INC Summer School 2014/7/14

Instrumentation and applications of liquid-environment FM-AFM (Part I)

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Outline

1．FM-AFM in Liquid

2．Force Sensitivity

3．Imaging Speed

4．Stability & Reproducibility

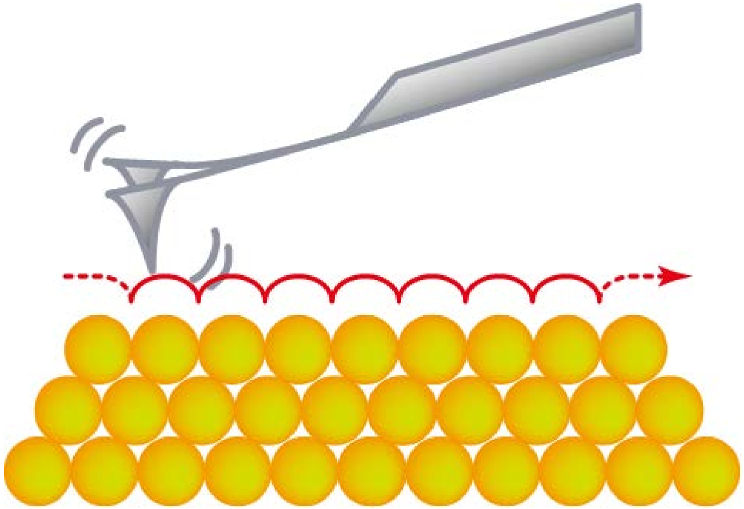
5．Summary

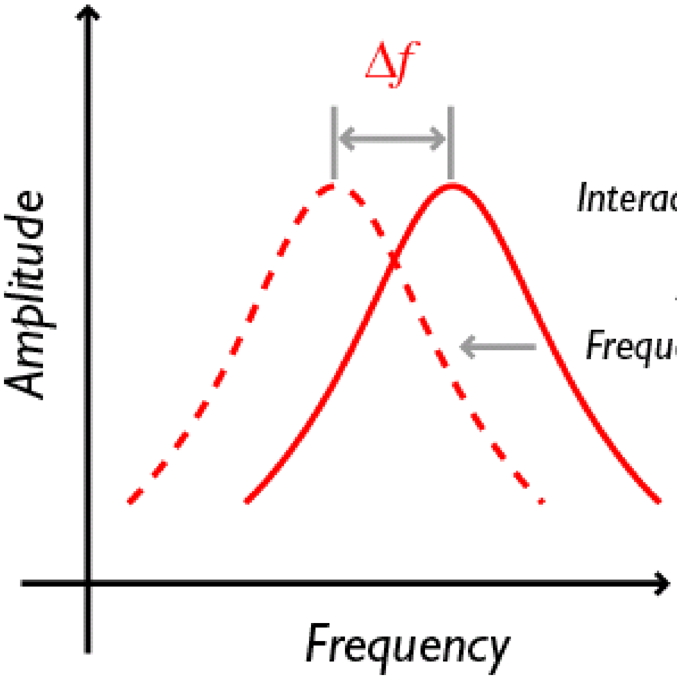
Outline

1. **FM-AFM in Liquid**
2. Force Sensitivity
3. Imaging Speed
4. Stability & Reproducibility
5. Summary

Frequency Modulation AFM (FM-AFM)

Principle



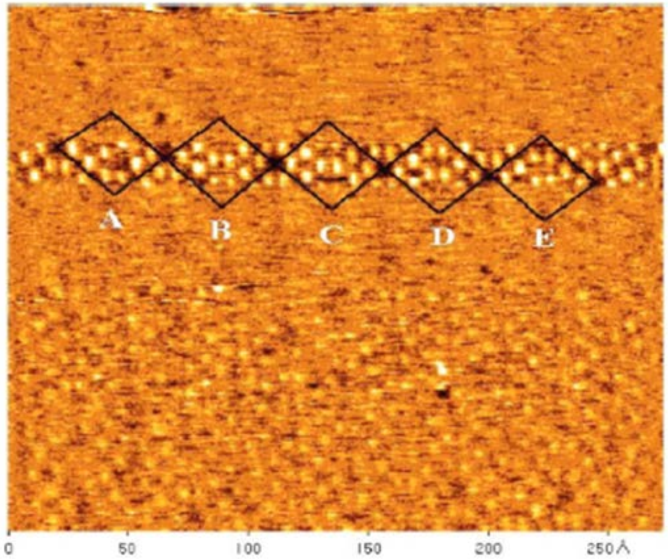


- True atomic resolution
- Conductive & Non-conductive surfaces
- Small loading force

True Atomic-resolution FM-AFM Imaging

In Vacuum

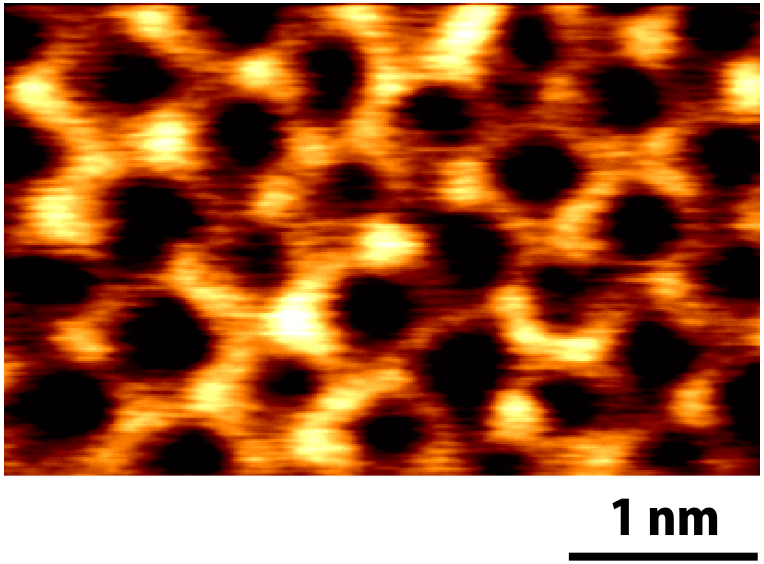
Si(111) in Vacuum



F. J. Giessibl, Science 267 (1995) 68

In Liquid

Mica in Water



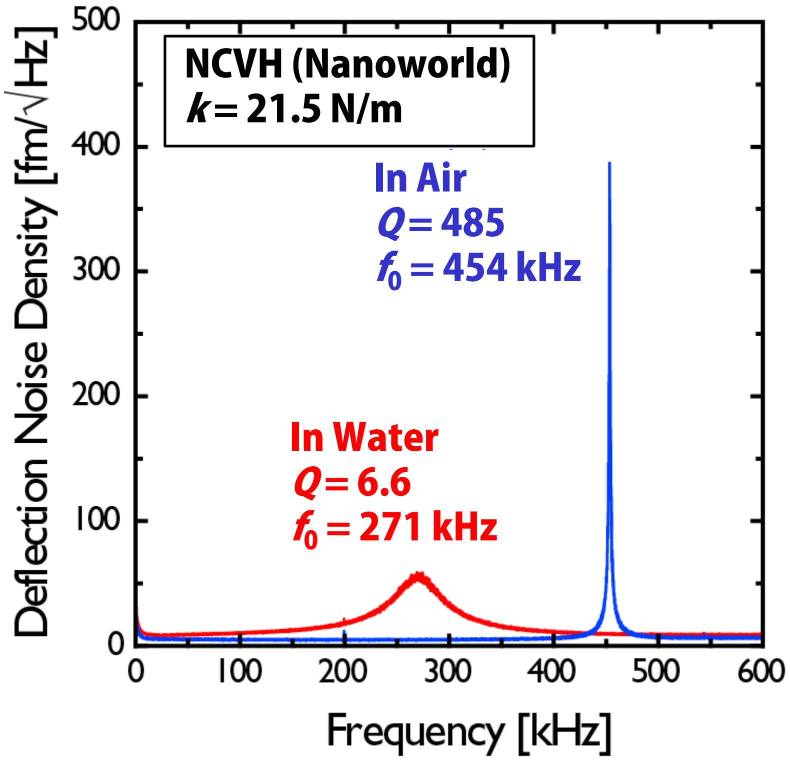
Fukuma *et al.* APL 87 (2005) 034101

Operating environment of FM-AFM was limited to vacuum for 10 years

Difficulties in Liquid

Hydrodynamic Damping

Cantilever Thermal Vibration



Low Q Factor

Vacuum	1,000 – 100,000
Air	100 – 1,000
Liquid	1 – 10

Minimum Detectable Force

$$F_{\mathrm{min}} = \sqrt{\frac{4kk_BTB}{\pi f_0 Q}}$$

F_{min} was considered to be limited **mainly** by cantilever

Major Improvements

Stiff Cantilevers

Thermal Vibration

$$\boxed{z_{\text{th}} = \sqrt{\frac{k_B T}{k}}}$$

Conventional

$k = 0.4$ N/m

$z_{\text{th}} = 100$ pm

→

Improved

$k = 40$ N/m

$z_{\text{th}} = 10$ pm

Small Oscillation Amplitude

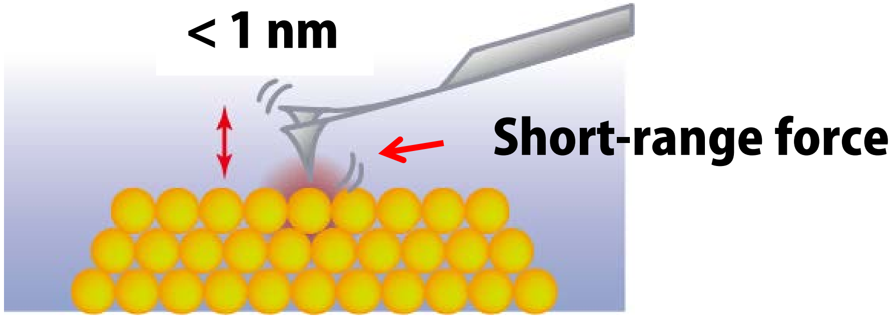
Conventional

$A = 1\text{-}10$ nm

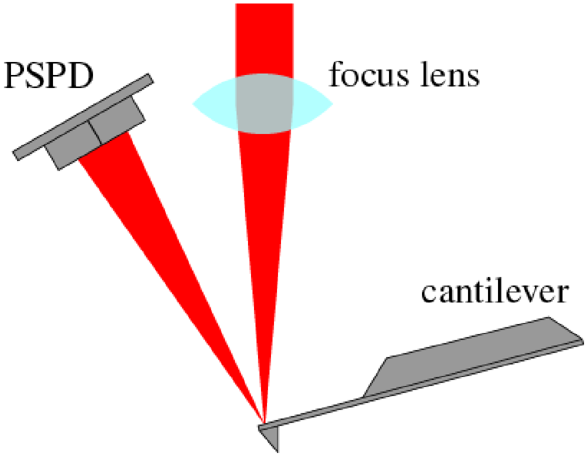
→

Improved

$A = 0.1\text{-}1$ nm



Low-noise Cantilever Deflection Sensor



Conventional

$n = 100\text{-}1{,}000$ fm/√Hz

↓

Improved

$n = 40$ fm/√Hz (2005)

$n = 7.3$ fm/√Hz (2006)

$n = 4.7$ fm/√Hz (2009)

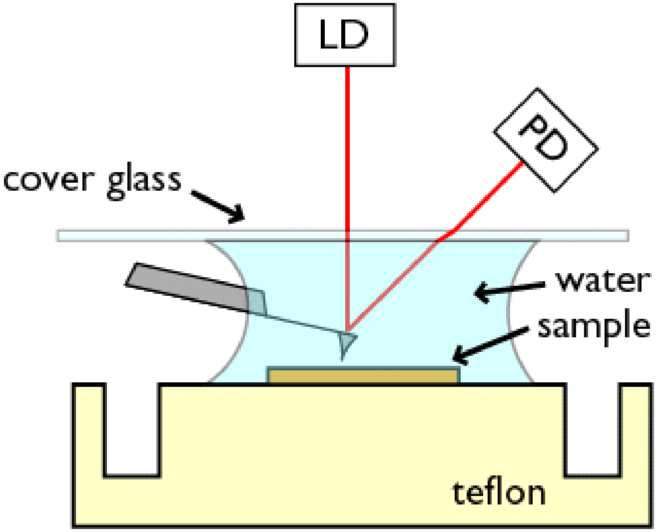
Fukuma *et al.* RSI 76 (2005) 053704

Fukuma *et al.* RSI 77 (2006) 043701

Fukuma RSI 80 (2009) 023707

Reduction of Deflection Sensor Noise

Noise from Laser



Interfaces in the optical path

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Reflection, Scattering

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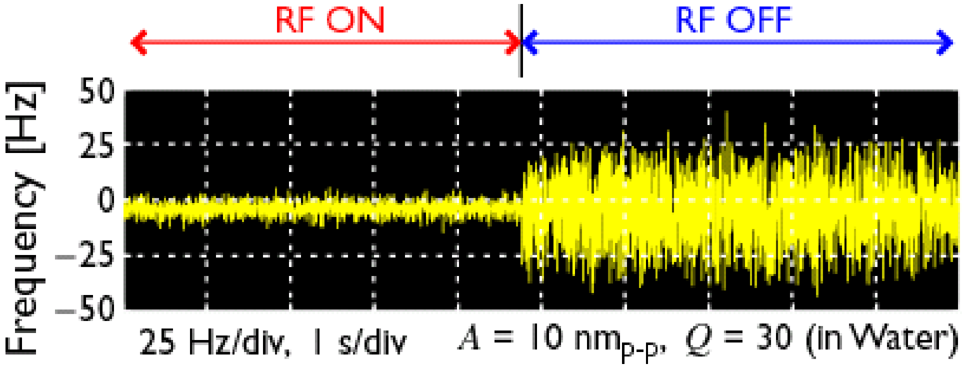
- Optical feedback noise
- Interference noise

RF Modulation of Laser

Frequency Shift



RF modulation of laser at 300 MHz

⬇

Suppression of coherence

⬇

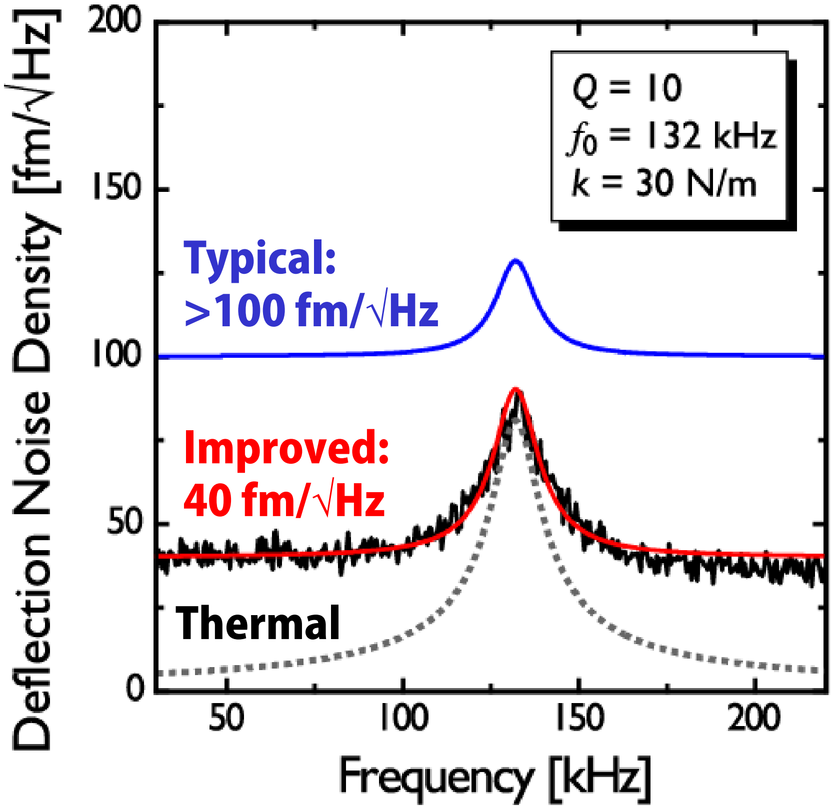
Reduction of noise
- **Mode hop noise**
- **Interference noise**

Fukuma *et al.* RSI 76 (2005) 053704

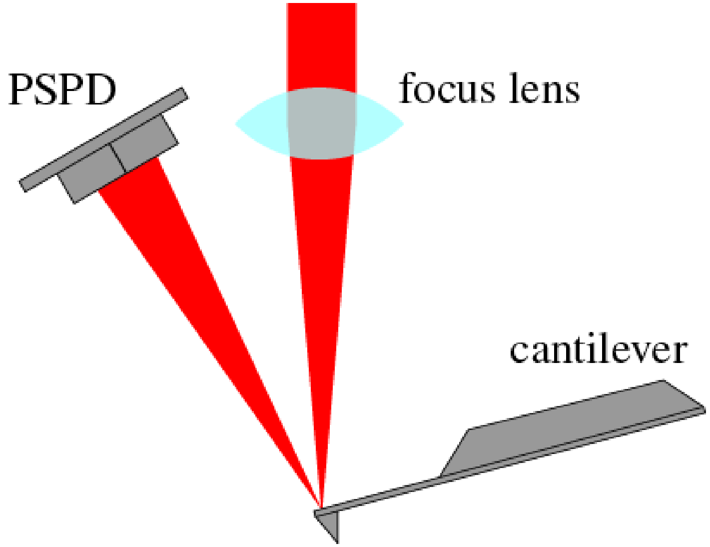
Atomic-resolution FM-AFM in Liquid

Thermal-noise-limited F_{min}

FFT Spectrum of Deflection Signal



Low Noise Deflection Sensor



Fukuma *et al.* RSI 76 (2005) 053704

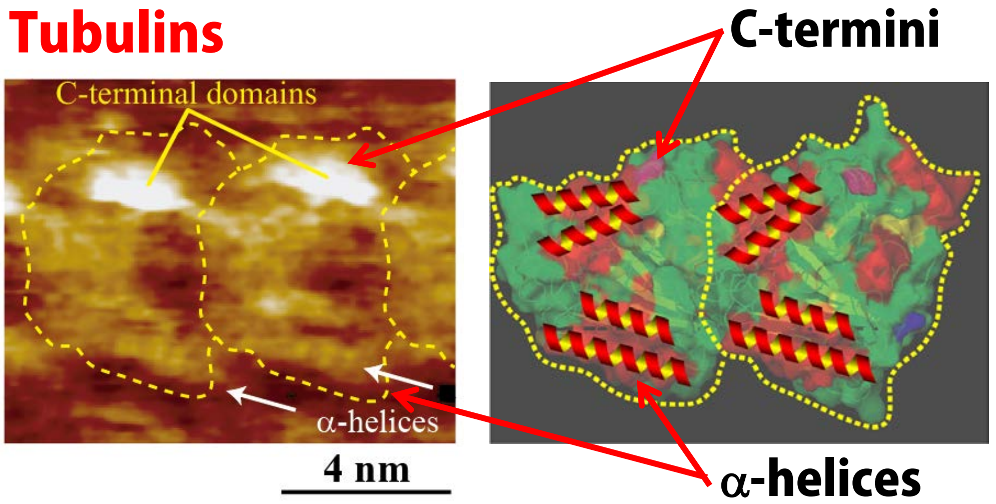
- Thermal-noise-limited F_{min} → True atomic resolution
- Now, F_{min} is indeed limited mainly by cantilever

Liquid-environment FM-AFM

Biological Systems

- Hoogenboom et al. APL 88 (2006) 193109
- Higgins et al. BPJ 91 (2006) 2532
- Fukuma et al. PRL 98(2007) 106101
- Yamada et al. APEX 2 (2009) 095007
- Nagashima et al. JVSTB 28 (2010) C4C11
- Asakawa *et al.* BPJ 110 (2011) 1270

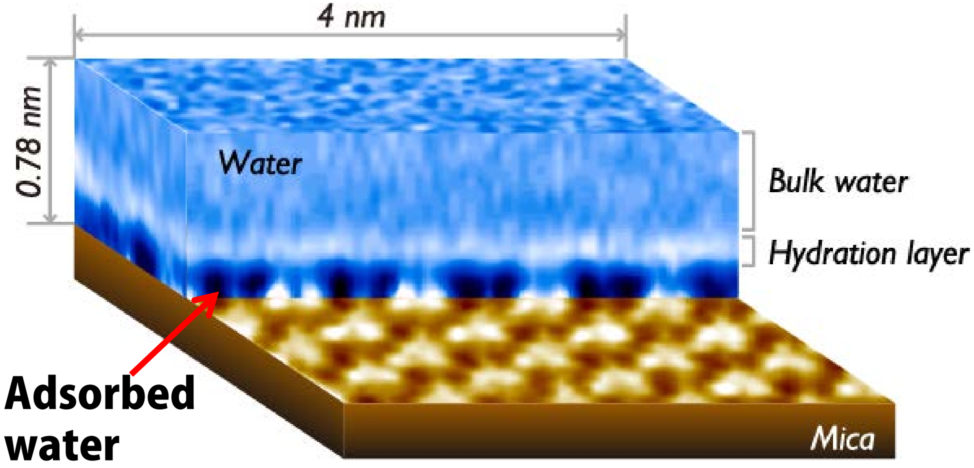
Tubulins



3D Hydration Structures

- Fukuma *et al.* PRL 104 (2010) 016101
- Kimura *et al.* JCP 132 (2010) 194705
- K. Suzuki *et al.* APEX 4 (2011) 125102
- H. Asakawa *et al.* ACS NANO 6 (2012) 9013
- T. Hiasa *et al.* PCCP 14 (2012) 8419

Mica/Water



- Application techniques significantly advanced
- F_{min} is still limited by cantilever

Outline

1. FM-AFM in Liquid
2. **Force Sensitivity**
3. Imaging Speed
4. Stability & Reproducibility
5. Summary

Theoretical Limit of FM-AFM

Minimum Detectable Force

Small Amplitude Approx.

$$F_{\min} = \sqrt{\frac{4kk_BTB}{\pi f_0 Q}}$$

k: Spring constant
Q: Q factor
f_0: Resonance Freq.

Influence of Fluids

Typical Values (NCH)

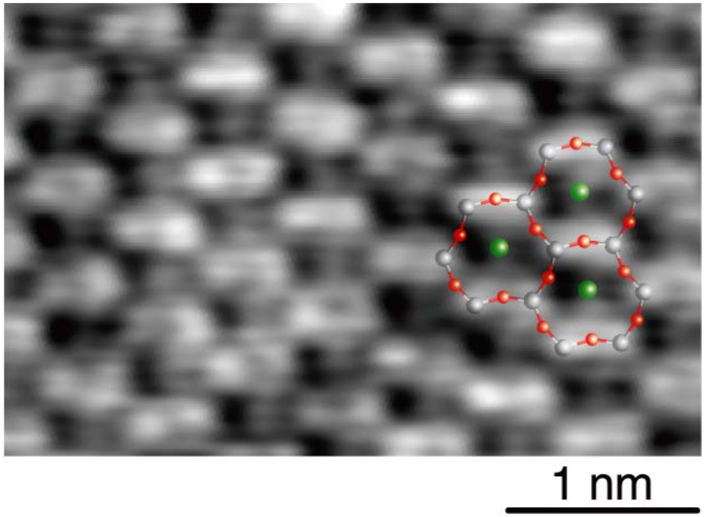
	Vacuum	Liquid
Q	30,000	8
f_0	300 kHz	130 kHz
$F_{\min}$ (B:100 Hz)	0.04 pN	4 pN

- $F_{\min}$ is determined by cantilever parameters
- $F_{\min}$ in liquid is much worse than that in vacuum

Required Force Resolution

Atomic-resolution Image

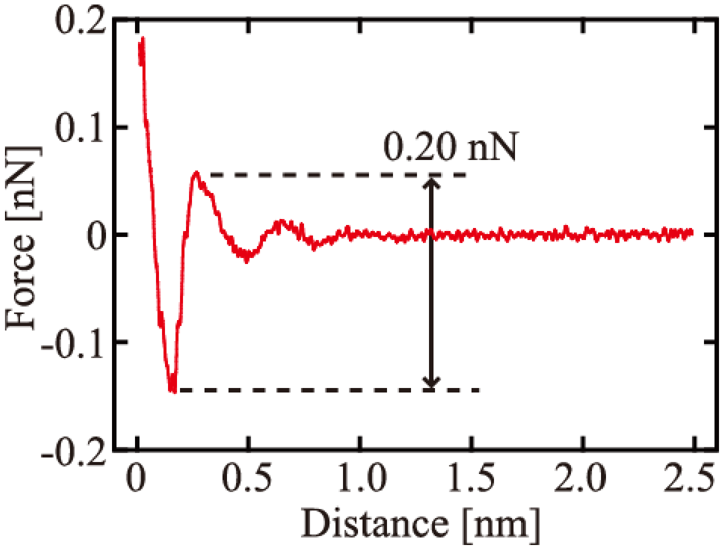
Mica in Liquid



Corrugation : 10 - 100 pm
Force gradient : 0.3 - 3 N/m
→ F_{min} : 3 – 300 pN

Hydration Force

Mica/Water Interface



Hydration force : 3- 300 pN
→ F_{min} : 3 – 300 pN

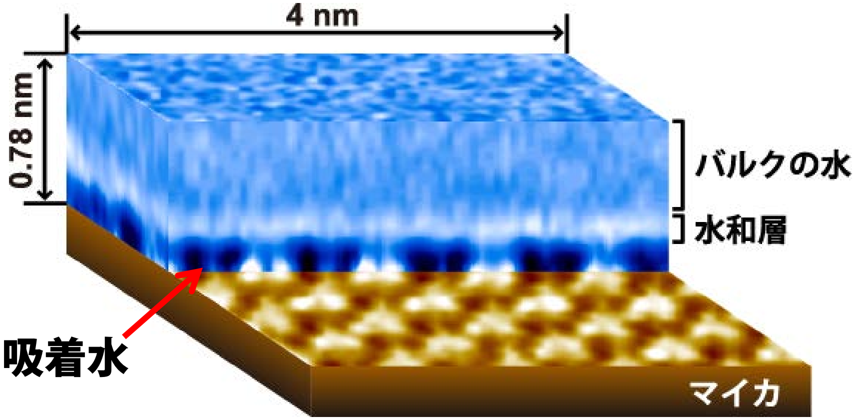
Present AFM barely satisfies these requirements
→ **Low reproducibility, reliability**
→ **Dependent on skills, samples, solution**

Required Force Resolution

3D Hydration Structure

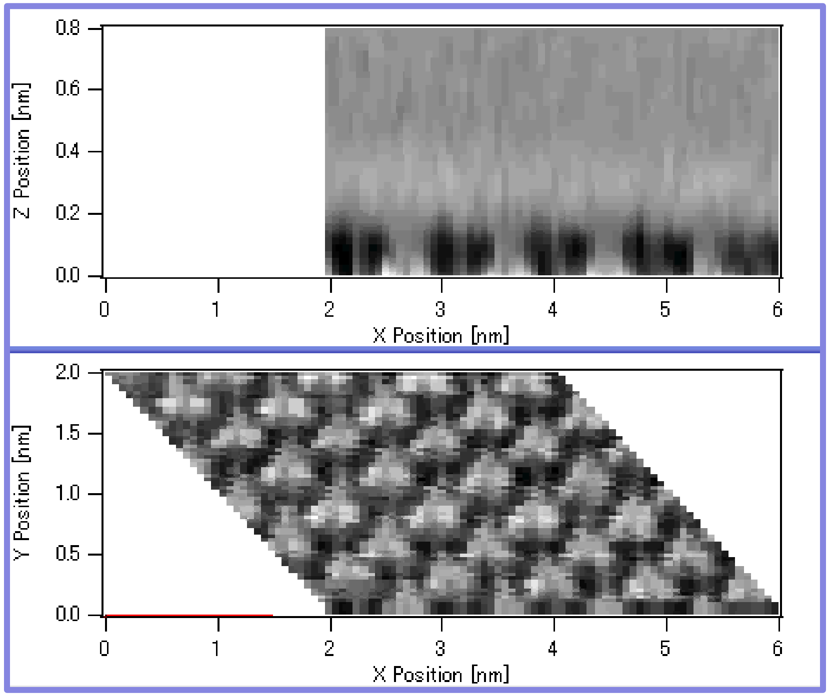
Fukuma *et al.* PRL 104 (2010) 016101

Mica/Water Interface



- XZ Image: 0.82 sec/frame
- 3D Image: 53 sec/frame

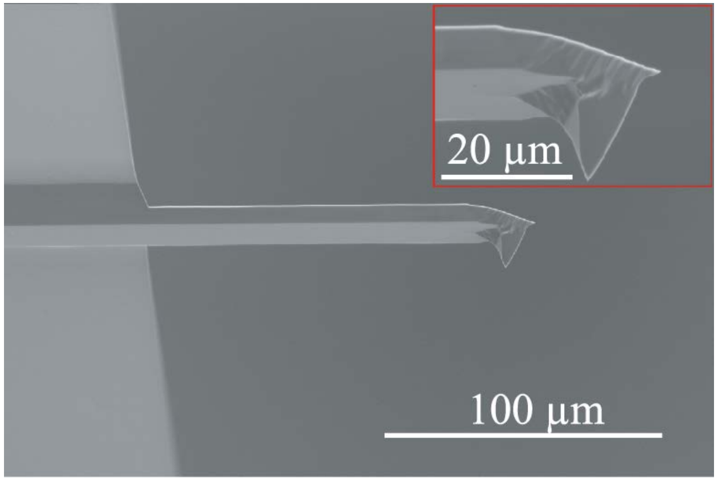
XY & Z Cross Sections



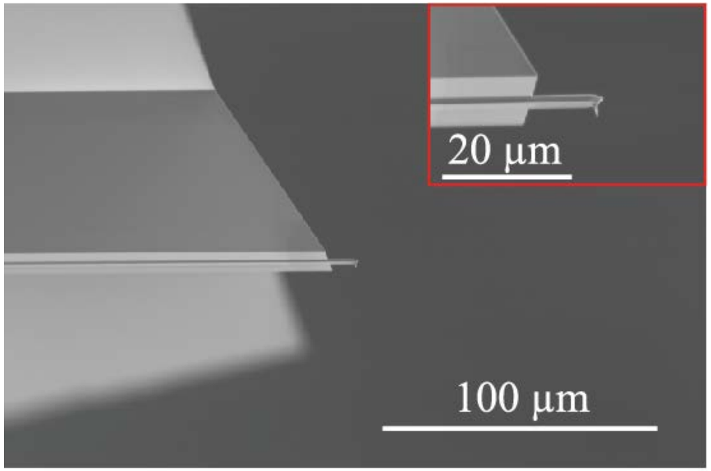
- 3D force measurement requires $B > 1$ kHz
- F_{min} of present AFM is not necessarily sufficient

Small Cantilevers (Nanoworld)

Conventional (NCH)



Small (USC - Prototype)



	ℓ [µm]	t [µm]	w [µm]	k [N/m]	Q	f_0 [kHz]	F_{min} @ $B = 100$ Hz [pN]
Conventional	136	3.7	30	26	6	130	4.2
Small	11	0.8	4.8	29	5	2800	1.0

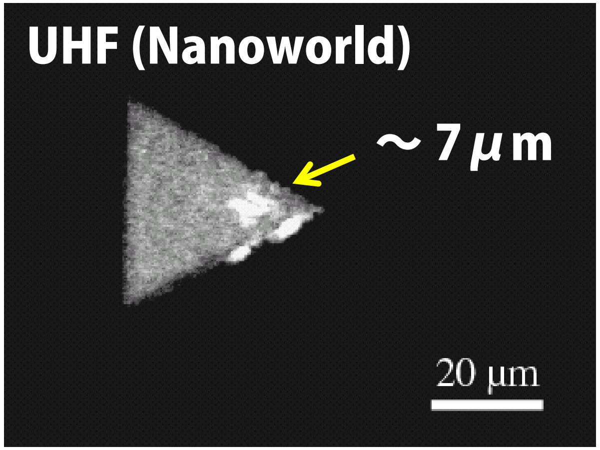
Deflection Sensor

Special Requirements

Wideband

Bandwidth: ～10 MHz

High-Mag. Optics



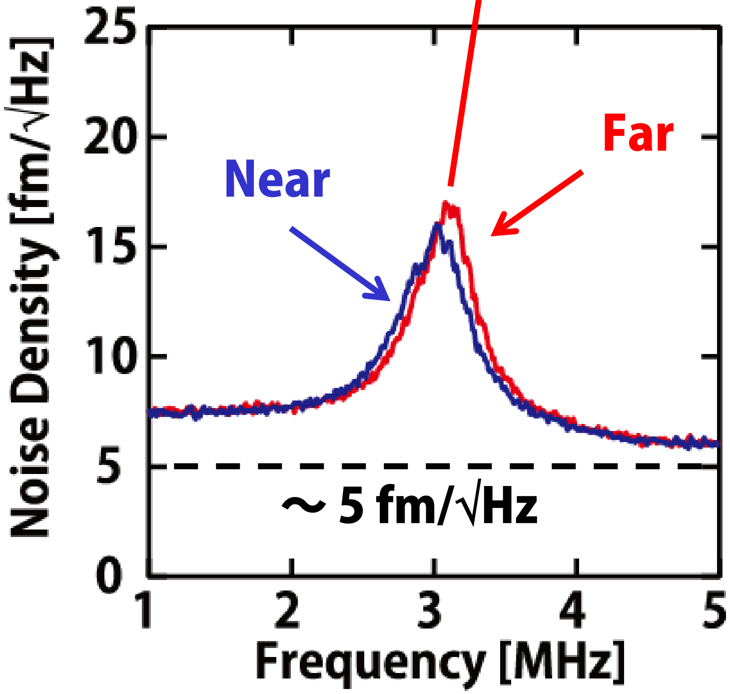
Fukuma et al. RSI 77 (2006) 043701

Fukuma RSI 80 (2009) 023707

Low Noise

$$n_{zB}(f_0)=\sqrt{\frac{2k_BTQ}{\pi k f_0}}$$

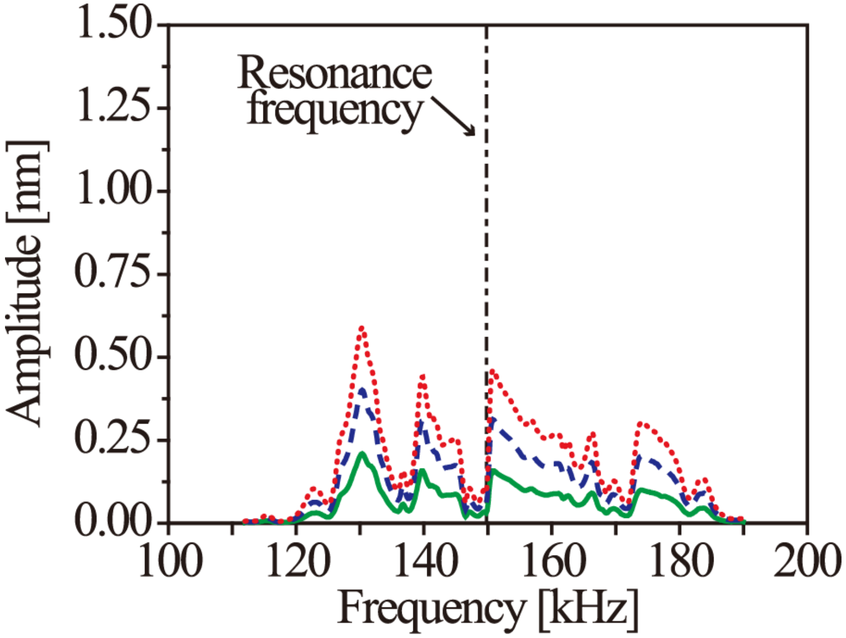
Thermal noise spectrum (USC in water)



- **Clear thermal vibration peak**
- **Sensor noise is negligible**

Cantilever Excitation

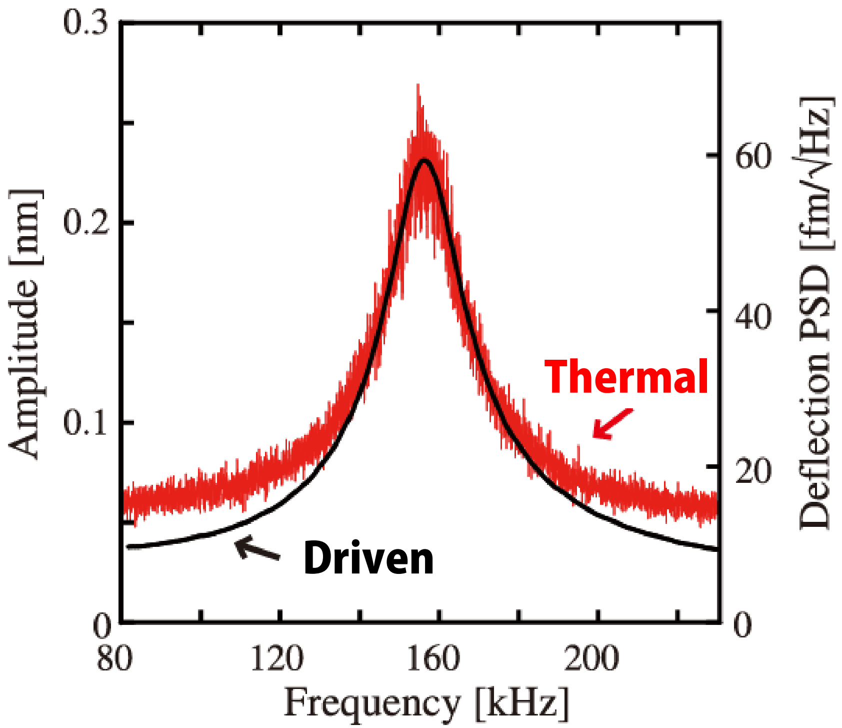
Piezoelectric Excitation



Asakawa et al. RSI 80 (2009) 103703

- **Forest of peaks**
- **Narrow bandwidth: < 1 MHz**

Photothermal Excitation



Fukuma RSI 80 (2009) 023707

- **Ideal cantilever response**
- **Wide bandwidth: > 10 MHz**

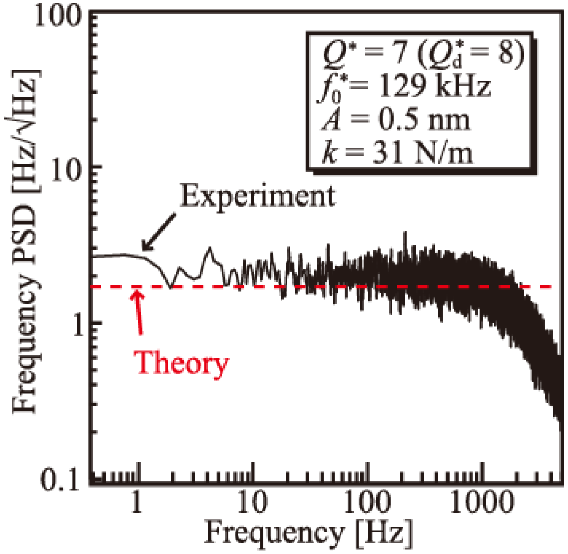
Instability of Excitation

FM Noise

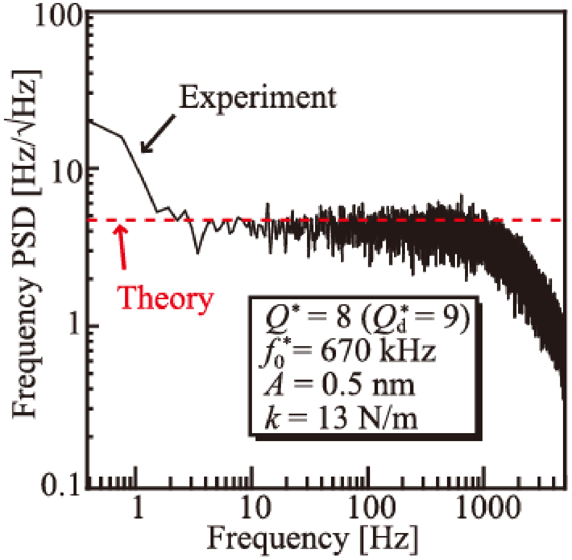
Cantilever Size

Large ↔ Small

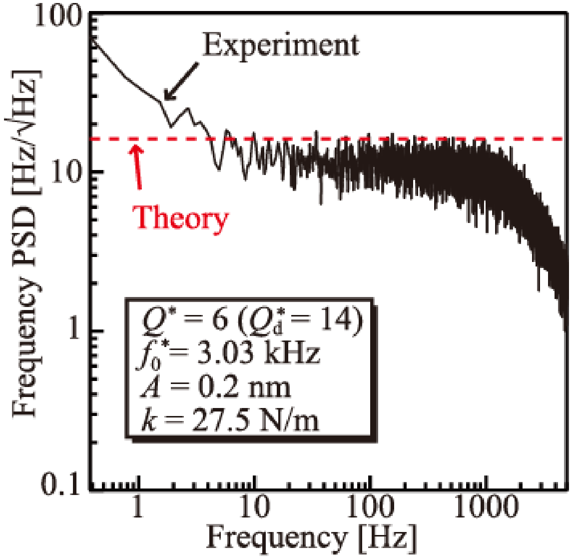
NCH



UHF



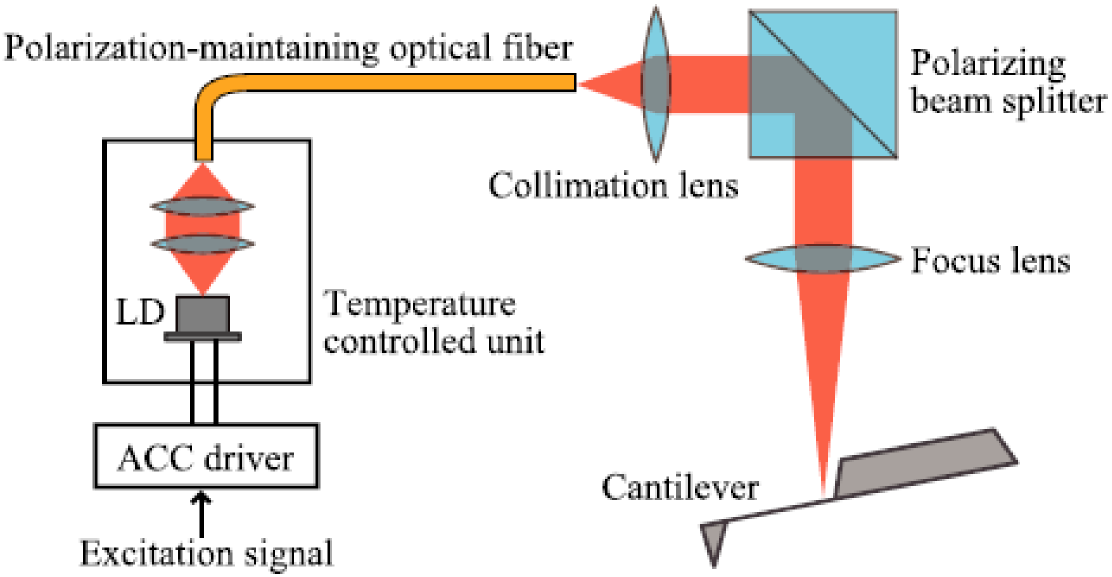
USC



Smaller cantilever shows larger Instability

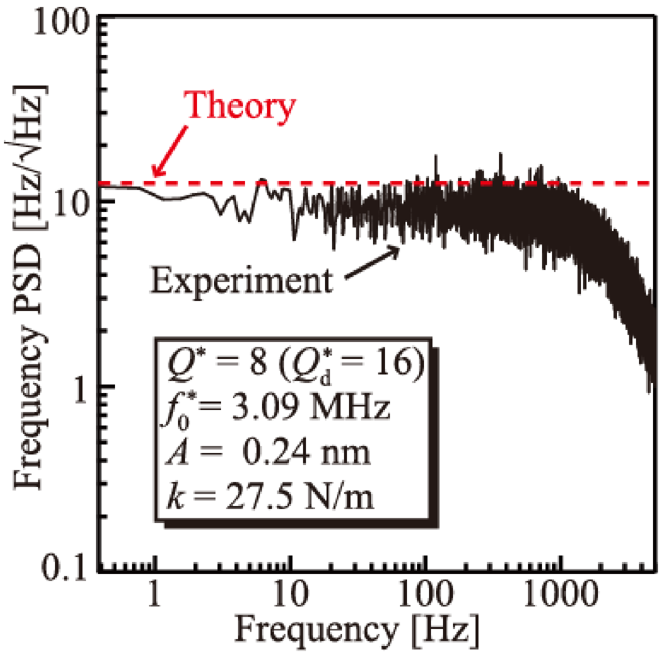
Improvement in Stability

Improved Photothermal Excitation Setup



- **APC → ACC + TEC**
- **LD+Lens → LD + PMF + Lens**

FM Noise (USC)

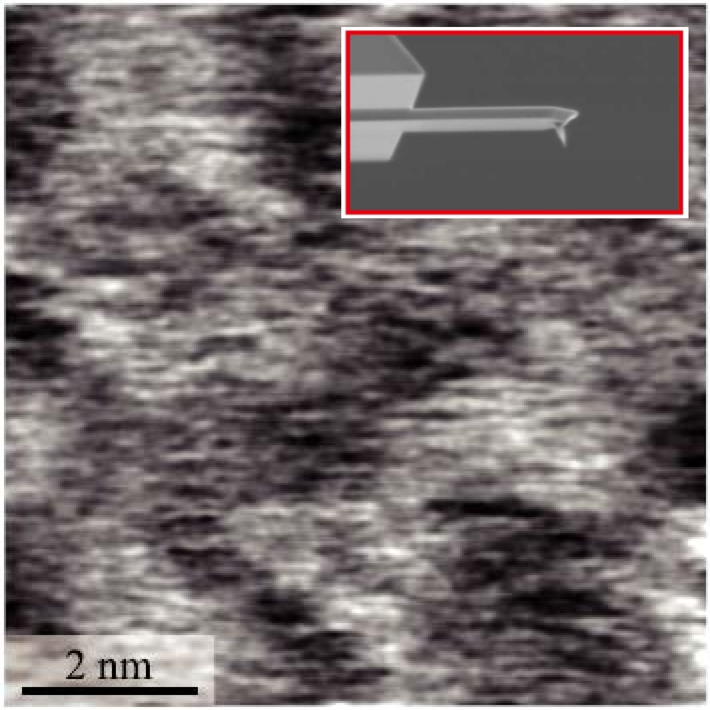


- **ACC + TEC + PMF → Sufficient stability**
- **Theoretically-limited performance with USC**

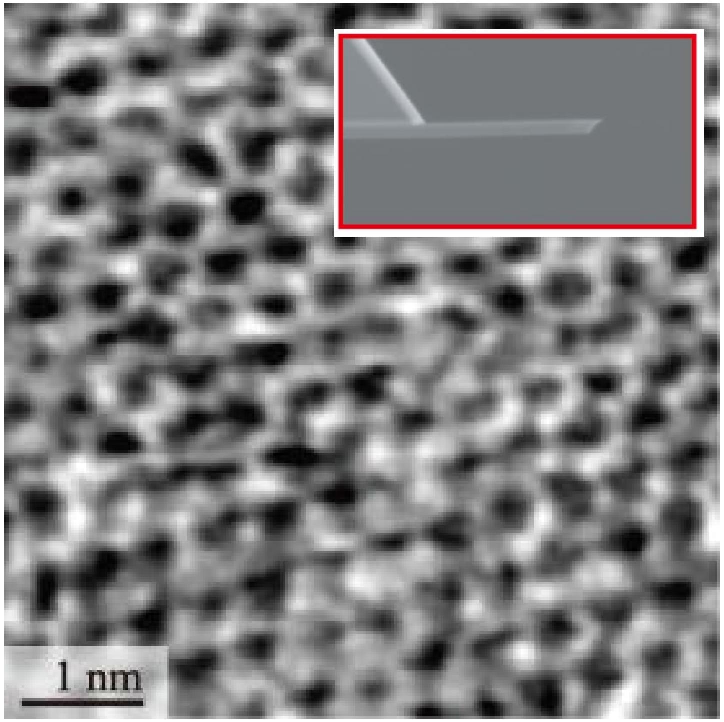
Problem in Atomic-scale Imaging

Mica in PBS Solution

USC with EBD tip



USC without Tip

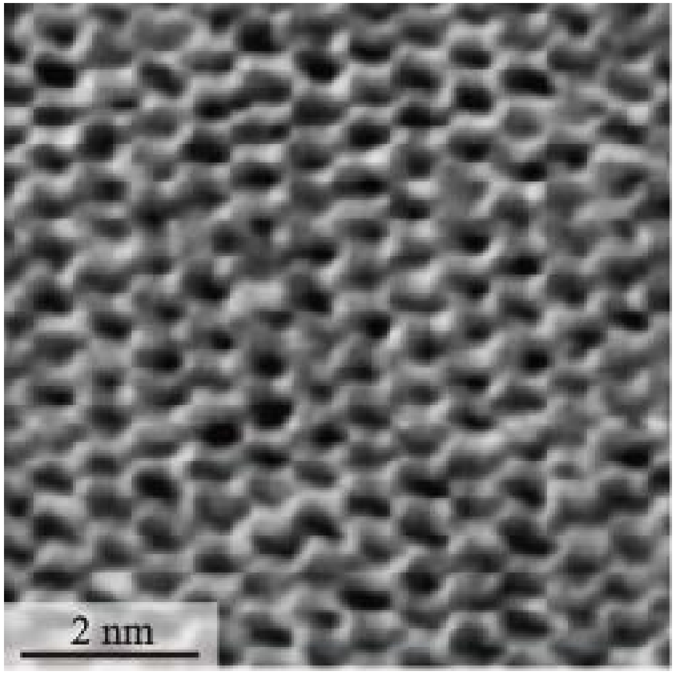


- **EBD tip prevents atomic-resolution imaging**
- **Contamination is one of the reasons**

Surface Treatment of Tip Apex

Mica in PBS Solution

USC with Si Coat（30 nm, Tip Side）



- **High reproducibility**
- **High stability**

- **The tip problem was solved by Si coating**
- **Atomic-resolution imaging by small cantilever !**

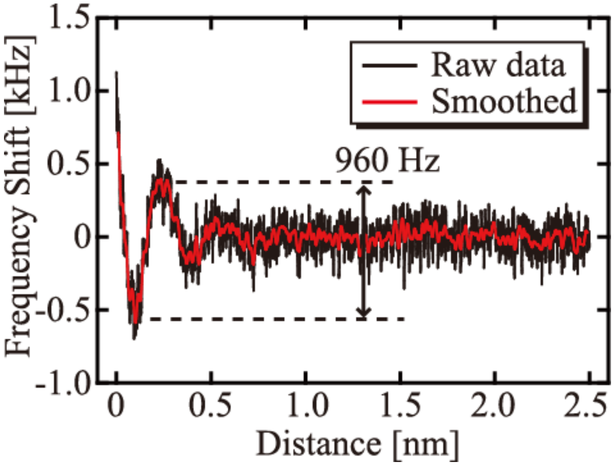
Force Measurements on Mica in Water

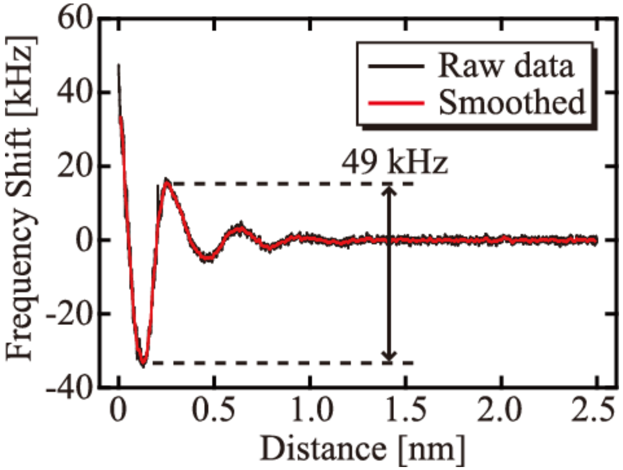
Conventional

Small

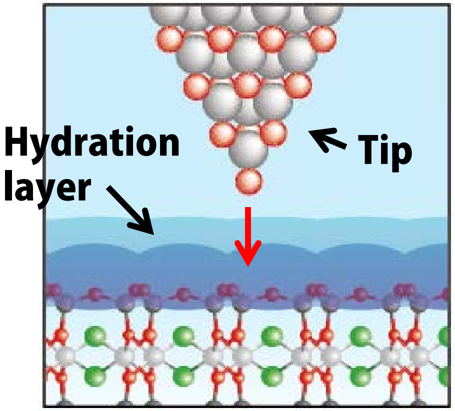
Fukuma *et al.* Nanotechnol. 23 (2012) 135706

Sens.: 5.7 THz/N → **X 43** → **Sens.： 245 THz/N**





Mica/water interface



7.4 times improvement in F_{min}

- 11 → 1.4 pN @ B = 100 Hz
- 34 → 4.6 pN @ B = 1 kHz

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Required F_{min}

- 2D：~10 pN @100 Hz
- 3D：~10 pN @ 1 kHz

Outline

1. FM-AFM in Liquid
2. Force Sensitivity
3. **Imaging Speed**
4. Stability & Reproducibility
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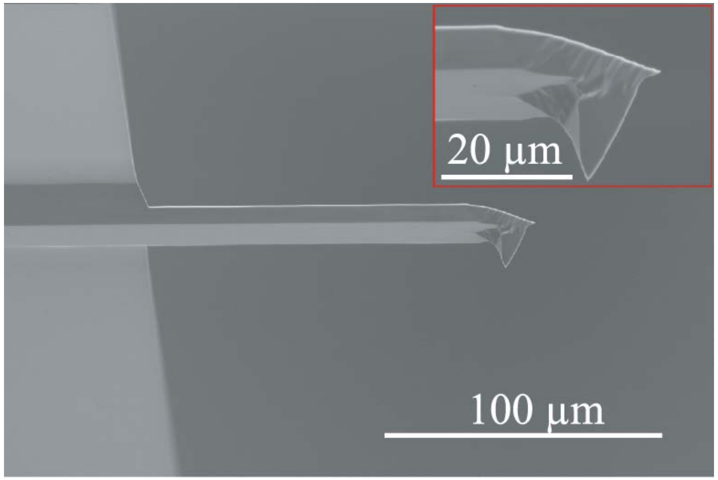
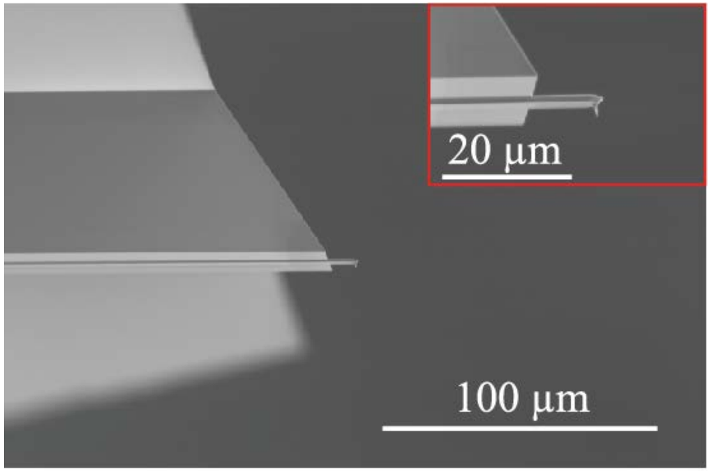
Another Benefit of Small Cantilever

Conventional (NCH)



Small (USC)

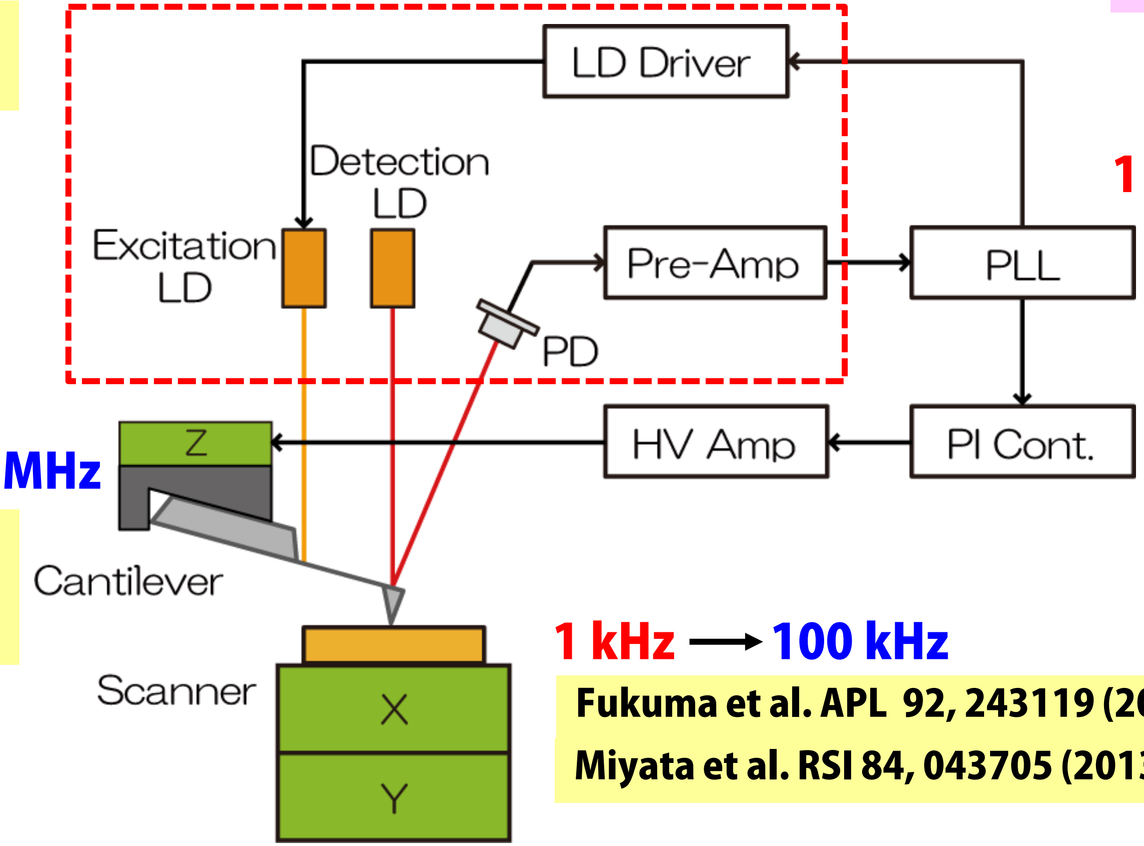


	F_{min} @ B = 100 Hz	B @ F_{min} = 10 pN	Imaging time
Conventional	11 pN	87 Hz	~60 s
Small	1.4 pN	4.8 kHz	~1.1 s
Ratio	×7.4	×55	×1/55

Small Cantilever：B = 5 kHz @ F_{min} = 10 pN
→ Atomic-resolution imaging at 1 s/frame

Improvement of *B*

Before／After



1 MHz → 10 MHz

Fukuma et al. RSI 80, 023707 (2009)

1 kHz → 100 kHz

Mitani et al. RSI 80, 083705 (2009)

Miyata et al. APL 103, 203104 (2013)

150 kHz → 3.5 MHz

Fukuma et al. Nanotechnol. 23 (2012) 135706

1 kHz → 100 kHz

Fukuma et al. APL 92, 243119 (2008)

Miyata et al. RSI 84, 043705 (2013)

Improvements of individual components

Outline

1. FM-AFM in Liquid
2. Force Sensitivity
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4. Stability & Reproducibility
5. **Summary**

Summary

FM-AFM in Liquid

- Stiff cantilever ($k > 10$ N/m)
- Small amplitude ($A < 0.5$ nm)
- Low-noise deflection sensor ($n < 40$ fm/√Hz)

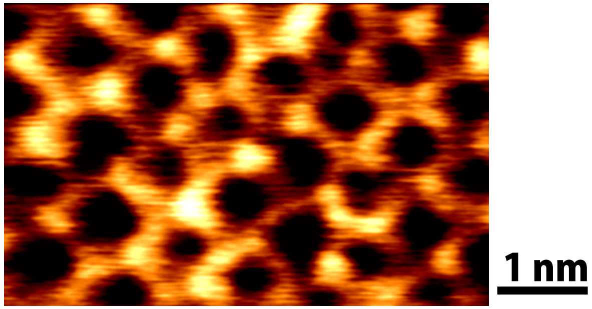
Force Sensitivity

- Small cantilever ($L < 10$ μm)
- High resonance frequency ($f_0 > 3.5$ MHz)
- Low noise deflection sensor ($n < 10$ fm/ √ Hz)
- Stable photothermal excitation

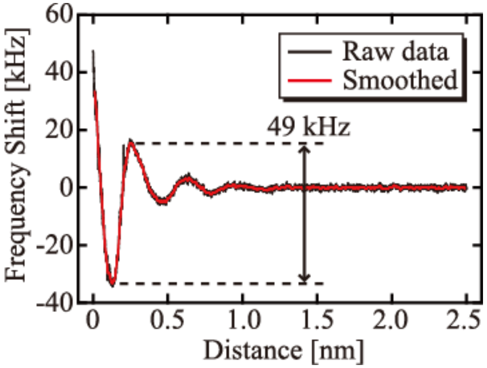
Imaging Speed

- Small cantilever ($f_0 > 3.5$ MHz)
- High resonance freq. scanner ($f_0 > 100$ kHz)
- Wideband & Low-latency PLL ($\tau < 1.4$ μs)

Atomic-resolution Imaging



~1 pN Force Resolution

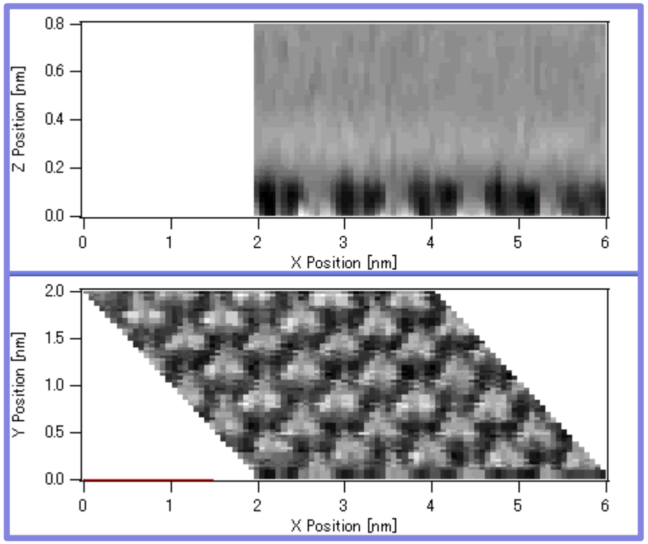


Summary

Future Prospects

- High-speed 3D Imaging
  - -> Time-resolved measurements
- Single-molecular-level tip modifications
  - -> 3D mapping of molecular interactions
- Surface property measurements
  - -> Surface potential & charge

High-speed 3D Imaging



Acknowledgements

Collaborators

Kanazawa Univ.
Hitoshi Asakawa
Kazuki Miyata
Kyosuke Onishi
Shunsuke Yoshioka
Yasumasa Ueda

Aalto Univ.
Adam Foster
Bernhard Reischl
Peter Spijker

Kyoto Univ.
Hirofumi Yamada
Kei Kobayashi

Trinity College Dublin
Suzanne Jarvis
Michael Higgins

Funding

JSPS
Japan Society for the Promotion of Science

JST Japan Science and Technology Agency