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Nanomechanical standards based on the intrinsic mechanics of molecules and atoms

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ABSTRACT

For more than a decade, instruments based on local probes have allowed us to "touch" objects at the nanoscale, making it possible for scientists and engineers to probe the electrical, chemical, and physical behaviors of matter at the level of individual atoms and molecules. In principle, physical interactions on this scale are characterized by fixed, unique values that need only be reliably measured in terms of accurately realized units of force and length to serve as standards. For example, the silicon lattice spacing is often used as a convenient ruler for estimating length in atomic scale images, since this lattice spacing has been independently measured using x-ray interferometry. Recently, the force-induced failure of DNA, often referred to as the overstretch condition, has been proposed as both a standard of force and length in single-molecule bio-physics experiments. Still other nanomechanics researchers have suggested that the rupture force of a single-atom chain is unique to a given metal, and that this intrinsic force can be used to calibrate atomic break junction experiments. In both these examples, a fundamental assumption is that the irreducible nature of nanoscale experimentation, in this case tensile testing, yields consistency befitting a standard. This paper offers context and a condensed overview of recently published results from the NIST Small Force Metrology Laboratory regarding new instruments and capabilities we have developed to examine this fundamental assumption. The reviewed papers describe new test platforms, techniques, and calibration procedures that allow us to bring accurate picoscale measurements of both length and force to bear on the problems of single-molecule and single-atom tensile testing.

Keywords: small force, electrostatic force balance, atomic force microscope, colloidal probe calibration.

INTRODUCTION

An intrinsic standard is an invariant of nature that can be linked to a unit of measure. The triple point of water as a calibration reference in thermometry is a familiar example; the silicon lattice spacing, often used as a convenient ruler for estimating length in atomic scale images, is another. In the realm of piconewton to nanonewton forces, there are a handful of phenomena already referred to as "standards" in biophysical investigations of single-molecule responses to mechanical deformation and also in similar nanomechanical studies of atomic-size metal contacts. These phenomena, which have been measured in numerous experiments using a variety of techniques, are beginning to be used as convenient reference points for the calibration of the very instruments used in such experimentation. The National Institute of Standards and Technology (NIST) is seeking to securely anchor these reference points to known values by measuring intrinsic force interactions using rigorously calibrated experiments, both physical and computational, that emphasize absolute accuracy through traceability to accepted standards of force and length as defined in the International System of Units (SI). The following paper is drawn from the major published results of these efforts, using the notion of an intrinsic standard to provide a unifying backdrop for the discussion.

The paper is organized into four sections; the first two sections deal with specific intrinsic forces, while the latter two sections focus on the more general problems associated with calibrating force and length at the nanoscale. In

general, the sections comprise previously published source material assembled and edited here to support the keynote address delivered at the 2010 Annual Meeting of the Society for Experimental Mechanics. For example, the first section, **Au Break Junctions**, provides a brief review of Reference [1] where we describe new NIST capabilities developed to study the mechanics and electrical properties of gold nanowires. Gold nanowires apparently neck down under tension to form a single chain of atoms, a physical constriction that leads to the coincidence of quantized force and quantized electrical impedance. It is believed that gold nanowires form in at least three different atomic arrangements. It is not known if all such structures form single-atom chains when stretched to failure and, if so, whether or not the strength of the final bond depends on the initial structure. NIST has been seeking to quantify, to the extent possible, these potential systematic variations. First principles quantum mechanics models along with a new Feedback Stabilized Break Junction (FSBJ) experimental platform have been developed and used at NIST to examine how structure and conductance evolve during elongation, with the ultimate aim to reveal their effect on force at rupture; here, we offer a brief snapshot of this exciting new work. Obviously, the interested reader is encouraged to read the source material for more detail.

The intrinsic force associated with the overstretching-induced conformation change of DNA is reported to occur under a tensile force of approximately 65 pN. This force has been measured using both scanning probe microscope (SPM) and optical trapping instruments and has been proposed as both a length and force standard. The quoted force value has known dependencies on environmental factors such as pH, salinity, and temperature. NIST is working to determine how to accurately control these variables to yield reliable data, and we present a small indication of our new single-molecule expertise in the section headed **DNA Overstretch**.

The experimental platforms necessary to investigate these disparate physical phenomena share two things in common. First, both require the accurate measurement of forces at levels at or below a few nanonewtons. Second, because the primary experiments are analogous to macroscale tensile testing, they each require a means of monitoring the elongation of a mechanical specimen with resolution of a few picometers or less. Consequently, **Picometer Fiber Interferometry** reviews recent developments at NIST regarding the use of fiber interferometry to measure displacements of a nanometer or less. This section provides a highly condensed introduction to the topic; for details the reader should see Reference [2]. Finally, **Piconewton Force Calibration** summarizes our attempts to improve the calibration of atomic force microscope (AFM) cantilever stiffness and to create known forces at or below the level of a nanonewton. It provides a succinct review of our previous research, and then communicates the key findings from Reference [3] regarding the influence of friction in cantilever-on-cantilever calibration, and from References [4-7] regarding our new capabilities to apply electrostatic forces of known magnitudes directly to electrically conducting instrumented indentation and AFM probes.

Au Break Junctions

We have developed an experimental platform, which we refer to as a feedback-stabilized break junction (FSBJ), to create and deform stable atomic-scale contacts, and have used that platform to probe the phenomenon of quantized electrical conductance in Au nanowires (NWs) and single-atom chains (SACs) [1]. In such a system, electrical conductivity, σ, is known to be quantized in units of $G_0 = 2e^2/h$; that is, $\sigma = nG_0$ for integer n, with e the charge of the electron and h Plank's constant [8-10]. The conductivity for the $n = 1$ state corresponds to a contact resistance of 12.9 kΩ. Quantized conductance has been observed many times, but experimental instabilities typically limit the time a given contact stays in a low-n state to milliseconds [11], and often the presence of quantized states must be inferred from histograms compiled from hundreds or thousands of junction breaks [12].

Because the $n = 1$ conduction state is believed to occur when there is only one electron conduction channel through the contact [13,14], the ability to maintain that state indefinitely would clearly demonstrate exceptional experimental stability. The NIST FSBJ described in [1] and shown in the photos of Figure 1 is proving to be just such an exceptionally stable experimental platform. By positioning an interferometer cavity directly between an Au surface and probe mount, we have significantly tightened the displacement measurement frame relative to that achieved in prior work. This has allowed us to close a servo loop around the junction separation with long-term, picometer stability, so as to remove thermal drift and low-frequency vibration artifacts and thereby reduce the need for rigorous environmental isolation that is often encountered in these types of experiments. In the near future, the NIST FSBJ will incorporate a stiff elastic force sensor (e.g., an AFM style colloidal probe) coupled with a high resolution fiber interferometer (see Figure 1), so that direct measurements can be made of bond stiffness and breaking force in SACs.

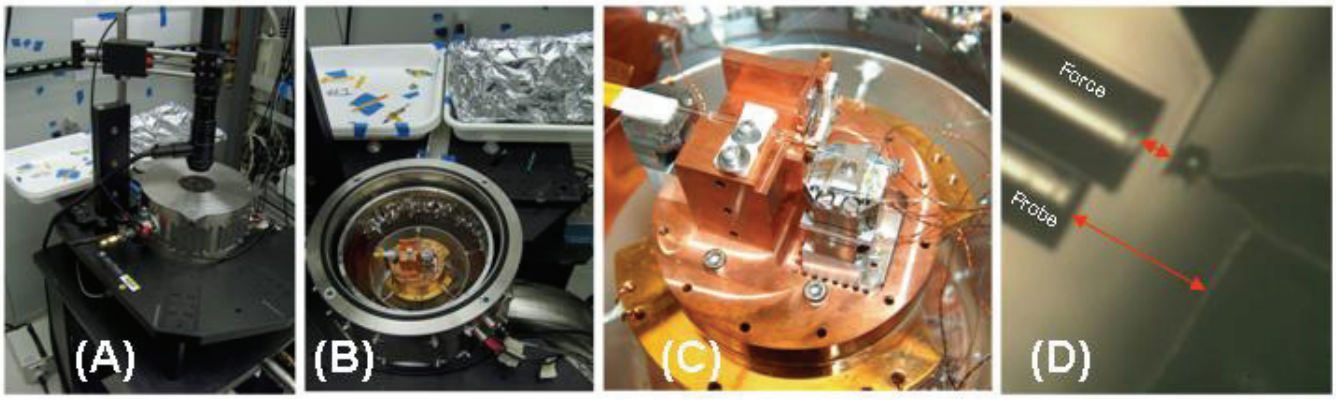

Figure 1. Feedback-stabilized break junction platform (A) high-vacuum cryogenic chamber with long standoff microscope (B) chamber lid removed (C) mechanics including probe positioning stage (D) view of tip approaching an AFM colloidal probe as seen using the long standoff microscope. The fiber labeled force records the deflection of the colloidal probe cantilever, while the fiber labeled probe monitors the displacement of the probe stage with respect to their common plane (both fibers are in a single, double bore ferrule that is rigidly attached to the cantilever holder base) for the feedback stabilization of the probe sensor separation.

DNA Overstretch

Another example of an intrinsic force is the overstretch transition of DNA [15, 16]. During single-molecule force measurements, a transition occurs at approximately 65 piconewtons in which the DNA molecule elongates significantly with very little extra applied force. The force-displacement curve of a single molecule of DNA measured with a force-calibrated AFM is shown in Figure 2, as described previously [17]. This particular molecule was amplified from a segment of the plasmid vector pBR322, and was measured in Tris/sodium chloride buffer. The transformation can be seen as a plateau in the curve. The methods developed for small force measurement at NIST are being used to calibrate the force at which this plateau occurs. The DNA itself then will become a force reference that will allow the calibration of a wide variety of force measuring instruments such as optical, magnetic, and dielectrophoretic tweezers.

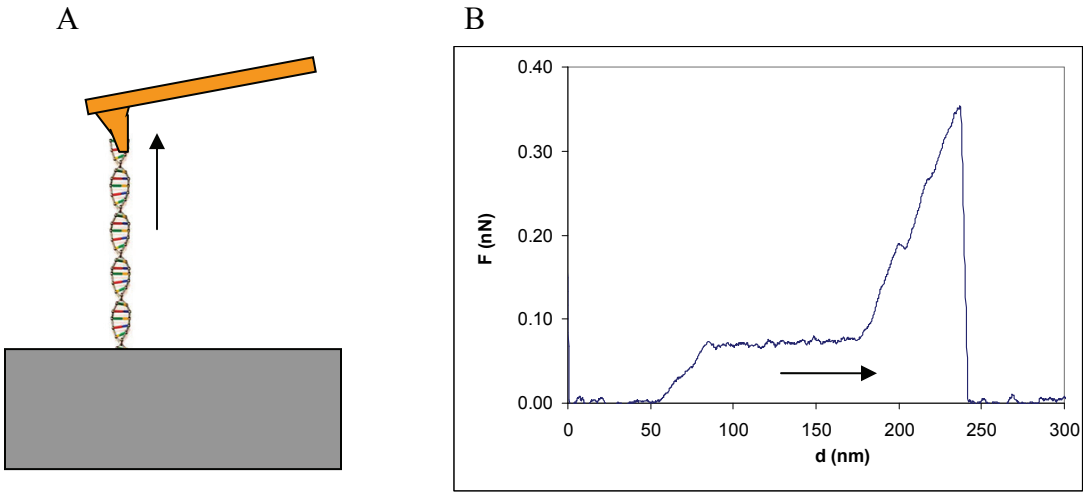

Figure 2. DNA as an intrinsic force standard. (A) Schematic of a single molecule of DNA being stretched by an AFM cantilever. (B) Force displacement curve showing the overstretch transformation of a single DNA molecule measured using an AFM. Arrow indicates the direction in which the DNA was stretched.

Picometer Fiber Interferometery

Clearly, when dealing with single-atom contact mechanics, such as that realized by the interaction of a probe tip with a flat surface, relative displacement of the tip with respect to the substrate must be monitored with resolution well below the lattice spacing of the atoms (< 0.1 nm). Similarly, the interaction forces must be resolved to within at least a few percent of the rupture force of an atomic bond, which has been observed to be between 1 nN and 2 nN for a pair of gold atoms [18]. Assuming that this force is measured using a spring sufficiently stiff to avoid snap in, a stiffness anticipated to be around 50 N m^{-1}, the detector on the force sensor must resolve relative displacement of the spring to 1.5 pm to achieve even a 5 % uncertainty in determination of the rupture force. The requirements for atomic-scale length metrology in these experiments are clear, and point to the need for an accurate sensor capable of recording full-scale relative displacements on the order of 10 nm with percent-level linearity and a noise floor of picometers, in a bandwidth from DC to hundreds of Hertz.

Accurate measurement of displacement requires calibration via comparison to an absolute standard. The unit of length in the International System of Units (SI) is most accurately realized in terms of the wavelength of light; thus, the most accurate determinations of displacements are typically achieved by incorporating measurement tools developed around optical interference, where the displacement is directly compared to the absolute SI standard, minimizing the accrual of uncertainty due to successive calibrations. Simple homodyne interferometers are often employed when the displacement of interest is expected never to exceed the fringe spacing. Robust interferometers based on the low-finesse Fabry-Perot (FP) cavity formed between the end of an optical fiber and the reflective surface of the cantilever spring have been demonstrated for scanning probe microscopes, and we have developed such a fiber-optic interferometer (see schematic in Figure 3) optimized for best performance in the frequency range from DC to 1 kHz, with displacement linearity of 1 % over a range of ± 25 nm, and noise-limited resolution of 2 pm [2]. The interferometer uses a tunable infrared laser source (nominal 1550 nm wavelength) with high amplitude and wavelength stability, low spontaneous self-emission noise, high sideband suppression and a coherence control feature that broadens the laser linewidth and dramatically lowers the low-frequency noise in the system. The amplitude stability of the source, combined with the use of specially manufactured “bend-insensitive” fiber and all-spliced fiber construction, result in a robust homodyne interferometer system that achieves resolution of 40 fm·$Hz^{-1/2}$ above 20 Hz and approaches the shot-noise-limit of 20 fm·$Hz^{-1/2}$ at 1 kHz for an optical power of 10 μW, without the need for differential detection.

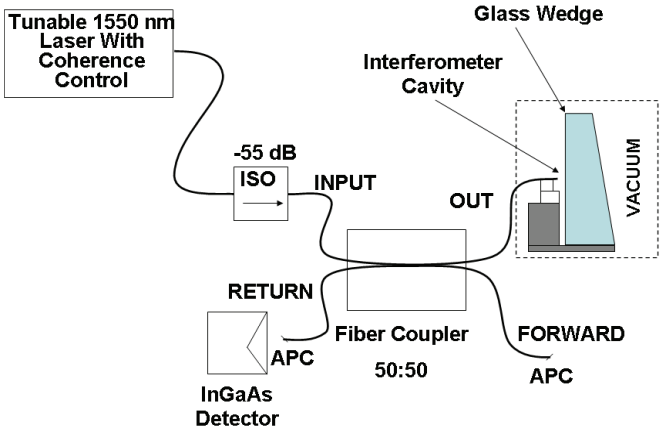

Figure 3. Schematic diagram of the fiber-optic interferometer components showing the laser, optical isolator (ISO), evanescent wave coupler, single InGaAs detector, and a test interferometer cavity. Note that the forward and return ports of the coupler are terminated using angle polished connectors (APC) to minimize interference in the parasitic cavities along these fiber runs.

The light source for our interferometer can be tuned stably and accurately over the wavelength range 1440 nm to 1640 nm. This tuning range enables two very convenient operational features. First, when we either have no control over the macroscopic cavity spacing, as for example in the case of measuring the deflection of a cantilever

force sensor, or we choose not to change the cavity out of concern for dimensional stability, we can still operate the interferometer at its maximum sensitivity by tuning λ, so long as the cavity is large enough to contain a quadrature point within the tuning range of the laser. Second, we can make an absolute determination of a fixed cavity length h by sweeping wavelength. Since maxima in reflected intensity occur when $4h/\lambda = 2m+1$, assuming no phase shift at the interfaces (other than standard phase inversion), and minima occur when $4h/\lambda = 2m$, it follows directly that h can be calculated from the measured wavelength values λ_m and λ_{m+1} of two consecutive fringe maxima or minima:

$$h = \frac{1}{2}\frac{\lambda_m \lambda_{m+1}}{(\lambda_{m+1} - \lambda_m)}.$$

For the tuning range of our laser, this means that we can make an absolute determination of cavities as small as h = 6 μm. If a consecutive maximum and minimum are used to calculate h, 3 μm cavities can be measured. Accuracy is limited by our ability to measure λ_m and λ_{m+1}. With curve fitting, wavelengths of maxima and minima can typically be determined within a range of ± 0.1 nm, permitting cavity length determination to better than one part in 1000.

Piconewton Force Calibration

We have been exploring methods to calibrate microcantilever force sensors, such as those used in atomic force microscope experiments. Our initial work in this field focused on creating a system for accurately realizing or creating known forces of appropriate magnitudes. The NIST Electrostatic Force Balance (EFB), which we created for this purpose [19], is an electromechanical balance system that we have used to measure the force versus displacement response of so-called reference cantilevers [20] for use in cantilever-on-cantilever calibrations, and the force sensitivity of piezoresistive cantilever force sensors that can be similarly used to calibrate the force sensitivity of AFMs [21,22]. This work has been extended recently in two important directions.

First, we have found that there are systematic differences between loading and unloading force versus displacement curves obtained using an AFM to probe another cantilever. In Reference [3], the appearance of hysteresis in the slopes of loading curves when probing compliant surfaces with AFM has been explained with an analytical model describing the bending of the test cantilever under the combined influence of a normal contact force and a tangential sliding frictional force. Expressions derived in the paper allowed us to determine coefficients of sliding friction, as well as the stiffness of a sample, provided the spring constant of the AFM cantilever was known. More importantly within the present context, the results were also applied to determine the stiffness of an AFM cantilever using a cantilever-on-cantilever spring constant calibration. A unique aspect of this investigation was that the stiffness of both the AFM cantilever and reference cantilevers was known *a priori*, based on absolute calibrations performed using the NIST EFB. Making use of corrections described in the paper, it was possible to measure the unknown cantilever stiffness using an accurately calibrated cantilever reference within a relative standard uncertainty of approximately 3 %. Remarkably, similar precision was achieved in the determination of the coefficient of sliding friction. From a practical standpoint, a very useful observation made in the paper is that the accuracy of cantilever-on-cantilever calibration can be markedly improved by simply taking the mean of the slopes recorded during loading and unloading against the reference cantilever.

The second important direction of our recent work has been extending the use of calculable electrostatic force to the direct calibration of indentation and colloidal probe force sensors [4-6]. In Reference [4], the capacitance gradient between a spherical indenter probe and a flat electrode was measured. The flat electrode was then used to apply calculable electrostatic forces directly to the spherical indenter, which was mounted on a commercially available force sensor. In essence, the experiment demonstrates the direct application of a force standard to a target instrument without recourse to a transfer artifact, in much the same way calibration has been achieved by hanging known masses on springs in the past. Electrostatic forces ranging from 10 μN to 200 μN were realized with uncertainties estimated less than 1 % (k = 1). Forces were compared in an indirect fashion to deadweights through evaluation of the sensor stiffness, with the relative difference between measured stiffness recorded via the two approaches less than 1 %. In follow up papers [5,6], we have demonstrated calculable electrostatic forces nominally ranging from 320 pN to 100 nanonewtons with uncertainties of a few percent in experiments to perform a direct force calibration of colloidal probe AFM, as illustrated in Figure 4.

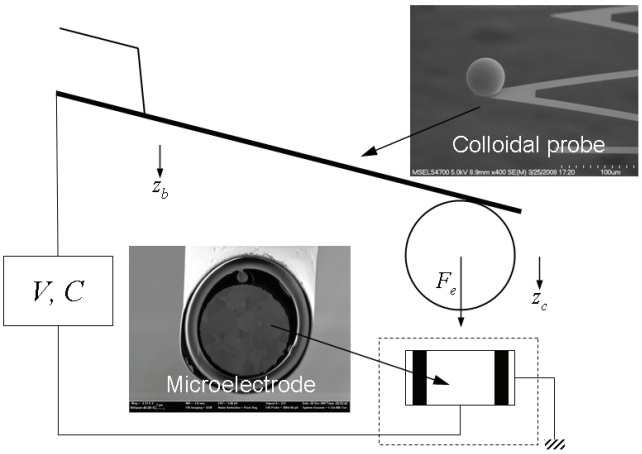

Figure 4. Schematic of an electrostatic force probe experimental setup as in References [5,6]. Insets show scanning electron microscope micrographs of devices as constructed.

CONCLUDING REMARKS

A brief overview of NIST's pioneering work in the field of intrinsic force standards has been presented. The concept of an intrinsic force standard has been introduced, and two candidate physical phenomena have been discussed to describe the current status of this measurement science at NIST. The physical measurements necessary to support the foundational single-molecule and single-atom contact experiments, namely pico-scale force and length metrologies, were reviewed. At present, NIST's Feedback Stabilized Break Junction platform has demonstrated the stability necessary to perform single-atom contact mechanics experiments with traceable force and length metrology, largely thanks to NIST innovations in the application of fiber interferometery, electrostatic force calibration, and micro-cantilever stiffness calibration. The force curve presented in Figure 2 provides a glimpse of a tantalizing future where accurately determined force transitions that occur in the tensile loading of DNA can serve as readily accessible calibration references for a variety of single-molecule science platforms, including optical and magnetic tweezers. DNA can be manufactured with atomic precision in large quantities, and could provide a very cost-effective reference material for single-molecule nanomechanical experimentation.

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