van der Waals and Electrostatic Forces in Particle Adhesion

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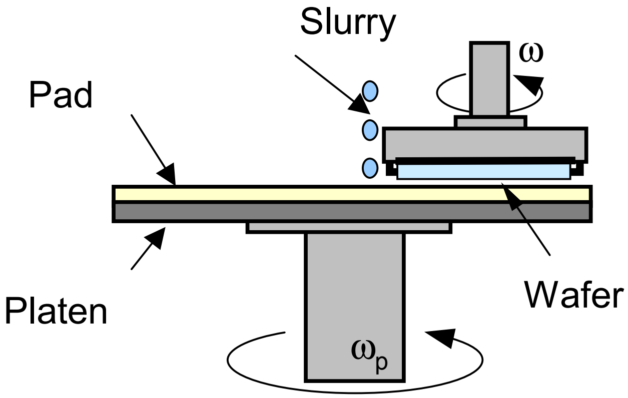
NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing Teleseminar

November 13, 2003

Importance of Adhesion

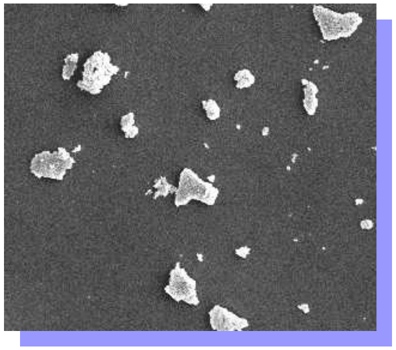
In the Semiconductor Industry

Chemical Mechanical Planarization



Post-CMP Cleaning

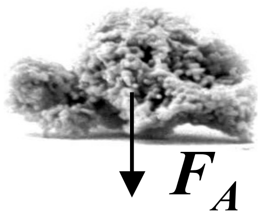
Al_2O_3 Slurry on SiO_2 wafer

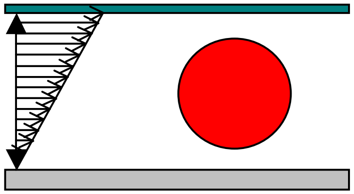


Post-CMP Cleaning Model

- Input: substrate, polishing slurry, post-CMP solutions
- Output: cleaning conditions

Adhesion
Model





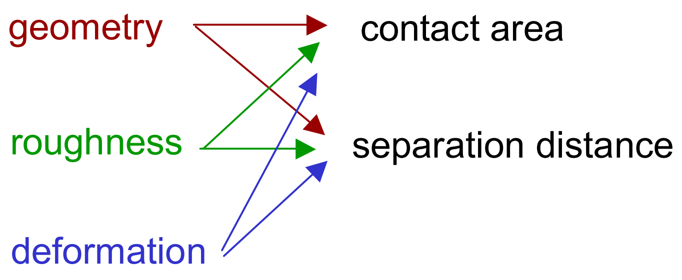
Flow
Dynamics

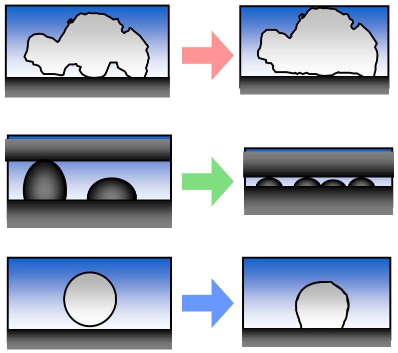
Forces In Particle Adhesion

Comparison of Adhesion Forces

				Order of Magnitude Change in Interaction due to:		
Interaction Force	Magnitude (kJ/mol)	Range (nm)	Presence	Geometry	Roughness	Deformation
Chemical Bonds	100--1000	0.1--0.2	Ocasionally	1--2	1--2	1--3
van der Waals	10--100	0.4-->100	Always Present	1--3	1--2	1--2
Electrostatic (non double layer)	0.1--10	0.4--20	In Air or Vacuum	0--1	0--1	0--1
Electrostatic (double layer)	1--20	2--100	In Electrolyte Solutions	0--2	0--2	0--2
Hydrophobic	10--100	0.4-75	Between Hydrophobic	1--3	1--2	1--2

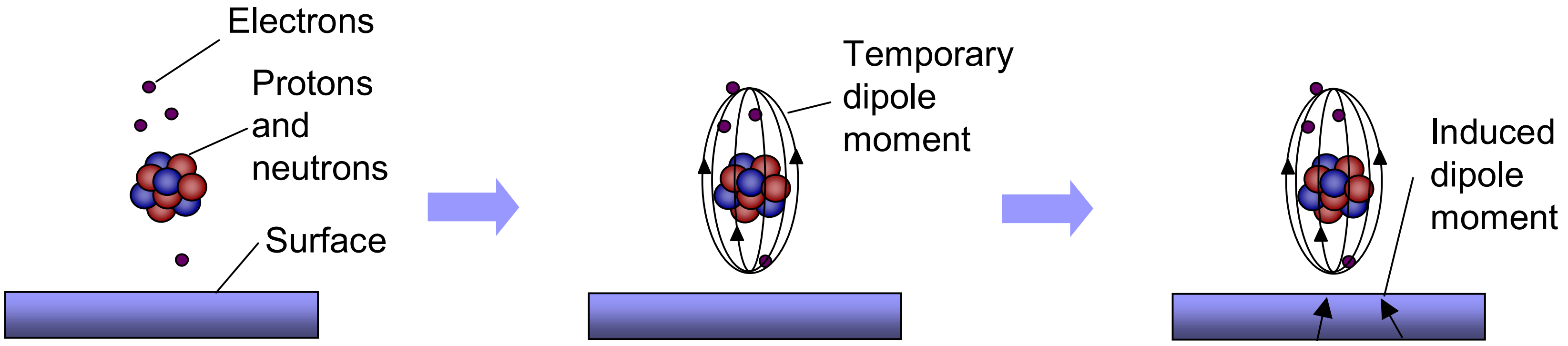
How Factors Affect Force



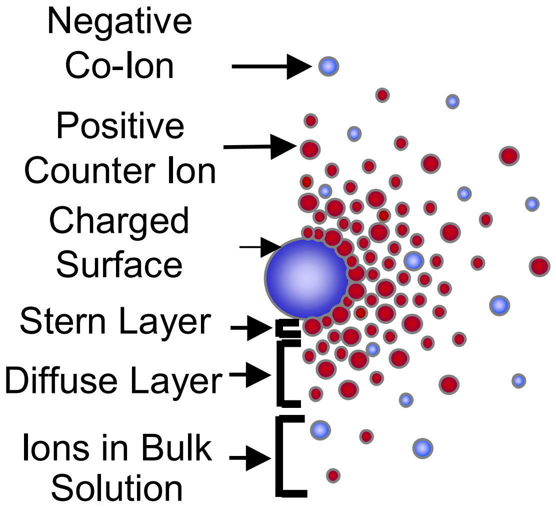


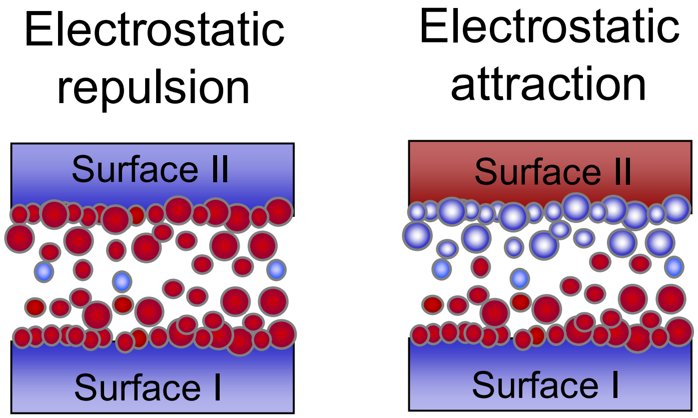
Adhesion Forces Considered

van der Waals



Electrostatic Double Layer

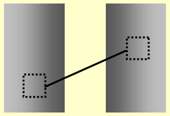




Current Adhesion Models

van der Waals

Point-by-point additivity



$$dU_{12} = -\frac{C_{12}\rho_1\rho_2 dV_1 dV_2}{\left\{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right\}^3}$$

Hamaker Constant, A_{12}

Analytical & Approximate Solutions

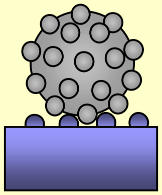
$$F = \frac{A_{12}R_1}{6h^2}$$

+

$$F = \frac{-A}{6h}\frac{R_1 R_2}{R_1+R_2}$$

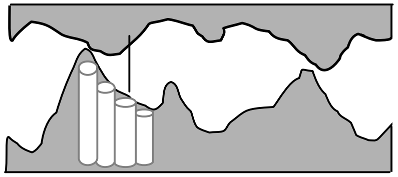
+

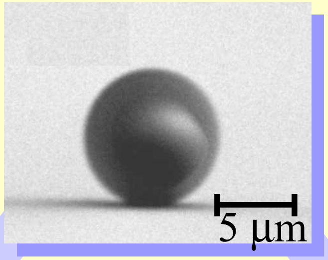
$$F = \frac{A_{12}}{12\pi h^3}$$



Computational Solutions

Integration Over Both Surfaces





Combination of ideal shapes

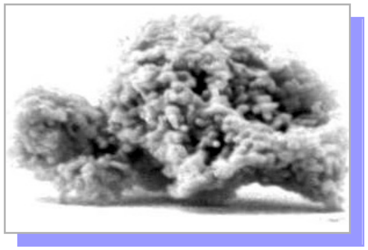
sphere-plate

+

sphere-sphere

+

plate-plate



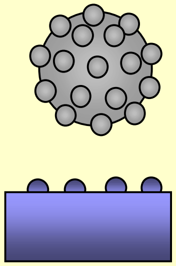
Electrostatic

Poisson-Boltzmann Equations

$$\nabla^2\psi = \kappa^2\psi$$

$$\kappa = \sqrt{\frac{e^2\sum_i z_i^2 n_{io}}{\varepsilon_0\varepsilon_r k_B T}}$$

Analytical & Approximate Solutions



$$F = \frac{\varepsilon\varepsilon_0 d}{4}\frac{\kappa e^{-\kappa h}\left(\psi_p^2+\psi_s^2\right)}{\left(1-e^{-2\kappa h}\right)}\left(\frac{2\psi_p\psi_s}{\left(\psi_p^2+\psi_s^2\right)}+e^{-\kappa h}\right)$$

+

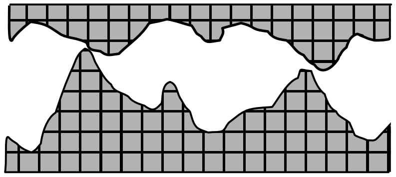
$$F = \frac{\kappa^2\varepsilon_0\varepsilon_r}{2\sinh^2(\kappa h)}\left(2\psi_1\psi_2\cosh(\kappa h)-\psi_1{}^2-\psi_2{}^2\right)$$

+

$$F = \frac{\kappa^2\varepsilon_0\varepsilon_r}{2\sinh^2(\kappa h)}\left(2\psi_1\psi_2\cosh(\kappa h)-\psi_1{}^2-\psi_2{}^2\right)$$

Computational Solutions

Numerical Solutions



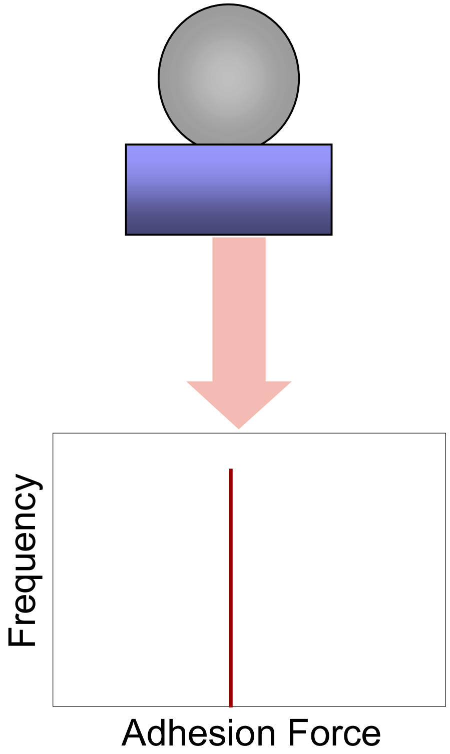
Importance of More Realistic Models

Distribution of Adhesion Forces

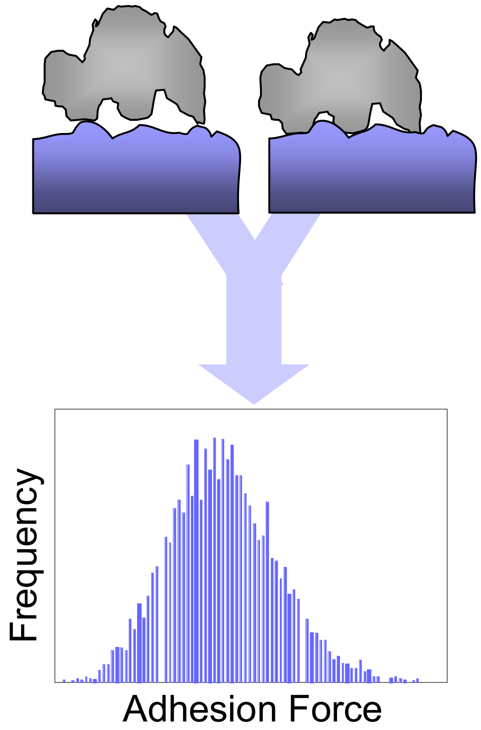
Predicted Adhesion Force(s)

Effect on Removal Model

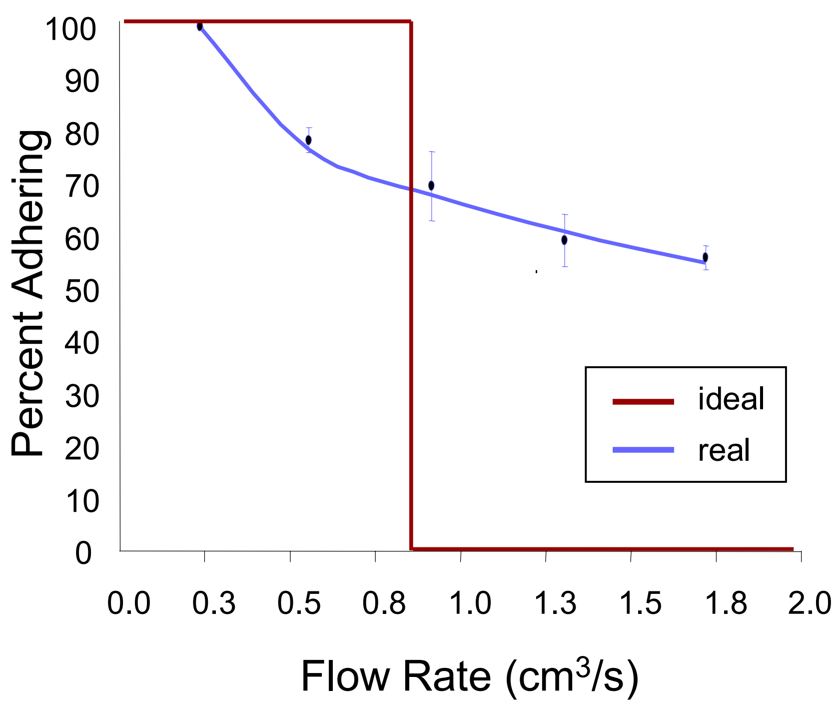
Ideal



Real



Percentage of Particles Removed†



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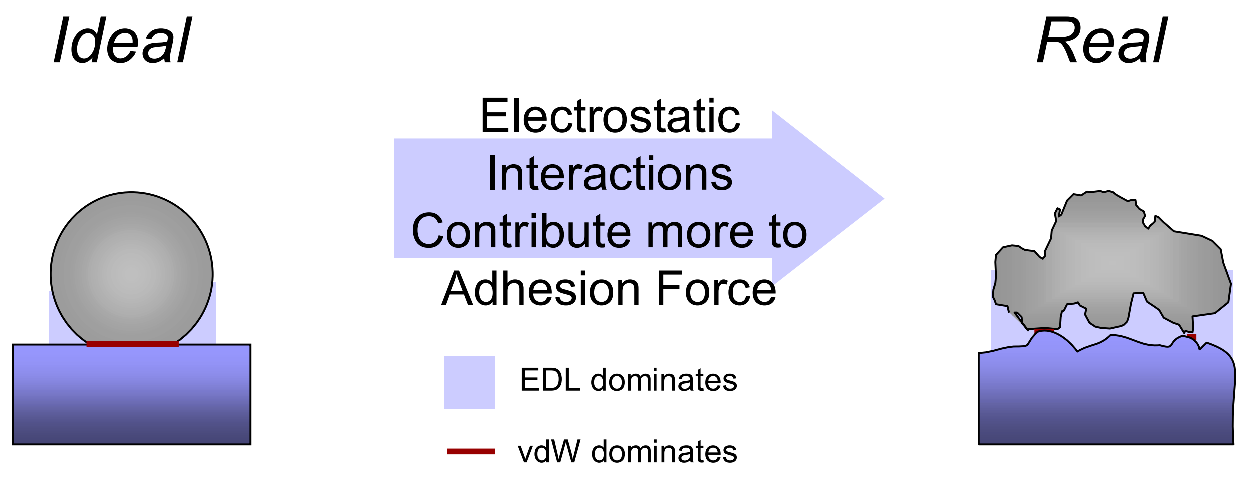
† *G. M. Burdick, N. S. Berman, and S. P. Beaudoin, J. Nanoparticle Res. 3 (2001) 455*

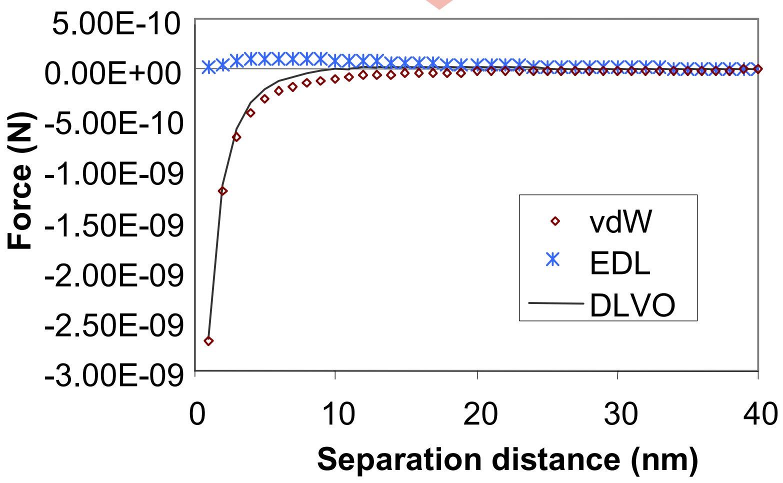
Importance of More Realistic Models II

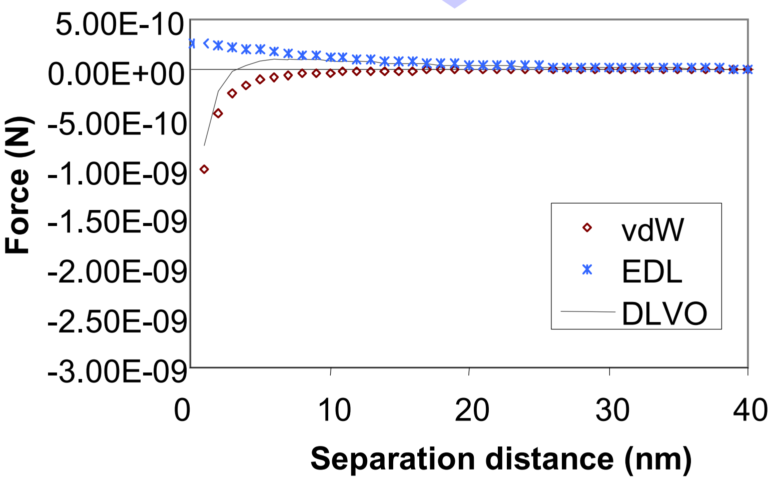
Relative Contribution of Each Force



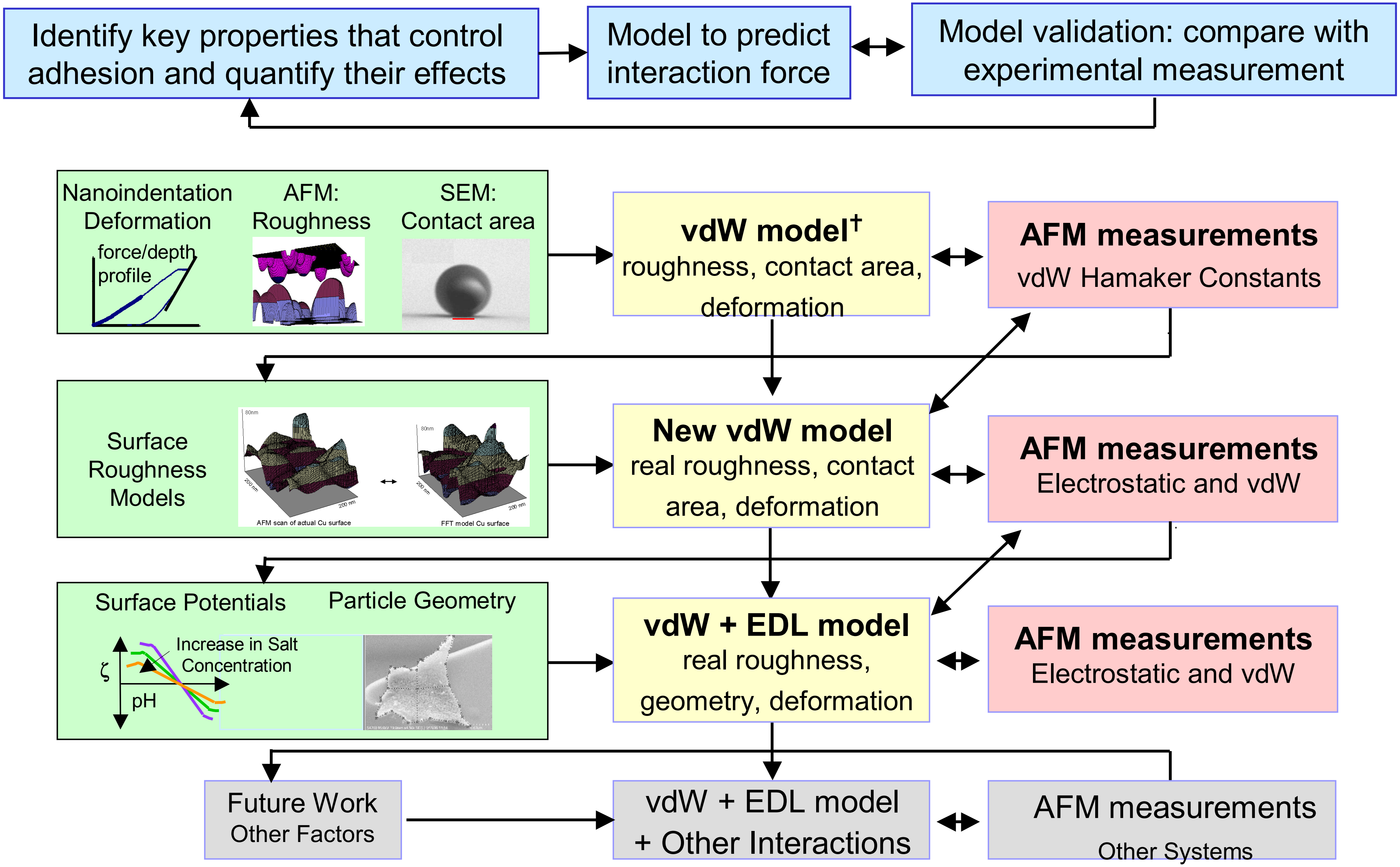
Electrostatic Interactions Contribute more to Adhesion Force

Interactions between a PSL Particle and Silicon Dioxide Surface





Experimental Approach Overview



Identify key properties that control adhesion and quantify their effects

Model to predict interaction force

Model validation: compare with experimental measurement

Nanoindentation
Deformation

AFM:
Roughness

SEM:
Contact area

vdW model†
roughness, contact area, deformation

AFM measurements
vdW Hamaker Constants

Surface
Roughness
Models

New vdW model
real roughness, contact area, deformation

AFM measurements
Electrostatic and vdW

Surface Potentials

Particle Geometry

vdW + EDL model
real roughness, geometry, deformation

AFM measurements
Electrostatic and vdW

Future Work
Other Factors

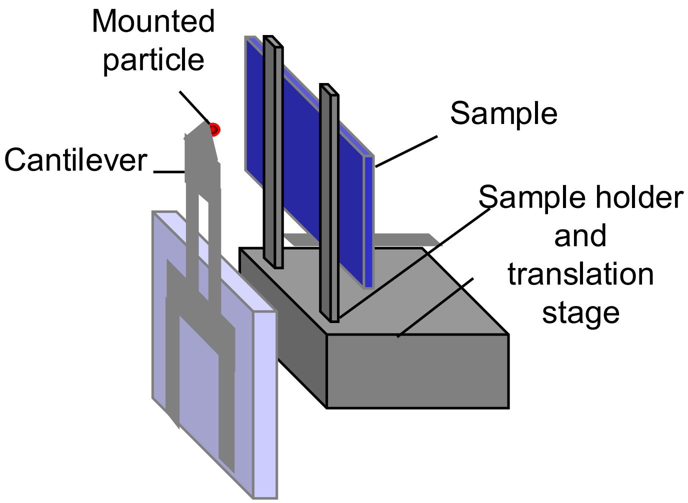
vdW + EDL model
+ Other Interactions

AFM measurements
Other Systems

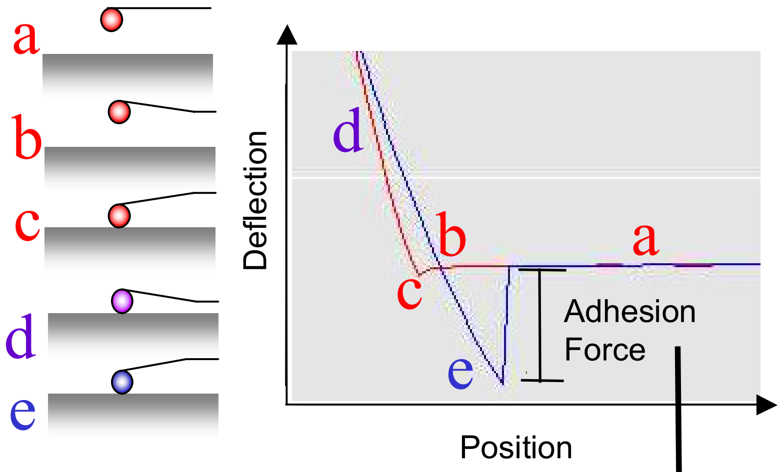
† *K. Cooper, A. Gupta, and S. Beaudoin, J. Colloid and Interface Sci. 234 (2001) 284.*

Experimental Measurements

AFM Schematic

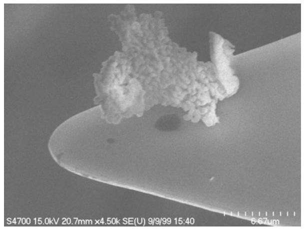


AFM Force Curve

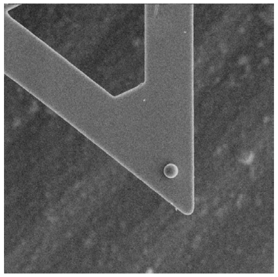


Particles Mounted on AFM Cantilevers

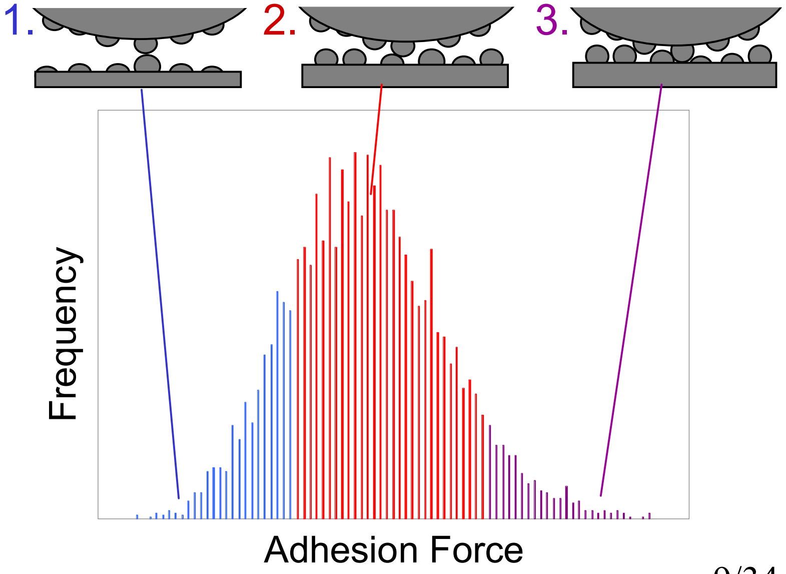
Al_2O_3 Particle



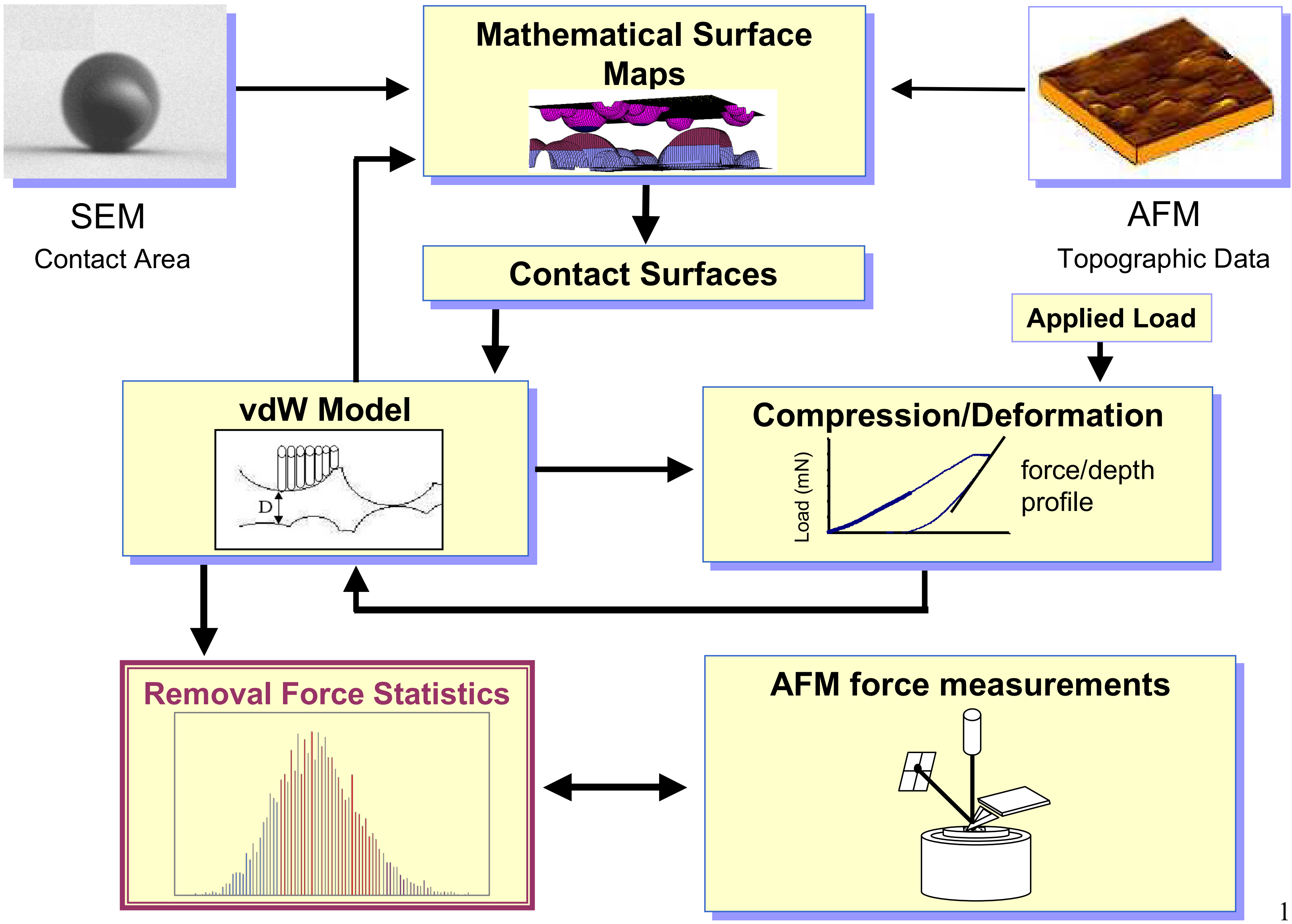
PSL Particle



Distribution of Interactions



van der Waals Adhesion Model



SEM

Contact Area

Mathematical Surface Maps

AFM

Topographic Data

Contact Surfaces

Applied Load

vdW Model

Compression/Deformation

force/depth profile

Removal Force Statistics

AFM force measurements

van der Waals Adhesion Model

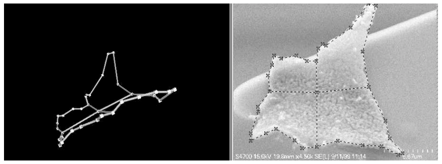
Determination of Hamaker Constants, A_{123}

Provides

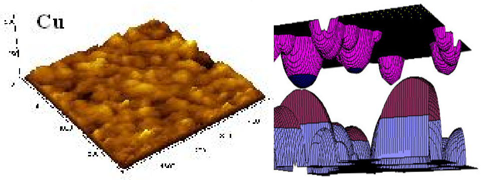
- Further validation of the vdW adhesion model
- An intrinsic measure of the forces important in thin film adhesion

Model Parameters

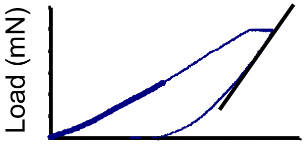
Contact Area



Surface Roughness



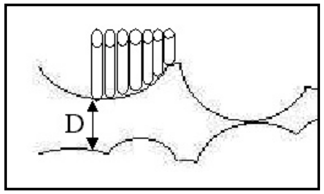
Deformation



force/depth profile

Isolate Intrinsic Adhesion

van der Waals Model:



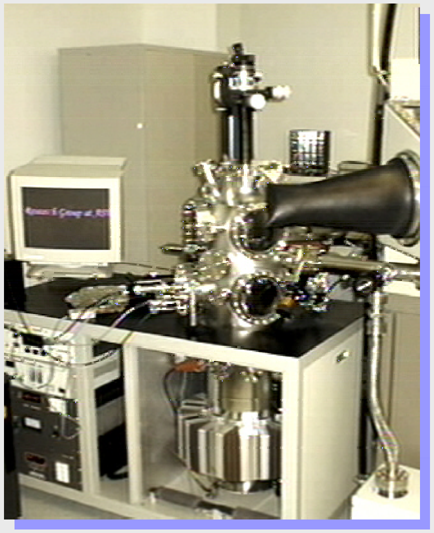
Integrate vdW Force over Surfaces

AFM Measurements

Hamaker Constant

Validation

UHV AFM

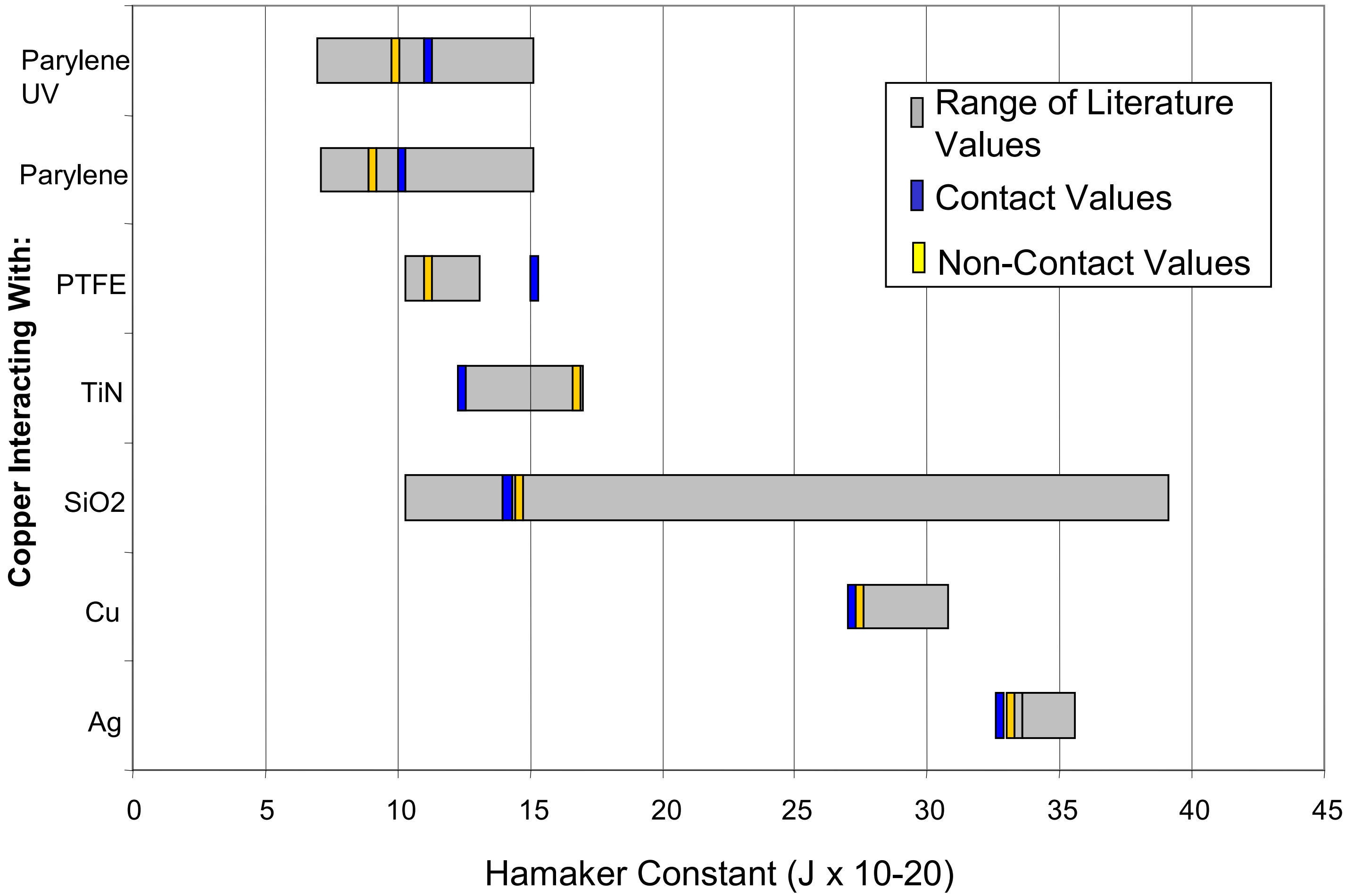


- AFM Measurements of A_{123}
  - Out of contact
- Theoretical
- Literature Values

For Systems of PTFE, Cu, Ag, TiN, SiO_2, Parylene

Hamaker Constants

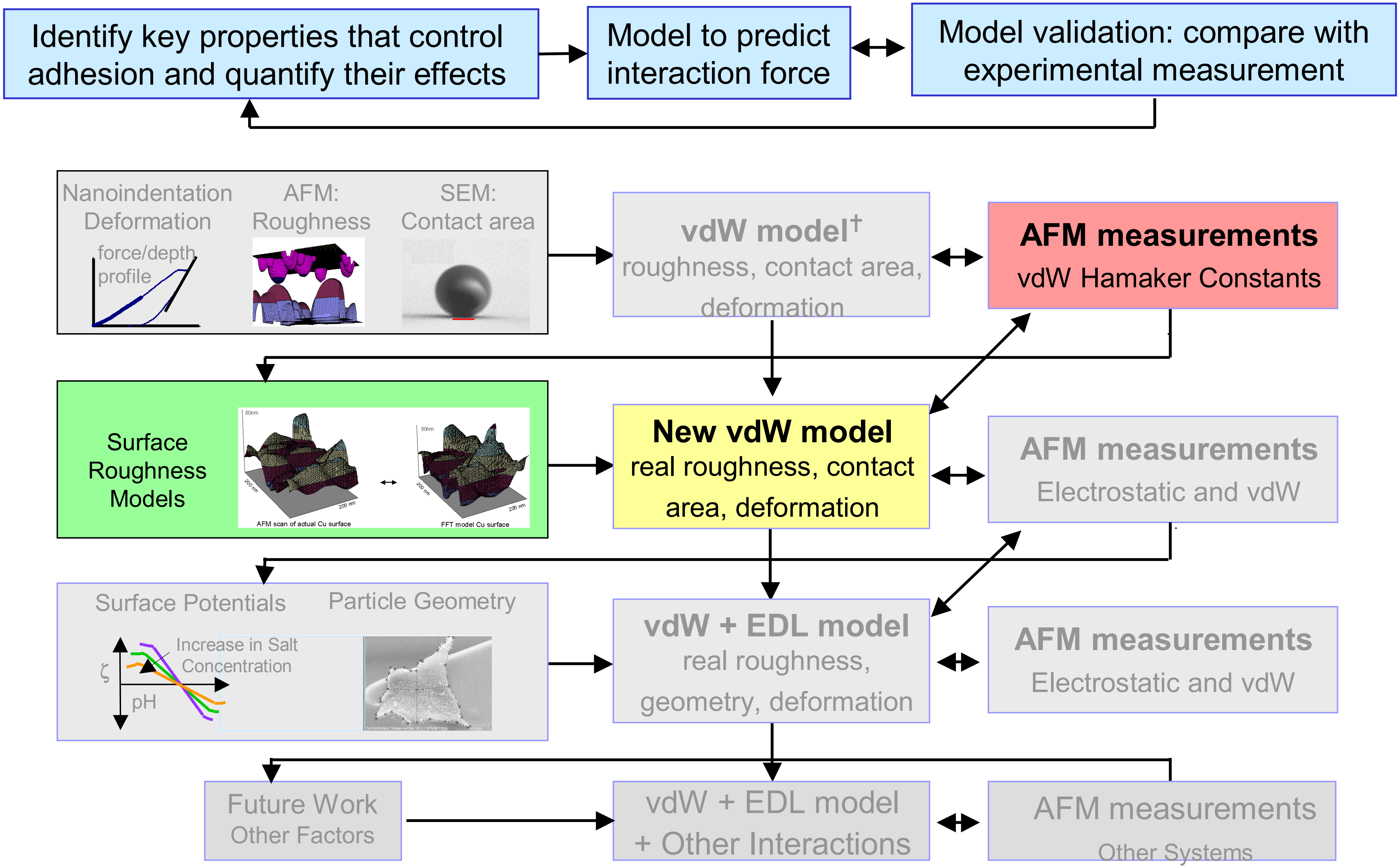
Comparison of Experimental and Literature Hamaker Constants



- Good agreement for surfaces with <u>small</u> asperities: Ag, Cu, SiO_2
- Poorer agreement for surfaces with <u>large</u> asperities: Parylene, PTFE, TiN

(Roughness generated with hemispherical asperities)

Surface Roughness Models



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Nanoindentation Deformation

AFM: Roughness

SEM: Contact area

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roughness, contact area, deformation

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Particle Geometry

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Future Work
Other Factors

vdW + EDL model
+ Other Interactions

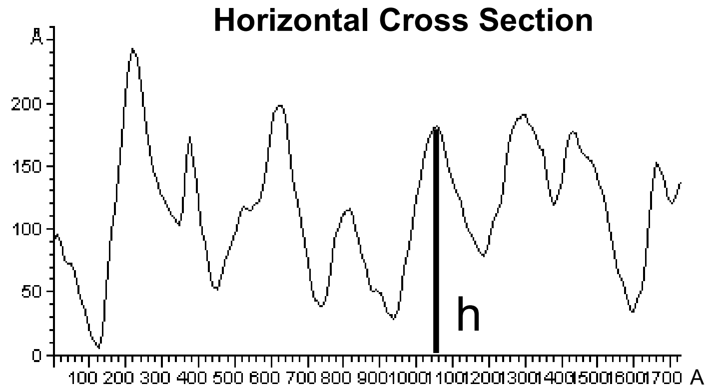
AFM measurements
Other Systems

Limitations of vdW Model

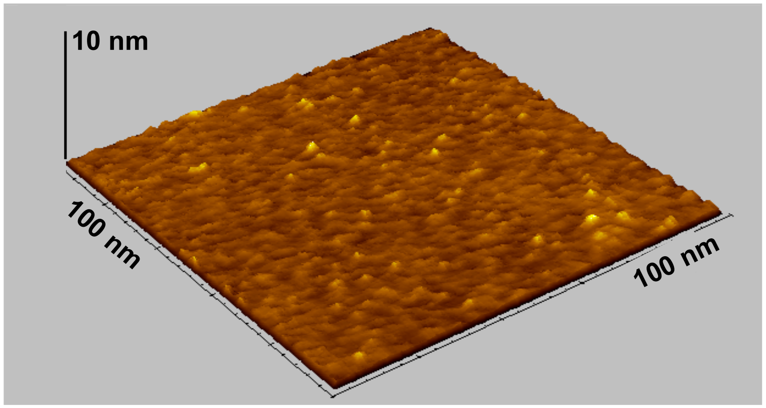
Hemispherical Asperity Surface Roughness

Measured parameters (constraints)

- Heights of asperities, h
- Standard deviation of asperity height
- Fractional surface coverage by the asperities

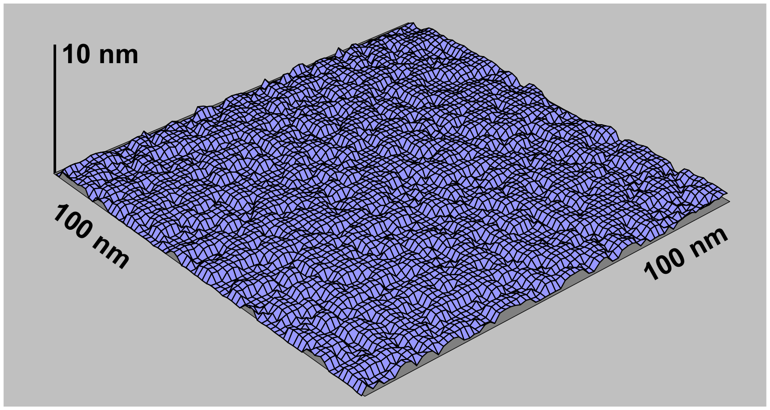


Hemispherical asperities placed on surface until constraints are met



AFM scan of actual Cu surface

↔



Hemispherical asperities model of Cu surface

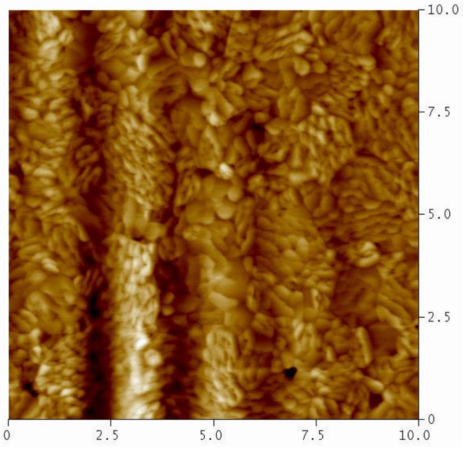
Limitations of vdW Model II

Hemispherical Asperity Restrictions

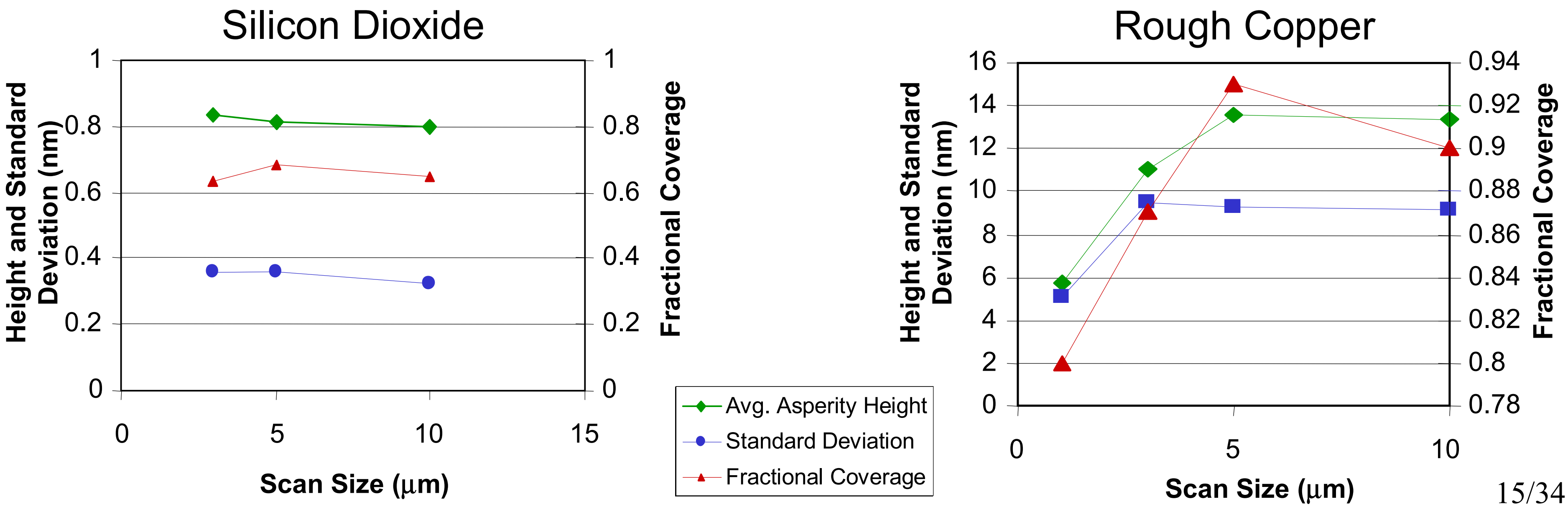
Measured parameters

- Distribution of asperity heights must be normal
- Parameters don't vary with AFM scan size
- Individual asperities present

AFM Scan of Aluminum



Parameters determined at various scan sizes


Silicon Dioxide

Rough Copper

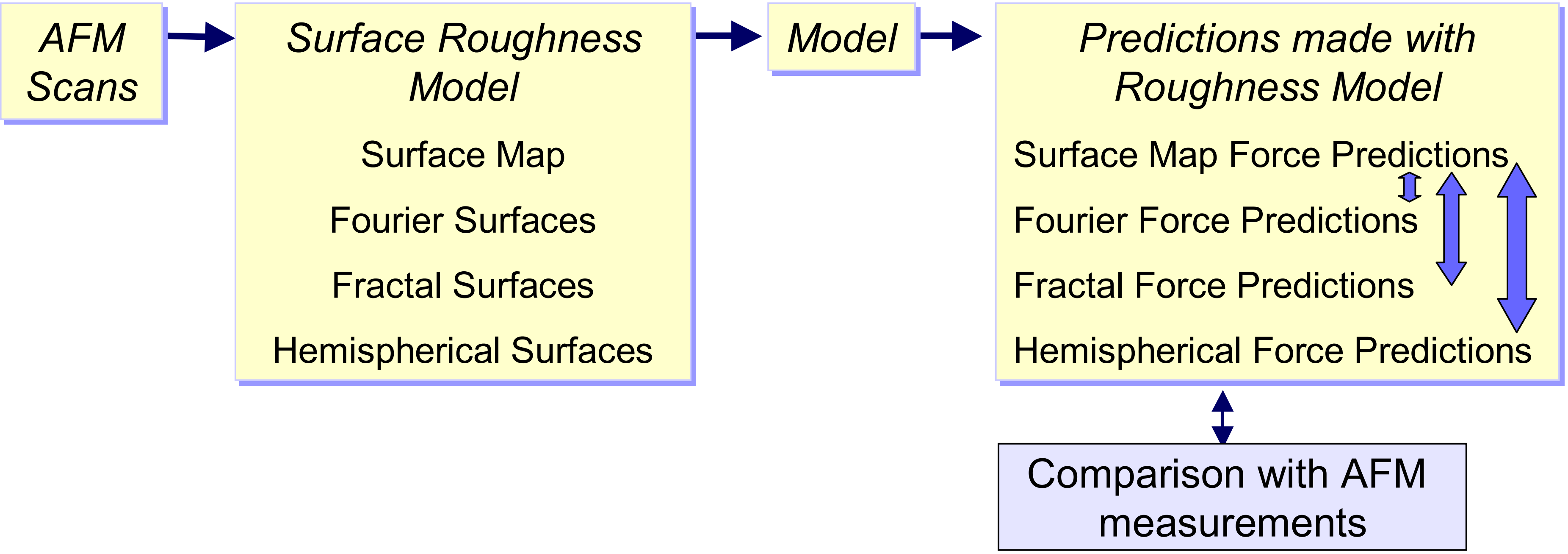
New Surface Roughness Models

Provides

- Ability to generate rough complex surfaces
- More accurate surface models
- More accurate adhesion model predictions

Combination of Ideal Shapes

Summation of Sine Waves



AFM Scans

Surface Roughness Model

Surface Map

Fourier Surfaces

Fractal Surfaces

Hemispherical Surfaces

Model

Predictions made with Roughness Model

Surface Map Force Predictions

Fourier Force Predictions

Fractal Force Predictions

Hemispherical Force Predictions

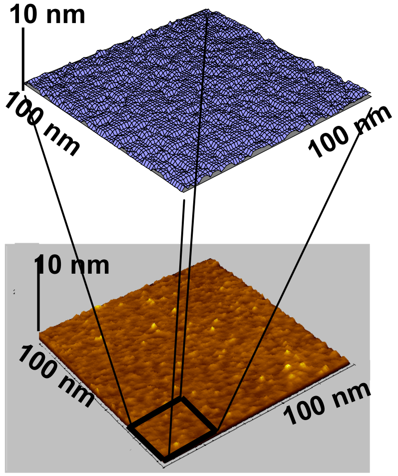
Comparison with AFM measurements

Hemispherical Asperity Model

Smooth Copper Surface

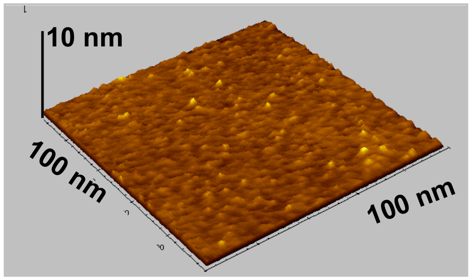
Direct Surface Map

Section of AFM Scan

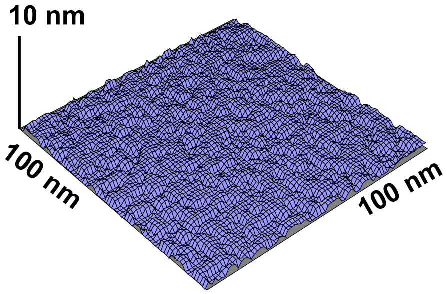


AFM scan

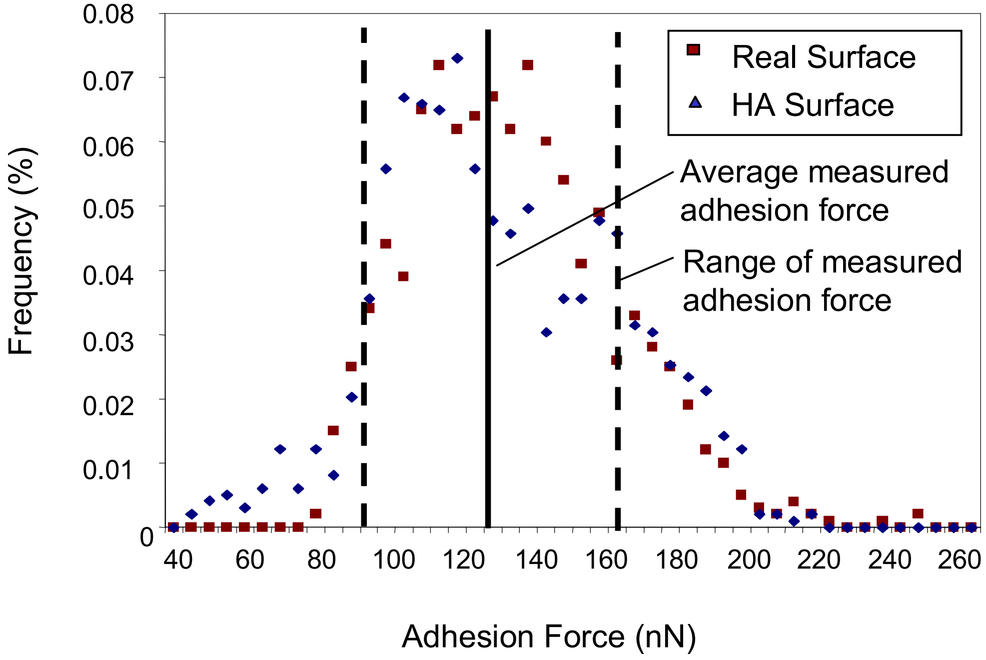
AFM Scan



Model Surfaces



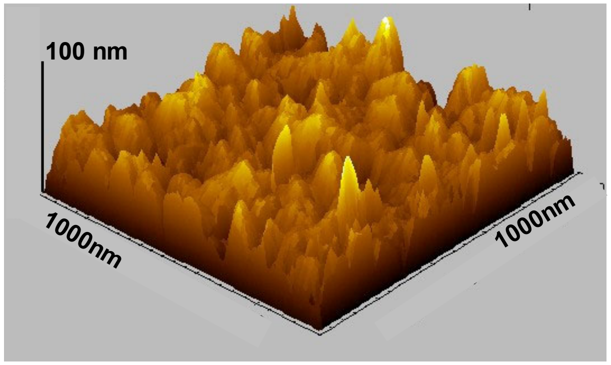
Histogram Comparing Predicted Adhesion Forces



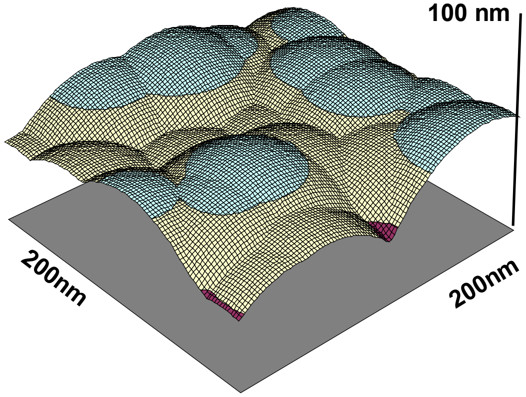
Hemispherical Asperity Model

Rough Copper Surface

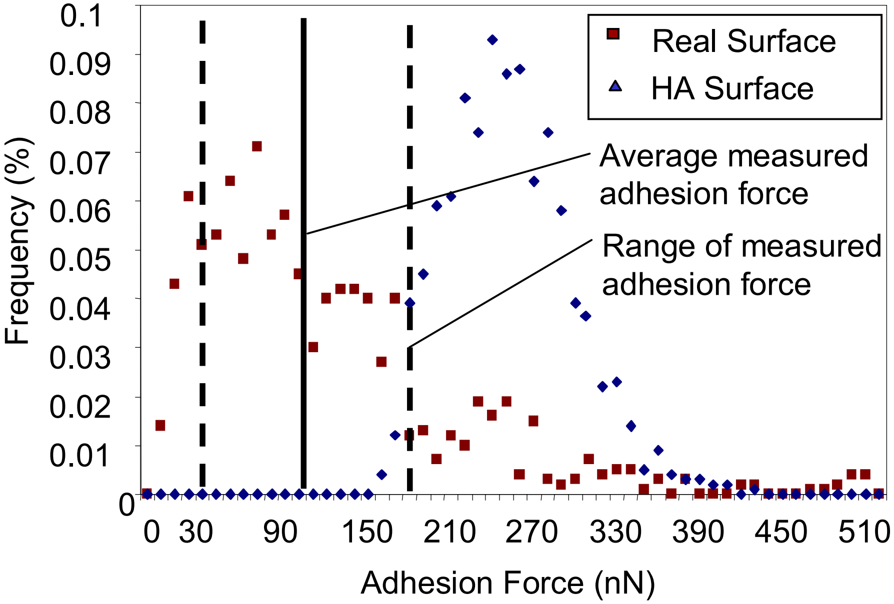
AFM Scan



Model Surface



Histogram Comparing Predicted Adhesion Forces

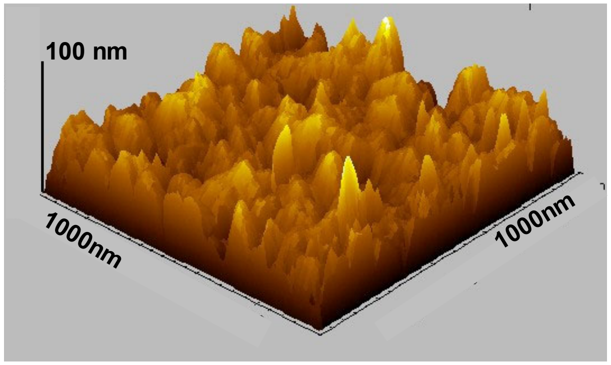


Average measured adhesion force

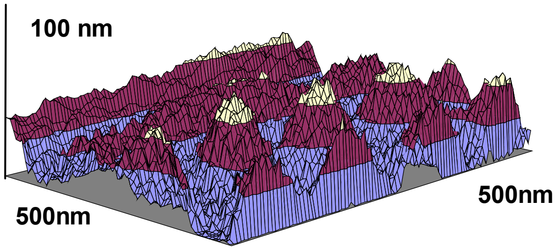
Range of measured adhesion force

Model Surfaces Generated with Fractals

AFM Scan



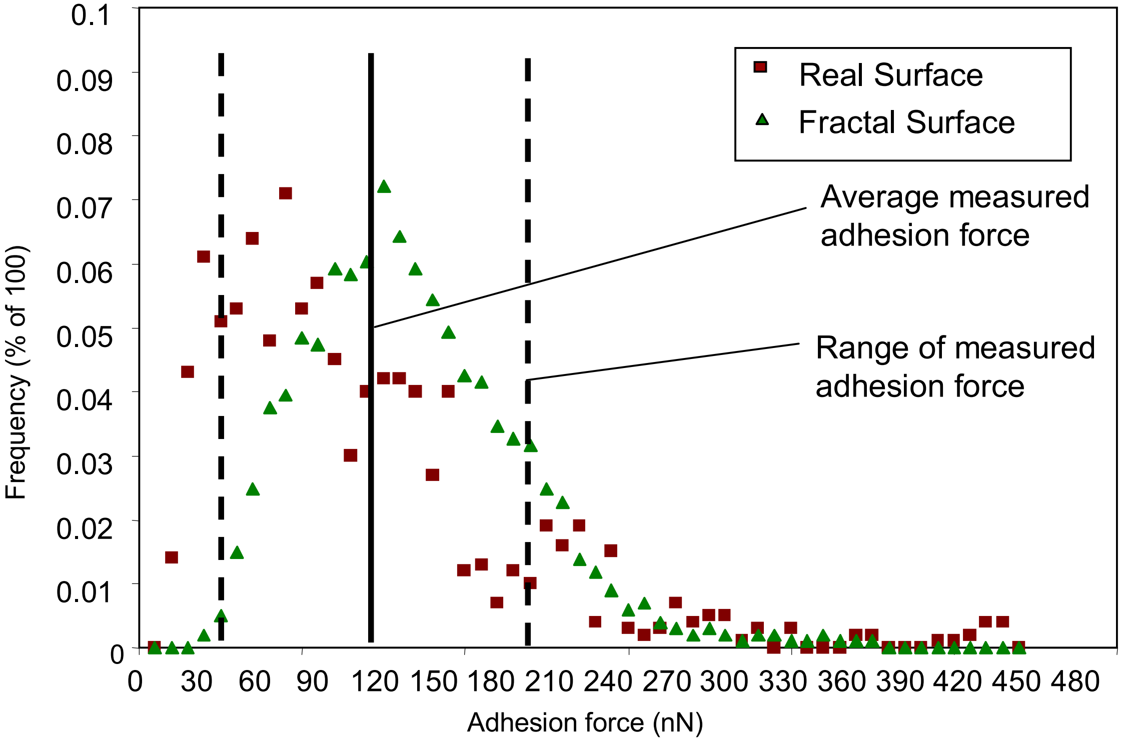
Model Surface



Weierstrass-Mandelbrot equation

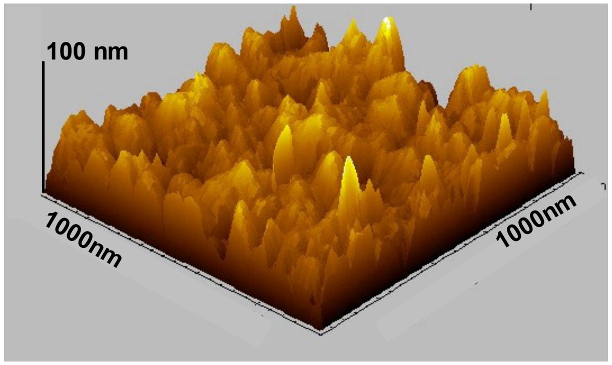
$$W(r) = ((\ln \gamma)^{1/2} / M^{1/2}) \sum_{m=1}^{M} A_m \sum_{n=-\infty}^{\infty} \left[1 - e^{\left(ik_0 \gamma^n r \cos(\theta - \alpha_m)\right)}\right] e^{\left(i\phi_{m,n}\right)} \left(k_0 \gamma^n\right)^{D-3}$$

Histogram Comparing Predicted Adhesion Forces

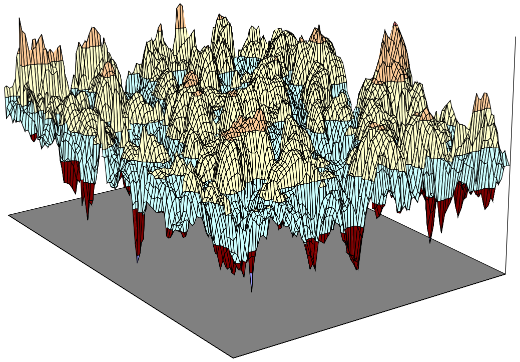


Model Surfaces Generated with Fourier Transform

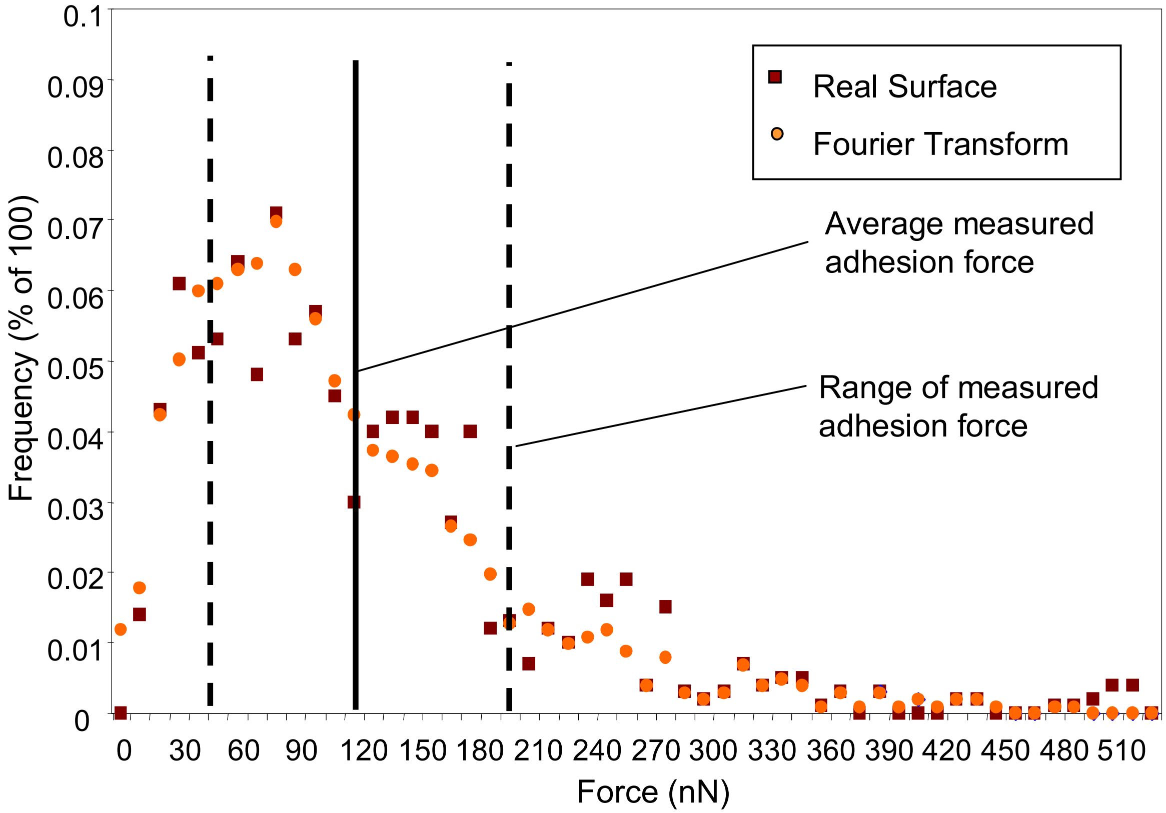
AFM Scan



Model Surface



Histogram Comparing Predicted Adhesion Forces



Fourier transform equation:

$$f(k) = \int_{-\infty}^{\infty} f(x) e^{-i2\pi fx}\, dx$$

Fourier transform of surface profile

$$f(x) = \sum_{k=0}^{n-1} F_k e^{i2\pi \frac{kx}{n}}$$

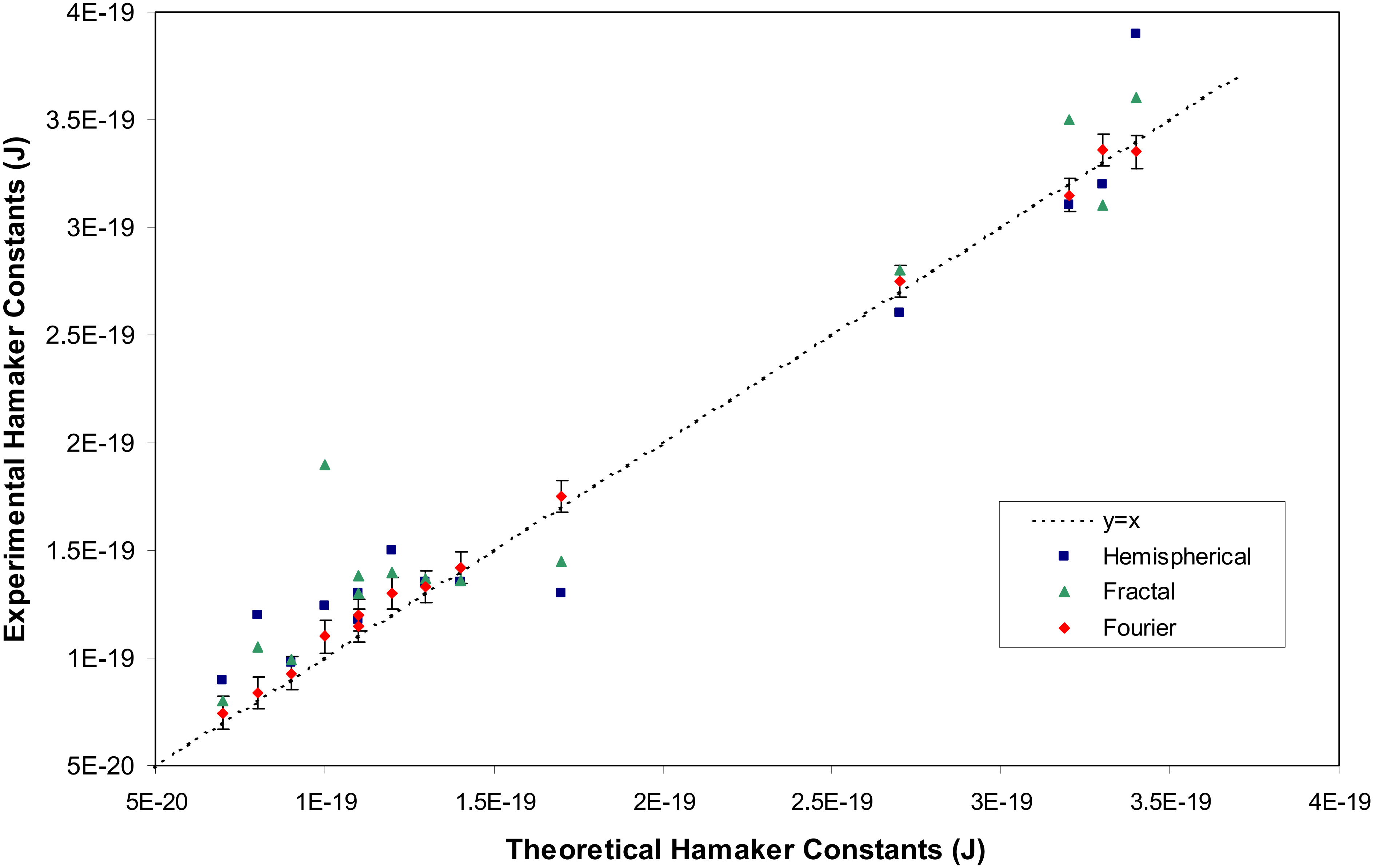
$$\hat{f}_k = \frac{1}{n} \sum_{j=0}^{n-1} f(x_j) e^{i2\pi k x_j / n}$$

Addition of random phase angle

$$f(x) = \sum_{k=0}^{n-1} F_k e^{i2\pi \left[\phi_k + \frac{kx}{n}\right]}$$

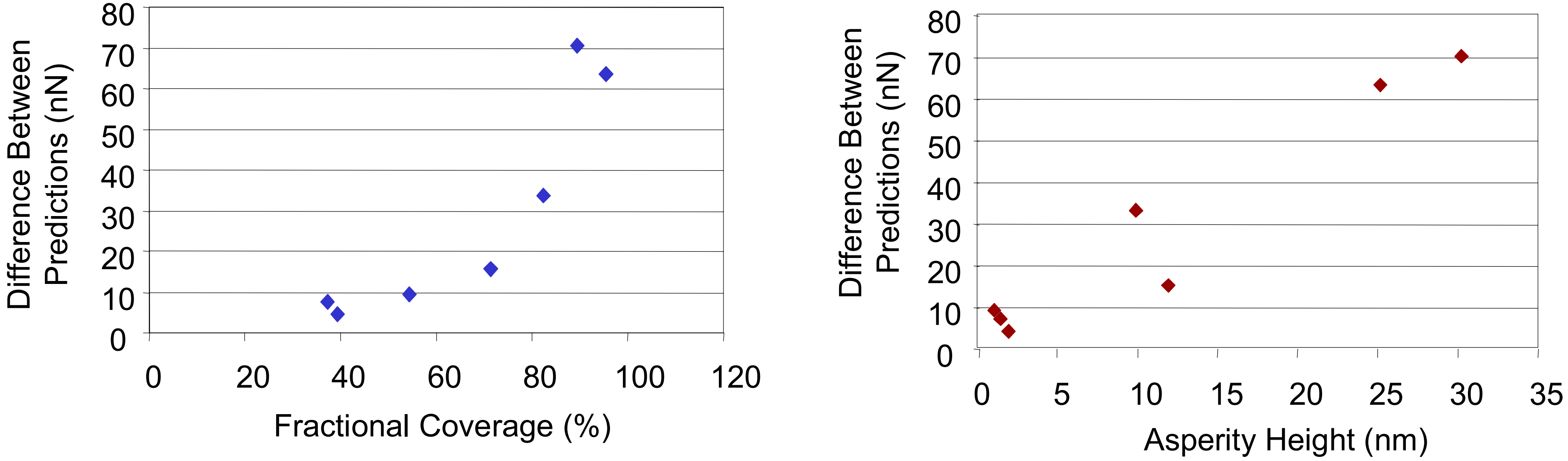
$$f(x,y) = \sum_{k=0}^{n-1} \sum_{l=0}^{m-1} F_{k,l} e^{i2\pi \left[\phi_{k,l} + \frac{kx}{m} + \frac{ly}{n}\right]}$$

Improvement in vdW Model Hamaker Constants with New Surface Roughness Models



Limitations on Hemispherical Asperity Model

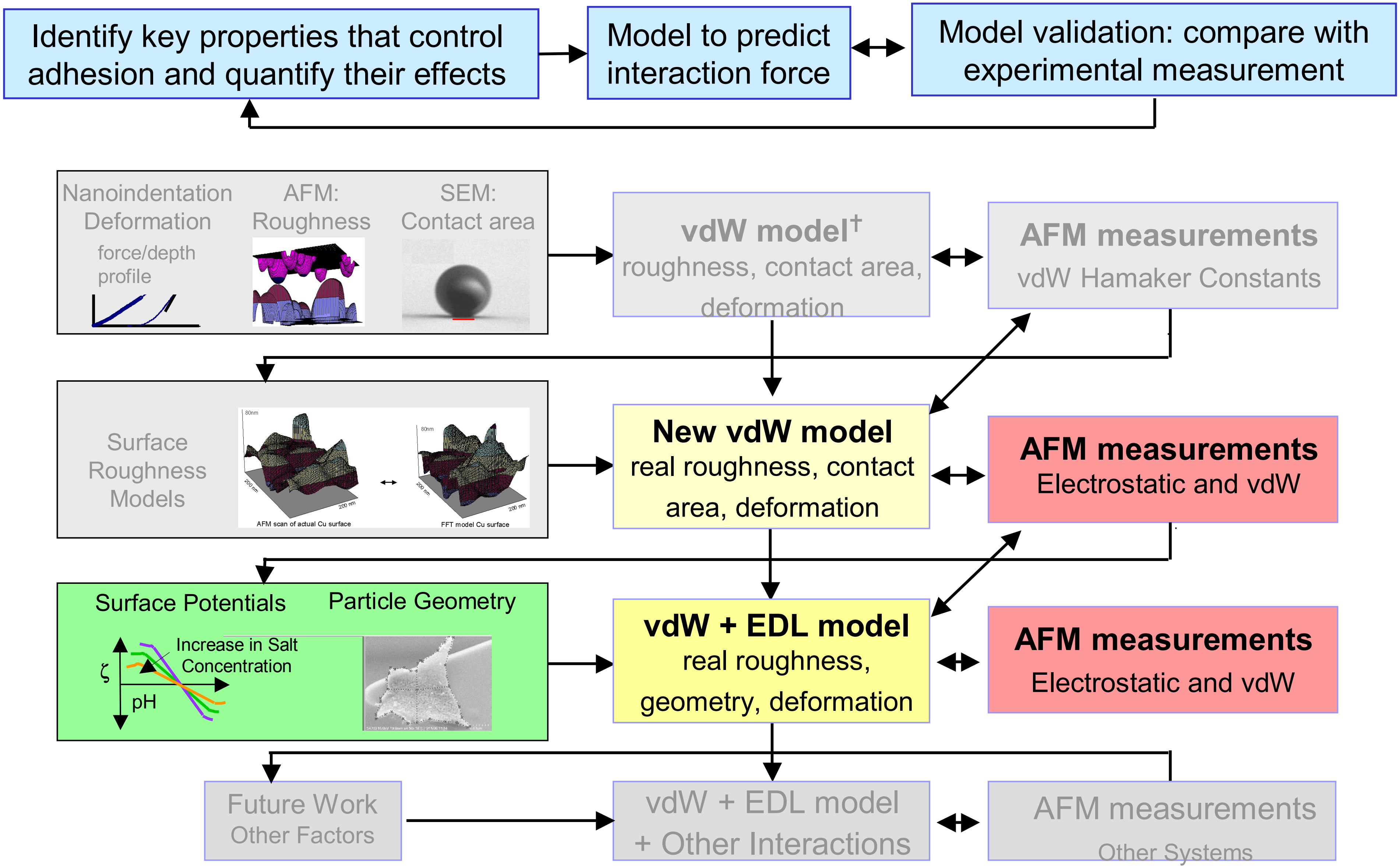
Difference Between Average Predicted Adhesion Forces
Using Hemispherical Asperities and FFT



To use Hemispherical Asperity Model

- Fractional coverage must be less than 70 percent
- Asperity Height must be less than 10 nm
- Larger fractional coverages and asperity heights result in poor predictions

Electrostatic Interactions



Identify key properties that control adhesion and quantify their effects

Model to predict interaction force

Model validation: compare with experimental measurement

Nanoindentation Deformation

force/depth profile

AFM: Roughness

SEM: Contact area

vdW model† roughness, contact area, deformation

AFM measurements vdW Hamaker Constants

Surface Roughness Models

New vdW model real roughness, contact area, deformation

AFM measurements Electrostatic and vdW

Surface Potentials

Particle Geometry

vdW + EDL model real roughness, geometry, deformation

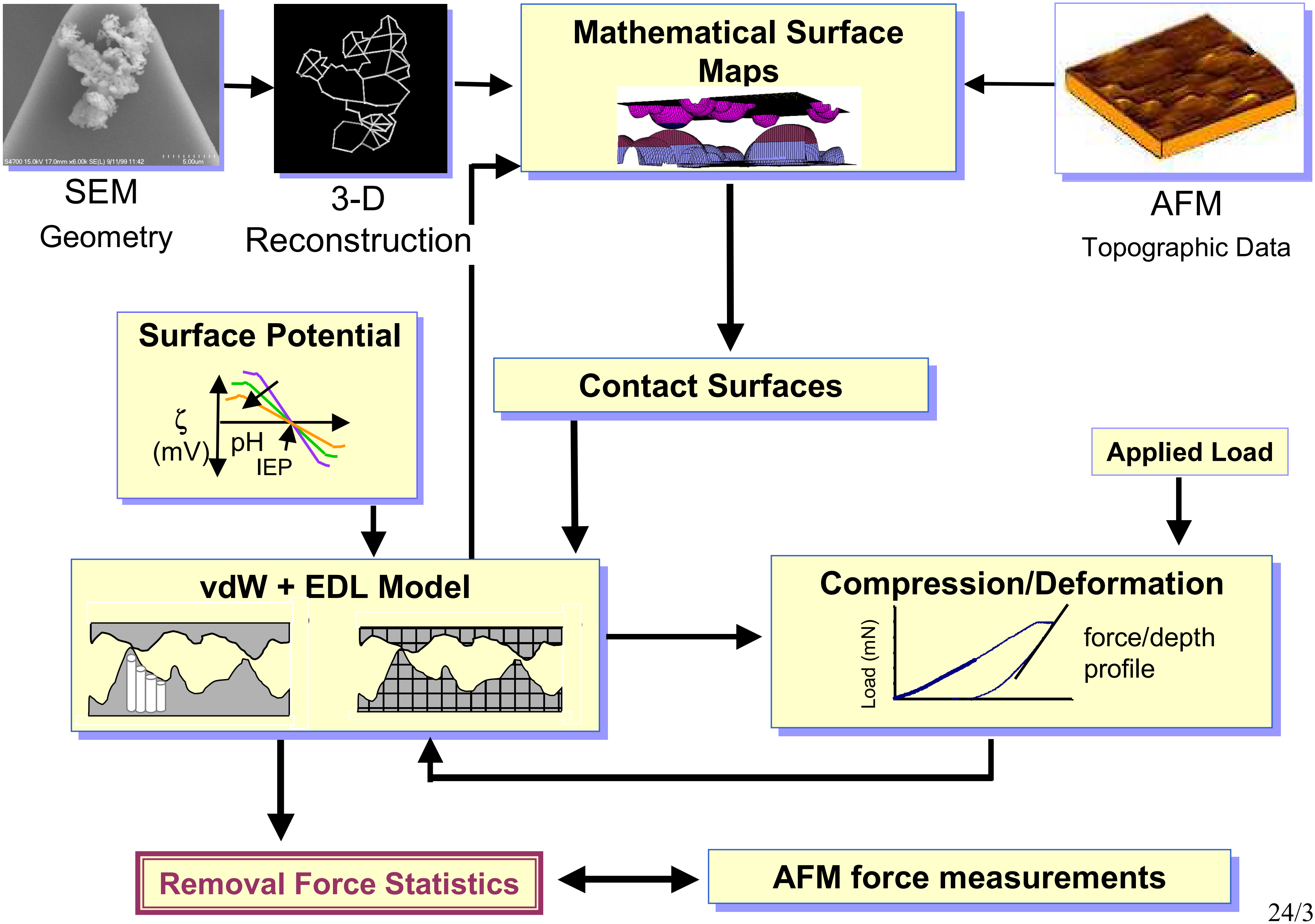
AFM measurements Electrostatic and vdW

Future Work Other Factors

vdW + EDL model + Other Interactions

AFM measurements Other Systems

Electrostatic Adhesion Model



SEM

Geometry

3-D

Reconstruction

Mathematical Surface Maps

AFM

Topographic Data

Surface Potential

Contact Surfaces

Applied Load

vdW + EDL Model

Compression/Deformation

force/depth profile

Removal Force Statistics

AFM force measurements

Calculation of Electrostatic Forces in Adhesion Model

1.) Find ψ, q ρ

Reduce equation to a system of algebraic equations

$$\nabla^2\psi = \kappa^2\psi \qquad \psi = \psi_0 \text{ on } \Gamma_1 \qquad q_0 = \partial u_0 / \partial n \text{ on } \Gamma_2$$

Weighted Residuals

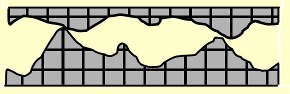
$$\psi = \alpha_1\phi_1 + \alpha_2\phi_2 + \ldots \quad q - q_0 \neq 0 \quad \text{on } \Gamma_1$$

$$w = \beta_1\psi_1 + \beta_2\psi_2 + \ldots. \quad \psi - \psi_0 \neq 0 \quad \text{on } \Gamma_2$$

$$\psi_j = \int \psi^* q_0 d\Gamma - \int q^* \psi_0 d\Gamma \qquad \psi^* = \frac{1}{4\pi r} e^{-\kappa r}$$

$$c_j \psi_{0j} = \int \psi^* q_0 d\Gamma - \int q^* \psi_0 d\Gamma \qquad q^* = \nabla \psi^* \cdot \mathbf{n}_\alpha$$

Apply to Discretized Boundary



$$\psi_j = \sum_{i=1}^{N}\left(\int_{\Gamma_i} \underline{\psi^* d\Gamma_i}\right) q_{0i} - \sum_{i=1}^{N}\underline{\left(\int_{\Gamma_i} q^*\right)}\psi_{0i} \quad \frac{1}{2}\psi_{0j} = \sum_{i=1}^{N}\left(\int_{\Gamma_i} \underline{\psi^* d\Gamma_i}\right) q_{0i} - \sum_{i=1}^{N}\underline{\left(\int_{\Gamma_i} q^*\right)}\psi_{0i}$$

Solve with quadrature

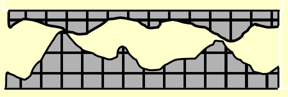
System of linear algebraic equations, solve for ψ or q

2.) Calculate force

Solve for ρ

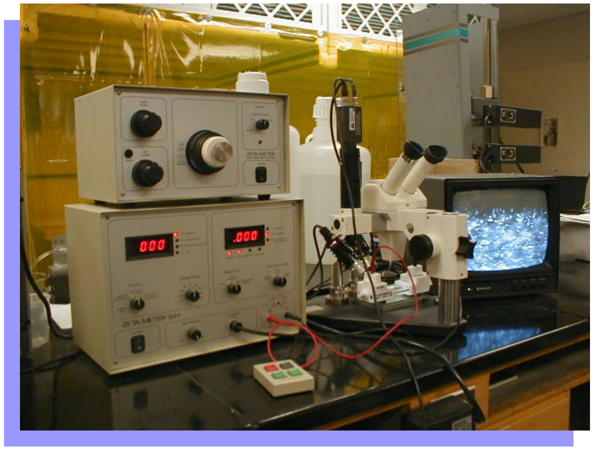
$$\frac{F}{Area} = -\frac{\sigma^2}{2\varepsilon_0\varepsilon_r} + kT\sum_i\left(c_i^*(0) - c_{io}^*\right)$$

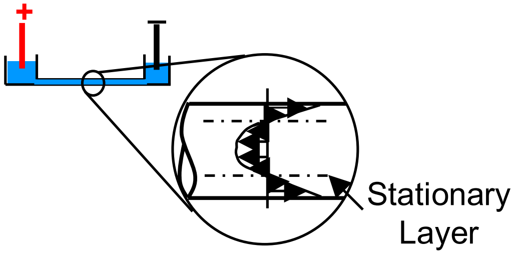
Integrate over surfaces



$$F = \sum\left[-\frac{\sigma^2}{2\varepsilon_0\varepsilon_r} + kT\sum_i\left(c_i^*(0) - c_{io}^*\right) * Area\right]$$

Surface Potentials

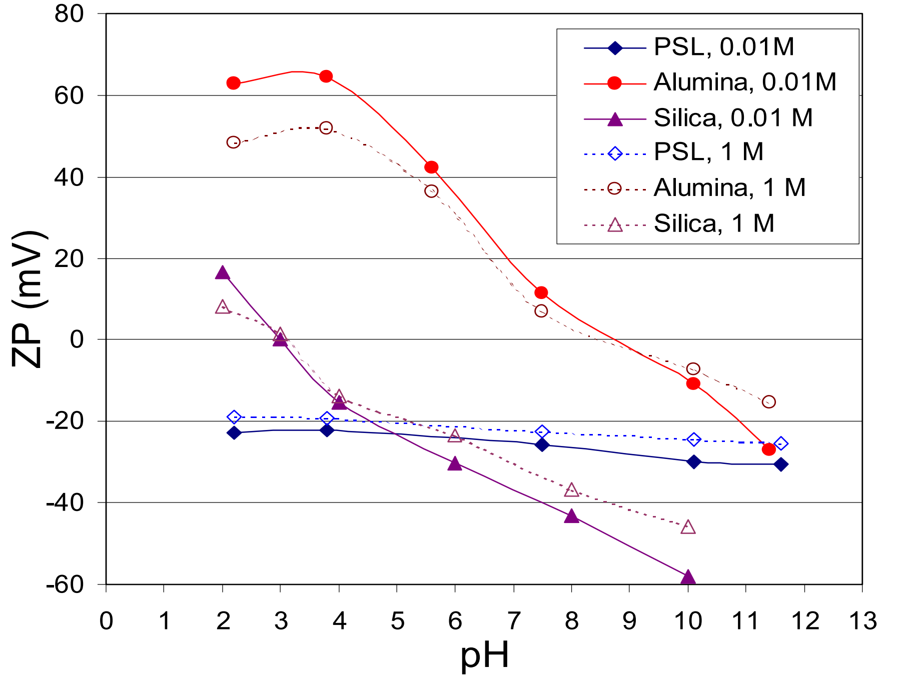


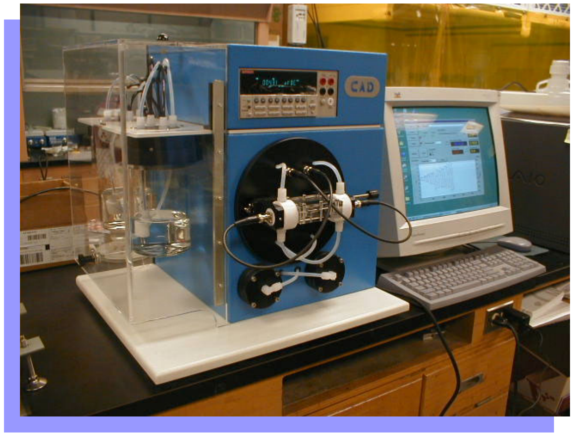


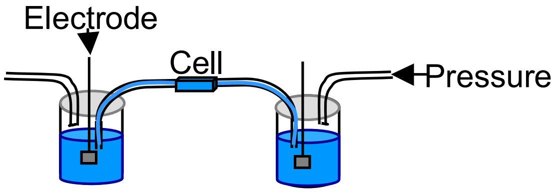
Smoluchowski Equation

$$\xi = 113{,}000\frac{\mu}{\varepsilon}\,\mathrm{EM}\ (\mathrm{mV})$$

Zeta Potential as a Function of pH and Ionic Strength





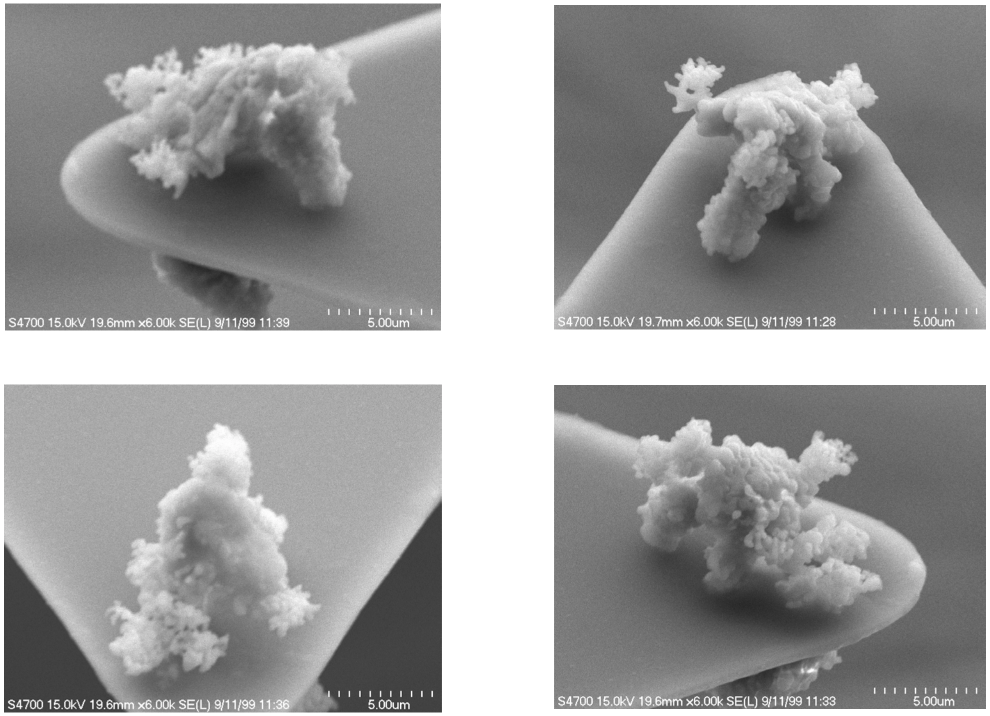


Streaming Potential Equation

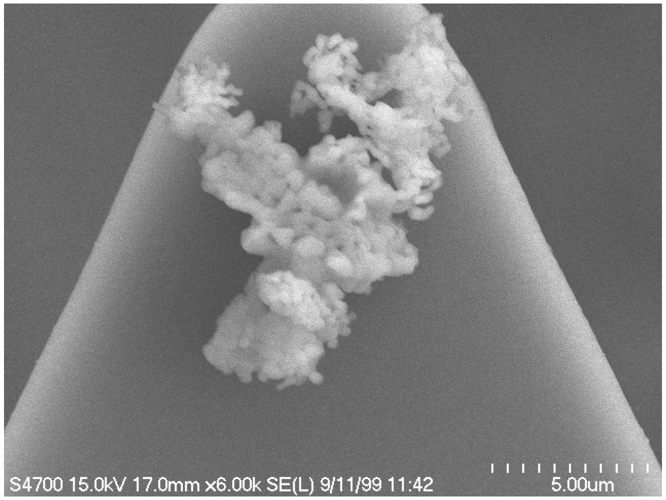
$$\xi = 135500\frac{\Phi\mu k_e}{\Delta P\varepsilon\varepsilon_o}\ (\mathrm{mV})$$

Particle Geometry

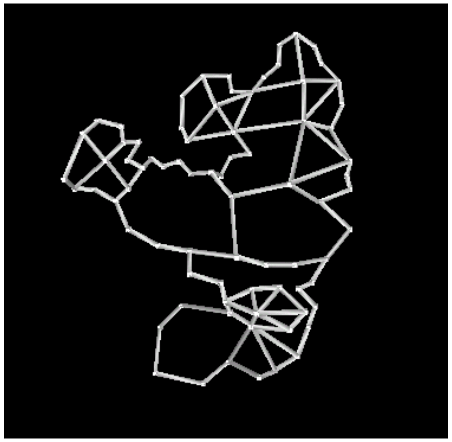
SEM Characterization



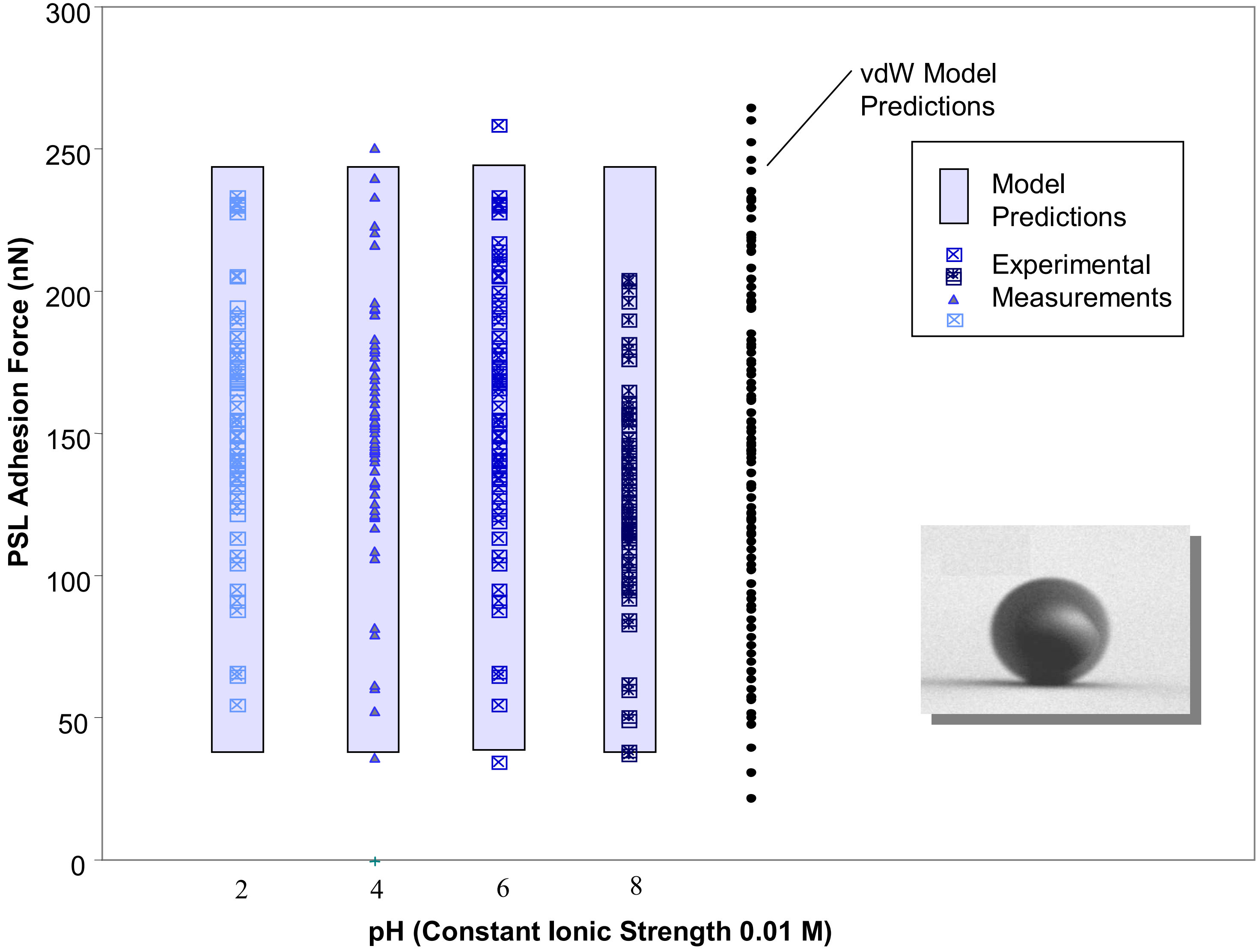
+



Photomodeler® Pro
Reconstruction

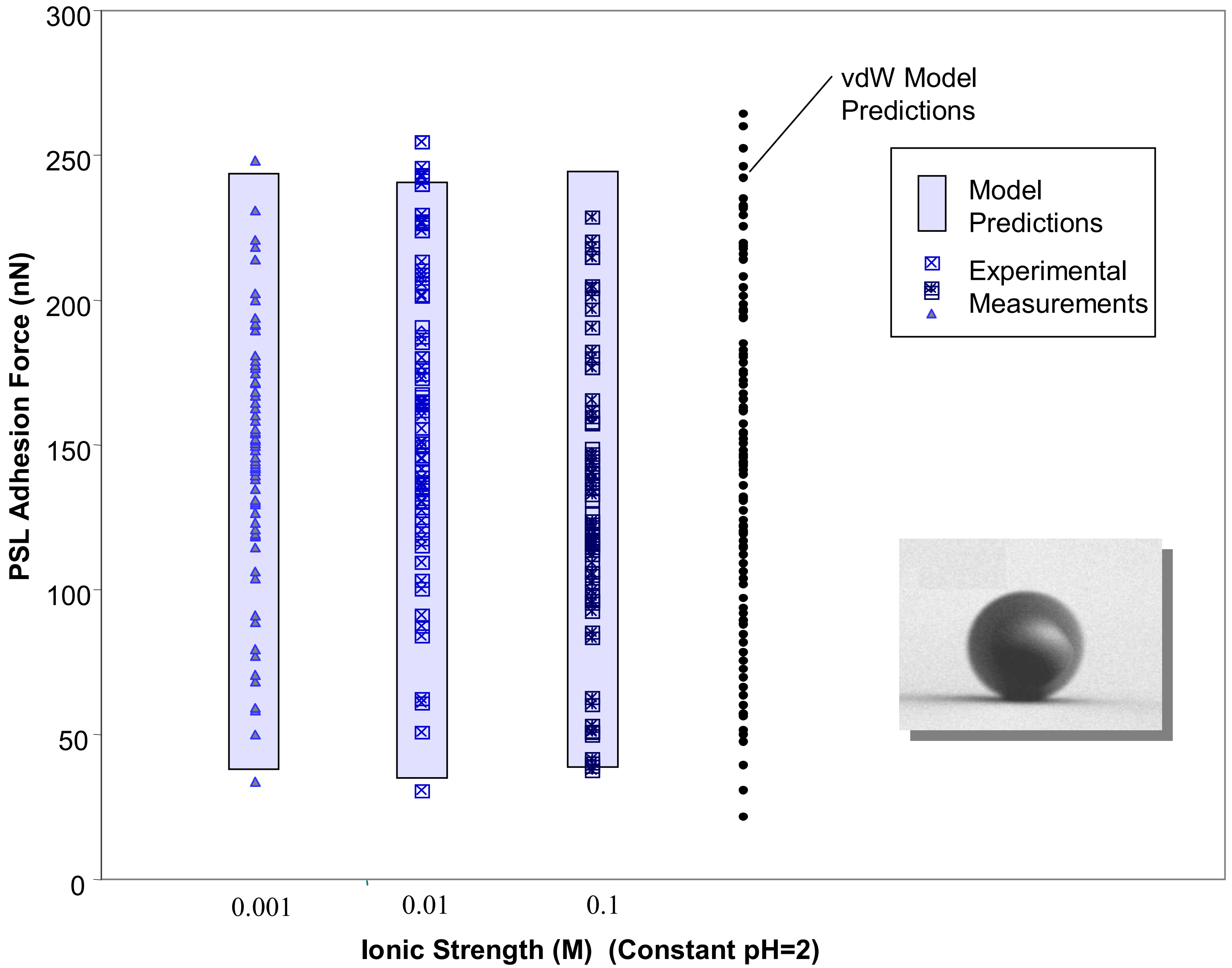


PSL Interactions with SiO_2



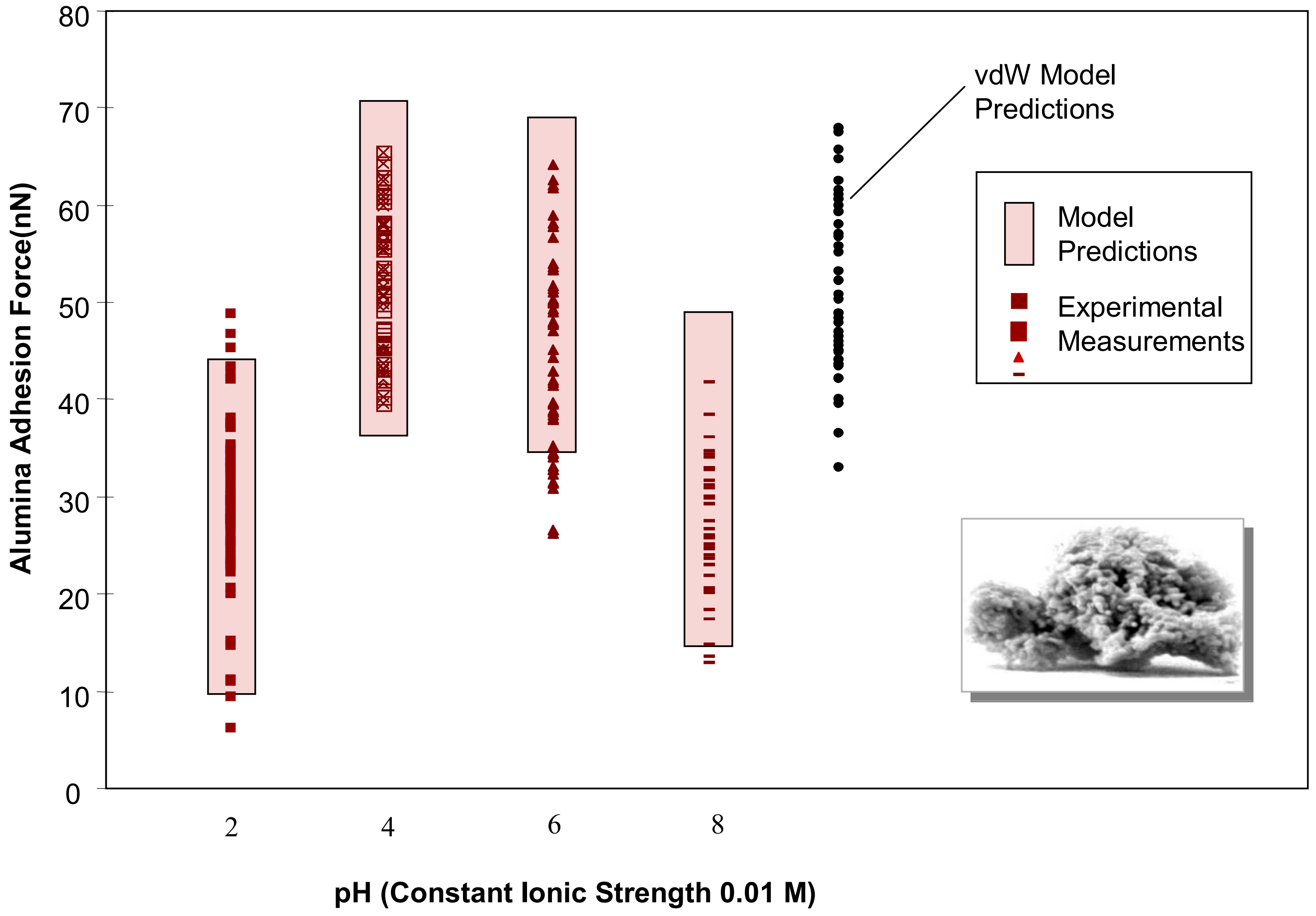
- Electrostatic interactions do not have a significant effect at different pHs
- Large contact area between sphere and wafer dominated by vdW

PSL Interactions with SiO_2



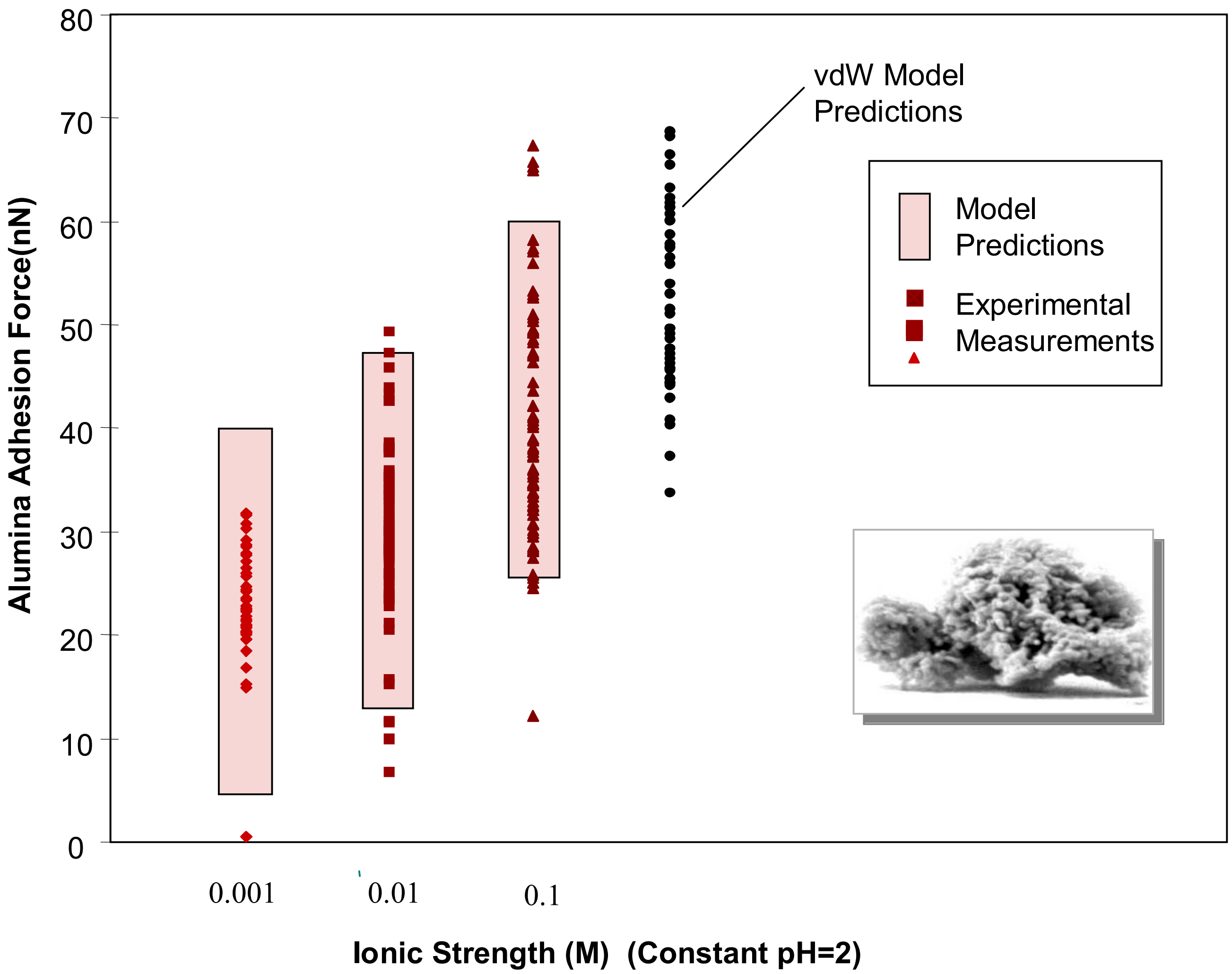
- Electrostatic interactions do not have a significant effect at different ionic strengths
- Large contact area between sphere and wafer dominated by vdW

Alumina Interactions with SiO_2



- Electrostatic interactions do affect the adhesion force, which varies with pH
- Large area between particle and wafer out of contact
- Small contact area

Alumina Interactions with SiO_2



- Electrostatic interactions do affect the adhesion force, which varies with ionic strength
- Large area between particle and wafer out of contact
- Small contact area

Conclusions

Hamaker Constants

- Measured Hamaker constants for:
  - SiO_2, Cu, Ag, TiN, PTFE, and Parylene,
- Method of measuring Hamaker constants for new materials
- Further validation of vdW adhesion model
- Limitations of surface roughness models

Surface Roughness Models

- Examined effects of model surface generated with fractals, Fourier transforms and hemispherical asperities
- Hemispherical asperity models
  - Parameters cannot vary with AFM scan size
  - Accurate for surfaces with small roughness
- Fractal surfaces
  - Difficult to generate and cannot be generated for all surfaces
- Surfaces generated with Fourier transforms
  - Accurate for all surfaces
- Validation of roughness models through comparisons with AFM measurements

Electrostatic Double Layer Interactions

- Small for particles with ideal geometry, vdW dominate
- Contribute to adhesion force for asymmetrical particles
- Modeled with boundary element method
- Validated model through comparison with AFM measurements

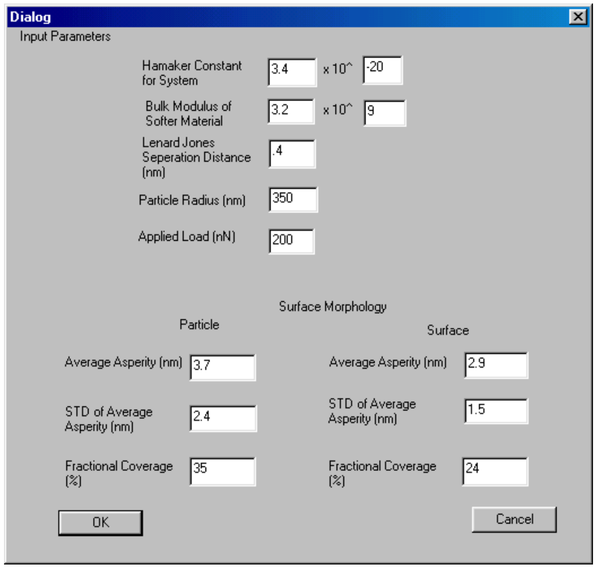
Future Work

Theory

- Particle geometry characterization
- Examine electrostatic interactions for the particle not in contact
- Cohesive failure of the particle or surface
- Investigation of other forces
  - Isolate force with adhesion model

Applied

- Tailor systems to control adhesion force
  - Strengthen adhesion force when desired
  - Weaken adhesion force when particles must be cleaned from surface
- Use model to examine other systems of interest in other industries
- Combine all interactions and removal model in software package



Hamaker Constant for System: 3.4 x 10^ -20

Bulk Modulus of Softer Material: 3.2 x 10^ 9

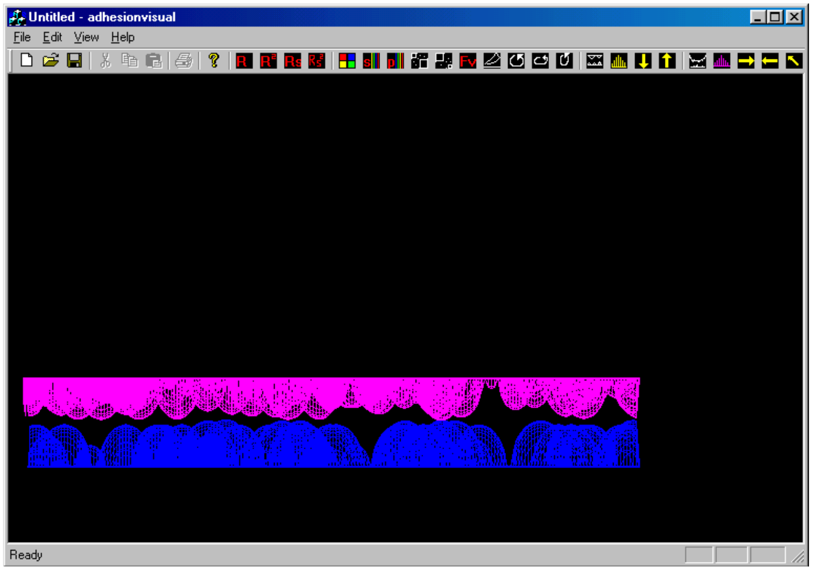
Lenard Jones Seperation Distance (nm): .4

Particle Radius (nm): 350

Applied Load (nN): 200

Surface Morphology

	Particle	Surface
Average Asperity (nm)	3.7	2.9
STD of Average Asperity (nm)	2.4	1.5
Fractional Coverage (%)	35	24



Acknowledgments

Advisor and Committee

- Steve Beaudoin, Terry Alford, Veronica Burrows, Michael Kozicki, Greg Raupp

Experimental Contributions

- Carlota Holland, Harriet Gu, Carly Chan, and Heather Stanfield

Funding provided by

- NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
- NSF Career Grant
- NSF Graduate Research Traineeship

Technical support provided by

- Fred Pena
- Center for Solid State Science, Arizona State University
- Center for Solid State Electronics Research, Arizona State University
- Interactive Nano-visualization in Science and Engineering Education, Arizona State University