Manipulation of the Electrode/Electrolyte Interface of Gold via the Application of an External Electric Field

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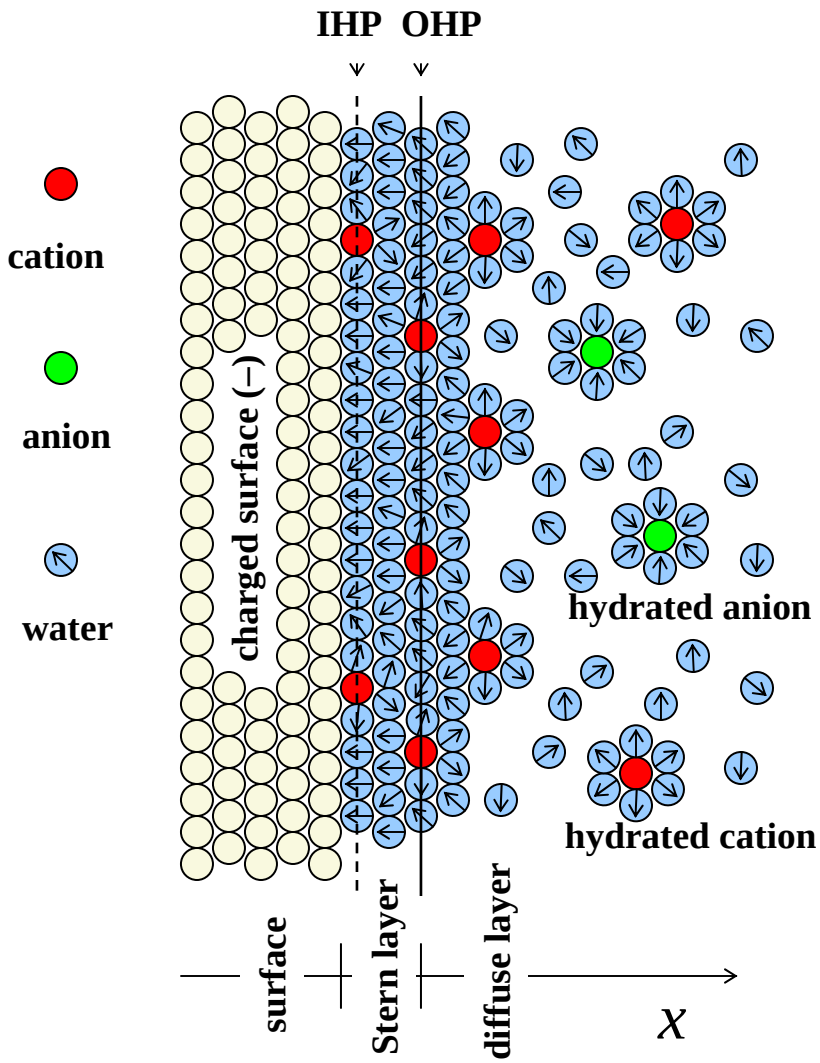
Outline

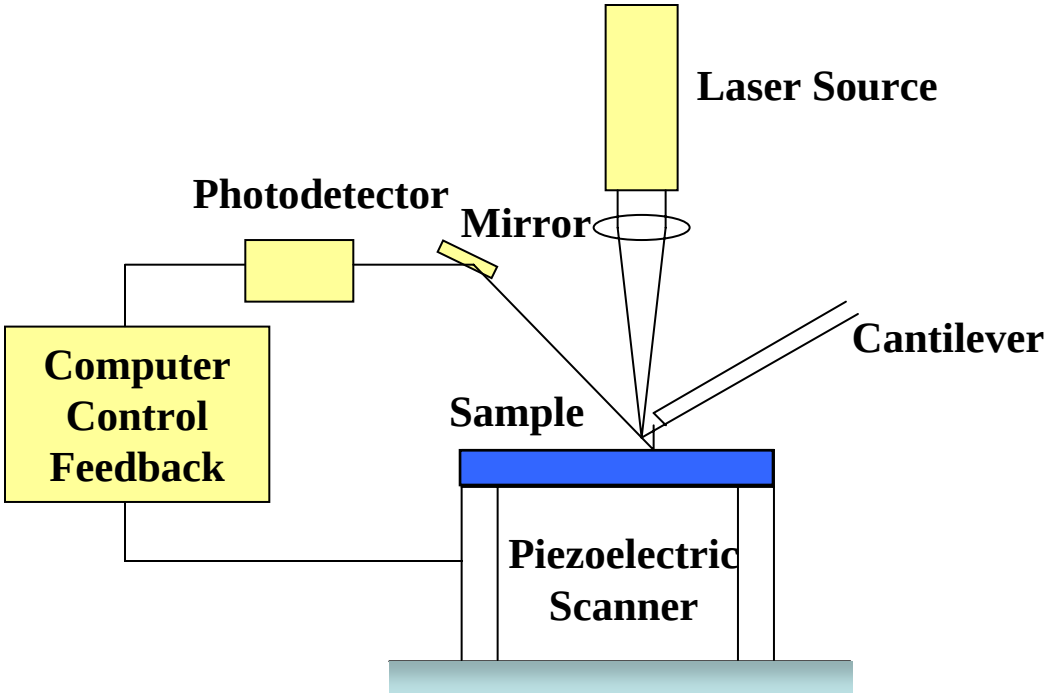
- Introduction
- Overview on atomic force microscopy (AFM)
- Experimental set-up
- Theoretical calculation of interparticle forces
- Low pH
- Intermediate pH
- High pH
- Conclusions

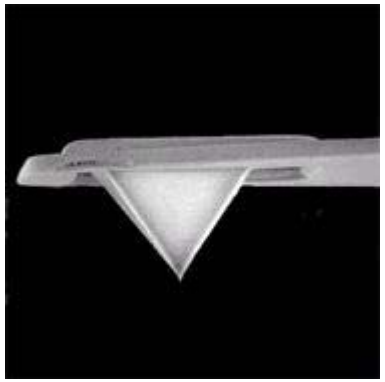
Introduction

- Electric fields modify the structure of the layers adjacent to the interfaces resulting in modification of the interaction force between surfaces.
- H+, OH-, and halide ions are believed to associate with "inert" electrodes like gold and platinum at the solid/liquid interface.



Atomic Force Microscopy (AFM)

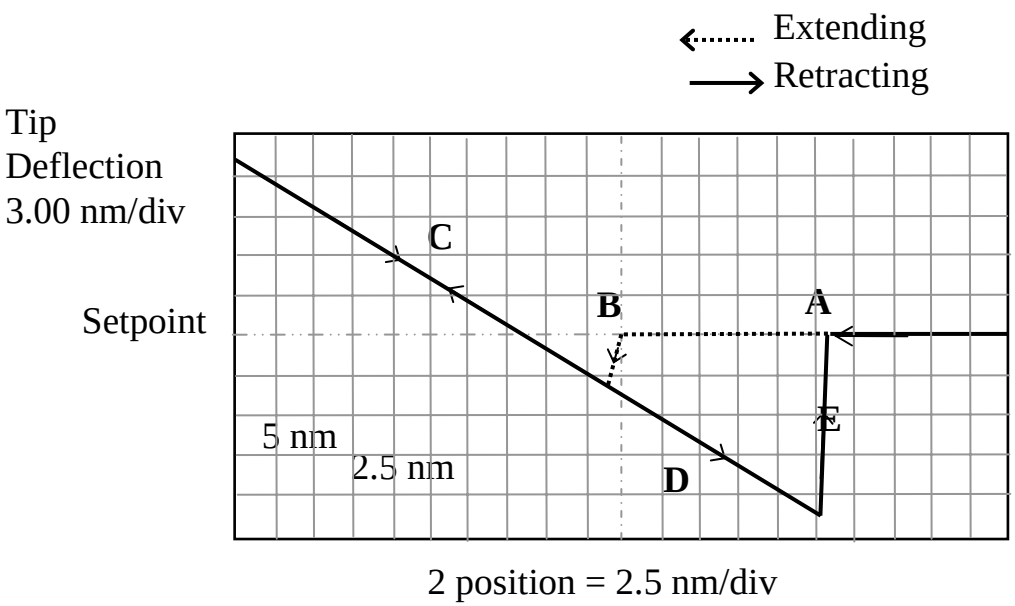


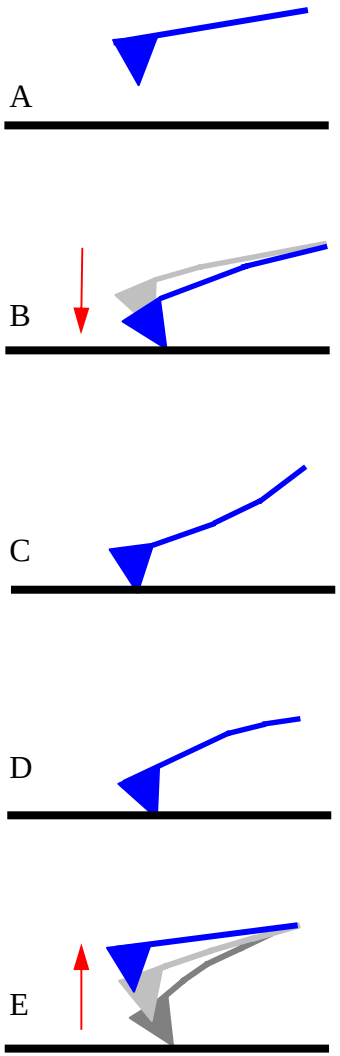


Invented in 1986 by Binnig, Quate, and Gerber, AFM is a form of scanning force microscopy in which the interaction forces between a sharp tip and a sample are monitored.

Force Curves Obtained by AFM

Force Calibration Plot



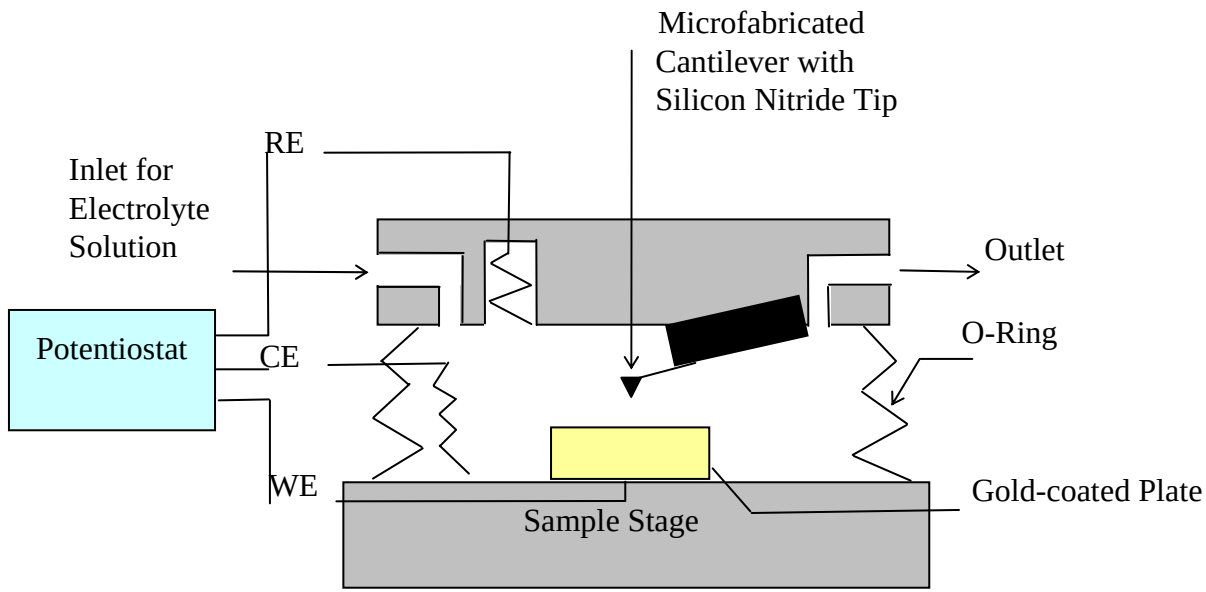


Interaction forces are calculated through the application of Hooke's Law:

$$F = kx$$

k = cantilever spring constant
x = cantilever deflection

System of Study: Experimental Setup



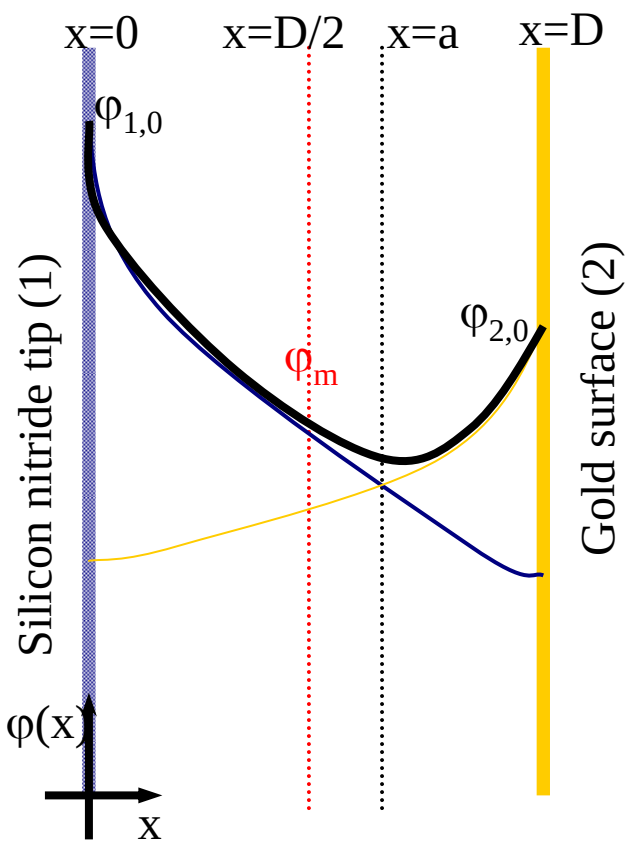
Working electrode: gold coated plate

Counter electrode: platinum wire

Reference electrode: Ag/AgCl standard

pH I [M]	5.0	6.0	9.0
0.0005	+500 mV…–500 mV	+500 mV…–500 mV	+500 mV…–500 mV
0.005	+500 mV…–500 mV	+500 mV…–500 mV	+500 mV…–500 mV
0.05	+500 mV…–500 mV	+500 mV…–500 mV	+500 mV…–500 mV

Prediction of Interaction Forces



Net force includes two terms: Van der Waals and electrostatic forces (solution of the non-linear Poisson-Boltzmann equation for 1:1 electrolyte).

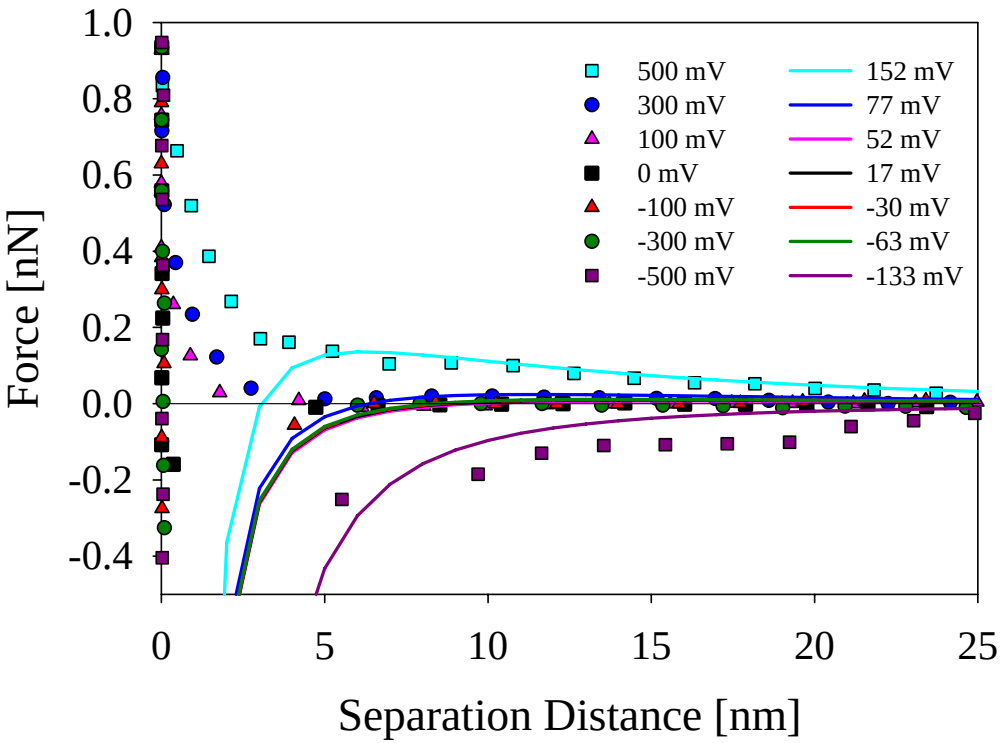
$$\frac{d^2\varphi}{dx^2} = \frac{2z\bar{e}N_0}{\varepsilon}\sinh\left(\frac{z\bar{e}\varphi}{k_B T}\right)$$

$$\varphi(x=0) = \varphi_{1,0} \qquad \left.\frac{d\varphi}{dx}\right|_{x=a} = 0$$

$$\Gamma[\varphi(x)] = \mathrm{A}(x)\cdot\mathrm{H}[\varphi_1(x)] + \mathrm{B}(x)\cdot\mathrm{K}[\varphi_2(x)]$$

$$F = \left\{ kT\left[\exp(e\varphi_m/kT) + \exp(-e\varphi_m/kT) - 2\right] - \frac{\varepsilon}{2}\left(\frac{d\varphi}{dx}\right)^2\Bigg|_{x=D/2} \right\}\cdot A_{eff} - \frac{A_H}{12\pi D^2}$$

Low pH: H^+ Are the Charge Determining Ions



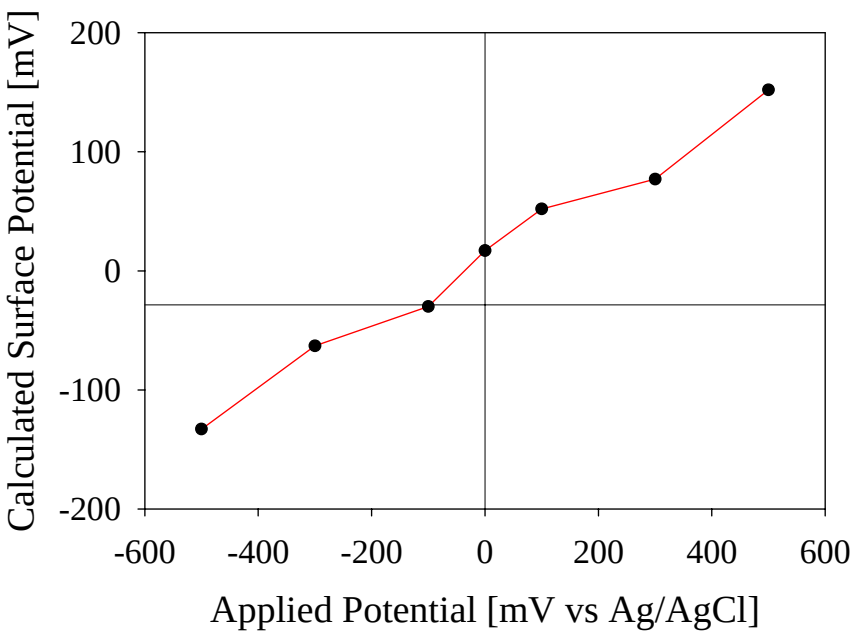
Strong adsorption of H+ ions on the gold/electrolyte interface takes place at conditions of low pH.

pH ~ 5.2 – 5.3, I = 0.0005 M NaCl

Epzc = -50 mV

$\varphi_{o.c.}$ = + 17 mV

φ_0 = +152…–133 mV



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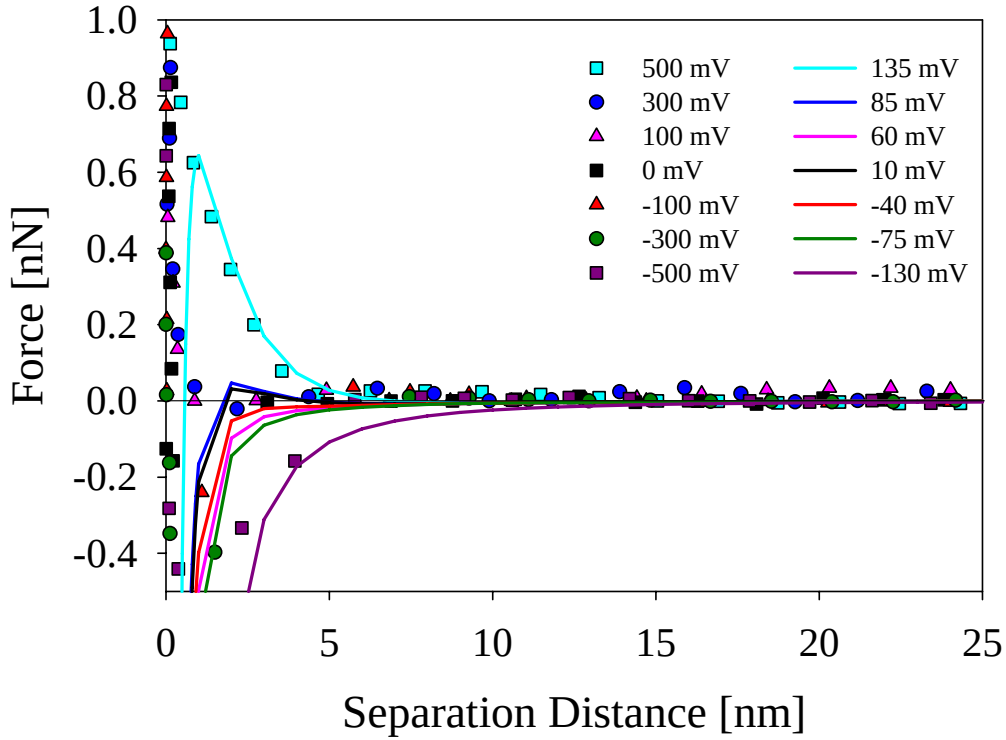


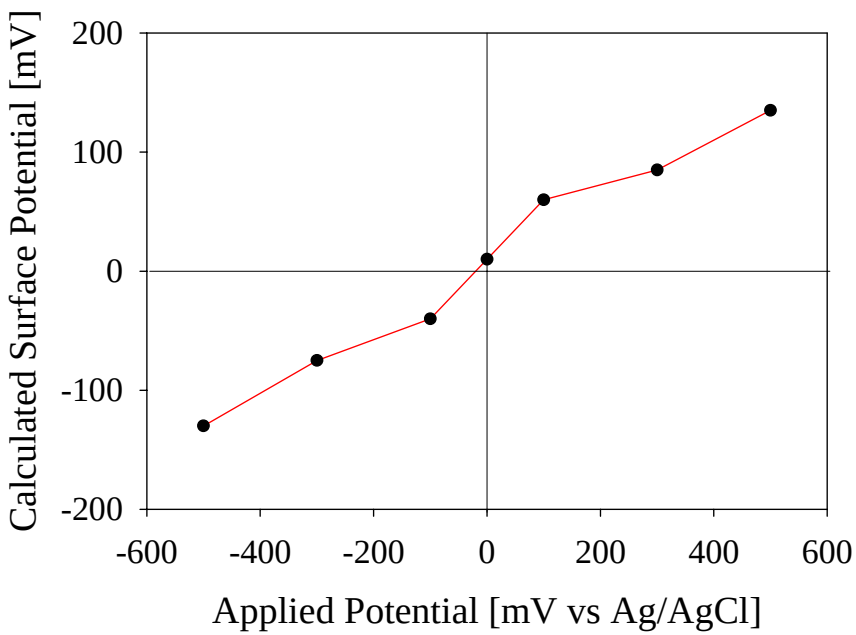
The extent of adsorption of H^+ ions is reduced by the presence of the competitive Cl^-.

pH ~ 5.2 – 5.3, I = 0.05 M NaCl

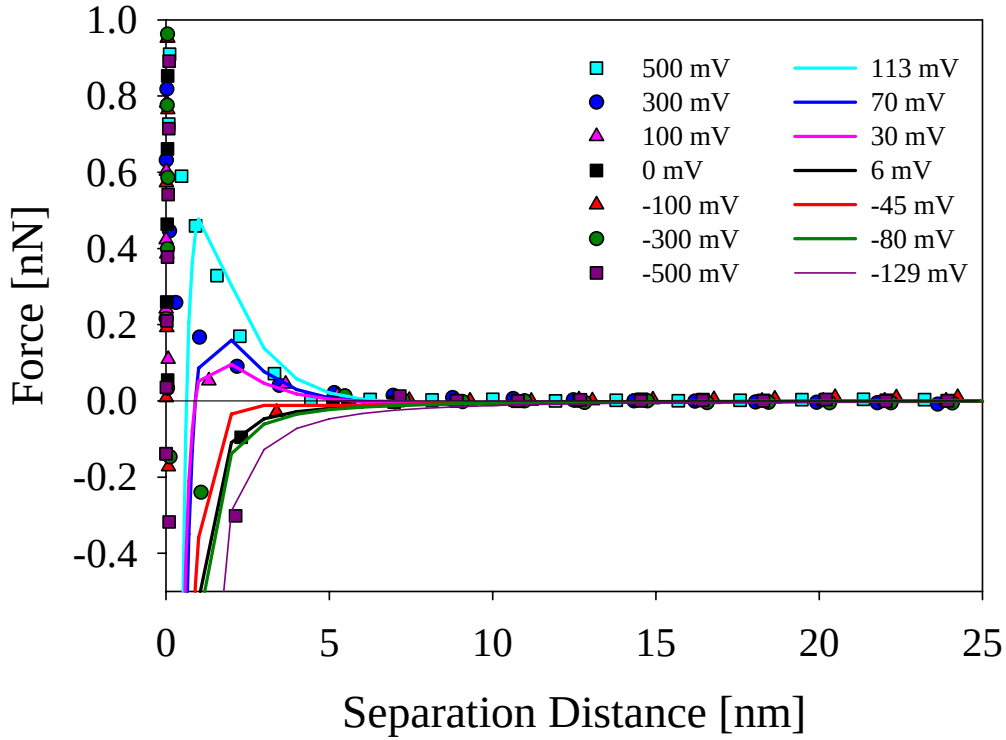
Epzc = -50 mV

$\varphi_{o.c.}$ = + 10 mV

φ_0 = +135…–130 mV



Intermediate pH: H^+ vs Cl^-



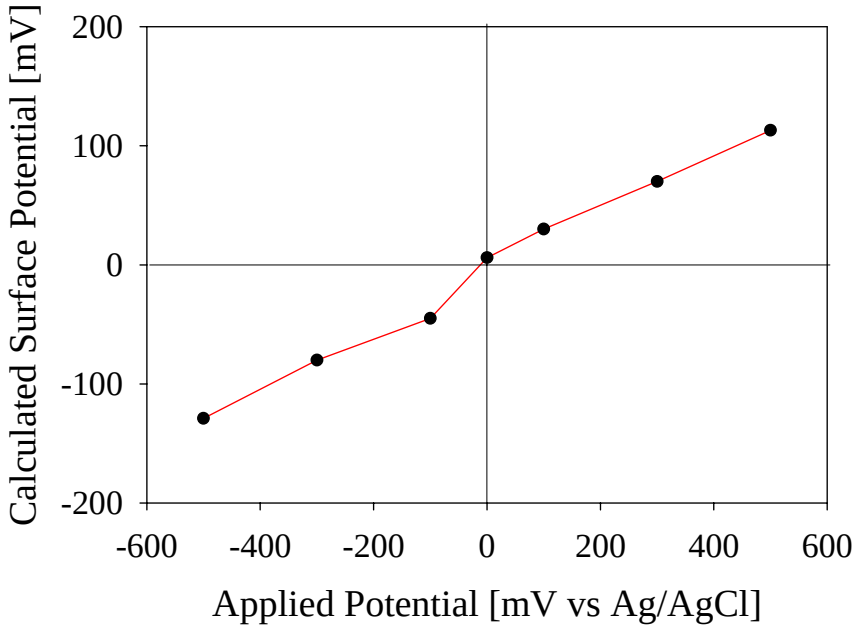
Cl^- ions become important in the determination of the gold/electrolyte interface charge as pH increases.

pH ~ 6.0, I = 0.05 M NaCl

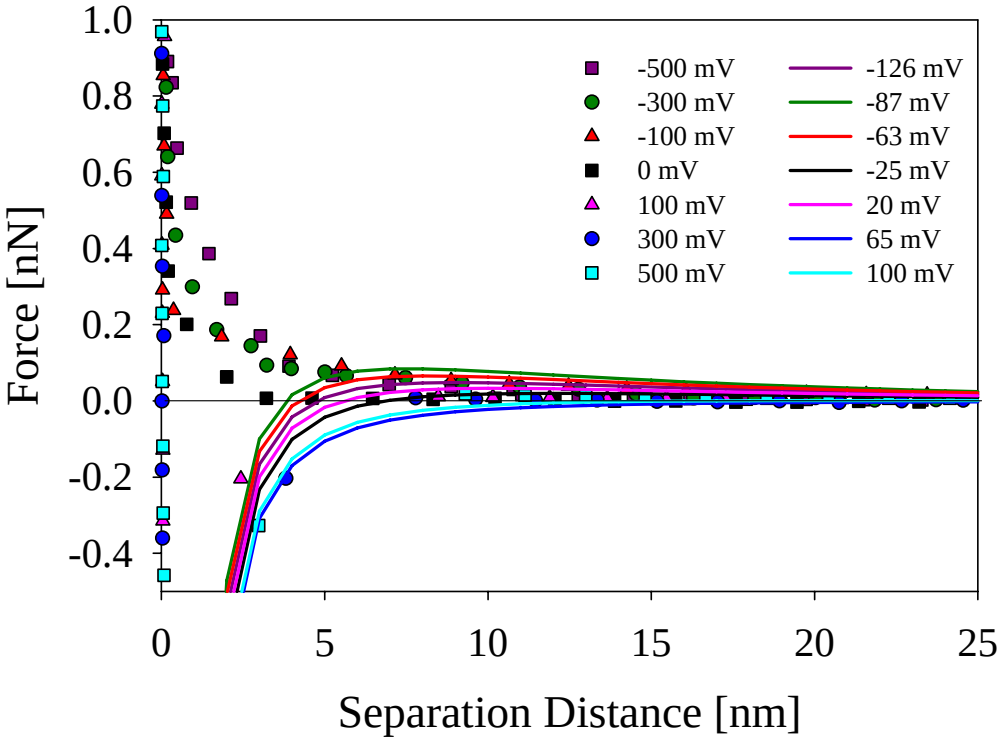
Epzc = -3 mV

$\varphi_{o.c.}$ = + 6 mV

φ_0 = +113…–129 mV



High pH: OH^- Are the Charge Determining Ions



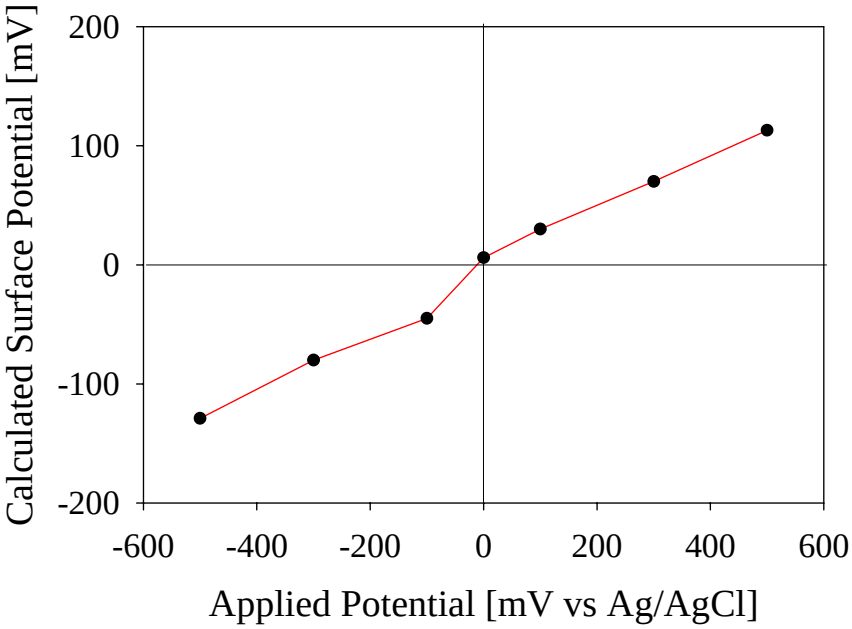
Strong adsorption of OH^- ions on the gold/electrolyte interface takes place at conditions of high pH.

pH ~ 9.1 – 9.2, I = 0.0005 M NaCl

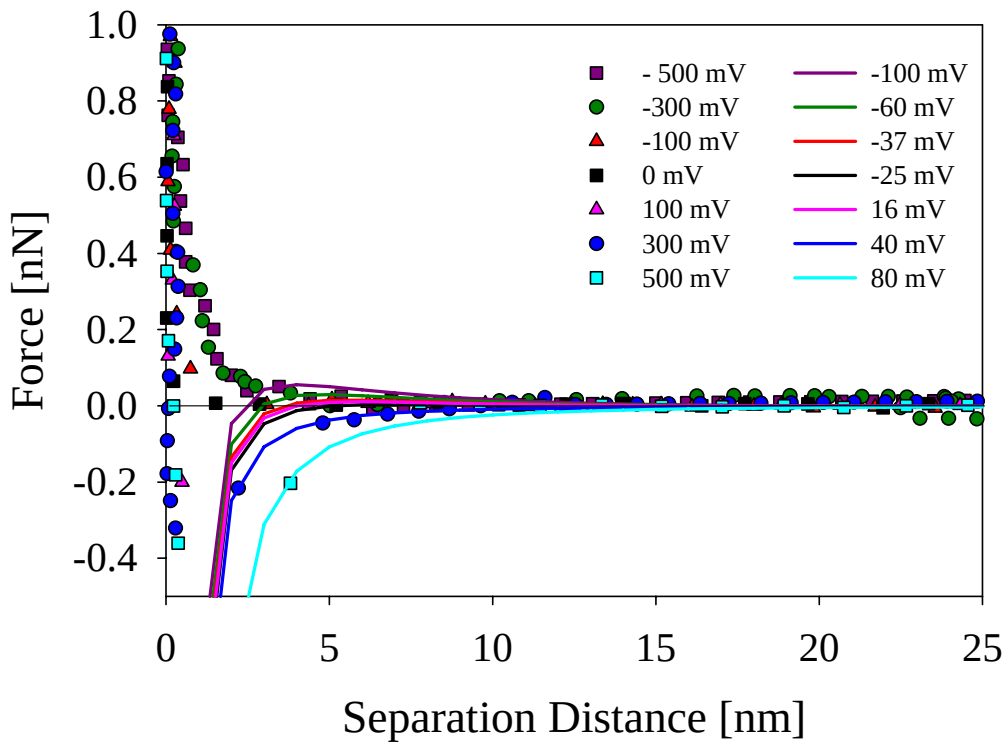
Epzc = +50 mV

$\varphi_{o.c.}$ = –25 mV

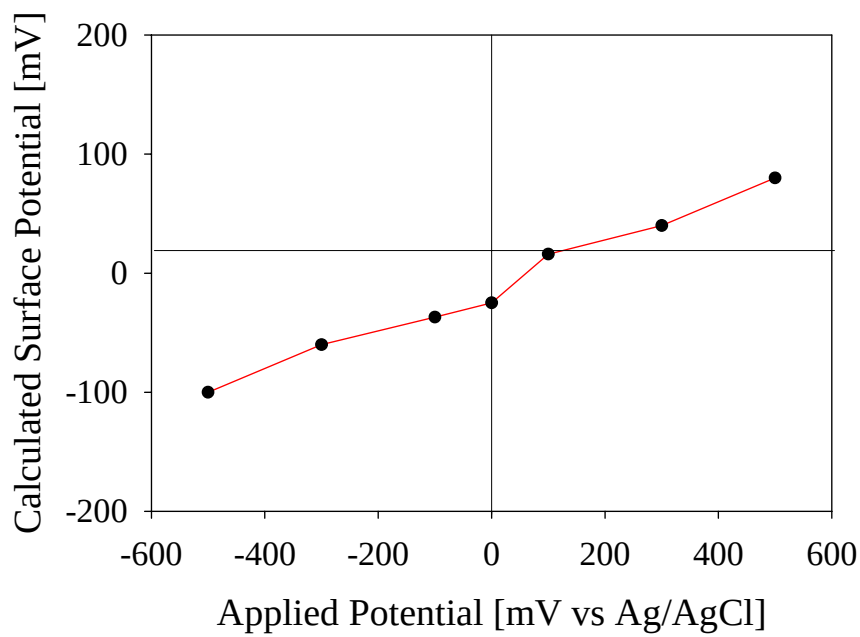
φ_0 = +100…–126 mV



High pH: OH^- Are the Charge Determining Ions



Cl^- competitive adsorption increases with increasing absolute value of applied potential.



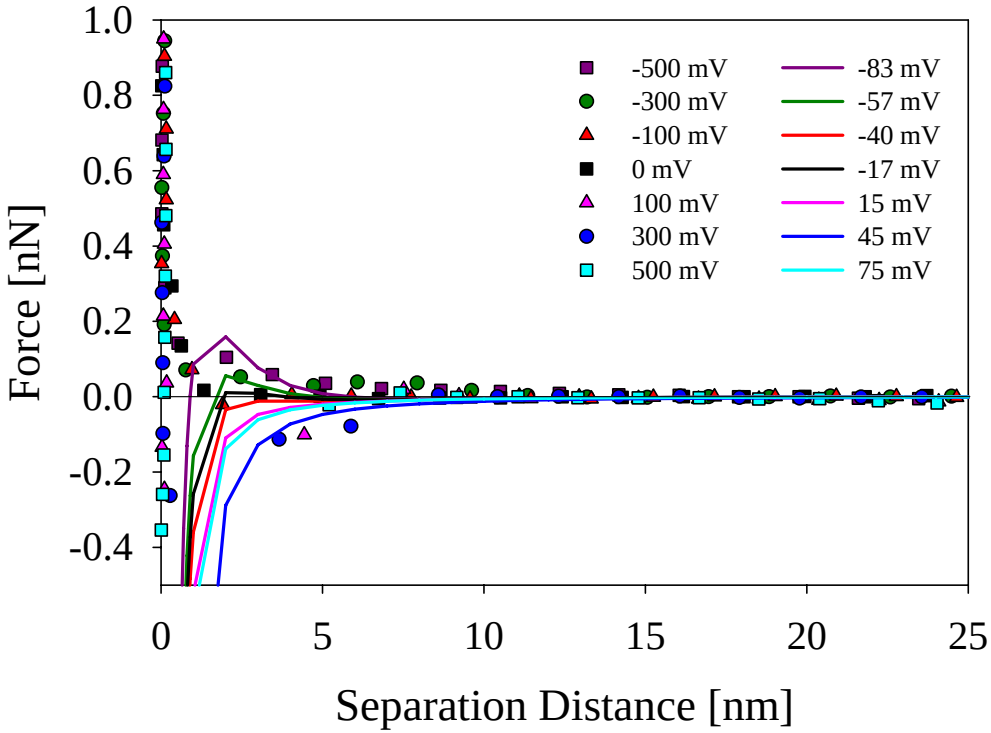
pH ~ 9.1 – 9.2, I = 0.005 M NaCl

Epzc = +50 mV

$\varphi_{o.c.}$ = –25 mV

φ_0 = +80…–100 mV

High pH: OH^- Are the Charge Determining Ions



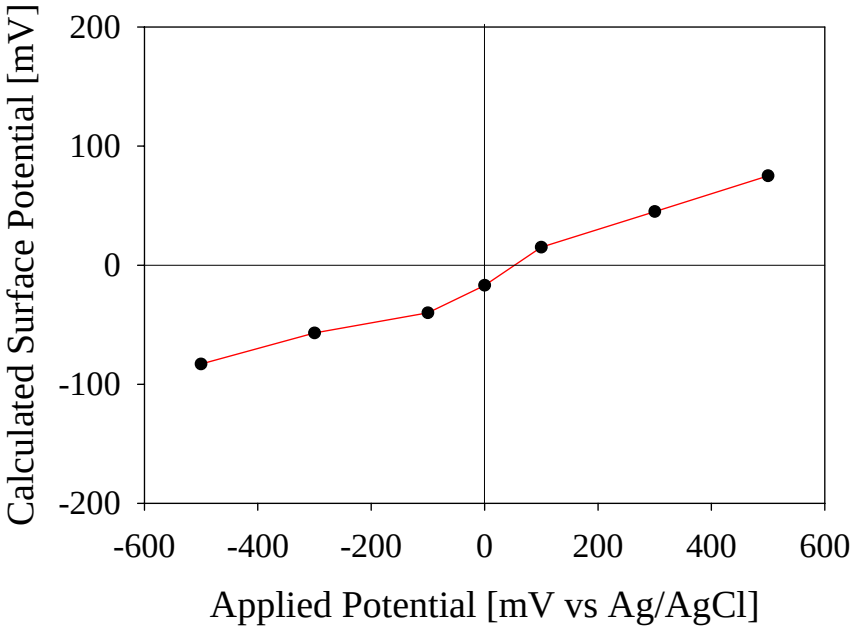
Cl^- ions determine the surface charge at the gold/electrolyte interface at high applied potentials.

pH ~ 9.1 – 9.2, I = 0.05 M NaCl

Epzc = +50 mV

$\varphi_{o.c.}$ = –17 mV

φ_0 = +75…–183 mV



Conclusions

- The applied potential on a gold electrode is much higher than the effective potential at the interface.
- Adsorption of ions at the gold/electrolyte interface determines the surface charge at open circuit conditions.
- Externally applied electric fields can modify the nature and concentration of ions present at the solid/liquid interface and, thus, modify surface forces.
- Additional experimental validation is needed to confirm the results and unequivocally identify the ions present at the gold/electrolyte interface.

Acknowledgments

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