presented. Forces presented include the physical van der Waals forces, which act independently of the chemical nature of the particle or medium, and electrostatic forces which occur when particles are charged through surface charge groups or by specific ion adsorption from a solution. When these two forces are operating simultaneously, one turns to the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory in order to explain the resulting phenomena. The DLVO theory relates the two forces, and predicts that a stable colloidal system can be achieved only when the two forces balance.

Also in this section, the development of theories relating interactions at contact are presented. As the surfaces come into contact, another set of theories, which are used to explain the adhesion and deformation forces, applies. In addition to the prominent role at finite separations, the van der Waals forces continue to have an influence at contact as well. When the surfaces are very close to contact the van der Waals forces dominate over the electrostatic forces. At contact, the van der Waals forces are assisted by a contribution from the deformation of the surfaces. Depending largely on the size of the contact area, this additional contribution has been the focus of much research such that various theories have developed to describe this relationship between deformation and adhesion.

After the presentation of the involved theories, a review that covers various experiments relating these ideas, is given.

2.1 Long Range Forces Before Contact

2.1.1 *van der Waals Forces*

Van der Waals forces are physical forces, which Israelachvili (1) identifies as polarization forces. The three basic mechanisms of van der Waals forces are the Keesom interaction, the Debye interaction, and London dispersion interaction. The Keesom interaction comes from the interaction between two dipoles; the Debye interaction is from the dipole non-dipole interaction; and the third, and perhaps the most important contribution of the three, comes from the London dispersion interaction, which is between two non-polar molecules. To understand how the London dispersion force comes about, one must visualize the following model. Imagine a non-polar atom where the time average of its dipole moment is zero; however, at any instant there exists a finite dipole moment given by the instantaneous position of the electrons about the nucleus. This instantaneous dipole generates an electric field which polarizes any nearby neutral atom, inducing a dipole moment in it. The resulting interaction between the two dipoles gives rise to an instantaneous attraction between the two atoms, and the time average of this force is nonzero and finite.

Van der Waals forces are effective from an interatomic spacing of 0.2 nm to large distances (greater than 10 nm). They can be either attractive or repulsive depending on

the system. The interaction is always attractive between two similar particles in a medium and can be either attractive or repulsive for dissimilar particles. The van der Waals force between any two condensed bodies in a vacuum or air is always attractive.

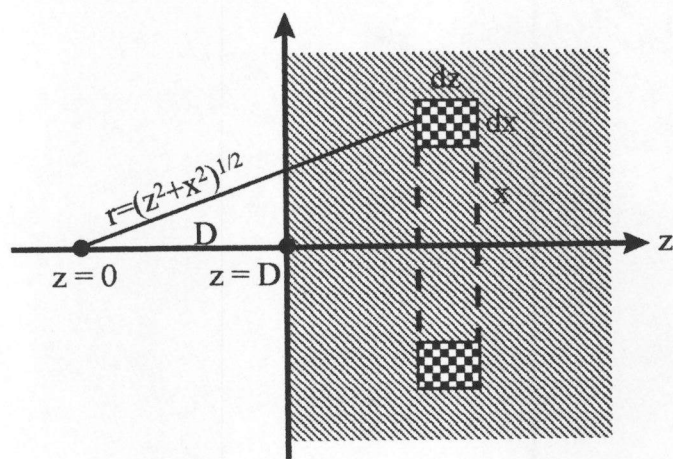
The development of the van der Waals forces begin with the simplest model for the intermolecular pair potential, $w(r)$, between two molecules. This relationship is given in the following equation:

$$w(r) = -\frac{C}{r^6} \quad (1)$$

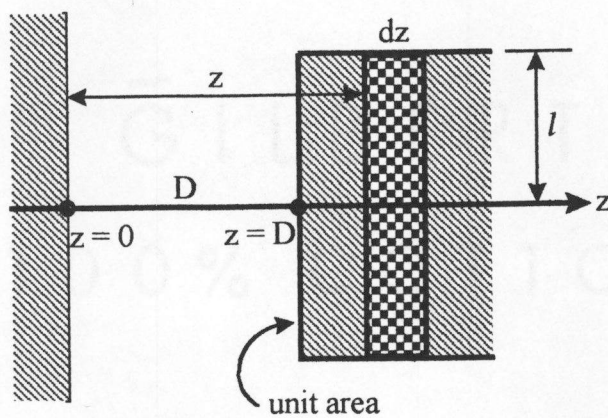
where the strength of the intermolecular interaction between two molecules is represented by C , and the distance between them is given by r . Assuming pairwise additivity, the net interaction energy can be developed between a molecule and a planar macroscopic body (made up of identical molecules). This is achieved by integrating over all the molecules in the macroscopic body. For the molecules in a circular ring of cross-sectional area dx and radius x (Figure 1a), the number of molecules is represented by $2\pi x\rho dx$, where ρ is the number density of molecules in the solid. Following from equation 1 with $r = (z^2 + x^2)^{1/2}$, the net interaction energy for a molecule at a distance D away from a planar macroscopic body is

$$w(D) = -2\pi C\rho \int_{z=D}^{z=\infty} dz \int_{x=0}^{x=\infty} \frac{x dx}{(z^2 + x^2)^3} = -\frac{\pi C\rho}{6D^3} \quad (2)$$

From this result, it is now possible to calculate the interaction energy between two planar surfaces a distance D apart. This must be done on a unit area basis, because if an infinite surface area is used, the result would be an infinite energy. Hence, the number of molecules for a sheet of unit area and thickness dz is simply ρdz (Figure 1b). Following



(a)



(b)

Figure 1. Models for summing interaction energies of macroscopic bodies from individual molecules (1). (a) Molecule and a planar surface. (b) Two planar surface where $l \ll D$.

from equation 2 for a distance z away from another planar surface, the net interaction energy per unit area between two planar surfaces can be obtained by

$$W(D) = -\frac{\pi C \rho^2}{6} \int_D^{\infty} \frac{dz}{z^3} = -\frac{\pi C \rho^2}{12 D^2} \quad (3)$$

For macroscopic bodies such as a sphere and a planar surface, it is generally the forces that are often easier to measure, and of greater interest than their interaction energies. To arrive at the corresponding force, one must take the derivative of the intermolecular potential. However, because of complex geometries, many systems have very complicated interaction energies, making it undesirable to obtain the force relationship through this method. For this reason, the Derjaguin approximation was developed. The Derjaguin approximation (1) relates the force versus distance relationship $F(D)$ between two curved surfaces such as spheres to the interaction energy $W(D)$ of two planar surfaces.

$$F(D)_{sphere} = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) W(D)_{planes} \quad (4)$$

This relationship is only valid when R_1 and $R_2 \gg D$. If one sphere is much larger than the other such that $R_1 \gg R_2$, then one can obtain a limiting case for the force law between a sphere of radii R_2 and a planar surface as

$$F(D) = -\frac{\pi^2 C \rho^2 R_2}{6 D^2} \quad (5)$$

It is interesting to observe that the interaction energy is proportional to the radius of the sphere and decays at a much weaker dependence ($1/D^2$) than for the intermolecular pair potential of two molecules ($1/r^6$).

Equation 5 is further simplified with the use of the Hamaker constant A , which is defined as $\pi^2 C \rho^2$, to give the van der Waals equation for the force between a sphere and a planar surface as

$$F(D) = -\frac{AR}{6D^2} \quad (6)$$

The Hamaker constant plays a central role in the description of the van der Waals forces between particles. It has the dimensions of energy, and depends on both the strength of the intermolecular interaction through C and on the density of the particle. Common notation for Hamaker constants of similar and dissimilar particles in various media is described in Table 1.

Table 1. Hamaker Constant Notation For Various Media

Hamaker constant	first medium	intervening medium	second medium
A_{11}	polystyrene	vacuum	polystyrene
A_{22}	mica	vacuum	mica
A_{33}	water	vacuum	water
A_{12}	polystyrene	vacuum	mica
A_{13}	polystyrene	vacuum	water
A_{23}	mica	vacuum	water
A_{132}	polystyrene	water	mica
1 = polystyrene 2 = mica 3 = water			

The Hamaker constants for pure systems, such as A_{11} for the interaction of polystyrene separated by a vacuum, are readily accessible (1). Combining relations are available to approximate unknown Hamaker constants in terms of known ones. The

Hamaker constant for the system of polystyrene and mica separated by a vacuum can be approximated by

$$A_{12} = \sqrt{A_{11}A_{22}} \quad (7)$$

Likewise through analogy the following expression can be deduced

$$A_{23} = \sqrt{A_{22}A_{33}} \quad (8)$$

This expression is similar to equation 7 except the media represented are mica and water separated by a vacuum.

These constants depend solely on the material composition of the contacting substances. They are not dependent on the geometry of the system. Ranade (30) extrapolated this idea of combining laws to the case of two materials, 1 and 2, in an intervening medium 3. This yields

$$A_{132} = (A_{12} + A_{33} - A_{13} - A_{23}) \quad (9)$$

Visser (31), however, provides a modified equation for the Hamaker constant of a system of three materials. The value for material 1 and material 2 in medium 3 is given by

$$A_{132} = c(A_{12} + A_{33} - A_{13} - A_{23}) \quad (10)$$

where c is a constant dependent on the surrounding medium. The value of c for a water medium is given by Visser as 1.6.

2.1.2 Electrostatic Forces

Electrostatic forces are important for the stability of systems because they balance the inherently attractive van der Waals force. Electrostatic forces develop when particles are charged through surface charge groups or by specific ion adsorption from solution. When immersed in liquids, this charged surface develops a diffuse layer of counterions that is often called the double layer or Debye screening length. Upon overlapping, these double layers exert forces that are generally repulsive and are characterized in terms of a surface charge density σ and an electrostatic surface potential ψ_o . It is important to determine the relationship between σ and ψ and how the potential and distribution of ions in the solution vary with distance from the charged interface. The Boltzmann distribution gives the counterion distribution at any point x between two surfaces by the following relationship

$$\rho = \rho_o e^{-ze\psi_o/kT} \quad (11)$$

For two surfaces separated by a distance D (Figure 2), $x = 0$ at the midplane, $\psi_o = 0$, and ρ_o is the ionic concentration of valency z . Equation 11 also includes the Boltzmann constant k and the temperature T . A second important equation is the Poisson equation, which relates the excess charge density at x :

$$ze\rho = -\epsilon\epsilon_o \left(\frac{d^2\psi}{dx^2} \right) \quad (12)$$

where ϵ and ϵ_o are the dielectric constants of the liquid medium and free space, respectively. A combination of the Poisson equation with the Boltzmann distribution of

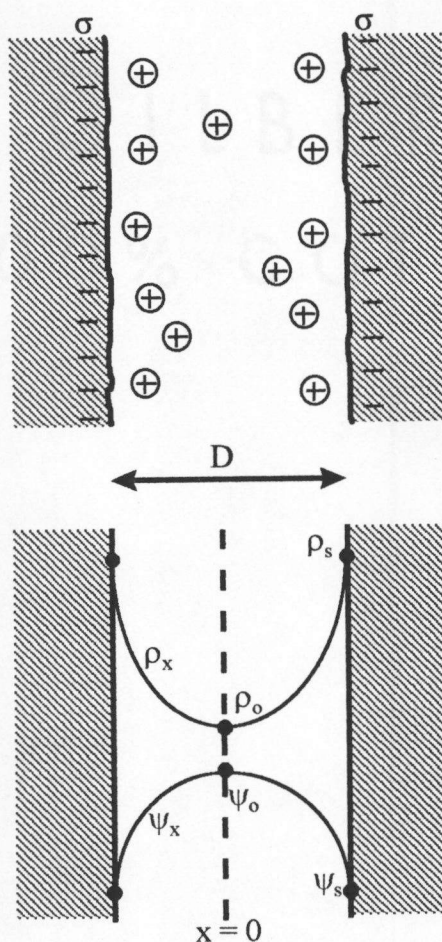


Figure 2. Model of two negatively charged surfaces with a surface charge density σ (1). (a) Display of the dissociation of counterions from the surface. (b) Graph of the counterion density profile ρ_x , and the electrostatic surface potential ψ_x . The subscript "s" denotes the values on the surface, and $x = 0$ is the midplane between the surfaces.

counterions provides an expression that gives the electrostatic potential ψ , electric field $E = -\partial\psi/\partial x$, and counterion density ρ , at any point x away from the charged surface. The name of this expression is the Poisson-Boltzmann (PB) equation, and it is obtained by combining equations 11 and 12. For a uniformly charged planar surface exposed to an electrolyte solution the PB equation becomes

$$\frac{d^2\psi}{dx^2} = -\frac{ze\rho_o}{\epsilon\epsilon_o} \exp\left(\frac{-ze\psi}{kT}\right) \quad (13)$$

After taking the derivative of equation 11, and using equation 13 and the following relations

$$\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2 = 2\left(\frac{d\psi}{dx}\right)\left(\frac{d^2\psi}{dx^2}\right) \quad (14)$$

it is possible to obtain

$$\frac{d\rho}{dx} = -\frac{ze\rho_o}{kT} e^{-ze\psi/kT} \left(\frac{d\psi}{dx}\right) = \frac{\epsilon\epsilon_o}{kT} \left(\frac{d\psi}{dx}\right) \left(\frac{d^2\psi}{dx^2}\right) = \frac{\epsilon\epsilon_o}{2kT} \frac{d}{dx} \left(\frac{d\psi}{dx}\right)^2 \quad (15)$$

By integrating equation 15 and using the relation for the electric field on the surface

$$E_s = \left(\frac{d\psi}{dx}\right)_s = \frac{\sigma}{\epsilon\epsilon_o} \quad (16)$$

one obtains

$$\rho_s = \rho_o + \frac{\sigma^2}{2\epsilon\epsilon_o kT} \quad (17)$$

which gives the ion concentration at the surface ρ_s , in terms of ion concentration at the midplane ρ_o , and the surface charge density σ .

The force between two planar surfaces can be derived from the osmotic pressure that develops between them from the presence of ions in the solution. At equilibrium the pressure should be uniform throughout the gap, and equal to the pressure acting on the two surfaces. The pressure is expressed in terms of ion concentration and is based on the assumption that the surface charge density remains constant ($\sigma = \epsilon\epsilon_o\kappa\psi_o$) and independent of D .

$$P(D) = kT[\rho_o(D) - \rho_o(\infty)] = kT\left[\rho_s(D) - \frac{\sigma_1\sigma_2}{2\epsilon\epsilon_o kT}\right] \quad (18)$$

Following from equation 18, for low surface potentials, the pressure between two planar surfaces simplifies to

$$P(D) = \frac{2\sigma_1\sigma_2}{\epsilon\epsilon_o} e^{-\kappa D} \quad (19)$$

where κ is the reciprocal Debye screening length defined as $(z^2 e^2 \rho_\infty / \epsilon\epsilon_o kT)^{1/2}$. By integrating equation 19 with respect to D , the electrostatic interaction energy per unit area for two planar surfaces becomes

$$W(D) = \frac{2\sigma_1\sigma_2}{\kappa\epsilon\epsilon_o} e^{-\kappa D} \quad (20)$$

Using the Derjaguin approximation in equation 4, the electrostatic double layer interaction for a sphere and a planar surface can be derived from equation 20 as

$$F(D) = \frac{4\pi\sigma_1\sigma_2 R}{\kappa\epsilon\epsilon_o} e^{-\kappa D} \quad (21)$$

In recent studies (6, 24), the linearized Poisson-Boltzmann theory was shown to give a satisfactory representation of the double layer force between a sphere and a planar surface.

It was concluded (24) that the use of the Derjaguin approximation not only was adequate for the analysis of sphere and planar surface force curves, but also that it improves at higher surface potentials.

2.1.3 *The Derjaguin, Landau, Verwey and Overbeek (DLVO) Theory*

In the 1940s two independent groups of scientists, Boris Derjaguin and Lev Landau from the Soviet Union, and Evert Verwey and Theo Overbeek from the Netherlands, accomplished a major advance in colloidal science by presenting quantitative theoretical analyses on colloidal stability. This work became known as DLVO theory.

In DLVO theory, competition between an electrostatic repulsion and a van der Waals attraction determines the stability or instability of many colloidal systems. The resulting equation for the force law between a large sphere of radius R and a planar surface separated by a distance D is simply a combination of equations 21 and 5 as

$$F(D) = \frac{4\pi\sigma_1\sigma_2R}{\epsilon\epsilon_0\kappa} e^{-\kappa D} - \frac{AR}{6D^2}, \quad (22)$$

where the first term on the right represents the repulsive electrostatic double-layer interaction and the second term is the van der Waals interaction. Equation 22 is based on the assumption that the surface charge remains constant as the sphere and surface approach one another, and is developed for surface potentials smaller than kT and for low salt concentrations. The van der Waals attractive term dominates over the repulsive term when the distance between the two surfaces is either very large or very small as shown in Figure 3. At intermediate separations the electrostatic term creates an energy barrier.

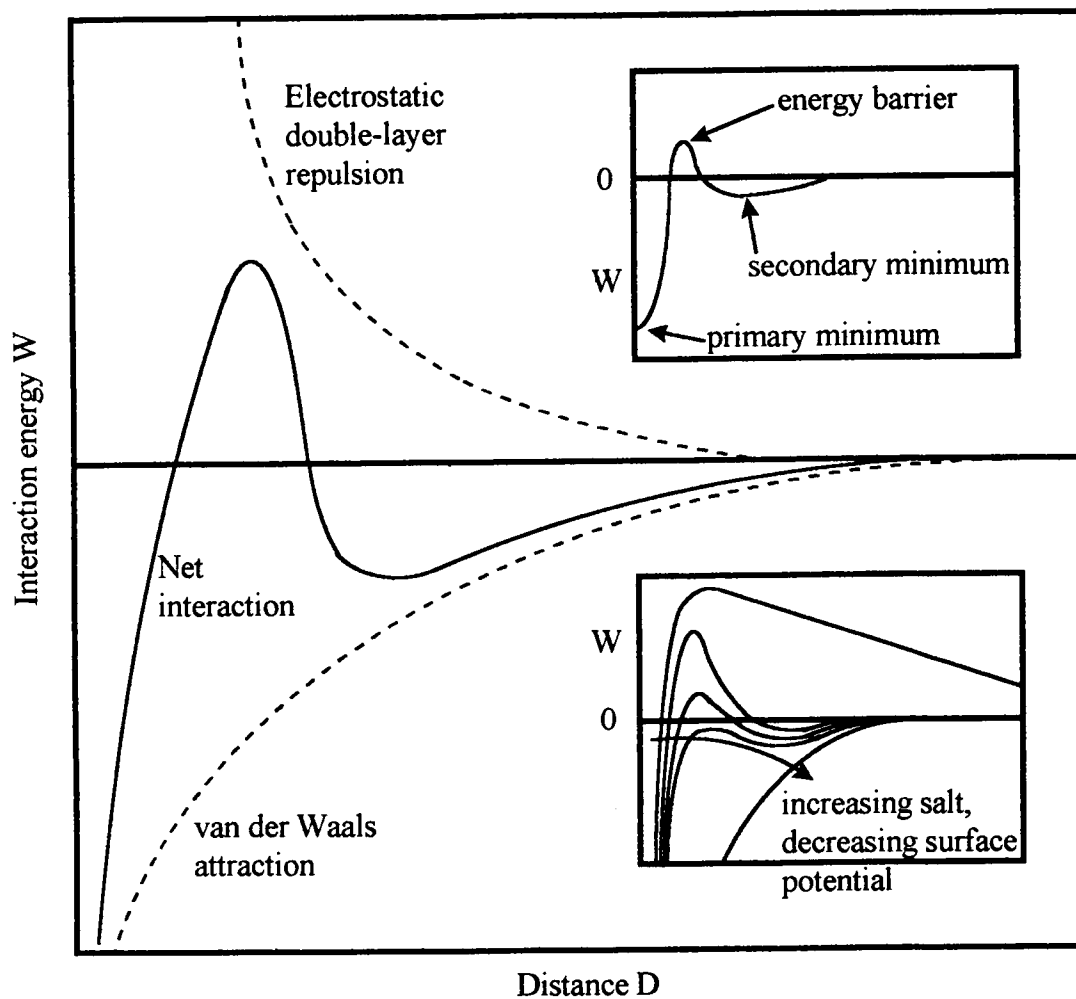


Figure 3. Derjaguin, Landau, Verwey, and Overbeek (DLVO) model of interaction energy versus distance displaying the effect of added electrolyte while defining the energy barrier and primary and secondary minimums (1).

This is especially apparent for highly charged surfaces in dilute electrolyte. At contact there exists a potential energy minimum called the primary minimum from the balance of the attractive van der Waals and the physical repulsive forces at contact. In addition, there is a secondary minimum in concentrated electrolyte solutions. Often when the energy barrier is too high, colloidal particles remain in the secondary minimum. Since the electrostatic force is controlled by charge density and surface potential, it can often be used to lower the energy barrier, which leads to slow coagulation or flocculation. As the concentration of electrolyte is increased, the energy barrier decreases until the energy barrier crosses the zero axis after which time the particles rapidly coagulate. This point is defined as the critical coagulation concentration.

2.2 Adhesion and Deformation Forces After Contact

Up to this point we have focused on forces that operate primarily at finite separations. In this section a review of the current theories for interactions at contact is given. It is interesting to note that the van der Waals forces, which play an important role for colloidal stability at separations, continue to have a prominent role in attraction of surface at contact as well. As an overview of all the adhesion forces, a classification by Krupp (18) is presented. According to Krupp, adhesion forces are classified into three categories:

- 1) The adhesion forces that prevail in the region of contact and at finite separations (electrostatic and van der Waals forces).

- 2) The adhesion forces that result from chemical bonding as well as intermediate energy bonding such as hydrogen bonding.
- 3) The adhesion forces caused by interfacial processes such as diffusion, condensation, and diffusive mixing.

In the present work, the materials are polystyrene and mica immersed in pure water. These materials are neither reactive nor porous. Therefore, the adhesion forces from chemical bonding and interfacial processes can be neglected. This assumption is supported by the work of Bowling (19), who postulated that the primary force of adhesion for small uncharged particles ($< 50 \mu\text{m}$) on uncharged substrates comes from the van der Waals interactions. In addition, this primary force of adhesion between a sphere and a planar surface depends largely on the contact area between them. Therefore, any deformation in the contacting surfaces can increase the adhesion forces. When a sphere and a planar surface come into contact with each other, the attractive force causes the interface to deform such that a circular adhesion area is formed between the two surfaces. The total adhesion force (19,32) is represented by two components.

$$F_T(D) = -\frac{AR}{6D^2} - \frac{A}{6\pi D^3} \pi a^2 \quad (23)$$

The first term comes directly from the van der Waals interaction, and is the force acting between the two surfaces before and at the moment of contact before any deformation occurs. The second term represents the contribution from the extended contact area due to deformation. By direct measurement of the adhesive force between a particle and a planar surface, one can use equation 23 to derive the contact area and thus contact radius, a , between the two materials.

Many theories have been developed to characterize the deformation between spherical particles and planar surfaces (22-23, 12, 15). In 1934, Derjaguin (23) calculated the contact area between two surfaces assuming only van der Waals interactions. In addition, he assumed the particle to be a Hertzian indenter with an initial radius R , contact radius a , and under an applied load P^o . This relationship is given by

$$a^3 = \frac{3}{4} P^o \frac{(1-\nu^2)}{E} R \quad (24)$$

where E and ν are the Young's modulus and Poisson's ratio, respectively.

In 1984, Maugis and Pollock (15) (MP) extended this concept to include plastic deformation of the contacting materials. They proposed that the contact radius is related to the externally applied load P^o , the hardness of the deforming material H , the work of adhesion ω_A , and the particle radius R , by

$$P^o + 2\pi\omega_A R = \pi a^2 H \quad (25)$$

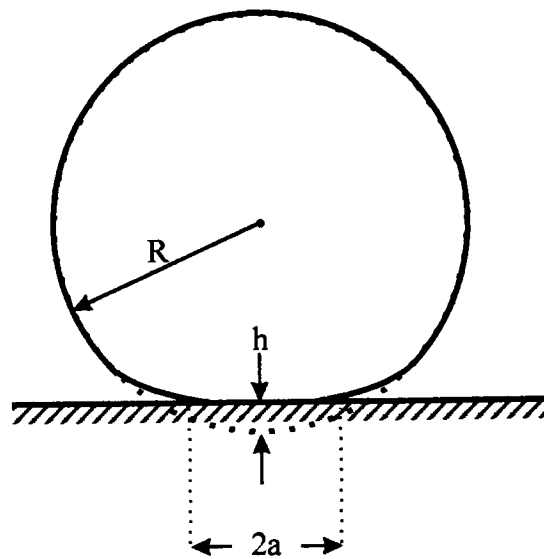
where the hardness H is related to the yield strength Y of the material by

$$H = 3Y \quad (26)$$

By using the relationship $a^2 = Rh$ from the Derjaguin, Muller, and Toporov (14) theory (Figure 4), the contact area can be related to particle deformation, h . When this relation is substituted into equation 25, one achieves a linear equation relating the particle deformation with the applied force.

$$h = \frac{P^o}{3\pi RY} + \frac{2\omega_A}{3Y} \quad (27)$$

Equation 27 can be used to predict material yield strength and work of adhesion from the relationship of deformation and contact force.



$$a^2 = Rh$$

Figure 4. Model for Relating Vertical Particle Deformation, h , with Contact Radius, a (14).

In Table 2, a summary is displayed of the various theories presented thus far including the DLVO theory for finite separations and the elastic and inelastic theories relating deformation and adhesion forces at contact.

Table 2. Summary of theoretical equations for interactions at finite separations and contact

At Separation		eq.
Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory (2,3)	$F(D) = \frac{4\pi\sigma_1\sigma_2R}{\epsilon\epsilon_0\kappa} e^{-\kappa D} - \frac{AR}{6D^2}$	(22)
At Contact		
Total adhesion force (19,32) including deformation contribution	$F_T(D) = -\frac{AR}{6D^2} - \frac{A}{6\pi D^3} \pi\alpha^2$	(23)
Elastic Theory		
Derjaguin theory (23) assuming a Hertzian indenter	$a^3 = \frac{3}{4} P^0 \frac{(1-\nu^2)}{E} R$	(24)
Inelastic Theory		
Maugis and Pollock theory (15)	$P^0 + 2\pi\omega_A R = \pi\alpha^2 H$	(25)
Maugis and Pollock theory (15) upon the substitution of $\alpha^2 = Rh$	$h = \frac{P^0}{3\pi RY} + \frac{2\omega_A}{3Y}$	(27)

2.3 Overview of Experimental Literature

Seminal work on the measurement of the attractive van der Waals forces was done by Derjaguin and co-workers (Derjaguin and Abrikossova, 1954; Derjaguin et al., 1956) using a convex lens and a flat glass surface in a vacuum. As the field developed, better techniques became available. Tabor and Winterton (1969) and Israelachvili and Tabor (1972, 1973) developed what is known today as the surface forces apparatus (SFA) for measuring the van der Waals forces between molecularly smooth mica surfaces in air or vacuum. Further development of the SFA led to the first experiments immersed in liquids which were done by Israelachvili and Tabor in 1978 (2). Since 1978 various methods have been employed to measure these types of forces, including Total Internal Reflection Microscopy (TIRM) and especially Atomic Force Microscopy (AFM).

Atomic force microscopy measurements have been taken in a variety of media using numerous materials. In such experiments one can measure the force-distance function (F/D) of individual forces such as the van der Waals forces. Moreover, interactions between specific geometries can be evaluated.

In 1991 Ducker, Senden and Pashley (5,6) were the first to publish work on the measurement of the interaction forces between a colloidal particle attached to a cantilever (colloidal probe) and a flat surface. The interaction of a silica sphere and a silicon surface in solutions of sodium chloride was studied. The measurements were found to be consistent with double-layer theory of colloidal forces. As predicted by Derjaguin, Landau, Verwey and Overbeek (DLVO) theory (2,3), the measured forces decayed exponentially at large separation, and both decay length and electrostatic potential

decreased with concentration. The predicted force was fitted to the measured force at distances greater than about one decay length by adjusting the surface potential for the silica.

Since 1991, much attention has been given to the development of experiments based on the interaction between a colloidal probe and a surface. In 1993, Li, et al. (9) developed a method to measure the forces between a colloidal probe and another individual colloidal particle attached to a flat surface immersed in electrolytes. For pairs of polystyrene spheres, a reproducible long-range repulsion was observed. Data for repulsion were fitted by a simple form of the DLVO theory based on the linearized Poisson-Boltzmann equation, the Derjaguin approximation, and a sum of the van der Waals interactions found in equation 22. This fit yielded a surface potential and a Debye length in reasonable agreement with the expected Debye length and the measured zeta potential. Then Li, et al. compared this simple form of the DLVO theory to a full numerical solution of the Poisson-Boltzmann equation, and the simple form was shown to work reasonably well.

Many other studies using AFM have dealt with the interaction of a colloidal probe with a similar surface in various media. A dependence on concentration of numerous electrolytes such as sodium chloride (5,6,40), calcium chloride (39), and potassium chloride (6,47), has been examined. Hydrophilic and hydrophobic interactions (40,43) have also been studied. Furthermore, media such as the medium of cetyltrimethyl ammonium bromide (44) (CTAB) have been considered. In addition, interactions between colloidal particles immersed in solutions of a non-adsorbing polymer (41) have been

investigated to verify theories on the depletion interaction, an interaction related to the repulsion of polymers from surfaces. A summary of literature for the preceding discussion is given in Table 3.

Table 3. A Summary of Literature for Atomic Force Microscopy
Colloidal Probe Interactions

Materials and Shapes	Intervening Media	Forces Studied	References
silica sphere / silicon wafer	aqueous CaCl_2	force vs. distance	Meagher (39)
silica sphere / silicon wafer	aqueous NaCl	force vs. distance	Ducker, Senden, and Pashley (5,6)
silica sphere / silicon wafer	water, aqueous NaCl	hydrophobic, DLVO interactions	Ducker, Xu, Israelachvili (40)
silica sphere / polished silica plate	aqueous nonadsorbing polymer	depletion forces	Milling and Biggs (41)
silica sphere / drops of water or air	entering air bubble and drop	force vs. distance	Butt, 1994 (42)
silica sphere / polished stainless steel plate	water	hydrophobic forces	Mantel, Rabinovich, Wightman, Yoon (43)
Au coated silica sphere / polished Au plates	water, CTAB	Hamaker constant H_{121} ($\text{Au}/\text{H}_2\text{O}/\text{Au}$)	Biggs and Mulvaney (44)
Zr agglomerates / polished Zr plate	air, polyacrylic acid, aqueous KNO_3	steric and bridging forces	Biggs (45)
polystyrene sphere / polystyrene block	water, surfactant solutions	force vs. distance	Karaman, Meagher, Pashley (46)
polystyrene sphere / polystyrene sphere	aqueous KCl	force vs. distance	Li, Tao, Pan, Garcia, Lindsay (9)
various tips on mica	aqueous KCl	force vs. distance	Butt, 1991 (47)

3. EXPERIMENTAL ASPECTS

3.1 Synthesis of Polystyrene Particles

When synthesizing large particles of greater than 1 micron in diameter, it is very common to use a seed particle as a nucleation site. Usually seed particles are less than one micron in diameter and can be of practically any substance. In these experiments, previously prepared polystyrene particles were used as the seed particles.

The procedure for making pure polystyrene consists of having two beakers with the following contents:

Table 4. Individual beaker contents for the synthesis of pure polystyrene

Beaker 1	Beaker 2
seed particles	potassium persulphate (KPS)
styrene monomer	pure water
pure water	

Each beaker was mixed thoroughly, and separately brought to a constant temperature of 60°C. The styrene monomer coats the surface of the seed particles in beaker 1, and then the seed particles act as nucleation sites for the growth of the polystyrene polymer. After waiting about 30 minutes, the mixtures are at constant temperature, and the two beakers are mixed together. The KPS is the initiator for the reaction, and after waiting approximately 12 hours, the result is a stable solution of pure polystyrene particles with diameters as large as 4 microns for use in many applications requiring the absence of emulsifiers, etc.

The particles supplied by Mitsubishi Rayon company, Ltd. were produced by a very similar method as the pure polystyrene, except that they added another component called n-butyl acrylate (BA) monomer with the styrene monomer. They also have a slightly more complicated temperature cycle. To achieve varying transition temperatures in the final product, they varied the weight ratios of n-butyl acrylate (BA) monomer and styrene (St) monomer. The resulting transition temperatures of the final particles were calculated using the Fox equation (29) based on transition temperatures for the pure components of BA and St ($T_g = -47^{\circ}\text{C}$ and 100°C , respectively). As shown in Table 5, the PS29 sample contains a BA/St weight ratio of 40/60, and the PS57 sample contains 20/80.

Table 5. Polystyrene samples supplied by Mitsubishi Rayon company, Ltd.

Sample identification	Seed 6.7 % BA/St	Final 93.3 % BA/St	T_g, °C
PS29	60/40	40/60	29
PS57	60/40	20/80	57

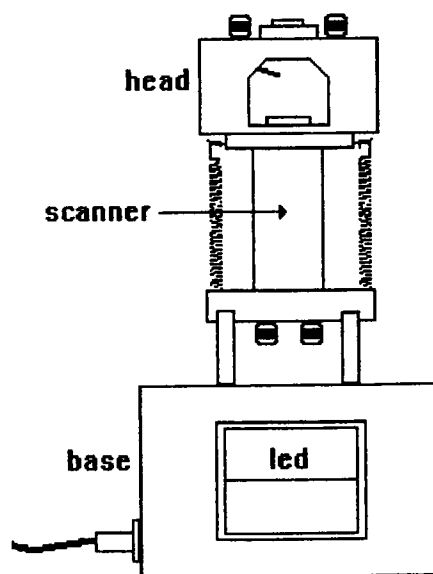
3.2 Atomic Force Microscopy

The atomic force microscope (AFM) was invented by Binnig, Quate and Gerber (5) in 1986. Its ability to image and measure forces of non-conductive material has made it a paramount discovery in the world of microscopy. Force microscopes operate by means of raster scanning a probe across the surface of a sample. Forces between the probe and surface cause deflections to occur in the cantilever. These deflections of the

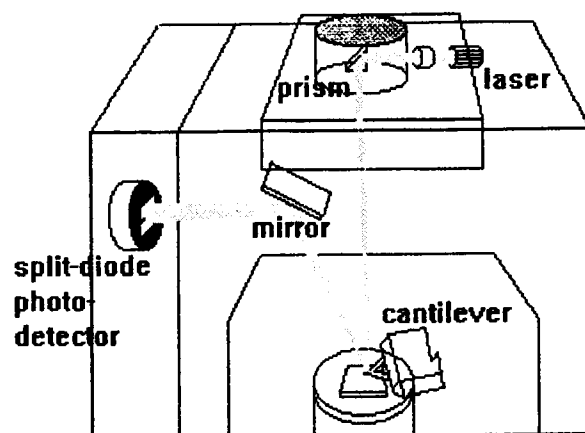
cantilever are used to obtain force data and to reconstruct the surface topography. In this section the operational modes and physical apparatus of the AFM are described.

There are three modes of operation. In the constant force mode, the deflection of the cantilever is held constant by an adjustment of the vertical position of the tip or the sample with a feedback loop using a proportional-integral-derivative (PID) controller. In a second arrangement, the sample is kept at a constant height and the deflection of the cantilever is recorded. The last operational mode is mostly used to measure long range forces. In this mode, the cantilever is modulated at its resonant frequency and the amplitude of the vibration is monitored as the tip is brought near the surface.

A typical apparatus, the Digital Instruments Nanoscope III, contains a head and a base, as shown in Figure 5. The base contains a piezo sample scanner and an L.E.D. to display parameters and deflection settings. A piezo electric scanner is a device that moves by a microscopic amount when a voltage is applied across its electrodes. Piezoelectric scanners for AFMs usually can translate in three directions (x, y, and z axes) and come in different sizes to allow maximum scan ranges of 0.5 to 125 μm in the x and y axes and several microns in the vertical (z) axis. A well built scanner can generate stable motion on a scale below 1 Angstrom. Figure 5b shows the head unit in more detail, including the laser diode deflection detection system developed by Sarid et al. in 1988. In this system a laser is reflected off the back of the cantilever into a bank of photo diodes, which records the vertical motion of the cantilever. Three-dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position.



(a)



(b)

Figure 5. Atomic force microscope (AFM) apparatus (26). (a) schematic of Digital Instruments Nanoscope III, Santa Barbara, California. (b) enlargement of the AFM head unit.

In addition to topographical data, the AFM can also provide much more information. The AFM can also record the forces felt by the cantilever as it approaches, comes in contact, and as it is pulled away from a surface. This technique can be used to measure the long range repulsive or attractive forces between the cantilever and the sample surface. With the recent addition of attaching a particle to the tip of the cantilever, the forces between an individual particle and another surface can be examined, elucidating local chemical and mechanical properties such as adhesion and elasticity, and even thickness of adsorbed molecular layers.

3.3 Sample Preparation

3.3.1 *Description of Colloidal Probes and Cantilever Modification*

Although many cantilevers exist, two main types are most popular. For the repulsive interactions, a standard V-shaped contact mode cantilever was used. This cantilever has a spring constant of 0.58 N/m, and is made of silicon nitride. This spring constant is sensitive enough that the repulsive forces can be measured between a polystyrene particle and mica surface immersed in water, but too weak to measure adhesive pull-off force. Therefore, the experiments studying the adhesive pull-off forces require stiffer cantilevers. For these experiments a cantilever made of pure silicon with a spring constant of 53 N/m was used.

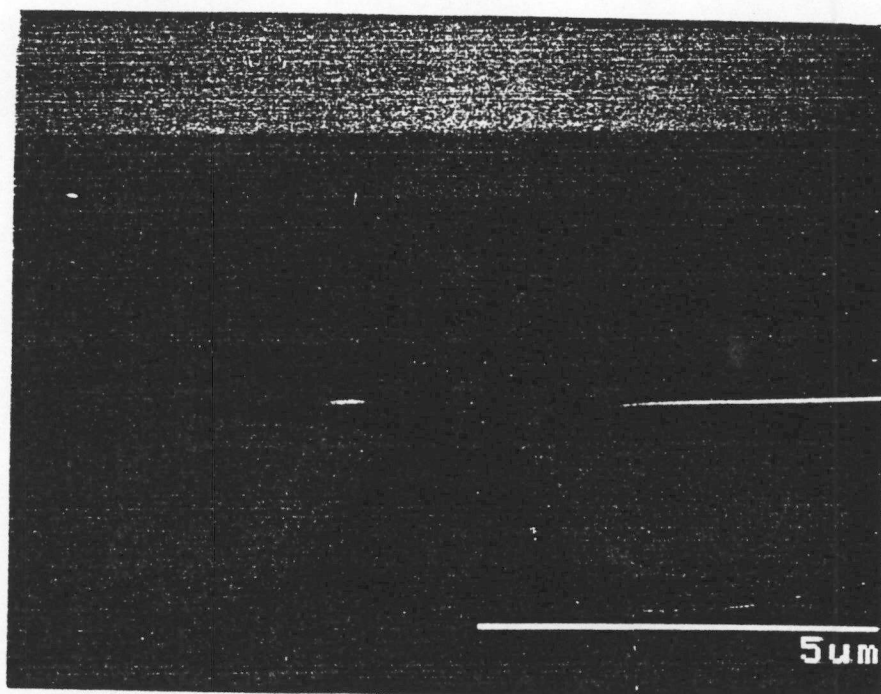
Both PS29 and PS57 particles were attached to 0.58 N/m and 53 N/m spring constant cantilevers with epoxy resin. Scanning electron microscope (SEM) images of the

cantilevers used for measurement are shown in Figure 6. These images were taken after all experiments were completed.

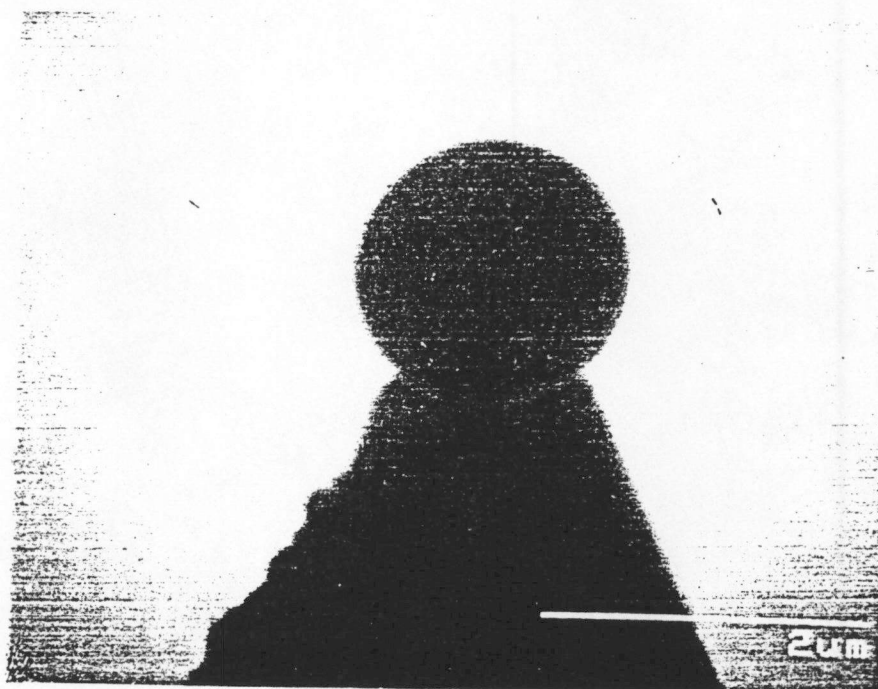
When measuring the interaction of an individual colloidal particle with an AFM, the particle is often greater than 4 μm . This allows the particle to be attached to the base of the cantilever without having to attach it directly to the tip. With a particle this large, the tip should never be able to touch the flat substrate. When studying the interactions of particles smaller than 4 μm , however, one must use either specially designed tipless cantilevers, or the method described in the following paragraphs.

For the 0.58 N/m cantilevers, the tip has a relatively low perspective (ratio of height to width). This, accompanied with the fact that only small forces can be applied and measured, allows the direct use of this cantilever without any modifications. The relative forces with the 0.58 N/m cantilever were low enough that the resin was sufficient to hold the particle in position on the tip throughout the repulsive force experiments.

However, with the 53 N/m cantilever, a different effect was observed. The high tip perspective accompanied with the larger forces made it almost impossible for the particles to remain glued to the side of the tip (near the apex) as in the case of the 0.58 N/m cantilever. With this cantilever, a different approach was needed. To overcome this attachment problem, a procedure was devised for dulling the tip leaving a flat spot on the contacting portion of the tip as shown in Figure 7. Typical dulling parameters include using the maximum scan area ($>10 \mu\text{m}^2$) with a rate of at least 10 Hz. With a force of 10 Volts and a scan angle of 90 degrees, one can obtain a modified tip as shown in Figure 7 after approximately 2 hours. It is important to note that although the above dulling



(a)



(b)

Figure 6. SEM photos of samples used for experimental measurement. (a) repulsive interactions studied using a 0.58 N/m cantilever. (b) contact interactions studied using a 53 N/m cantilever

procedure worked well for tip of spring constant 50 N/m, it was not as effective for higher spring constant cantilevers (~ 80 N/m). Once the tip was properly modified, the particles were glued directly on the flat surface, which provided an ideal supporting surface that was parallel to the mica surface.

3.3.2 *Procedure for Attaching a 2 μm Particle on the Tip of a Cantilever*

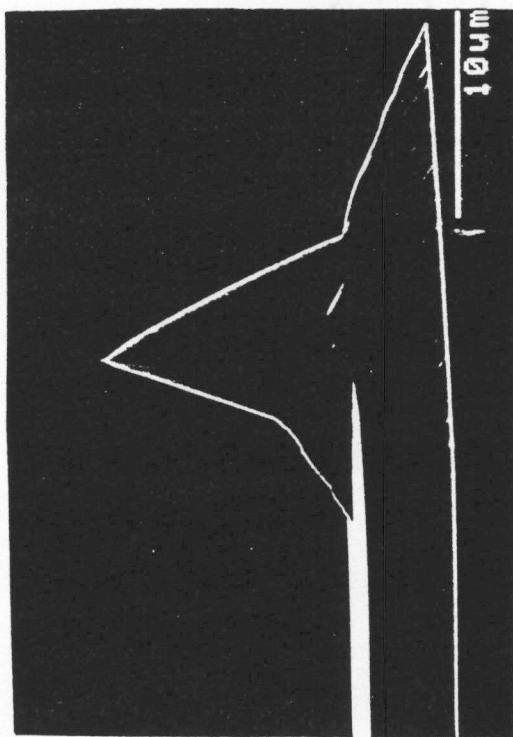
Attaching 2 μm particles to the tip of cantilevers requires a delicate procedure. Given the fact that a human hair is 80 microns in diameter, one can quickly imagine the relatively small sizes involved and the precision needed in the equipment. The system used consists of two microscopes placed side by side. One microscope is used for viewing the action of attachment. On the sample stage of this first microscope there is the cantilever (tilted 90° on its side), a freshly cleaved sheet of mica (titled 45° with the colloidal sample on its surface), and a copper fiber (with a relatively large drop of glue on its tip). The second microscope is used for movement of a manipulator. On the manipulator, there is an arched glass fiber (used for picking up the particles), and a small piece of straight copper wire (used for picking up a very small amount of glue).

Both copper wires were pre-cleaned and sharpened by placing in nitric acid for approximately 30 seconds, and subsequently rinsed in pure water. The copper wire on the manipulator is used to pick up a small mount of resin and place it on the cantilever tip. The arched fiber is rinsed with pure water by wiping with a water droplet attached to a pipette. This action greatly decreases the contaminants on the surface of the fiber. Once

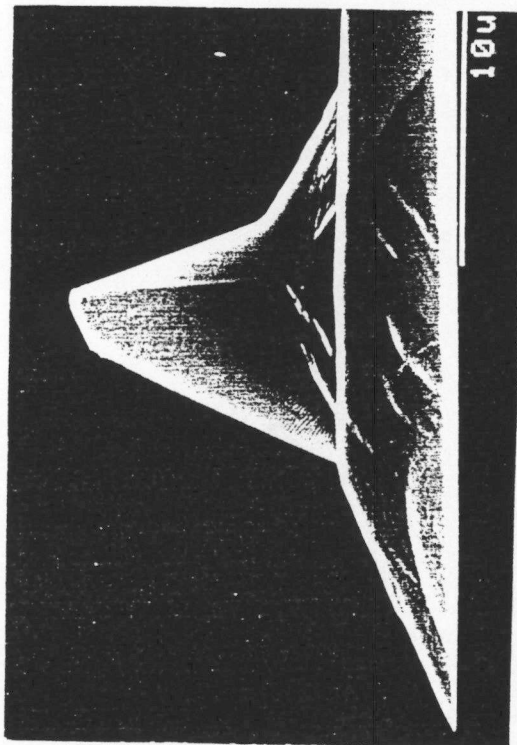
the fiber is satisfactorily clean as viewed through the microscope, it can be dipped into the colloidal sample located in the sample stage of the first microscope. This method easily picks up particles, so that it is only a matter of choosing the desired particle. Since the glue is already on the cantilever, the particle is easily pulled from the fiber onto the cantilever. Very fine movements in the manipulator can be achieved by applying a small pressure to the base of the microscope holding the manipulator. This causes the rubber legs to compress slightly, which translates to a more precise control in the manipulator. In addition, it is very important to have a stable desk or table for both microscopes to set. In the present case, the microscopes were resting on concrete tables that were part of the building structure. This provided a steady surface that minimized vibration.

3.4 Force Measurement

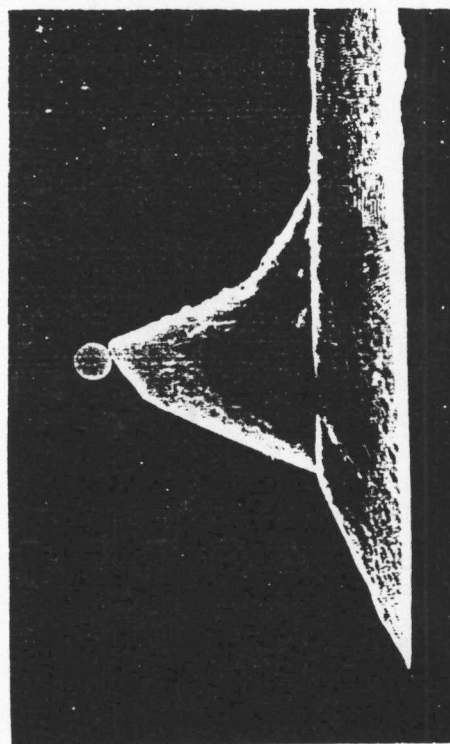
Force measurement from cantilever deflections is the heart of the operation for an AFM. Even deflections interpreted as topographical data for use in recreating surface images still require a calibration of the force curve. The standard force curve represents the movement of the cantilever upon interaction with a surface (Figure 8). This detection is measured using a laser that is reflected off the back of the cantilever. As the sample is raised toward the cantilever, the cantilever initially experiences a repulsive force from the electrostatic forces present and moves slightly upward away from the surface. As the sample is continually raised, the cantilever continues to move upward until it reaches a maximum point where the maximum repulsive forces occur (Figure 8b). After which, the



(a)



(b)



(c)

Figure 7. Scanning electron microscope (SEM) photos of AFM cantilevers.
 (a) new tip before use; (b) after dulling; (c) after attachment of the polystyrene particle

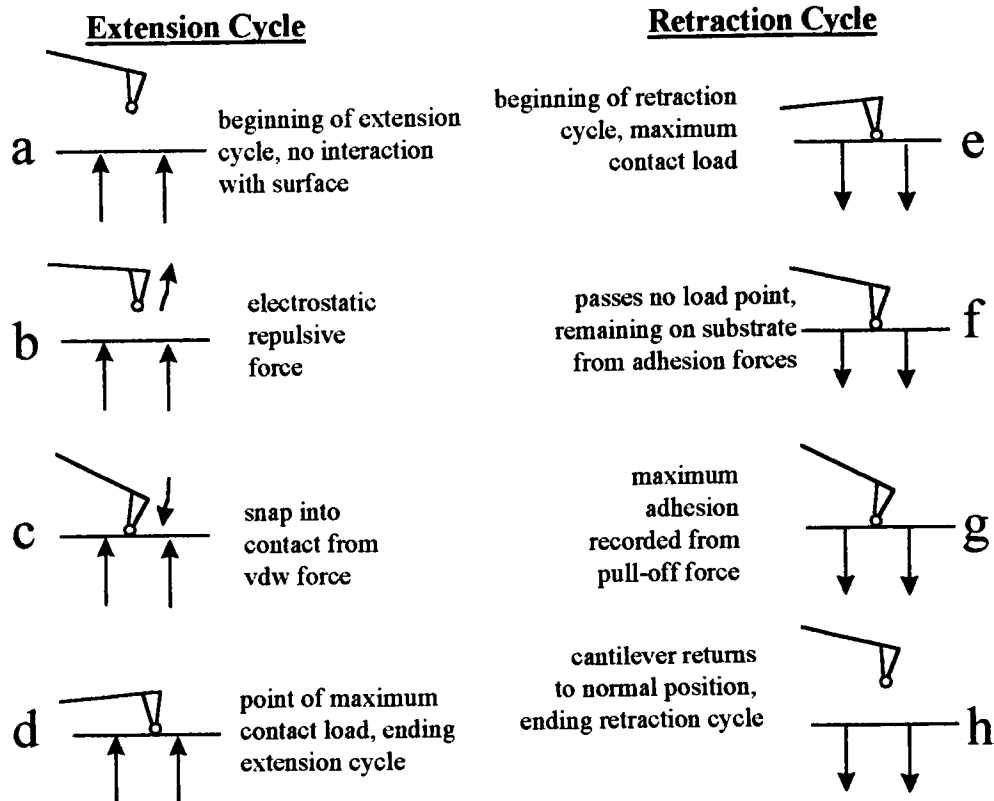
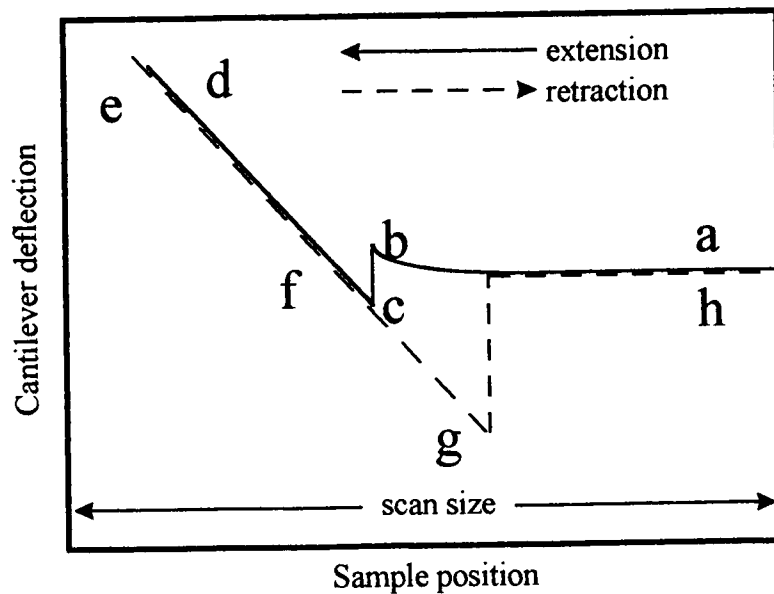


Figure 8. Model of an ideal AFM force curve (displaying both the extension and retraction sections of the curve)

cantilever snaps into contact with the sample surface from the strong van der Waals forces (Figure 8c). The sample is further raised until it reaches the maximum applied contact load ending the extension part of the cycle (Figure 8d). Then, the retraction part of the cycle begins as the sample is lowered releasing the load from the cantilever (Figure 8e). As the sample is lowered beyond the point of initial contact, the particle remains in contact with a negative load from the cantilever (Figure 8f). This continues until the force from the cantilever equals a maximum pull-off value (Figure 8g) from the adhesion forces causing the cantilever to snap back to its resting position (Figure 8h). The scan size represents the total distance traversed by the sample stage. The scan rate is the frequency of the total cycle, and the approach velocity can be calculated by multiplying the scan rate and the scan size.

When analyzing data, it is often necessary to obtain it in a more accessible form. After using the ASCII output function of the AFM software, the output file is not in a completely usable format. Since all data were taken with 512 data points, the output listed two series of data with the first 512 data points as the extension curve, and the last 512 points were the retraction curve. The output file was setup such that a program had to be written to convert the data into two vertical columns. Once the data are in form of two columns, it is relatively easy to recreate the as-measured AFM format as well as the more useful force versus distance format. The Z position or distance between each data point is obtained by dividing the scan size by the number of data points. After contact, the cantilever and flat substrate are moving vertically upward at the same rate (Figure 8d). The slope of this section of the curve is used as the sensitivity to convert voltage data

(used for manipulating the piezo) to distance data. This distance data is then converted to cantilever deflection data by an equation supplied by the AFM manufacturer, which changes depending on the software version used. Now the as-measured force curve obtained by the AFM can be recreated by plotting Z position (nm) versus cantilever deflection (nm) (Figure 9a). From here it is simple to convert to force versus distance curves. The force is simply the product of the cantilever spring constant (k) and the cantilever deflection (δz). The distance from the surface is obtained by adding the value of Z position (Z) and cantilever deflection (δz) at each data point (Figure 9b). The surface will be marked by a sharp increase in force with very little difference in distance.

In this form of force versus distance (Figure 9b), physically meaningful quantities can be easily extracted. The maximum repulsive force before contact is represented by F_R , and the snap-on deformation (d_{on}) is defined as the compressed distance from initial contact to the point of maximum compression. After contact, the maximum load applied by the cantilever is represented by F_C . When the cantilever remains on the surface with a negative load, it finally reaches the maximum pull-off force represented by F_A . In addition, the pull-off deformation of the particle is measured from the reference of maximum compression to the point of release. The remaining data will be discussed in terms of these variables.

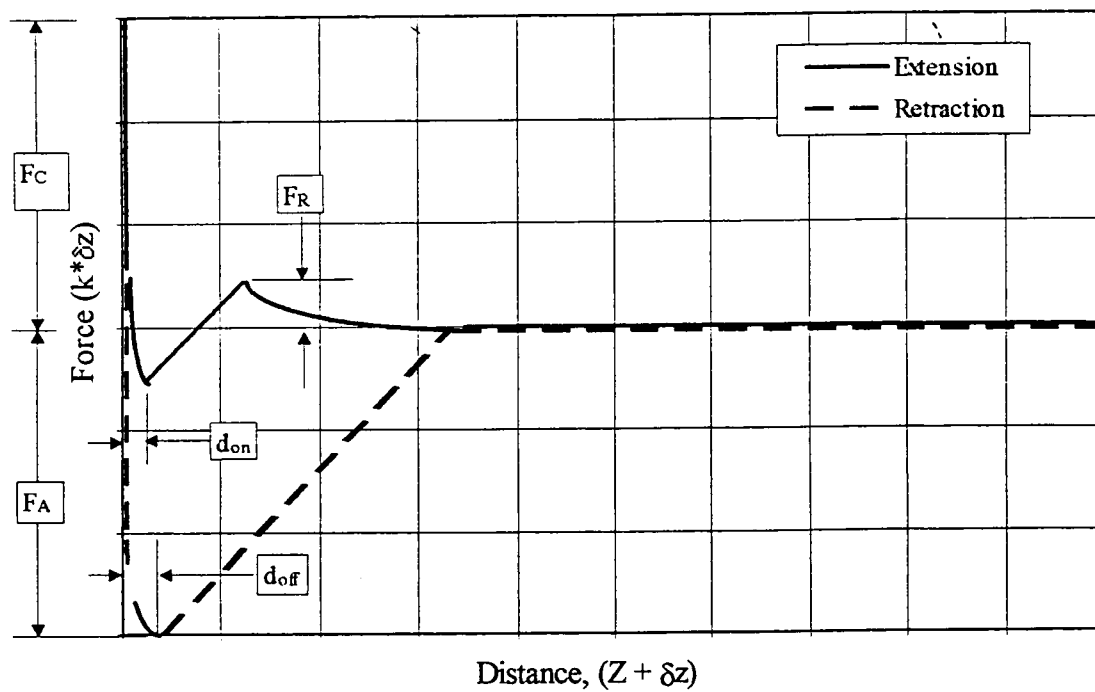
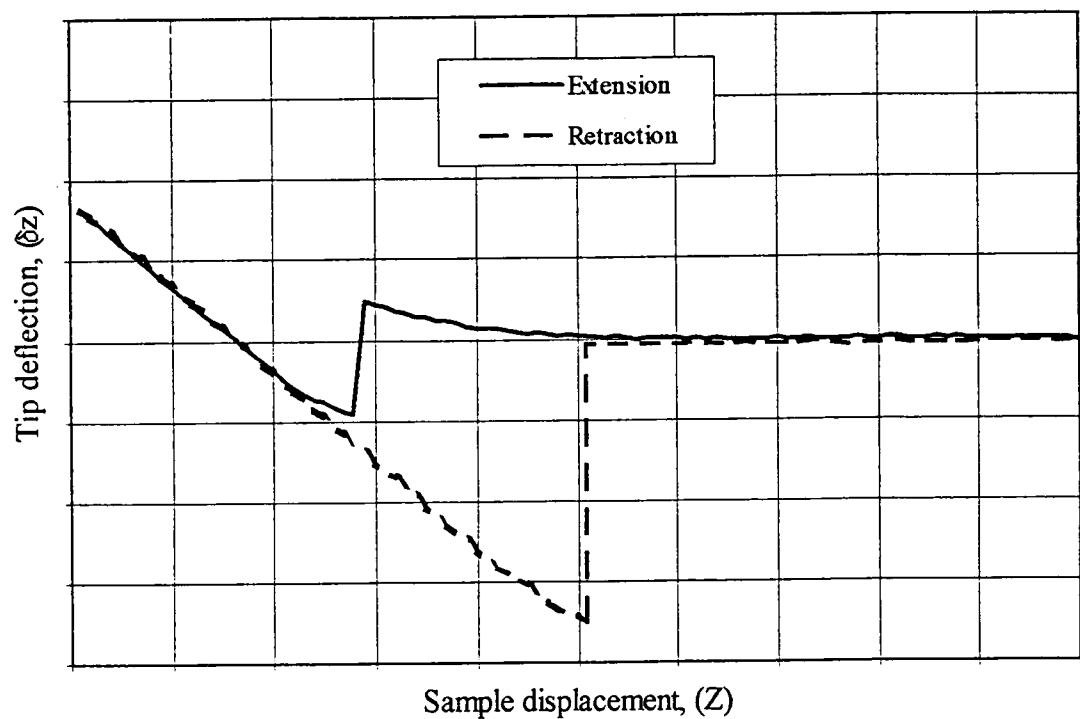


Figure 9. Force curve analysis. (a) Typical force curve with slight deformation. (b) Normalization and variable definition for a force curve with slight deformation

4. RESULTS AND DISCUSSION

Much has been learned about the interaction, adhesion, and deformation forces between spherical particles of polystyrene and mica in aqueous solutions. In this section, a discussion is presented on the typical force curves obtained from the atomic force microscope. Depending on the elasticity of the materials being tested, deformation of the particle or surface can be observed in the force curve. Examples are shown for rigid and compliant contacts between surfaces. Next, repulsive interactions have been observed that cause noticeable deformation of the particle even before the surfaces come into contact. Once in contact, the particle were found to display both elastic and inelastic responses depending on the magnitude of the applied force. While still in contact, adhesion and deformation forces between the polystyrene particles and mica were studied elucidating relationships with contact force and contact time. Based upon a well-known theory for adhesion of particles to substrates (19,32), the contact radius was calculated from adhesion measurements and compared with contact radii derived from direct measurements of particle deformation.

4.1 Typical AFM Force Curves

After attaching a colloidal particle to the tip of the cantilever, the forces between the particle and another surface can be measured. A typical force curve for the interaction of a silica particle and a mica surface in water is included in Figure 10 as a reference for

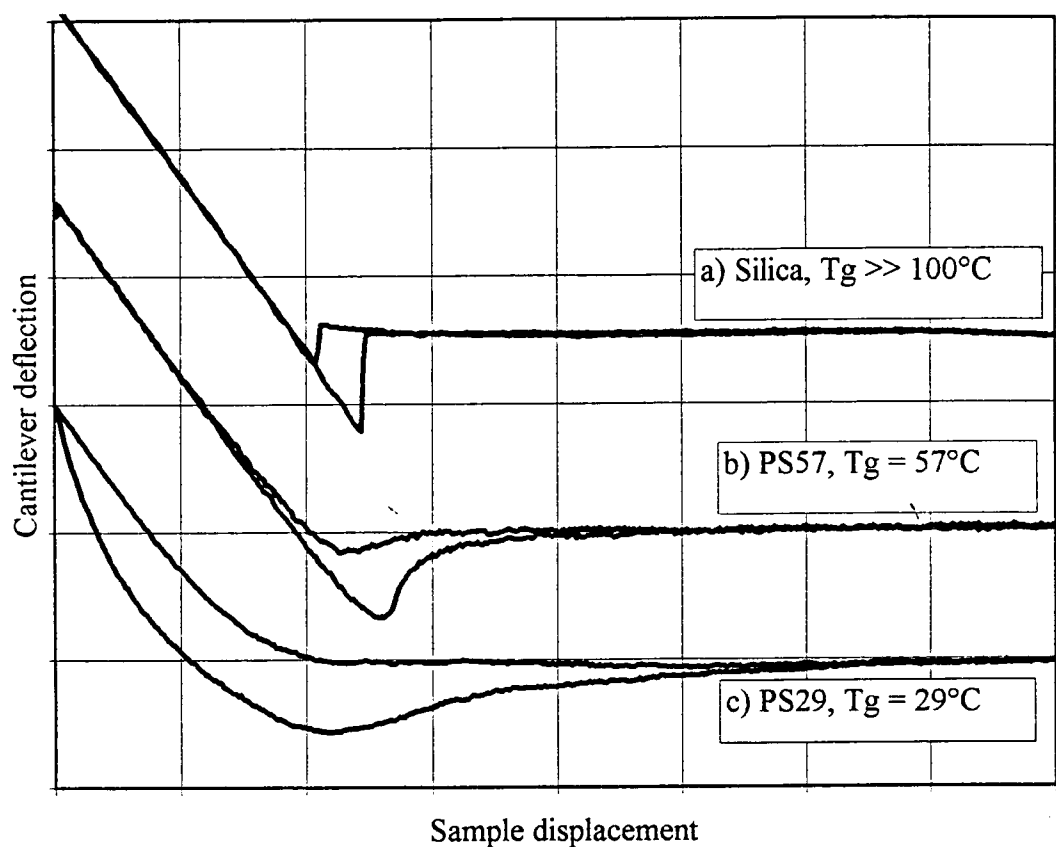


Figure 10. Typical atomic force microscope (AFM) force curves displaying rigid and compliant contact. (a) silica particle and mica in water; (b) PS57 particle and mica in water; (c) PS29 particle and mica in water.

the effect of rigid contact. This curve was obtained using a cantilever with a spring constant of 0.58 N/m, and displays sharp and instantaneous snaps into and away from the surface, much like an ideal force curve in Figure 8. Characteristic force curves between polystyrene particles and mica in pure water are also shown in Figure 10. Deformation of the PS particles is evident in both force curves. The absence of a repulsive force in the PS force curves is the result of using a large spring constant cantilever. To record the maximum pull-off force of PS on mica in water, cantilevers with a spring constant of 53 N/m were required. For the PS29 particle, the retraction cycle indicates major particle deformation. For both PS curves, after passing the maximum pull-off force, the cantilevers do not “snap” back from the contacted position. This is the result of the strong attractive forces that are induced from the temporary increase in effective contact area of the particle. Just after detachment, the particle's surface area closest to the mica surface is increased from the flattening of the particle's surface due to deformation from the applied force.

Figure 11 displays the as-measured AFM data for the spectrum of force curves obtained at various applied forces for the PS57 sample and mica in water. Slight deformation is evident when the particle first makes contact with the surface, but does not continue as the applied force is increased. Also it is interesting to notice the trend in adhesive force as the applied force is increased.

Figure 12 displays the as-measured AFM data for the spectrum of force curves obtained at various applied forces for the PS29 sample and mica in water. This series of curves has very large observed deformations with increased applied force. All curves have

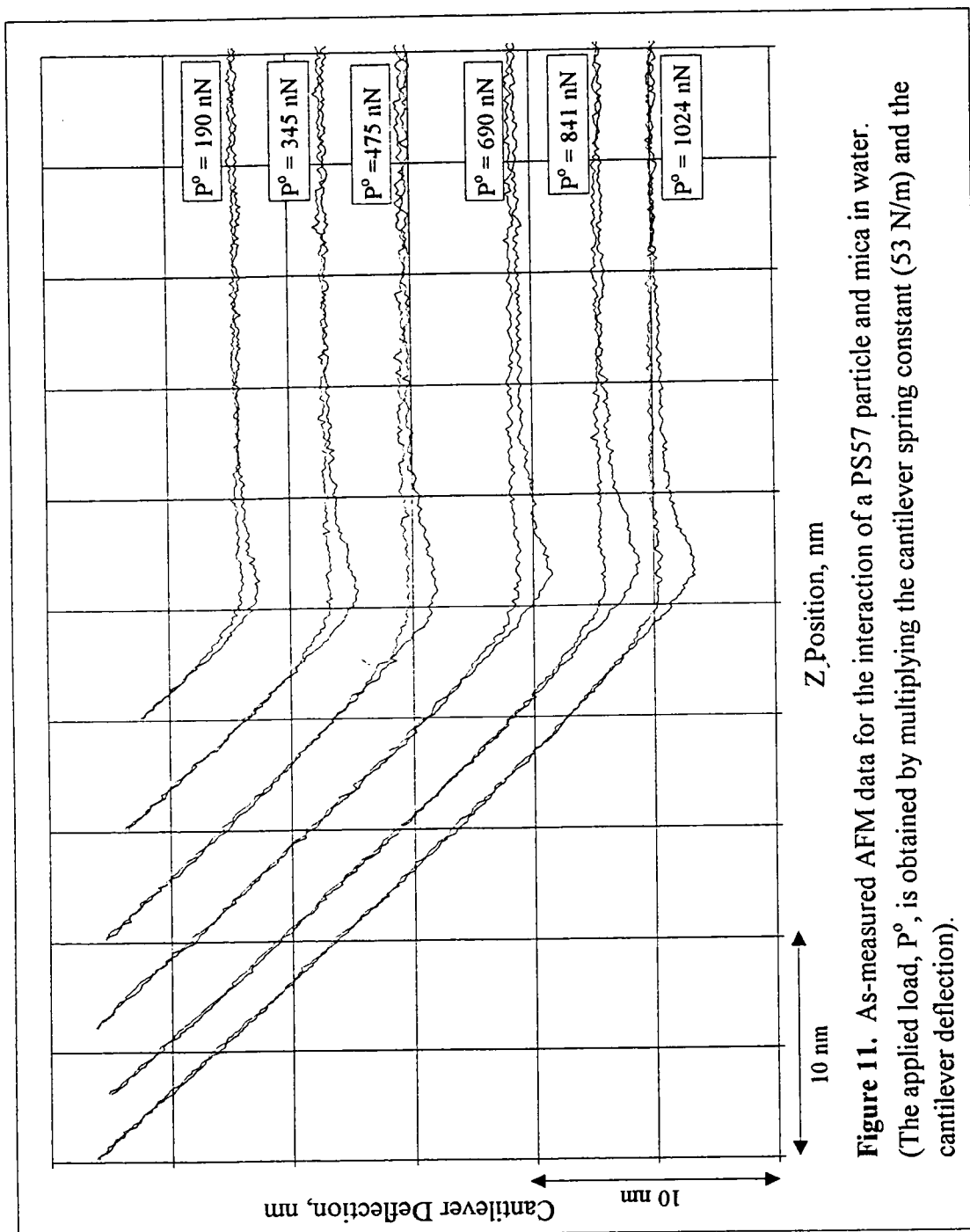


Figure 11. As-measured AFM data for the interaction of a PSS7 particle and mica in water. (The applied load, P^0 , is obtained by multiplying the cantilever spring constant (53 N/m) and the cantilever deflection).

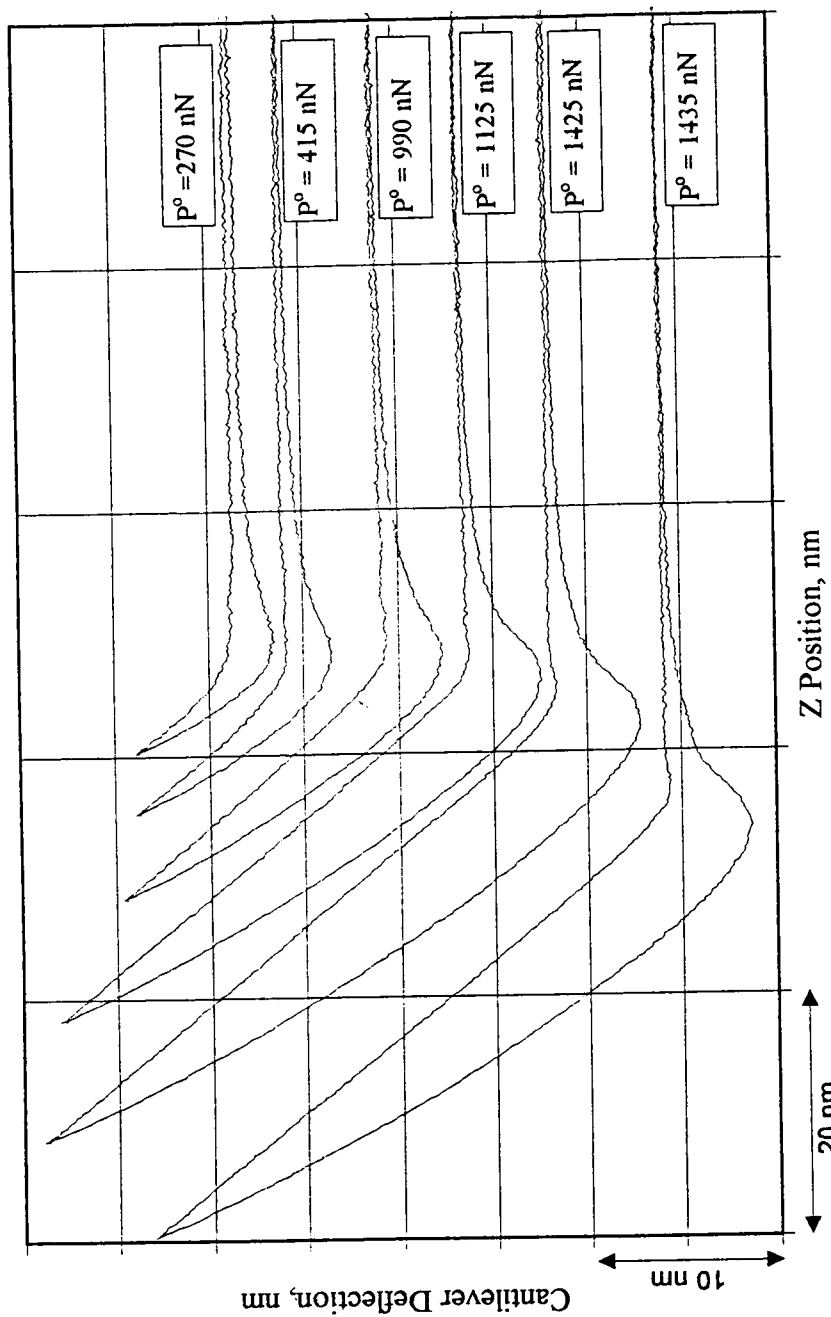


Figure 12. As-measured AFM data for the interaction of a PS29 particle in water. (The applied load, P^0 , is obtained by multiplying the cantilever spring constant (53 N/m) and the cantilever deflection).

an observed hysteresis that is caused from the compression of the particle's vertical diameter during both the extension and retraction sections of the force cycle. For the relatively short time period of these curves, as long as there exists an applied force, the particle continues to compress even at the lower applied forces.

Figure 13 displays the normalized form of the AFM force curve for a PS57 particle. This form is obtained by first converting the axes to force versus distance from the as-measured tip deflection versus sample displacement data (Figure 9). The conversion method is explained in Section 3.4 of the chapter under Experimental Aspects. After conversion, one must adjust a value called the sensitivity, which converts the values obtained directly from the AFM (volts) to values understood in terms of distance from the surface (nanometers). For the PS57 particle the adjustment was relatively simple. The optimum shape of the curve occurred when the data near maximum applied load were vertical. Curves are also displayed for sensitivities that are factors of 0.7 and 1.2 of the optimum value to show the adverse effect of incorrect adjustment.

Figure 14 displays the normalized form of the AFM force curve for a PS29 particle. The sensitivity adjustment for this curve is more complicated than with the PS57 curve. Because of the large deformation in the particle from the applied forces, the force curve contains a large hysteresis that must be considered when determining the optimum sensitivity adjustment. As before, the sensitivity has an adverse effect on the shape of the normalized force curve. Since the shape of the curve is linear during extension under an applied load, it is possible to locate the optimum sensitivity. It is very fortunate that the compression of the particle's vertical diameter is linear with the rate of increase in the

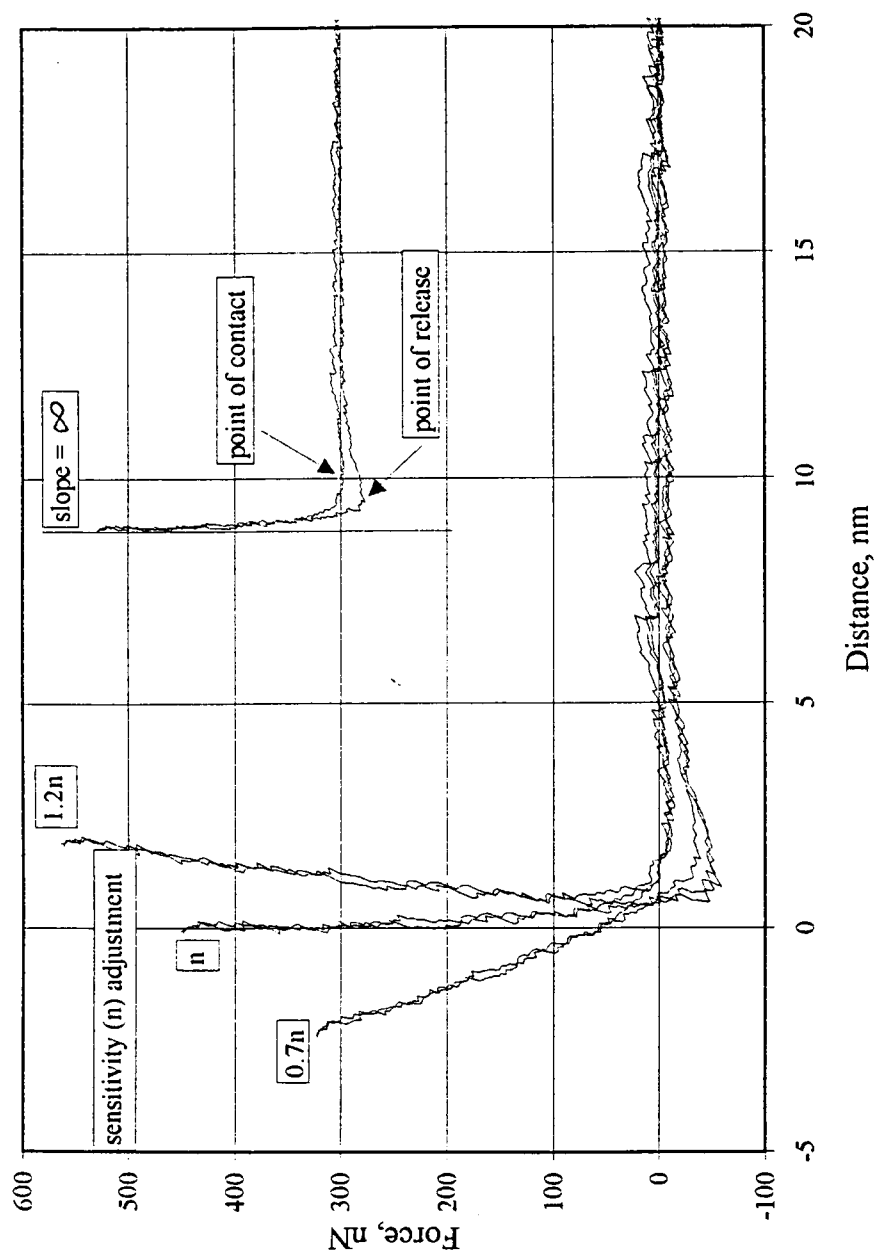


Figure 13. Normalization of the atomic force microscope force curve of a PSS7 particle and mica in water. (Deformation is observed only when the surfaces first meet and does not occur at large applied loads).

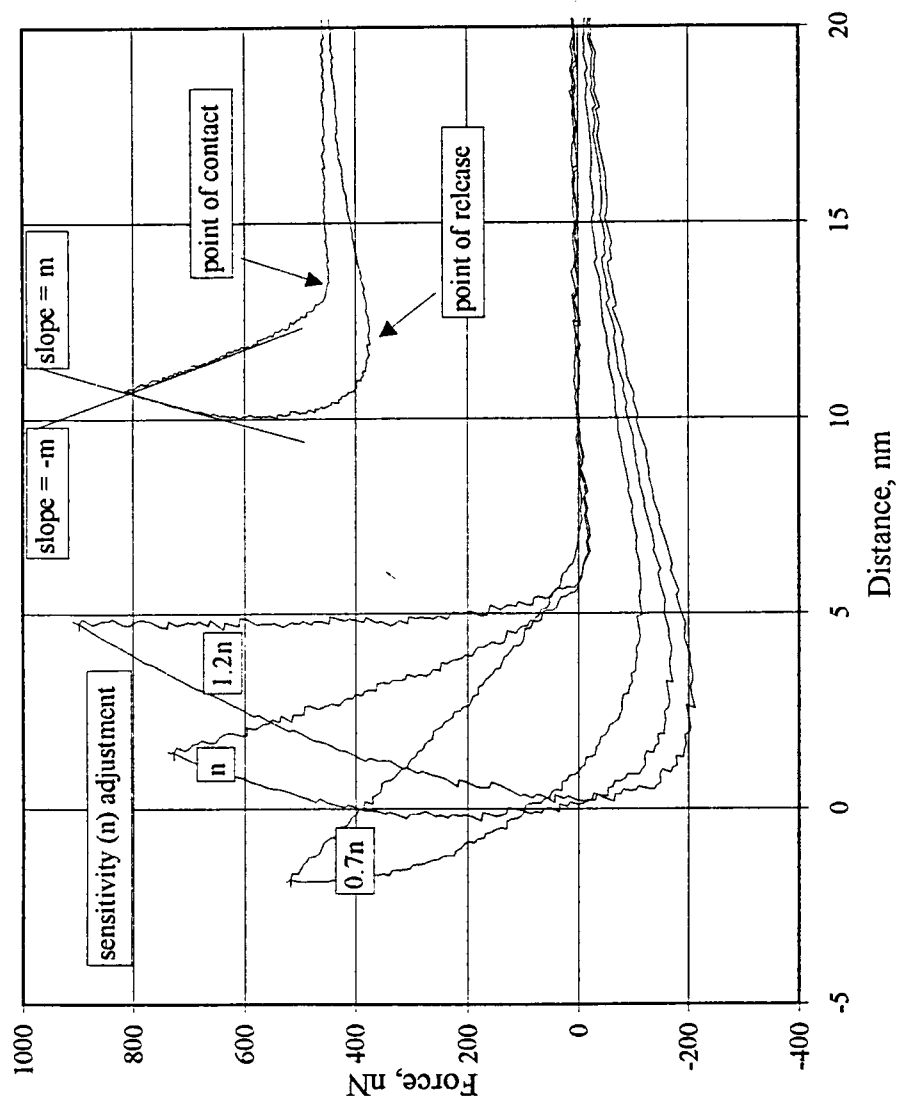


Figure 14. Normalization of the atomic force microscope force curve of a PS29 particle and mica in water. (Since the deformation is linearly increasing with the applied force during compression of the particle, the linearity will continue just past the point of maximum load. The sensitivity is adjusted until the slopes, before and after maximum load, are equal, but opposite sign.)

applied force. From this artifact, it is assumed that the particle is compressing at the same rate just before and after maximum contact load such that the slopes are equal, but opposite in sign.

Figure 15 gives a description of the physical conditions at various positions along the normalized force curve of a PS29 particle and mica surface in water. The curve represents the deflection of a cantilever from the interactions of another surface that is raised to and lowered from the cantilever. At position a , the particle and surface are separated by a large distance sufficient that no forces are observed in the cantilever. At point b , the mica surface is close enough such that the cantilever deflects slightly downward and the particle comes into contact with the mica surface from the attractive van der Waals forces. This marks the point of initial contact between the polystyrene particle and the mica surface. At point c , the particle and cantilever have been raised by the mica surface such that they are in the same location as steady state, a , where no load is applied on the particle. At point d , the mica surface is continually raised until it reaches a maximum height corresponding to a specified maximum applied force from the cantilever. After reaching the maximum height, the mica surface stops rising and is immediately lowered. At no other position in the curve does the mica surface stop its vertical motion. During the condition where the deflection of the cantilever causes an applied force the PS29 particle continues to deform until it reaches point e . At this stage the cantilever is at the position of no contact load once again, and no deformation is observed at this location. The mica surface is continually lowered past point e , where a negative load occurs on the cantilever. At point f , the cantilever detaches from the mica surface and slowly moves

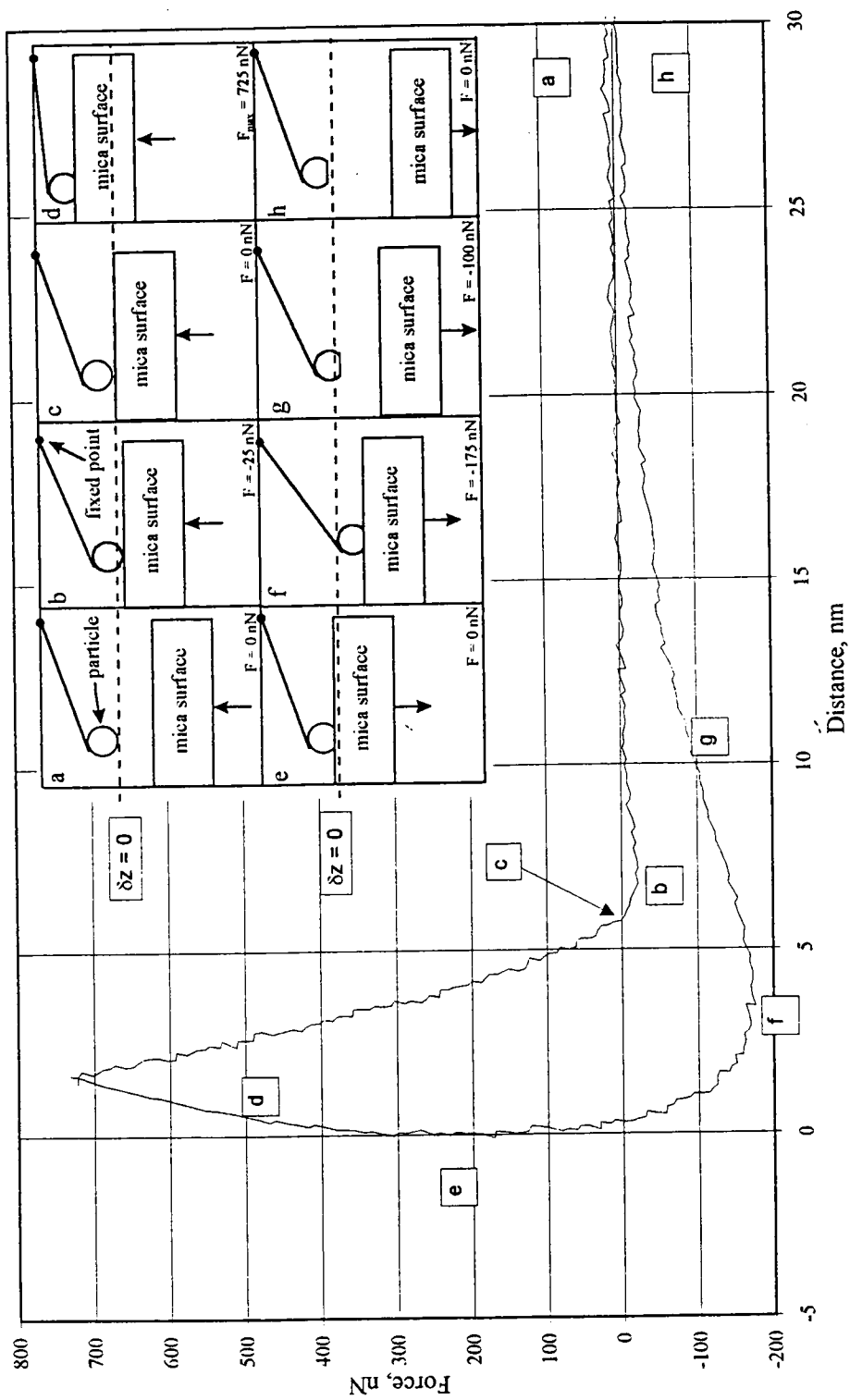


Figure 15. Description of the physical condition at various points along the normalized force curve for a PS29 particle and mica in water.

back to the steady state position h . The reason for the slow return to steady state at point g is because the particle's surface area closest to the mica surface is now increased from the deformation. This increase in surface area induces a much larger attractive force causing the force curve to display a slower return to the steady state position.

Clearly, much information is gained by simply examining the force curves. By comparing the curves of rigid and compliant contact, it is possible to gain further insight into the realm of deforming media. With the ability to directly measure the precise deformation of individual particles and/or surfaces on this level, various forms of characterization such as microhardness and other physical testing can be greatly enhanced.

4.2 Repulsive Interactions at Finite Separations

The repulsive interactions between polystyrene particles and mica surfaces in water can be studied using a 0.58 N/m cantilever as shown in Figure 16. In this figure, only the extension part of the force curve cycle was studied. All three curves represent the repulsive interaction of the same PS29 particle with a mica surface in pure water. The only parameter adjusted was the scan rate (approaching velocity). Depending on the velocity at which the surface and particle were brought together, noticeable trends were discerned for the maximum repulsive forces, the attractive pull-on forces, and the particle deformation after contact. At the highest velocity, the repulsive force was the highest, the pull-on force during the snap to the surface was the lowest, and particle deformation after contact was the largest (see Figure 16). However, as the approaching velocity was

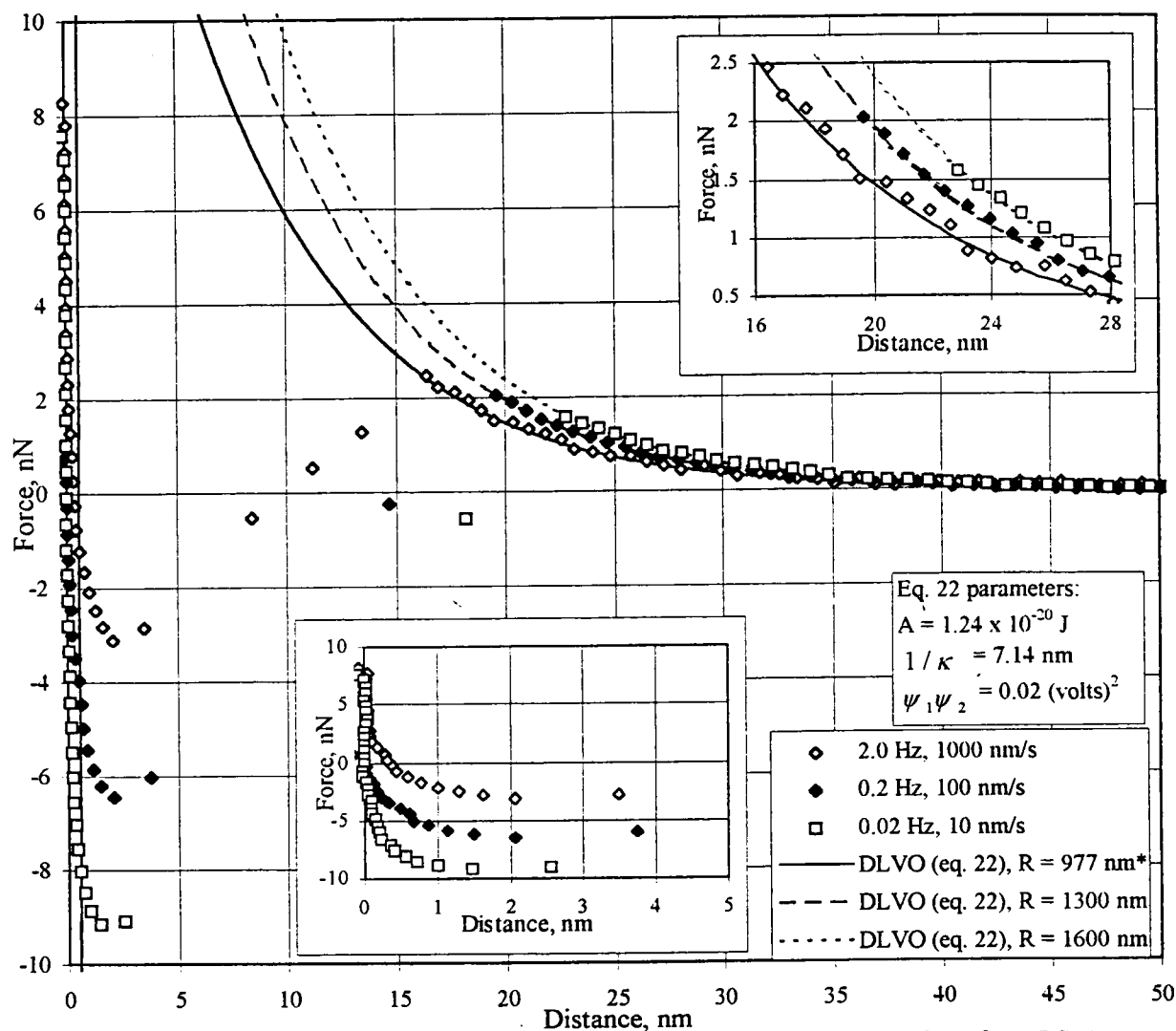


Figure 16. Dependency of approach velocity on observed repulsive interactions for a PS29 particle with mica in water. (* The measured radius is 977 nm. This radius was used in fitting eq. 22 to the force curve of the highest velocity. In fitting the other velocities, the radius was used as the adjustable parameter.)

lowered, a very interesting effect was observed. The repulsive forces lowered, the pull-on forces increased, and the particle deformation after contact decreased.

Before the analysis is presented on varying the approach speed, it is important to acknowledge the fact that at all approach velocities, the particle snaps into the surface at large distances (16-23 nm). Recalling that van der Waals forces occur only at very close distances of 0.2-10 nm, the larger distance is unexpected from DLVO theory. According to DLVO theory, the maximum repulsive forces should be predicted by the peak in the DLVO curve. It is apparent that an additional attractive force is balancing the electrostatic term, causing the peak to be much lower and at a further distance away from the surface. This phenomena has been observed in many previous studies using the AFM. Karaman et al. (46) observed this same effect with a polystyrene particle and a flat sheet of premelted polystyrene in water. Their conclusion was that the longer range attraction force was attributed to hydrophobic interactions, which are still under intense study by many researchers. They reasoned that this was not unexpected because of the hydrophobic nature and correspondingly high water contact angle ($> 90^\circ$) of polystyrene.

4.2.1 *Influence of Drag Force on Observed Repulsive Forces*

In an attempt to understand the reasons for the observed differences in the force curves, an evaluation using Stokes law of resistance from particle sedimentation theory was completed. The relationship for Stokes law of resistance is given by the following

$$F_D = 3\pi\mu D_p u \beta \quad (28)$$

where

$$\beta = \frac{6\bar{h}^2 + 13\bar{h} + 2}{6\bar{h}^2 + 4\bar{h}} \quad \text{and} \quad \bar{h} = \frac{2h}{D_p} \quad (29)$$

In determining the drag force from Stokes equation, the primary variable is the velocity (u) at which the particle moves toward the surface. The second important parameter is the distance from the surface (h). In the present case the velocity is determined, but the exact distance at which the force should be obtained is somewhat unclear. Nevertheless, a sequence of distances has been chosen that allows comparison of the relevant forces present. Table 6 displays a summary of the evaluation. It is evident that at the velocities of 1000 nm/s and 100 nm/s the calculated differences in drag forces (0.4 nN at 20 nm from the surface) are the correct order of magnitude for the measured differences in maximum repulsion (0.4 nN). However, for the comparison of 100 nm/s and 10 nm/s, the difference in drag force drops an order of magnitude (0.04 nN), while the measured difference in maximum repulsion remains relatively high (0.36 nN), which results in unexplained behavior. In conclusion, this result confirms that although the drag force contribution to the observed decrease in repulsion is the correct order of magnitude for the two higher velocities (1000 and 100 nm/s), the same explanation does not hold true for the lower two velocities (100 and 10 nm/s).

Table 6. Calculated drag forces and their effect on observed repulsive interactions

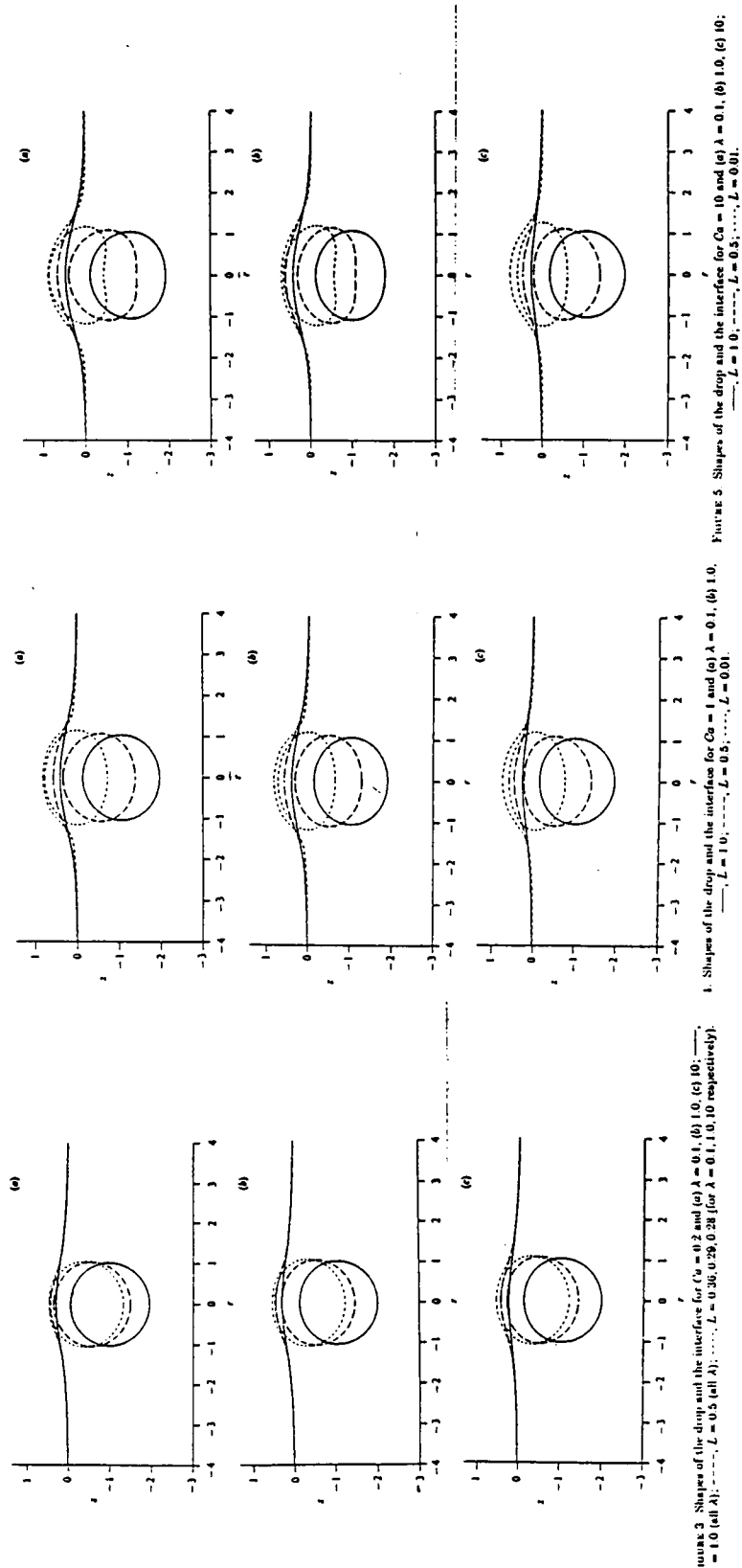
Particle velocity nm/s	Maximum repulsion measured (Fig. 16) nN	Drag force calculation at distances				
		10 nm	20 nm	30 nm	40 nm	50 nm
1000	2.52	0.845	0.442	0.308	0.241	0.200
100	2.12	0.084	0.044	0.031	0.024	0.020
10	1.76	0.008	0.004	0.003	0.002	0.002

4.2.2 Influence of Particle Deformation on Observed Repulsive Forces

The next plausible explanation for this phenomena is that the particle is deforming as a result of the repulsive forces acting on it. The particle is deforming at different amounts depending on the time scale of the force curve measurement. For the lowest velocity, the particle has time to deform to compensate for the repulsive forces allowing the cantilever to deflect less (giving a lowered maximum observed repulsive force). This is achieved by a slight compression of the particle's vertical diameter. However, this slight compression in vertical diameter causes the particle to have an increased effective surface area near the mica surface. This increase in surface area causes an increase in the van der Waals and hydrophobic forces (resulting in larger pull-on forces). In addition, since the particle has already compressed slightly before contact, when it reaches the surface it compresses less for the same applied force (supporting the observed lowered compressive deformation). To test this idea, the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory was compared. This was done by fitting the DLVO theory (equation 22) to the force curve measured for the highest velocity. For this case the radius was assumed to be

the measured value of 977 nm. The fitting parameters of the DLVO theory in equation 22 are the inverse Debye length (κ) and the product of the surface potentials ($\psi_1\psi_2$). The Hamaker constant was calculated from equations 7-10 as 1.24×10^{-20} J. After fitting with the DLVO theory for the highest velocity force curve, where the particle displays rigid characteristics, the remaining force curves were fitted by adjusting only the particle radius until an adequate fit was established. Despite adjusting with only the radius, it was possible to make the subsequent curves from the DLVO theory agree with the other velocity force curves, supporting our theory of increased effective particle size due to deformation. As will be shown in the next section, these values of increased effective radii are very reasonable.

To further support the idea of large particle deformations, models from fluid mechanics have been included. Models for the motion of a viscous drop toward a fluid interface (Figure 17) and toward a planar wall (Figure 18) are presented. In Figure 17, the drop is defined as a light liquid rising through an immiscible heavy liquid, toward an initially flat interface which separates the heavy bulk fluid and another lighter fluid. For Figure 18, the model is comparing the photographic results of a drop of golden syrup containing potassium iodide falling under the influence of gravity through sextol phthalate towards a planar wall. In both figures, the various sub-figures are displaying the differences of varying Ca , the capillary number, (function of: viscosity, surface tension, and buoyancy) and λ (ratio of viscosities). Both models display a spherical drop that exhibits large deformation as it approaches an interface. A similar trend in these figures for a relatively large sphere gives insight into the deformation that is occurring in the



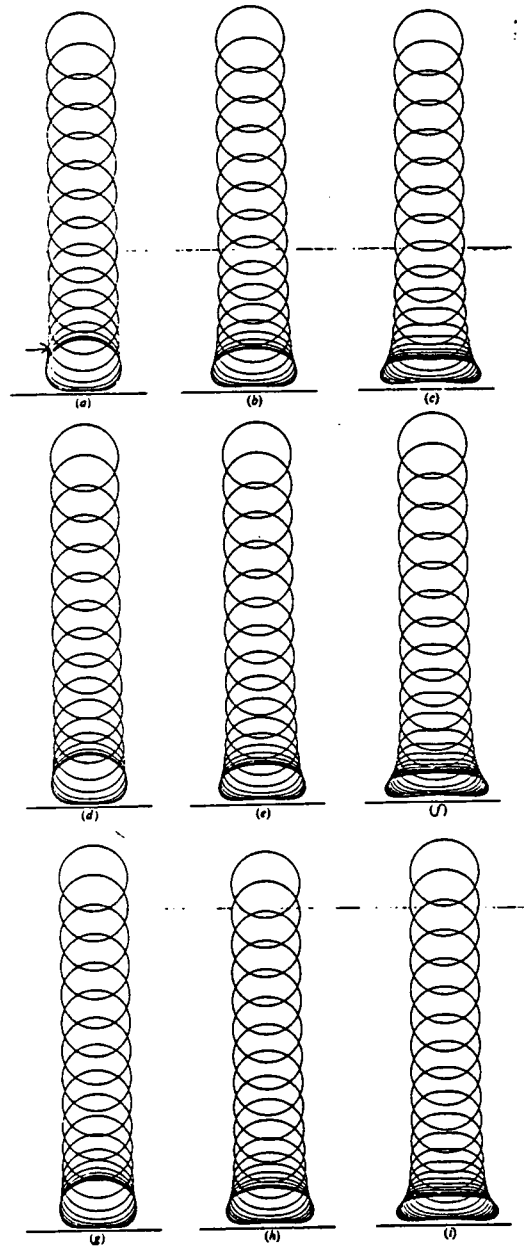


FIGURE 3. Evolution of drop shape. The dimensionless time between shape curves is 1. (a) $Ca = 0.3$, $\lambda = 0.3$; (b) $Ca = 1$, $\lambda = 0.3$; (c) $Ca = 3$, $\lambda = 0.3$; (d) $Ca = 0.3$, $\lambda = 1$; (e) $Ca = 1$, $\lambda = 1$; (f) $Ca = 3$, $\lambda = 1$; (g) $Ca = 0.3$, $\lambda = 3$; (h) $Ca = 1$, $\lambda = 3$; (i) $Ca = 3$, $\lambda = 3$.

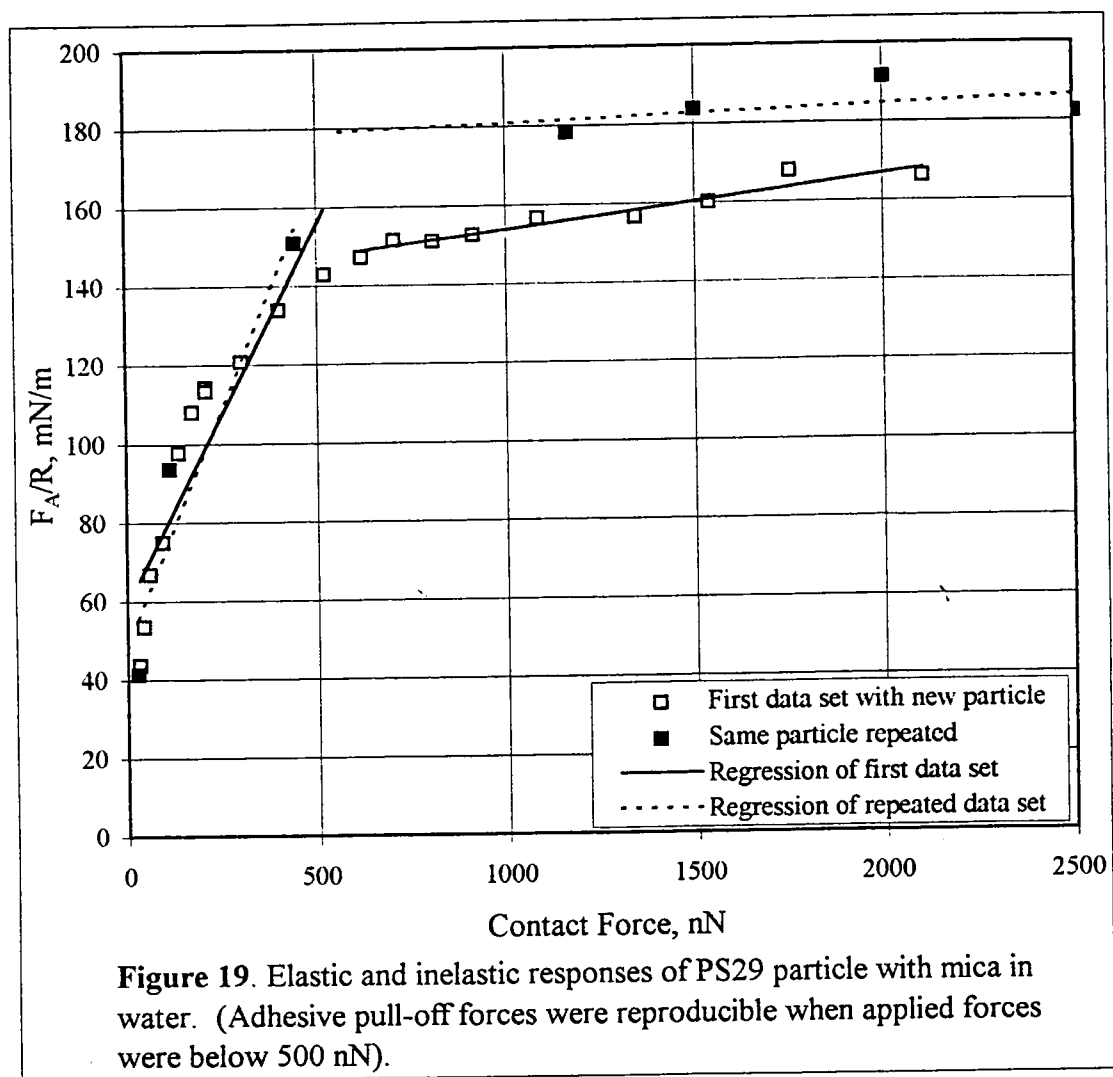
Figure 18. Model of the motion of a deformable drop toward a rigid planar surface (35).

present study where the sphere is very small. In addition, the relative amounts of particle deformation determined with the polystyrene are only a fraction of these observed in the fluid mechanics models, which further supports the plausibility of this particle deformation explanation.

4.3 Adhesion and Deformation Forces at Contact

4.3.1 *Elastic and Inelastic Responses to Contact Load*

As the sphere and planar surface are brought together and the adhesive pull-off force is measured, the data show characteristics of both elastic and inelastic deformation. This study was completed by taking the first set of data using a new particle, and then repeating under the same conditions with the same particle. At applied forces below 500 nN, the force curves for both PS29 and PS57 particles were reproducible for a given experiment (see Figures 19 and 20). Regression lines have been included for sets of data both above and below the applied force of 500 nN. The regression lines convey the reproducibility at lower applied force and accentuate the difference when the applied force is increased beyond 500 nN. The repeated data set should overlap if the particle deforms elastically. Instead, the repeated data set shows a larger adhesion force than the first data set at applied loads larger than 500 nN. Previous studies from Rimai et al. (16, 17) suggest an inelastic response while experimenting with micron-sized polystyrene particles. Their studies support this observed phenomena. Therefore, the remaining evaluation will concentrate on the data taken at applied forces below 500 nN to improve reproducibility.



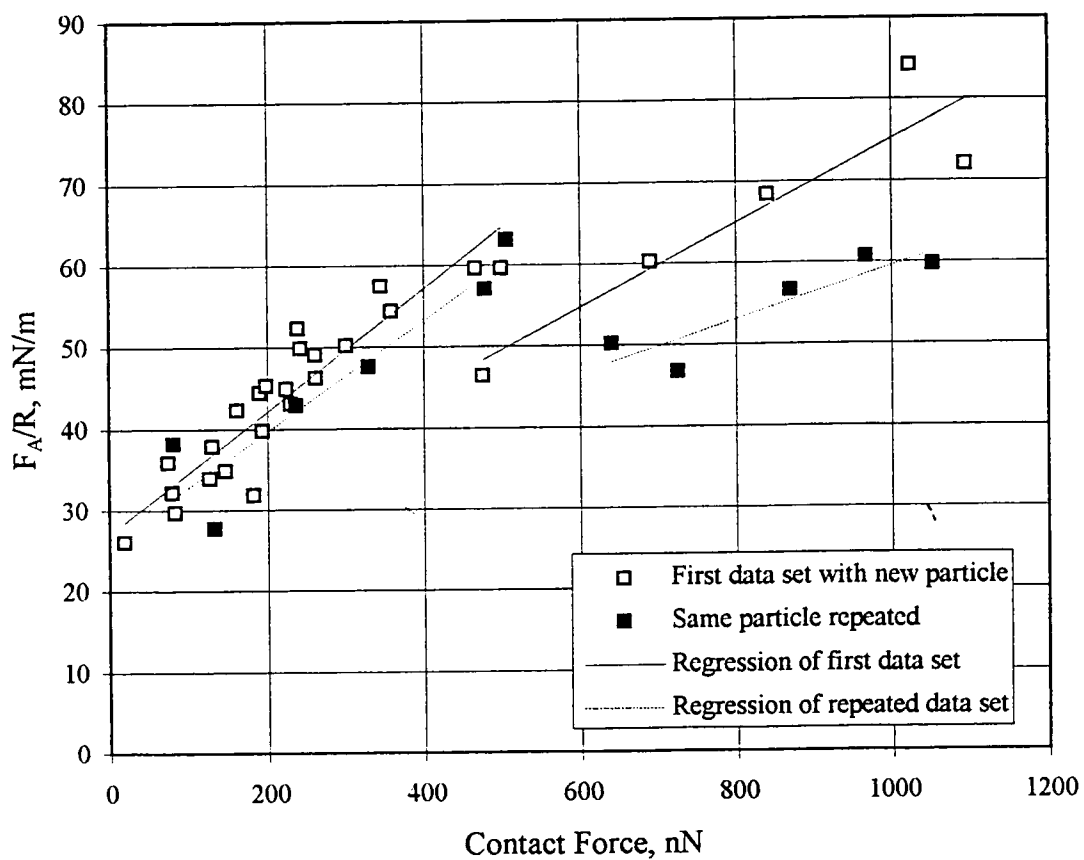


Figure 20. Elastic and inelastic responses of a PS57 particle with mica in water (Adhesive pull-off forces were reproducible when applied forces were below 500 nN).

4.3.2 *Contact Force Measurements*

The relationships of adhesive pull-off force and particle deformation with applied force were studied between PS29 and PS57 particles and mica in water. Figure 21 relates the applied force with the corresponding pull-forces for both PS29 and PS57 particles. In these measurements the contact time was held relatively constant by taking all data at the same scan rate (2 Hz). The maximum contact time for these data is 0.24 seconds. The adhesive force has been divided by the particle radius to remove the slight difference in particle diameters between samples. The linear regression lines are included to display the no-load adhesive force (intercept). The no-load value represents the adhesive force without any applied force, which best describes a real system. As expected, the PS29 particle was found to have a much higher no-load adhesive force (97.2 mN/m) than the PS57 particle (30.3 mN/m). In addition to the increased adhesion, the PS29 particle displays a greater dependence with applied force denoted by the higher slope of the data.

Figure 22 relates both the snap-on and pull-off particle deformation with contact force. The deformation also has been normalized to remove particle size dependencies by dividing by the particle radius. Again the PS29 particle displays a greater dependency with deformation from applied force, while the PS57 particle shows a very weak dependency. As expected for both particles, the snap-on deformation is larger than the pull-off deformation. This is because of the way the deformations are defined. For the case of the snap-on deformation, the measurement refers to the distance between initial contact and maximum compression. However, for the pull-off deformation, this refers to

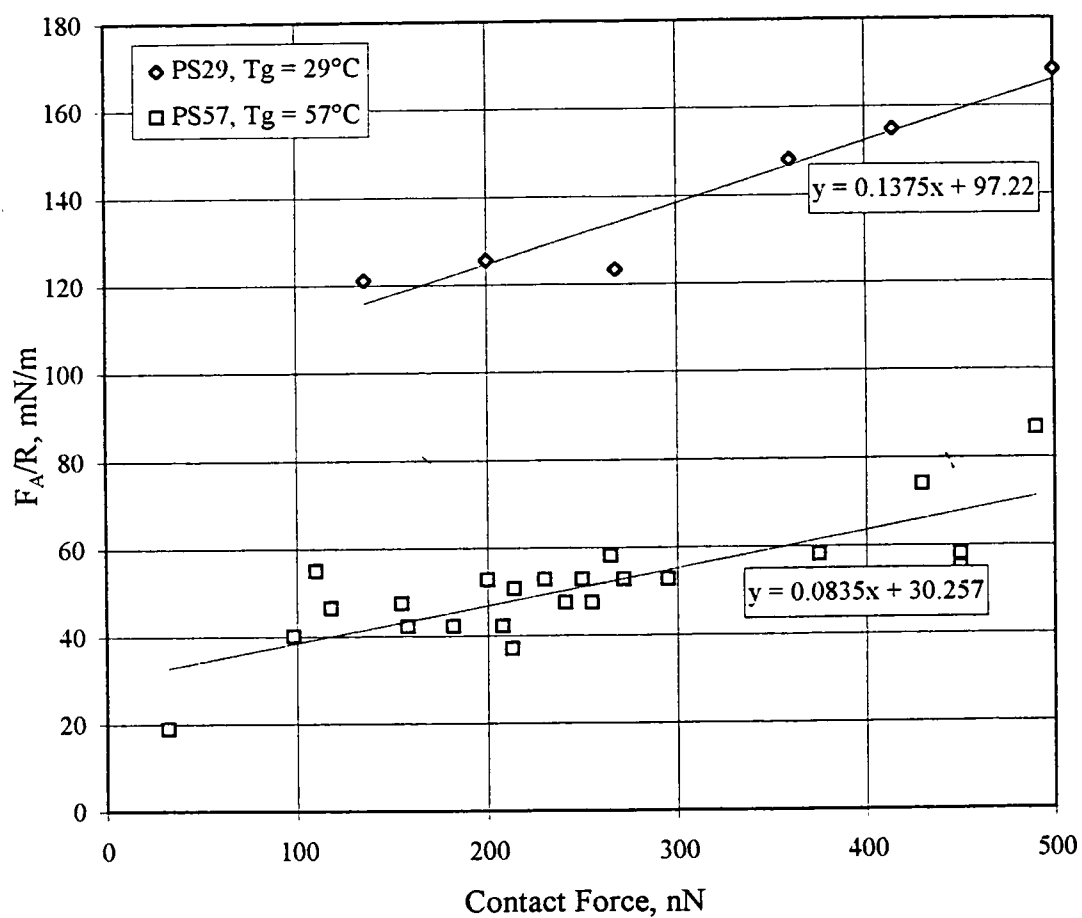


Figure 21. Comparison of behavior for PS29 and PS57 particles with maximum pull-off force as a function of contact force (constant contact time).

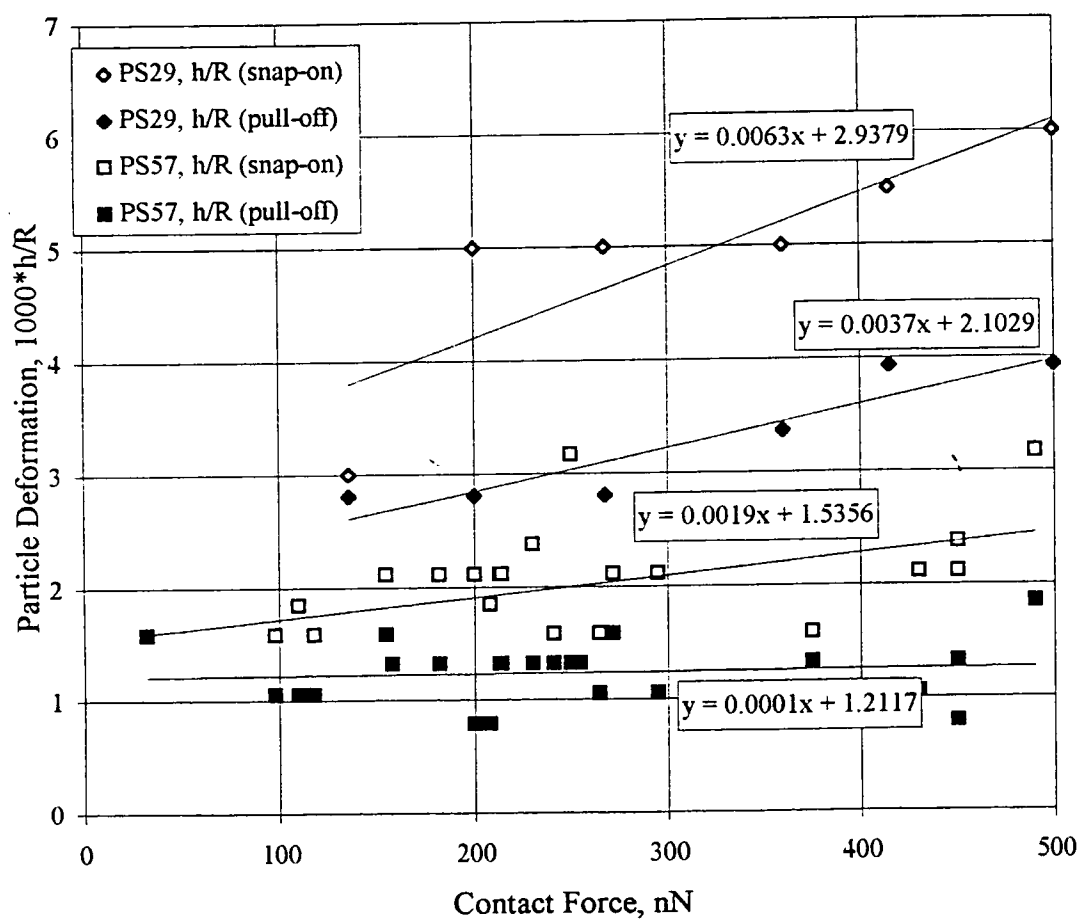


Figure 22. Comparison of behavior for PS29 and PS57 particles with particle deformation as a function of contact force (constant contact time).

the distance between maximum compression and the point of release. Therefore, the reason for the decrease in pull-off deformation is because the particle has a temporary flattened surface upon release, which is responsible for the cantilever displaying a slow return to the steady state position in Figure 15g.

The ability to measure the deformation dependence with applied force for an individual particle is very advantageous. In addition, the linearity of the results allows the comparison to the Maugis and Pollock (MP) theory. By comparing the regression lines in Figure 21 with equation 27, it is possible to determine the yield strength Y , and the corresponding work of adhesion ω_A , for the interaction between a polystyrene particle and mica in water. Table 7 contains a summary of results for this evaluation.

Table 7. Use of Maugis and Pollock (15) theory to determine the yield strength (Y) and work of adhesion (ω_A) from the regression lines on Figure 22

Sample deformation	$y = mx + b$		MP theory (eq. 27)	
	m	b	Y , MPa	ω_A , J/m ²
PS29 snap-on	0.0063	2.9379	0.021	0.08
PS29 pull-off	0.0037	2.1029	0.036	0.10
PS57 snap-on	0.0019	1.5356	0.062	0.14
PS57 pull-off	0.0001	1.2117	1.183	2.04

Recent work using the MP (15) theory was presented by Rimai et al. (21). In their study, the dependence of particle radius with contact radius was determined visually from photographs taken by SEM. This method is very useful for studying the effect of different particle radii, but in their analysis, the determined work of adhesion (0.32 J/m² for PS particles and silicon substrate) was very dependent on a previously measured yield strength (10.8 MPa) for bulk polystyrene. In addition, questions were raised about the

assumption of the measured yield strength for the bulk polymer being equal to the yield strength of individual particles. In the present evaluation, both yield strength and work of adhesion are determined from the same figure, which is very beneficial. As expected, the values for yield strength and work of adhesion for PS29 and PS57 particles and mica in water were much lower, but of the correct order of magnitude when compared with Rimai et al. for pure polystyrene. The results of the pull-off deformation for the PS57 particle do not seem to obey the trend of the remaining values. This is because the pull-off deformation from that particle remained relatively constant for all applied forces. This is an interesting effect. This is not observed in the PS29 particle, because that particle was soft enough to slightly deform before release, displaying an increasing pull-off deformation with increased applied force.

Another approach for the comparison of adhesion and deformation forces is to examine the contact radii. Figure 23 displays the calculated contact radii from the adhesion force and snap-on and pull-off deformations. The contact radius obtained from the adhesion force was derived by setting the measured pull-off force equal to equation 23 and solving for the contact radius. The method for calculating the contact radii from the deformation measurements comes from Figure 4 (14). The two contact radii calculated from deformation measurements were compared with the contact radii calculated from adhesion measurements to ascertain which deformation measurement more closely follows the adhesion measurements. The contact radii determined from the adhesion force for the PS29 particle fell intermediate between the two contact radii obtained from the deformation methods. However, for the PS57 particle, the contact radii calculated from

adhesion data more closely followed the contact radii calculated from the pull-off deformation.

Since the direct measurement data are now represented through calculations as contact radii, the relationship to contact force can now be examined. The previously described MP theory is identically transferred to Figure 23 as the regression line through the data. The regression line (MP theory) was included to display the contact area at zero-load. The main reason for converting the data to the form of contact radii is for the comparison to the Derjaguin (23) relationship for contact radii and applied force. Since the snap-on deformation is the most suitable form for measuring the contact radii, the Derjaguin relationship was fitted to this contact radii by adjusting the Young's modulus. For the PS29 particle, the Young's modulus was determined as 0.62 GPa, whereas the PS57 particle was 1.83 GPa. Typical values for the Young's modulus of pure polystyrene are 3.4 GPa (37). However, using Figure 9 in reference (25), the Young's modulus can be estimated for two-phase polyblends and block polymers of widely different T_g values, which is the same as the present case. The values for the Young's modulus approximated with this Figure (0.42 and 1.8 GPa) are remarkably close to the determined values from the Derjaguin relationship (0.62 and 1.83 GPa, respectively).

While the responses to applied loads are important, characteristics for the condition of zero-applied loads are also significant, because they best represent the case of a real system. Table 8 contains a summary of the extrapolated data obtained for the condition of zero applied load; and from the measured values, the calculated contact radii are also included. As expected, the PS29 particle has an adhesion of more than three

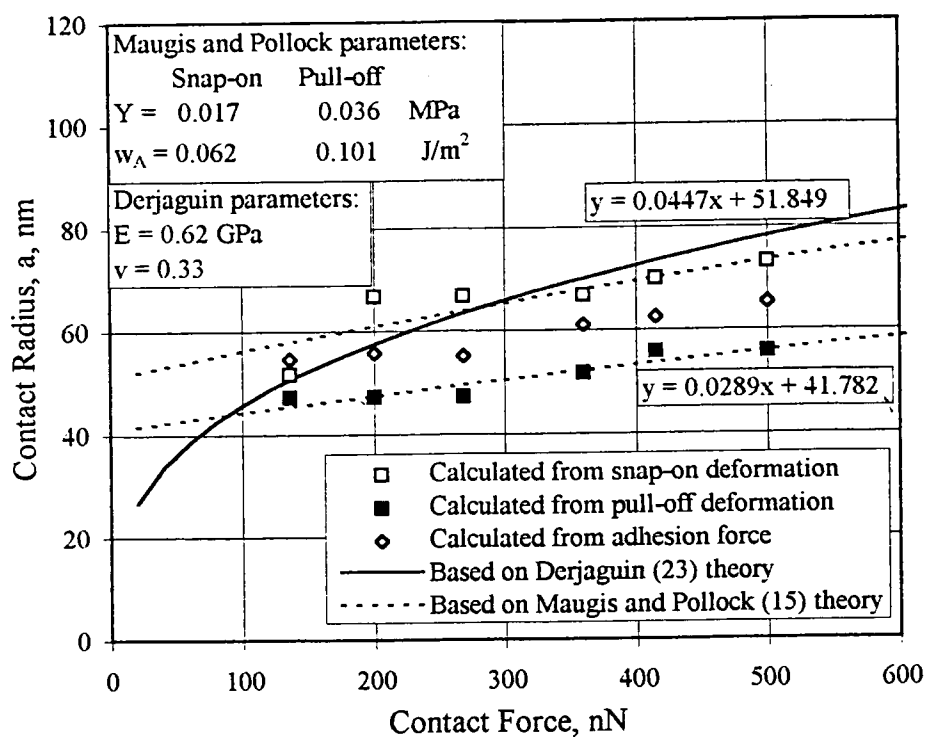


Figure 23. Comparison of contact radius (PS29) when calculated from adhesion force and deformation and compared with contact force (contact time is constant).

times that of the PS57 particle. In addition the corresponding vertical deformation is almost twice as large.

Table 8. Evaluation of the extrapolated conditions of zero applied load for the interaction between PS29 and PS57 particles and mica in water

Particle	Measured values			Calculated contact radius		
	F_A/R , (Fig. 21) mN/m	snap-on (Fig. 22) $1000*d/R$	pull-off (Fig. 22) $1000*d/R$	a, nm (eq. 23) (adhesion)	a, nm (Fig. 4) (snap-on)	a, nm (Fig. 4) (pull-off)
PS29	97.2	2.94	2.10	49.2	48.4	41.8
PS57	30.3	1.54	1.21	26.2	37.3	32.9

4.3.3 Contact Time Measurements

Another major benefit of using the AFM is the ability to take measurements at short contact time measurements, which were previously inaccessible to experimental investigation. The effect of increased contact time has been studied by examining the adhesive pull-off force, particle deformation, and contact radii (calculated from the pull-off force and deformation). Figure 25 displays the relationship of pull-off force and particle deformation with contact time, while holding the contact force constant. In these measurements, the applied force was held constant (400 nN) while the scan rate was adjusted to allow the particle to remain on the surface for periods of time ranging from 0.01 seconds to 10 seconds.

The PS57 particle displayed a slight increase in pull-off force resulting from an increase in contact area with time, but the measured pull-off deformation remained relatively constant for all contact times. It is possible that the PS57 particle will deform,

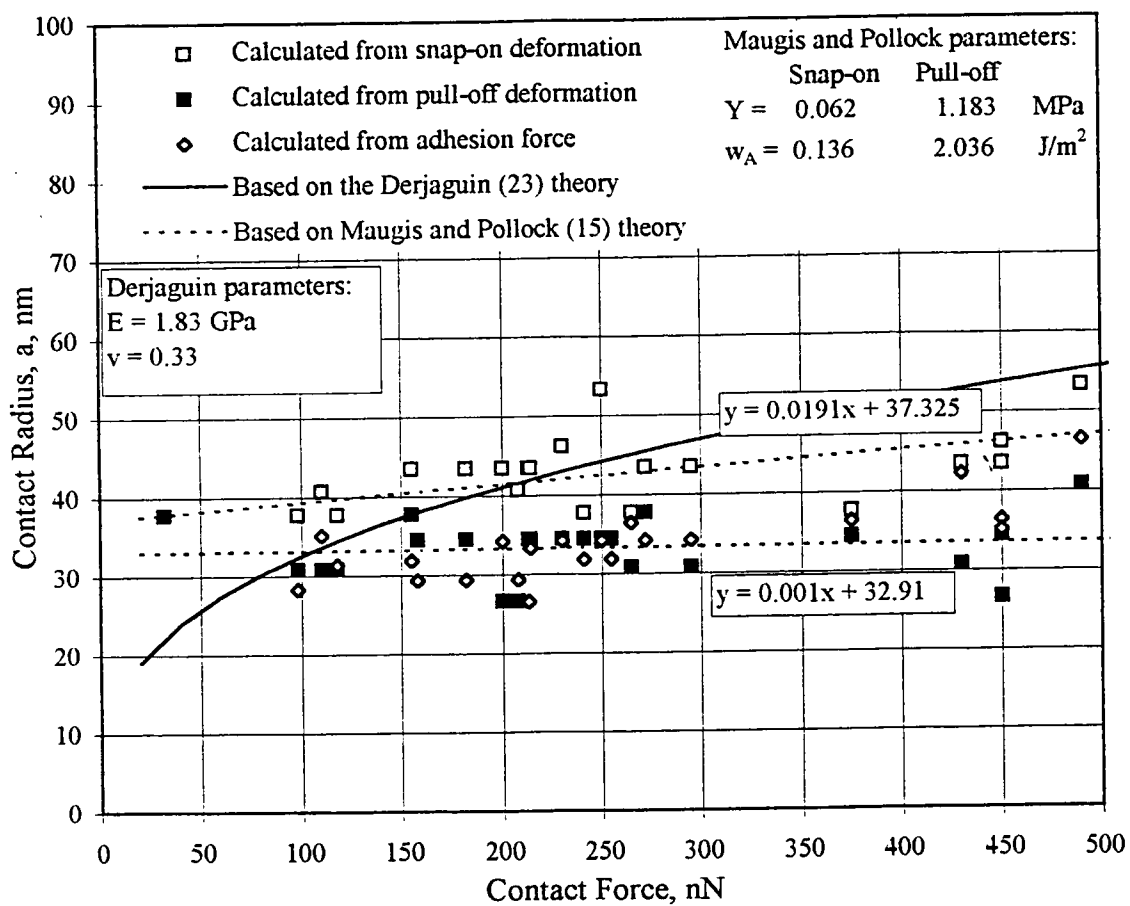


Figure 24. Comparison of contact radius (PS57) when calculated from adhesion force and deformation and compared with contact force (contact time is constant).

but maybe not in the time frame of these experiments (< 10 seconds). The PS29 particle displayed a similar dependence for the adhesion strength with contact time, but the relative forces were roughly three times larger than the PS57 particle. In addition, at contact times greater than 0.5 seconds, the PS29 particle displayed a large increase in pull-off deformation which was accompanied by a large decrease in adhesive pull-off force. It is evident that something is occurring after the particle remains on the surface longer than 0.5 seconds. Possibly, the particle is starting to creep, causing the contacting surface to soften, resulting in the increased pull-off deformation and decreased adhesion.

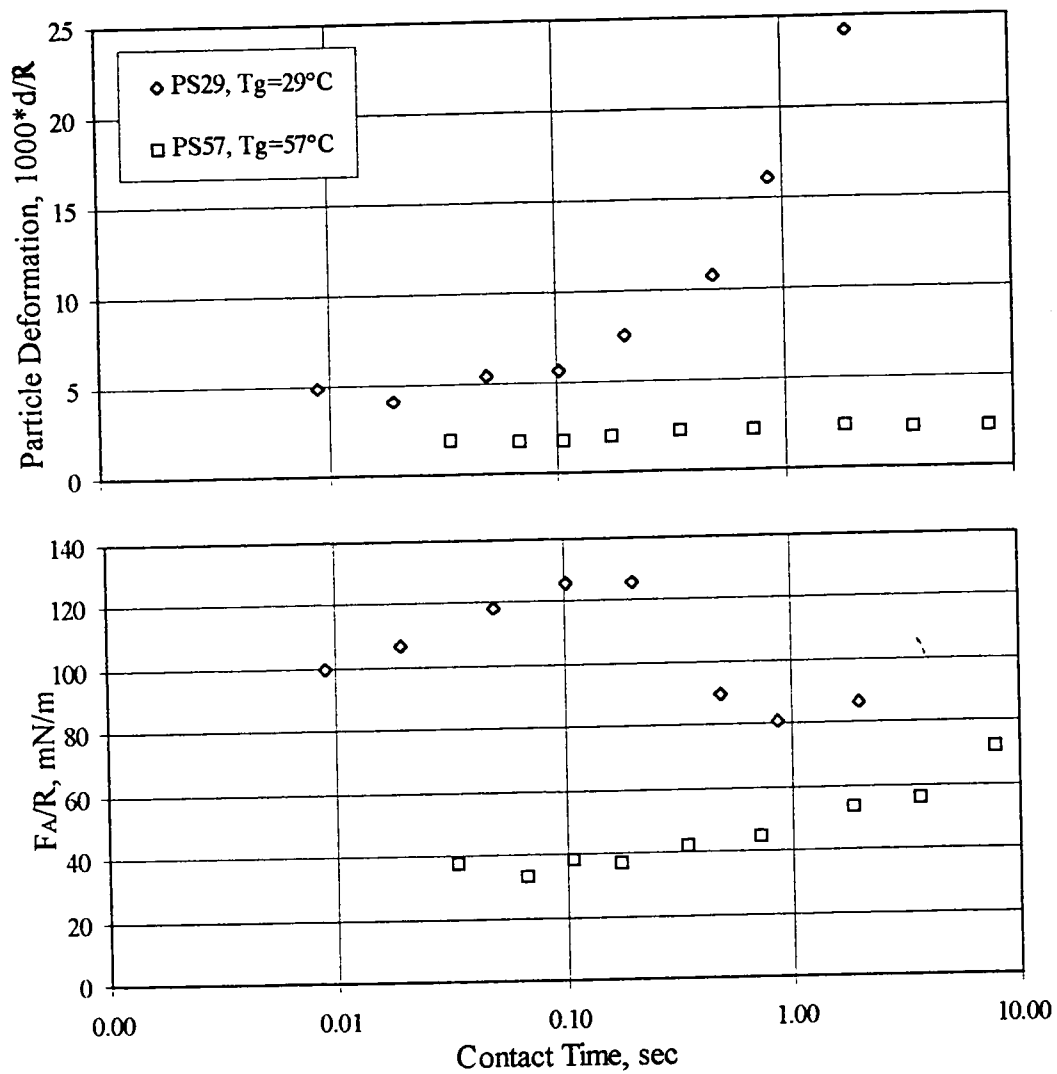


Figure 25. Comparison of behavior for PS29 and PS57 particles with maximum pull-off force as a function of contact time (contact force is constant).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Interaction and adhesion forces of soft polymer particles with various glass transition temperatures have been studied in some detail. In prior work, little was known about how the softness, as characterized by the transition temperature, affects the interaction and adhesion forces and deformations of individual particles. The direct measurements of the present work open the way for identifying and characterizing these phenomena.

An atomic force microscope has been used to measure the interaction and adhesion forces between a 2 μm polystyrene particle and a mica surface in aqueous solutions. The interaction and adhesive pull-off forces, as well as particle deformation, have been measured as a function of contact force and contact time for particles with glass transition temperatures of 29°C and 57°C. These results indicate that a noticeable deformation occurs during approach of the particle and surface and after contact. Various relationships were established elucidating a more complete understanding of the interaction forces of soft particles at the microscopic level, including repulsive interactions before contact and attraction forces and particle deformations after contact.

For the experiments studying the repulsive interactions before contact, a noticeable difference in the repulsive forces (observed at approximately 20 nm from the surface) was found to be dependent on the approach velocity of the particle and planar surface. In

these studies, the force curves displayed a snap onto the mica surface at large distances (20 nm), which are unexpected from van der Waals forces alone. This observation is believed to be caused by hydrophobic forces (46), which are expected from polystyrene's high water contact angle ($>90^\circ$). In the case of repulsive force deviations with approach velocity, explanations were examined for two mechanisms influencing this phenomena. The first mechanism was the drag force, but this effect only partially accounted for the observed effect. The second mechanism was that of time-dependent particle deformation resulting from repulsive forces. After fitting the DLVO theory to the highest velocity force curve, where the particle is assumed to display rigid characteristics, the remaining force curves were fitted by adjusting only the particle radius. The subsequent radii obtained were plausible when compared with fluid mechanics models for the motion of deformable drops.

When the surfaces came into contact, the applied force and the contact time were controlled to determine relationships with adhesive pull-off force and particle deformation. Preliminary evaluations showed that when repeating experiments with the same particle, the adhesive pull-off forces increased with applied loads greater than 500 nN, suggesting inelastic flattening of the contact surface. Previous studies (16,17) have also observed inelastic responses from micrometer-sized polystyrene particles.

Continuing with interactions after contact, contact force measurements were used to evaluate both the maximum adhesion forces and corresponding vertical deformation of the particle. From a linear relationship with contact force, the adhesive pull-off forces and deformation values were extrapolated to zero contact load for both samples. For the

PS29 particle, the zero load pull-off force was found to be roughly three times that of the PS57 particle. The Maugis and Pollock (15) theory was used to calculate the yield strength and work of adhesion independently from the deformation versus contact force relationships. Availability of force measurements in the present work made possible a more direct physical use of this theory. Earlier methods required an input of a previously determined value for the yield strength, which greatly influenced the calculated value for the work of adhesion.

In addition, the measured values for adhesion and deformation were converted to contact radii to compare with the Derjaguin relationship (23). The adjustable parameter in this relationship is the Young's modulus. Upon fitting to contact radii calculated from snap-on deformations, Young's moduli were determined, which gave results similar to those predicted by Nielsen and Landel (25).

Another novel aspect of the AFM is the ability to control the amount of time the particle and surface are in contact. Contact time measurements were studied to gain further information on the rate at which the deformation occurs. Following with the trends of the contact force measurements, based on increased contact area, similar dependencies were obtained from increased contact time. The PS29 particle, however, exhibited an abrupt increase in pull-off deformation accompanied by a decrease in adhesion at contact times greater than 0.5 seconds. This was possibly the result of particle creep, causing the contacting surface to soften, which resulted in an increased pull-off deformation and decreased adhesion.

Finally, then, the AFM instrument used here allows one to measure both force and deformation of soft polymer particles (2 μm) interacting with mica surfaces in aqueous solutions. As the above discussion makes clear, it has been concluded that deformation of soft particles can be detected in the repulsive regime.

5.2 Recommendations For Further Work

Extensive research has been completed on the repulsive interaction before contact, the deformations during contact, and adhesive pull-off forces during removal. In most experimental studies involving the use of an atomic force microscope, including those of the present work, there has been a focus on particles of a single diameter, whereas many theories for adhesion and deformation were developed to study the relationship of particle size with interaction, adhesion, and deformation forces. Therefore, it would be of interest to study the particle size dependencies of various interactions (repulsive, attractive, long range, short range), using various experimental conditions (different surfaces and intervening materials). In addition, for soft particle interactions, the time dependency of particle deformation and inertial effects can be analyzed by studying force curves obtained from varying the approach velocity.

REFERENCES

REFERENCES

- (1) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, (1991).
- (2) Derjaguin, B. and Landau, L. *Acta Physiochem.* **14**, 633 (1941).
- (3) Verwey, E. G. W. & Overbeek, J. J. G. *Theory of the stability of Lyophobic Colloids*. Elsevier: Amsterdam, (1948).
- (4) Binnig, G.; Quate, C.; and Gerber, C. *Phys. Rev. Lett.*, **56**, 930-933, (1986).
- (5) Ducker, W. A.; Senden, T. J.; and Pashley, R. M. *Nature*. **353**, 239 (1991).
- (6) Ducker, W.; Senden, T.; and Pashley, R. *Langmuir*, **8**, 1831-1836 (1992).
- (7) Zimon, A. *Adhesion of Dust and Powder*. 2nd ed.; Consultants Bureau: New York (1982).
- (8) Busnaina, A.; Taylor, J.; and Kashkoush, I. *J. Adhesion Sci. Technol.* **7**, No. 5, 441-455 (1993).
- (9) Li, Y. Q.; Tao, N. J.; Pan, J.; Garcia, A. A.; and Lindsay, S. M. *Langmuir*, **9**, 637-641 (1993).
- (10) Rimai, D. S.; Demejo, L. P.; and Bowen, R. C. *J. Appl. Phys.* **68**, 6234 (1990).
- (11) Rimai, D. S.; Demejo, L. P.; and Bowen, R. C. *J. Appl. Phys.* **66**, 3574 (1989).
- (12) Johnson, K. L.; Kendall, K.; and Roberts, A. D. *Proc. R. Soc. London, Ser. A* **324**, 301 (1971).
- (13) Kendall, K. and Padget, J. C. *Int. J. Adhesion Adhesives* **2**, 149 (1982).
- (14) Derjaguin, B. V.; Muller, V. M.; and Toporov, Y. P. *J. Colloid Interface Sci.* **53**, 314 (1975).
- (15) Maugis, D. and Pollock, H. M. *Acta Metall.* **32**, 1323 (1984).
- (16) Schaefer, D. M.; Carpenter, M.; Reifenberger, R.; Demejo, L.P.; and Rimai, D. S. *J. Adhesion Sci. Technol.* **8**, No. 3, 197-210 (1994).
- (17) Rimai, D. S.; Moore, R. S.; Bowen, R. C.; Smith, V. K.; and Woodgate, P. E. *J.*

Mater. Res. **8**, 662 (1993).

- (18) Krupp, H. *Adv. Colloid Interface Sci.* **1**, 111 (1967).
- (19) Bowling, R. A. in: *Particles on Surfaces I: Detection, Adhesion and Removal*, Mittal, K. L. (ed.), pp. 129-142. Plenum Press: New York (1988).
- (20) Hamaker, H. C. *Physica* **4**, 1058 (1937).
- (21) Rimai, D. S.; Demejo, L. P.; and Bowen, R. C. *J. Adhesion Sci. Technol.* **8**, No. 11, 1333-1355 (1994).
- (22) Bradley, R. S. *Philos. Mag.* **13**, 853 (1932).
- (23) Derjaguin, B. V. *Kolloid Z.* **69**, 155 (1934).
- (24) Carnie, S. L.; Chan, D. Y. C.; Gunning, J. S. *Langmuir* **10**, 2993-3009 (1994).
- (25) Nielson, L. E. and Landel, R. F. *Mechanical Properties of Polymers and Composites*. 2nd ed.; Marcel Dekker, Inc.: New York (1994).
- (26) Digital Instruments User's Manual, Santa Barbara California.
- (27) Krishnan, S.; Busnaina, A. A.; Rimai, D. S.; and Demejo, L. P. *J. Adhesion Sci. Technol.* **8**, No. 11, 1357-1370 (1994).
- (28) Busnaina, A.; Taylor, J.; and Kashkoush, I. *J. Adhesion Sci. Technol.* **7**, No. 5, 441-455 (1993).
- (29) Meares, P. *Polymers: Structure and Bulk Properties*. Van Nostrand Reinhold Company: London (1965).
- (30) Ranade, M. B. *Aerosol Sci. Technol.* **7**, 161-176 (1987).
- (31) Visser, J. *Adv. Colloid Interface Sci.* **2**, 331-363 (1972).
- (32) Visser, J. in: *Surface and Colloid Science*, Matijevic, E. (ed.), Vol. 8. John Wiley: New York (1976).
- (33) Wust, Jr., John, M.S. thesis, University of Tennessee, 1978.
- (34) Chi, B. K. and Leal, L. G. *J. Fluid Mech.* **201**, 136-146 (1989).
- (35) Ascoli, E. P.; Dandy, D. S.; and Leal, L.G. *J. Fluid Mech.* **213**, 287-311 (1990).

- (36) Wust, Jr., C. J. and Bogue, D. C. *J. Appl. Poly. Sci.* **28**, 1931-1947 (1983).
- (37) Nielson, L. E. *Mechanical Properties of Polymers*. Reinhold Publishing Corporation: New York (1962).
- (38) Higashitani, K. and Ishimura, K. general discussions, Kyoto University, Japan (1996).
- (39) Meagher, L. *J. Colloid Interface Sci.* **152**, 293 (1992).
- (40) Ducker, W. A.; Xu, Z.; & Israelachvili, J. *Langmuir*. **10**, 3279 (1994).
- (41) Milling, A. & Biggs, S. *J. Colloid Interface Sci.* **170**, 604 (1995).
- (42) Butt, H. J. *J. Colloid Interface Sci.* **166**, 109 (1994).
- (43) Mantel, M.; Rabinovich, Y. I.; Wightman, J. P.; & Yoon, R.-H. *J. Colloid Interface Sci.* **170**, 203 (1995).
- (44) Biggs, S. & Mulvaney, P. *J. Chem. Phys.* **100**, 8501 (1994).
- (45) Biggs, S. *Langmuir*. **11**, 156 (1995).
- (46) Karaman, M. E.; Meagher, L.; & Pashley, R. M. *Langmuir*. **9**, 1220 (1993).
- (47) Butt, H.-J. *J. Biophys.* **60**, 1438 (1991).

VITA

Kevin D. Heath was born in Knoxville, Tennessee on March 21, 1971. He attended public schools in East Tennessee, where he graduated the top 10% of his class in June, 1989. He entered the University of Tennessee the fall semester of the same year, where in August, 1994 after completing 4 semesters of Co-op work experience at General Electric Aircraft Engines in Cincinnati, Ohio, he received the Bachelor of Science in Chemical Engineering with honors of Magna Cum Laude. He then entered the Master's program in Chemical Engineering at the University of Tennessee; and through a special program called "A year in Japan", he was able to complete his research work at Kyoto University in Kyoto, Japan for a period of 1.5 years, which was fully funded through the Japanese government. He officially received his Master's degree in May of 1997.

He is presently working towards the Ph.D. degree in Chemical Engineering at the University of Tennessee through support from the Chemical Technology Division of Oak Ridge National Laboratories.