

Supporting Information

Experimental

Magnetic Tip Preparation. An inverted optical microscope equipped with micromanipulators was used to prepare the magnetic tips by gluing small SmCo magnets onto FESP cantilevers (Digital Instruments, $k = 2\text{-}5\text{ N/m}$) with UV and heat curable adhesive. Small magnets ($5\text{-}20\mu\text{m}$ in diameter) were prepared by crushing a larger SmCo magnet (Edmond Scientific), spreading the resulting powder on a plastic film, and stretching the film to separate small pieces. The inverted microscope (Epiphot 200, Nikon) was equipped with three micromanipulators (461-XYZ-M, Newport), which were used to manipulate the cantilever, a sharpened tungsten wire probe, and the plastic film with magnet fragments. A small magnet was attached to the cantilever using the following sequence: (i) the tungsten wire probe, which was dipped in UV cure glue (optical adhesive #63, Norland Products), was used to deposit a small patch of glue on the backside of the cantilever; (ii) the wire was used to pick up a single magnet fragment from the plastic film and deposit this on the back of the cantilever; (iii) the glue was cured for at least 1 h using an UV lamp (UVGL-25 mineralight lamp, UVP Inc., San Gabriel, CA); (iv) the tungsten probe, now coated with heat cure glue (#377, Epoxy Technologies), was used to smother the magnet with glue; (v) and cure the glue at 110 C for one hour. Smothering the magnet with heat cure glue sealed the magnet from contaminating the surfaces during imaging and strengthened the attachment. UV cure could not be used as the sealant since it was too viscous and would remove the magnet upon withdrawal of the tungsten probe. Conversely, heat cure glue could not be used for initially affixing the magnet because it is not viscous enough to pick up magnets from the plastic film with the tungsten probe. After curing the glue, a thermal evaporator (Sharon Vacuum, $P_B \sim 7 \times 10^{-8}$ torr) was used to apply a chromium and gold layer of 70 and 400 Å respectively at a rate of 1 Å/s. For the probe used to produce the energy dissipation image in figure 1, heat cure glue was placed on the tip apex to blunts the tip and promote adhesion of the metal film. The probe used to produce the force curves in figures 2 and 3 was blunted by annealing the tip in a tube furnace at 700 C overnight. The probes retain a small interaction area because the contact radius is defined by a single gold grain (10 nm diameter).

Flat Gold Surface Preparation. Atomically flat gold surfaces reduce variations between force curves caused by sample drift and reduce the error signal caused by topography while scanning. Flat gold for the patterned SAM surface in figure 1 was prepared using a thermal evaporator (Sharon Vacuum, $P_B \sim 7 \times 10^{-8}$ torr) to deposit 300 Å of gold at 2 Å/s on freshly cleaved mica surfaces. The samples were removed from the chamber and placed in a tube furnace at 300 C for one hour. The “flat gold” surface was polycrystalline with facets in some regions but much of the surface contained atomic steps and the total rms roughness was $9\text{ Å}/\mu\text{m}^2$. Flat gold surfaces for the force curves presented in figures 2 and 3 were prepared in an ion pumped load-locked UHV thermal evaporator at 2×10^{-9} torr. The mica was annealed at 400 C overnight before evaporation and for at least 2 hours after evaporation before slowly cooling. The evaporation deposited 100 nm of gold at 7 Å/s. With this technique, atomically flat regions with areas as large as $0.1\text{ }\mu\text{m}^2$ are common.

Surface Functionalization. Tips were placed in 1 mM 11-mercapto-1-undecanol (Aldrich) ethanolic solution immediately after removal from the chamber. The surfaces

formed a self-assembled monolayer (SAM) for at least an hour. The patterned SAM surface for figure 1 was made using soft lithography techniques.¹ A PDMS stamp with 1 μm lines spaced by 1 μm is doused with 1 mM 11-mercapto-1-undecanol ethanolic solution. After letting dry, the stamp is pressed against the gold surface and removed after 10 s. The stamp is doused again and the process repeated after a 90 degree rotation and the gold is allowed to stand for 10 minutes to allow SAM formation. The surface is then immersed in a 1 mM 16-mercaptohexadecanoic acid (Aldrich) ethanolic solution for 10 minutes. The carboxyl terminated thiol binds to the square gold regions that did not have hydroxyl terminated thiol deposited by the stamp. Migration of the 11-mercapto-1-undecanol before submersion in the carboxyl terminated thiol solution causes the carboxyl terminated region to be slightly smaller than 1 μm^2 . The flat gold surfaces for the force curves in figures 2 and 3 were immersed in either carboxyl or hydroxyl terminated thiol solution for over 2 hours to produce homogenous SAMs.

Data Collection. A multimode AFM (Digital Instruments), which was modified to achieve a 36 fm/ $\sqrt{\text{Hz}}$ baseline noise and less than 10 pm noise in a 1 mHz to 1 kHz bandwidth,² was used during the experiments. The quartz fluid cell was thoroughly cleaned using ethanol and blown dry with ultra pure nitrogen. Similarly, the sample surfaces and tips were rinsed and dried. Surfaces were affixed to an electromagnet composed of 400 turns of 32 gauge wire wrapped around a hollow aluminum spindle, producing an inner diameter of 1.5 mm for the wound wire. The electromagnet was mounted atop the E scanner. Power dissipation greater than 5 μW heated the solenoid and caused sample drift, thus enormous cantilever magnetic moments are necessary to reduce the solenoid current and still actuate cantilever motion in high damping environments. The fluid cell was injected with 10 mM phosphate buffer pH 2 and allowed to equilibrate.

A home built Q-control feedback system was used to implement active modulation of the cantilever damping.³ A breakout box between the head and base accessed the photodiode voltages and contained an instrumentation amplifier to produce a low noise deflection signal. This low noise signal was high pass filtered near 1 Hz to remove the DC components and subsequently amplified with a variable gain amplifier. The resulting signal was phase shifted 90 degrees using a single pole low pass filter and then summed with the tapping mode drive signal, retrieved from a breakout box between the base and phase extender. Finally, a booster stage using a power amplifier (PA10 Apex Microtechnologies) drove the solenoid mounted on the scanner.

During imaging experiments, an external lock-in amplifier (SR830, Stanford Research) was used to produce amplitude and phase data. An external lock-in was required since the phase extender produces an error signal, amplitude minus setpoint, instead of an amplitude signal and the phase is in Bocek degrees which only approximates the true phase shift. The output amplitude and phase were recorded using the Nanoscope software and the auxiliary ADC inputs on the controller. At the end of collecting an image in feedback, the free amplitude and phase were recorded by increasing the setpoint until the tip lost contact with the surface so that all the variables needed to compute energy dissipation, excluding the cantilever parameters, were included in each image. The intrinsic Q of the cantilever was used during image collection.

Contact mode and tapping mode force curves were performed with a separate set of tip and samples. For contact mode force curves (equilibrium), the deflection was recorded

using the Nanoscope software. For tapping mode force curves (energy dissipation), the low noise deflection signal was recorded using a high-speed DAQ card (4911, National Instruments). Data was collected at 16-bit resolution using a separate computer equipped with Labview and sampling at 1 MHz while the sample continuously rastered back and forth near the tip. The high sampling rate enabled calculation of amplitude for the fundamental and all higher harmonics that are a part of the energy dissipation equation. Tapping mode force curves were collected for numerous combinations of Q and free amplitude values.

For each experiment, the deflection was recorded using the high-speed DAQ card with the tip in the hard contact region of contact mode force curves for detector sensitivity calculations. The deflection without any tip-sample contact was also recorded to determine the cantilever parameters. After imaging, a deflection time course while tapping was recorded such that the amplitude could be numerically calculated for the calibration of the lock-in amplifier amplitude signal.

Data Analysis. All calculations and data analysis were performed using Igor Pro (v 4, Wavemetrics). For image analysis, the detector sensitivity was calculated from the slope of the contact region in hard contact with the surface and used to scale all deflection data. Cantilever parameters were calculated from the power spectrum of the deflection without tapping drive using the thermal noise technique.⁴ Numerical lock-in techniques, described below, were used to calculate the amplitude of a tapping time course and used to determine the sensitivity of the lock-in amplifier. The images were loaded and scaled for amplitude and phase. Then, the phase offset was carefully calculated from the cantilever parameters and tapping frequency since the drive electronics contribute unknown phase lag. Phase and amplitude data were combined to produce the energy dissipation data. Signals and noise were calculated from the upper and lower right corners of the image for the hydroxyl terminated region and a rhombus fit to the inside of the carboxyl region.

Contact mode force curve analysis similarly started by calculating the sensitivity and cantilever parameters. Numerous force curves were loaded, scaled for force, and offset to zero force in the region of no tip-sample interaction. The curves were subsequently interpolated to be a function of tip-sample distance and offset in the tip-sample distance axis so that each curve overlapped in the contact region. Twenty-eight curves were averaged together to produce the advancing and receding force profiles from the carboxyl terminated SAM surface. Likewise, the force profiles for the hydroxyl terminated surface were the average of nine and seven force profiles for the advancing and receding force profiles, respectively.

For energy dissipation force curve analysis, numerical lock-in techniques were used to calculate phase and amplitude of each harmonic as follows. The deflection time course was multiplied by reference waves to produce in-phase, x_n , and quadrature, y_n , components: $x_n = Deflection \cdot 2\sin(2n\pi ft + \delta)$ and $y_n = Deflection \cdot 2\cos(2n\pi ft + \delta)$, where f is the tapping frequency, δ is an arbitrary phase shift, and n is the index of the harmonic. The products are filtered to remove the high frequency components and phase and amplitude information was computed from the components using $A_n = \sqrt{x_n^2 + y_n^2}$ and $\phi_1 = \tan^{-1}(y_1/x_1)$. Numerical lock-in techniques lack a phase lock loop so the reference frequency needed to be determined with millihertz accuracy, otherwise the phase signal would have a noticeable slope over the length of the time course. Subsequently, the lock-in phase was

corrected and the free amplitude of the fundamental calculated. The amplitudes of numerous higher harmonics of the fundamental motion were included during calculation of the energy dissipation such that the summation in energy dissipation equation converged. During the transition from the repulsive to attractive tapping regime, the amplitude typically increased by as much as 5 Å. Thus, the data for the two regimes were separated so that the Energy Dissipation could be interpolated to be a function of tapping amplitude. Eight curves were averaged together to produce each energy dissipation force curve shown in figure 3.

Derivation of Energy Dissipation equations.

The common paradigm in Atomic Force Microscopy focuses on forces between the tip and sample. During tapping mode, the tip and sample interact with every oscillation and the interaction forces change very rapidly, yet the observational bandwidth is quite small. Understanding the physical origin of the low bandwidth signals requires a shift in thinking from instantaneous forces to accumulated force over a trajectory. Cleveland pioneered this effort by developing a model of cantilever dynamics based on time-averaged power balance.⁵⁻⁷

Cantilever oscillations are maintained by viscous drag, P_{drag} , and tip-sample interaction, P_{tip} , continuously dissipating the power flowing into the system from the sinusoidal drive, P_{in} .

$$\overline{P_{\text{in}}} = \overline{P_{\text{drag}}} + \overline{P_{\text{tip}}}. \quad (\text{S1})$$

The instantaneous power is calculated by multiplying sinusoidal driving force times the velocity of the cantilever,

$$P_{\text{in}} = F_d \sin(2\pi ft) \cdot v(t), \quad (\text{S2})$$

where F_d is the magnitude of the driving force, f is the tapping frequency, and $v(t)$ is the velocity of the cantilever. The cantilever position is not sinusoidal as a result of the tip-sample interaction, but the motion is conveniently expressed as a Fourier expansion of sinusoidal basis functions,

$$x(t) = x_0 + \sum_{n \geq 1} A_n \sin(n2\pi ft - \varphi_n), \quad (\text{S3})$$

where x_0 is the mean deflection, A_n is the amplitude of the n^{th} harmonic, φ_n is the phase change of the n^{th} harmonic, and n is an integer. The velocity is the first derivative,

$$v(t) = \sum_{n \geq 1} 2n\pi f A_n \cos(n2\pi ft - \varphi_n). \quad (\text{S4})$$

The resulting time-averaged power applied to the cantilever is the integral over one period of the force-velocity product,

$$\overline{P_{\text{in}}} = \pi F_d A_1 f \sin(\varphi_1). \quad (\text{S5})$$

Only the phase of the fundamental is important since higher harmonic terms integrate to zero.

The drive force, F_d , is not readily measurable but it can be inferred from the free tapping amplitude, A_{free} , the frequency, f , and the cantilever parameters using the transfer function,⁸

$$F_d = A_{\text{free}} k \frac{f}{f_0} \left(\left(\frac{f_0}{f} - \frac{f}{f_0} \right)^2 + \frac{1}{Q^2} \right)^{1/2}. \quad (\text{S6})$$

Although the convention in AFM is to use A_0 as the free amplitude of the fundamental oscillation, A_{free} is used here for labeling consistency between harmonics. Previously, it

was assumed that the tapping frequency was equal to the resonant frequency such that equation S6 simplified to $F_d = A_{1free}k/Q$. Since the tapping frequency is frequently chosen to be less than the resonant frequency to achieve stable feedback, this assumption is invalid and can lead to inaccuracies. Similarly, off resonance tapping and electronic circuit delays change the free phase lag. The proper free phase lag can be calculated from the transfer function,

$$\varphi_{1free} = \tan^{-1} \left(\frac{ff_0}{Q(f_0^2 - f^2)} \right). \quad (S8)$$

The viscous drag is calculated from the dampening force times the velocity. The dampening force is the damping constant b times the velocity such that

$$\overline{P_{drag}} = \int_{t \rightarrow t+1/f} b \cdot v(t)^2 dt = 2b\pi^2 f^2 \sum_{n \geq 1} n^2 A_n^2 = \frac{\pi k f^2}{Q f_0} \sum_{n \geq 1} n^2 A_n^2. \quad (S9)$$

Every cross harmonic term integrates to zero but the diagonal terms are non-zero. The final equality substitutes the damping b for cantilever parameters, k , f_0 and Q , using $b = k/2\pi Q f_0$. If the repulsive interaction is stiff and the cantilever Q is low, then nontrivial drag power is contained in the higher harmonics, which must be included during the calculation.

From the input power and viscous dissipation, the energy dissipated by the tip-sample interaction is easily calculated,

$$\overline{P_{ip}} = \frac{\pi k f^2}{f_0} \left[A_1 A_{1free} \left(\left(\frac{f_0}{f} - \frac{f}{f_0} \right)^2 + \frac{1}{Q^2} \right)^{1/2} \sin(\varphi_1) - \frac{1}{Q} \sum_{n \geq 1} n^2 A_n^2 \right]. \quad (S10)$$

To obtain the energy dissipation per tap divide by f .

References

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