Scaling of the Adhesion between Particles and Surfaces from Micron-Scale to the Nanometer Scale

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Abstract

Particulate contaminants adhering to surfaces are of great concern in many applications. A detailed understanding of particle adhesion, including the nature of the scaling of adhesion forces as particle sizes are reduced from micron- to nano-scale, is essential to the development of protocols to control particle contamination. This work employed micron-scale model particles to determine adhesion forces to model surfaces. Force measurements were obtained in both air and liquid environments. Particles were mounted onto tipless atomic force microscope (AFM) cantilevers and the forces required to pull the particles out of contact with the substrate surfaces were measured. A distribution of adhesion forces was observed in each case, resulting from particle and surface roughness and geometry variations. Particle and surface morphologies and mechanical properties were considered in modeling the measured adhesion force distributions, using adhesion models which have been previously validated. The predicted force distributions showed good agreement with the experimental data.

In order to demonstrate the viability of scaling adhesion force predictions from the micron- to nano-scale, Si_3N_4 AFM cantilevers whose tips had radii of curvature ranging from 8 - 60 nm were acquired. Micron-scale Si_3N_4 particles were mounted on separate AFM cantilevers, and the interaction forces between model surfaces and the nano- and micron-scale Si_3N_4 were measured. Two nano-scale tip sizes were used in each case. As observed with the micron-scale particles, a distribution of adhesion forces was obtained for each cantilever. The geometry of the cantilevers and the morphology of the surfaces were inputs to a previously-developed and validated adhesion force model that describes adhesion based on both electrostatic and van der Waals (vdW) forces. The surface potentials and Hamaker constants used to describe the micron-scale adhesion forces were used as model inputs to describe the nano-scale behavior. The modeled force distributions at both length scales showed good qualitative and quantitative agreement with the measured forces.

Introduction

When particles adhere to surfaces, a macroscopic approach to describing the adhesion force includes two forces: van der Waals (vdW) forces and electrostatic interactions. Often the dominant interactions between the particles and the surface when the particles are in contact with the surface are the vdW forces [1-3]. In certain cases in which the particles have highly nonuniform geometry, it is possible that the particle-wafer contact region where vdW forces dominate can be sufficiently small and the area of the particle where electrostatic forces dominate can be sufficiently large that electrostatic interactions can significantly affect the adhesion force for particles that are in contact with surfaces. The total adhesion force with which a particle adheres to a substrate is given by:

$$\overline{F_A} = \overline{F_{vd}} + \overline{F_E} \tag{1}$$

where F_A is the total adhesion force, F_{vd} is the van der Waals force and F_E is the electrostatic force, which is usually considered to be the electrostatic double-layer force if the contact occurs in aqueous solution.

The roughness of two interacting surfaces has a large effect on the adhesion force observed. The effects of surface roughness on vdW forces have been examined previously, and several models for describing the adhesion between rough surfaces have been proposed. One approach is to describe the roughness as a film that varies from 100% particle to 100% solution and then integrate across the film varying the Hamaker constant based on the fraction of solution and particle [4, 5]. A second approach is to develop a mathematical model to describe the roughness on the surfaces and then integrate the forces between elements within the two rough surfaces. For example, ideal shapes have been used to model asperities or surface roughness [2, 6-11]. The model developed by Cooper *et al*. [1] was used to investigate the vdW forces between different film materials, and it was determined that in some cases surface roughness cannot be represented by ideal shapes. In this work, the roughness of each interacting surface was represented by a series of sine waves using the Fourier transform to generate model surfaces which were statistically similar to the actual surfaces [12]. These model surfaces were then brought in contact and each surface was discretized into cylindrical volume elements as shown in Figure 1.

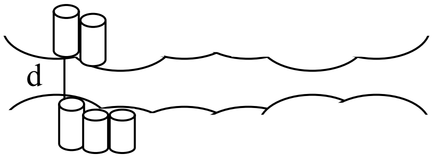

Figure 1. Division of two interacting surfaces into cylindrical volume elements

Assuming pairwise additivity, the interaction force between two opposing elements separated by a distance *d* is

$$F_{vdW-cylinder} = -\frac{A \cdot (Area\, of\ cylinder)}{6\pi D^3} \tag{2}$$

The vdW force is computed by integrating Equation 2 between opposing volume elements in the two interacting surfaces. The computational scheme has been described in detail separately [12].

The electrostatic double layer force (present only in electrolyte systems) is computed using a boundary element method to solve the linearized Poisson-Boltzmann equation

$$\nabla^2\psi = -\kappa^2\psi \tag{3}$$

where Ψ is the electrical potential on the two interacting surfaces and κ is the reciprocal of the Debye length. The two interacting surfaces are divided into boundary elements which were approximately 1nm in width. The boundary conditions account for constant potential on the two surfaces and the following set of linear equations is solved in order to obtain the charge in each node:

$$\psi_j = \sum_{i=1}^{N}\left(\int_{\Gamma_i}\psi^* d\Gamma_i\right)q_{0i} - \sum_{i=1}^{N}\left(\int_{\Gamma_i} q^* d\Gamma_i\right)\psi_{0i} \quad \textit{in the domain of computation} \tag{4a}$$

$$\frac{1}{2}\psi_{0j} = \sum_{i=1}^{N}\left(\int_{\Gamma_i}\psi^* d\Gamma_i\right)q_{0i} - \sum_{i=1}^{N}\left(\int_{\Gamma_i} q^* d\Gamma_i\right)\psi_{0i} \quad \textit{on the surfaces} \tag{4b}$$

where *j* denotes the location where the electric potential is calculated (this is influenced by the electric fields generated by all elements on both interacting surfaces), *i* denotes the i^{th} element, *N* is the total number of elements and Γ_i is the surface area of the i^{th} element. Since the constant potential boundary conditions are used, Ψ_{0i} is equal to the known surface potential Ψ_0 and all q_{0i} are unknown. By solving the above equations, the potentials and hence the ion concentrations are known at every point in the domain between the surfaces. The force is then calculated by taking the derivative of the free energy of the interaction

$$\frac{F_E}{Area} = \Pi = -\frac{\sigma^2}{2\varepsilon_0\varepsilon_r} + kT\sum_i\left(c_i^*(0) - c_{io}^*\right) \tag{5}$$

Force measurements between micron-scale Si_3N_4 particles and surfaces were made by mounting the particles on AFM cantilevers and measuring the pull-off force. In order to demonstrate the scaling of adhesion forces, Si_3N_4 AFM cantilevers with tips with nanometer-scale radii of curvature were used to make interaction force measurements. For both the micron-scale particles and nano-scale cantilevers, adhesion forces were measured against quartz and tetraethyl orthosilicate (TEOS)-sourced silicon dioxide surfaces. The adhesion model summarized in Equations 1-5 was used to compute the vdW and electrostatic interactions between the particles/tips and the surfaces. The modeling results were then compared to the experimental data to demonstrate that the adhesion model scales down to the nanometer scale.

Experimental

Micron-scale experiments

Si_3N_4 particles were obtained from Atlantic Equipment Engineers and were 1-5μm in size, with irregular geometries. Tipless AFM cantilevers were purchased from Veeco and the Si_3N_4 particles were mounted on cantilevers using a UV cured epoxy. The glue was cured by exposing it to UV light for 15min and then baking it on a hotplate at 90°C for 15min to remove any moisture. Cantilever resonant frequency measurements were made before and after the particle mounting and the spring constants were calculated using the added mass method [13]. Force measurements were made using a Veeco Nanoscope IV AFM with a Picoforce scanner. Two substrates were used in the study – TEOS - sourced silicon dioxide (thickness ~ 5000Å) and quartz. Pull-off force measurements were made for each of these substrates in air and water at three different locations. The particle was allowed to come into contact with the surface 100 times at each location. The resulting distribution of forces was used for comparison with the modeling output. A Hitachi FESEM was used to obtain images of each

Si_3N_4 particle glued to the cantilever from 5 different angles. These images were used to generate a 3-D wireframe mesh model of the particle using Photomodeler Pro. Tapping mode AFM was used to scan the particle to determine roughness. The 3-D geometry and the roughness were used as inputs to the adhesion model.

Nano-scale experiments

Si_3N_4 AF cantilevers were purchased from Veeco. The MSCT cantilevers had nominal tip radii of curvature of 40nm and the OTR8 cantilevers had nominal tip radii of curvature of 15nm. These two tip types were used for the nano-scale experiments in order to demonstrate the scaling of adhesion forces. Pull-off force measurements were made using MSCT and OTR8 tips on TEOS-sourced silicon dioxide and quartz substrates in air and water. In each case 100 measurements were made at three different locations. FESEM images were obtained using a Hitachi FESEM and the exact tip size and geometry was determined. The measured force distributions were used for comparison with modeling results.

Results and Discussion

The objective of this work was to demonstrate the scaling of a macroscopic adhesion model to describe micron- and nano-scale adhesion. Figures 2a and 2b present the measured and modeled interaction forces between Si_3N_4 particles/tips and TEOS-sourced silicon dioxide in air and water. Figures 3a and 3b present the measured and modeled interaction forces between Si_3N_4 particles/tips and quartz in air and water. Comparison of Figs. 2a and 3a shows that the adhesion force is reduced by roughly an order of magnitude when the adhering particle shrinks from the micron- to the nano-scale. In each case, the modeling results bound the experimentally measured force distributions. The Hamaker constants used in the nano-scale modeling are the same as used in the micron scale modeling. Thus, the model is able to predict interaction forces down to the nanometer scale without a significant increase in error.

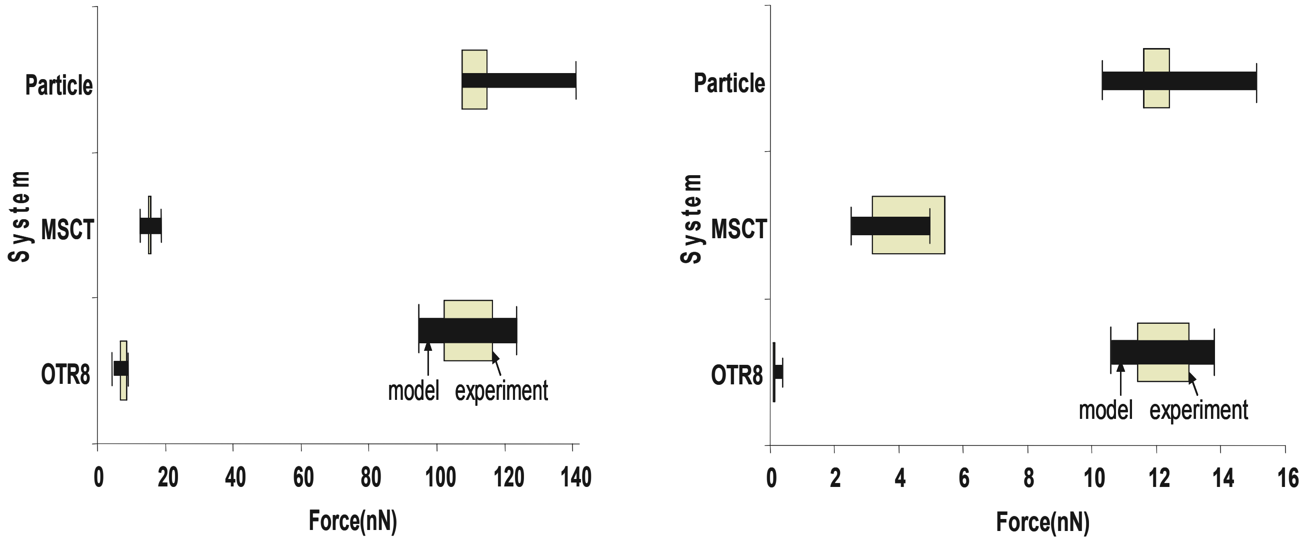

Figure 2. Measured and modeled forces between silicon nitride particles/tips and TEOS-sourced silicon dioxide (a) in air (b) in water

Figs. 2b and 3b represent measurements in water. It was observed in each case that there was a significant reduction in interaction force as compared to the forces measured in air. This reduction in force has been observed before and is consistent with previous measurements [3, 14]. In either case, the modeling results bound the experimental data. The Hamaker constants used in this case were the same for the micron scale and the nano-scale simulations.

Comparison between figs. 2a, 3a and 2b,3b show that in general, silicon nitride is more adhesive to silicon dioxide than quartz. Such comparisons have important implications in terms of being able to predict particle removal using various cleaning protocols and can be used specifying a process window in each case[15-17].

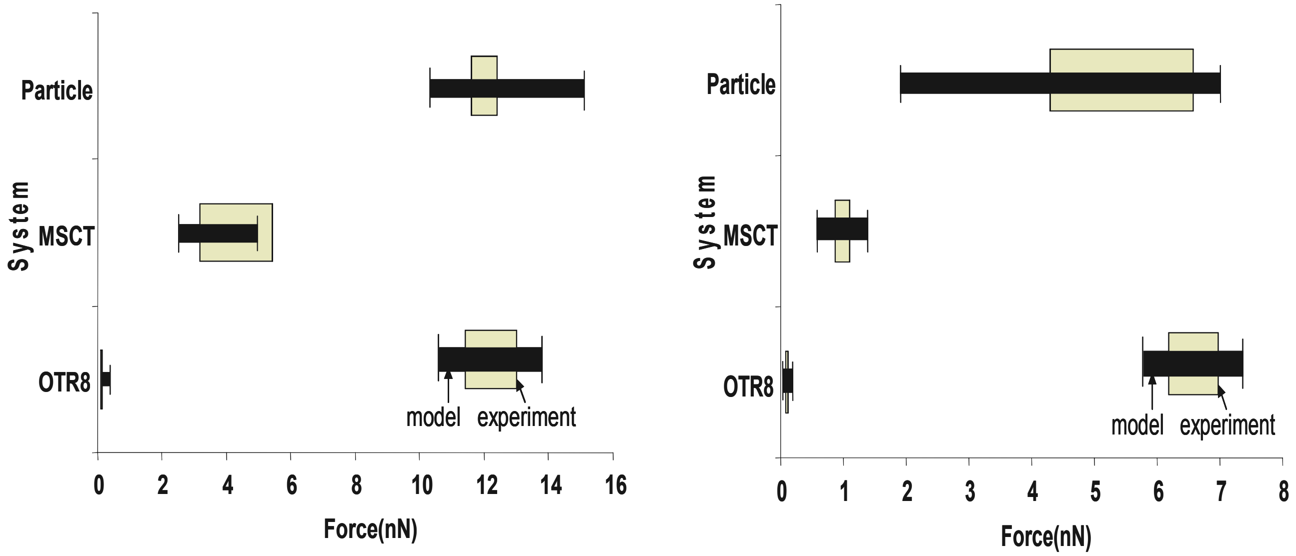

Figure 3. Measured and modeled forces between silicon nitride particles/tips and quartz (a) in air (b) in water

Conclusions

Scaling of adhesion force predictions between particles/tips and surfaces were demonstrated in two systems. An existing adhesion model was used to describe the interaction forces in each case. The model was found to predict force distributions which showed good qualitative as well as quantitative agreement with the measured interaction forces in each case. It is evident that the macroscopic model is valid for adhering objects as small as nanometers in diameter.

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