Measurements of Colloidal Forces Using an External Magnetic Field and Atomic Force Microscopy

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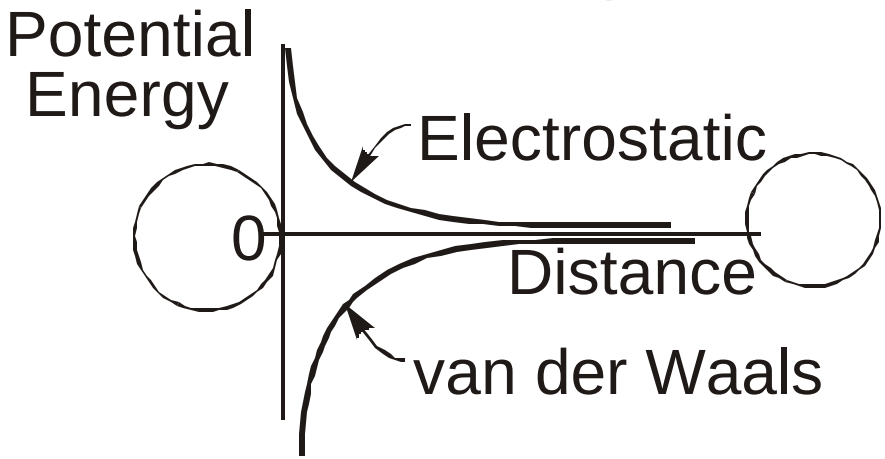
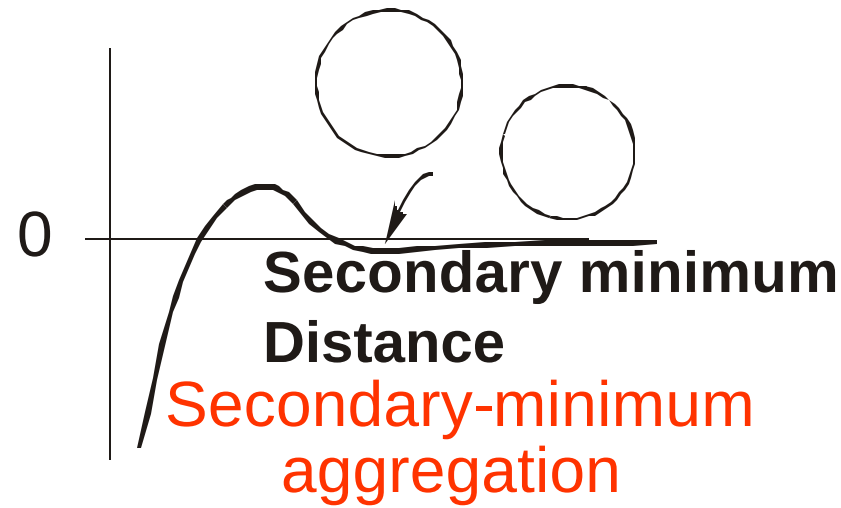
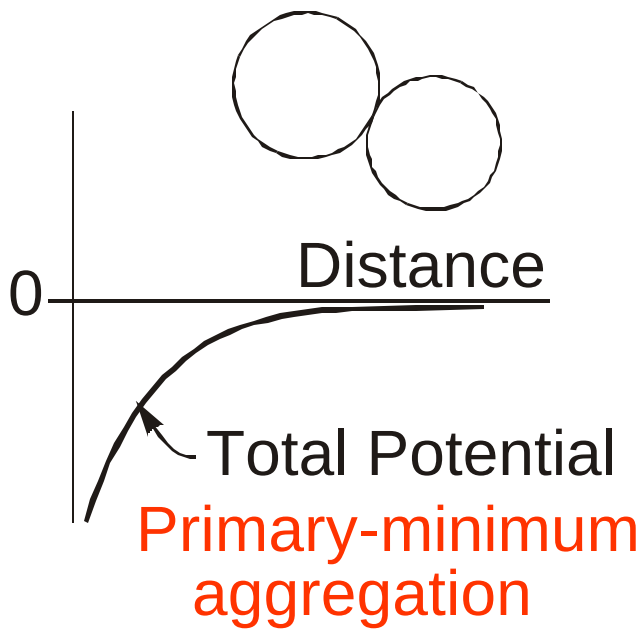
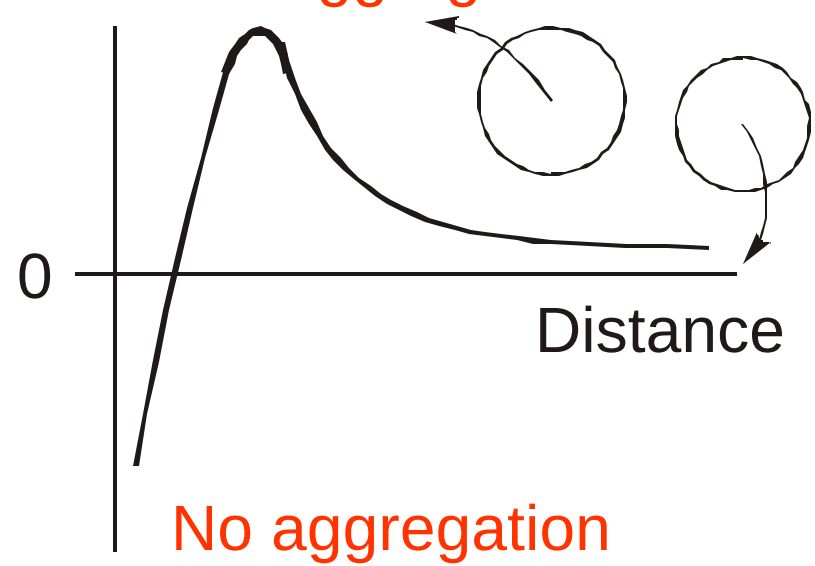
Potential Energy for DLVO Forces

DLVO: Derjaguin-Landau-Verwey-Overbeek









Objectives

- **Investigate primary-minimum and secondary-minimum aggregation by visualizing chain formation and breakup.**
- **Examine aggregation of magnetic particles and breakup of magnetic chains based on extended DLVO theory including:**
  - **DLVO Forces:**

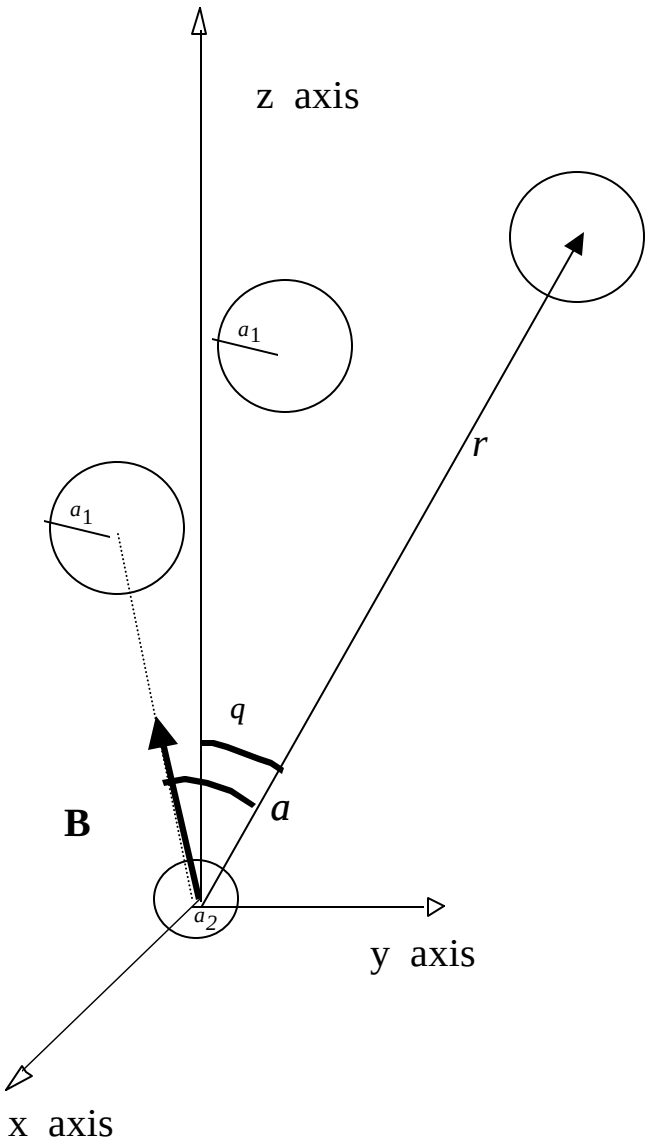
    van der Waals, electrostatic, magnetic-dipole
  - **Non-DLVO Forces:**

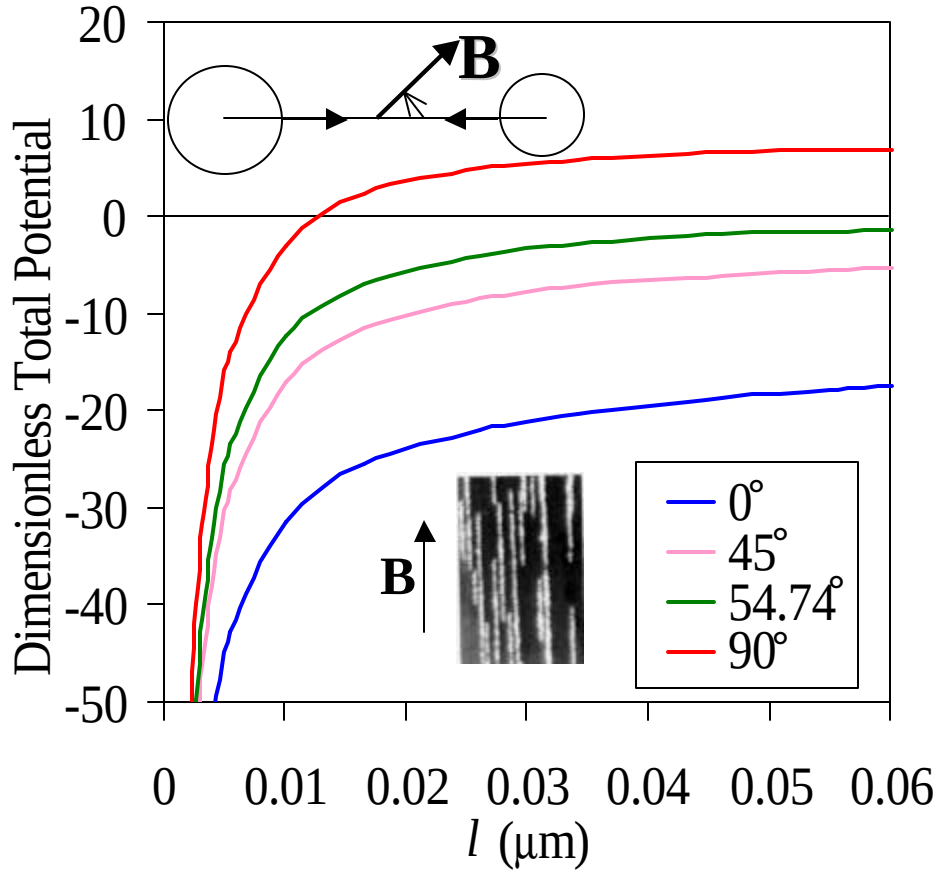
    hydrophobic attraction, steric
- **Investigate the influence of surfactant on breakup of magnetic chains.**

Manipulation of Interparticle Forces

- A magnetic force is introduced as an additional interparticle force to probe DLVO forces.
- The total potential between initially stable particles is manipulated at different aggregation regimes.
- By examining the breakup of magnetic chains after the additional force is removed, the aggregation regime is determined.
- Potential Applications:
  - Environmental separations (aggregation, filtration)
  - Hydrometallurgy (metal recovery)
  - Magnetorheological fluids
  - Medical applications (cancer treatment, drug delivery)
  - Paper industry (toner removal, recycling of pulp fibers)

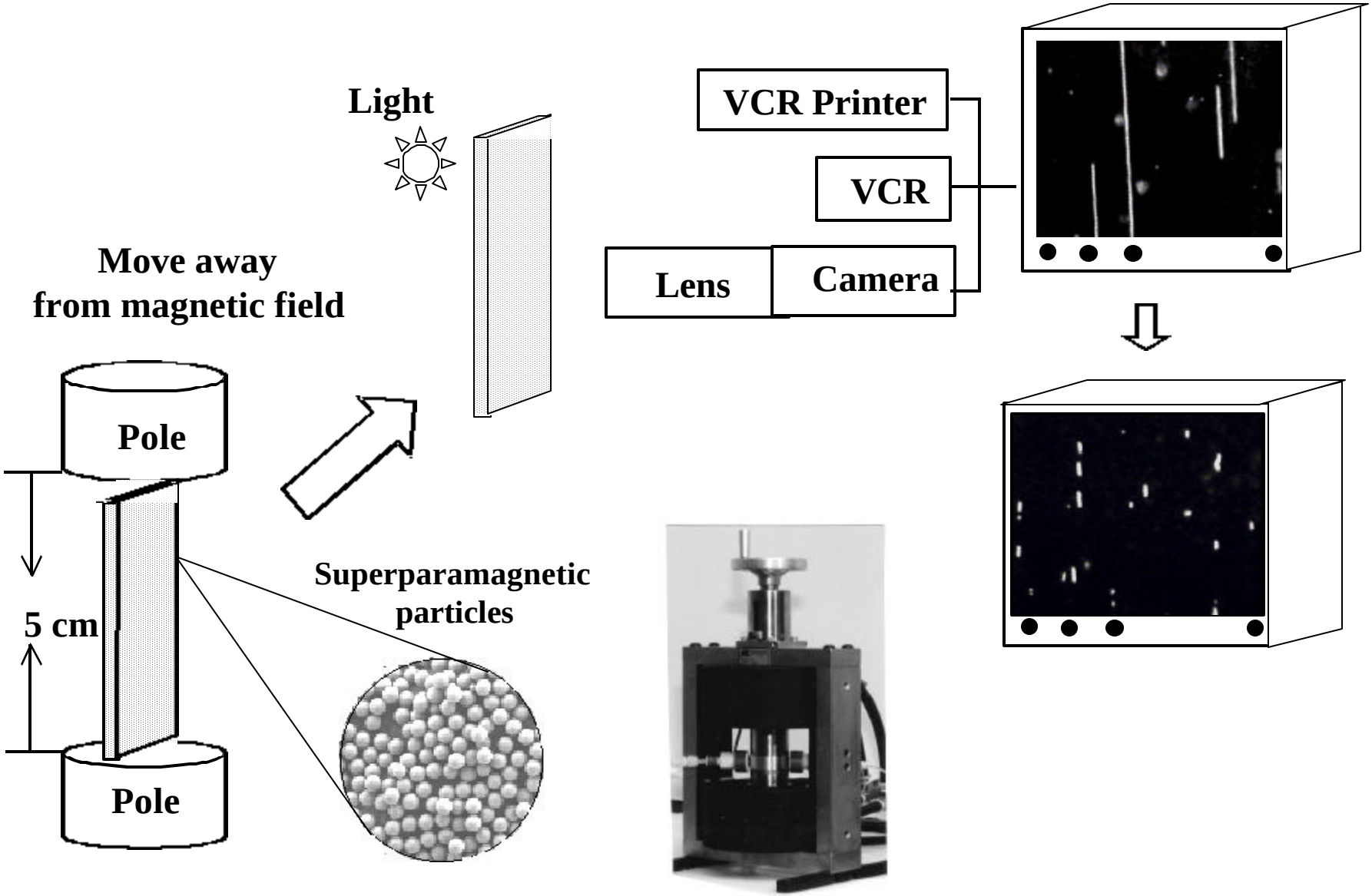
Magnetic Dipole Force



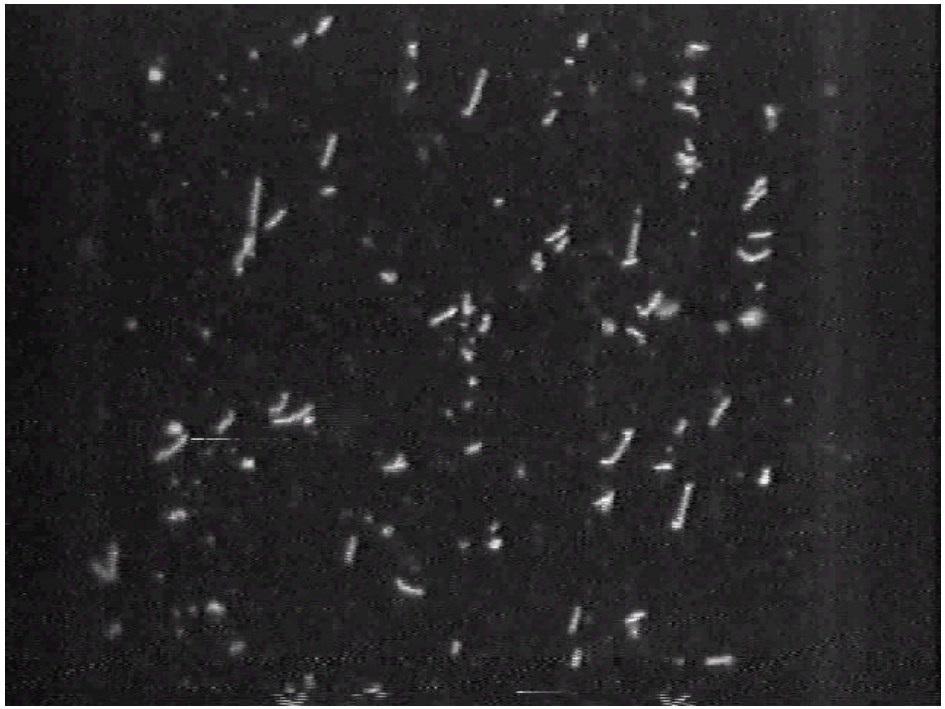


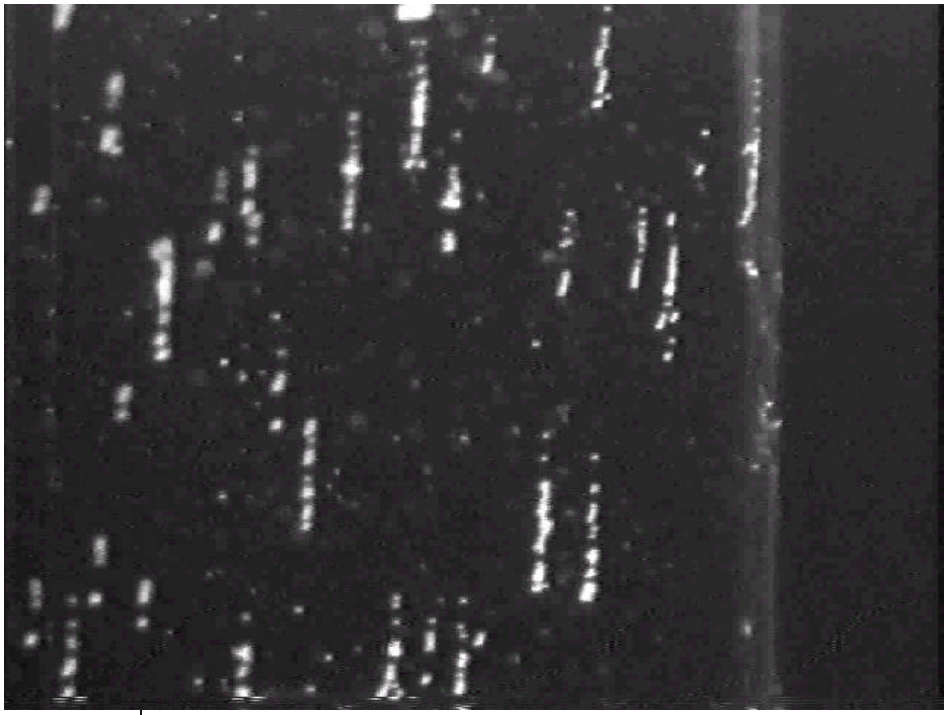
Dimensionless total potential at different angles (a-q): *A* = 1.6 E-20 J, *I* = 0.1 *M*, *c* = 0.6, zeta potential = -3.2 mV, *B* = 0.003 T.

Experimental Setup

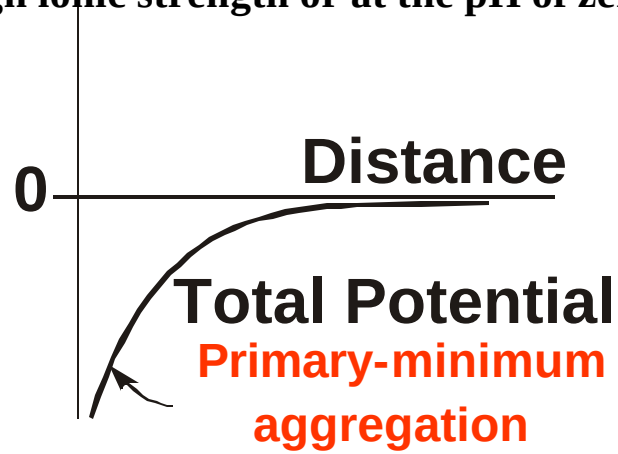


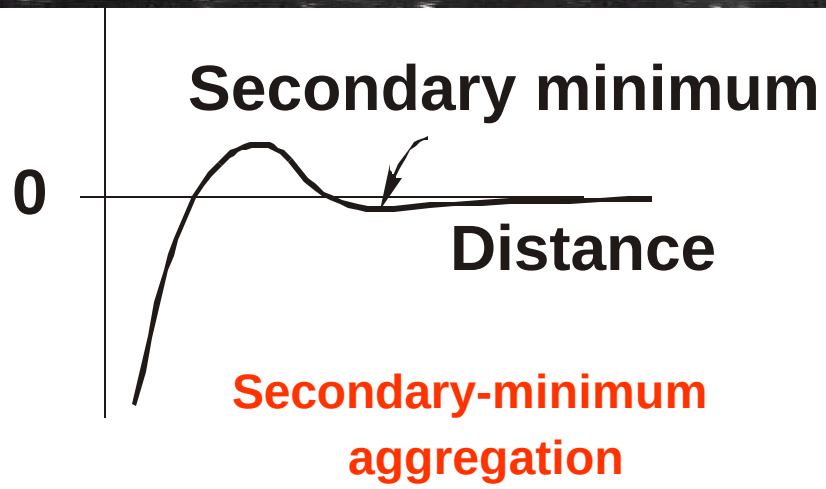
Breakup of Aggregates



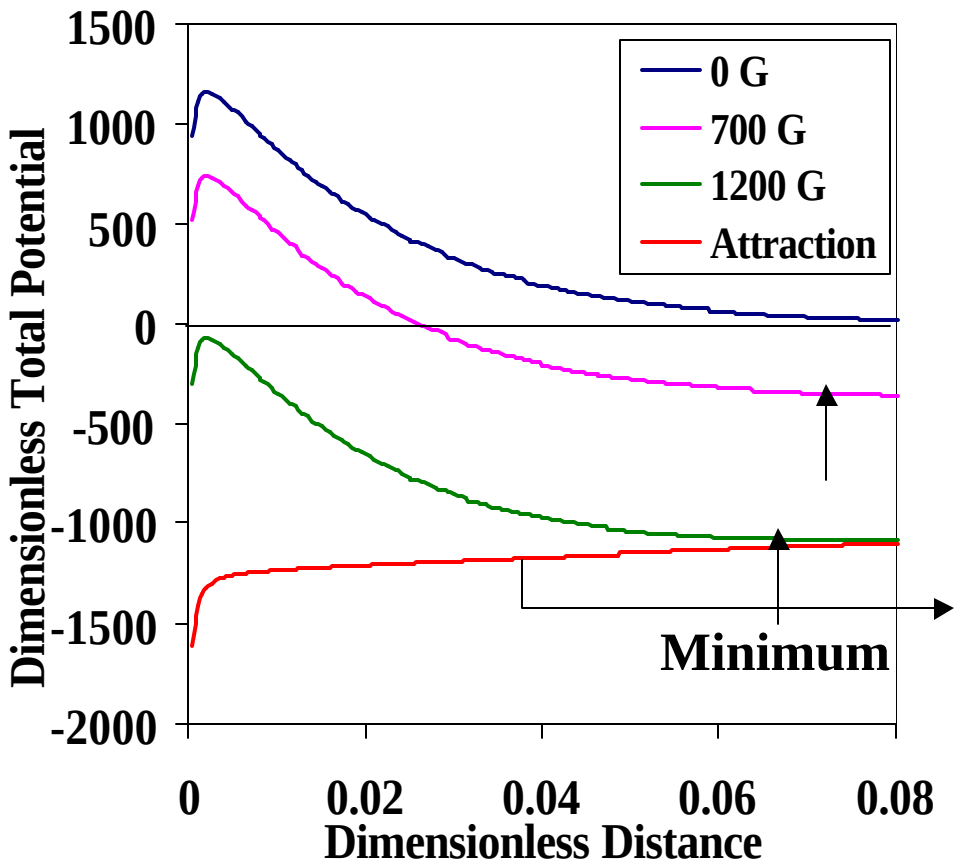


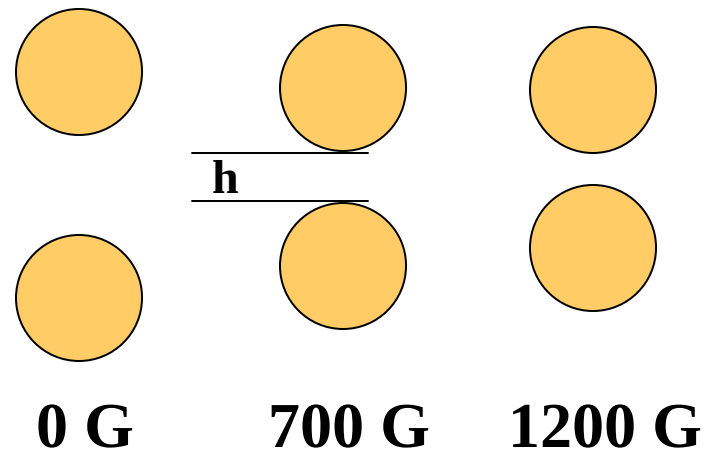
High ionic strength or at the pH of zero charge



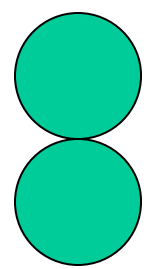


Transition from Secondary to Primary Minimum Aggregation Using the Magnetic Dipole Force





h decreases as B is increasing



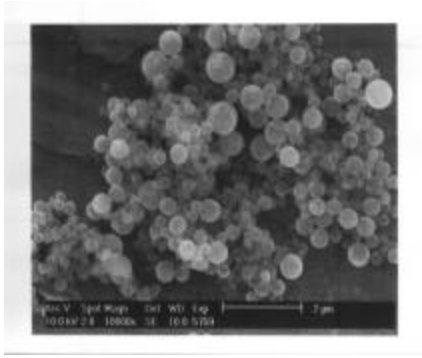
Particles in contact

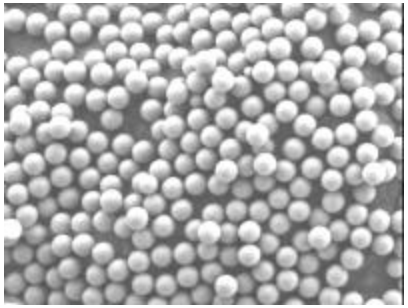
Dimensionless total potential at different magnetic field strengths: A = 1.6E-20 J, I = 0.001, *c* = 0.1, zeta potential = -60 mV.

C.J. Chin, S. Yiacoumi, C. Tsouris, S. Relle, S.B. Grant, *Langmuir*, **16**, 3641 (2000).

Particle Properties and Characterization

Property	Small particles	Large particles
Average size of composite particles measured from SEM images (mm)	0.23	4.5
Weight % magnetite in polystyrene	38 %	20 %
Density (g/cm^3)	1.504	1.5
Volumetric magnetic susceptibility	0.19	0.24
Hamaker constant (J)	2.228E-20	1.436E-20
Zeta potential (mV) at pH 11	- 49.0	- 50.0
Particle concentration (number of particles/mL)	2.0E+8	4.0E+7





Transitional Magnetic Induction

Magnetic induction at which secondary-minimum aggregation changes to primary-minimum aggregation

Particle Suspension	Small Particles	Large Particles
Average size of composite particles measured from SEM images (μm)	0.23	4.5
Experimentally determined transitional magnetic induction (T)	0.46 – 0.52	0.0030 – 0.0040[1] 0.0610 – 0.0717[2]
Calculated transitional magnetic induction using the pair-dipole model (T)	0.482	0.0656
Calculated transitional magnetic induction using the chain-dipole model (T)	0.4512	0.0595

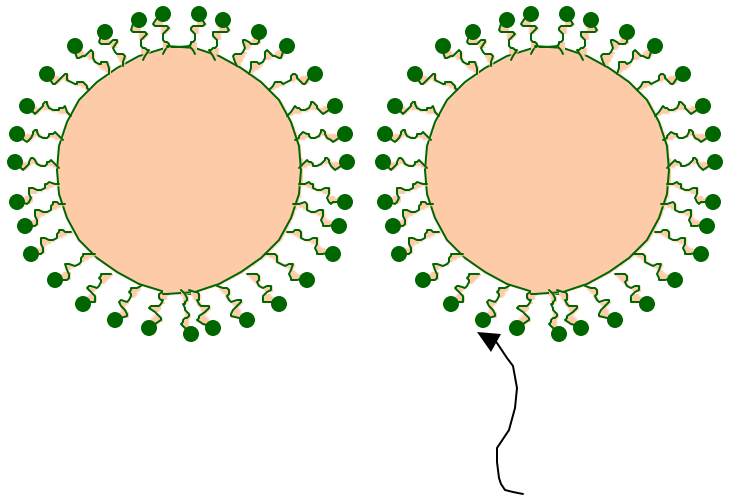
[1] **Narrow capillary tube: 50-mm length ´ 1-mm width ´ 50-mm thickness**

[2] **Wide capillary tube: 50-mm length ´ 2-mm width ´ 100-mm thickness**

Formation and Breakup of Chains in Surfactant Solutions

Non-Equilibrium Steric Repulsion

Non-equilibrium steric repulsion between two equal spheres (Israelachvili, 1991) :



$$V_{steric} = 3\pi r_i G k T l_p \exp\left(-D/l_p\right)$$

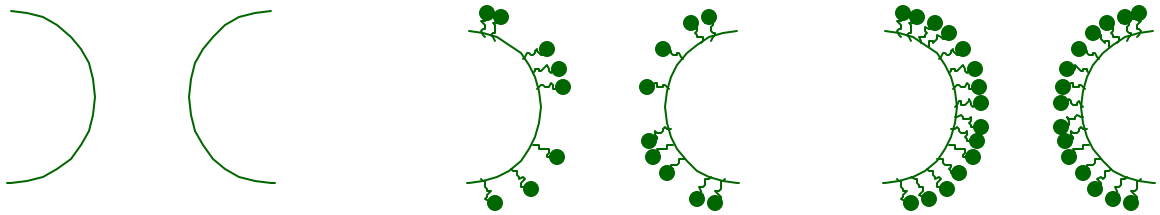
***G*: surface coverage, number of grafted chains per unit surface area of particle**

***k*: Boltzmann constant**

***T*: absolute temperature**

***l_p*: protrusion decay length**

Influence of Surfactant Concentration on Transitional Magnetic Induction



Concentration of SDS (x CMC)	0.01	0.1	1	10	50
Transitional Magnetic Induction (T)	0.082–0.099	0.1150–0.1220	0.1515–0.1650	0.1794–0.2150	0.1794–0.2150

- **The transitional magnetic induction increases with increasing surfactant concentration until the particles are completely covered by surfactant molecules.**
- **Theoretical transitional magnetic induction for particles completely covered by surfactant: 0.1803 T.**

Summary of Work with Magnetic Particles

- An external magnetic force is used to study interparticle forces.
- Particles form chains in a magnetic field. Chain breakup after magnetic force is removed indicates secondary-minimum aggregation.
- The transitional magnetic induction, at which secondary-minimum aggregation changes to primary-minimum aggregation, is determined experimentally and theoretically.
- The transitional magnetic induction increases with increasing surfactant concentration and reaches a maximum after the particles are completely covered by surfactant molecules.
- Experimental and theoretical values of transitional magnetic induction for small particles, large particles in wide tubes, and large particles in high SDS concentration are in good agreement.
- DLVO theory and existing force formulae for potential energy calculations are reliable.

Measurements of Colloidal Particle Forces Using Atomic Force Microscopy (AFM): Effects of Sorption of Metal Ions

Introduction

- AFM has been used to measure surface colloidal forces in various systems (e.g., Ducker et al., 1991; Larson et al., 1993; Camesano and Logan, 2000).
- The constant-surface-charge model was reported to describe electrostatic forces better than the constant-surface-potential model.
- Sorption of metal ions changes the surface charge density of sorbent materials.
- Sorption of metal ions on oxide surfaces involves specific interactions between ions and surface groups.

Sorption/Precipitation

Oxide particles **Metal cations** **charge neutralization**

Objectives

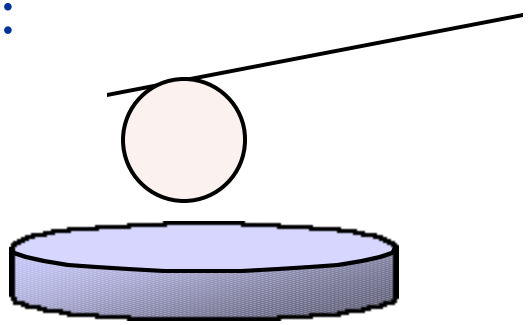
- Directly measure surface colloidal forces during sorption of metal ions using AFM.
- Compare direct force measurements with theoretical calculations to probe the DLVO theory.
- Investigate the influence of metal ion sorption on surface forces using a single colloidal particle.

AFM is one form of scanning probe microscopy (SPM), a family of microscopy in which a surface is scanned by a sharp probe and the tip-surface interactions are monitored.

Force Determination

Force, F, between a sphere and a smooth plate for the constant-surface-charge model (Israelachvili, 1991) :

$$F = \frac{4\pi \sigma_1 \sigma_2 R}{\varepsilon \kappa} e^{-\kappa D} - \frac{AR}{6D^2}$$



σ_1, σ_2: charge densities of the sphere and the plate, respectively

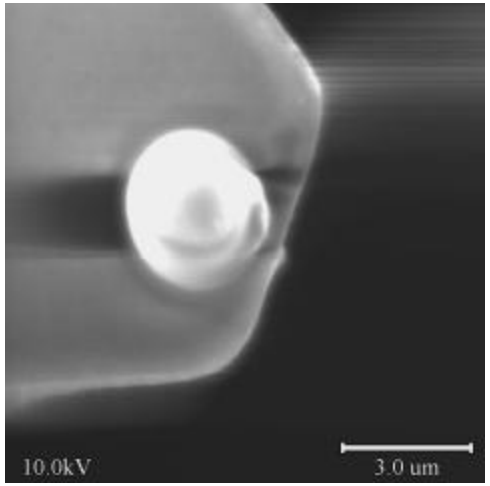
R: radius of the silica particle tip

ε: permittivity of water

κ: inverse of the double–layer thickness

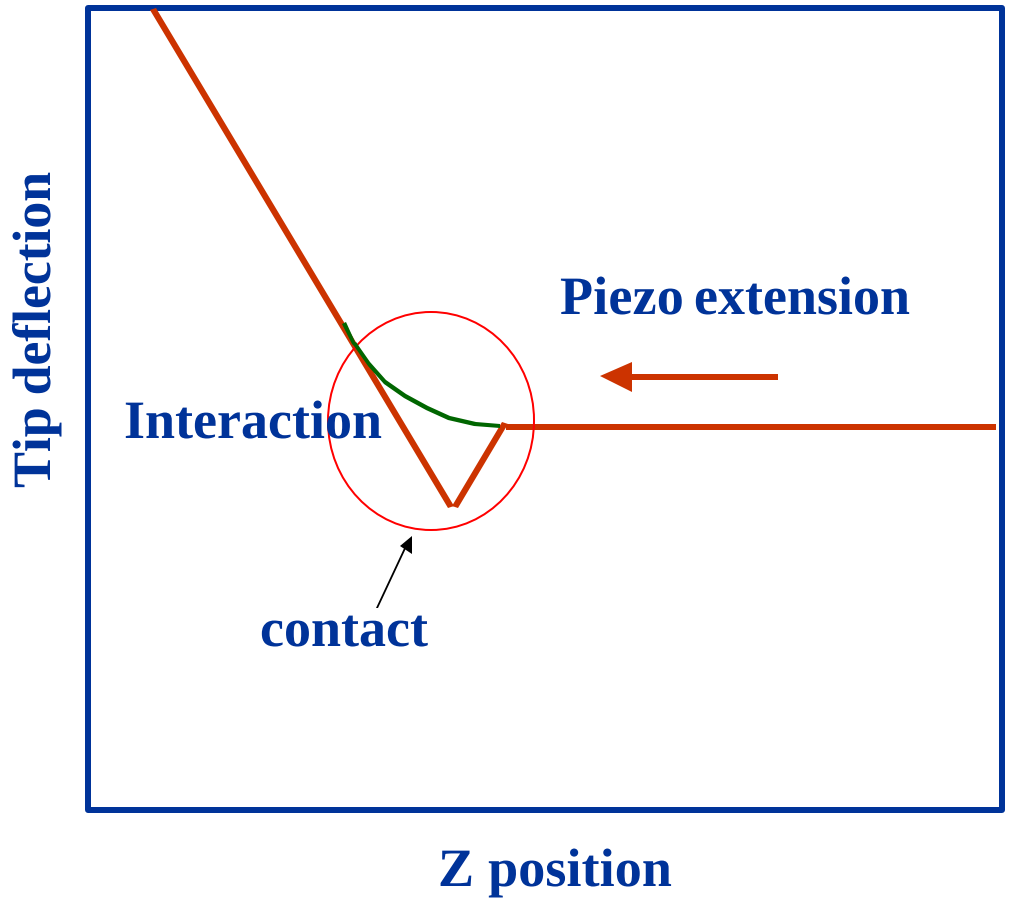
A: Hamaker constant

D: separation distance



Size of silica particle: 3 mm

Force Curve



Force, F:

From Hook's Law,

$$F = -kx$$

k: spring constant

x: deflection of tip

Spring constant determination:

Cleveland method

$$M + m^* = k / (2pn)^2$$

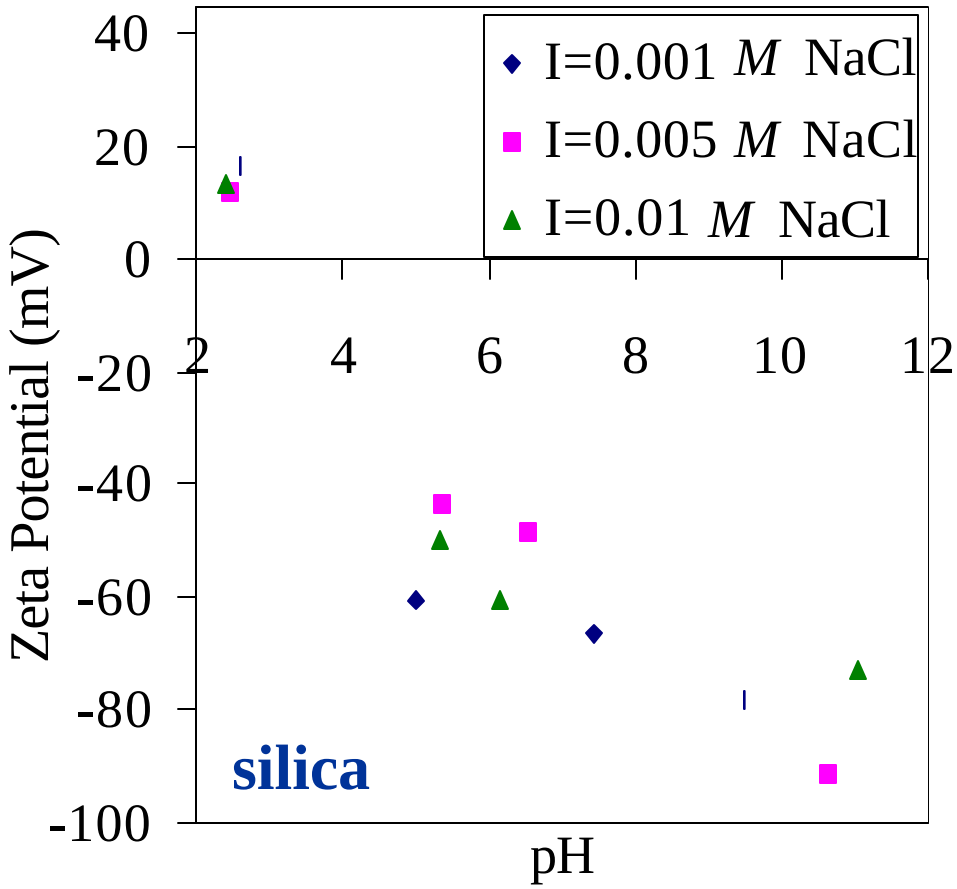
M: mass of cantilever

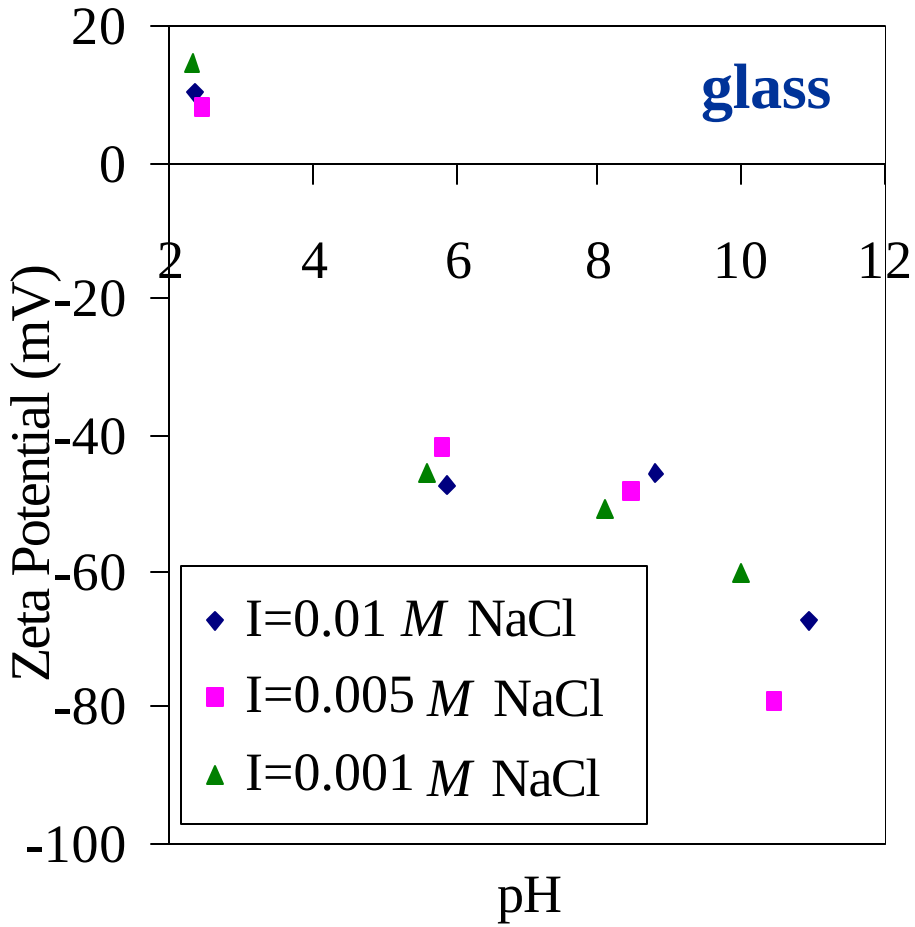
m^*: added mass

n: resonance frequency

J. P. Cleveland, S. Manne, D. Bocek, and P. K., Hansma, *Rev. Sci. Instrum.*, **64**, 403 (1993)

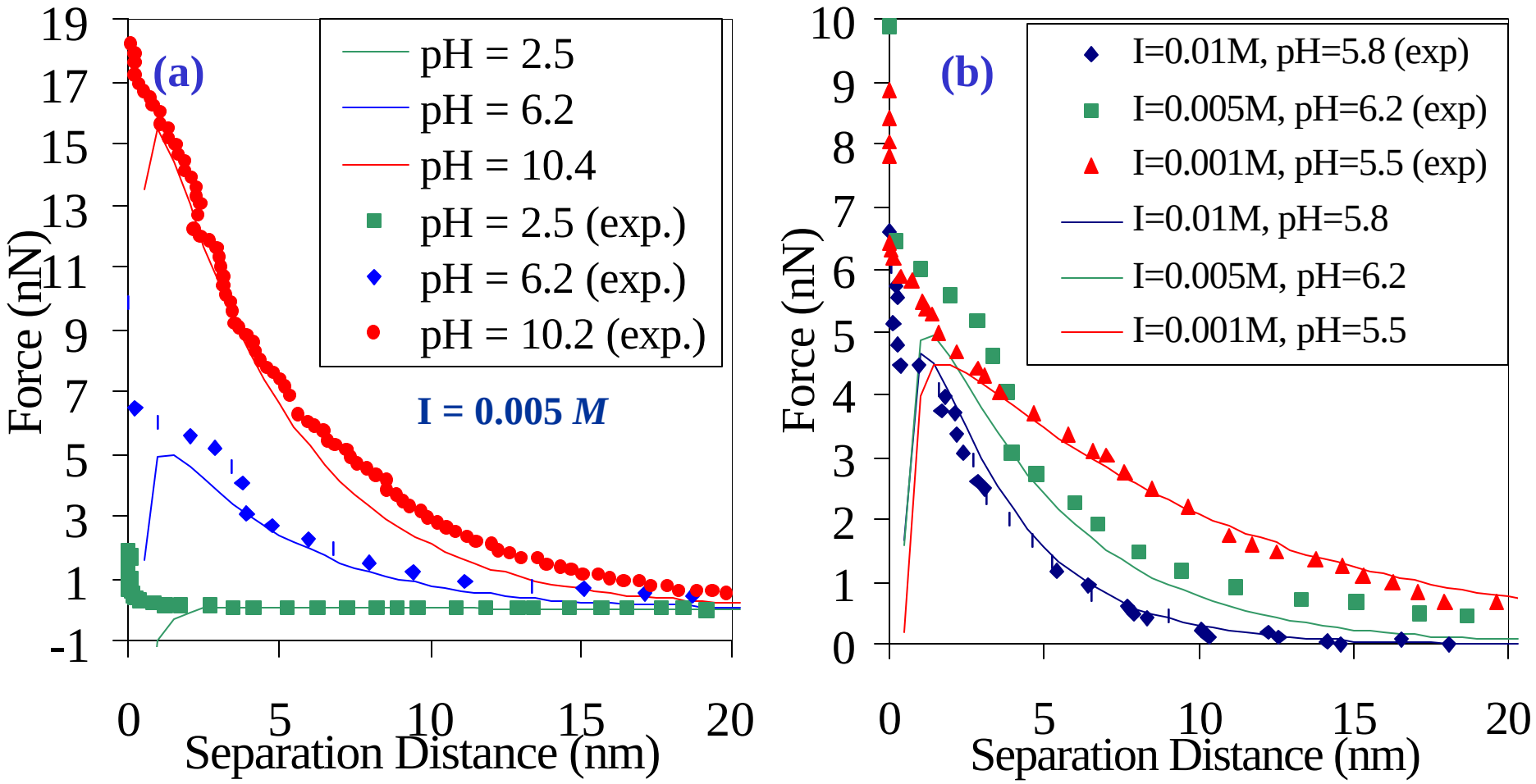
Zeta Potential of Silica Particles and Glass Beads





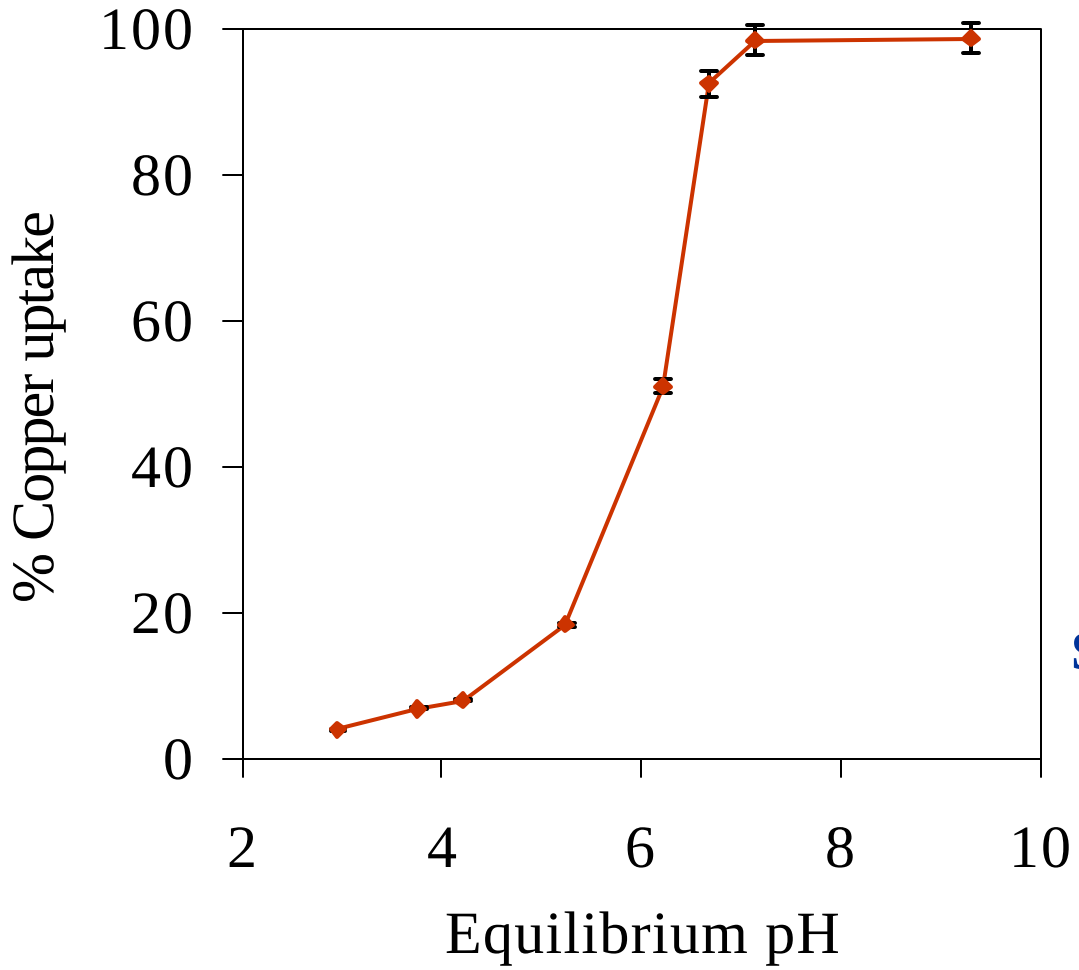
Silica particles and glass beads have similar values for zeta potential.

Force Measurements between a Silica Particle and a Glass Plate



Effects of (a) pH and (b) ionic strength on the force between a silica particle and a smooth glass plate.

Equilibrium Copper Uptake by Silica Colloidal Particles



The uptake of copper ions by silica particles increases dramatically from zero to nearly 100 % at a critical pH.

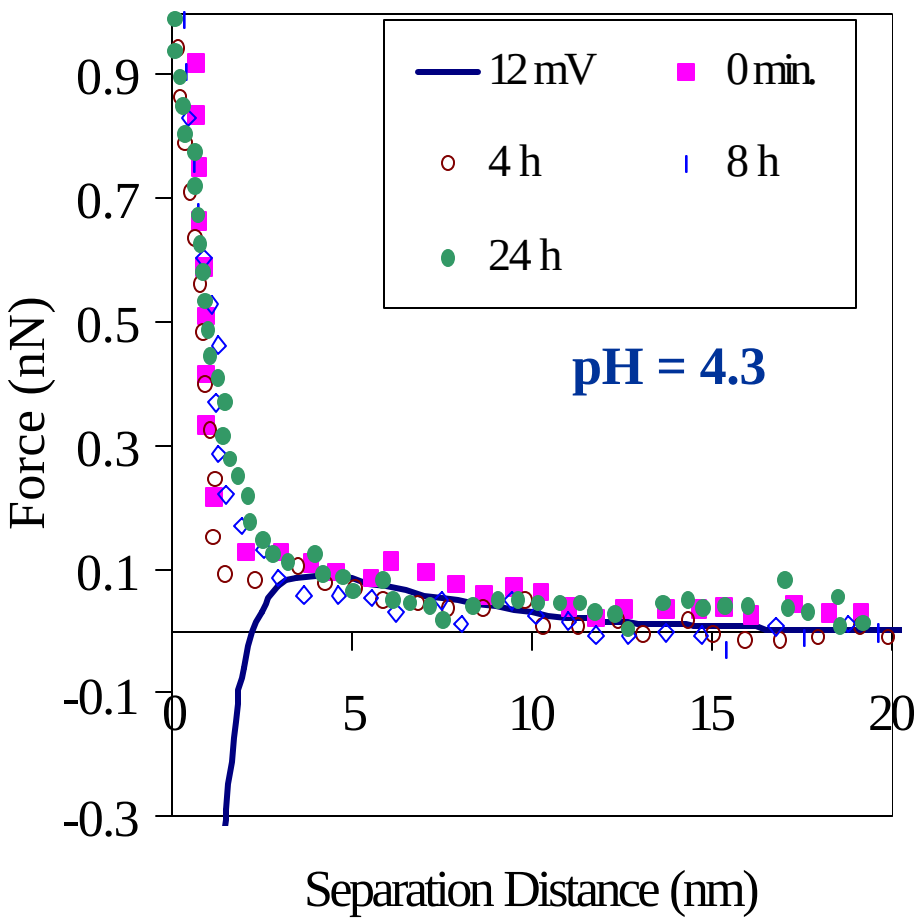
$$SOH + Cu^{2+} + H_2O \text{ Û } SOCuOH + 2H^+$$

$$Cu^{2+} + 2OH^- \text{ Û } Cu(OH)_{2(s)}$$

Silica particle concentration = 250 ppm, copper concentration = 1.6E-4 *M*, I = 0.001 *M*.

Subramaniam, K., Yiacoumi, S., and Tsouris, C., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **177**, 133–146 (2001).

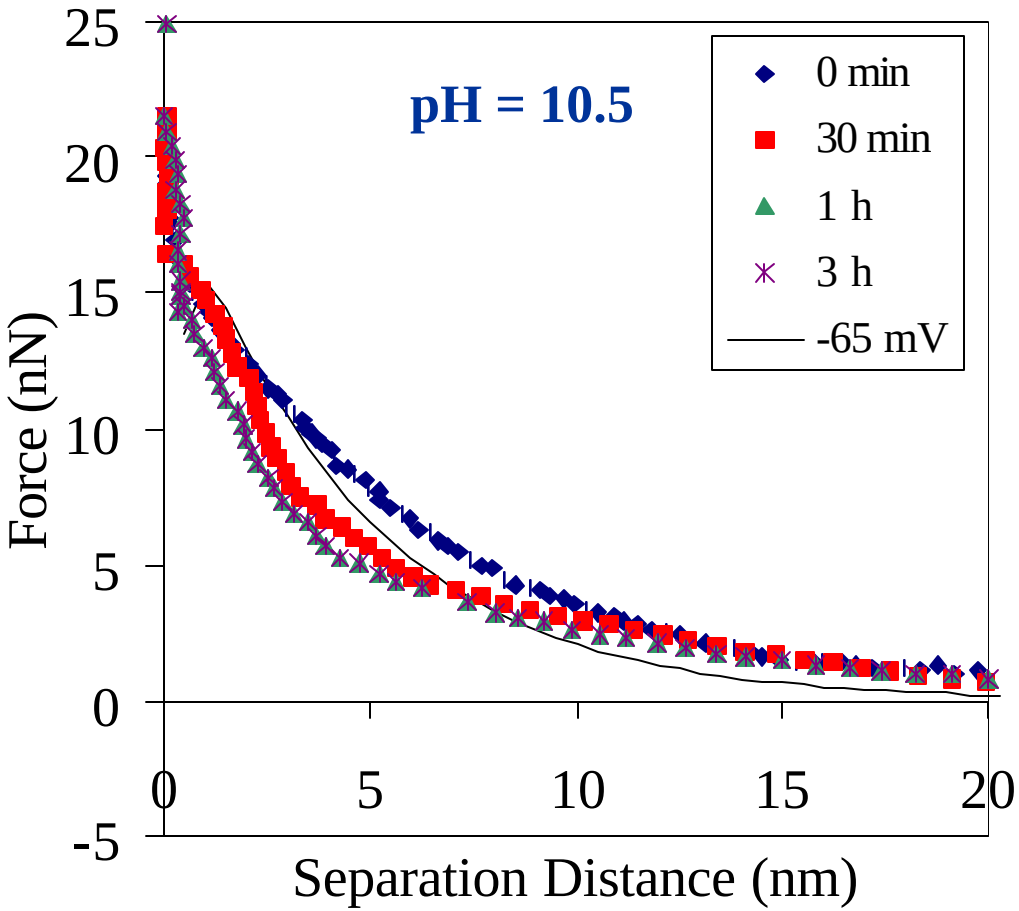
Interaction Force During Copper Uptake at Low pH



I= 0.005 *M* NaCl, *A* = 5.43E-21 J, copper concentration = 5 ppm.

At low pH, the dominant copper species is Cu^{2+}, which has a low sorption affinity for oxide surfaces. Therefore, due to lack of sorption, the electrostatic force between a silica tip particle and a smooth glass plate in the copper solution remains similar to that in the solution without copper ions.

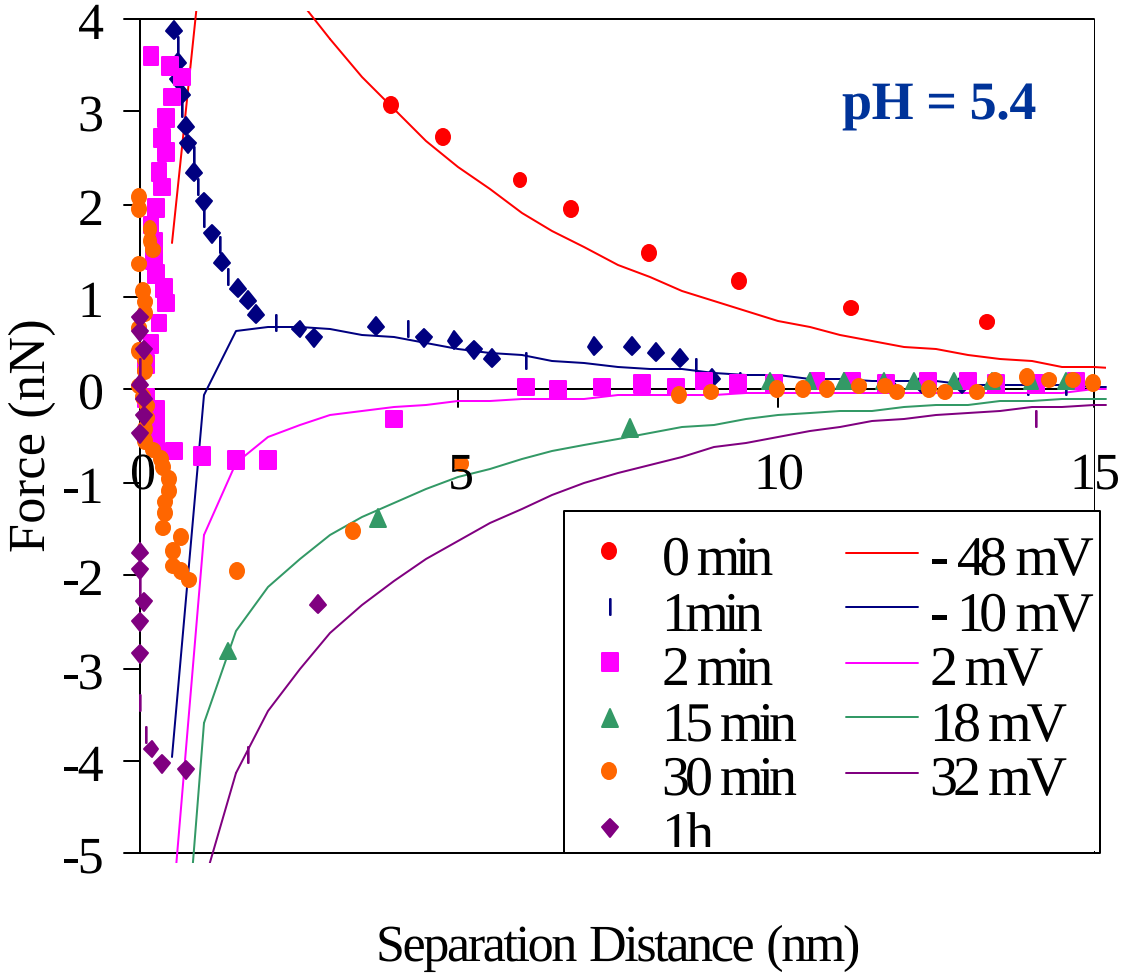
Interaction Force During Copper Uptake at High pH



I= 0.005 *M* NaCl, *A* = 5.43E-21 J, copper concentration = 5 ppm.

No sorption of copper ions occurred on the surface of silica particles. At high pH, tenorite (CuO) and metastable copper hydroxide are the dominant copper species and the removal of metal ions is attributed to precipitation of tenorite.

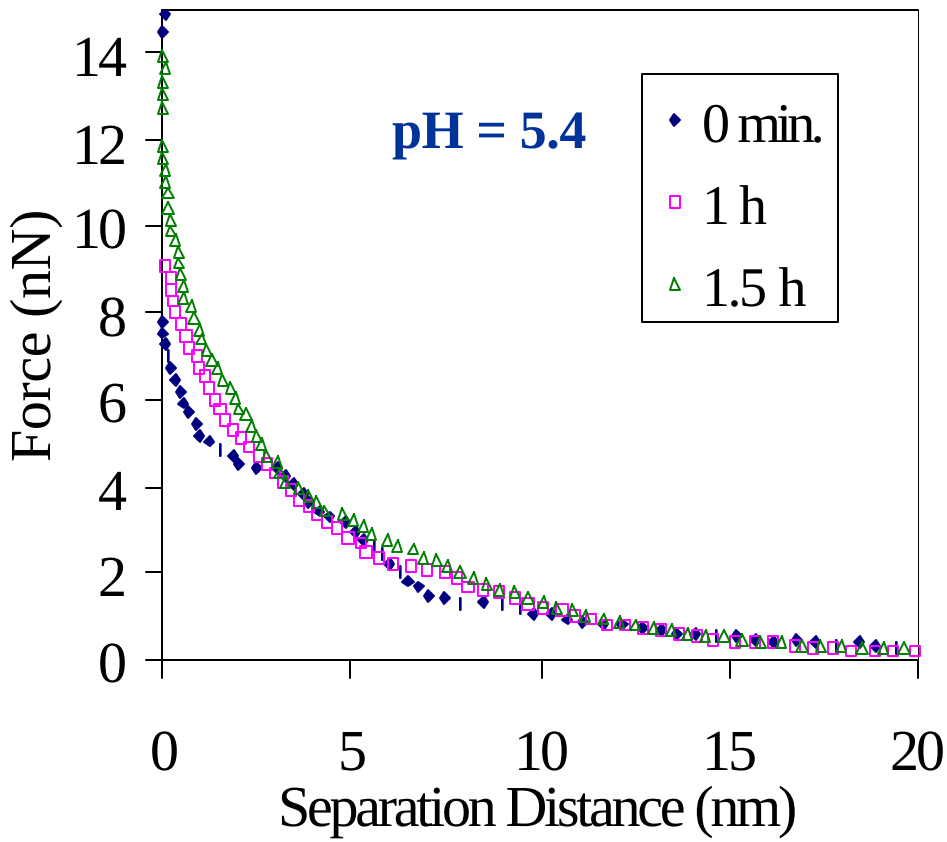
Interaction Force During Copper Uptake at Intermediate pH



I = 0.005 *M* NaCl, *A* = 5.43E-21 J, copper concentration = 5 ppm.

Sorption of copper ions caused an immediate change in the measured force. This change is brought out by charge reversal of the silica tip particle from negative to positive. This behavior concludes that sorption of copper ions on the surface of silica particles is significant and is a relatively fast process.

Interaction Force During Copper Uptake at Intermediate pH by Polystyrene



The interaction forces between a polystyrene tip particle and a smooth glass plate in the copper solution remains the same with time. Therefore, there is no sorption of copper ions on both the polystyrene tip particle and the glass plate.

I = 0.005 *M* NaCl, copper concentration = 5 ppm.

Zeta Potential History of Oxide Surfaces during Copper Sorption

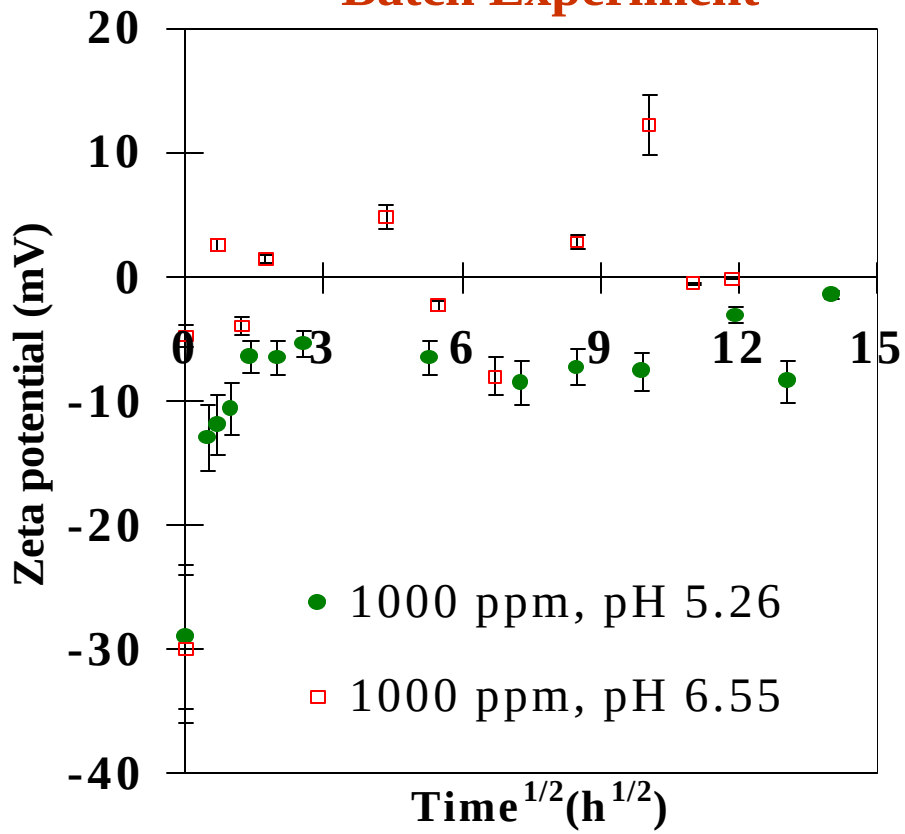
Microscopic
AFM Experiment

pH = 5.4

Time (min)	Zeta potential (mV)
0	-48
1	-10
2	2
30	18
60	32

With AFM, sorption is studied using a single colloidal particle.

Macroscopic
Batch Experiment



Subramaniam, K., and Yiacoumi, S., *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **191**, 145–159 (2001).

Summary of AFM Work

- AFM measurements showed that the electrostatic repulsion between a silica particle and a smooth glass plate decreases with increasing ionic strength and decreasing pH.
- Good agreement between AFM force measurements and DLVO theory was observed in all the solution conditions examined, except at very small separation distances, suggesting that the constant–surface–charge model correctly describes the interaction force between two charged surfaces.
- A discrepancy between experimental data and predicted results from the DLVO theory is consistently shown at short distances, where a maximum in the force is predicted. This is probably due to non-DLVO repulsion.

- At high and low pH values, the forces with and without the presence of copper ions are identical. This observation suggests that there is no sorption of copper ions on the silica particles.
- At intermediate pH values, the force changes from strongly repulsive to attractive. This observation indicates that there is a significant sorption effect from copper ions sorbed on the silica particle causing charge reversal on the surface.
- AFM force measurements were used to determine the zeta potential of colloidal particles during sorption of metal ions.
- Further investigation of sorption dynamics and equilibrium is needed to determine whether AFM can be reliably used to provide sorption data using a single colloidal particle.