

MY 5580: Laboratory #5

Colloidal Force Measurements with Nanoscope II

Objective: To learn how to operate the Nanoscope II AFM and to measure the long-range surface forces between a probe and a substrate in aqueous solution of electrolyte.

Background: In this lab, colloidal forces between a probe and a mirror-polished multi-phase specimen of Duluth Gabbro will be measured in a liquid using Nanoscope II. The instructor will provide the specimen and its characteristics during the lab. A v-frame cantilever will be utilized in the force measurements under contact mode.

When two surfaces/interfaces approach each other, colloidal forces become significant at separations of a few tens of nanometers. These forces arise from molecular interactions between charged and uncharged atoms or molecules of the interacting bodies and the surrounding medium. According to the DLVO model proposed by Derjaguin, Landau, Verwey and Overbeek, the net interaction between two surfaces/interfaces in a liquid medium is the arithmetic sum of van der Waals and electrostatic (electric double layer) forces. The van der Waals forces arise from dipole-dipole (Keesom), dipole-induced dipole (Debye) and/or instantaneous dipole-dipole (London) interactions. In a polar solvent, like water, most interfaces become electrically charged due to either dissociation of ionizable groups present at the interface or preferential hydration of lattice ions or adsorption/reaction of ions at the interface, and they repel or attract each other through Coulombic interactions.

Atomic force microscopy (AFM) is capable of characterizing solid surfaces at microscopic and sub-microscopic resolutions by providing three-dimensional images of surfaces and probing materials properties such as adhesion, elasticity, friction, and magnetic properties. The AFM is also commonly used in the measurement and identification of long-range and short-range surface forces for microscopic particles or nano-scaled probes through the colloidal probe technique. Analysis of AFM-measured forces based on theoretical models can also be used to either compare model predictions with experimental results, or to calculate parameters such as the Hamaker constant, surface potentials, or surface charge densities.

In this laboratory session, students will measure colloidal forces for selected phases of the specimen and then use the DLVO model to analyze the force curves. Theoretical portion of the exercise will be limited to calculation of the surface charge density for the substrate-water interface and analysis of the surface charge density variation.

Experimental Procedure: Students will operate the Nanoscope II AFM following the guidelines of demonstration provided by the instructor.

All the experiments will be conducted in a fluid cell. The electrolyte solution of 1 mM KCl having pH of about pH 9 will be used. From 10 to 15 force curves will be collected for each of the three-to-four different phases of the rock sample. Each student will be responsible for capturing a set of force curves for one of the phases.

The deflection-distance data will be converted to force distance curves using the SPIP software. The processing of the force-distance curve will include baseline and hysteresis corrections.

Report. In the report, the students should present all three/four graphs with the force – separation curves. All 10 to 15 force curves that were captured for each phase should be presented on one graph and a scatter of the curves should be discussed. Each graph should also include a theoretical force-separation curve that represents an “average” of experimental results. Equations needed to plot the theoretical curve are provided below and are limited to equations describing long-range electrostatic forces. Forces at distances less than a few nanometers (van der Waals forces and solvation forces) will not be analyzed in this exercise.

Parameters used in modeling, including surface charge density, need to be listed in the table. Students should also discuss differences, if any, in surface charge density values determined for different phases.

Theoretical Model:

Electrostatic Forces:

We only consider the electrostatic force in calculation. The total tip-substrate electrostatic force is divided into two parts that represent interactions of the substrate with spherical and conical parts of the tip.

$$F_{TS}^S = \frac{4\pi}{\epsilon_0 \epsilon \kappa^2} \sigma_T \sigma_S (a_0 e^{-\kappa D} - a_1 e^{-\kappa L_1}) + \frac{2\pi}{\epsilon_0 \epsilon \kappa^2} (\sigma_T^2 + \sigma_S^2) (a_2 e^{-2\kappa D} - a_3 e^{-2\kappa L_1})$$

$$F_{TS}^C = \frac{4\pi}{\epsilon_0 \epsilon \kappa \tan \alpha} \left[b_1 \sigma_T \sigma_S e^{-\kappa L_1} + b_2 \frac{(\sigma_T^2 + \sigma_S^2)}{2} e^{-2\kappa L_1} \right]$$

$$\text{where } b_1 = \left[R \sin \alpha - \frac{D + R(1 - \cos \alpha)}{\tan \alpha} \right] + \frac{1}{\tan \alpha} \left[\left(L_1 + \frac{1}{\kappa} \right) \right]$$

$$b_2 = \left[R \sin \alpha - \frac{D + R(1 - \cos \alpha)}{\tan \alpha} \right] + \frac{1}{\tan \alpha} \left[\left(L_1 + \frac{1}{2\kappa} \right) \right]$$

$$L_1 = D + R(1 - \cos \alpha), a_0 = \kappa R - 1, a_1 = \kappa R \cos \alpha - 1, a_2 = a_0 + 0.5, \text{ and } a_3 = a_1 + 0.5$$

$$\alpha=55^\circ, R=70\text{nm}, \frac{1}{\kappa} = \frac{3.043 \times 10^{-10}}{(c_0)^{1/2}} m, \epsilon=79.5, \epsilon_0=8.854 \times 10^{-12} \text{C}^2/\text{Jm}$$

The total electrostatic force is equal to:

$$F^e = F_{\text{TS}}^S + F_{\text{TS}}^C$$

Symbols:

c_0 – concentration of electrolyte (=0.001 M)

F_{TS}^S . electrostatic force for spherical part

F_{TS}^C . electrostatic force for conical part

ϵ - dielectric constant of the medium separating surfaces

ϵ_0 - permittivity of vacuum

σ_T - surface charge density for tip¹

σ_S - surface charge density for the substrate

$1/\kappa$ - Debye length

D - surface to surface separation

R - radius of tip apex

α - geometrical angle for the spherical cap at the tip end

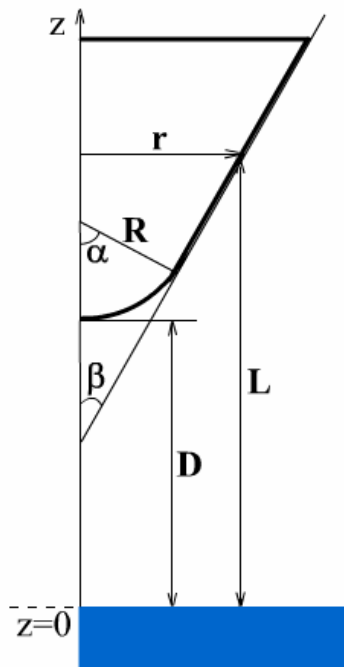


Figure 1. Geometry of the tip and parameters used in the theoretical model.

¹ If not stated otherwise, assume the surface charge density for the Si_3N_4 tip at pH 9 equal to -0.01 C/m^2