SHIMADZU
Excellence in Science

C147-E016

High Resolution Scanning Probe Microscope

SPM-8100FM

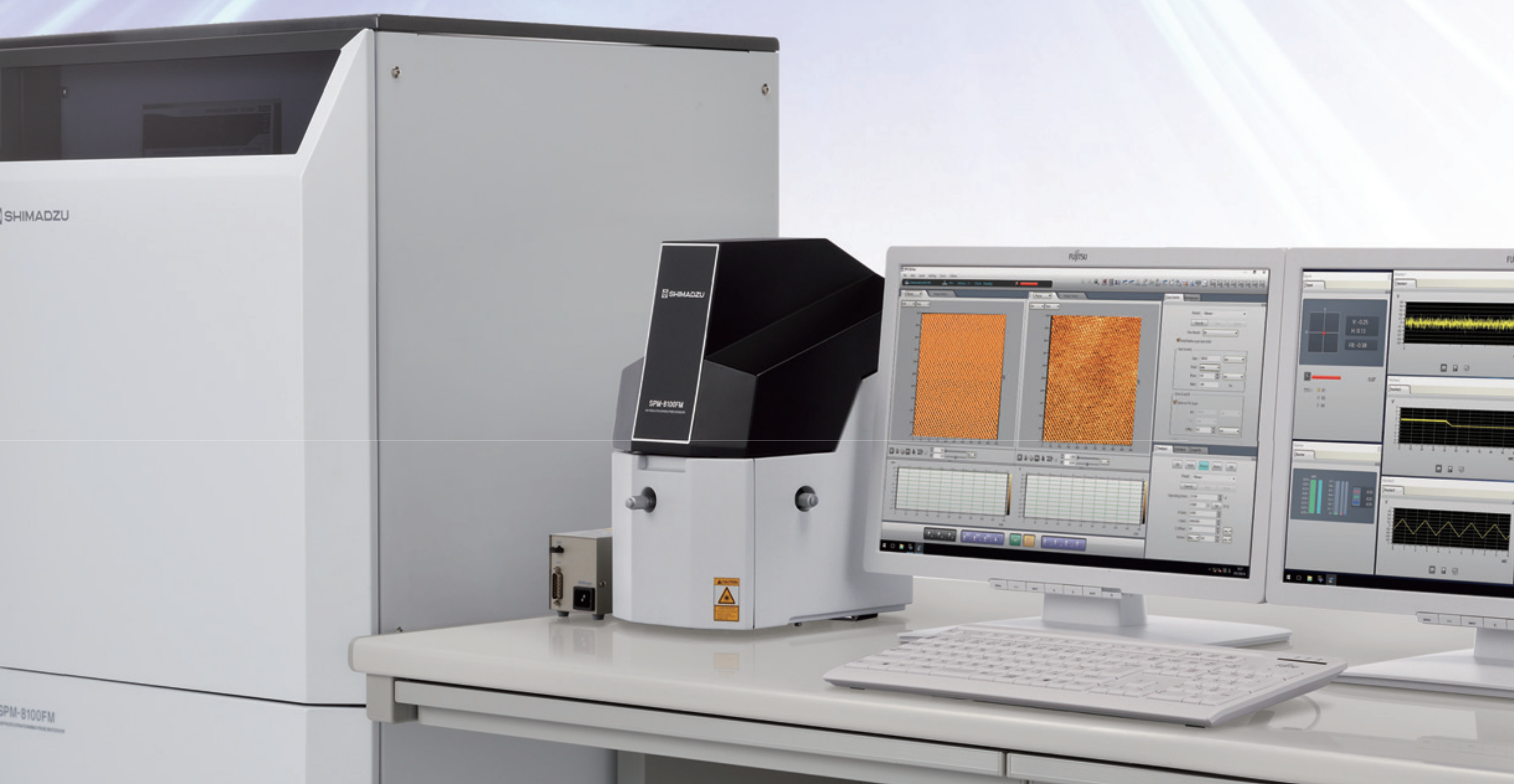
HR-SPM

HR-SPM

See the Nano World Come to Life

The new HR-SPM scanning probe microscope uses frequency detection.
This instrument is not only capable of ultra-high resolution observations in air or liquids, but for the first time enables observations of hydration/solvation layers at solid-liquid interfaces.

HR-SPM: High Resolution Scanning Probe Microscope



This product was developed as part of the Development of Systems and Technologies for Advanced Measurement and Analysis program, conducted by the Japan Science and Technology Agency (JST).
Some of the data in this brochure was obtained using instruments with a different configuration than the SPM-8000FM.

Features of the HR-SPM

High Resolution

- Uses the FM method
- Noise in air and liquids is reduced to 1/20 that of existing methods.
- Achieves the performance level of a vacuum-type SPM, even in air and liquids.
- Enables measurement of the local structure at the solid-liquid interface.

Improved Usability

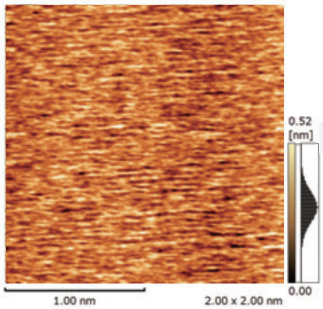
- HT scanner extends observation area and shortens observation times.
- Dual monitors and signal indication function provide significant improvement in flexibility.

Existing SPMs (Scanning Probe Microscopes) and AFMs (Atomic Force Microscopes) generally use AM (Amplitude Modulation).
In principle however, the FM (Frequency Modulation) measurementmethod enables higher imaging resolution.

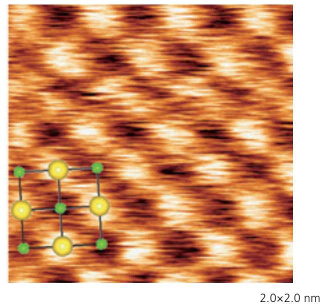
SPM : Scanning Probe Microscope
AFM : Atomic Force Microscope
AM : Amplitude Modulation
FM : Frequency Modulation

Differences From Existing SPM/AFM

Atomic Resolution Observations in Solution



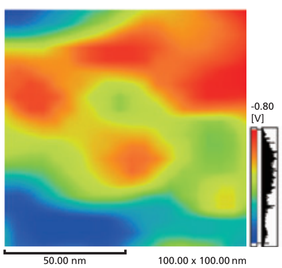
AM Method



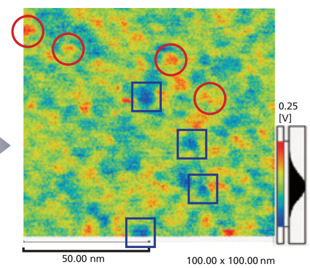
FM Method

Observations were made of the arrangement of atoms on a NaCl surface in a saturated aqueous solution. Atoms hidden by noise in existing AFM observations (AM method, left) are clearly visible when the FM method (right) is used. The FM method provides true atomic resolution.

Pt Catalyst Particles Observation in Air [1)]



AM Method



FM Method

KPFM: Kelvin Probe Force Microscope

Pt catalyst particles in a TiO_2 substrate were identified, and the surface potential was measured using a KPFM. Pt particles several nm in size were observed in the exchange of charges with the substrate. In the figure on the right, the red circles indicate positive potential, and the blue circles indicate negative potential. It is evident that the resolution has been dramatically improved, even for a KPFM. 50.00 nm 100.00 x 100.00 nm 50.00 nm 100.00 x 100.00 nm

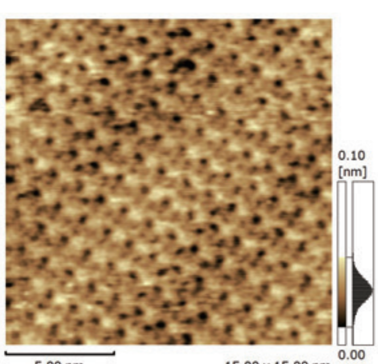
Note: KPFM functionality is available on a special order basis.

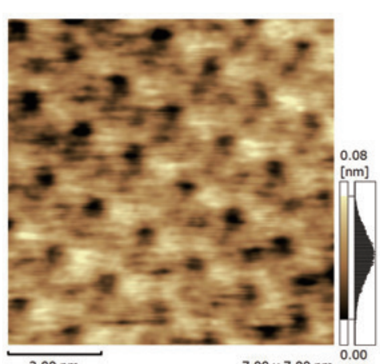
Examples of Observations in Air

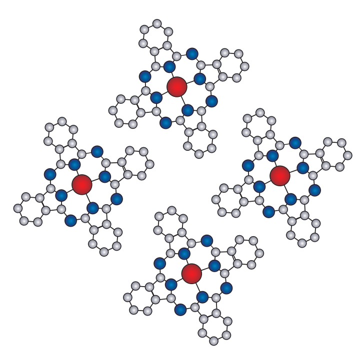
In Air

The Molecular Structural Arrangement of a Thin Film of Lead Phthalocyanine Crystals

These figures show phthalocyanine crystals, which are commonly used in organic light-emitting displays, and in dye-sensitized solar cells. The four-leaf structure surrounding the metal atom at the center of the molecule can be clearly observed.







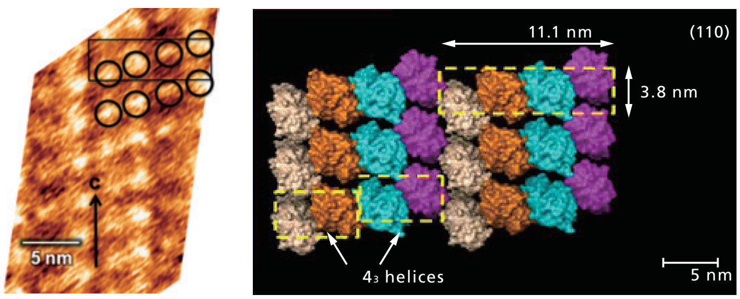
Sample : $PbPc/MoS_2$

Examples of Observations in Liquids

In Liquid

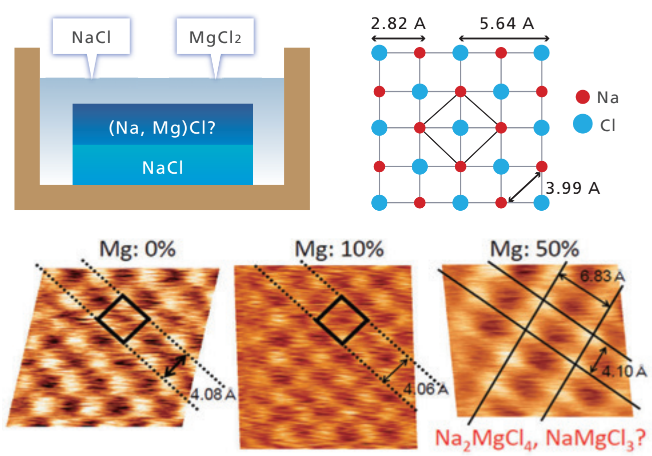
Molecular Structure of Proteins [2)]

Egg-white lysozyme was observed in a saturated aqueous solution. Protein molecules (the circles in the figure at left) can be observed within the surface unit cell (the square in the figure at right). The inside of the unit cell can not be observed using the existing AFM, while four protein molecules were observed using HR-SPM and the images are consistent with the model image shown in the figure at right.



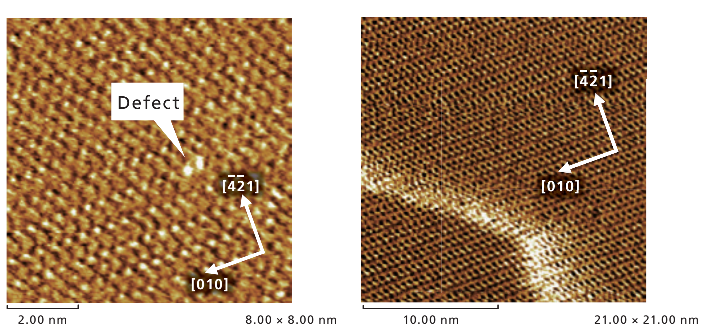
Model of the Crystalline Structure of the Surface of Lysozyme (110)

Mixed Crystalline Structures



This illustrates the observation of epitaxially-grown Na_2MgCl_4 crystals on a single NaCl crystal surface in a mixed solution. Because the crystalline structure can be observed, this technique can be used to identify the structure of mixed samples.

Atomic Structure of a Calcite Cleavage Plane [3)]



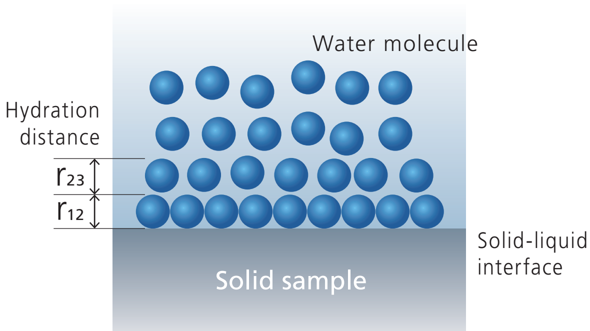
This is an atomic-resolution observation of surface structure in a liquid medium. Defects in the calcite surface are evident in the figure at left.

All data on this page was obtained using the petri dish type solution cell (option).

Observational Examples of Hydration/Solvation Structure

What are Hydration and Solvation?

It is known that liquids in contact with solids become stratified, a phenomenon called solvation, or in the case of water, hydration. It is believed that this characteristic structure, which is different from that of a bulk liquid, is the main influence on the various roles played by solid-liquid interfaces, such as dissolution, chemical reactions, charge transfers, wetting, lubrication, and heat transfer in the liquid phase. However, because this layer is extremely thin, the hydration/solvation structure is not easy to measure experimentally. In particular, non-uniform structures in the in-plane direction of the surface have not yet been detected.



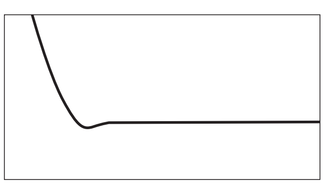
Model of Hydration Structure

Differences from Existing AFM Technology

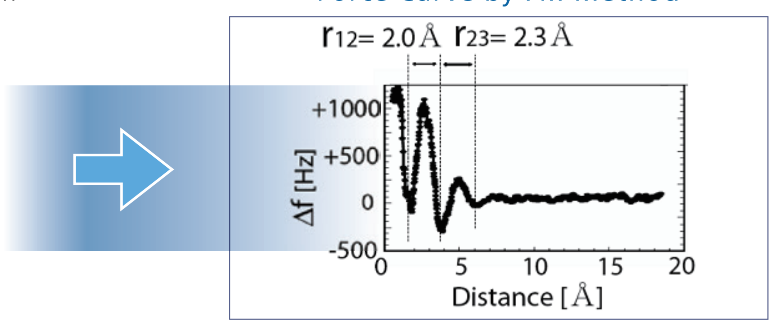
When measuring hydration/solvation, the variation in the force on the cantilever is very small. However, by using an ultra-high sensitivity FM method, this can now be measured for the first time.

Such methods enable not only the measurement of hydration/solvation structures in the Z-X direction, but also the analysis of 3D Z-XY structures. HR-SPM capabilities have now advanced from mere surface observations to measurements of the structure of solid-liquid interfaces.

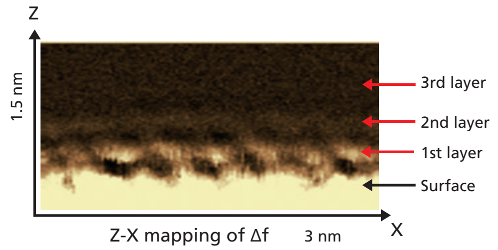
Force Curve by Existing AFM



Force Curve by FM Method

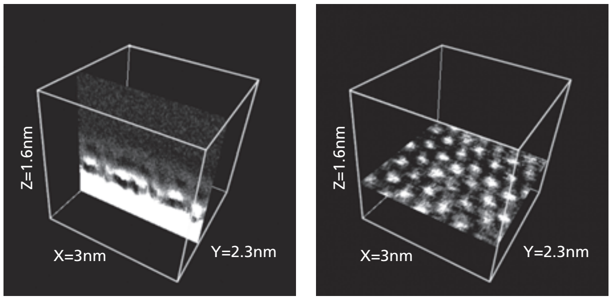


Hydration Measurement Using the FM Method [4]



The layered hydration structure of a mica surface can be visual

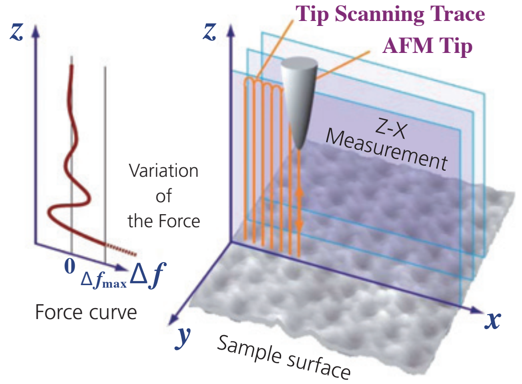
Observation and Analysis of 3D Hydration Structures at a Solid-Liquid Interface [5]



All data on this page was obtained using the petri dish type solution cell (option).

The Hydration/Solvation Measurement Method

1. Run the HR-SPM in a solution, bringing the cantilever close to the surface of the solid sample with high precision, up to the settings value (fmax).
2. Use the force curve method to measure the force on the probe on the tip of the cantilever.
3. Variations in characteristic power (f) in accordance with the sample can be obtained in the immediate vicinity of the solid-liquid interface.
4. Variation of the force is due to hydration/solvation, which provides insight into the stratification structure in the liquid.
5. A cross section of the hydration/solvation structure can be visualized by performing continuous acquisition in the X-direction (Z-X measurement).
6. Furthermore, the 3D structure of the solid-liquid interface can be analyzed by acquiring Z-X measurements in the Y direction.



Pattern Diagram of Hydration/Solvation Measurement

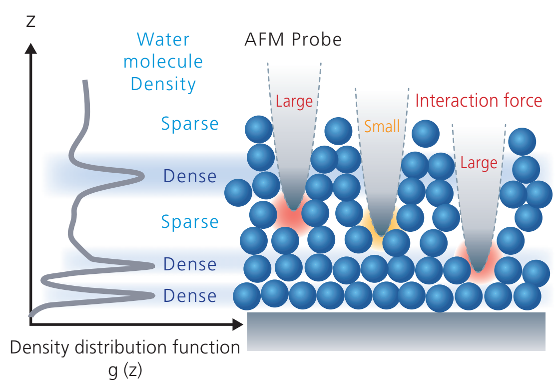
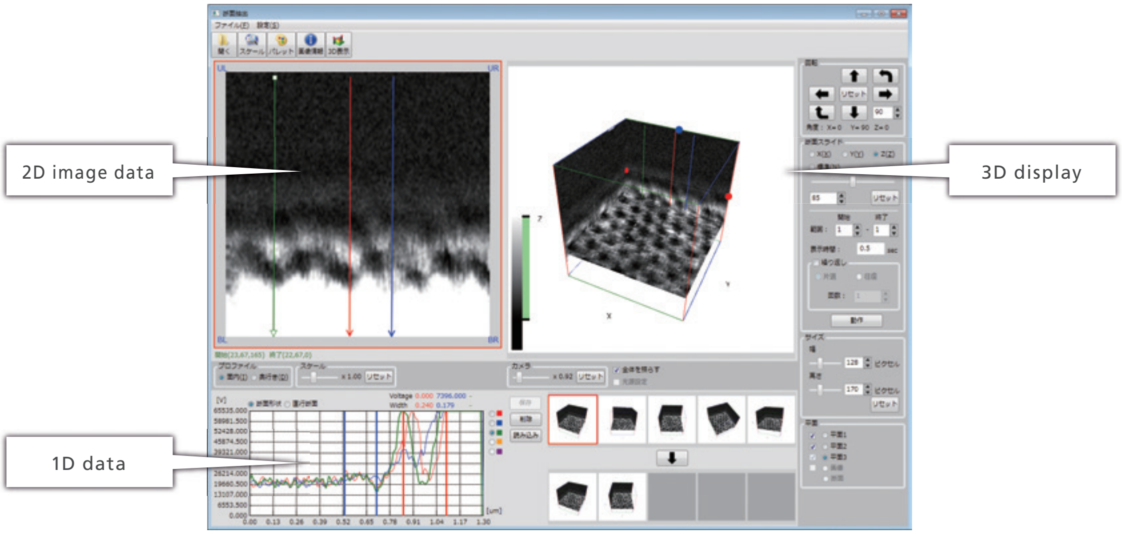


Diagram of Hydration/Solvation Measurement

Data Analysis Software

This software is designed specifically for 3D mapping data analysis. It provides powerful support for analyzing hydration and solvation structure data.

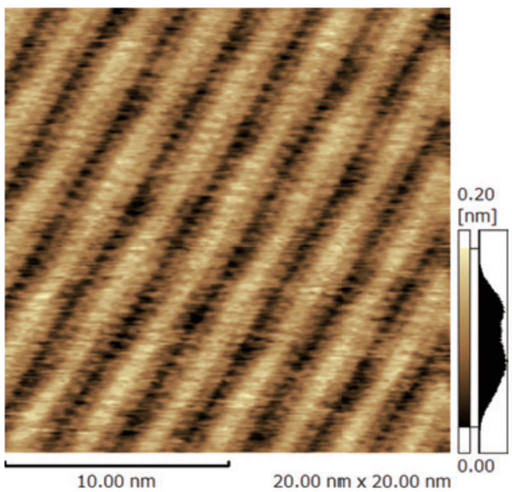


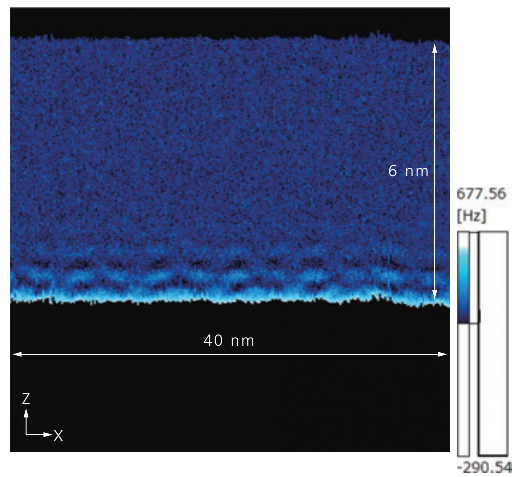
- Displaying 3D mapping data
- Extracting and displaying 2D images from the mapping data
- Displaying and analyzing specified 1D data over 2D image data

Examples of Hydration/Solvation Structure Measurements

Interface Structure of 1-Decanol Contact with Graphite

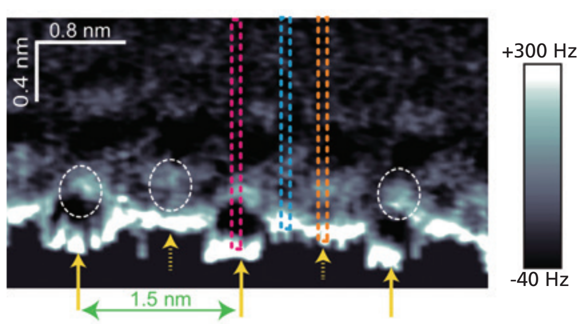
The molecular film of 1-decanol over graphite was observed (figure at left). The joining of two molecules of decanol and molecular film formation can be observed. The cross-section structure of decanol liquid contact with an adsorbed molecular layer was measured (figure at right). It was found that the decanol organized in a layer structure and there existed inhomogeneous distribution in an in-plane direction.



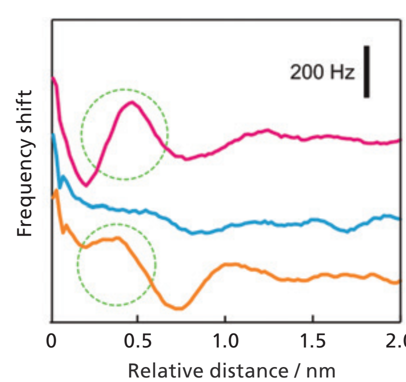


A Saturated Aqueous Solution in Contact with p-nitroaniline Crystals [6)]

In the Z-X in measurements on the left, the convex area is the position of the benzene ring, and the concave area is the position of the hydrophilic functional group. From the force curves at each position (Z- f curves), it is evident that there is strong hydration due to the localization of water molecules in the concave area representing the hydrophilic group. This data suggests that the structure is stabilized by hydrogen bonding of the water molecules with the polar groups, as shown by the model in the figure at the bottom.

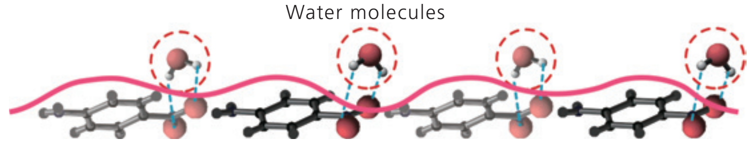


Z-X Measurement of p-nitroaniline interface



Force curve

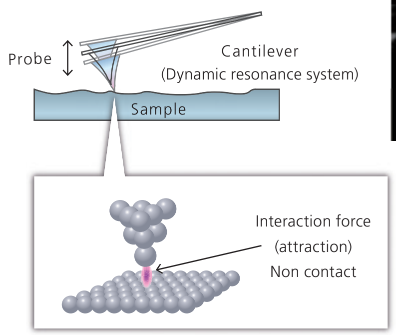
Water molecules



All data on this page was obtained using the petri dish type solution cell (option).

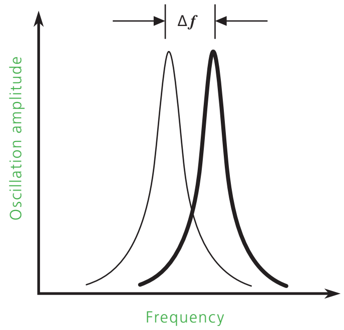
The Principle of FM-Type AFM

The frequency of a vibrating cantilever is measured in dynamic mode, and interactions with the sample are detected. Specifically, the cantilever is moved in a non-contact state, so that the cantilever frequency shift (Δf) is constant. This enables highly sensitive force detection, 20 times better than with existing methods, thereby improving the image resolution.



Cantilever

Cantilever resonance curve



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2) K. Nagashima, M. Abe, S. Morita, N. Oyabu, K. Kobayashi, H. Yamada, R. Murai, H. Adachi, K. Takano, H. Matsumura, S. Murakami, T. Inoue, Y. Mori, M. Ohta, R. Kokawa, Molecular resolution investigation of tetragonal lysozyme(110) face in liquid by FM-AFM, Journal of Vacuum Science and Technology B 28 (2010) C4C11-C4C14

3) Sebastian Rode, Noriaki Oyabu, Kei Kobayashi, Hirofumi Yamada, and Angelika Kuhnle, True Atomic-Resolution Imaging of (1014) Calcite in Aqueous Solution by Frequency Modulation Atomic Force Microscopy, Langmuir, 2009, 25 (5), pp 2850–2853

4) K. Kimura, S. Ido, N. Oyabu, K. Kobayashi, Y. Hirata, T. Imai, H. Yamada, Visualizing water molecule distribution by atomic force microscopy, Journal of Chemical Physics, 132, 19, 194705 (2010).

5) Kei Kobayashi, Noriaki Oyabu, Kenjiro Kimura, Shinichiro Ido, Kazuhiro Suzuki, Takashi Imai, Katsunori Tagami, Masaru Tsukada and Hirofumi Yamada, Visualization of hydration layers on muscovite mica in aqueous solution by frequency-modulation atomic force microscopy, Journal of Chemical Physics, 138, 184704 (2013).

6) Rina Nishioka, Takumi Hiasa, Kenjiro Kimura, and Hiroshi Onishi, Specific Hydration on *p* Nitroaniline Crystal Studied by Atomic Force Microscopy, J. Phys. Chem. C, 117, 2939–2943 (2013).

Instrument References

- Ryohei Kokawa and Masahiro Ohta, Development of a High Resolution FM-AFM Working in Air or Solution, Microscopy, Vol. 47, No. 1 (2012) (Japanese)
- Kei Kobayashi, Hirofumi Yamada, and Kazumi Matsushige, Reduction of frequency noise and frequency shift by phase shifting elements in frequency modulation atomic force microscopy, Rev. Sci. Instrum., 82, 033702 (2011).

Application Examples

- Shinichiro Ido, Kenjiro Kimura, Noriaki Oyabu, Kei Kobayashi, Masaru Tsukada, Kazumi Matsushige and Hirofumi Yamada, Beyond the Helix Pitch: Direct Visualization of Native DNA in Aqueous Solution, ACS Nano, 7, 1817-1822 (2013).
- Takumi Hiasa and Hiroshi Onishi, Competitive Adsorption on Graphite Investigated Using Frequency-Modulation Atomic Force Microscopy: Interfacial Liquid Structure Controlled by the Competition of Adsorbed Species, Langmuir, 29, 5801-5805 (2013).

This Instrument has been commercially developed through collaboration with the Yamada group at Kyoto University, the Morita group at Osaka University, the Onishi group at Kobe University, the Tomitori group at JAIST, and the Arai group at Kanazawa University.

Main Specifications

1. SPM Unit

Resolution	X, Y: 0.2 nm, Z: 0.01 nm	
SPM Head	Displacement detection system	Light source/optical lever/detector
	Light source	Laser diode (635 nm, 5 mW max., switchable ON/OFF) Irradiates cantilever continuously, even while replacing samples.
	Detector	Photodetector
	Noise level converted to displacement	20 fm/√Hz max.
Scanner	Drive element	Tube piezoelectric element
	Max. scanning size	10.0 μm × 10.0 μm × 1.0 μm (X, Y, Z)
Stage	Max. sample size	38 mm dia. × 8 mm
	Sample replacement method	Head-slide mechanism
	Sample securing method	Magnet
	SPM head movement range	10 mm × 10 mm
Z-Axis Coarse Adjustment Mechanism	Method	Fully automatic, using stepping motor
	Max. stroke	10 mm
Optical Microscope	CCD	Element size: 1/3 inch
		Effective pixels: 1024 × 768
	Lens	Stroke: 65 mm Optical magnification: 4x
	Illumination	Coaxial incident illumination
Vibration Isolation System	Vibration damper	Built into SPM unit

2. Control Unit

Control Unit	Feedback	Digital control
	Communications Interface	1000Base-T, TCP/IP protocol
Drive Unit	X/Y-axis control	-211 to + 211 V, 16 bit
	Z-axis control	-211 to + 211 V, 16 bit
Analog Unit	Input voltage	-10 to 10 V
	Resolution	16 bit
	Sampling frequency	200 kHz
	Input signal	8 channels

3. Data Processing Unit

Host Computer	Main memory	16 GB min.
	External recording device	Internal hard drive with minimum 250 GB One CD-RW drive
	Communications interface	1000Base-T, TCP/IP protocol
	OS	Windows 10 Professional (64 bit), English version
Monitor	Panel	21-inch wide-screen TFT LCD Display resolution: 1920 × 1080 pixels

4. Software

Online	Observation window	Maximum 8 images can be displayed simultaneously. Cross section shape can be displayed during scanning
	Scanning mode	Switchable between XY, ZX, and ZXY
	Control screen	Observation parameters can be specified
Offline	Summary display	Summary of images can be displayed as thumbnails
	Image data display/analysis	Display, process, or analyze image data Display or analyze 3D mapping data

Optional Products

Narrow Range Scanner (2.5 μm)

Used for observation in a narrow range.
X·Y: 2.5 μm Z: 0.3 μm

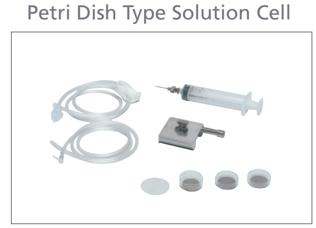
Middle Range Scanner (30 μm)

Used for observation in a wide range.
X·Y: 30 μm Z: 5 μm

Fiber Light

Used to provide angled illumination in addition to standard coaxial incident illumination.

Petri Dish Type Solution Cell



Used for observation in liquid.
The dedicated cantilever holder is included.

Cantilever Mounting Jig

This jig ensures easy and secure mounting of the cantilever.

Air-Cushioned Vibration Damper

This is a floor-type passive vibration damper. It requires a compressed air source.

Active Vibration Damper

This is a table-top active vibration damper. It only requires a power supply to function.

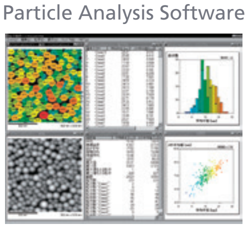
Active Vibration Damper with Dedicated Stand

This is the active vibration damper unit combined as a set with a matching dedicated stand.

Additional Monitor

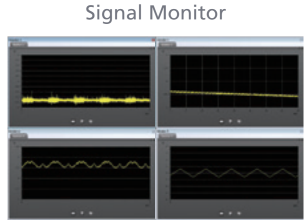
Add a second monitor (optional) for a dual monitor. The connection cable is included.

Particle Analysis Software



Extracts multiple particles from image data and calculates characteristic values for each particle.

Signal Monitor

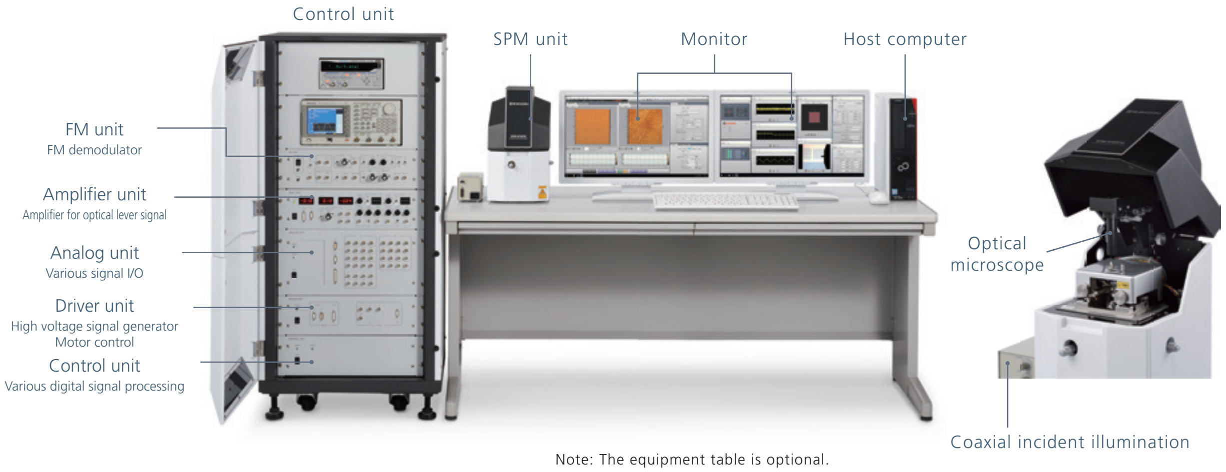


An arbitrary signal can be taken and shown on the screen using online software.

Static Eliminator

This is used to eliminate static charge from samples or cantilevers.

External Appearance of Instrument



Note: The equipment table is optional.
Note: Dual monitors setup is available as an option.

Installation Specifications

Installation Room Environment

The installation room environment should meet the following conditions.

Temperature: 23°C ± 5°C
Humidity: 60% max. (no condensation)

Power Supply

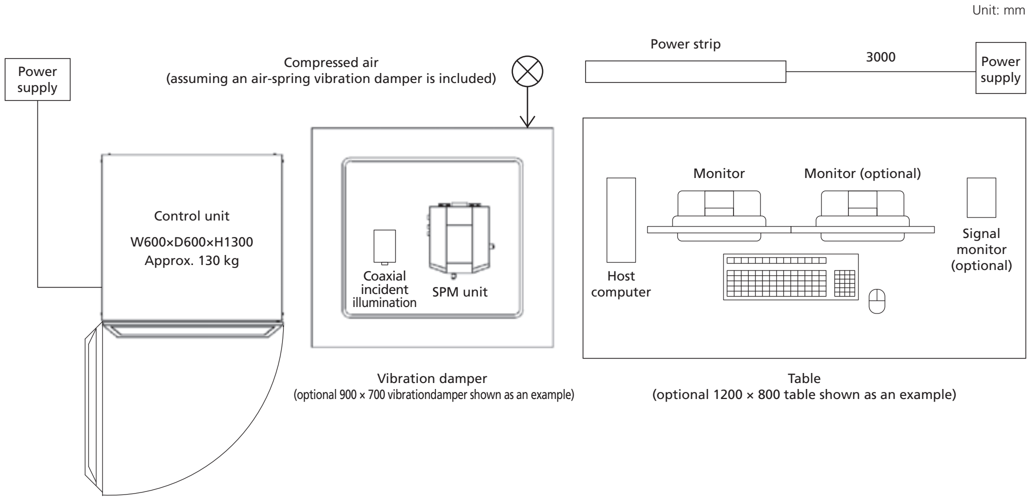
The following power supply is required to operate this system.

Single-phase 100 V AC, 50/60 Hz, 15 VA, 2-prong
Ground resistance 100 Ω max.

Instrument Size and Weight

SPM unit : W200 × D220 × H370 mm; approx. 10 kg
Control unit: W600 × D600 × H1,300 mm; approx. 130 kg

Installation Example



Related Product

SPM-9700HT

Scanning Probe Microscope

This microscope enables high-magnification observations of the three-dimensional structure and local properties of samples. With a wealth of functions and expandability, this instrument is capable of meeting a variety of demands. Thanks to a revolutionary software interface, all operations are straightforward, from observation through to analysis.

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