Fundamentals of Atomic Force Microscopy
Part 2: Dynamic AFM Methods

Week 5, Lecture 4
Dynamic AFM in Liquids I

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From the last lecture

- MFM methods
Why dynamic AFM in liquids?

- Biological structures in native state
- Complementary to EM and x-ray crystallography
- Material properties
- High resolution imaging and property mapping of liquid solid interfaces

- Microtubules (P. J. de Pablo, Madrid)
- ATPase molecular motors (J. Stahlberg et al, 2001)
- \(\phi 29\) virion on graphite (80 nm), cryo EM
Sample preparation

- Most effort in bio sample imaging is in sample preparation
- In particular binding DNA, virus, cells to the substrate is a key issue
- Many specialized techniques exist that are documented in papers and we suggest following established protocol carefully
Tip sample interaction forces in liquids

- Electrostatic + van der Waals forces (DLVO theory Derjaguin-Landau-Verwey-Overbeek)
- Hydration forces
- Hydrophobic interactions
- Steric forces
Tip and sample placed in electrolytic solution

Surface charges develop on tip and sample due to surface adsorption of ions + native charge/contact potential

Oppositely charged ions in the solution are attracted and create two layers called the electric double layer, screening the electrostatic interactions

Double layer forces decay exponentially as a function of tip-sample gap, the decay length is called the Debye length \( \lambda_D \)

\[
\lambda_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2ce^2}}
\]  

(1)

For a monovalent salt (NaCl, KCl etc.)

\( c \): Salt concentration in mol/L

\( k_B \): Boltzmann constant (1.381 *10^{-23} \text{ J/K})

\( e \): unit charge (1.602 *10^{-19} \text{ C})

\( \varepsilon \): dielectric constant of the medium

\( \varepsilon_0 \): vacuum permittivity (8.854 *10^{-12} \text{ A s V}^{-1} \text{ m}^{-1})

**DLVO model**

- Electrostatic + van der Waals forces (DLVO theory Derjaguin-Landau-Verwey-Overbeek)
  - Correctly computed using Poisson-Boltzmann equation (constant charge or constant potential)
  - Van der Waals and electrostatic forces are additive
  - Used to explain coagulation of colloids

For the tip (radius $R_{tip}$) and sample (flat) at constant potentials $\psi_T$ and $\psi_S$:

$$ F_{ts,el} = \frac{2\pi R_{tip} \varepsilon \varepsilon_0}{\lambda_d} \left[ 2\psi_S \psi_T e^{-d/\lambda_d} - \left( \psi_S^2 + \psi_T^2 \right) e^{-2d/\lambda_d} \right] $$

For the tip (radius $R_{tip}$) and sample (flat) at constant charge densities $\sigma_T$ and $\sigma_S$:

$$ F_{ts,el} = \frac{2\pi R_{tip} \lambda D}{\varepsilon \varepsilon_0} \left[ 2\sigma_S \sigma_T e^{-d/\lambda_d} + \left( \sigma_S^2 + \sigma_T^2 \right) e^{-2d/\lambda_d} \right] $$

Valid for $R_{tip} > \lambda_d$ for $d > \lambda_d$

As we have seen from Part I:

$$ F_{ts,VdW} = -\frac{HR_{tip}}{6d^2} $$

$$ F_{ts,DLVO}(d) = F_{ts,VdW} + F_{ts,el} = -\frac{HR_{tip}}{6d^2} + \frac{2\pi R_{tip} \lambda D}{\varepsilon \varepsilon_0} \left[ 2\sigma_S \sigma_T e^{-d/\lambda_d} + \left( \sigma_S^2 + \sigma_T^2 \right) e^{-2d/\lambda_d} \right] $$


Understanding DLVO forces

- Model provides good predictions.
- Which version to constant potential or charge?
- Charge density on SiN/SiO₂/mica depends on the pH of the solution.
- SiN tip on Mica as a function of salt concentration. Prediction made using Eq. (5). The parameters used are $\sigma_s$ (mica) = $-0.032 \text{ C/m}^2$, $\sigma_t$ (SiN) = $-0.0025 \text{ C/m}^2$, $H$ (between mica and SiN in water) = $3.4 \times 10^{-20} \text{ J}$, $\varepsilon_0$ = $8.85 \times 10^{-12} \text{ F/m}$, (de-ionized water) = 80, and $R_{\text{tip}}$ = 10 nm.

Examples

J. Sotres, PhD thesis (A. Baro, Universidad Autonoma de Madrid)

Muller and Engel *Nature Protocols* 2007

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Fig. 21. Force between a silica (SiO$_2$) microsphere of 2.5 μm radius and a titania (TiO$_2$) crystal vs. distance. The force is scaled by the radius of the sphere. The curves were recorded at pH values of 8.8, 7.2, 6.3, 5.3, and 3.0 from top to bottom with 1 mM KNO$_3$ background electrolyte. The figure is reproduced with kind permission from Drummond [339].

From Butt, Cappella, and Kappl, 2005
Other forces of relevance

- Solvation+Hydration forces
- Hydrophillic/hydrophobic forces
- Nanobubbles
- Steric forces

From

Also see H. J. Butt, B. Cappella, M. Kappl, “Force measurements with the atomic force microscope: Technique, interpretation and applications”, Surface Science Reports, 59 (1-6), 1, 2005

Tapping mode topology image of nanobubbles on the surface of a d-PS coated silicon substrate in distilled water, and result of a manipulation of the nanobubbles with the AFM tip, by which several nanobubbles have coalesced into one bigger object.