The NanomechPro™ Toolkit: Accurate Tools for Measuring Nanoscale Mechanical Properties for Diverse Materials

Understanding nanoscale mechanical properties is of fundamental importance for evaluating the behavior and performance of a wide variety of industrially, biologically and structurally important materials. An Atomic Force Microscope (AFM) tip interacting with a sample experiences forces originating from many different sources – elasticity, viscosity, adhesion, van der Waals – to name a few. Hence, it has become increasingly clear that reliable and accurate materials properties measurements require looking at your sample in more than one way. Single techniques are simply insufficient for accurately and rigorously revealing sample properties and can often yield misleading and even inaccurate results and conclusions.

Figure 1: The NanomechPro Toolkit comprises a suite of accurate tools for measuring the nanoscale mechanical properties of diverse materials. The various tools are complementary – each technique probes and records different responses of your samples.

The NanomechPro™ toolkit (Figure 1) for Asylum's Cypher™ and MFP-3D™ AFMs provides a suite of tools to meet the requirements of the nano-mechanics researcher and is both impressively powerful and rapidly expanding. The various tools are complementary – each technique probes and records different responses of your samples – and often can be used simultaneously (e.g. Figures 2a - d). Additionally, with the Cypher AFM, many of these new techniques can be combined with small, fast, low noise cantilevers, enabling measurements at noise levels and speeds previously impossible.

Combined Loss Tangent and AM-FM Imaging

Amplitude-modulated (AM) atomic force microscopy, also known as tapping mode or AC mode, is a proven, reliable and gentle imaging method with widespread applications. Previously, the contrast in tapping mode has been difficult to quantify. However, in this work we introduce two new techniques that allow unambiguous interpretation of material properties in tapping mode: AM-FM and Loss Tangent. Because these measurements are made simultaneously, there is a built-in check for self-consistency in the measurements. The new AM-FM imaging technique combines the features and benefits of normal tapping mode with the quantitative, high sensitivity of Frequency Modulation (FM) mode. Both Loss Tangent and AM-FM imaging can be performed simultaneously at high data acquisition rates. These techniques are exclusively available from Asylum Research, US patents 8,024,963, 7,937,991, 7,603,891, 7,921,466 and 7,958,563 with others pending.

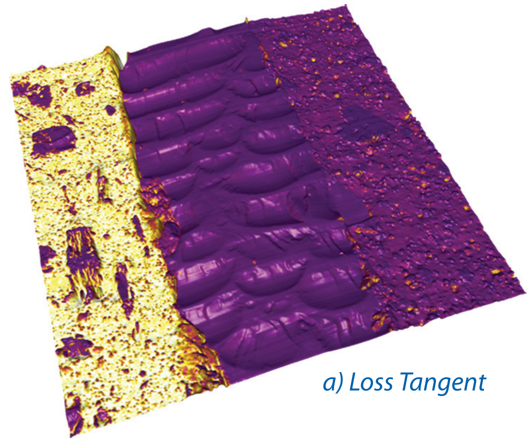
Loss Tangent

Loss Tangent imaging (Figure 2a) is a recently introduced quantitative technique that recasts the interpretation of phase imaging into one term that includes both the dissipated and stored energy of the tip sample interaction. At the same time, tip-sample interaction modulates the frequency of the second resonant mode. The quantitative frequency shift depends on the sample stiffness and can be applied to a variety of physical models. These techniques allow high speed, low force imaging in tapping mode while providing quantitative elasticity and Loss Tangent images.

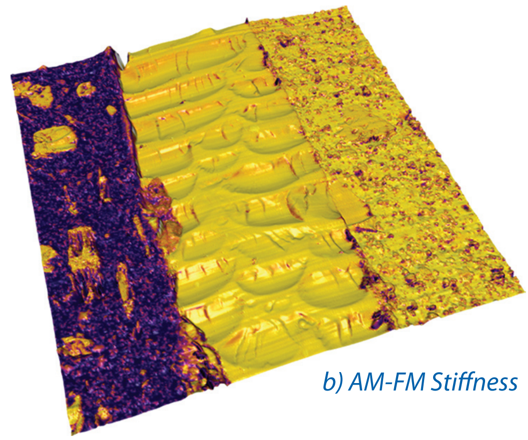
AM-FM Imaging

AM-FM imaging (Figure 2b, c) combines the features and benefits of normal tapping mode (also called AM) with fast scanning and quantitative, high sensitivity Frequency Modulation (FM) mode. The topographic feedback operates in normal tapping mode, providing non-invasive, high quality imaging. The second mode drive frequency is adjusted to keep the phase at 90 degrees, on resonance. This resonant frequency is a sensitive measure of the tip-sample interaction. Simply put, a stiffer sample shifts the second resonance to a higher value while a softer sample shifts it to a lower value. This can be converted into a quantitative modulus measurement through a variety of mechanical models (see below).

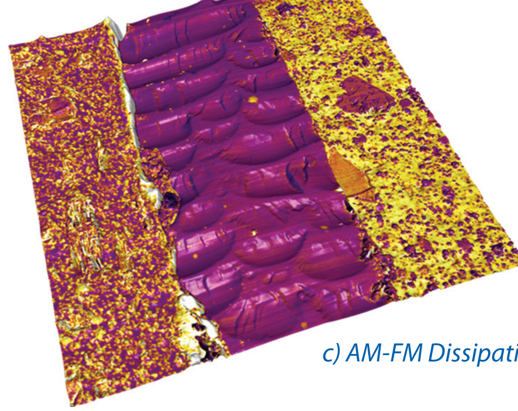
As with conventional FM mode, AM-FM is a quantitative technique where the conservative and dissipative tip-sample interactions can be separated. Where AM-FM differs from FM is that the Z-feedback loop is completely decoupled from the FM loop, both greatly simplifying and stabilizing operation.



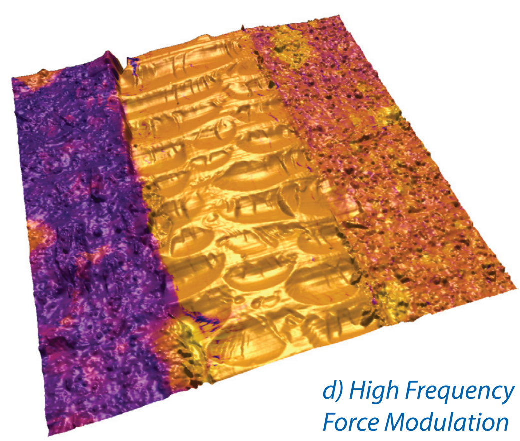
a) Loss Tangent



b) AM-FM Stiffness



c) AM-FM Dissipation



d) High Frequency Force Modulation

Figure 2: Images of a Viton®/epoxy/EPDM (left to right) sandwich. The quantitative Loss Tangent data shown in (a) clearly indicates the higher Loss Tangent of the Viton. The stiffness is measured by tracking the resonance frequency of the second mode (b), clearly resolving the difference in the elastic moduli of the Viton (Shore A 78) and the EPDM (Shore A 58). The AM-FM dissipation, related to the loss modulus is shown in (c). Finally, the Force Modulation Amplitude image (d) also shows the stiffness measured with a second technique, at much higher penetration depth, providing complementary information to the AM-FM results in (b).

High Frequency Force Modulation

Using a new high frequency cantilever holder (Figure 3), we have breathed new life into the technique of traditional force modulation. The high frequency cantilever holder allows force modulation to be performed over a wide range of frequencies at high amplitudes. Thus the new high frequency force modulation provides increased and often uniquely different contrast to reveal sample mechanical properties with applications in many new areas (Figure 2d).

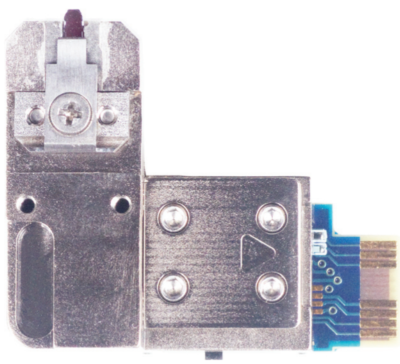


Figure 3: The high frequency cantilever holder is required for AM-FM imaging and has also rejuvenated the traditional force modulation technique with added capability and broader applications (shown is the Cypher High Frequency Cantilever Holder).

Contact Resonance

Contact Resonance (CR) AFM is a contact mode technique in which the sample is actuated at the contact resonance frequency to yield quantitative measurements of elastic modulus (Figure 4). Developed in the late 1990s for use on very stiff materials (>50 GPa), CR techniques originally involved measurements at a fixed position on a sample. In the last decade, CR methods were adapted for quantitative imaging (mapping) of elastic modulus. In the last two or three years, CR techniques have been further modified for use on more compliant materials (modulus ~1 GPa to 10 GPa) and for measurements of viscoelastic properties. Our proprietary Dual AC™ Resonance Tracking (DART) and Band Excitation (BE) techniques allow the contact resonance to be imaged at high rates on a variety of samples. Figure 4 shows a DART image of a 80/20 polypropylene/ polystyrene blend. Because both the resonance frequency and quality factor are measured with DART, we can detect both differences in the elasticity and differences in the dissipation.

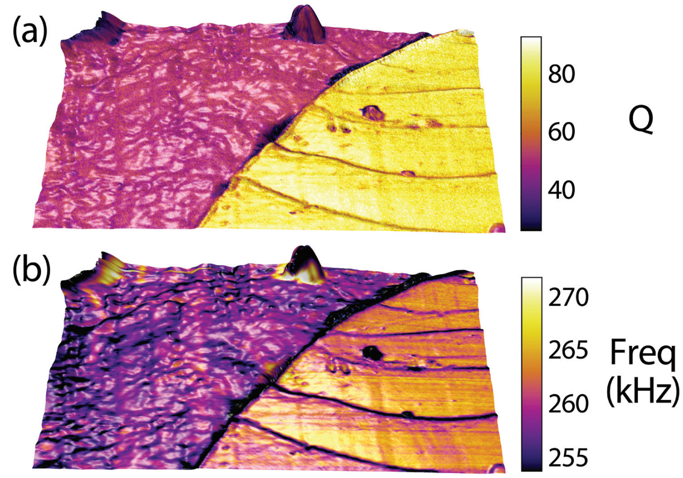


*Figure 4: A 4.5µm x 9µm contact resonance image of the cryotomed surface of an 80/20 polypropylene/polystyrene blend. The calculated Quality factor painted on the rendered topography is shown in (a) and contact resonance f_0 on topography is shown in (b). The PP and PS regions display less contrast in f_0 consistent with a small difference in their bulk storage moduli, while the higher contrast in Q between PP and PS is consistent with a large difference in their bulk loss moduli. Adapted from Gannepalli et al. Nanotechnology **22** 355705 (2011).*

Vertical Nanoindenting

The MFP NanoIndenter is a true instrumented indenter and is the first AFM-based indenter that does not use cantilevers as part of the indenting mechanism. These characteristics and the use of state-of-the-art AFM sensors provide substantial advantages in accuracy, precision and sensitivity over other nanoindenting systems. Unlike cantilever indenters, the MFP NanoIndenter moves the indenting tip perpendicular to the surface. This vertical motion avoids the lateral movement and errors that are inherent in cantilever-based systems. Compared to conventional commercially-available instrumented nanoindenters, the MFP NanoIndenter provides lower detection limits and higher resolution measurements of force and indentation depth with the superior precision of AFM sensing technology.

The indenter is completely integrated with the AFM, providing the unique ability to quantify contact areas by performing AFM metrology of both the indenting tip and the resulting indentation (Figure 5 and 6). These direct measurements enable analysis of material properties with unprecedented accuracy relative to indirect calculation methods. The design uses passive actuation through a monolithic flexure, minimizing drift and other errors in depth measurement.

The positioning accuracy in the sample plane is sub-nanometer using the MFP-3D's closed loop nanopositioning sensors. The NanoIndenter Head utilizes advanced diffraction-limited optics coupled with CCD image capture for precision navigation of the tip to areas of interest on the sample.

This highly quantitative tool, combined with high-end AFM capabilities, breaks new ground in the characterization of diverse materials including thin films, coatings, polymers, biomaterials, and many others.

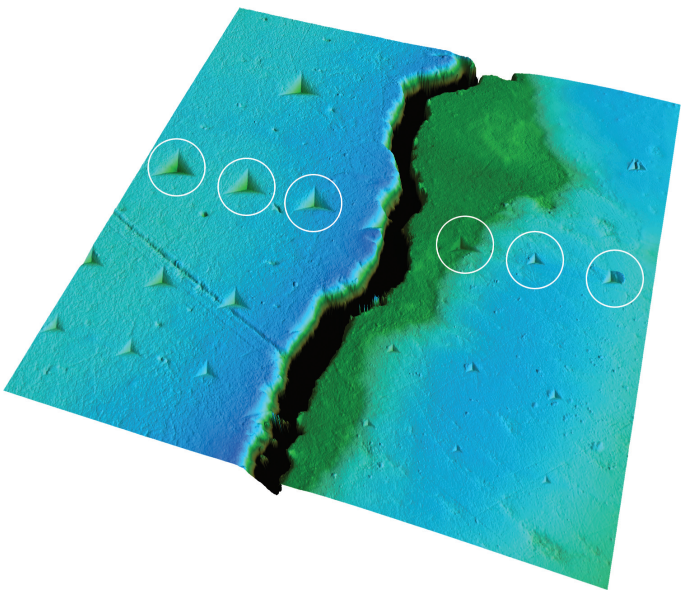


Figure 5: Indentation on dentin (left of crack) and enamel (right). The indentations in each row (one row is circled) were all created with the same maximum force. The smaller indents on the enamel demonstrate that it is harder than the dentin, 70µm scan. Corresponding force curves are shown in Figure 6. Sample courtesy D. Wagner and S. Cohen, Weizmann Institute of Science.

Force Curves, Force Mapping and Force Modeling

Force Curves

Force curves measure the amount of force experienced by the cantilever as the probe tip is brought towards, in contact with, and/or pulled away from the sample surface (Figure 7). This process can be repeated at a single location or as the probe is moved to different positions on the sample surface (Figure 6).

Force curves can be used to examine mechanical properties of materials (hardness, adhesion, elastic-

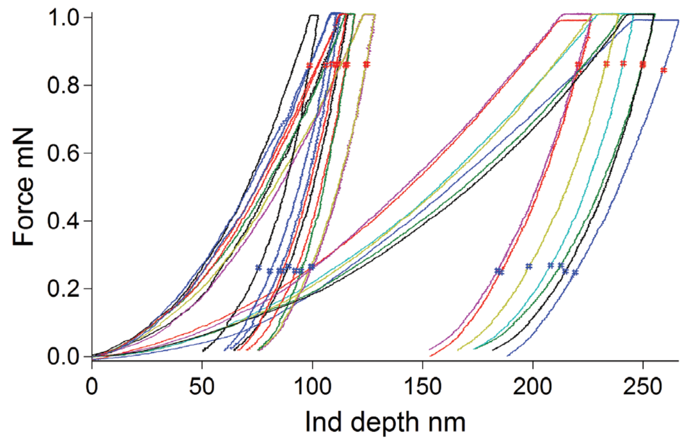


Figure 6: Indentation force curves on enamel (left set of curves, stiffer) and dentin (right set of curves, softer). Variability obeys both real material variation and contact area effects which can be quantified with AFM images of indents.

ity...), chemical characteristics (such as affinity of various functional groups for others), as well as intra- and intermolecular bond strengths and folding strengths.

Force Mapping

Force mapping is a data acquisition technique that is used in concert with various force curve analysis routines for visualization of the 2D distribution of sample properties. For force mapping, an XY array of force curves is taken at regularly spaced intervals

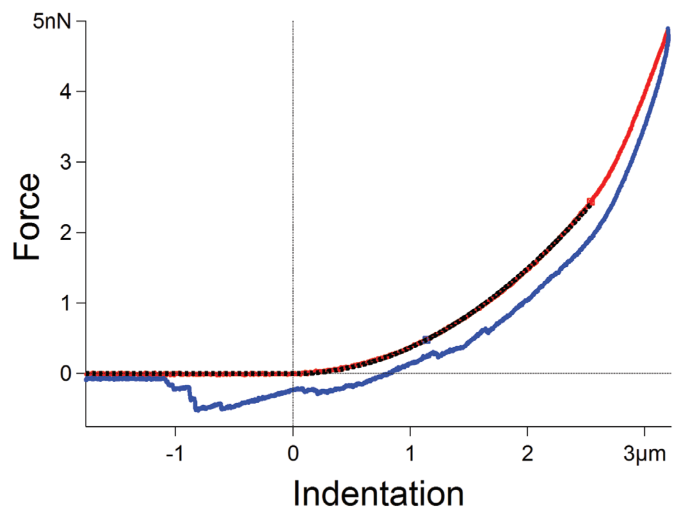


Figure 7: Force curve showing indentation onto a polyacrylamide gel. An AFM tip was indented onto a polyacrylamide gel substrate used for cell culture. The gel was fabricated to have a modulus of approximately 700 Pa. Applying the Hertz model (dashed black line) to the indentation part of the curve (red) shows a measured modulus of 720 Pa, in good agreement with the expected value.

across the sample surface. The resulting array of force curves is often referred to as a Force Map or a Force Volume. The user first specifies an area of interest, usually by either taking an AFM scan of the area or by optically aligning the AFM scan area with the sample. Once the desired array size and data density (or, number of force curves per area) are set, the XY piezo moves the sample under the tip and force curves are taken at the specified locations. Data are saved as discrete force curves for later analysis and various automated analysis routines can then be performed. For example, a height map can be calculated from the trigger point of each curve, adhesion maps can be calculated from the maximum point of adhesion at each location, and elasticity models can be applied to each force curve. The results of the analysis are plotted as a 2D pseudo-color image. This 2D image can be adjusted just as any AFM image, and can also be used for overlay with 3D topography data or with optical microscopy data (Figure 8). This is a powerful technique, as it allows for direct correlation of functional information to structural data.

Force Modeling

Asylum's AFM software includes various mathematical models that are applied to force curve data to determine a sample's mechanical properties (e.g. Figure 7). Due to the wide variety of sample types that can be analyzed with AFM, no single model can be used to correctly determine the properties of all samples. Further, most models rely on assumptions about the tip, the sample, or the tip-sample contact that can change among different samples or, perhaps more importantly, even across different force curves for the same sample. For example, tip geometry is crucial when analyzing indentation data, so various geometries can be modeled (cone, sphere, punch, cube corner, Berkovich, etc...) to account for the wide variety of standard and modified AFM tips, in addition to instrumented indenter tips. In each model the Asylum software allows for various assumptions to be modified as needed by the investigator. Included in the Asylum software are:

- **Hertz/Sneddon Model:** This popular model is applied to many samples analyzed by AFM, and is generally used when the indentation is assumed to be on a fully elastic, non-adhesive, homogenous material (Figure 7). This model is used widely in biology, where the mechanical properties of cells and their environment have been found to influence function.
- **Oliver-Pharr Model:** This model is used when the sample exhibits permanent, plastic deformation. It is mostly used on data obtained with instrumented indentation devices like the Asylum Research NanoIndenter. It is used extensively in materials sciences.
- **Johnson-Kendall-Roberts (JKR) Model:** The JKR model is used when there is strong adhesive contact between the tip and the sample, and when the size of the tip is large compared to the indentation on the sample.

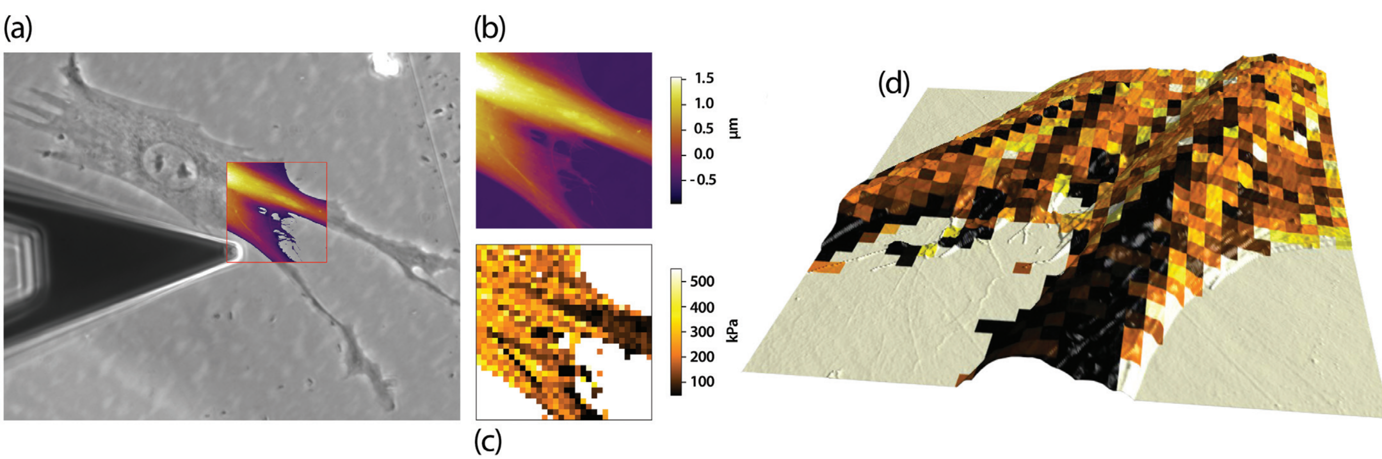


Figure 8: Force Mapping used for imaging and sample property measurements. The optical phase contrast image of a cell with the cantilever hovering over it, and with an optically defined region of interest (red box) for force mapping is shown in (a). After the AFM topographic scan (b), the elasticity force map was taken and analyzed using the Hertz model (see explanation below) and the modulus values were plotted and displayed as a 2D image (c). The modulus map was overlaid onto the AFM topography image and rendered in 3D using the Asylum ARgyle software in (d).

- **Derjaguin-Muller-Toporov (DMT) Model:** The DMT model is useful for samples that have weak but detectable adhesive forces, and when the tip size is small compared to sample indentation. Like the JKR model, DMT is starting to see more widespread application to various areas of indentation analysis.
- **Model Selection Guide,** including plasticity index, force/adhesion ratio, and Tabor Coefficient calculation.

Asylum's exclusive model selection guide analyzes various parameters to guide the user to the most appropriate mechanical model for their data. For example, when there is tip-sample adhesion, the software will notify the user that the Hertz model is not appropriate, and that a model that includes adhesion should be used. The calculated selection parameters are always displayed to the user so that an informed decision can be made.

Additional detail and examples of the various force modeling techniques is provided elsewhere.

Summary

As discussed, understanding nanomechanical properties is of fundamental importance for evaluating the behavior and performance of a wide variety of industrially, biologically and structurally important materials. Because of the complexity of these materials, no single tool provides the detailed and accurate information required for these evaluations.

The NanomechPro toolkit for Asylum's Cypher and MFP-3D AFMs provides a suite of tools to help the researcher examine and understand these nanoscale mechanical properties for a wide range of materials – these include elasticity, viscosity, adhesion, and van der Waals forces, among others. The various NanomechPro tools are complementary – each technique probes and records different responses of your samples. These tools can often be used simultaneously and several of these techniques are proprietary to Asylum Research, providing the researcher with accurate and unambiguous information not available with any other tool.

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