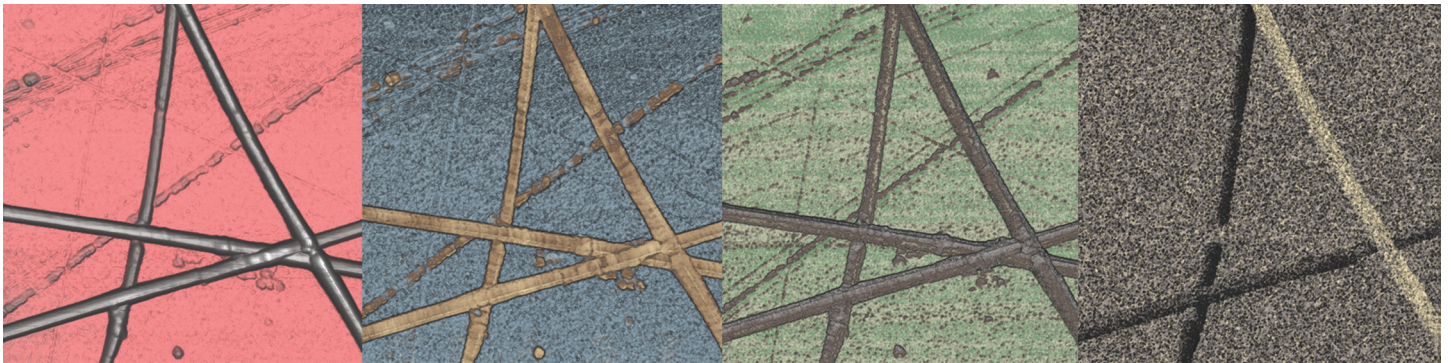


HybriD Mode

Rebirth of Force Spectroscopy: Advanced Nanomechanical, Electrical, Optical, Thermal and Piezoresponse Studies

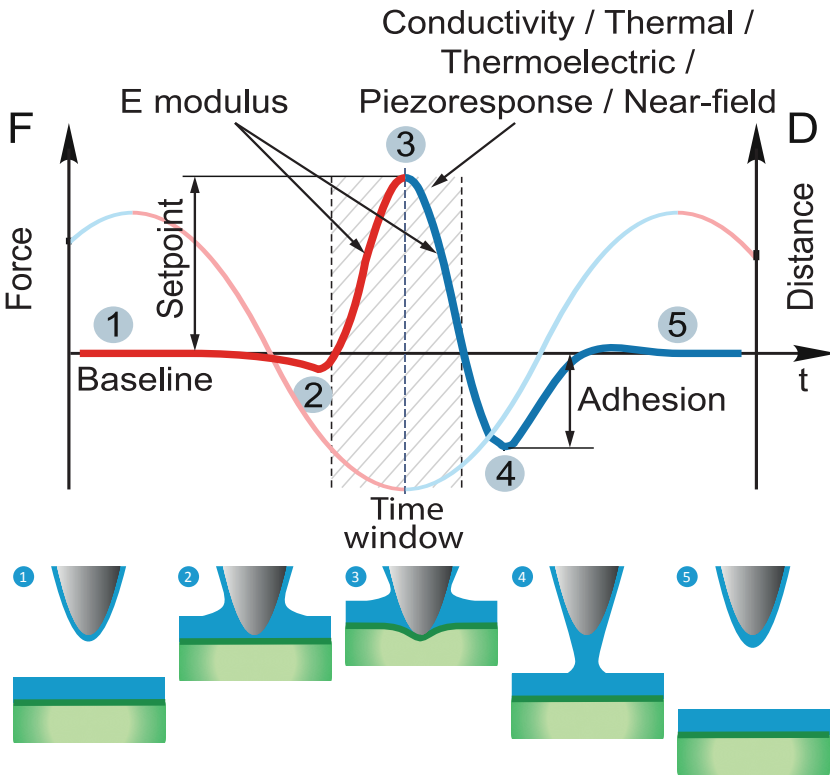
- Fast Quantitative Nanomechanical Measurements and Force Volume
- Simultaneous Electrostatic and Non-destructive Conductivity, Piezoresponse and Thermal Studies
- Advanced Cantilever-Type Tip-Enhanced Raman Scattering and Scanning Near-Field Optical Microscopy



Non-destructive HybriD PFM study of diphenylalanine peptide nanotubes. From left to right: topography, adhesion, Young's modulus and in-plane piezoresponse phase. Scan size: 7×7 μm

GENERAL INFORMATION

HybriD mode (HD mode) – scanning technique based on fast force-distance curves measurements with real-time processing of tip response.



HybriD (HD) mode operation principle: time dependency of tip trajectory (dashed) and tip-sample force interaction (solid)

Measured properties:

- Topography in Attraction and Repulsive Regimes
- Young's Modulus and Force Volume
- Adhesion and Work of Adhesion
- Conductivity
- In-Plane and Out-of-Plane Piezoresponse
- Temperature and Thermal Conductivity
- Thermoelectric
- Electrostatic: Kelvin Probe Force, Electrostatic Force and Scanning Capacitance Force Microscopy
- Near-Field Component of Optical Response
- Tip-Enhanced Raman Scattering

HybriD mode working principle

In HybriD mode the tip-sample distance is modulated according to the quasi-harmonic law. Thus tip enters a force interaction with the sample thousands times per second. Force-distance curve analysis enables maps of topographical, nanomechanical, electrical, thermal and piezoelectric properties of the sample to be extracted with high spatial resolution and minimized lateral forces.

High-performance electronic components and unique algorithms implemented in

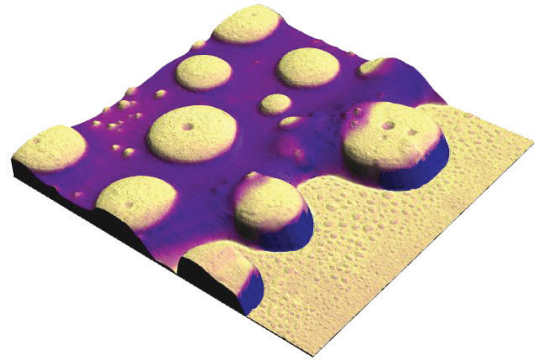
the state-of-the-art HybriD 2.0 Control Electronics provide superb level of real-time signal processing and analysis.

Combining mode with cutting-edge optical microscopy and spectroscopy techniques opens-up novel opportunities of cantilever-based tip-enhanced Raman scattering (TERS) and scattering scanning near-field optical microscopy (s-SNOM).

HD QUANTITATIVE NANOMECHANICAL MEASUREMENTS

Fast mapping and real-time calculation of quantitative nanomechanical properties (QNM)

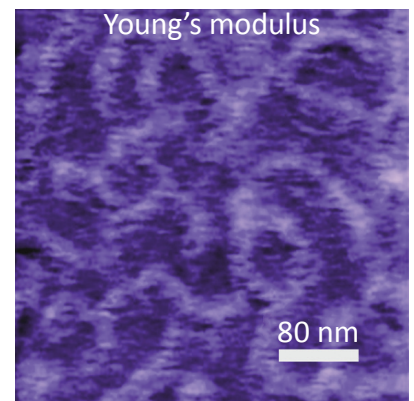
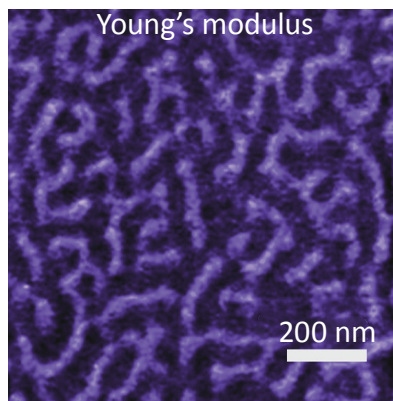
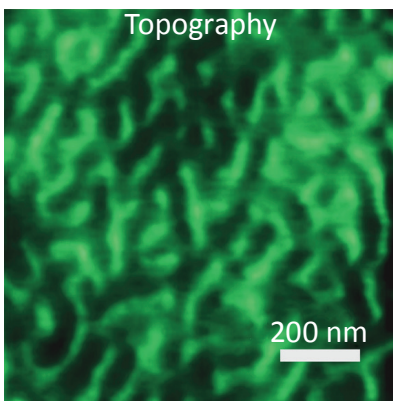
Force spectroscopy is a well-known AFM technique for quantification of local nanomechanical properties. HD mode allows fast, more than 1000 force curves per second measurements, real-time calculation of Young's modulus according to Hertz, DMT, JKR and other mathematical models and automated cantilever force constant calibration.



Polystyrene-polybutadiene blend on silicon substrate. Topography is overlaid by Young's modulus maps. Scan size: $4 \times 4 \mu\text{m}$

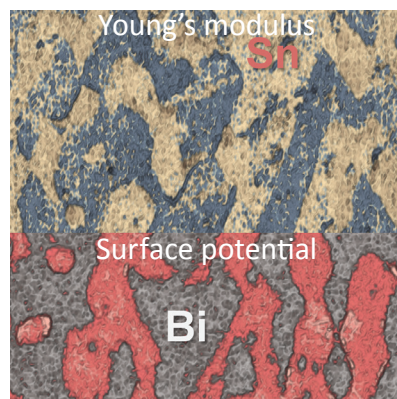
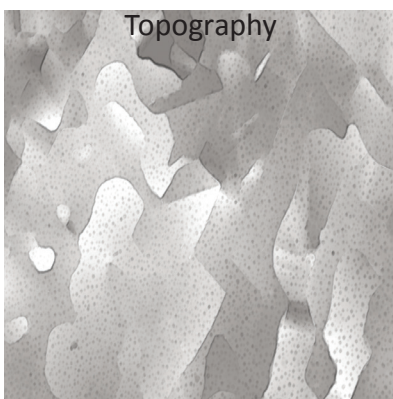
Ultimate spatial resolution

HD mode ensures less than 10 nm spatial resolution of QNM maps.



HD QNM study of PS-b-PMMA. Right image demonstrates around 10 nm spatial resolution

Braking the force limit



HD QNM study of Tin-Bismuth alloy. Scan size: $10 \times 10 \mu\text{m}$

HybriD Mode uniquely enables stiff materials to be distinguished from each other by means of an AFM probe. Areas corresponding to Bismuth (32 GPa, blue color) and Tin (50 GPa, yellow color) are clearly identified. The mechanical properties map corresponds well with the surface potential image.

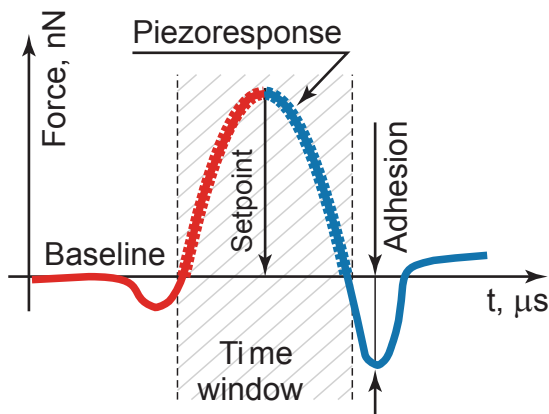
HD PIEZORESPONSE FORCE MICROSCOPY

Non-destructive PFM studies simultaneously with QNM and Electrostatic measurements

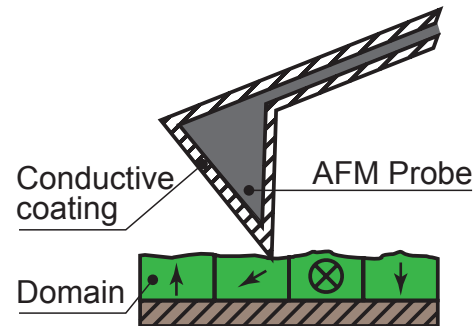
In HD Piezoresponse Force Microscopy mode (HD PFM) an AC voltage is applied to the conductive AFM cantilever when the tip comes in contact with the sample during each fast force spectroscopy cycle. Applied AC voltage causes mechanical oscillations of the piezoelectric (ferroelectric) sample. Corresponding vertical and lateral motions of the AFM tip are recorded and processed to get the amplitude and phase characterizing the local piezoelectric coefficient and local polarization direction respectively. Since the AFM tip retracts from the surface in each scanning point, the lateral tip-sample interaction force is significantly reduced in

comparison to the conventional contact PFM technique. This provides new capabilities for piezoresponse studies of soft, loose and fragile objects like biological samples, nanoparticles etc.

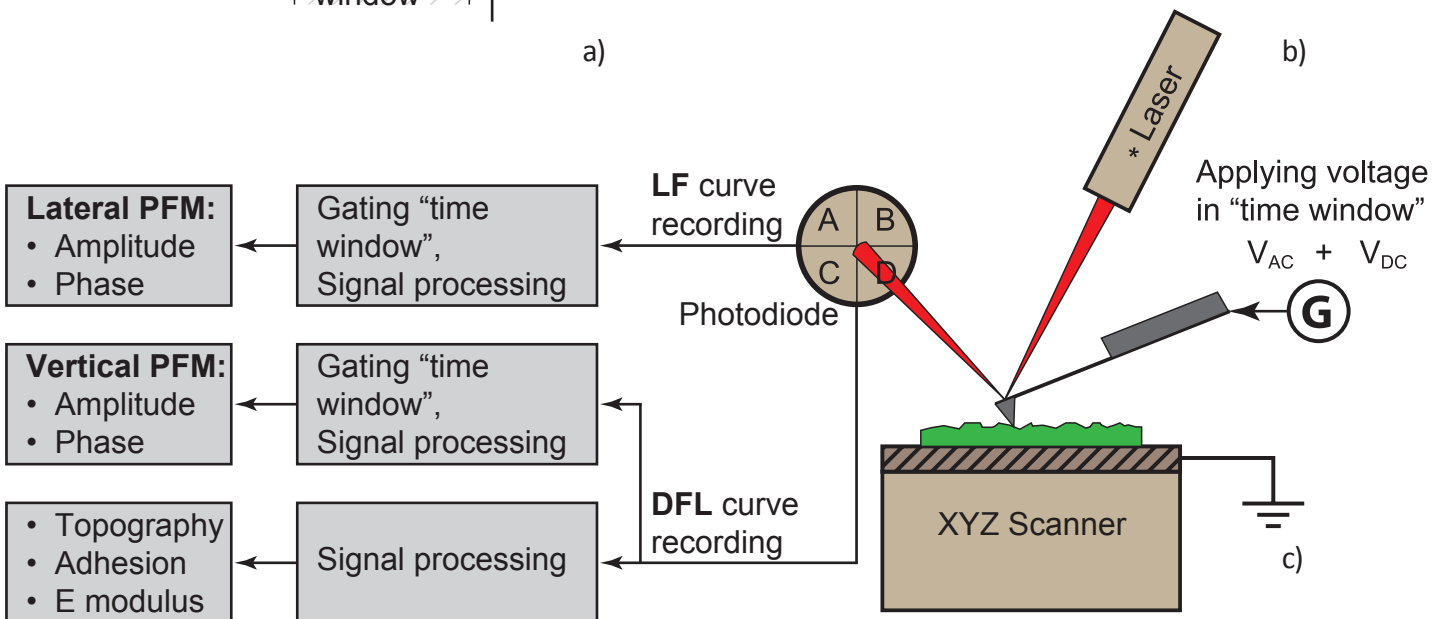
Furthermore an AFM cantilever of higher stiffness and resonance frequency can be used. Therefore the ability of two-pass resonant electrostatic measurements was implemented: Kelvin probe microscopy or Electrostatic force microscopy can be used simultaneously with topography, adhesion, E modulus and piezoresponse studies.



a)

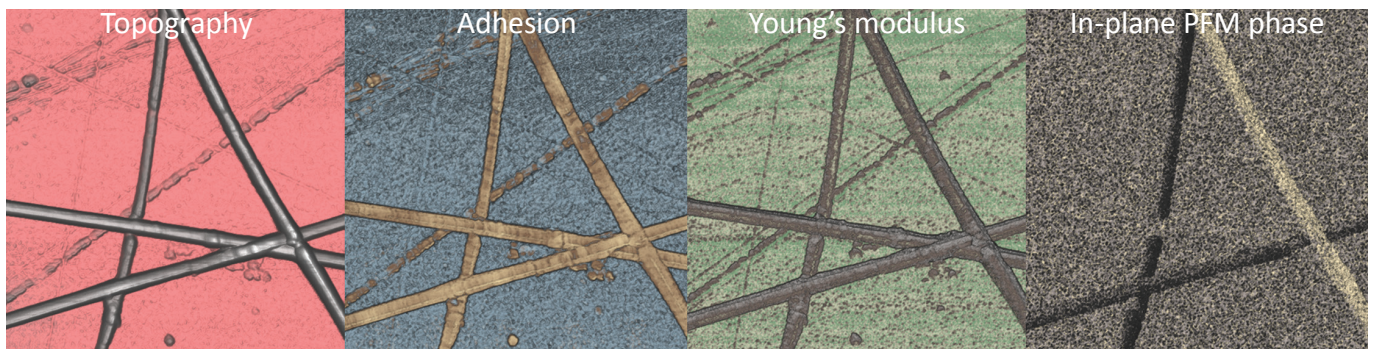


b)

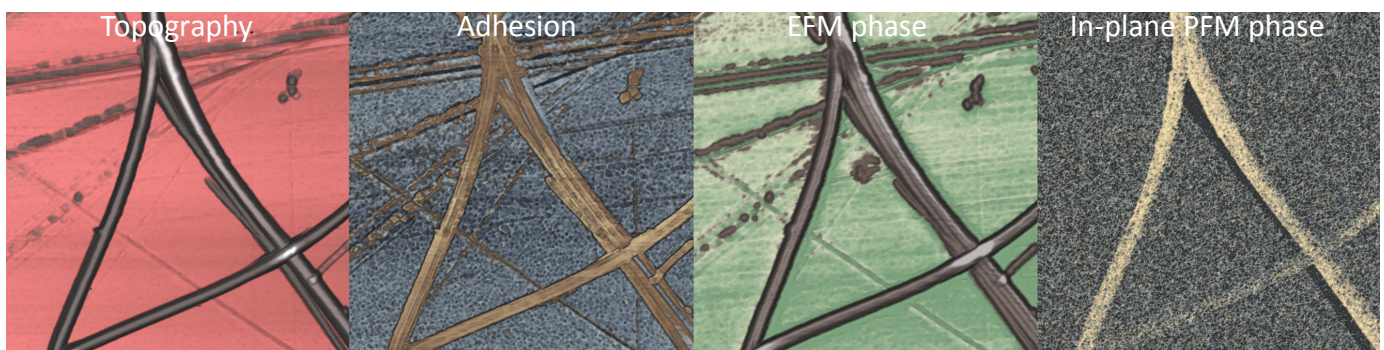


c)

HD PFM working principle: a) an idealized temporal deflection curve during an oscillatory cycle, b) tip-sample interaction in "time window", c) measurement scheme

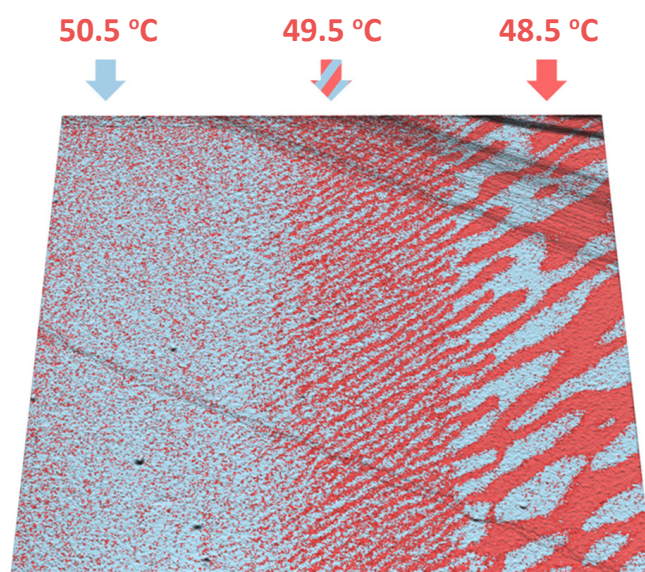


Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Sample courtesy: Dr. A. Kholkin, University of Aveiro.
Scan size: $7 \times 7 \mu\text{m}$, nanotubes diameter: $70 \pm 100 \text{ nm}$



Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Sample courtesy: Dr. A. Kholkin, University of Aveiro.
Scan size: $8 \times 8 \mu\text{m}$, nanotubes diameter: $30 \pm 150 \text{ nm}$

Real-time PFM studies under varying temperature

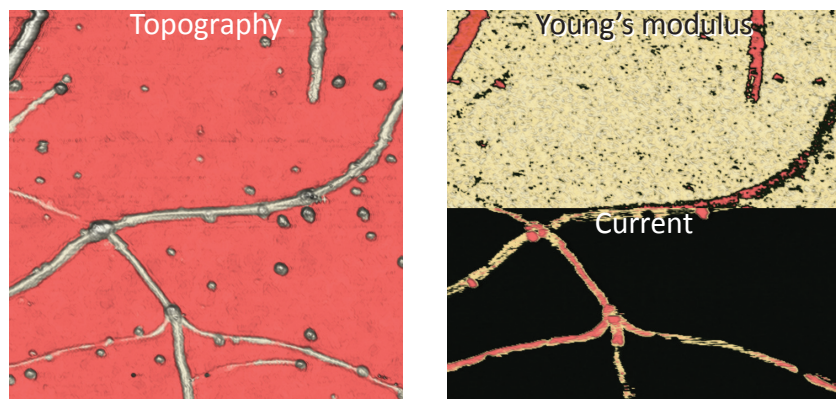


Topography of triglycine sulfate crystal overlaid with vertical piezoresponse phase. Image illustrates real-time observation of the second-order phase transition. The sample temperature was changed during scanning. Sample courtesy: Dr. R. Gainutdinov, IC RAS.
Scan size: $15 \times 15 \mu\text{m}$

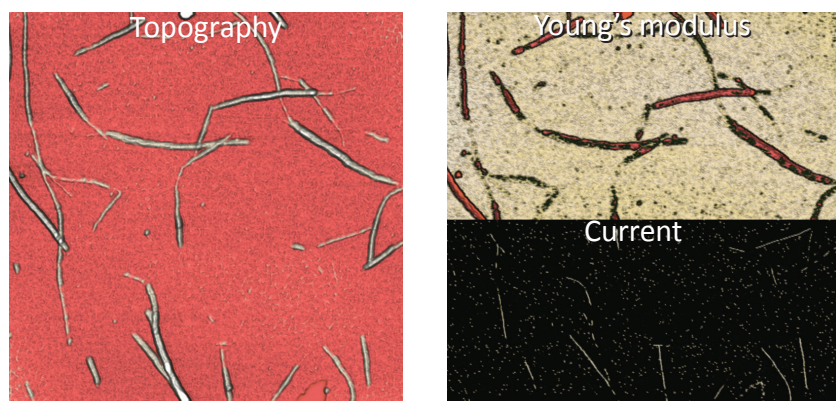
Another important characteristic of HybriD Piezoresponse Force Microscopy is its ability to perform electromechanical studies under varying temperature of the sample. A unique feature implemented in this mode is an automatic compensation of the thermal drift of the AFM probe at each point.

HD CONDUCTIVE & ELECTROSTATIC STUDIES

Non-destructive Conductive studies simultaneously with QNM measurements



HD C-AFM study of carbon Nanotubes on Silicon. Sample courtesy: Dr. Kuljanishvili, Saint Louis University, Department of Physics. Scan size: $1 \times 1 \mu\text{m}$



HD C-AFM study of coupled carbon and peptide nanotubes. Sample courtesy: Dr. J. Montenegro, University Santiago de Compostela. Scan size: $3 \times 3 \mu\text{m}$

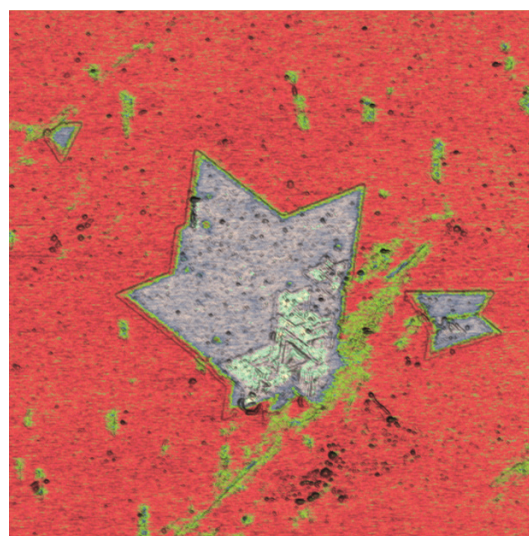
Electrical characterization of objects, that are weakly attached to the surface, has always been a challenge when using standard AFM modes like Conductive AFM. This was because often the tip moved or abraded the objects of interest. HybriD Mode drastically decreased the impact of lateral forces and simplified these experiments.

Comparison of conductive and mechanical maps shown in this example allows the clear identification of single nanotubes and bundles.

Simultaneous electrostatic studies: HD KPFM, HD EFM and HD SCFM

New state-of-the-art HybriD 2.0 control electronics allows simultaneous resonant electrostatic studies using two-pass technique:

- Kelvin Probe Force Microscopy
- Electrostatic Force Microscopy
- Scanning Capacitance Force Microscopy



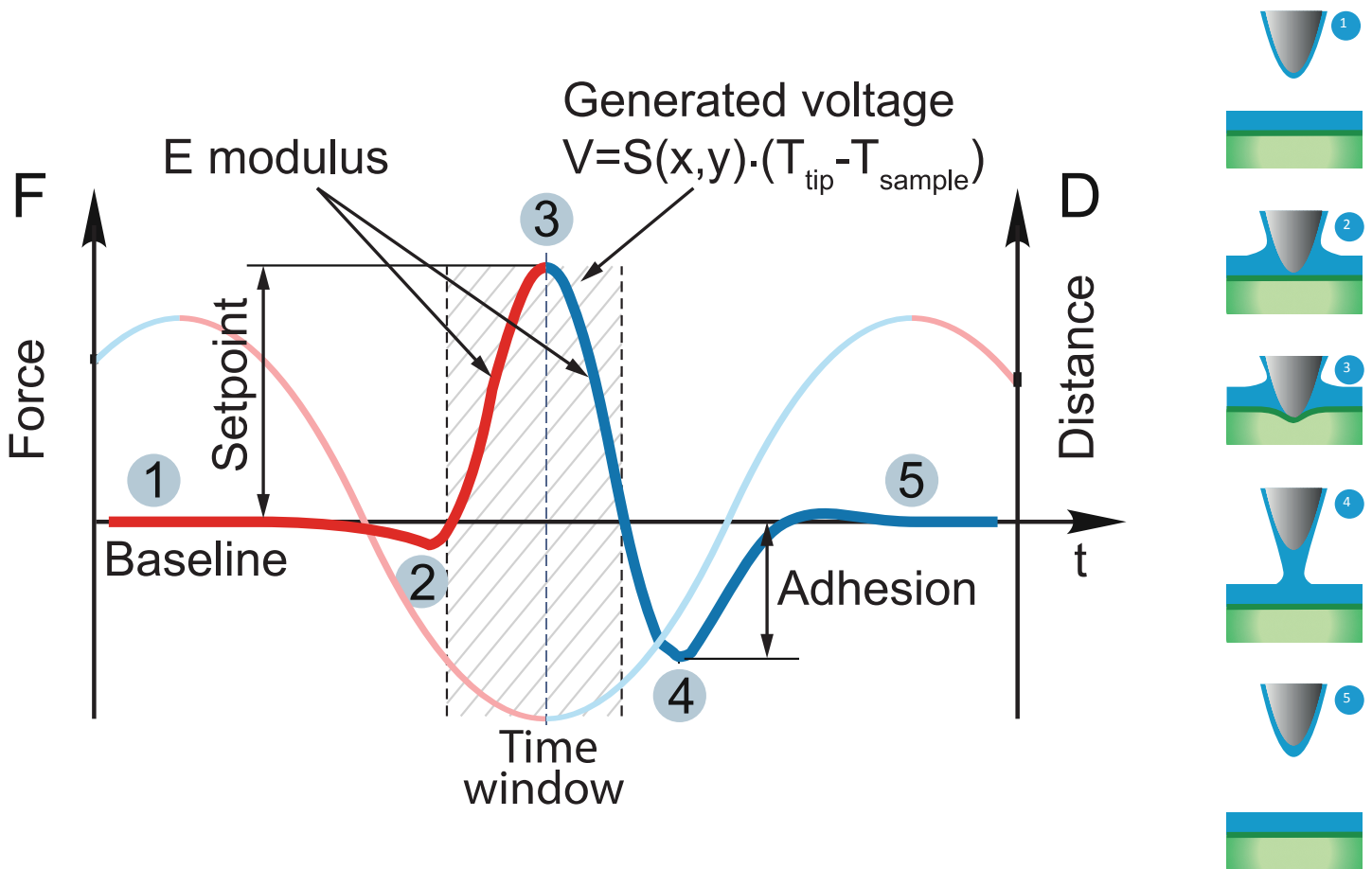
HD KPFM study of WS_2 monolayers grown on epitaxial graphene measured in vacuum. Topography is overlaid with surface potential. Sample Courtesy: Dr. Cristina Giusca, NPL, Prof. Mauricio Terrones, PSU Scan size: $14 \times 14 \mu\text{m}$

HD SCANNING THERMOELECTRIC MICROSCOPY

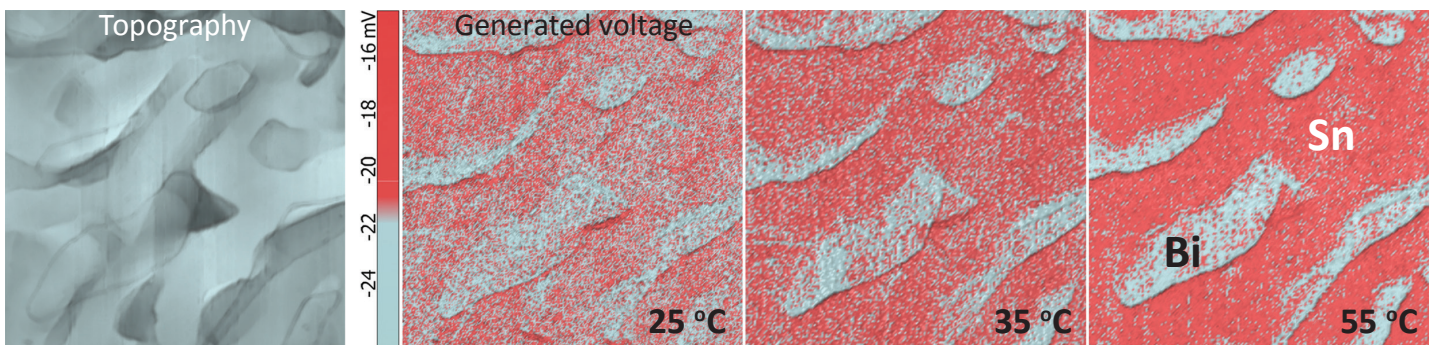
Mapping of local Seebeck coefficient by HD Scanning Thermoelectric Microscopy

Thermoelectric studies of nanoscale structures like n-p junctions, conductive nanowires, graphene oxide etc. are currently of a great interest. HD Scanning Thermoelectric Microscopy (HD SThEM) allows non-destructive mapping of Seebeck coefficient with tip radius-limited spatial

resolution. HD SThEM working principle is based on direct measurement of generated voltage when conductive tip and sample under different temperatures contact each other during fast force spectroscopy measurements.

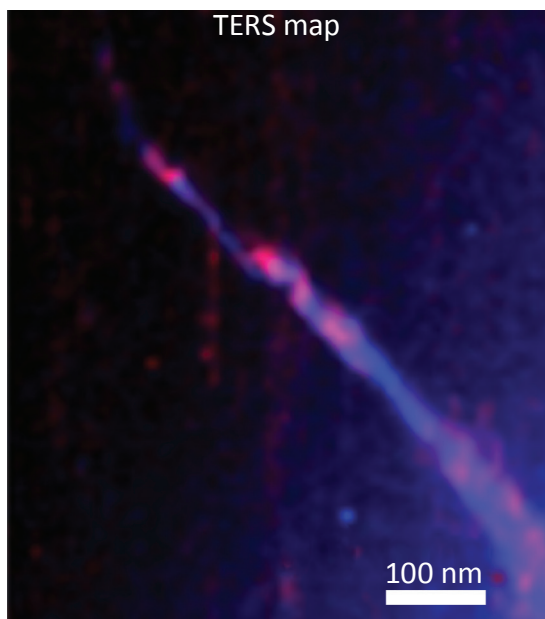


HD Scanning Thermoelectric Microscopy working principle, V – generated voltage, $S(x,y)$ – Seebeck coefficient



HD SThEM study of Tin-Bismuth alloy. Seebeck coefficient, S : Bi -72 mV/C, Sn -1.5 mV/C. Scan size: $7 \times 7 \mu\text{m}$

HD TERS: cantilever-type tip-enhanced Raman scattering



High resolution TERS map of carbon nanotubes on Au substrate. Resolution: ~ 10 nm. Overlay of G-band (blue) and D-band (red)

Tip Enhanced Raman Scattering (TERS, nano-Raman) is the technique for enhancement of weak Raman signals and for super-resolution Raman imaging with spatial resolution less than 10 nm.

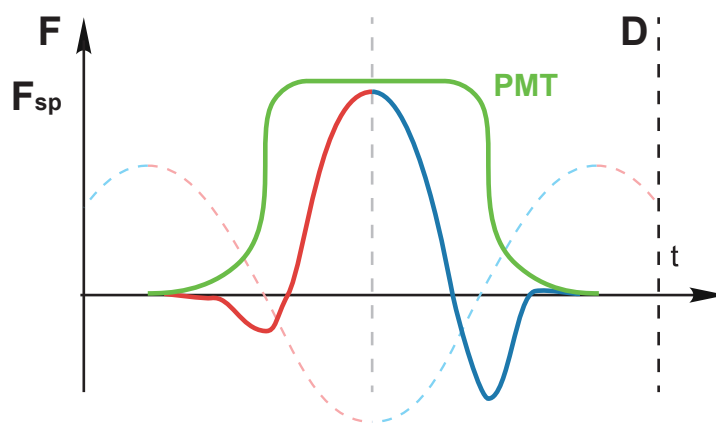
As a result of comprehensive research performed together with NT-MDT SI customers and partners, we are now able to offer to AFM-Raman customers mass produced reproducible TERS probes.

TERS imaging requires prolonged tip-sample contact at each scanning point but Contact AFM is destructive for both the tip and the sample. Thereby, HD mode is a superior technique for cantilever-type TERS since it noticeably increases the tip lifetime and makes possible TERS imaging of soft, loose and fragile samples.

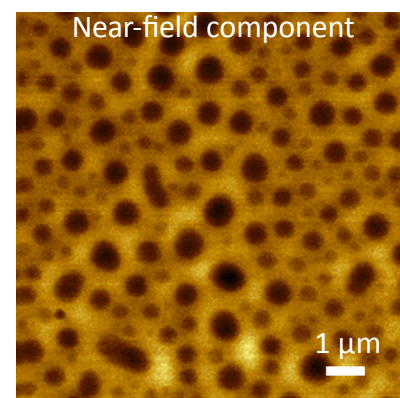
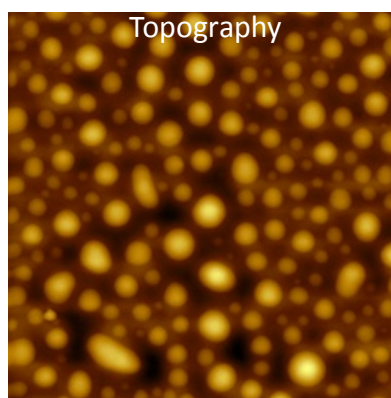
Advanced Scattering Scanning Near-field microscopy

Thanks to high-speed HybriD 2.0 Control Electronics the approach and withdrawal optical response signal curve (PMT) can be recorded and processed in real-time. This allows to separate a near-field from far-field component of optical response and to map it spatial resolution limited by the tip radius.

Here we demonstrate its application to PS/PBD polymer blend study with less than 100 nm optical resolution.



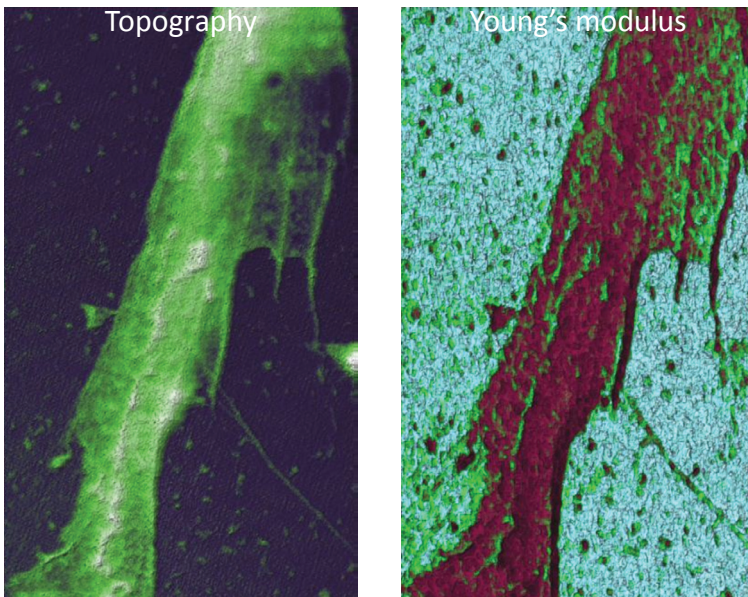
HD s-SNOM working principle



HD s-SNOM study of PS/PBD film

BIO HD & VACUUM HD MEASUREMENTS

Bio HD: long-term liquid measurement combined with QNM



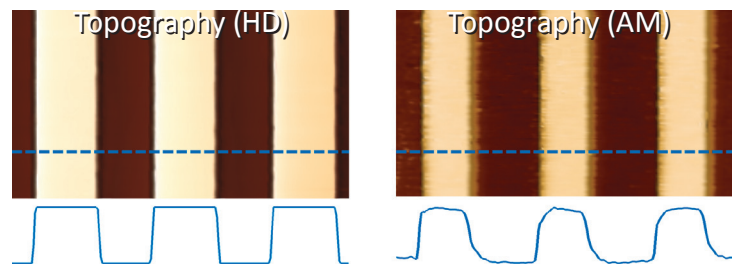
Bio HD study of Stem Cell fragment in Liquid. Elastic Modulus range: 0.2-1.5 kPa.
Scan size: 18×30 μm

Hybrid mode uniquely enables long-term experiments in liquid medium allowing the lowest force interaction and eliminating force sensor drift.

Additional information about mechanical properties of the sample significantly increases the value of experimental data. Furthermore, since Hybrid mode is a non-resonant mode there is no need to determine the resonance peak of cantilever.

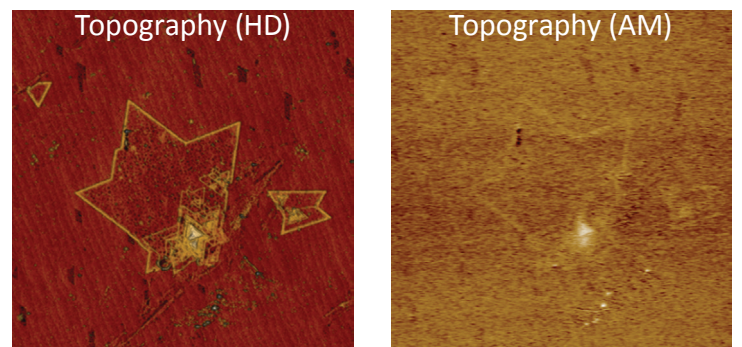
Fast and artifact-free studies with Vacuum HD

Vacuum measurements in amplitude modulation (AM) mode requires unacceptably low scanning speeds because of extremely high Q-factor of AFM probes. Being a non-resonant mode, HD mode allows at least 10 times faster imaging speed.



Topography of TGZ₂ calibration grating measured in vacuum with use of HD and AM modes. Scanning speed is 1 Hz.
Grating period is 3 μm, height is 100 nm

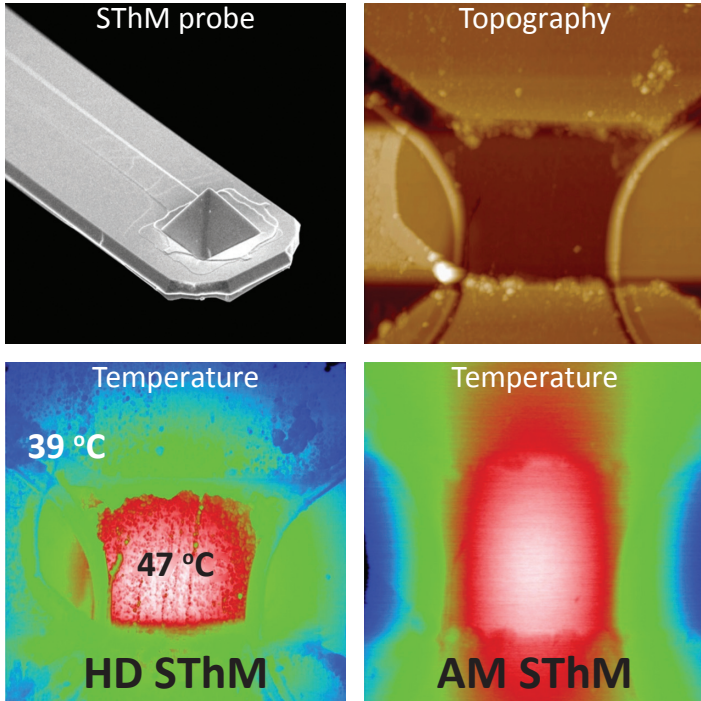
Another issue of AM mode in vacuum is that it is influenced by the electrostatic forces while the HD mode working principle allows automatic compensation of long-distance forces at each scanning point.



WS₂ monolayers grown on epitaxial graphene measured in vacuum with use of HD and AM modes. The influence of electrostatic forces is demonstrated. Sample Courtesy: Dr. Cristina Giusca, NPL, Prof. Mauricio Terrones, PSU. Scan size: 14×14 μm

HD SCANNING THERMAL MICROSCOPY

HD Scanning Thermal Microscopy working principle



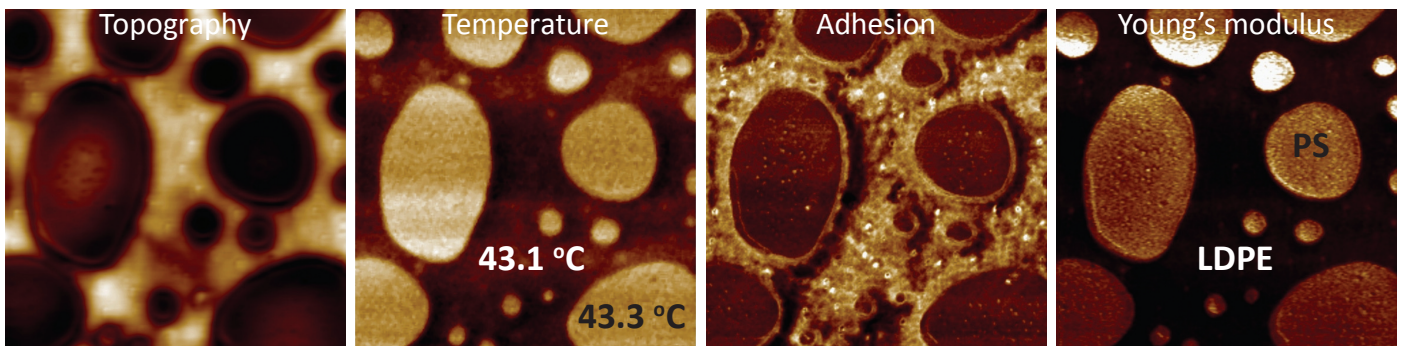
SEM image of AppNano VertiSense™ thermocouple probe and comparison of HD SThM and AM SThM techniques.
Scan size: 17×17 μm

HD Scanning Thermal Microscopy (HD SThM) allows studying local thermal properties simultaneously with QNM measurements. From the hardware point of view it was implemented using AppNano VertiSense™ thermocouple probes. The thermal conductivity and temperature mapping modes (CMM, TMM) can be realized by positioning the AFM laser at the end or the central part of the probe, respectively. HD mode working principle allows exceptional spatial resolution of SThM measurements in comparison to conventional Amplitude Modulation (AM) mode. That was demonstrated in TMM of a micro-heater sample.

Simultaneous Thermal and QNM measurements

SThM and HybriD mode is the winning combination for distinguishing between the constituents of polymer blends as demonstrated in the example of a blend of polystyrene (PS) with low density polyethylene

(LDPE) (see below). The difference in thermal conductivity of the polymers (PS – 0.12 W/mK; LDPE – 0.33 W/mK) allows the assignment of the colder matrix to LDPE and the hotter islands to PS.

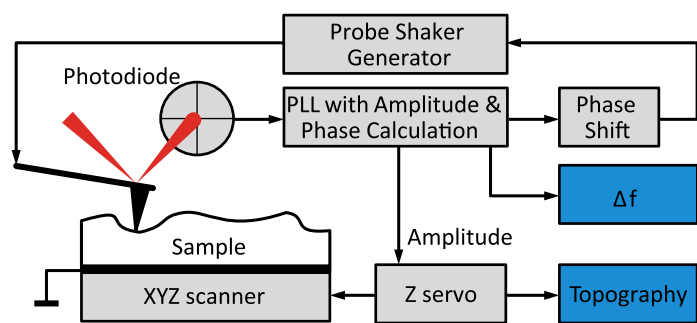


HD SThM study of PS-LDPE. Scan size: 10×10 μm

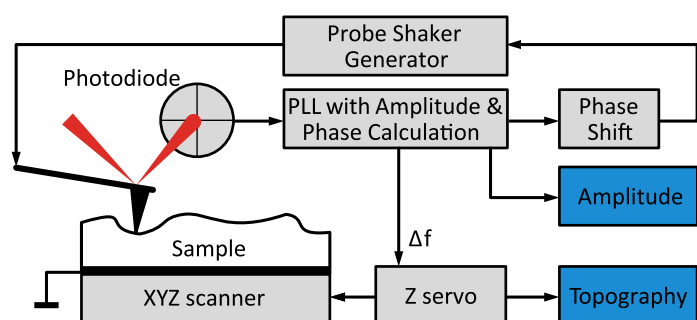
HD PHASE-LOCKED LOOP STUDIES

State-of-the-art HybriD 2.0 Control Electronics incorporates high-speed digital lock-in amplifiers (LIA) and phase locked loop detector (PLL) for advanced oscillatory resonance modes: Amplitude Modulation with Frequency Imaging (AM-FI) and Frequency Modulation (FM) modes. They

provide exceptional level of spatial resolution of challenging flat and soft samples (self-assembled molecular structures etc.) thanks to ultra-precise control of the tip-sample interaction force. Additionally they allow mapping of its mechanical properties.

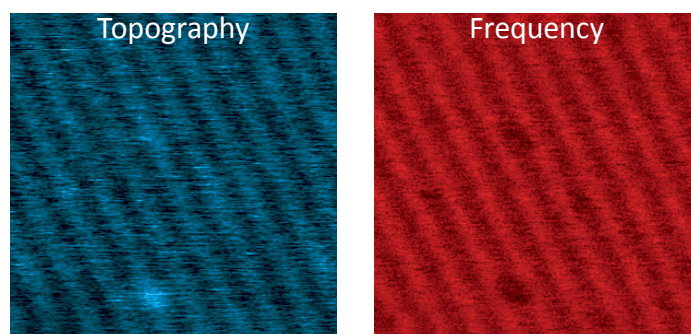


Schematics of AM-FI mode

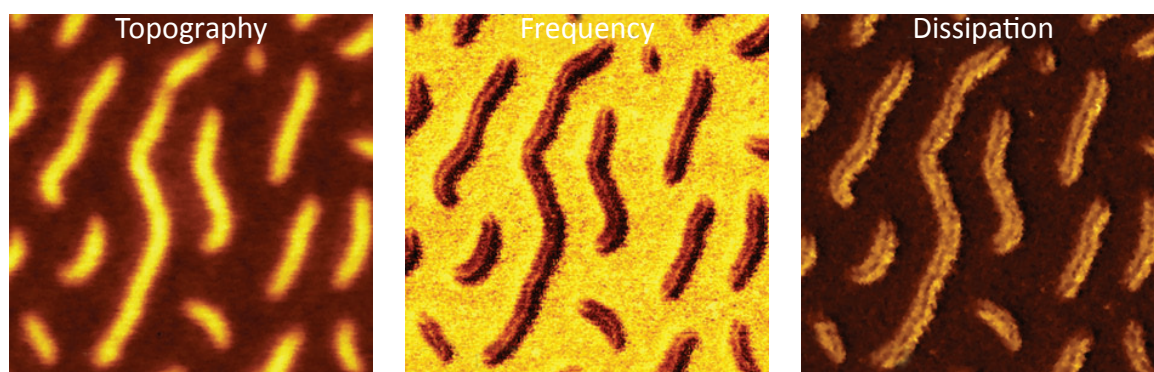


Schematics of FM mode

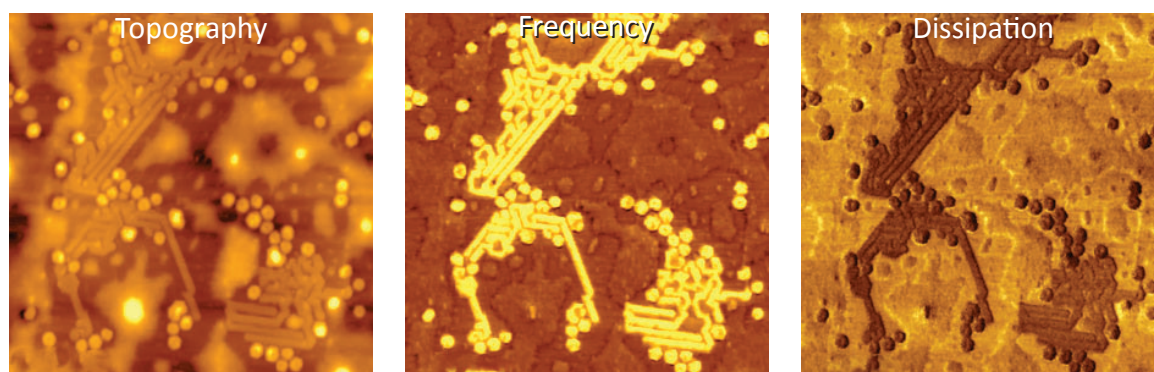
The two images below show topography and probe resonant frequency distribution over lamellar arrangement of short alkane $C_{36}H_{74}$ on graphite with a spacing of 4.5 nm. One can also see a couple of adsorbates formed on the lamellar surface by disordered alkane chains which are rarely observed by the traditional AM mode.



AM-FI mode images of $C_{36}H_{74}$ lamellae on graphite. Scan size 40×40 nm



FM mode images of brush-like macromolecules on mica. Scan size 500×500 nm



AM-FI mode images of F14H20 adsorbate on graphite. Scan size 1.5×1.5 μm



Parameter	Value
High Speed ADC-s	2 × 20 MHz, 16 bit
High Precision ADC-s	4 × 1 MHz, 18 bit
DAC-s	20 x 16 bit 1 MHz 2 x 12 bit 20 MHz
FPGA	120 MHz, Floating Point
DDS (Direct digital synthesizer)	2 × 20 MHz
Lock-in Amplifier Band	4 MHz
High Voltage Amplifier	+/-150 V, slew rate 32 V/uSec (limited to 33 kHz at 150 V) small signal band- width 500 kHz at < 10V Amplitude
Number of curves per second	Limited only by Z scanner resonance frequency
PLL	
Operational Modes	Self-exciting oscillation, constant amplitude, constant excitation
Measurement Resolution	0,3 Hz at 10 kHz BW; 0,02 Hz at 600 Hz BW
Demodulation Bandwidth	500 kHz
Digital Phase Shifter	0 – 360° (20 bit); 0,34 millidegree step
Spectrum Analysis	Amplitude, Phase
Probe Safety	Yes
Output Modulation	P-p 10 V, resolution 0,15 mV
Input Signal	10 kHz - 1 MHz; 70 mV - 10 V
Common	
PC Interface	USB 2.0, Ethernet
Program SDK	Labview
Power Supply	100-240 V (50/60 Hz)
Set of modes	
Topography, Elastic modulus, Lift and Land Adhesion, Work of Adhesion, Current, Force Volume, PFM, KPFM, MFM, EFM, SThM, SThEM	