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Byung I. Kim

Boise State University

Luke Smith

Boise State University

Thanh Tran

Boise State University

Steven Rosland

Boise State University

Erik Parkinson

Boise State University



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Byung I. Kim,^a Luke Smith, Thanh Tran, Steven Rossland, and Erik Parkinson

Department of Physics, Boise State University, Boise, Idaho 83725, USA

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We developed a novel cantilever-based optical interfacial force microscope (COIFM) to study molecular interaction in liquid environments. The force sensor was created by attaching a chemically etched optical-fiber tip to the force sensor with UV epoxy, and characterized by imaging on a calibration grid. The performance of the COIFM was then demonstrated by measuring the force between two oxidized silicon surfaces in 1 mM KCl as a function of distance. The result was consistent with previously reported electrical double layer forces, suggesting that a COIFM using an optical-fiber tip is capable of measuring force in a liquid environment. *Copyright 2013 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [<http://dx.doi.org/10.1063/1.4795761>]

Probing the forces between two surfaces as a function of distance is important to understanding the nature of interactions between two objects such as colloidal particles, bio-molecules, and other organic or inorganic molecules.¹ Because some biological samples such as DNA and living cells must remain immersed in liquids to retain biological activity, a way to study them in liquid environments is needed.² Interfacial force microscopy (IFM) was developed twenty years ago to avoid the snap-to-contact problem present in atomic force microscopy (AFM),³ and has been applied to liquid studies by attaching a tip to the cantilever to isolate it from the liquid environment. Using this method, IFM has been applied to various systems in liquid such as thermally switchable bioactive surfaces and hydration forces of interfacial water.⁴⁻⁷ However, IFM is limited in its use due to the low force resolution of 10 nN of its electrical sensing methods.³

As an approach to solve this limitation, two scanning probe techniques, AFM and IFM, were integrated, resulting in the development of a cantilever-based optical interfacial force microscope (COIFM).⁸ The COIFM solved the IFM's low sensitivity problem by using an optical detection method⁹ used in AFM in combination with a commercially available dimension micro-actuated silicon probe (DMASP)¹⁰ [Figure 1(a)]. Since its development, the COIFM's improved interfacial force resolution in air has been demonstrated by observing large oscillatory forces generated by interfacial water under lateral modulation between two hydrophilic surfaces.^{11,12} The COIFM has also been applied to the investigation of the mechanical properties of soft materials,¹³ and its use of force feedback has been applied to high-speed atomic force microscopy to image biofilms at a rate of one frame per second.¹⁴ The force resolution of the COIFM in these measurements was 150 pN, two orders of magnitude better than the 10 nN in IFM.⁸ This is due to the use of an optical detection method and the DMASP, which is twenty times smaller in the long axis and forty times smaller in the short axis than the sensors commonly used by IFM. However, these studies with COIFM have been limited to studies in air because liquid could interfere with the cantilever's electrical feedback signal. Here we developed a novel COIFM which is capable of measuring molecular interactions in liquid, which has not been reported previously.

We developed chemically etched optical-fiber tips to be used as sensors in combination with DMASP cantilevers to probe the biomolecular interaction in fluid. We chose to make the tips out of

^aE-mail: byungkim@boisestate.edu

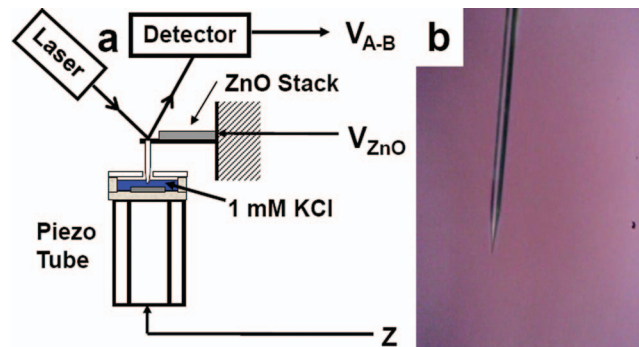


FIG. 1. (a) A schematic diagram of the COIFM with voltage activated force feedback using an optical-fiber probe. (b) Close-up (200X magnification) of an optical-fiber tip after etching it with a HF solution.

optical-fiber because the oxidized silicon surface can be covalently functionalized with organic- or bio-molecules through silane coupling agents.⁴⁻⁷ The optical fibers used (obtained from ThorLabs Inc. Newton, NJ) had a diameter of 125 μm without the protective coating layer, and were cut into 10-15 cm long segments for handling. To use the optical-fibers, the protective coating was removed by submerging them in a CH_2Cl_2 solution for 60 seconds. To sharpen the tips by chemical etching a solution of 48-51% HF, provided by Fluka Analytical (St. Gallen, Switzerland), was prepared with a layer of toluene on top. The optical fibers were suspended over the solution with enough of the tip submerged in the solution to pass the layer of toluene by a few millimeters, creating a meniscus on the optical-fiber at the interface between HF and toluene. As the HF dissolves the tip, it results in the sharpening of the optical-fiber tip. The required etching time was approximately 90 minutes. After the tips were etched, they were cleaned with ethanol and their radii were measured using an Optizoom obtained from Digital Instruments (Santa Barbara, California), to make sure they had a radius under 10 μm . Figure 1(b) shows a finished optical-fiber tip at 200X magnification.

Once an optical-fiber tip was finished it had to be attached to the COIFM probe in order to be used for microscopy. The first step in the attachment process was to trim the tip to 5 mm. This length was chosen because it was long enough to measure forces in liquid while keeping the force sensor unexposed to the liquid environment, and it was light enough that it would not break the AFM cantilever. After trimming the tip, we applied a UV epoxy (Norland Optical Adhesive 81, Norland Products Inc. Cranbury, NJ) to the non-sharpened end. The tip was then placed on a horizontal plane, and the cantilever picked up the non-sharpened end of the tip. For this attachment, an optical microscope and an X-Y-Z translation stage were used. The prepared optical-fiber tip was attached directly to the ZnO stack (consisting of 0.25 μm Ti/Au, 3.5 μm ZnO, 0.25 μm Ti/Au) at the base of the probe,¹⁰ because the cantilever is so fragile that direct attachment to the ZnO stack provides more robustness. After picking up the tip, we straightened it with tweezers so that it hung vertically and perpendicularly to the cantilever. The epoxy was then exposed to UV light for about 30 seconds so it would harden and bond to the cantilever.

Before attempting to measure forces in liquid, the tip was characterized by imaging on a platinum-coated calibration grid with a 1 μm period in the lateral direction and 100 nm ($\pm 10\%$) pit depth.¹⁰ Figures 2(a) and 2(b) show the images obtained with the AFM tip bought from VEECO and the optical-fiber tip, respectively, on the calibration grid, showing that the optical-fiber tip creates a degraded image when compared to the AFM tip. Figures 2(c) and 2(d) display sectional profiles over the black lines shown in Figures 2(a) and 2(b), respectively. While both graphs display an accurate period of 1 μm , the AFM tip measured a height change of 100 nm between the top and bottom of the pits, a significant difference from the 60 nm measured by the optical-fiber tip. The 100 nm height measured by the AFM tip agrees with the height provided by the manufacturer.¹⁰ A previous study has shown that these differences result from each tip's specific size and shape.¹⁵ Due to the degraded resolution of Figure 2(b) and the height change of only 60 nm in Figure 2(d), it can be concluded

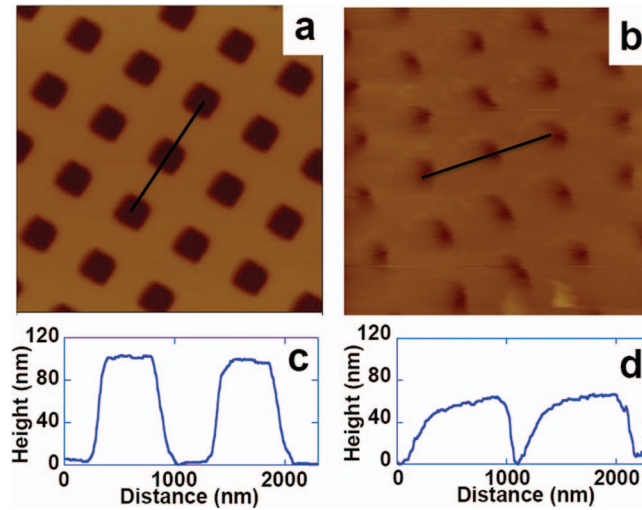


FIG. 2. (a) A comparison of an image and plot diagram obtained on a two-dimensional grating sample with $1\ \mu\text{m}$ periodicity with a normal AFM tip (b) to our optical-fiber tip (c) Sectional profiles comparing a normal AFM tip to (d) the optical-fiber tip.

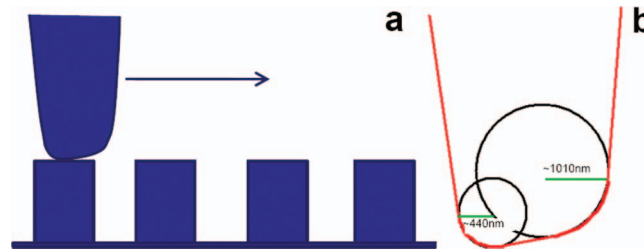


FIG. 3. (a) Graphic representation of an optical-fiber tip moving along the calibration grid. (b) A two-dimensional representation of the optical-fiber tip.

that the optical-fiber tip is much bigger than the AFM tip, and is unable to reach the bottom of the calibration grid [Figure 3(a)].

In previous studies,^{16,17} the radius of the tip was critical in determining the particle size when the curvature of the tip was larger than the particle. The tip-radius of the optical-fiber tip was determined by analyzing Figure 2(d), with the equation $R = (x^2 + y^2)/(2y)$, where R is the tip radius, y is the y-axis distance between the maximum height and the minimum height of the tip, and x is the x-axis distance between the same points. As seen in Figure 2(d) the height changed from 64.4 nm to 0.3 nm as the tip moved along the x-axis from 873 nm to 1102 nm, yielding $x = 229$ nm, $y = 64.1$ nm, and $R = 441$ nm. The height then changed from 0.3 nm to 56.6 nm as tip moved along the x-axis from 1102 nm to 1434 nm, yielding $x = 332$ nm, $y = 56.3$ nm, and $R = 1007$ nm. These findings show that the optical-fiber tip is composed of two spheres with radii of 440 nm and 1010 nm merged together [Figure 3(b)].

After it was calibrated, the performance of the optical-fiber tip was demonstrated by measuring the force-distance curves between the optical probe and an oxidized silicon surface in 1 mM KCl with feedback-on, using the setup in Figure 1(a). We used a room temperature fluid cell with a glass slip with a hole on top to avoid exposing the DMASP sensor to water vapor. The rest of our setup is the same as our previously reported COIFM in air.⁸ The voltage signal to the ZnO material (V_{ZnO}) and the error signal (V_{A-B}) were recorded as a function of tip to sample distance. Figure 4(a) shows that the V_{A-B} signal remains zero during the force measurement, indicating that all forces on the cantilever remain balanced, or the cantilever has zero compliance by relieving the strain built up in the ZnO stack through force-feedback. As the noise level in Figure 4(b) is 100-200 pN at

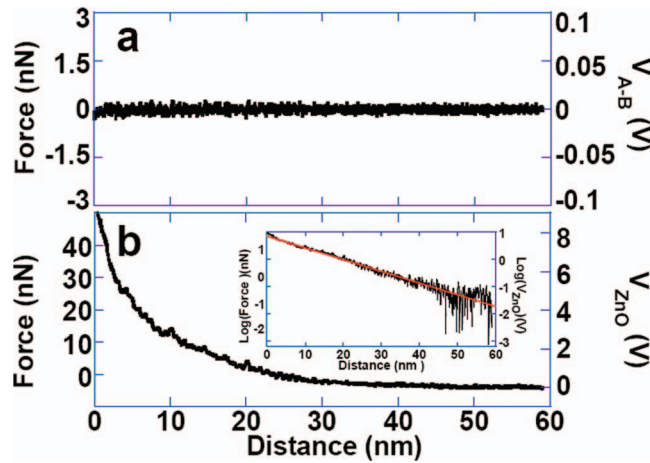


FIG. 4. (a) The error signal caused by the bending of the tip, obtained with a force activated voltage feedback system. (b) The force applied to the ZnO stack material graphed as a function of tip and silicon sample distance. (inset) The logarithm of the force applied to the ZnO stack material graphed as a function of tip and silicon sample distance. The red line is the linear fitting of the data.

distances between 45-55 nm, the force resolution of the COIFM is comparable to that without the optical fiber tip, which is known to be 150 pN. Due to being measured in 1 mM KCl, there was an electrical double layer effect in the force measurement.¹⁸ Figure 4(b) shows the electrical double layer repulsion between the two silicon surfaces as a function of distance. In a previous study,¹⁹ the double-layer force between a flat sample and a spherical tip has been given by

$$F = \frac{2\pi R}{\varepsilon\varepsilon_0 K_D} [(\sigma_T^2 + \sigma_S^2)e^{-2K_D D} + 2\sigma_T\sigma_S e^{-K_D D}] \quad (1)$$

where F is the force between the tip and the surface, R is the tip radius, $1/K_D$ is the Debye length, σ_T and σ_S are the surface charge densities of the tip and the sample, respectively, ε is the dielectric constant of water, ε_0 is the permittivity of free space, and D is the distance between the sample and the tip. Because $\sigma_T = \sigma_S$ the second term is always dominant, and for $10 \text{ nm} < D < 45 \text{ nm}$ Equation (1) can be simplified to

$$F = \frac{4\pi R\sigma^2}{\varepsilon\varepsilon_0 K_D} (e^{-K_D D}) \quad (2)$$

where σ is the surface charge density of both the tip and the sample. An exponential fitting of our data yielded the curve $F = 35.563e^{-0.09858D}$, giving a Debye length of 10.144 nm. Using $R = 1007 \text{ nm}$, $\varepsilon = 80.1$, and $K_D = 0.09858 \text{ nm}^{-1}$, Equation (2) was fitted to find the surface charge densities of the tip and the sample surface, yielding $\sigma = 0.014 \text{ C/m}^2$. The theoretical Debye length can be calculated using $1/K_D = 0.304/\sqrt{[X]}$ where $[X]$ is the electrolyte concentration in moles.¹⁹ Solving this equation yields $1/K_D = 9.613 \text{ nm}$, which is consistent with our result with 10% error. In a previous experiment we found the surface charge density of glass to be 0.008 C/m^2 , which is comparable to our findings. The error could be explained by the two spherical forms that make up the optical-fiber tip, instead of the one spherical form used in our analysis.

The consistencies between our findings and the theoretically predicted values in the above analysis confirm that an electrical double layer repulsive force appears at distances up to 45 nm from the silicon surface. This is further confirmed by the fact that when the force is graphed in the logarithmic scale [inset of Figure 4(b)], a linear line is produced. This clearly shows the electrical double layer repulsion between the two oxidized silicon surfaces, and demonstrates the feasibility of the combined approach between the ambient COIFM and the optical-fiber probe for biological studies in fluid.

In conclusion, we developed a COIFM that functions in liquid by isolating the cantilever from the liquid environment through the use of an optical-fiber tip. The COIFM has a force resolution

of less than 150 pN, which is greater by two orders of magnitude than the existing IFM with the electrical detection method.³ This force resolution is achieved through the use of the DMASP cantilever and the optical detection method. This is comparable with the sensitivity of our existing COIFM reported in previous works,^{8,11,12} indicating that the effect of the optical-fiber tip on the force resolution is negligible. The force measurement between two oxidized silicon surfaces in 1 mM KCl as a function of distance suggests that a COIFM using an optical-fiber tip is capable of measuring force in a liquid environment. Although our tip had a radius of 1 μm , future optical-fiber development of a nanometer-scale tip could improve the force resolution when measuring the intermolecular interaction at the single molecular level between the tip and surface. Considering the recent demonstration of the unprecedented capability of COIFM in probing interfacial water structures in ambient environments,^{11,12} the new capability of the developed COIFM in interaction measurements in liquid would significantly contribute to our understanding of molecular interactions.

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