

# Lecture 25

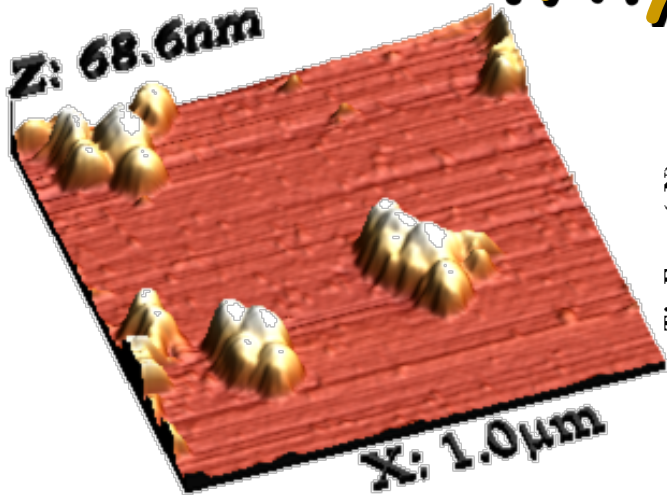
## AFM in liquids I

Arvind Raman

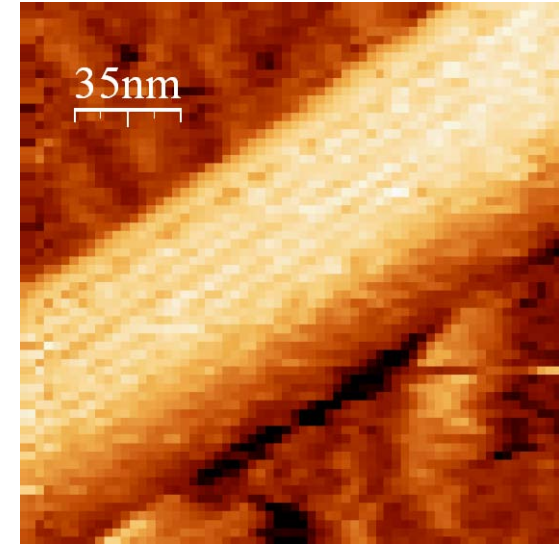
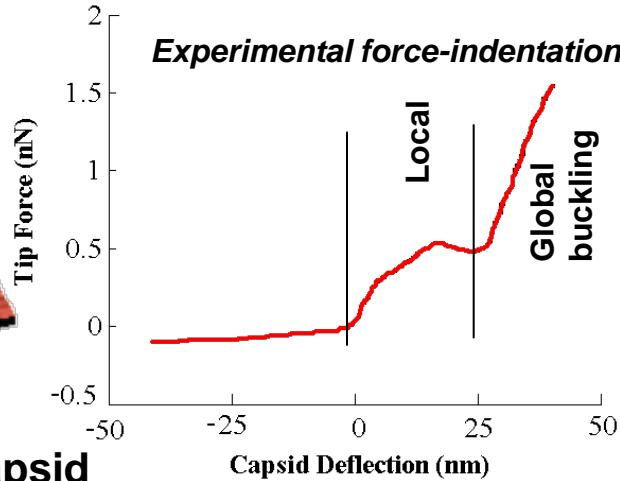
*Mechanical Engineering*

*Birck Nanotechnology Center*

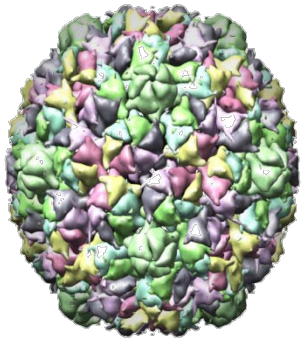
# Why AFM in liquids



Bacteriophage P22 virus procapsid  
(supplied by C.Teshcke)



Microtubules (P. J. de Pablo, Madrid)



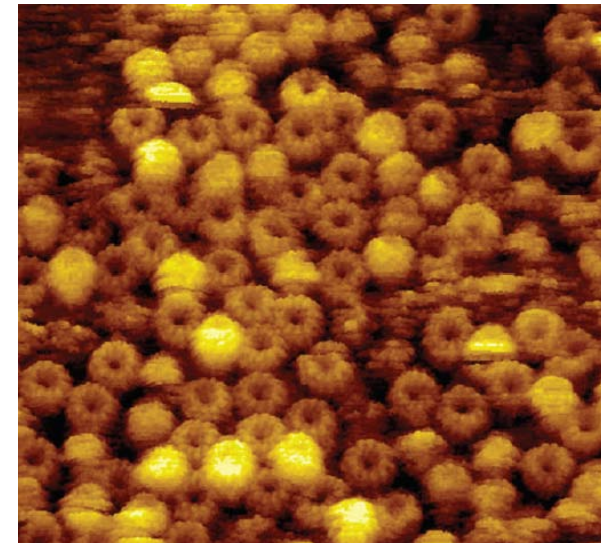
P22 protein structure  
(T. Ferrin UCSF)

- Biological structures in native state
- Complementary to EM and x-ray crystallography
- Material properties
- High resolution

“Being able to see small molecules binding to proteins would vibrate the whole community.”

— Daniel Müller *Nature*, 440, 2006

ATPase molecular motors  
J. Stahlberg et al (2001)

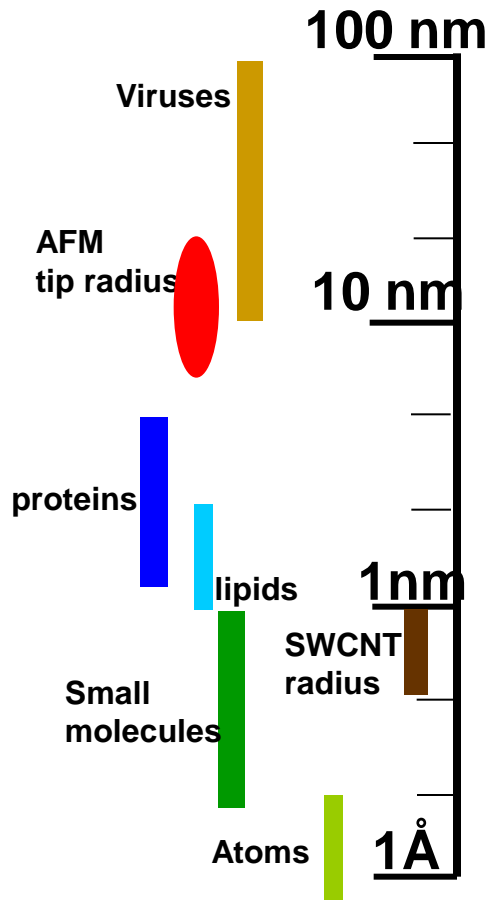


# Sample preparation

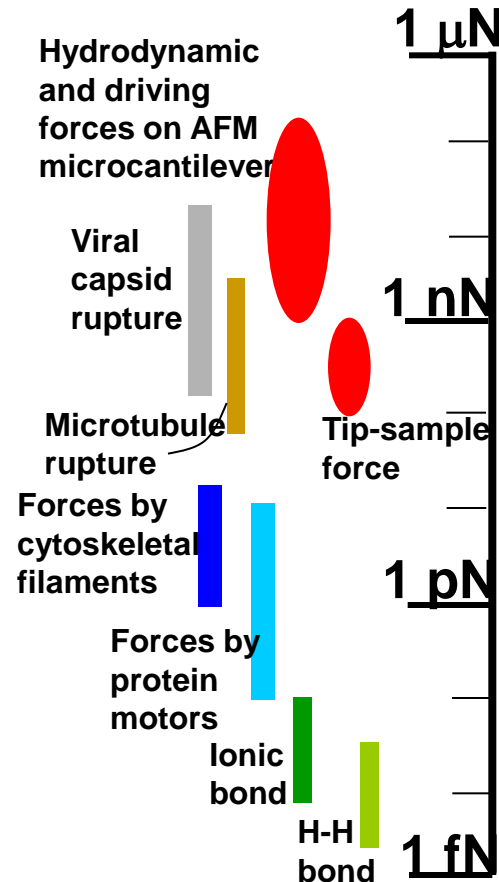
- Most effort in bio sample imaging is in sample preparation
- In particular binding DNA, virus, cells to the substrate is a key issue
- Many specialized techniques exist that are documented in papers and we suggest following established protocol carefully

# AFM challenges in biology\*

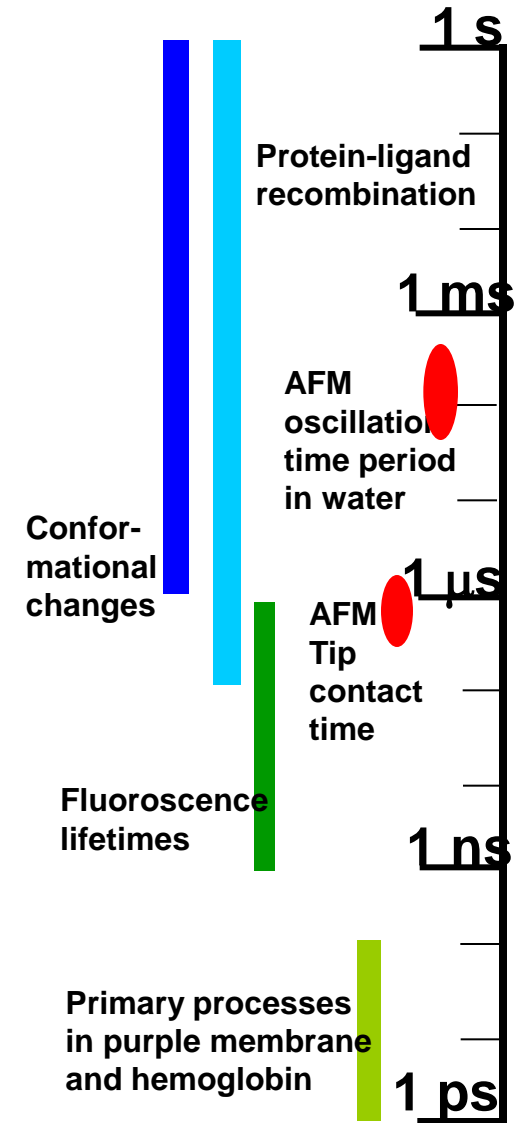
## Relevant length scales



## Forces in water



## Relevant time scales



- High-resolution imaging?
- Imaging with sub-piconewton forces?
- Imaging with sub-nanosecond contact time?

# Tip sample interaction forces

- Electrostatic + van der Waals forces (DLVO theory Derjaguin-Landau-Verwey-Overbeek)
  - Used to explain coagulation of colloids
  - Electrostatic forces arise due to surface charges on interaction surfaces
  - Surface charge balanced by dissolved counterions
  - Correctly computed using Poisson-Boltzmann equation (constant charge or constant potential)
  - However simple expression arises when  $D \gg \lambda$

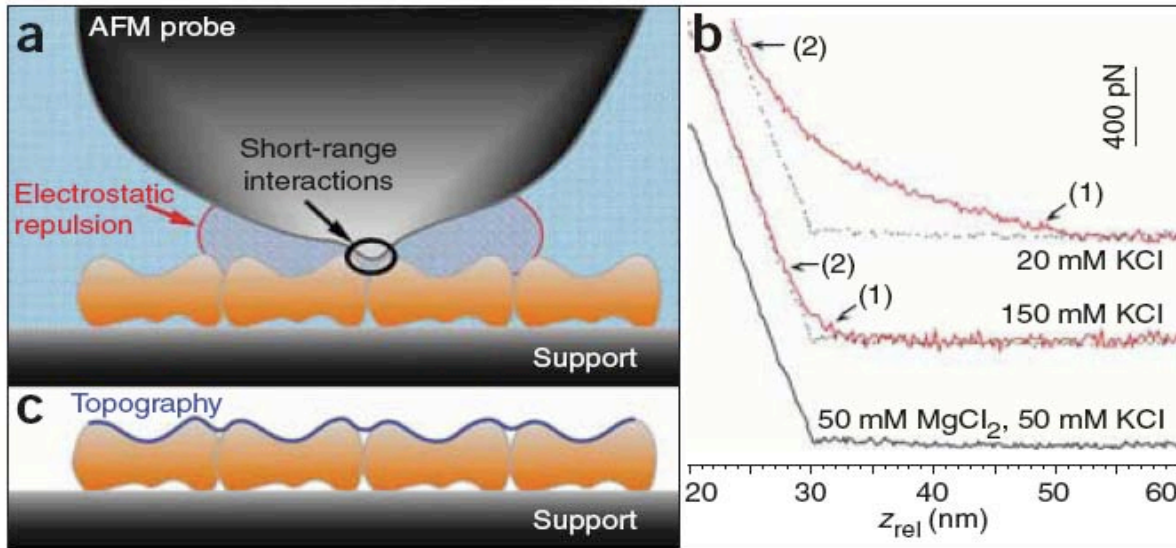
$$F_{dlvo}(D) = \frac{4\pi R\lambda}{\epsilon\epsilon_0} \sigma_T \sigma_S e^{-D/\lambda} - \frac{AR}{6D^2},$$

- $\lambda$  is the Debye length

$$\lambda_D = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{2ce^2}}$$

- Based on  $\sigma_T$  or  $\sigma_S$ , elect. forces are attr. or rep.

# Tip sample interaction forces



Muller and Engel *Nature Protocols* 2007, also A. Baro et al

■ *Butt, Cappella, and Kappl, Reader*

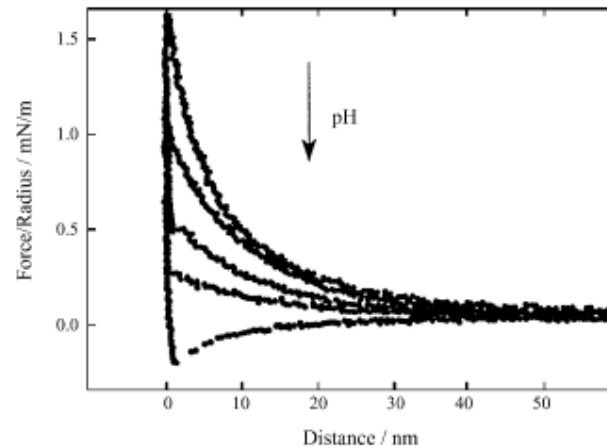
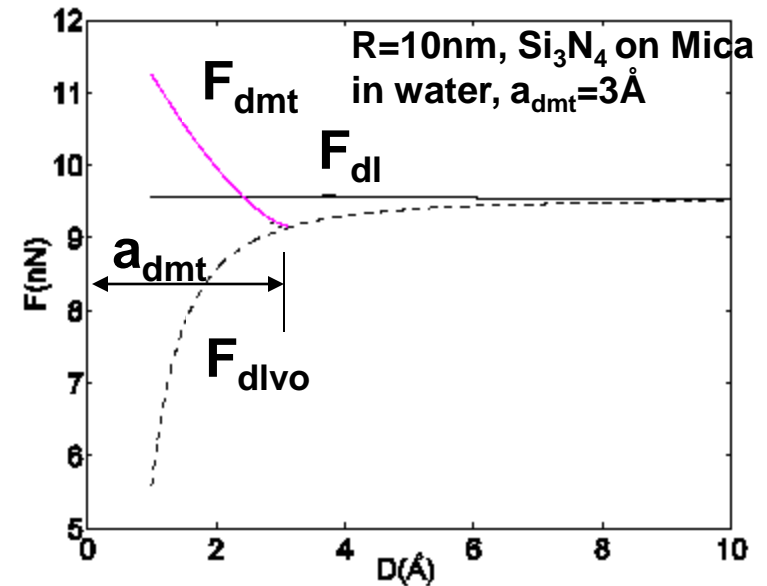
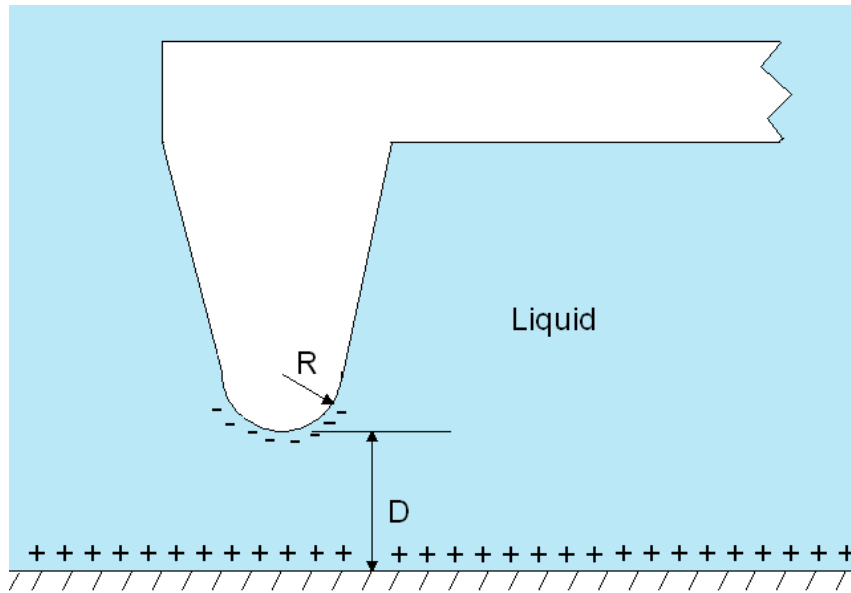


Fig. 21. Force between a silica (SiO<sub>2</sub>) microsphere of 2.5 μm radius and a titania (TiO<sub>2</sub>) crystal vs. distance. The force is scaled by the radius of the sphere. The curves were recorded at pH values of 8.8, 7.2, 6.3, 5.3, and 3.0 from top to bottom with 1 mM KNO<sub>3</sub> background electrolyte. The figure is reproduced with kind permission from Drummond [339].

# Tip-Sample Interaction Force



- Derjaguin-Landau-Verwey-Overbeek (DLVO):

$$F_{dlvo}(D) = \frac{4\pi R\lambda}{\epsilon\epsilon_0} \sigma_T \sigma_S e^{-D/\lambda} - \frac{AR}{6D^2}, \quad D \geq a_{dmt}$$

- Derjaguin-Muller-Toporov (DMT):

$$F_{dmt}(D) = \frac{4E'\sqrt{R}}{3} (a_{dmt} - D)^{\frac{3}{2}} + F_{dlvo}(a_{dmt}), \quad D < a_{dmt}$$

$$F_{dlvo}(a_{dmt}) \equiv F_{adhesion}(a_{dmt})$$

# Tip-Sample Interaction Force

- Solvation+Hydration forces
- Hydrophilic/hydrophobic forces
- Nanobubbles

- *Butt, Cappella, and Kappl, Reader*

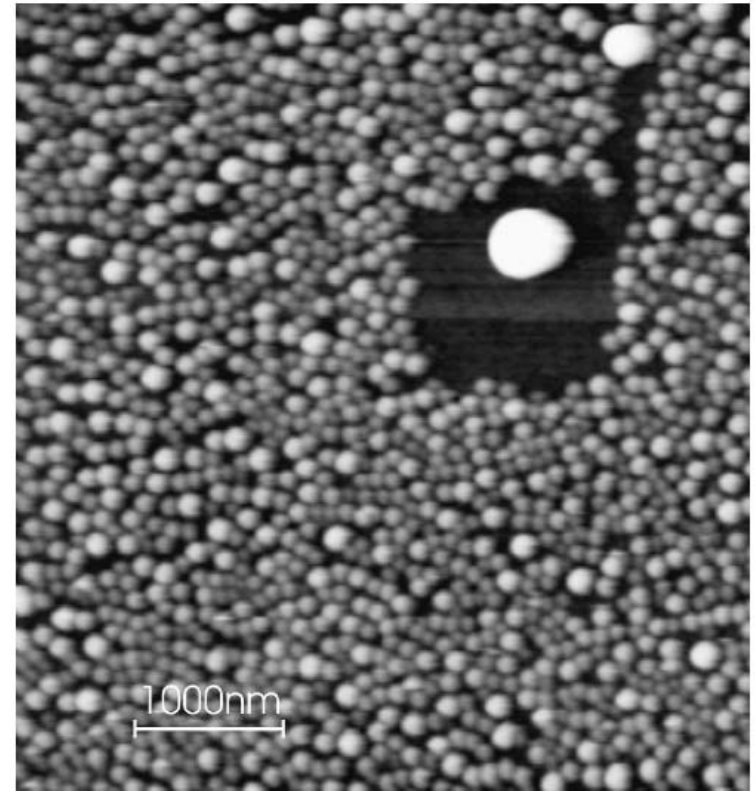
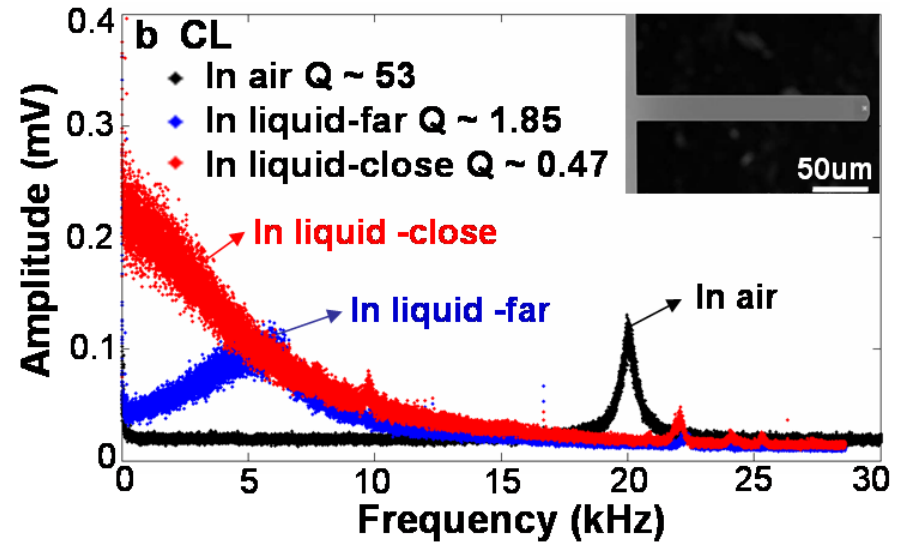
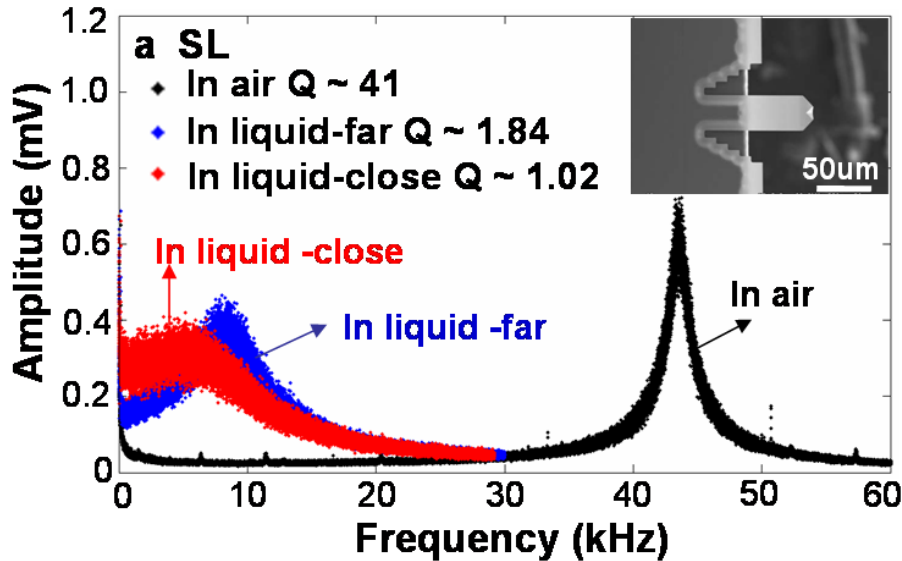


Fig. 23. AFM image of nanobubbles spontaneously formed by immersion of a hydrophobic polystyrene surface. The image was taken in tapping mode. By scanning a small region with increased tapping amplitude, the nanobubbles in this region fused to one bigger bubble. The figure was kindly provided by Klösgen [546].

# Cantilever dynamics in liquids

- Resonance frequency and Q-factor

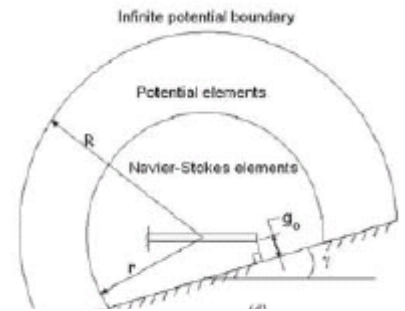
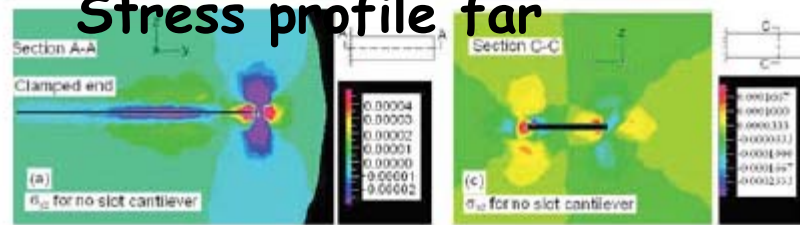
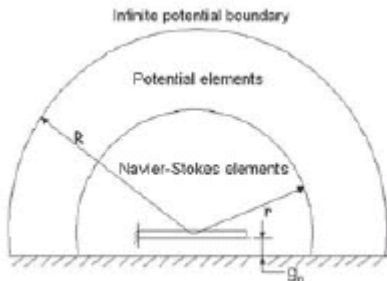


- Resonance freq in water can be 3-5 times less than in air
- Surrounding fluid adds inertia and damping

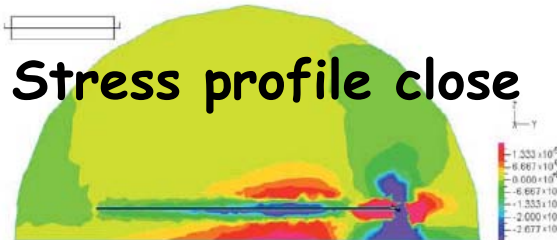
# Cantilever dynamics in liquids

## Effect of closeness to surface

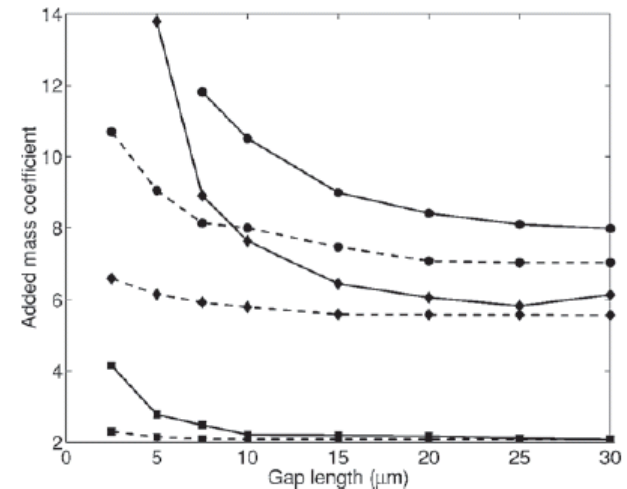
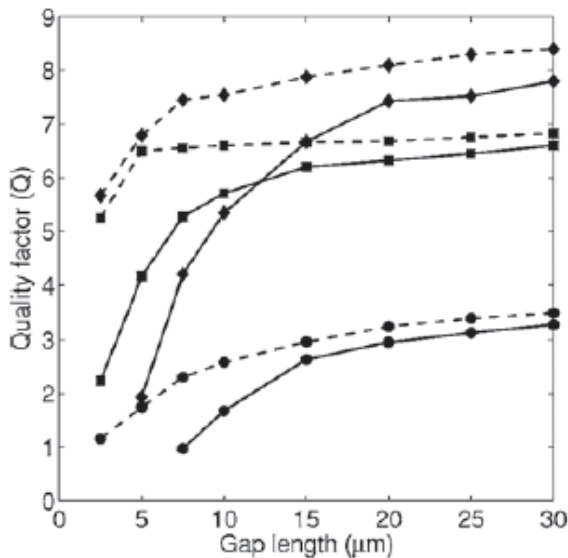
### Stress profile far



### Stress profile close



- Depends on boundary layer thickness
- Occurs over long Z ranges



Basak, S., Raman, A., Garimella, S., "Hydrodynamic loading of microcantilevers vibrating in viscous fluids", *Journal of Applied Physics*, 99(11), 114906, 2006.

Tung, R., Jana, A., Raman, A., "Hydrodynamic loading of microcantilevers near rigid walls: semi-analytical expressions and validation", *Journal of Applied Physics*, 104(11), 114905, 2008.

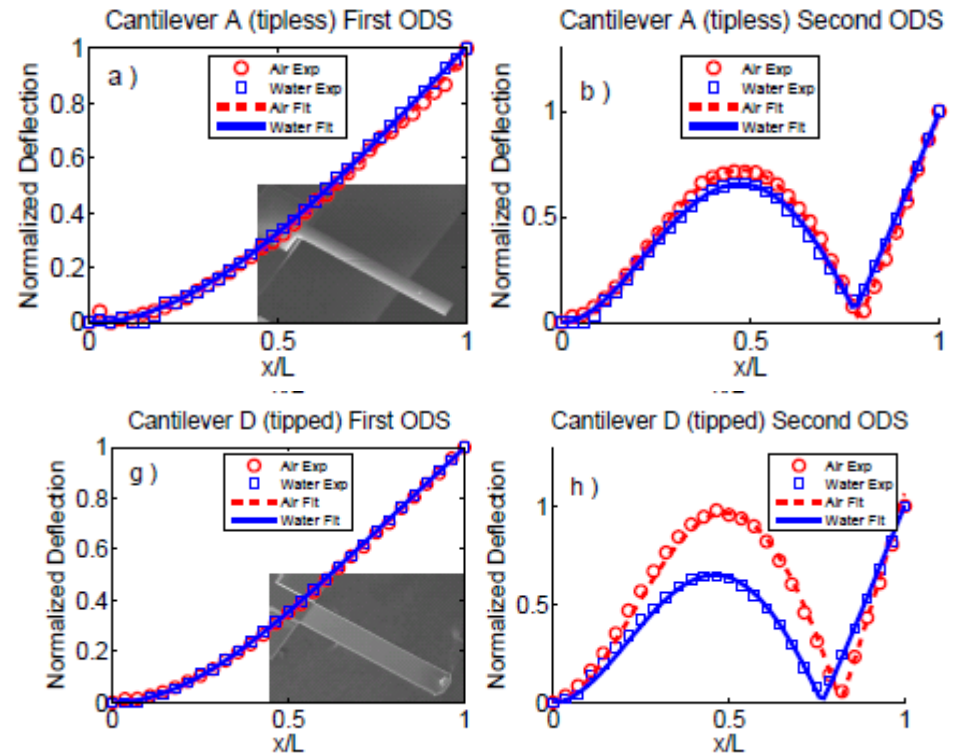
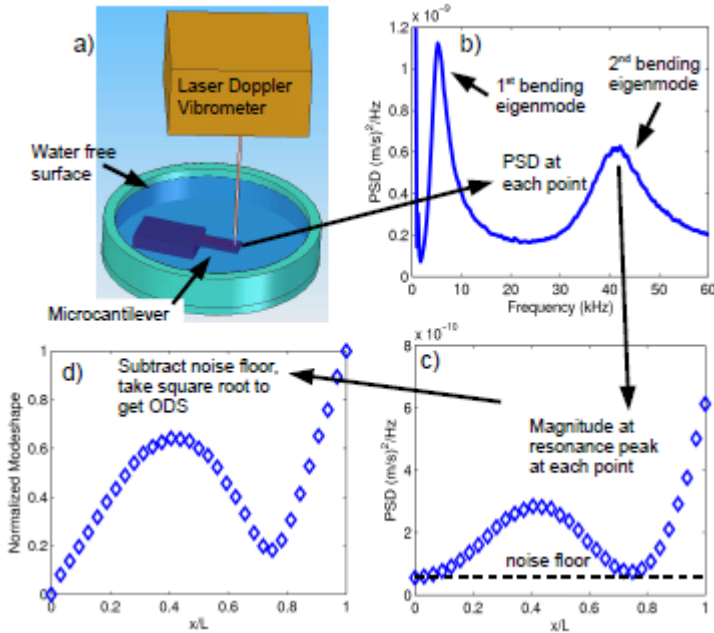
J. E. Sader et al, "Small amplitude oscillations of a thin beam immersed in a viscous fluid near a solid surface", *Physics of Fluids*, 17, 73102, 2005.

O. E. Jensen et al., "The drag on a microcantilever oscillating near a wall", *Journal of Fluid Mechanics*, 545, 397, 2005.

P. Hinterdorfer et al., "Hydrodynamic damping of a magnetically oscillated cantilever close to a surface", *Ultramicroscopy*, 100, 301, 2004.

# Cantilever dynamics in liquids

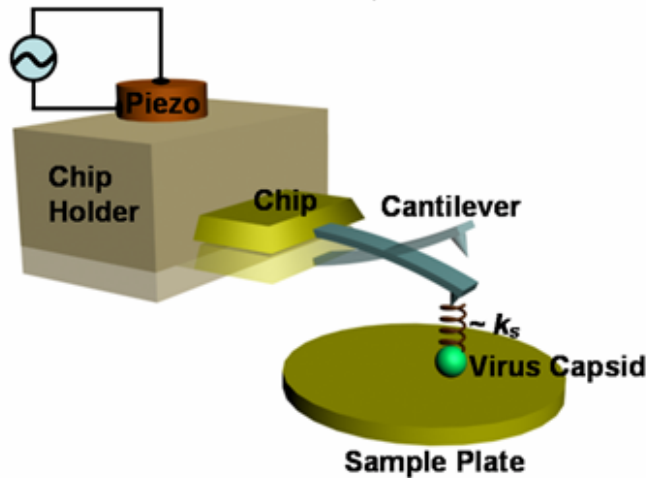
## Eigenmodes



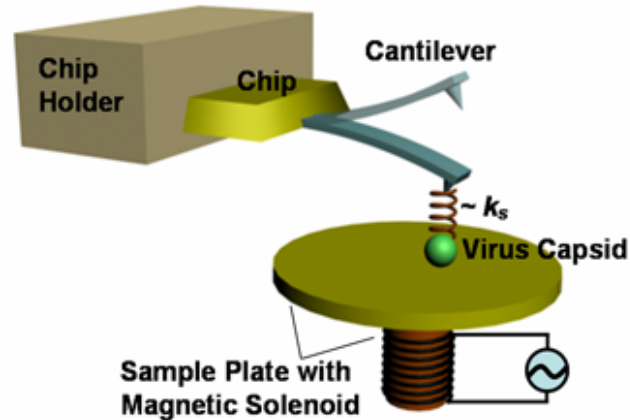
- Added liquid mass dilutes the effect of tip mass
- Stiffness of second mode in water is much smaller than in air

D. Kiracofe, A. Raman "On eigenmodes, equivalent stiffnesses, and sensitivity of AFM microcantilevers : air vs. liquids", *Journal of Applied Physics*, in press, 2009.

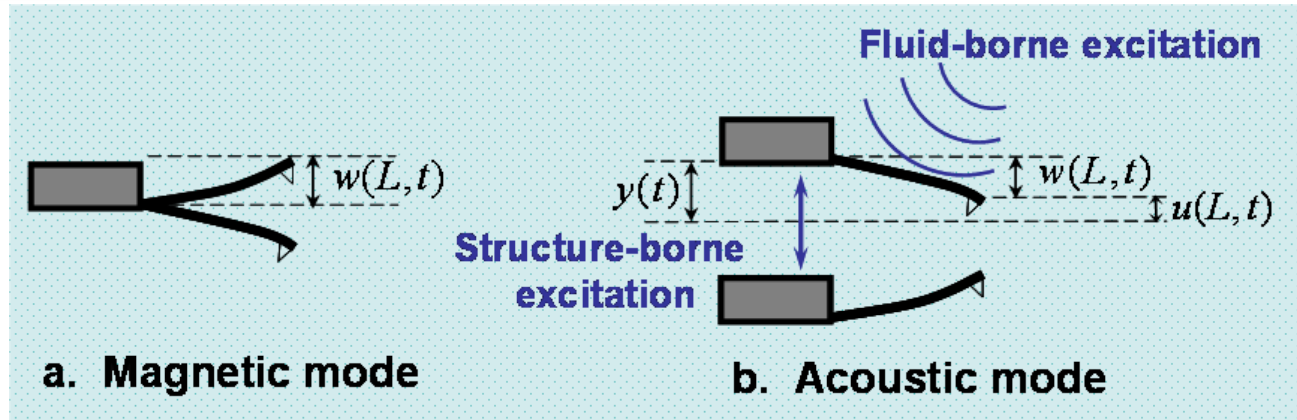
# Acoustic vs. direct (magnetic) excitation



a Acoustic Mode



b Magnetic Mode



a. Magnetic mode

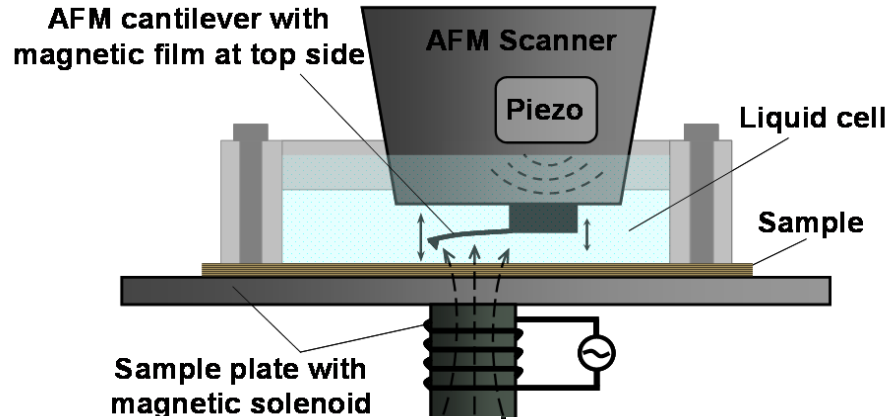
b. Acoustic mode

Xu, X., Raman, A., "Comparative dynamics of magnetically, acoustically, and brownian motion excited microcantilevers in liquid atomic force microscopy", *Journal of Applied Physics*, 102(3), 2007.

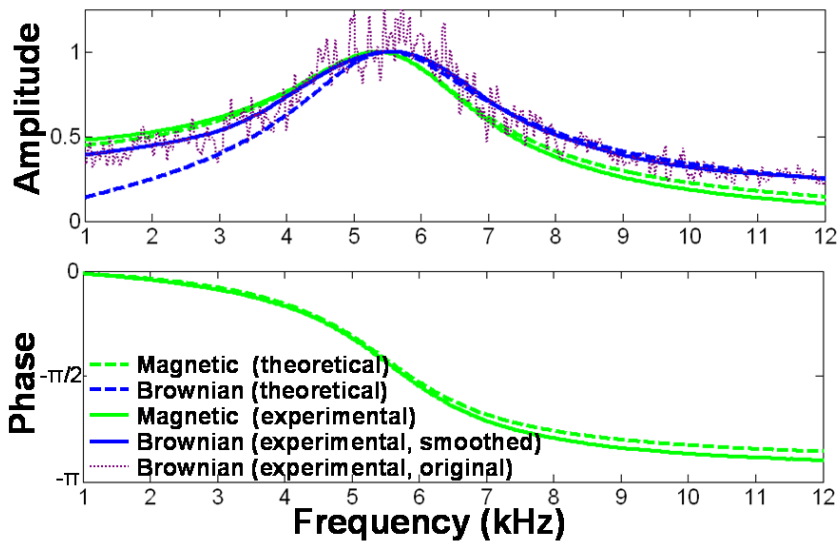
E. T. Herruzo and R. Garcia. Frequency response of an atomic force microscope in liquids and air: Magnetic versus acoustic excitation. *Applied Physics Letters*, 91(14): Art. No. 143113, 2007.

■ Mechanisms and observables are different!

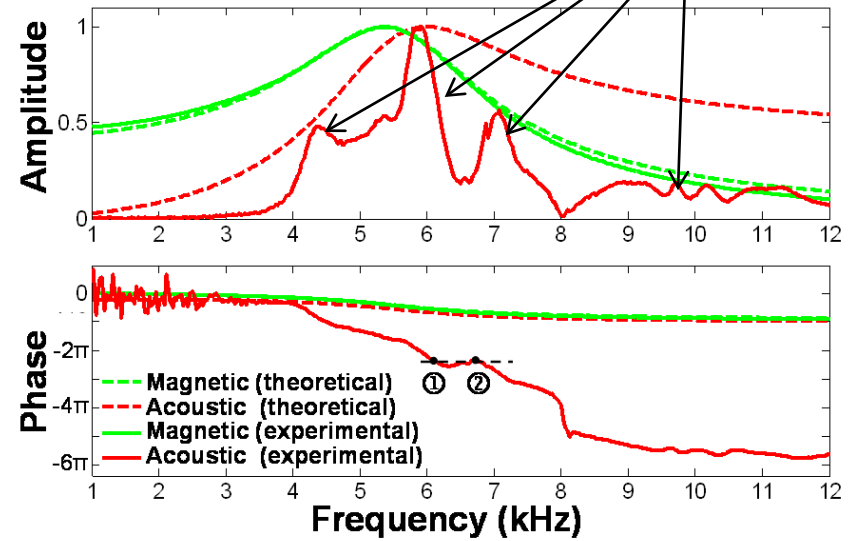
# Acoustic vs. direct (magnetic) excitation



“Forest” of peaks



a. Magnetic vs. thermal

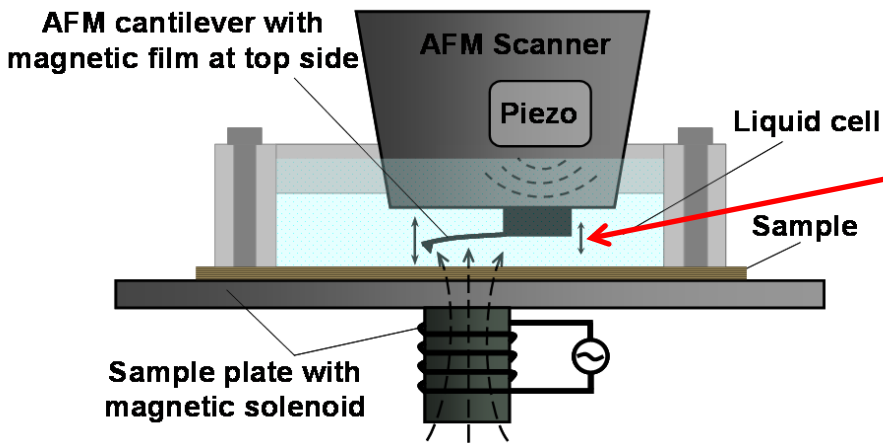


b. Magnetic vs. acoustic

- T.E. Schaffer, J.P. Cleveland, F. Ohnesorge, D.A. Walters, and P.K. Hansma. *Studies of vibrating atomic force microscope cantilevers in liquid.* *Journal of Applied Physics*, 80(7): 3622-3627, 1996.
- I. Revenko and R. Proksch. *Magnetic and acoustic tapping mode microscopy of liquid phase phospholipid bilayers and DNA molecules.* *Journal of Applied Physics*, 87(1): 526-533, 2000.

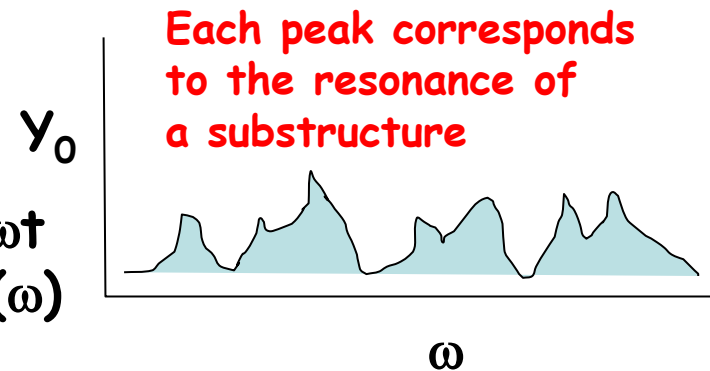
# Fundamental reasons for forest of peaks

- The dither piezo, the chip holder, the chip are all “sub-structures” with their own resonances
- As a result the base motion for cantilever is not constant with drive frequency



$$y(t) = Y_0 \sin \omega t$$

But  $Y_0 = Y_0(\omega)$

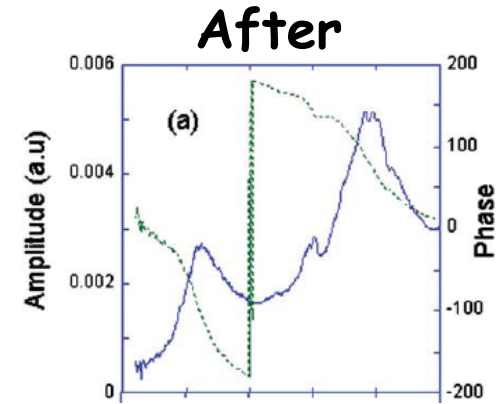
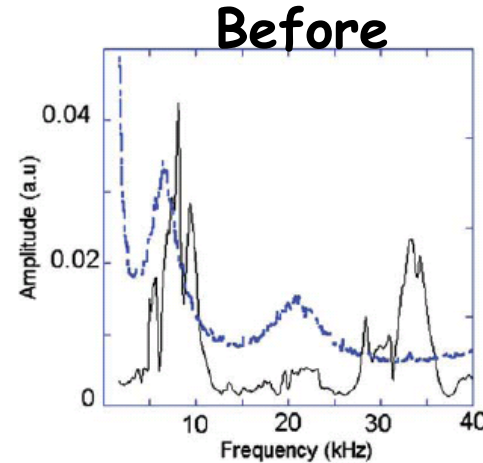
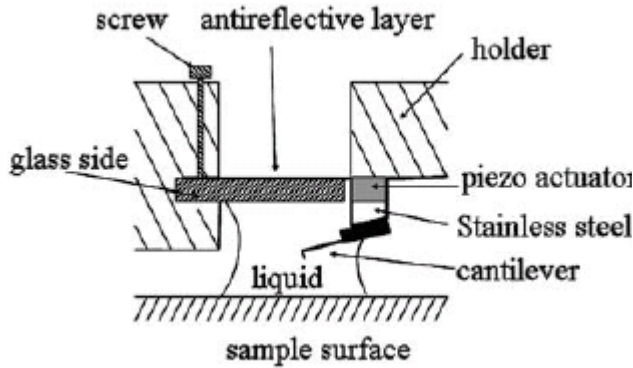


- These peaks generally have Q factors around 10
- So in air cantilever  $Q > 100$  so no problem and a clean peak appears
- However in water cantilever  $Q < 5$  so the sharpest peaks are in fact the substructure resonances

# "Solving" the forest of peaks problem

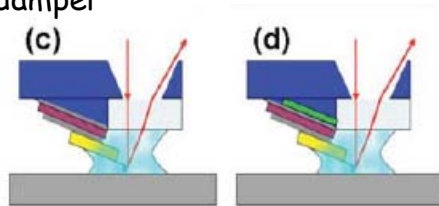
- Maali, Marsaudon, Aime et al., *App. Phys. Lett.*, 88, 163504, 2006

- Brought dither piezo much closer to cantilever

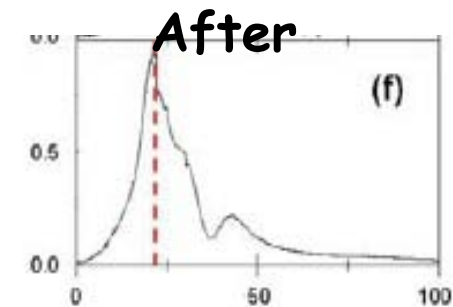
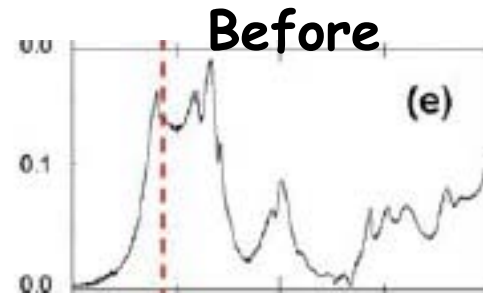


- Carrasco, de Pablo, Gomez-Herrer et al, *Rev. Sci. Instrument*, 79, 126106, 2008

- Inserted clay damper

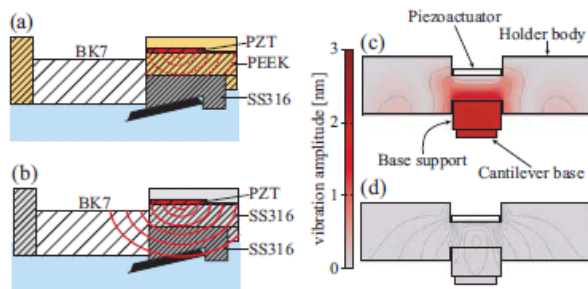


- Aluminum support
- Clay vibration absorber
- Stainless steel 0.2x7.5x5 mm<sup>3</sup> plate
- 0.2x5x5 mm<sup>3</sup> Dithering piezo element



- Asakawa, Fukuma, *Rev. Sci. Instrument*, 80, 103703, 2009

- Acoustic impedance mismatch using PEEK+flexure stage



**Before** **After**

