

NOVEL TECHNIQUES IN MULTI-FREQUENCY ATOMIC FORCE MICROSCOPY AND SPECTROSCOPY

A THESIS

SUBMITTED TO THE PROGRAM OF MATERIALS SCIENCE AND

NANOTECHNOLOGY

AND THE INSTITUTE OF ENGINEERING AND SCIENCE

OF BILKENT UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

By

Musa Kurtuluş Abak

March, 2009

I certify that I have read this thesis and that in my opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Salim Çıracı (Advisor)

I certify that I have read this thesis and that in my opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

Assist. Prof. Aykutlu Dâna (Co-Advisor)

I certify that I have read this thesis and that in my opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

Prof. Dr. Abdullah Atalar

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assist. Prof. Mehmet Bayındır

I certify that I have read this thesis and that in my opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Assist. Prof. Ceyhun Bulutay

Approved for the Institute of Engineering and Science:

Prof. Dr. Mehmet B. Baray
Director of the Institute Engineering and Science

ABSTRACT

NOVEL TECHNIQUES IN MULTI-FREQUENCY ATOMIC FORCE MICROSCOPY AND SPECTROSCOPY

Musa Kurtuluş Abak

M.S. in Materials Science and Nanotechnology

Supervisor: Prof. Dr. Salim Çıracı

March, 2009

The capability of measuring material properties of nanostructures simultaneously with their size and shape is very desirable for characterization of novel materials and devices at the nanoscale. Here we present two novel techniques for imaging and spectroscopy of mechanical and electrical properties of surface nanostructures simultaneously with topographic imaging.

First we present a scanning probe technique that can be used to measure charging of localized states on conducting or partially insulating substrates at room temperature under ambient conditions. Electrostatic interactions in the presence of a charged particle between the tip and the sample is monitored by the second order flexural mode, while the fundamental mode is used for stabilizing the tip-sample separation. Cycling the bias voltage between two limits, it is possible to observe hysteresis of the second order mode amplitude due to charging. Results are presented on silicon nitride films containing silicon nanocrystals.

Second we report use of nonlinear tip-sample interactions to convert the frequency components of periodic tip-sample interaction forces to frequencies where they can be resonantly detected by resonant heterodyne mixing. One flexural mode of a cantilever is used for tapping-mode imaging and another flexural mode is used for detection of forces converted in presence of an externally injected mechanical oscillation at the difference frequency of the detecting mode and a harmonic of the tapping mode. Material contrast in attractive and repulsive regimes are demonstrated on samples with polymethyl methacrylate patterns and with deoxyribonucleic acid strands on silicon.

The techniques can be implemented using standard force microscopy systems

and cantilevers, which make them potentially useful to a greater scientific community.

Keywords: atomic force microscopy, electrostatic force microscopy, multi-frequency force microscopy.

ÖZET

ÇOK-FREKANSLI ATOMİK KUVVET GÖRÜNTÜLEMESİ VE SPEKTROSKOPİSİNDE YENİ YÖNTEMLER

Musa Kurtuluş Abak
Malzeme Bilimi ve Nanoteknoloji , Yüksek Lisans
Tez Yöneticisi: Prof. Dr. Salim Çıracı
Mart, 2009

Nanometrik yüzeylerin ya da parçacıkların yüzey şekillerini Atomik Kuvvet Mikroskobu(AKM) ile görüntülerken, aynı zamanda bu nesnelerin farklı özelliklerinin de aynı zamanda görüntülenebilmesi çok ihtiyaç duyulan ve istenen bir özelliktir. Biz burada bu isteği gerçekleştirecek iki yeni teknik ortaya koyacağız.

İlk olarak iletken yada kısmi olarak yalıtkan alttaşların oda sıcaklığında normal şartlar altında yerleşmiş durumların yüklenmesini ölçebilecek taramalı uç tekniğini ortaya koyacağız. Uç ve numune arasındaki yüklenmiş parçacıkların varlığından kaynaklanan elektrostatik etkileşme ikinci dereceden bükülme kipleriyle görüntülenmiştir. Burada temel kip, uç ve numune arasındaki mesafeyi kararlaştırmak için kullanılmıştır. Uygulanan gerilimin iki sınır değeri arasında kendini tekrar eder şekilde değiştirilmesiyle, ikinci kipi genliğinin yüklenme dolayısıyla gösterdiği histeresisin gözlemlenmesi mümkündür. Sonuçlar silikon nanokristaller içeren silisyum nitrit filmler üzerinde gösterilmiştir.

İkinci olarak ise kendini tekrar eden uç numune etkileşim kuvvetlerinin frekans bileşenlerinin, doğrusal olmayan uç numune etkileşimleri yardımıyla, çınlanımlı olarak algılanabilecekleri frekanslara dönüştürülmesini göstereceğiz. Sallanan ucun bir bükülme kipi yarı-değme durumunda görüntüleme yaparken, diğer bükülme kipi, dışardan gönderilen algılama kipi ve yarı-vurma kipi bir harmoniğinin frekansları farkında uygulanan mekanik titreşimin varlığı ile, dönüştürülmüş kuvvetleri algılamak için kullanıldı. Çekici ve itici bölgelerde malzeme zıtlığı silisyum alttaşlar üzerine konan polimetil metakrilat şekilleri ve deoksiribonükleik asit zincirleri ile gösterilmiştir.

Teknikler, standart kuvvet mikroskobu sistemleri ve uçları kullanılarak uygulanabilmektedir, ki bu da bu teknikleri bilimsel topluluğun kullanımı için yararlı kılmaktadır.

Anahtar sözcükler: atomik kuvvet görüntülemesi, elektrostatik kuvvet görüntülemesi, çok-frekanslı kuvvet görüntülemesi.

Acknowledgement

I would like to thank to Assist. Prof. Aykutlu Dâna for letting me involve in the realization of this work and sharing his knowledge. It is a pleasure to me working with him and learn from him.

I would like to thank to the director of The Institute of Materials Science and Nanotechnology, Prof. Dr. Salim Çıracı for his support.

I would like to thank to Hasan Güner, Sencer Ayas, Ozan Aktaş and Özlem Yeşilyurt for being good friends and research partners.

I would like to thank to my friends Mutlu Erdoğan, Seydi Yavaş, Mustafa Ürel, Sencer Ayas and Güneş Kaya for sharing the same office with me and bearing with me to my questionable questions and loud disturbing voice. I would like to thank them for always being there, when i need them. Also I would like to thank all my friends in the Institute of Materials Science and Nanotechnology and Department of Physics.

To my parents and my sister, I would like to give them special thanks for supporting me and giving their love and respect for who I am.

I would like to thank to everybody whom I learned something.

Contents

1	Introduction	1
1.1	Motivation	3
1.2	Organization of the Thesis	4
2	Scanning Probe Microscopy	5
2.1	Anatomy and Working Principles of AFM	6
2.2	Calibration of spring constants of AFM cantilevers	8
2.2.1	Added mass method	10
2.2.2	Sader method	10
2.2.3	Determination with a calibrated cantilever	10
2.3	Operation Modes of AFM	11
2.3.1	Static Mode	11
2.3.2	Dynamic Mode	12
2.4	Factors Affecting the Imaging	12
2.4.1	Tip Effects	13

2.4.2	Thermal Drift	15
2.4.3	Mechanical Vibrations	15
2.4.4	Piezoelectric Transducer and Thermal Noise Related Creep	15
2.5	Noise in AFM	17
3	Tip-Sample Interactions and Force-Distance Curves	22
3.1	Forces In Tip-Sample Interactions	22
3.1.1	Van der Waals Forces (Long-range attractive interactions)	23
3.1.2	Contact and Short-Range Repulsive Forces	24
3.1.3	Electrostatic Forces	25
3.1.4	Capillary Forces	25
3.2	Constructing the Total Tip Sample Interaction	26
3.3	Force-Distance Curves	28
4	Simulation Strategy for AFM	32
4.1	Tip-Cantilever System Models	33
4.1.1	1-D Beam Model	33
4.1.2	Point Mass Model	36
4.2	Numerical Simulation Method	38
4.2.1	Numerical Strategy Used in This Work	39
5	Multifrequency Electrostatic Force Spectroscopy	48

5.1	Introduction	48
5.2	Description of extended interaction model including electrostatic effects	49
5.3	Description of new technique, multifrequency electrostatic force spectroscopy	51
5.4	Spectroscopy of Carbon Nano Tubes	59
5.5	Conclusion	60
6	Resonant Heterodyne Force Imaging	65
6.1	Introduction	65
6.2	Numerical Investigation of Resonant Heterodyne Force Imaging .	66
6.3	Description and implementation of the new technique	70
6.4	Conclusion	74
7	Conclusion	84
Appendix:		
A	Amplitude and Phase distance curve simulator code 1	86
B	Amplitude and Phase distance curve simulator code 2	88

List of Figures

2.1	AFM apparatus principle. Cantilever movement on a substrate under controlled constant force or other parameters	7
2.2	AFM working principle described for dynamic mode with closed loop for keeping amplitude constant while imaging	8
2.3	Nanoparticle capturing of the blunt tip and sudden improvement in imaging quality 1	14
2.4	Nanoparticle capturing of the blunt tip and sudden improvement in imaging quality 2	16
2.5	Visualization of the elongation of the features on the images of silver nanoparticles and DVD gratings caused by the thermally induced piezocreep	19
2.6	Representative noise spectrum for commercial instrument showing 1/f, electronic noise and brownian components.	20
2.7	Noise spectrum of instrument that we use in our experiments. Cleary 1/f component is mostly eliminated, and total noise is dominated by electronic noise and brownian components.	21
3.1	Graphical representation of combination of van der Waals and DMT model where interatomic distance parameter is 4 Angström	27

3.2	Force-distance curve from the experiment conducted on Si surface	28
3.3	Force-distance curve from the experiment conducted on PMMA surface	29
3.4	Force versus distance curve. For the example shown here, the tip first experiences a long-range repulsive force upon approaching the sample, even before the tip and sample are in physical contact. Close to the sample, the tip becomes strongly attracted by the van der Waals force. In this instance, the attractive force gradient becomes greater than the force gradient by the cantilever spring. This causes the tip to snap into physical contact with the sample (the perpendicular part of the approach curve). Once physical contact has been made, the cantilever is deflected linearly by the approaching scanner. When it is turning back, the tip may stick to the sample by adhesion until the pull by the cantilever forces it out of contact. Three types of hysteresis can occur: In the zero force line (green), in the contact part (yellow) and adhesion (squared purple)	30
4.1	Schematic description of the 1 dimensional beam cantilever	33
4.2	Illustration of the first four flexural eigenmodes of a freely vibrating rectangular cantilever beam	35
4.3	Schematic description of the point mass description of cantilever base and tip.	36
4.4	Amplitude distance, phase distance curves that are taken from the simulation results with the parameters $E_t = 130GPa, E_s = 1GPa, R = 50nm, H = 6.4 \times 10^{-20}, f_0 = 75kHz, k_0 = 2.5N/m, A_0 = 10nm$	42

4.5	Total force and potential energy of the cantilever(modeled as spring) and the tip-sample interaction at 24nm and 18nm respectively. Showing that tip and sample system, when the tip approaching the sample, has bistabilities at various points. This means, at those positions motion of the cantilever is chaotic and sudden jumps from one stable point to another, because of the tip-sample interaction, is possible.	44
4.6	Total force and potential energy of the cantilever (modeled as spring) and the tip-sample interaction at 12nm and 6nm respectively.	45
4.7	Amplitude distance, phase distance and stability map curves that are taken from the simulation results were no ferquency off-set is applied, with the parameters $E_t = 130GPa, E_s = 1.2GPa, R = 50nm, H = 6.4 \times 10^{-20}, f_0 = 75kHz, k_0 = 3N/m, A_0 = 10nm$	46
4.8	Amplitude distance, phase distance and stability map curves that are taken both in repulsive(above) and attractive(below) regions with same parameters were no frequency offset applied (previous figure)	47
5.1	Detailed representation of a tip with its geometrical characteristics.	49
5.2	Lumped electrostatic forces for excitation of the first two modes of a cantilever on a planar surface, plotted as a function of the tip-sample separation z_{cs}	52
5.3	The tip-sample separation during oscillation of the cantilever in the first and second order mode simultaneously. Tip-sample separation at closest approach is 0.6 nm. b) Electrostatic force resulting from AC excitation of the form $V_{ts}(t) = V_{DC} + V_{AC} \cos(\omega_2 t)$, during the oscillation shown in (a). The values used in the simulation are, tip length $H=15$ m, half-cone angle $\theta_0=15$ degrees, tip radius $R=15$ nm.	53

- 5.4 Dependence of the amplitude of the second order mechanical mode on DC bias voltage, during tapping with the fundamental mode. The ac frequency was on resonance with the second order mode. Smooth transition of the phase of the oscillation indicates finite capacitive coupling of the drive signal to the dither piezo. 56
- 5.5 Electrostatic excitation of the second order mode during a voltage sweep on a clean silicon surface. The arrows denote voltage sweep directions. No hysteresis can be observed. (b) Electrostatic excitation of the second order mode during a voltage sweep on silicon nitride layer with silicon nanocrystals embedded. Significant hysteresis is observable, indicating charging of nanocrystals. The arrows denote onset of charging and discharging events. The insets show capacitance-voltage traces of macroscopic capacitors fabricated using silicon nitride films without and with nanocrystals. 61
- 5.6 Oscillation amplitude vs tip-sample separation. When the cantilever is driven below its resonance frequency, peaking of the oscillation amplitude is observed (a) for 0 V bias and (b) for 2 V bias. If the drive frequency is above the resonance frequency, no such peaking occurs as seen in (c) for 0 V bias and (d) for 2 V bias. Representative theoretical fits obtained by using the same set of parameters and by only changing the bias parameter are shown as solid curves. (e) The inset shows amplitude vs tip-sample separation scans obtained at 0 V bias before and after charging the film by contacting with a 2 V biased tip. Shift of the curve and broadening of the peak after charging indicate a local surface potential shift. 62
- 5.7 These are taken from the silver nanoparticles on Si substrate. above is the topography and the below is the electrostatic image of the particles. Topography and the Electrostatic image recorded simultaneously 63
- 5.8 Topography image of the carbon nano tubes on silicon substrate. . 64

5.9	Representative spectroscopy datas taken on carbon nano tubes(CNT) and on silicon substrate	64
6.1	Stability map for the interaction amplitude with respect to distance. In figure repulsive branch is seen as the seperated part from the wide white region which is attractive branch	67
6.2	Calculation flow chart of amplitude of frequency components of interaction	75
6.3	Experimental data of tip sample seperation dependent amplitude of up-converted signal for different local oscillator frequencies . . .	76
6.4	Calculated data of tip sample seperation dependent amplitude of up-converted signal for different local oscillator frequencies	76
6.5	Flow chart of time dependent quality factor calculation	77
6.6	'Time dependant quality factor' corrected simulation result for tip sample seperation dependant amplitude of up converted signal for different local oscillator frequencies	78
6.7	The stability map, amplitude and phase distance curves that shows the switching behaviour of the sytem between attractive and repulsive branches.	79
6.8	Calculated data of tip sample seperation dependent amplitude of up-converted signal for different local oscillator frequencies with the switching behaviour of the system between attractive and repulsive regime	80

- 6.9 Excitation of the second order mode through resonant heterodyne mixing as a function of tip-sample separation. a) Typical Force-Distance and Amplitude-Distance curves acquired simultaneously with the up-conversion measurements. Second-order mode amplitude A_1 when b) $f_{LO} = f_1 - f_0$, c) $f_{LO} = f_1 - 2f_0$, d) $f_{LO} = f_1 - 3f_0$, e) $f_{LO} = f_1 - 4f_0$ and f) $f_{LO} = f_1 - 6f_0$. (Measurement bandwidth is 1 KHz.) g) Up-converted amplitude A_1 increases with increasing LO amplitude A_{LO} . (Measurement bandwidth is 100 Hz.) h) A_1 versus f_{LO} plot shows that up-conversion takes place at $f_{LO} = f_1 - nf_0$ (arrows). i) Perturbation of the dynamic properties of the fundamental mode as observed in the noise spectrum of the cantilever when the second mode is tapping in attractive (left arrow) and repulsive modes (right arrow). When the cantilever is lifted from the surface by a few micrometers, Brownian noise spectrum of the unperturbed cantilever can be observed (middle arrow). j) Down-converted amplitude A_0 at the shifted fundamental mode resonance frequency, during tapping with higher order flexural mode. As A_{LO} is increased down-converted signal amplitude increases. k) Down converted signal to 30 KHz (Non-resonant). 81
- 6.10 Simulation results for up-conversion process in pure repulsive regime. a) Amplitude vs z_{ts} for Si and Polystyrene samples for $Q_0=200$ and 150. b) Phase vs A_0 c) Up-converted force amplitude for $f_{LO} = f_1 - f'_0$ vs A_0 . d) Peak force vs A_{LO} . e) Up-converted signal vs. A_{LO} f) Average DC Force vs A_{LO} . g) Up-converted force vs A_0 for $f_{LO} = f_1 - nf'_0$ for $n=1, 2, 3, 4, 5, 6$ 82

- 6.11 Material contrast observed through up-conversion in the attractive regime. a) Phase contrast image of PMMA patterns on silicon. Up-converted force detected at the first-order mode frequency when sample is oscillated at b) $f_{LO} = f_1 - f_0$ c) $f_{LO} = f_1 - 2f_0$ d) $f_{LO} = f_1 - 3f_0$. Images acquired with 0.5 Hz per line. Material contrast observed through down-conversion in the repulsive regime. Images of plasmid DNA on silicon: e) Topographic (full scale 10 nm) f) Phase (full scale 30°) g) DC Force (full scale 0.5 nN) and h) PDC signal at 90 KHz. Double strand (arrow), curled particles and bundles of DNA can be discerned. Images acquired with 1.5 Hz per line, 1 μm image width. 83

List of Tables

- 5.1 Work function values taken from the spectroscopy experiments of the different points on either silicon or carbon nano tubes(CNT) . 60

Chapter 1

Introduction

As the science and technology proceeds towards smaller spatial dimensions, the requirement for the imaging lower scales become more and more important. This need is not impotant for looking at the smaller scale object but also for characterizing and manipulating them. The starting of the “nanotechnology revolution” coincides with, or closely follows the advancement and availability of imaging techniques with nanometer resolution. It’s well known that, in an imaging experiment, optical electronic or otherwise, when the probe is larger in size from the object that is to be investigated, resolution will be limited by the size of the probing agent. In optical microscopy for example, we are basically limited with “diffraction limit”; that is, the size of the waves that we use to probe is larger than the size of the objects that we want to see(However, recently, different techniques have been developed to overcome the diffraction limit). Electrons, neutrons, X-rays etc. provide naturally higher resolution. Electron microscopy and scanning probe microscopy are the two widely used techniques for nanoscale imaging. These two techniques(especially Atomic Force Microscopy) made a tremendous effect on micro and nano scale science and technology. Because the principles and the implementation of the technique is fairly simple and cheap, it had been rapidly developed and found vast number of application areas. Consequently, while it is rapidly developing, also the field of Nanotechnology accelerated and made a big jump. Today, we can find an atomic force microscope nearly in all universities or

research laboratories used for the purpose of imaging and characterization.

AFM overcomes certain problems that Scanning Tunneling Microscope (STM) faces. STM can be applied to samples that are conductive. Whereas AFM can operate under ambient conditions and can be applied not only to electrically conductive sample but also to semiconductors and to insulators. This advantage of AFM elucidated by scientists very well from the point of view of basic physics. In the mean time system is found very vast amount of application area in the semiconductor technology. It has been used as an ultimate surface characterization tool. It also revealed the atomic properties of surfaces.

From the fact that it is very flexible tool, people have perpetually developed the applications that can be implemented with an AFM system. With every application that is developed, AFM gains new features and find different application area. It became a tool of characterization for nano and micro devices, besides it was used as a novel device since it can reach and probe that very small scales.

It could only probe surface topography of the samples at first by the use of the static deflections of the cantilever. Soon after, dynamic methods broaden the operation technique and enabled to reach atomic resolution under ultra high vacuum with non-contact mode. Then tapping mode (intermittent contact mode) came to the scene and this became one of the most used characterization tools under ambient conditions for non destructive topography imaging. AFM modes go beyond these two basic and fundamental operation modes, below is a very short list of some of these modes.

- Contact mode
- Constant force mode
- Constant height mode
- Non-contact mode
- Tapping mode
- Static and dynamic force-distance mode

STM and after that AFM gives the opportunity to use the different forces and methods as probes for imaging and characterization such as

- Electrostatic Force Microscopy
- Magnetic Force Microscopy
- Kelvin Probe Microscopy
- NSOM (Near field Scanning Optical Microscopy)

As we mentioned above, been such a flexible tool, AFM finds application in biology, biophysics and even molecular biology. It is being used as characterization tool for microscale living organisms like bacteria, viruses. Chemists use the system as a tool for organic and inorganic characterization of surfaces.

AFM system also gain the ability to probe samples under different conditions such as, water, acids, bases etc. Being able to use AFM in these media gives chemists the ability to investigate reaction on surfaces, how surfaces react with chemical agents in time, the conformation of polymers and macromolecules in dry and aqueous conditions. Biologists use AFM to investigate living organisms in water or in their native living conditions.

Despite the richness of presently available AFM techniques, for imaging and characterization, AFM is still not a completely mature subject and it is still an open area to offer a lot more.

1.1 Motivation

In all imaging and characterization experiments, it is important to image the micro and nano scale feature with high resolution. But in addition to the topography, being able to acquire the information about the material properties of the features on the substrate is very crucial. With conventional dynamic force microscopy technique, we use the information coupled to the first or fundamental

mode of the mechanical resonator, namely cantilever. But the interaction between the tip and the sample is nonlinear because of this nonlinearity in every cycle of oscillation couples to whole of the participating spectrum of the cantilever. Mostly we single out the fundamental mode signal and waste the other portion of the spectrum. Utilizing higher harmonics of the cantilever system gives different kind of information about for instance stiffness of material, contact potential of sample etc. One of the important aspect of acquiring additional information from different modes, requires separately doing the experiment for each frequency component. If we could extract the information of these different modes and single out specific properties of materials at the same time with topography, this would be a great contribution to the AFM technique. In this thesis, we develop techniques for simultaneous imaging of the material stiffness or electrostatic contact potential difference and topography.

1.2 Organization of the Thesis

The thesis is organized as follows: Chapter 2 describes the AFM system, operation technique and related issues. Chapter 3 includes interactions between tip and the cantilever, and information we could get via force distance curves. Chapter 4 gives briefly simulation technique in AFM and explain modeling, simulation and related numerical approach that is used in this work. Chapter 5 introduces the Nanoscale charging hysteresis measurement by multifrequency electrostatic force spectroscopy. Chapter 6 introduces Resonant Heterodyne force imaging technique. Finally, Chapter 7 summarizes and gives some conclusive remarks for this thesis.

Chapter 2

Scanning Probe Microscopy

It was impossible to directly image individual atoms on a surface until the invention of the scanning tunneling microscope (STM) by Binnig, Rohrer, Gerber and Weibel in 1981.[1] In 1986 G.Binnig and Hrohrer won the Nobel Prize in Physics for imaging Si(111)-(7x7) surface. After that invention, surfaces of numerous metals and semiconductors have been investigated under STM. In today's scientific research world STM is an indispensable tool in many areas, such as surface science, superconductivity, biochemistry and semiconductor physics.

In spite of the widely usage of STM, it has a critical handicap. Since system uses the tunneling current between the tip and sample as control signal, the sample must be electrically conductive. Being electrically conductive is necessary but not sufficient for high resolution, high quality quantitative imaging with STM. Imaging procedure must be conducted under ultra-high vacuum conditions, to observe ideal surfaces, because surfaces of samples change under ambient conditions due to adsorption and desorption of atoms and molecules.

Experiments that are done with the STM revealed that, in the range of distances that tunneling current can flow, there are also different and significant atomic and molecular forces exists.[2] In 1986, Binnig invented a device that utilizes these significant forces for imaging purposes; that is the Atomic Force Microscope (AFM).[3]

The device Binnig invented beat the critical handicap which STM has, that is AFM can image any flat surface in ambient conditions and without the tedious procedure of surface preparation. Nevertheless for imaging surfaces on the atomic level still ultrahigh vacuum and special sample preparation is needed.

After the invention of the AFM, people developed lots of different imaging microscopies based on the knowledge of the AFM such as; electric force microscopy (EFM), magnetic force microscopy (MFM),[4] lateral force microscopy (LFM),[5] phase contrast imaging,[6] scanning conductance microscopy (SCM) [7] and scanning near field optical microscopy (SNOM).[8]

2.1 Anatomy and Working Principles of AFM

AFM structurally consists of three building block; first is the scanning block and, second is deflection detection block and third is the control block. Scanning of the sample is performed mostly by a piezoelectric scanner that can move in the X, Y, and Z directions. Deflection detection on the other hand is done in most of the commercial systems by beam bounce method; that consists of a laser source, a cantilever, a mirror, and a photodetector. Control block is a computer and additional hardware. Fig.2.1 shows the basic parts in the first and second block schematically.

AFM system uses a cantilever with a sharp tip at the end to sense the force and extract the topography of the sample surface. Most of the time, for scanning the sample, high voltage is applied to appropriate sides of the piezoelectric ceramic tube. Since these high voltages deform the piezoelectric ceramic tube, it can perform scanning process. Scanning can be done in two different ways. By a line scan or by a raster scan. In line scan, tip is scanned forward and backward over the same line before going to the next line, whereas in raster scan, each line is either recorded in forward or backward motion.

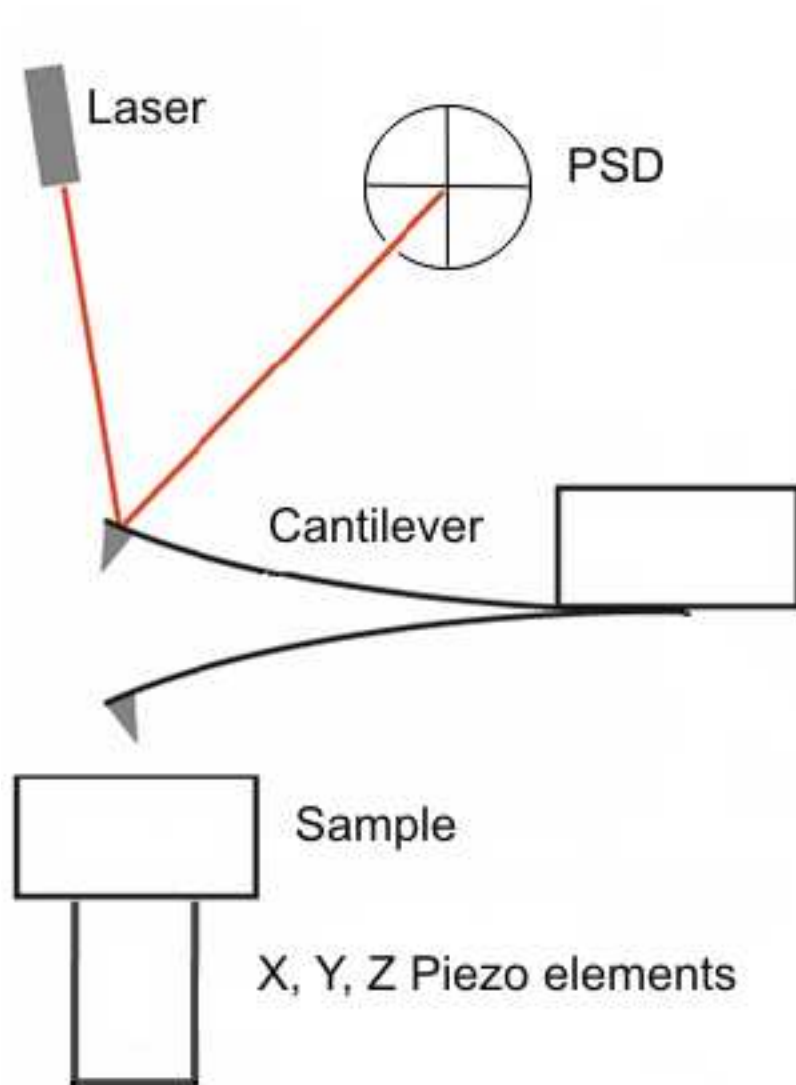


Figure 2.1: AFM apparatus principle. Cantilever movement on a substrate under controlled constant force or other parameters

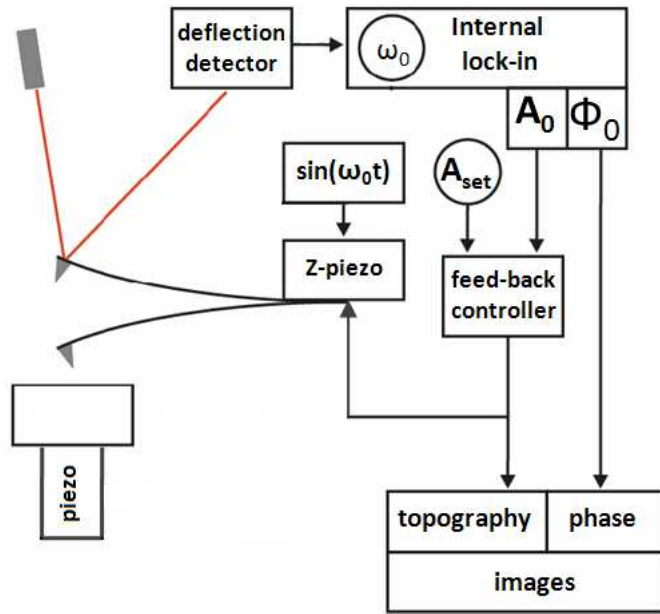


Figure 2.2: AFM working principle described for dynamic mode with closed loop for keeping amplitude constant while imaging

For keeping an interaction or parameter constant, control system uses a feed-back loop. While control system is keeping the predefined parameter constant, an error signal is recorded in addition to the topography signal. This error signal is the control signal of the closed loop system to keep the predefined parameter constant. The feedback loop is regulated by a PI controller where the proportional and integral factors of the system can be adjusted. Fig.2.2 shows the basic control loop for one of the modes of the AFM system.

2.2 Calibration of spring constants of AFM cantilevers

The cantilever is the component that plays the most important role in AFM system. Mechanical properties of cantilever determines the performance. Cantilevers

are fabricated mostly from silicon or silicon nitride. Back faces of the cantilevers are generally coated with a reflecting metal coating, because most commercial system uses beam reflection technique for detection. Also surface of silicon nitride or silicon has a native oxide of 1nm or 2nm. The spring constant and natural resonance frequency characterizes mechanical properties of the cantilever. By knowing material properties and dimensions of cantilevers we can theoretically calculate spring constant and natural resonance frequency. For example spring constant of a rectangular cantilever is

$$k = \frac{Ewt^3}{4L^3} \quad (2.1)$$

where E is Young's modulus of cantilever, w , t , L is width, thickness and length of the cantilever respectively.

Since we need to know the cantilever's spring constant, we have to determine it accurately. Generally we can classify four topics for the methods to determine spring constant.

- Dynamic methods, require analysing the resonance response of the cantilever.
- Theoretical methods, in this category, with the accurate knowledge of the cantilever's Young's modulus and dimensions, we can use simple theoretical expressions to calculate spring constant.
- Static response methods, by applying a known force and since we can monitor the deflection of the cantilever, we can calculate the spring constant
- Indirect methods

Here we briefly summarize three of these calibration methods.

2.2.1 Added mass method

In this technique we measure resonance frequency of the cantilever when a known mass is added and not added. [10] When we add an extra mass to a mechanical resonator its resonance frequency will change, we detect this change in frequency and use it to determine spring constant. This kind of measurement is also basic of some other sensor systems. The formula that can be used for calculating the spring constant is

$$k = 2\pi^2[M/(\nu_1^{-2} - \nu_2^{-2})] \quad (2.2)$$

2.2.2 Sader method

Here for using this technique we need to know the resonance frequency and the spring constant of the cantilever.[11] Also since it is always important we need to know the width and the length of the cantilever. With these parameters at hand we can calculate the spring constant with the formula

$$k = 0.1906\rho_f w^2 L Q \Gamma_i(Re) w_0^2 \quad (2.3)$$

where, ρ_f density of surrounding gas, Γ_i is the imaginary part of the so-called "hydrodynamic function", and Re is Reynolds number.

2.2.3 Determination with a calibrated cantilever

This technique is more experimental, meaning that we use another well calibrated cantilever for calibrating the cantilever. Basically we push the cantilever that is calibrated with the non-calibrated.[12] When one of the cantilever is attached to the piezoelectric holder and Z_p is height of it and Z_c is the deflection of other cantilever, then the formula for calculating the spring constant is

$$k = k_{ref} \frac{Z_c - Z_p}{Z_c} \quad (2.4)$$

2.3 Operation Modes of AFM

There are two basic techniques to probe the topography: static and dynamic mode. Although we can classify modes like contact, noncontact and intermittent-contact, we choose static and dynamic classification. Because, at the end, static mode corresponds to the contact mode and both noncontact and intermittent-contact mode included in the dynamic mode. Both of the modes changing of the cantilever position according to the sample due to the interaction with the surface.

2.3.1 Static Mode

In static mode, tip is directly in contact with the surface. Directly contact in the context of atomic force microscopy means very small tip surface separation that only repulsive interaction is dominant. Interaction force between the tip and sample is utilized as the imaging signal. This interaction force is transferred to the deflection of the cantilever by the Hook's law $d = F/k$. Cantilever must be very soft in order not to deform the surface, particularly not to break bonds between the surface atoms. Interatomic force constant are in the range of 10N/m and 100N/m for solids, in biological samples this value is even smaller. Because this force constant of the cantilevers proper for this mode are 0.01N/m to 5N/m. In constant height mode the distance between the tip and the surface kept constant by the feedback loop and the control signal gives the topography of the surface. Whereas in the constant force mode the interaction force between the tip and the sample kept constant by the feedback loop similarly control signal gives the topography. In addition to the restrictions of the spring constant, mode frequency of the cantilever f_0 has to be higher than the measurement bandwidth in order to prevent resonant excitation of the cantilever for imaging with atomic resolution.

2.3.2 Dynamic Mode

In contrast to the static mode, the cantilever is excited at its mechanical resonance frequency in dynamic mode. When the oscillating cantilever is approaching the surface because of the force gradient between the tip and the surface resonance frequency as well as the amplitude of the oscillation changes. Adjusting the control system, one of these parameter can be kept constant and system keeps track of the topography of surface. If we keep the oscillation amplitude constant, this operation technique is called Amplitude Modulation AFM(AM-AFM). The most important drawback of this technique is, it can not well suit to the vacuum applications. Because the response time of the cantilever can basically be expressed with $2Q/\omega_0$. This tells us that when the quality factor is very high, that is the common case for vacuum applications, measurement bandwidth is very small. This means that scanning speed is very slow and this is not practical. When we choose to use low Q cantilevers or damp cantilever or even use off-resonance techniques we sacrifice the signal to noise ratio. Although this technique can be optimized for the ambient conditions, this is not good for ultrahigh vacuum application. Luckily, Frequency-Modulation AFM can solve this problem[[45]]. Since system keeps track of the resonance frequency with a phase locked loop(PLL) to keep the amplitude constant, system can react frequency changes and can adjust in the time scale of $1/f_0$. This can increase the scan speed to reasonable values.

2.4 Factors Affecting the Imaging

Potentially, there exists artifacts in all kind of measurements and experiments. This is partially because the experimental conditions can not be perfectly controlled or there are some limits in the measurement process itself. Here we will consider only certain limiting factors. Particularly, in this part of the work we will mention about resolution limit due to tip effects, thermal drift, mechanical vibration and piezo creep briefly. And we will investigate noise(mechanical and electronic) in the following section.

2.4.1 Tip Effects

The main parameters that are affecting the image quality in terms of tip are geometry, size and the mechanical strength of the cantilever. In all microscopy techniques we use probes, and fundamental interactions to investigate the specimen. In AFM imaging we use one of the fundamental interactions; interatomic force interactions. To investigate this kind of potential interactions to control or interpret results we have to know the shapes. In this regard, the part that is encountering the force interaction must be well defined not only for calculations but also for the imaging quality.

In addition to the well defined shape, also the interacting part, the tip, must be chemically and mechanically strong. Because if the tip is not chemically stable, it may react with the sample and change interaction type and disturb image quality.

The size of the probe is maybe the most important criterion in imaging. When we are try to image sub-micron scale features, it is not suitable to use a micron-size probe; therefore, nanometer scale AFM tips should be used. Commercially available cantilever tips have 10nm to 30nm radius of curvature. While imaging, we assume that only the end atom interacts with the sample. But in reality this is not the case. The higher the radius of curvature, the more the interacting parts. Consequently, resulting image is convolution of the tip with the features that are imaged. To see this effect in action, we can investigate the images shown in (Fig.2.3, Fig.2.4). The sample is silver nanoparticles on silicon surface, casted by syring injection. The average diameter of particles are 5nm. The scan direction is from top to bottom, and at the upper part of the image we see that features are very big and triangle shaped. The reason for this is that the tip became blunt in the course of imaging and assumed as triangular shape. We see in Fig.2.3 around $y = 2.3\mu m$, instability occurs and then suddenly the image turns to be very clear. The reason is that the blunt tip captured a silver nanoparticle from the surface. Since this nanoparticle is now the foremost part of the tip, it is imaging the sample and after some time image gets blurred but not totally got worse. In this part we think that tip smashed the particle while imaging.

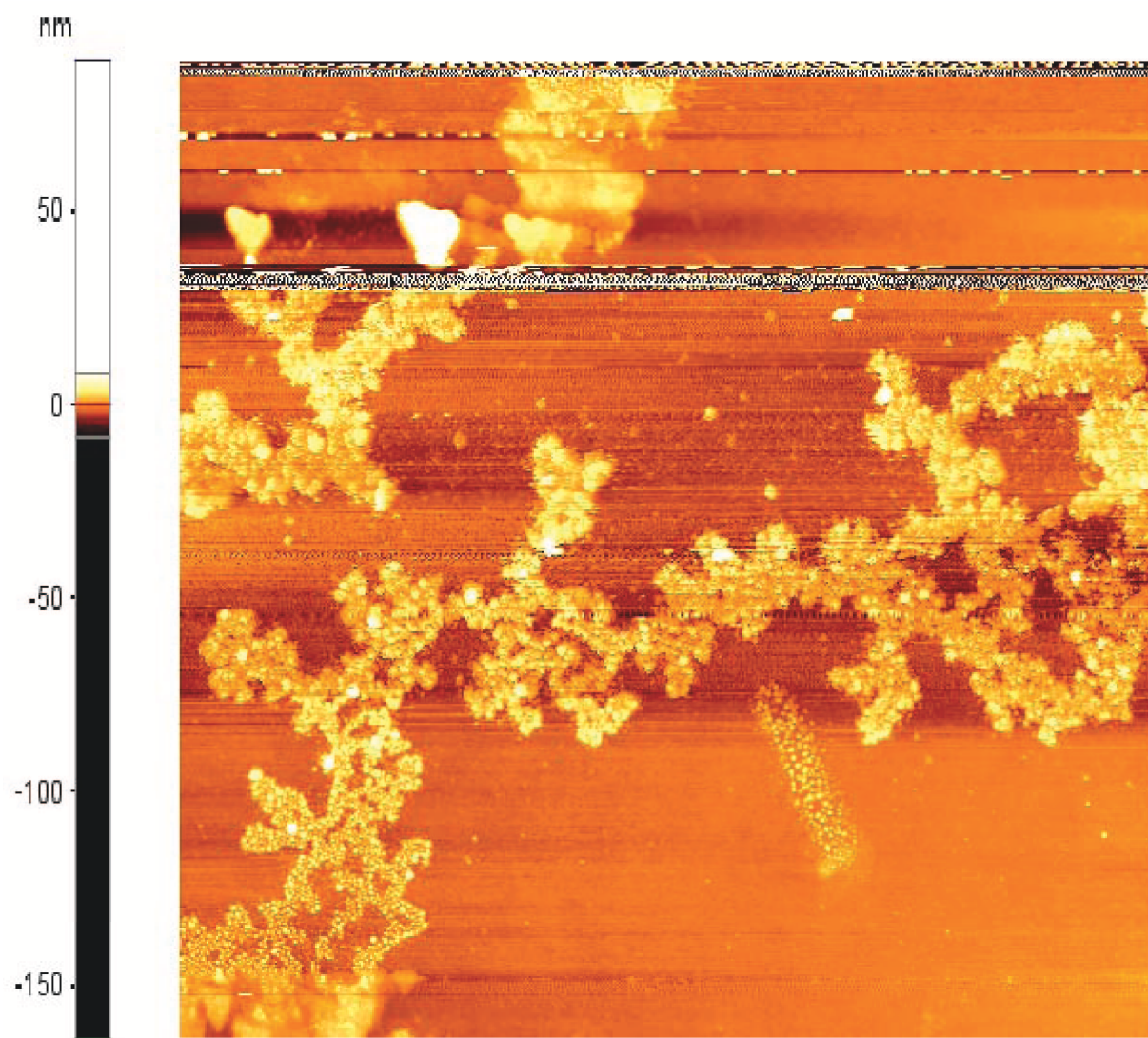


Figure 2.3: Nanoparticle capturing of the blunt tip and sudden improvement in imaging quality 1

2.4.2 Thermal Drift

Fluctuations in the temperature environment of the experiment can give rise a lot of different effects. For example, cantilever's dimensions, resonance frequency, and quality factor can change. Since the imaging system as a whole comprised of different circuits, these part's characteristics can change and as a result, image quality get worse. But most of the time, these effects are not important; because in order these effects to be significant, temperature changes must be severe.

2.4.3 Mechanical Vibrations

In all kind of microscopy experiments, external seismic and acoustic noise has to be kept in minimum. Since operation of AFM requires mechanical movement, if the mechanical vibrations could not be kept in minimum, this severely affects the quality of images. For avoiding this vibrations, special methods are used; such as suspension of instruments, use of vibration-free tables or suspension tables. If vibrations can not be eliminated, mechanical noise generally seen as artifacts in images.

2.4.4 Piezoelectric Transducer and Thermal Noise Related Creep

When sudden voltage changes applied to the scanner piezoelectric material, it can cause piezo displacement to nonlinearly follow the excitation signal. This effect happens for very short times; when the system settles down, it will disappear. To understand this effect clearly, see the Fig.2.5 below. First of the images is DVD-grating, and scanning starts from the bottom. As we can see, the bottom part of

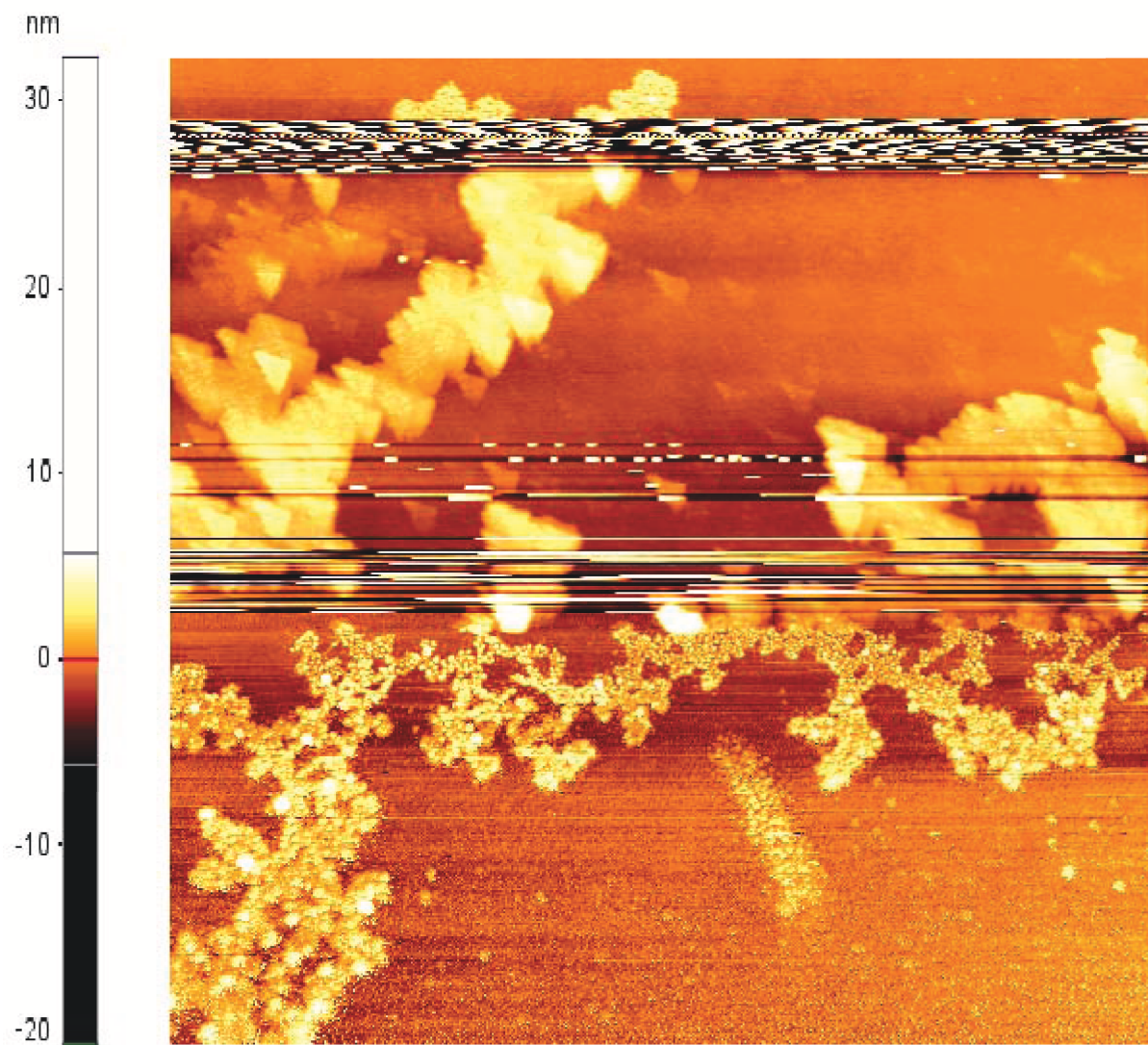


Figure 2.4: Nanoparticle capturing of the blunt tip and sudden improvement in imaging quality 2

the image seems like elongated to the left. This elongation effect may result from thermal fluctuations. We can observe the same phenomenon in the second image below too. But in the middle part of the image, the silver nanoparticles seems to be elongated because of the scanner creep.

2.5 Noise in AFM

The precision of the measurements of the forces is limited by the instrument and by the thermal noise sources. Noise consideration becomes more important when stiff cantilevers are used to avoid instabilities. Because using stiff cantilevers make the deflection smaller and signal to noise ratio lower. In Fig.2.6 we see a typical noise spectrum for AFM instrument. As we can observe, basically, there are three types of major noise source, namely $1/f$, electronic and thermal. $1/f$ noise is mainly dominant at lower frequencies where we make the force-distance curve measurements between 0 to 1kHz. In contrast to $1/f$ noise, electronic noise is dominant at high frequencies. Thermal noise is a function of cantilever properties and environment and it can be clearly seen around the resonance frequencies; because the gain of the mechanical system is high at that frequency range.

By their nature, all the semiconductor based electronic devices have the $1/f$ noise. The nature of the $1/f$ is not fully understood, but it is credited to the defects and contaminants in the crystal structure of the materials. All the electronic components that are used in AFM system have this type of noise, but the most dominant part is photodiode sensor parts of the deflection detection system. Also using better-performance devices reduce the $1/f$ noise. The probable source of $1/f$ noise in the spectrum is mode hopping of the laser light source. But this problem can be eliminated by using single mode fiber coupled devices.

Electronic noise content of the AFM spectrum mainly stems from photocurrent shot noise. The charge carriers that are stochastically passing a potential barrier, although the DC current is steady, is the basic explanation for the shot noise. Shot noise related current is $i = \sqrt{2qI}$, where q is charge of an electron, and I is

the measured current. Most of the AFM systems produce shot noise on the order of $1\mu v/\sqrt{Hz}$.

Thermal noise is caused by the hitting of the surrounding particles, driven by Brownian motion, to the cantilever.

The magnitude of this Brownian motion can be calculated by the wave equation and equipartition theorem. If we assume the cantilever as a simple harmonic oscillator, equation of motion for the cantilever is $kx + b\dot{x} + m\ddot{x} = F$, where x is displacement of the cantilever, $\dot{x}$ and $\ddot{x}$ first and second derivative of cantilever displacement, m is effective mass, b is the damping, k is spring constant and F is thermal force. To solve this equation, we can assume the form of the solution as $A(w)e^{i(wt - \phi)}$, where A is amplitude, t is time, ϕ is phase and w is angular frequency. This gives an amplitude spectrum as $|A(w)|^2 = \frac{F^2}{(k - mw^2)^2 + b^2w^2}$. If we rearrange this result with more experimental parameters, $w_0 = \sqrt{k/m}$ and $Q = \sqrt{km}/b$, amplitude spectrum becomes more intuitive as below

$$|A(w)|^2 = \frac{(F/k)^2}{(1 - (w/w_0)^2)^2 + (w/(w_0Q))^2} \quad (2.5)$$

This result consists of two parts: a transfer function $\frac{1}{(1 - (w/w_0)^2)^2 + (w/(w_0Q))^2}$ and a scalar $(F/k)^2$. The transfer function determines the spectral shape of the resonance. To compute the scalar, we must compute F via equipartition theorem. From the equipartition theorem each degree of freedom has thermal energy of the $\frac{k_bT}{2}$. This thermal energy corresponds to the average kinetic energy which is $k \langle x^2 \rangle / 2$. The integral of the amplitude function, $\int_0^\infty |A(w)|^2 dw$, is the average value of the square of the deflection $\langle x^2 \rangle$. This means that the F is only the function of temperature and its value is $F = \sqrt{4k_bTb} = \sqrt{4k_bTk/(w_0Q)}$.

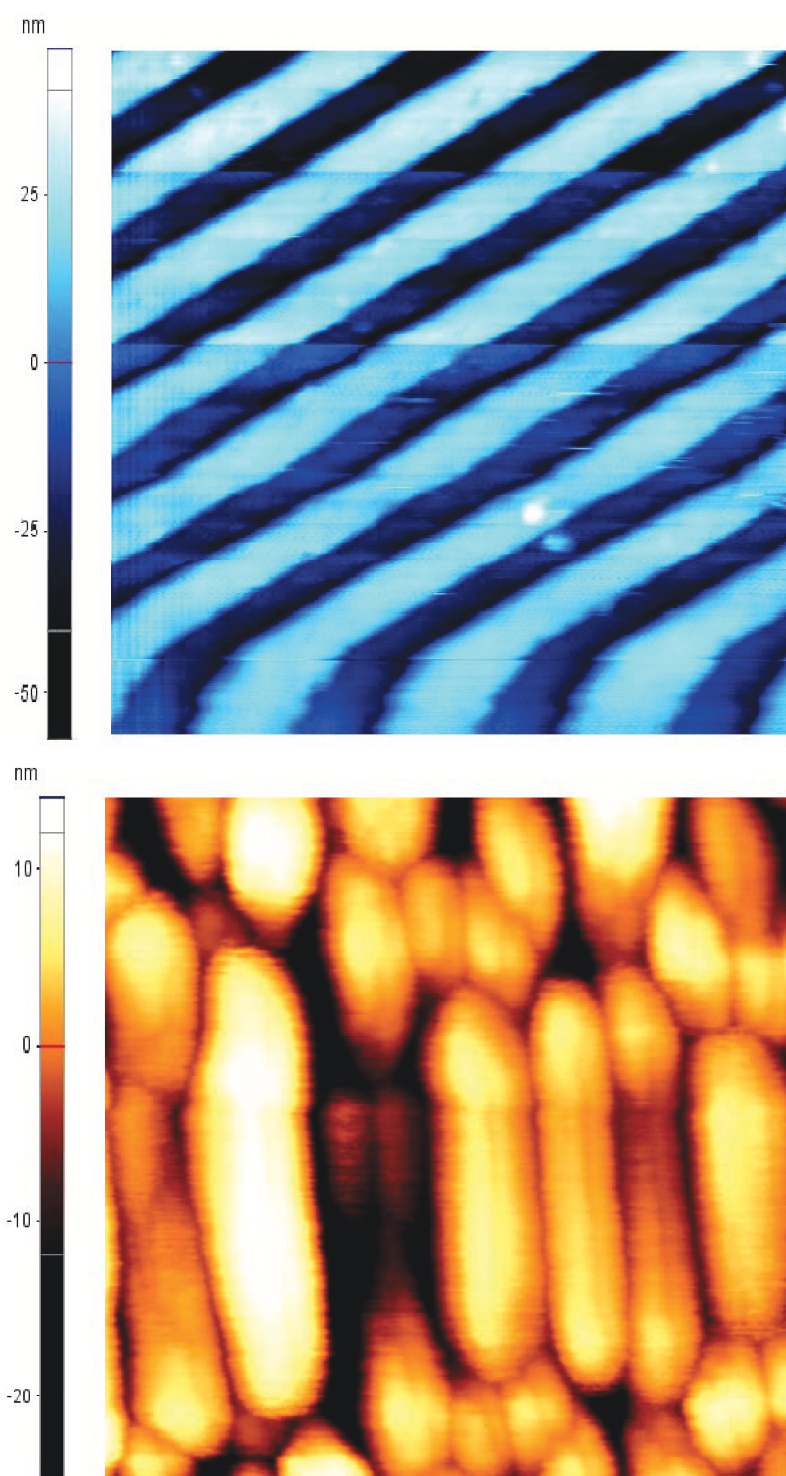


Figure 2.5: Visualization of the elongation of the features on the images of silver nanoparticles and DVD gratings caused by the thermally induced piezocreep

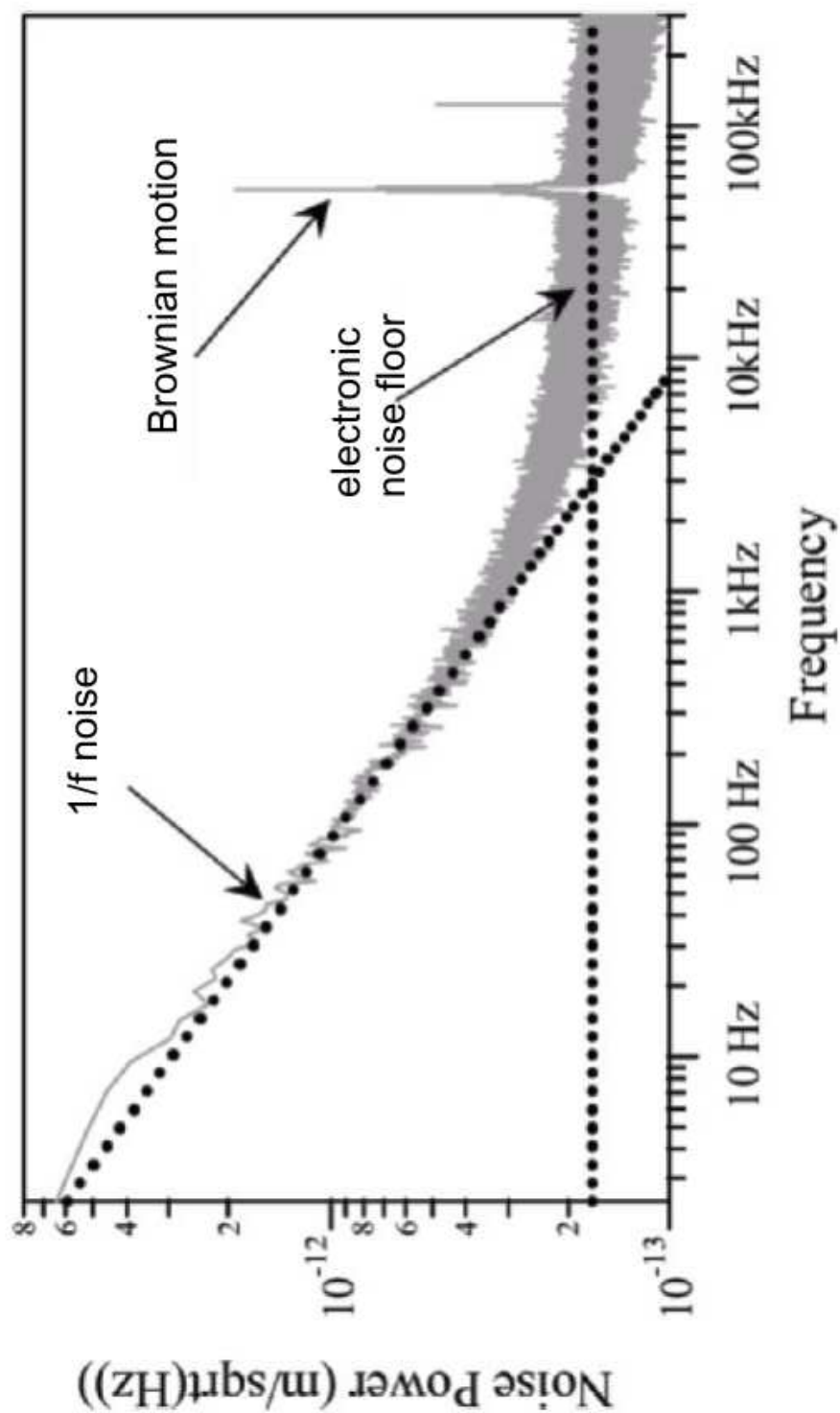


Figure 2.6: Representative noise spectrum for commercial instrument showing 1/f, electronic noise and brownian components.

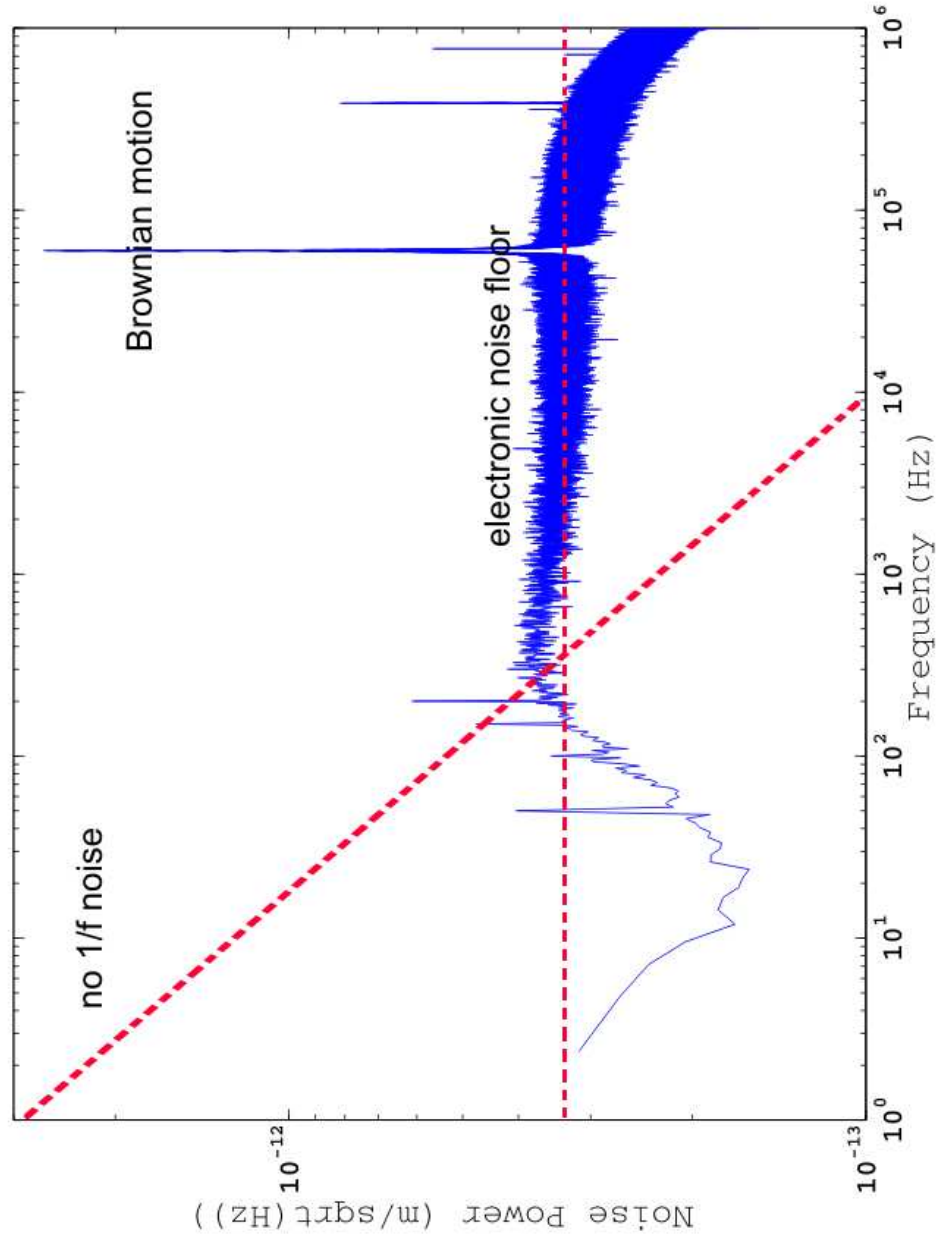


Figure 2.7: Noise spectrum of instrument that we use in our experiments. Clearly $1/f$ component is mostly eliminated, and total noise is dominated by electronic noise and brownian components.

Chapter 3

Tip-Sample Interactions and Force-Distance Curves

In the previous chapter we mentioned about the interaction forces, but did not clearly identify these forces; because we dedicate this chapter especially defining these forces and the information that we can gather from them.

3.1 Forces In Tip-Sample Interactions

It is obvious that when two bodies get in the proximity of each other, interaction between bodies is inevitable; but, the nature of the interaction differs from material to material, system to system and even more importantly size to size. Since this proximity range of the AFM experiments is on the order of microns to a few nanometers or even smaller, the nature of the interactions is very different from the macroscopic interactions. This difference manifests itself as various combinations of different types of interactions. Also, when the environment in which AFM experiment is conducted changes, new forces may also arise. And we will restrict ourselves to the dry, ambient conditions and to the forces that arise under these conditions. As usual, we will classify these forces into two broad groups, attractive and repulsive forces. Below, there is a list of different forces that show

up in different kinds of AFM experiments:

- Van der Waals Forces
- Electrostatic Forces
- Magnetic Forces
- Chemical Forces
- Interatomic and Intermolecular Forces
- Capillary Forces
- Viscoelastic Forces
- Double Layer Forces
- Contact Forces
- Adhesion Forces

As a terminology, we name attractive forces as long range forces. When we say long range, we mean a scale from a few nanometer up to hundred nanometers or larger distances. Some of the forces that are contained in this class are Van der Waals Forces, Electrostatic Forces, Magnetic Forces etc. Similarly we could name repulsive forces as short range forces. We can list some of the short range forces; such as Chemical Forces, Interatomic and intermolecular Forces. We will here briefly mention about the Van der Waals Forces, Contact Forces, Electrostatic Forces, Capillary Forces.

3.1.1 Van der Waals Forces (Long-range attractive interactions)

Van der Waals interactions stem from thermal or zero-point quantum fluctuations induced electromagnetic field fluctuations. This fairly weak interaction is

the main binding force which holds rare gas atoms together. It consists of three components:

- Fluctuations in the electron charge density create dipoles in neutral atoms. And this dipoles induce the formation dipoles in other atoms. This instantaneous dipole interaction is called the dispersion force (London Force). This type is the strongest one in all three.
- Also permanent dipoles in polar molecules can induce dipole formation in other atoms. This is called induction force.
- Polar molecules interact with each other via their permanent dipoles, and this is called orientation force.

As we name it this force is mostly attractive. Since both tip and the sample consists of many atoms, individual interaction of these atoms with each other can sum up to a few nanonewtons. Despite strength of this interaction seems weak, it can dominate chemical forces in tip-sample interactions. Deriving Van der Waals forces requires very tedious and lengthy treatment, so, here we will consider basic and most used sphere-flat geometry; because it is a good approximation for the tip-sample interface. Van der Waals force in flat-sphere geometry is $F_{ts} = -HR/(6d^2)$ where H is the Hamaker constant, R is the tip radius and d is the tip-surface separation.

3.1.2 Contact and Short-Range Repulsive Forces

Mainly Pauli exclusion principle and ionic repulsion give rise the repulsive interaction between atoms and molecules when they brought very small separations. But if the contact area is wide, that is, consists of tens or hundreds of atoms, there is no need to calculate effective repulsive force. When two objects made a mechanical contact, both of the objects deform; but there are differences because of the applied load and the material variations. First theory is set by Hertz in

1881 about contact of the different bodies using the continuum elasticity theory. He considered problem as contact between two spheres and did not account for the adhesion. After Hertz [13] a lot of different models developed; two of which become standard in AFM studies. Johnson-Kendall-Roberts(JKR) [14] and Derjaguin-Muller-Toporov (DMT) [15] models give analytical relations between deformation and applied force. In contacts studies with AFM, the DMT model is suitable for explaining stiff contacts with low adhesion forces and small tip radius. Whereas the JKR model is suitable for the contacts characterized by low stiffness, high adhesion forces and large tip radius.

3.1.3 Electrostatic Forces

If the electrostatic charges are trapped in the dielectric surface of the sample or an external electric field is applied between the tip and the sample, a long range attractive or repulsive force exists. In this situation, the sample and the surface behave like opposite sides of the capacitor. Using this approximation, the force between the tip and the cantilever can easily be calculated. Since the force between the opposite plates of the capacitor is proportional with the voltage applied, this interaction can be used as driving force or as a sensor mechanism for different applications.

3.1.4 Capillary Forces

In room conditions, a thin film of the water, approximately a few nanometer, is adsorbed on the sample surfaces. When the tip is approaching the sample surface, a liquid meniscus is formed between the tip and the sample. Because of this meniscus, an attractive force is exerted on the cantilever. This particular force is called Capillary Force. Also, the thin film of the water tends to be formed on the hydrophilic surfaces. Capillary force depends on the distance between the tip and the sample, also, strength of the meniscus is proportional to the size and the surface tension of the capillary.

3.2 Constructing the Total Tip Sample Interaction

Since we briefly examine the landscape of the forces and their importance, now we can construct the whole interaction that contains one or more of these components. To work interactions between tip and sample, the movements of the cantilever and inferring information, we need a model of the total force. At the beginning, we have made the classification of the attractive and the repulsive interactions. Now we will join these two parts together. For the long range attractive interactions we will use van der Waals interaction, since it is the dominant force at long distances from the sample. As for the repulsive interactions, neglecting the energy dissipation caused by the tip sample contact, we can use DMT model or JKR model. As mentioned above DMT is an appropriate model for the hard surfaces with low adhesion and small tip radius, whereas JKR is a suitable model for soft materials with high adhesion and large tip radius. For clarifying the parameter, we set $D = z_s + z$ as the tip sample distance where, z_s is distance between undeflected cantilever and the sample and z is the cantilever deflection. In order to prevent unphysical divergence, we introduce the parameter a_0 as the interatomic distance. Also a_0 separates the ranges of the interactions. Finally, tip-sample force can be written as

$$F_{ts}(z) = \begin{cases} -HR/[6(z_s + z)^2] & D \geq a_0 \\ -HR/6a_0^2 + \frac{4}{3}E^*\sqrt{R}(a_0 - z_s - z)^{3/2} & D < a_0 \end{cases} \quad (3.1)$$

where H is Hamaker constant, R is the radius of the tip and E^* is the effective Young's modulus or stiffness constant. Effective stiffness constant is defined as $E^* = [(1 - \nu_t^2)/E_t + (1 - \nu_s^2)/E_s]^{-1}$, where E_t is elastic modulus of the tip, E_s is elastic modulus of the sample, ν_t is Poisson ratio of tip and ν_s is Poisson ratio of the sample.

This basic formulation of the tip-sample interaction can be modified to include

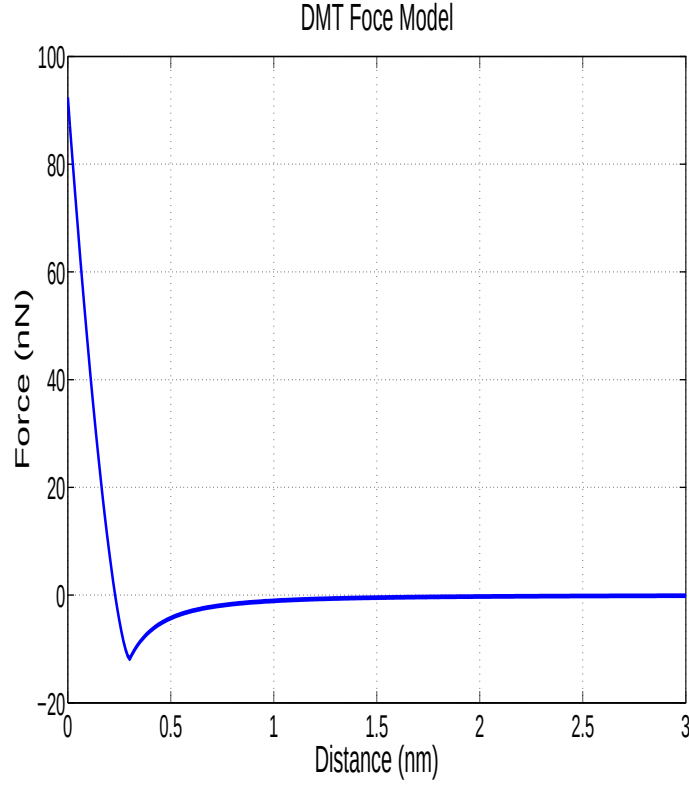


Figure 3.1: Graphical representation of combination of van der Waals and DMT model where interatomic distance parameter is 4 Angström

additional forces or effects; for example if the energy dissipation of tip-sample contact can not be neglected, we modify force interaction with viscoelastic damping term, consequently force interaction becomes

$$F_{\eta}(z) = \begin{cases} -HR/[6(z_s + z)^2] & D \geq a_0 \\ -HR/6a_0^2 + \frac{4}{3}E^*\sqrt{R}(a_0 - z_s - z)^{3/2} - \eta(a_0 - z_s - z)^{1/2}\dot{D} & D < a_0 \end{cases} \quad (3.2)$$

where η is viscoelasticity constant of the tip sample interaction in the normal direction.

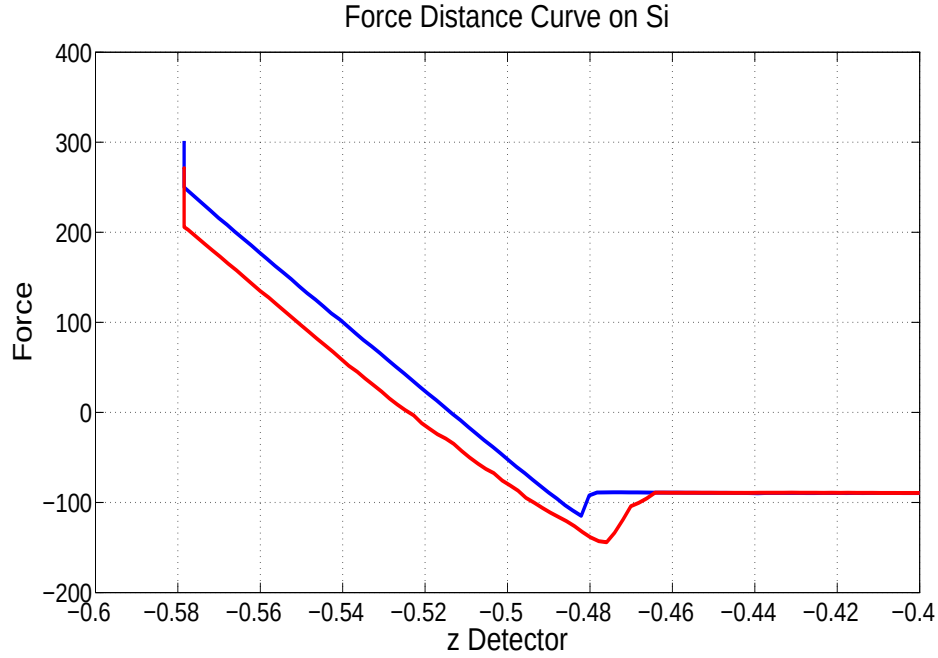


Figure 3.2: Force-distance curve from the experiment conducted on Si surface

Following Fig. 3.1 basically shows the graphical representation the force model.

3.3 Force-Distance Curves

Up to now, we have examined the interaction forces theoretically and tried to understand what is happening between the tip and the sample. The force-distance measurements complete this effort in terms of the experimental data gathered by AFM in which the force-distance curves are the representations of the constructed tip-sample interaction forces. By joining these two efforts together, we can interpret the properties of the materials that we are examining.

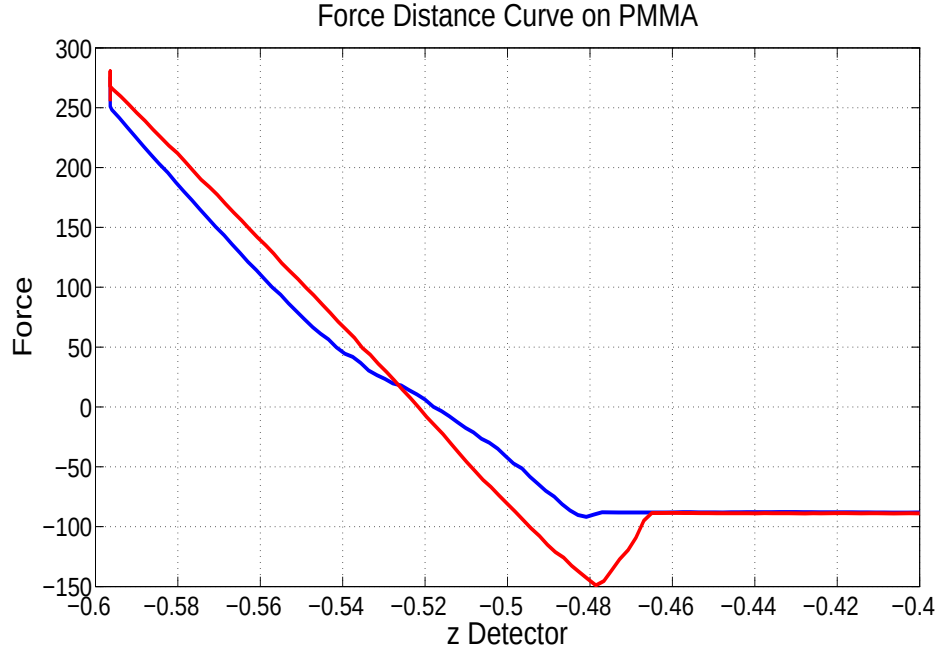


Figure 3.3: Force-distance curve from the experiment conducted on PMMA surface

Fig.3.2 and Fig.3.3 show the force-distance data that are taken on *Si* and *PMMA*. In a typical force-distance experiment, we choose a force set-point and optionally velocity set-point. Control system of the AFM approaches the sample vertically with the velocity that we set and records the deflection of the cantilever. When the tip reaches the sample and gets into contact with the sample, control system pushes the cantilever up to the force set point that we choose. Then control system retracts the tip from the surface with the same speed. In the course of approach and retract, deflection is recorded and when whole cycle is completed, system draws the force versus the piezo height on a plot. By examining the curve, we can get information about sample with the use of knowledge we got from the theoretical considerations. Again, if we theoretically know the experimental system parameters like spring constant of the cantilever, tip radius etc. we can easily calculate sample stiffness.

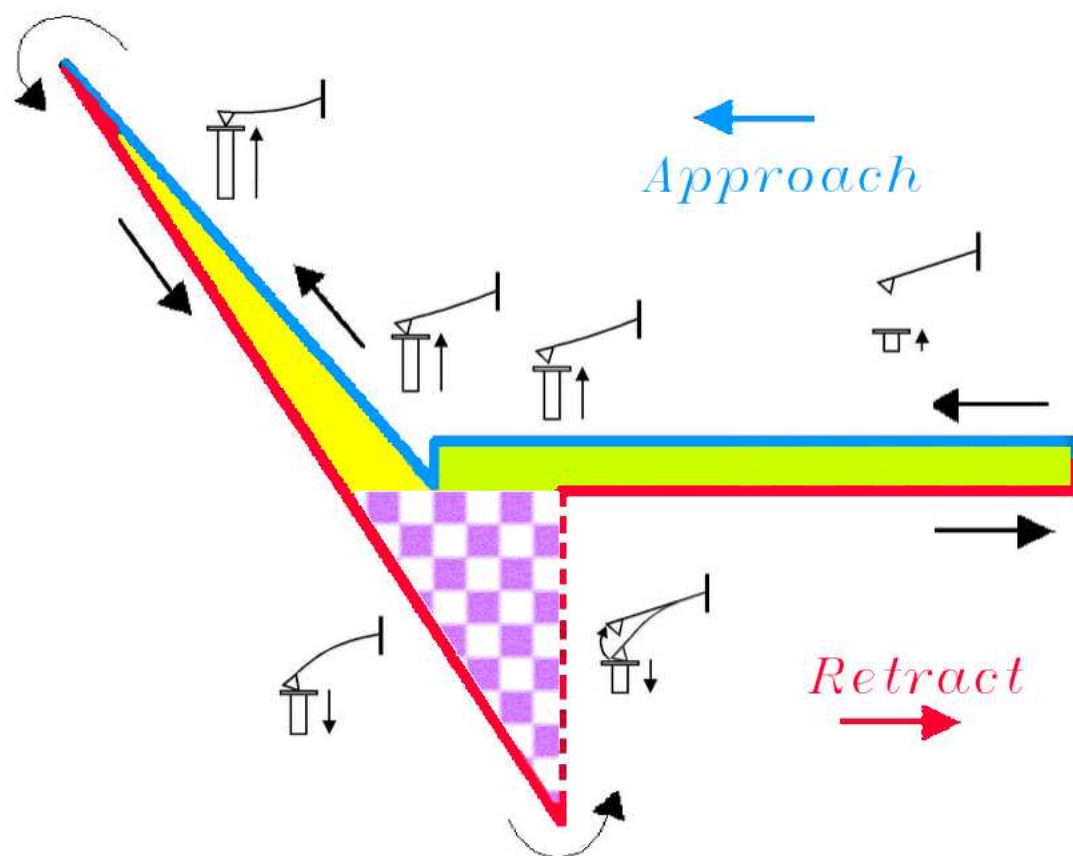


Figure 3.4: Force versus distance curve. For the example shown here, the tip first experiences a long-range repulsive force upon approaching the sample, even before the tip and sample are in physical contact. Close to the sample, the tip becomes strongly attracted by the van der Waals force. In this instance, the attractive force gradient becomes greater than the force gradient by the cantilever spring. This causes the tip to snap into physical contact with the sample (the perpendicular part of the approach curve). Once physical contact has been made, the cantilever is deflected linearly by the approaching scanner. When it is turning back, the tip may stick to the sample by adhesion until the pull by the cantilever forces it out of contact. Three types of hysteresis can occur: In the zero force line (green), in the contact part (yellow) and adhesion (squared purple)

Fig.3.4 explains schematically the force distance curve that are typically resulted from the experiment. With a quick review of the figure, we can easily notice the hysteretic behavior of the curve and the discontinuity of the curve. When we were constructing theoretical interaction force, we joined the attractive and repulsive parts of the interaction together. So here we can do the reverse and try to separate the attractive and repulsive parts. As we can clearly notice that the almost linear part is repulsive and the nonlinear part is attractive. By calculating the slope of the repulsive part of the curve, we can acquire informations about sample stiffness.

If we try to understand the discontinuity in the curve and the hysteretic behavior, we can also get additional information. The discontinuity that we see in the approach part of the curve is termed as “jump-to contact” phenomenon. To understand this phenomenon, we must remember one of the basic forces that can incorporate in experiments, that is capillary force. When approaching the surface, the adsorbant water layer exerts a force on the cantilever and when the force gradient that originates from the sample and capillary forces exceeds the cantilever’s spring constant, tip jumps to the surface. Similarly, when retracting from the surface the water layer keeps the cantilever on the surface until the ‘jump-off contact’ happens. This also causes the force distance curve to be hysteretic.

But interestingly, if we did this experiment under ultrahigh vacuum, we may see the same kind of discontinuity. If we could not see the discontinuity, we probably see the hysteresis. The reason for this is as the following: When the tip touches to the surface, chemical or physical bonds would form between the tip and the sample, and the tip adheres to the surface. Due to that adhesion, in order to tip to detach from surface while retracting, this extra bonds must be broken. So we would see the hysteresis but we can also take advantage of this phenomenon to measure adhesion forces by simply calculating the area between approach and retract.

Chapter 4

Simulation Strategy for AFM

Numerical models that can simulate dynamic properties of cantilever under tip-sample interactions is in the heart of interpreting AFM images and extracting different information like material properties. As we mentioned before in dynamic mode AFM cantilever is excited at its resonance frequency. Because of the tip-sample interaction during imaging, certain parameters (amplitude, resonance frequency, and phase angle) of the oscillating cantilever changes. Using feedback to stabilize one or more of the parameters, these changes are used to get the topography of the sample as well as the material properties. Since in this work we are introducing new characterization techniques, which utilize dynamic mode AFM, its crucial to touch briefly different modeling strategies and explain our method of simulation.

In this chapter, first we will give two tip-cantilever interaction models and mention about numerical techniques to simulate vibrating cantilever near the sample. Then we will present our numerical method.

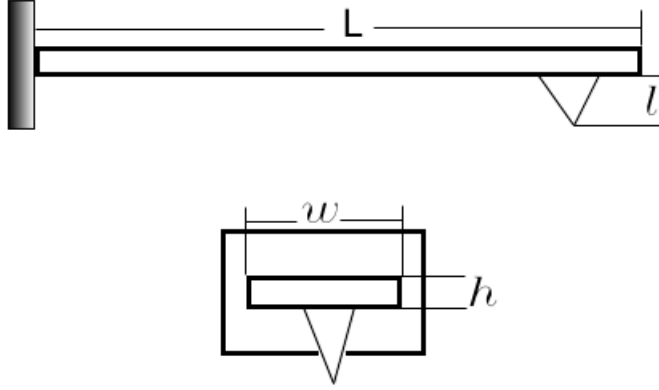


Figure 4.1: Schematic description of the 1 dimensional beam cantilever

4.1 Tip-Cantilever System Models

We can use different abstractions to model the system of the tip and the cantilever. The two abstraction that we will briefly mention about are, 1-D beam model and point mass model.

4.1.1 1-D Beam Model

The atomic force microscope cantilever seen in the Fig.4.1 is a sketch of the 1-D beam that is used in simulations of dynamic modes of force microscopy. Since it is a 1-D representation, it can only move in one direction and it corresponds to the flexural mode of the cantilever. The flexural bending of cantilever is governed by a differential equation that is fourth order in space and second order in time. This equation is called BernoulliEuler beam equation and it is given as

$$EI_y \frac{\partial^4 w(x, t)}{\partial x^4} + \rho A \frac{\partial^2 w(x, t)}{\partial x^2} + c_{vb} \frac{\partial w(x, t)}{\partial x} = 0 \quad (4.1)$$

where $w(x, t)$ is the cantilever's displacement in transverse direction, E is stiffness or Young's modulus, A is cross section area, I_y is the moment of inertia, ω is the natural vibration frequency of cantilever in flexural bending, and $c_{vb} = \omega \rho A / Q$ is the damping coefficient in air. For a cantilever, where its cross section is rectangular, where b is width and h is thickness of that cross section. The moment of inertia is defined as $I_y = bh^3/12$.

To simplify the solution of the problem, we can assume that cantilever is homogenous, isotropic and also it is linearly elastic with uniform cross section. While the cantilever is in free oscillation, we expect the modal shapes of the cantilever to be harmonic and the form of the solution is $w(x, t) = \phi_w(x) \exp i\omega t$. if we substitute this equation in above BernoulliEuler beam equation

$$\frac{d^4 \phi_W(x)}{dx^4} - a_{vb}^4 \phi_W(x) = 0 \quad (4.2)$$

$$a_{vb}^4 = \frac{\rho A}{EI_y} \omega^2 - i \frac{c_{vb}}{EI_y} \quad (4.3)$$

With these approximation we can write modal shape function as

$$\phi_W(x) = C_1 e^{-a_{vb}x} + C_2 e^{a_{vb}x} + C_3 e^{-ia_{vb}x} + C_4 e^{ia_{vb}x} \quad (4.4)$$

where a_{vb} is constant. Since this is a fourth order differential equation in space, we need four boundary condition. The boundary conditions for the cantilever beam with one end free and the other end clamped are:

$$\phi_W|_{x=0} = 0, \quad \phi'_W|_{x=0} = 0, \quad \phi''_W|_{x=0} = 0, \quad \phi'''_W|_{x=0} = 0 \quad (4.5)$$

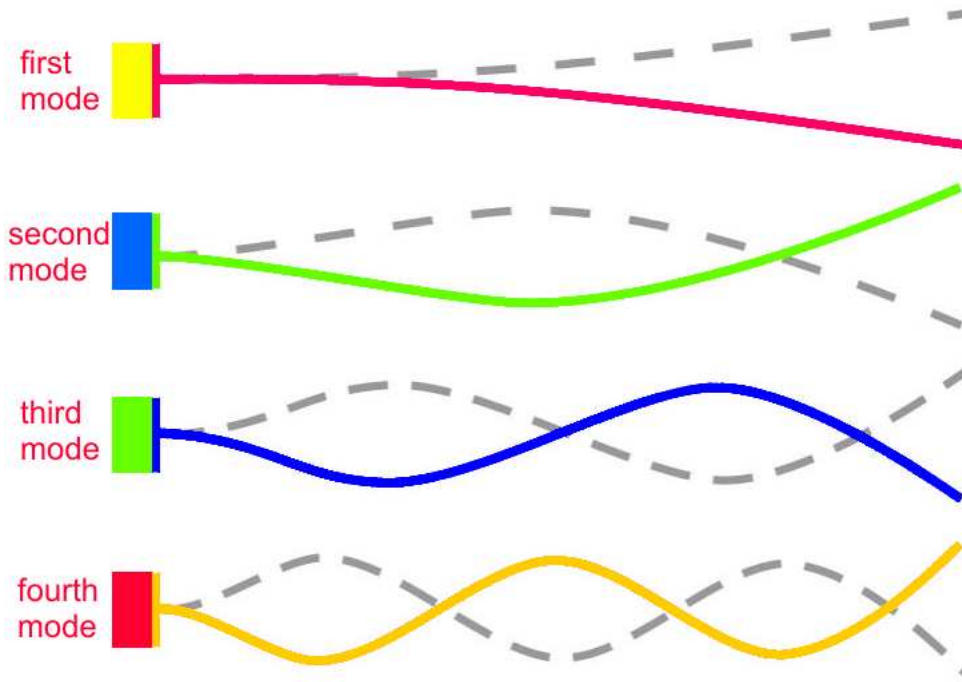


Figure 4.2: Illustration of the first four flexural eigenmodes of a freely vibrating rectangular cantilever beam

where L is the length of the cantilever and the superscripts stand for first, second and third differential of modal shape function with respect to space.

When we substitute the boundary conditions into the equation of modal shapes, by applying constraint that eigenvalue a_{av} have to take such values that nontrivial solutions guaranteed. The modal shapes that correspond to the each one of the resonance frequency can be found by determining the constants in Eq. 4.4 with the aid of boundary conditions in the Eq. 4.5. The mode shapes that are corresponding to the first few frequency is shown on the Fig.4.2.

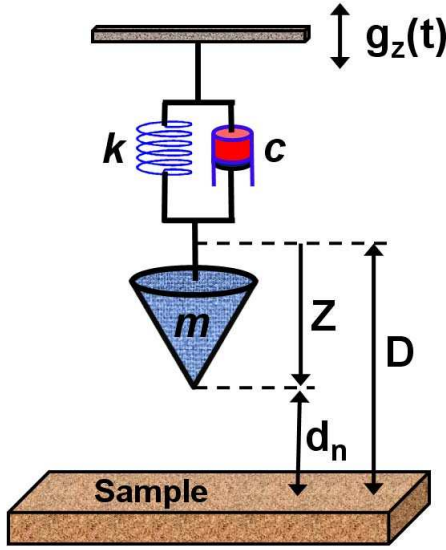


Figure 4.3: Schematic description of the point mass description of cantilever base and tip.

4.1.2 Point Mass Model

In contrary to the consideration above or 3D models which are using distributed masses, we can think all of the cantilever and tip system as one mass which is concentrated at tip position. By this abstraction we can get rid off many of the parameters and get the problem to a very well known ground, namely damped harmonic oscillator. Fig.4.3 shows the schematic of the motion of the cantilever described by the point mass model. The equation governing the system shown on the Fig.4.3 is a second order non-linear differential equation. The nonlinearity comes from the non-linear tip sample interactions.

$$m\ddot{Z} + c\dot{Z} + kZ = f_a + m\ddot{g}_z \quad (4.6)$$

where Z is the cantilever deflection, m is effective mass, k is spring constant, and c is damping coefficient. If we want to write this equation with more physical

parameters, we obtain the effective mass from $m = k/w_0^2$ where w_0 is fundamental resonance frequency of the cantilever. Also we can write damping coefficient in terms of mass, natural resonance frequency and quality factor as $c = mw_0/Q$. The quality factor Q can be defined as sharpness of the resonance. Since we are interested only in the modelling of cantilever-tip system, by neglecting the tip-sample interaction f_a , we can write the equation of motion with the term $g_z(t) = h_g \cos(\omega t)$ as the harmonic oscillation of the cantilever holder.

$$\ddot{Z} + \frac{w_0}{Q} \dot{Z} + w_0^2 Z = \Omega^2 h_g \cos(\Omega t) \quad (4.7)$$

The solution to the Eq. 4.7 is

$$Z = A_t e^{-w_0 t/Q} \sin(\sqrt{1 - (1/2Q)^2} w_0 t + \varphi) + A_0 \cos(\omega t + \varphi) \quad (4.8)$$

It can easily be noticed that the solution consists of two parts; one is exponentially decaying transient term and the other is a steady state term. In the steady state term, we have the same frequency ω of the driving oscillator with one exception, an additional phase lag ϕ . Also we can see that response time or decaying time of transient motion is $2Q/w_0$.

We can easily calculate the amplitude and the phase of the steady state motion as

$$A_0 = \frac{h_g \Omega^2}{\sqrt{(\Omega^2 - w_0^2)^2 + (\Omega w_0/Q)^2}} \quad (4.9)$$

$$\varphi = \tan^{-1}\left(\frac{\Omega w_0}{Q(\Omega^2 - w_0^2)}\right) \quad (4.10)$$

Free oscillations amplitude of the undamped cantilever ,when the resonance frequency is equal to the driving frequency, gives the relation

$$A_0 = Qh_g \quad (4.11)$$

4.2 Numerical Simulation Method

So far, we considered interaction forces and cantilever tip-model separately. Here we will combine these two parts and choose a numerical simulation method to mimic the AFM system. There are different numerical strategies to simulate, but we will not go into details of them, shortly mention about and then describe our strategy.

As all we can see, starting from the easiest one, we can try to solve the differential equations with methods like Runge-Kutta, Euler, etc. In 1-D beam and point mass model, we have different formulations and parameters. These, apart from each other, bring some advantages as well as disadvantages. Trying to solve the 1-D beam equation gives us the freedom on position of applying the force along the length of the cantilever. Also we don't have to separately or artificially introduce higher modes of the cantilever. But at the same, time calculation takes longer times and as we make a lot of assumptions, sometimes we introduce more unknowns than we solve for. In reality, the dimensions and the shape of the cantilever can not be perfect, so the resonance frequencies, especially the higher ones, do not correspond to the calculated ones. Of course, sometimes it is simply not practical to go into that much detail. In the case of point mass model, we do not have much freedom, but we have the easiness of handling of parameters, relatively short computation time and also we have analytical advantages. As we will see, we do not have to solve the differential equation in some formulations for the point mass model. Electrical equivalent of the differential equation can be devised and circuit analysis softwares could be used. Alternatively we can use

much more complex methods as finite element method (FEM) for both modeling of cantilever tip system and the dynamic simulation of all AFM system.

4.2.1 Numerical Strategy Used in This Work

In this work, when dealing with calculations, we use the simplest model of cantilever-tip system; that is point mass model. And for the tip-sample force interaction we choose the combination of van der Waals model for long range forces and DMT model for the repulsive interactions. We touched these issues in the previous parts of this chapters.

When we put all these together, we can write the equation of motion for this system as follows

$$m \frac{d^2 Z}{dx^2} + c \frac{dZ}{dx} + kZ = F_{ts} + A_d \cos(w_d t) \quad (4.12)$$

where the tip sample interaction F_{ts} is

$$F_{ts}(z) = \begin{cases} -HR/[6(z_s + z)^2] & D \geq a_0 \\ -HR/6a_0^2 + \frac{4}{3}E^* \sqrt{R}(a_0 - z_s - z)^{3/2} & D < a_0 \end{cases} \quad (4.13)$$

As previously discussed, we can prefer to solve this differential equation for the simple harmonic oscillator, in the field of a nonlinear force, in time domain with algorithms like Runge-Kutta or Euler. But it is obvious that when we operate the AFM, system has to be in a stable state. For the harmonic oscillator, simply stable states are the harmonic ones.

With this reasoning, we can solve this equation in frequency domain and get the information about amplitudes, phases, average forces, pressures for the

dynamic AFM mode. So we elaborate the transfer function method. In frequency domain the basic equation for this system is

$$Z(w) = h(w)F_{ts}(w) \quad (4.14)$$

where $Z(w)$ is the response of the system to the tip-sample interaction and $h(w)$ is the transfer function of the point-mass model that is damped harmonic oscillator. Here, basically transfer function of the system converts the force into the displacement of the cantilever. We can write the transfer function $h(w)$ for the damped oscillator as

$$h(w) = \left(\frac{1}{k}\right) \frac{1}{\left(1 - \frac{w_d^2}{w_0^2}\right) + j \frac{w_d}{Qw_0}} \quad (4.15)$$

We can say that amplitude of the oscillations in the force field is the modulus of the transfer function. Here k is spring constant of the cantilever and w_d is the drive frequency for the piezoelectric transducer. For the calculations, we can assume that k is not affected by the tip-sample interaction and since we set the value of the w_d , it is not changing. Eventually we need resonance frequency for the calculation of the amplitude and for other related information. We may think that the resonance frequency is determined by the thermal spectrum of the cantilever. But the real case is not that much simple, because in a force field, due to the force gradient between the tip and the sample, the natural resonance frequency of the mechanical oscillator changes.

To solve the problem in frequency domain and acquire the information, we need the frequency shifts of the oscillating cantilever for every point along the tip to the sample, while cantilever is both oscillating and approaching to the sample. Luckily, we can calculate the frequency shifts using the Giessible formula. Giessible calculated the frequency shift with first order perturbation theory using the HamiltonJacobi approach [45] as

$$\delta_f(z_b) = \frac{f_0^2}{kA} \int_0^{1/f_0} F_{ts}(z_b + A\cos(2\pi f_0 t))\cos(2\pi f_0 t)dt \quad (4.16)$$

where z_b is the base position of the cantilever relative to the sample position. Combining all these information we wrote a matlab code and numerically calculated amplitude and phase of the dynamic mode AFM experiments. The code is supplied in the appendices. Below one can see the resulting plots for a set of parameters in Fig.4.4.

Although we can calculate amplitude and phase distance curves for the Dynamic mode as in 4.4, the solution is not single valued. If we consider the forces and the potentials owing to the forces for the special separations, system has more than one minimum. This is made clear in the series of potential curves for the whole system (Figs. 4.5 and 4.6). We can construct these curves combining the potential of the cantilever and the tip sample equation at different distances between the cantilever and the sample.

As we set above, we must consider and adjust numerical approach by including this bistability effect.

For including this criterion, we use the idea of the fact that the resulting amplitude out of tip sample interaction, fixed tip sample separation and fixed driving amplitude can never be greater than the fixed driving amplitude. This is also a requirement for the stability of the state of the system. It actually means that when we drive the system at its resonance frequency, when there exists no tip-sample force, the cantilever is said to be free. Since free amplitude at resonance is at maximum, whatever the frequency shift is, due to the force gradient, it will change the resonance and then, because the driving frequency did not change, the amplitude certainly falls.

Numerically, we first calculate a matrix of frequency shifts for every tip sample separation and every amplitude in a range. Then we convert this frequency shift

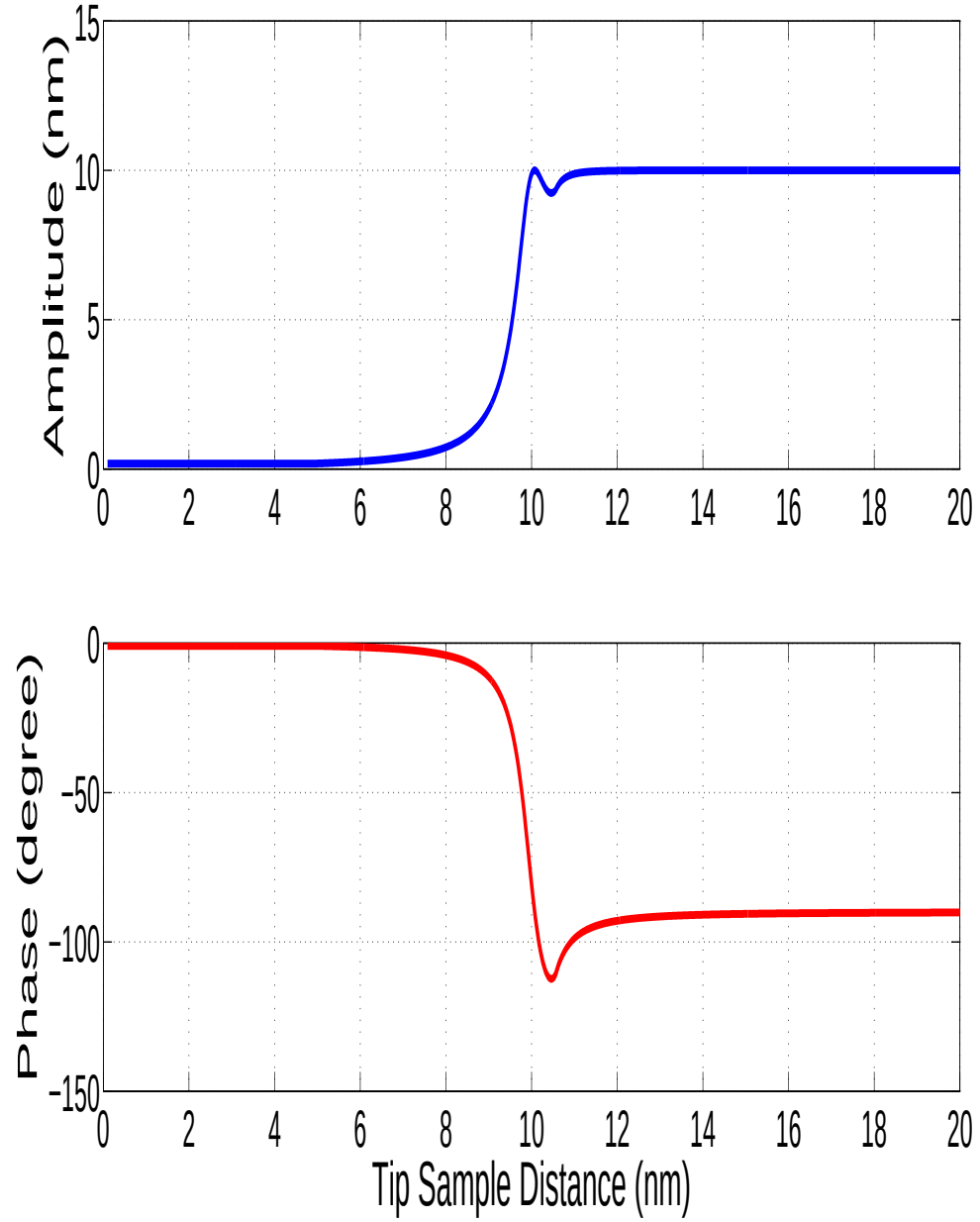


Figure 4.4: Amplitude distance, phase distance curves that are taken from the simulation results with the parameters $E_t = 130\text{GPa}$, $E_s = 1\text{GPa}$, $R = 50\text{nm}$, $H = 6.4 \times 10^{-20}$, $f_0 = 75\text{kHz}$, $k_0 = 2.5\text{N/m}$, $A_0 = 10\text{nm}$

matrix to the amplitude matrix by using the transfer function. Then we construct a matrix for each row, a specific tip-sample separation, we write all the starting or set amplitudes. Finally, comparing these two matrices, we get the stability map, those are amplitudes and phases. Code is supplied in the appendices. Below, in Fig. 4.7 and in Fig. 4.8, there is a plot of amplitude distance, phase distance and stability map for specific parameters.

Starting from the resulting amplitudes, we can also calculate the force spectrum of the tip-sample interaction at each tip-sample separation. We assume the resulting solution of the cantilever motion as sinusoidal and combine it with calculated stable amplitudes. Then we insert this motion of the cantilever to the force model and calculate the periodic force while cantilever is oscillating in the force field. After acquiring this periodic interaction force we can also calculate every single frequency component of it by using Fourier method. Going further, we can calculate average forces for any frequency component.

Including the effects of higher harmonics, we add a perturbation term in the frequency of higher harmonic with a small amplitude, to the solution. Then we follow the procedure above and calculate the spectrum of forces for the frequency that we want to measure.

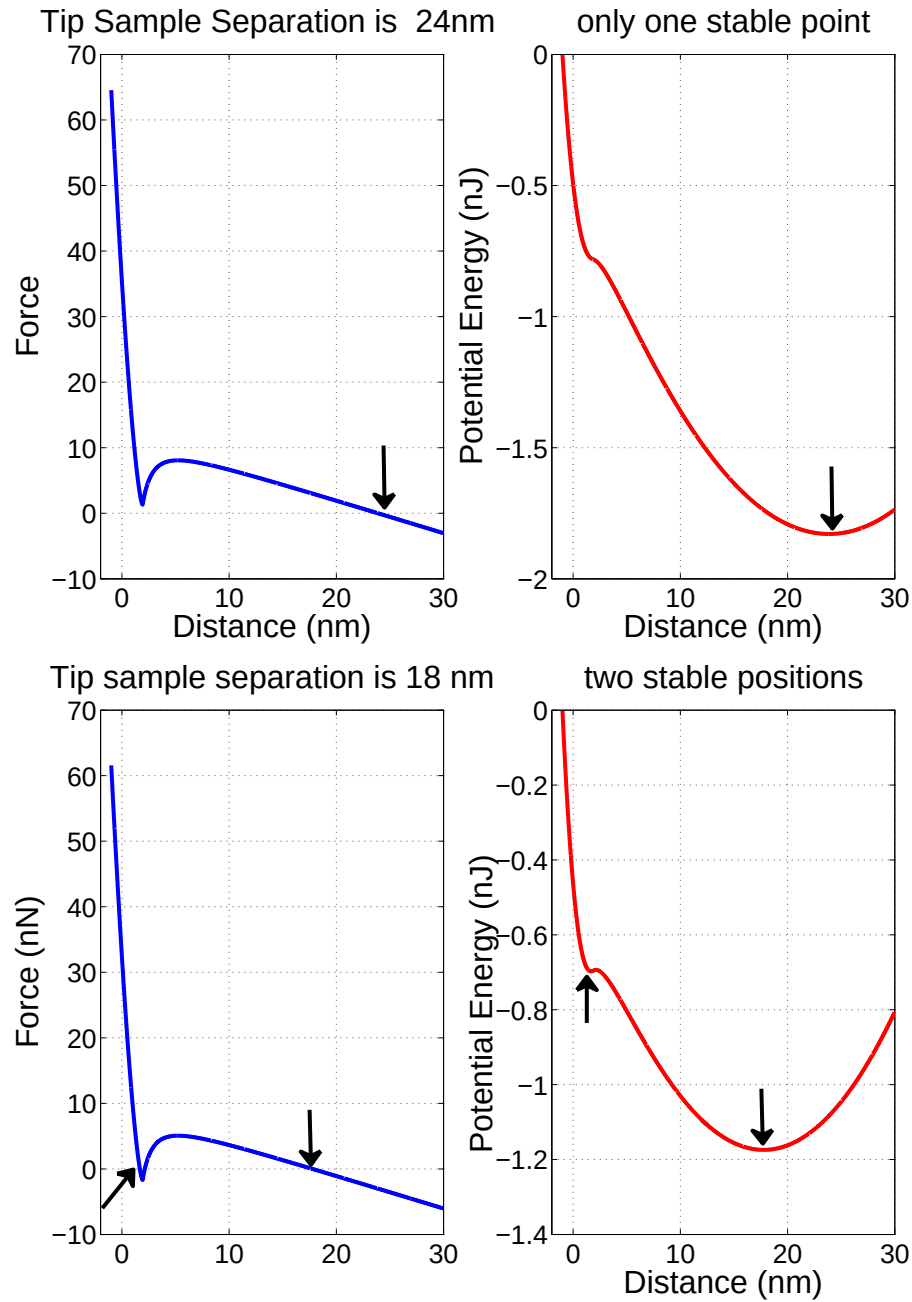


Figure 4.5: Total force and potential energy of the cantilever(modeled as spring) and the tip-sample interaction at 24nm and 18nm respectively. Showing that tip and sample system, when the tip approaching the sample, has bistabilities at various points. This means, at those positions motion of the cantilever is chaotic and sudden jumps from one stable point to another, because of the tip-sample interaction, is possible.

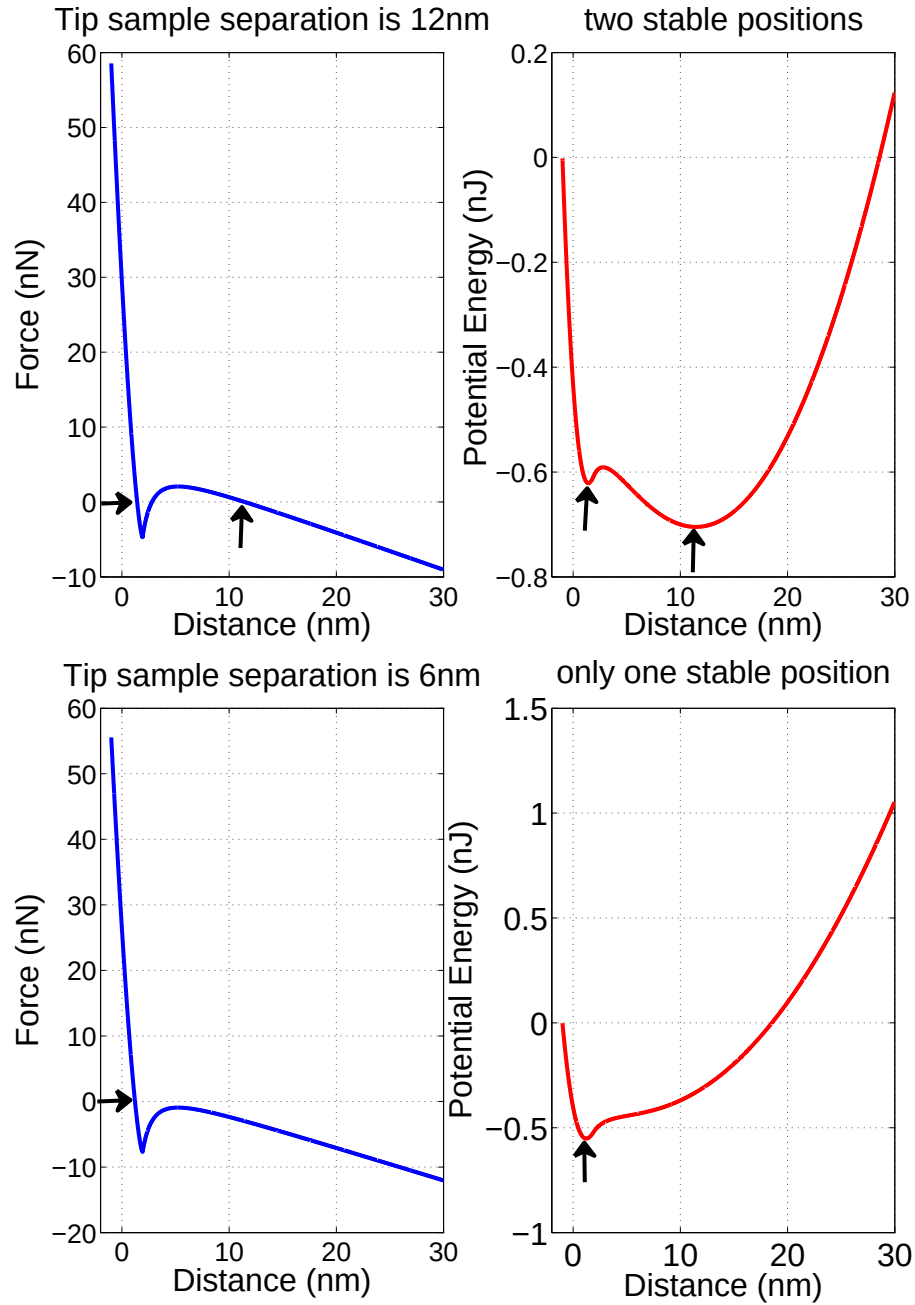


Figure 4.6: Total force and potential energy of the cantilever (modeled as spring) and the tip-sample interaction at 12nm and 6nm respectively.

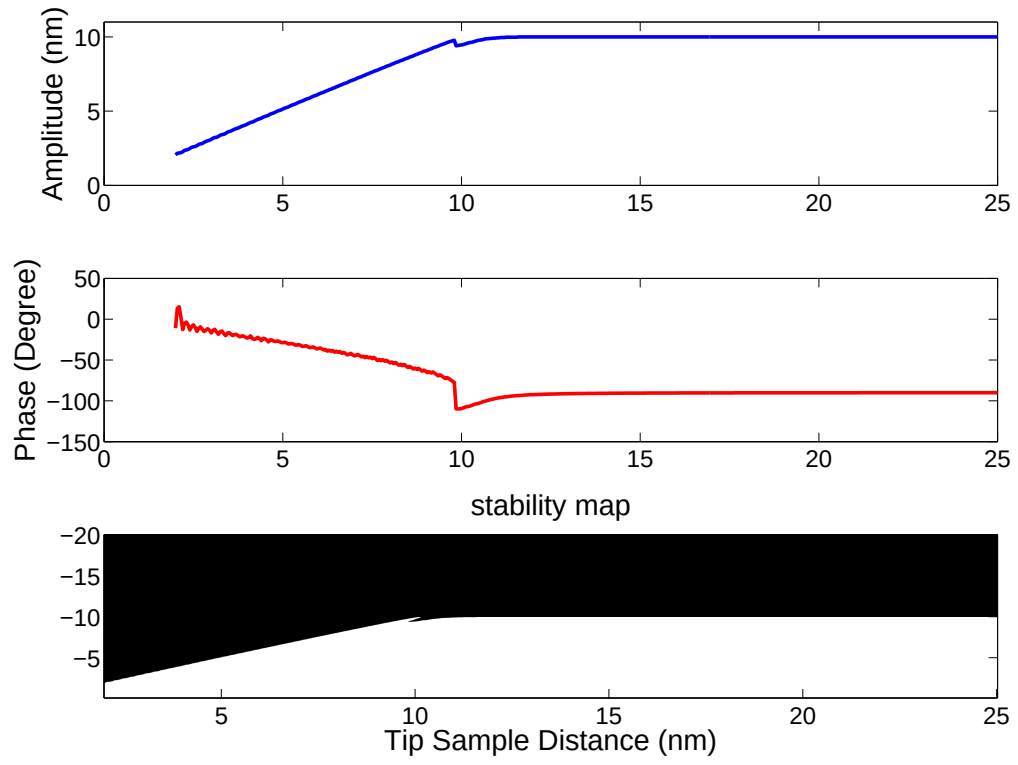


Figure 4.7: Amplitude distance, phase distance and stability map curves that are taken from the simulation results were no frequency off-set is applied, with the parameters $E_t = 130\text{GPa}$, $E_s = 1.2\text{GPa}$, $R = 50\text{nm}$, $H = 6.4 \times 10^{-20}$, $f_0 = 75\text{kHz}$, $k_0 = 3\text{N/m}$, $A_0 = 10\text{nm}$

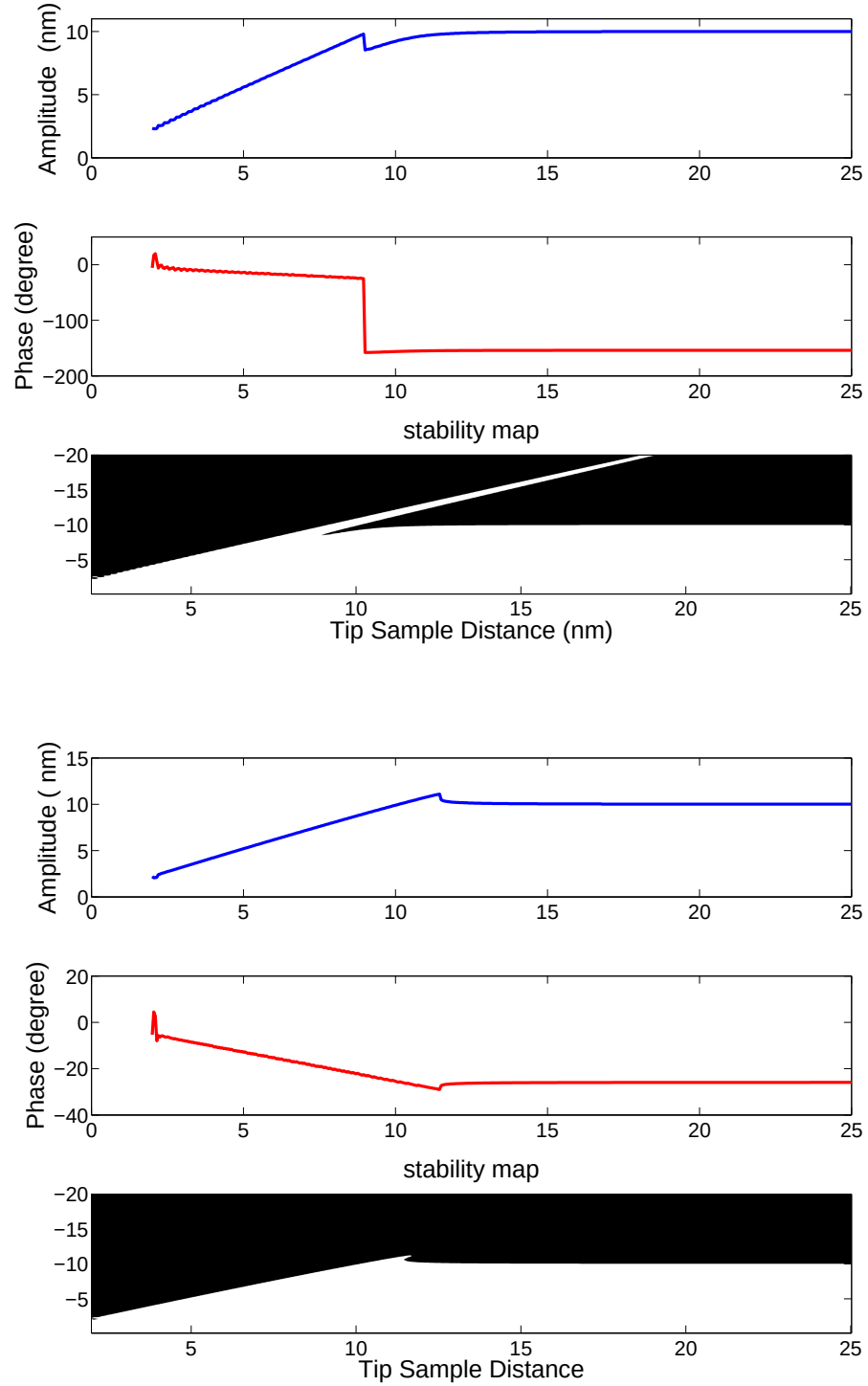


Figure 4.8: Amplitude distance, phase distance and stability map curves that are taken both in repulsive(above) and attractive(below) regions with same parameters were no frequency offset applied (previous figure)

Chapter 5

Multifrequency Electrostatic Force Spectroscopy

5.1 Introduction

As we mentioned in previous chapters, Atomic force microscopy (AFM)[17] is a powerful tool for imaging various tip-sample interactions on the nanometer scale. Imaging electronic properties are especially important for nanoelectronics; and electrostatic force microscopy has been applied to, for example, electrical characterization of carbon nanotubes,[18] DNA,[19] and nanoparticles.[20] Kelvin probe microscopy, which measures the contact potential difference between the tip and the sample, was applied to the label-free detection of nucleotides.[21] Electrostatic force microscopy has been used to study light induced carrier dynamics in organic conductors.[22] Single carrier charging events have been observed by AFM.[23, 24] Recently, multifrequency imaging has been applied to imaging of electrostatic forces on insulating substrates.[25]

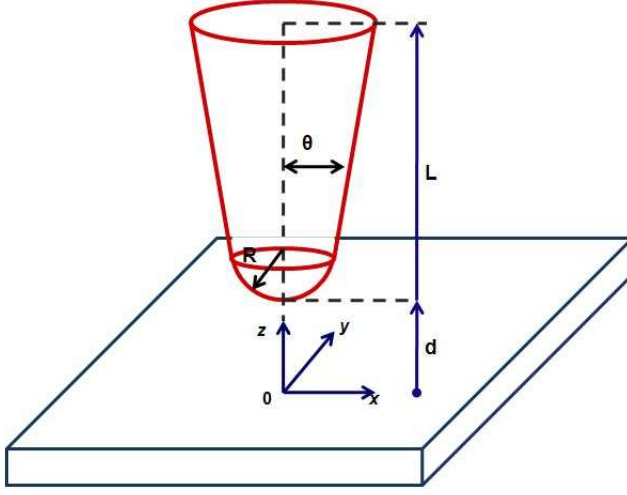


Figure 5.1: Detailed representation of a tip with its geometrical characteristics.

5.2 Description of extended interaction model including electrostatic effects

Before going into the detailed explanation of this technique, we must first mention about the nature of the electrostatic interaction between the tip and the sample and how we model and calculate this interaction. The electrostatic interaction between the tip and the sample can be modelled by addition of the contributions of the cantilever body and the tip cone and apex as

$$F_e = F_{e,body} + F_{e,tip} \quad (5.1)$$

where $F_{e,body}$ is an equivalent lumped force acting at the tip apex due to distributed capacitance of the cantilever body and $F_{e,tip}$ is the force due to the tip cone and apex. Both $F_{e,tip}$ and $F_{e,body}$ are dependent on the tip-sample separation z_{ts} and applied voltage $V_a(t)$. When exciting a particular mode n , a position dependent AC body force $F_{d,n}$ at frequency ω_n can be converted to an equivalent lumped force $F_{lumped,n}$ acting on the tip apex using[46]

$$F_{lumped,n} = \int_0^1 h_n(q) dF_{d,n}(q) \quad (5.2)$$

where $h_n(q)$ is the normalized mode shape[47], q is a normalized dimension such that $q = 0$ at the base and $q = 1$ at the tip of the cantilever. Using Eq. 5.2 and assuming infinitesimal parallel plate capacitors are responsible for the electrostatic interaction of the body and the sample, for exciting mode n of a rectangular cantilever of width w , at an inclination angle α with the planar ground plane, the lumped equivalent ω_n component of $F_{e,body,n}$ can be calculated as[48]

$$F_{e,body,n} = - \int_0^1 \frac{\epsilon_0 w L \Delta V V_{AC} \cos(\omega_n t) h_n(q) dq}{H^2 [z_{cs}/H + \cos\alpha + L/H(1-q)\sin\alpha]^2} \quad (5.3)$$

where $\Delta V = V_{DC} - V_s$, V_s being the average surface potential and z_{cs} is the distance between the conductive tip and the surface. Note that due to the dielectric separator of thickness t_d , the conducting tip separation is shifted with respect to the actual tip-sample separation, z_{ts} , i.e. $z_{cs} = z_{ts} + t_d$. The contribution of the cone and apex is modelled by a hyperboloid tip as[49]

$$F_{e,tip} = -\pi\epsilon_0(\Delta V + V_{AC}\cos(\omega t))^2 \left[\frac{\ln(1 + H/z_{cs}) - H \frac{z_{cs}-R/\tan^2(\theta_0)}{z_{cs}(H+z_{cs})}}{[\ln(\tan(\theta/2))]^2} \right] \quad (5.4)$$

The electrostatic AC lumped forces are plotted as a function of z_{cs} as shown in Fig. 5.2. It can be seen that, the contribution of the body to the overall electrostatic interaction is suppressed by more than an order of magnitude for the second order mode. This shows that we can consider the electrostatic interaction between tip and sample as dominant part and neglect the interaction due to cantilever body and the sample. When the cantilever is oscillated in its fundamental mode f_0 with an amplitude A_0 , and the second-order mode oscillation

amplitude is much smaller than A_0 , the tip sample separation can be written as $z(t) = z_0 + A_0 \cos(\omega_0 t)$ where $\omega_0 = 2\pi f_0$. If the tip-sample bias is of the form $V_{ts}(t) = V_{DC} + V_{AC} \cos(\omega_2 t)$ where $\omega_2 = 2\pi f_2$ is the resonance frequency of the second order mode, it is possible to calculate the time-dependent electrostatic force $F_e(t)$ through Eq. 5.4. Because of the nonlinear form of Eq. 5.4, in both the variables V_{ts} and z , multiple frequencies will be generated, including harmonics of f_0 and f_2 , and their sums and differences, namely $f_2 + f_0$, $f_2 - f_0$, $f_2 + 2f_0$, $f_2 - 2f_0$ etc. The frequency component at frequency f_2 can be calculated through Fourier analysis. Fig.5.3a shows tip sample separation, modulated by the oscillation of the cantilever. The cantilever displacement is the summation of the first and second order mode oscillations. Fig.5.3b shows the electrostatic force under AC excitation, during oscillation shown in Fig.5.3a. It can be seen from the waveform that, there are different frequency components in the time-dependent electrostatic force. Calculating the amplitude of the spectral component of the force at frequency f_2 using $\langle F_{e,tip,\omega_2} \rangle = | \int dt F_{e,tip}(t) \exp(-i\omega_2 t) |$ where the integral is taken over many cycles of the fundamental mode period, for typical tip and cantilever parameters and electrical excitation values, we find oscillation amplitudes of the second order mode to be about 0.1 to 1 nm. This is in good agreement with our measured results, considering the large number of variables. Also this result justifies the assumption that we make concerning the electrostatic interactions between tip and the sample.

5.3 Description of new technique, multifrequency electrostatic force spectroscopy

In this section, we will introduce an extension of multifrequency AFM to a spectroscopy technique similar to capacitance spectroscopy. We refer to the technique

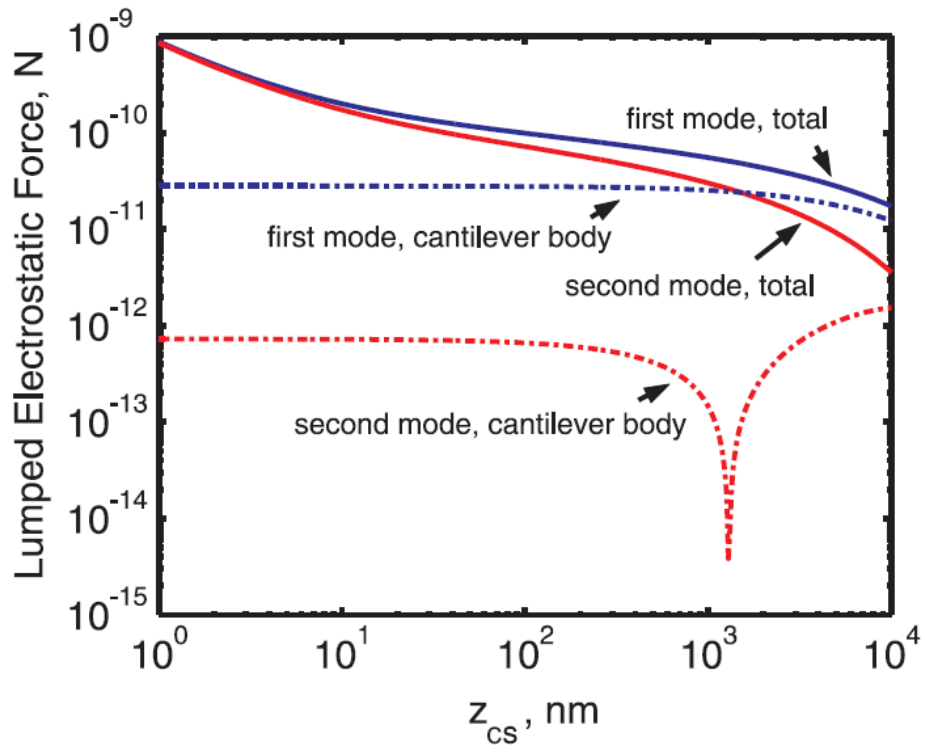


Figure 5.2: Lumped electrostatic forces for excitation of the first two modes of a cantilever on a planar surface, plotted as a function of the tip-sample separation z_{cs} .

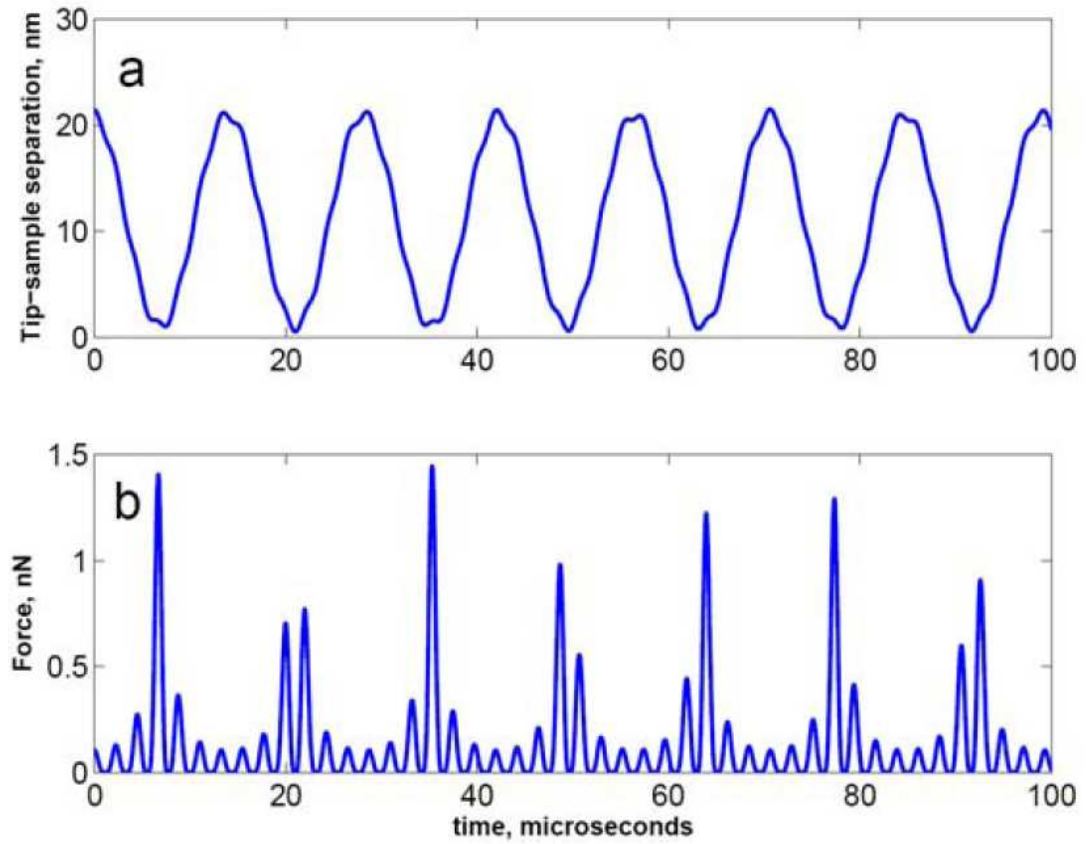


Figure 5.3: The tip-sample separation during oscillation of the cantilever in the first and second order mode simultaneously. Tip-sample separation at closest approach is 0.6 nm. b) Electrostatic force resulting from AC excitation of the form $V_{ts}(t) = V_{DC} + V_{AC}\cos(\omega_2 t)$, during the oscillation shown in (a). The values used in the simulation are, tip length $H=15$ m, half-cone angle $\theta_0=15$ degrees, tip radius $R=15$ nm.

as the multifrequency electrostatic force spectroscopy [MFEFS]. The technique is demonstrated by observing charging hysteresis of silicon nanocrystals in a silicon nitride matrix on silicon. In the experiments, a commercial AFM tip was used. The tip was a Pt/ Ir coated rectangular cantilever with a nominal length of $L=220$ nm, width of $w = 30\text{nm}$, tip height of $H = 15$ nm, tip half-cone angle of $\theta = 15^\circ$, and nominal tip radius of $R = 15$ nm. The fundamental mode of the cantilever is used to stabilize the average tip-sample separation, and the second order mode is used to resonantly measure electrostatic forces. In order to limit the charge transfer between the biased tip and the surface, and to avoid instabilities during tapping, the tip is coated with a nominal $t_d = 10\text{nm}$ thick Si_3N_4 layer in a plasma-enhanced chemical-vapor deposition [PECVD] reactor [PlasmaLab 8510C] using SiH_4 and NH_3 as precursor gases. This layer is analogous to the gate oxide in flash memory devices, and the tip can be considered as a metallic gate. The first and second eigenfrequencies of the cantilever were measured to be $f_0 \cong 70.01$ kHz and $f_2 \cong 448.83$ kHz, with quality factors of $Q_0 = 220$ and $Q_2 = 450$. The experiments were performed on a commercial AFM system [PSIA XE100E] under ambient conditions. During imaging, the cantilever is driven at a frequency slightly below f_0 by the dither piezo, and a sinusoidal voltage superimposed on a dc voltage is applied at a frequency that coincides with the second order flexural mode frequency $\omega_2 = 2\pi f_2$. The deflection of the second-order mode is measured using an external rf lock-in amplifier [Stanford Research Systems SR844]. It is known that, unless the second order mode frequency is an integer multiple of the fundamental mode frequency, tapping at the fundamental frequency does not generate significant oscillation of the second order mode.[26, 27] Using this fact and separate excitation sources for the two modes, it is possible to separate short and long range interactions by measuring the oscillation amplitudes and phase at f_0 and f_2 . In order to minimize the coupling of the two modes to each other through nonlinearities imposed by the tip-sample interaction, the second order mode amplitude A_2 was kept below 1 nm. Topographic feedback is maintained by the feedback loop of the AFM system using the fundamental mode. Typical fundamental mode amplitudes were $A_0 = 10\text{-}20$ nm defined by the adjustable set point. The tip-sample interaction force can be written as the sum of electrostatic and nonelectrostatic terms as $F_{ts} = F_e + F_{ne}$. The electrostatic component is

dependent on the tip-sample bias V_{ts} . In our experiments, the tip-sample voltage V_{ts} is of the form $V_{ts}(t) = V_{dc} + V_{ac}\cos(w_2t)$, V_{ac} typically being about 0.1 to 1 V. This modulated bias results in an average electrostatic force amplitude F_{e,w_2} at frequency f_2 that can be written as

$$F_{e,w_2} = \left\langle \frac{\partial C_{ts}(z)}{\partial z} \right\rangle (V_{dc} - V_{cpd}) V_{ac} \quad (5.5)$$

where $C_{ts}(z)$ is the tip-sample capacitance, V_{dc} is the tip-sample bias, and V_{cpd} is the contact potential difference. Brackets denote averaging over the oscillation period. When the ac excitation amplitude V_{ac} is kept constant, F_{e,w_2} is linearly proportional to $V_{dc} - V_{cpd}$. In order to verify that the second order mode oscillation is excited primarily by electrostatic interactions, we sweep the dc bias or the frequency of V_{ac} and record the second order mode amplitude and phase, while the first order mode is tapping a flat and clean silicon surface. The excitation amplitude of the second order mode follows the DC voltage bias, and is nulled when the contact potential difference is compensated around -0.3 V, as seen in Fig.5.4, in accordance with Eq.5.5. For large biases, detachment of the tip from the sample surface takes place. This effect is previously well studied and can be understood by considering the coupling of the dc electrostatic forces to the topography channel.[28] Tip retraction results in a reduced average electrostatic excitation of the second order mode, due to the increased average tip-sample separation. The feedback effect explains the observed deviation from linearity in the excitation amplitude at bias differences greater than 0.5 V shown in Fig.5.4. This effect must be avoided or be carefully considered when quantitative measurements under large biases are needed.

If a localized state is separated from the bulk of the substrate by a tunnel barrier, applying an electric field large enough to make the tunnel barrier transparent for carrier transport will result in accumulated charge in the localized state. When the field is reduced, the carriers will stay in the localized state until

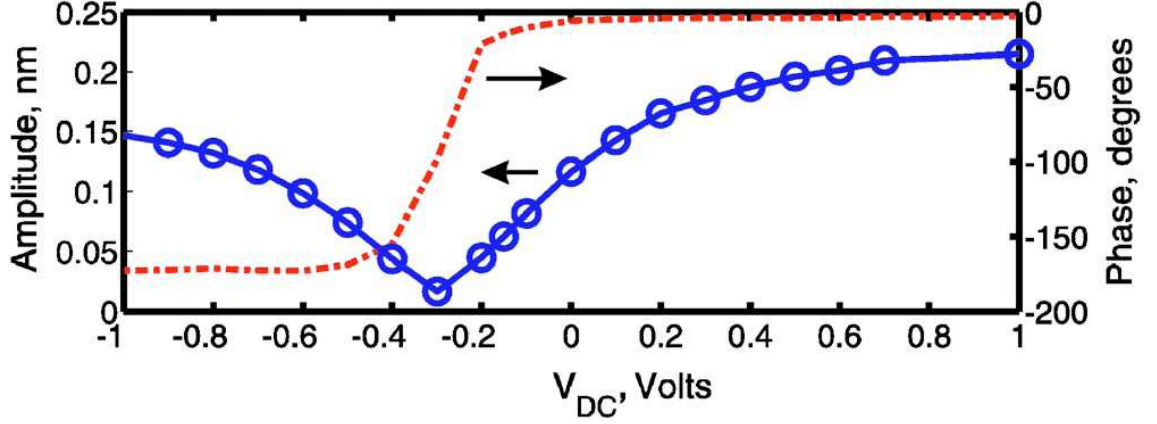


Figure 5.4: Dependence of the amplitude of the second order mechanical mode on DC bias voltage, during tapping with the fundamental mode. The ac frequency was on resonance with the second order mode. Smooth transition of the phase of the oscillation indicates finite capacitive coupling of the drive signal to the dither piezo.

they slowly tunnel out, or a large enough reverse polarity field causes them to escape. In order to interpret the data collected during a measurement of localized charging, the electrostatic model has to include the effect of localized charges. For the sake of simplicity, we consider the case of a nanocrystal below the tip. The electrostatic interaction energy between the tip and the sample with a charge trapped in a nanocrystal in between is given by [29, 30]

$$U = \frac{q^2}{2C_t} - \frac{C_1}{2C_t}qv - \frac{C_1C_2}{2C_t}V^2 - \frac{C_0}{2}V^2 \quad (5.6)$$

where C_0 is the tip-substrate capacitance, C_1 is the tipnanocrystal capacitance, C_2 is the nanocrystal-substrate capacitance and $C_t = C_1 + C_2$ total capacitance seen by the tip. The electrostatic force can be obtained from Eq.5.6 by differentiation with respect to the tip-sample separation z ,

$$F_e = \frac{1}{C_t} \frac{\partial c_1}{\partial z} \left(\frac{q^2}{2} - C_2 qV + \frac{C_2^2 V^2}{2} \right) + \frac{1}{2} \frac{\partial c_0}{\partial z} V^2 \quad (5.7)$$

Using Eq.5.7, and the ac modulated bias, different frequency components of the electrostatic force can be evaluated. When the electrostatic excitation is

measured as a function of the bias, the presence of charge in a state between the tip and the sample results in a shift of the curve along the bias coordinate. Using algebraic manipulation, Eq.5.7 can be used to calculate the hysteresis between the force-voltage curves with a charge q deposited in between the two curves, given by;

$$\Delta V_H = \frac{q}{C_2} \left[1 + \frac{\partial c_0}{\partial z} / \left(\frac{C_2}{C_1 + C_2} \right)^2 \frac{\partial c_1}{\partial z} \right] \quad (5.8)$$

The voltage ΔV_H is the charging voltage of the trap $V_c = q/C_2$, divided by a dimensionless factor that quantifies the shielding effect of the tip. Using Eq.5.8, by measuring the hysteresis at specific location, information about the local density of states and charging-discharging dynamics can be obtained. The technique was demonstrated on different sets of samples. Fig.5.5(a) shows the typical result for the amplitude of the second order mode during the cyclic voltage sweep on a clean silicon surface. No hysteresis can be observed, due to the low density of surface states on a clean silicon surface. Fig.5.5(b) shows the typical result of the same experiment performed on a 10 nm thick silicon nitride film with embedded silicon nanocrystals grown by PECVD. The average diameter of silicon nanocrystals is 5 nm inferred from photoluminescence measurements. Significant hysteresis of about 310 mV can be observed. Assuming a nominal nanocrystal diameter of 5 nm and a nominal conducting tip radius of 15 nm, through finite element analysis, the relevant capacitances and gradients are estimated as $C_1=1.05$ aF, $C_2=1.4$ aF, $\frac{\partial c_0}{\partial z}=120$ pF/m, and $\frac{\partial c_1}{\partial z}=25$ pF/m. These values give a hysteresis voltage of 56 mV per electron per nanocrystal. The measured hysteresis of 310 mV corresponds to about six electrons per nanocrystal, deposited between 0 and 2 V. Arrows in Fig.5.5(b) denote onset of charging and discharging of the nanocrystals. For our signal to noise ratio, single electron events should be observable for nanoparticles with up to 10 nm diameter, 3 nm away from the substrate, and using a 15 nm radius tip. The exact hysteresis value for a single electron depends on other parameters of the sample such as the thickness and dielectric constant of the tunnel barrier. In order to highlight the analogy of MFEFS with conventional capacitance spectroscopy, macroscopic capacitors (1 mm gate diameter) were fabricated on nonstoichiometric silicon nitride films containing nanocrystals

and on stoichiometric silicon nitride films without nanocrystals. The capacitance-voltage traces shown in the insets of Figs. 5.5(a) and 5.5(b) are acquired using an LCR meter and display similar hysteresis. In order to ensure that the observed effects are due to charging and not due to instability caused by tip-sample interactions, it is necessary to investigate the tip-sample interactions in greater detail. Figure 5.6 shows amplitude-distance data obtained at different biases. The inset of Fig. 5.6 shows that long-range electrostatic interactions are indeed perturbed as a result of charging of the film. Amplitude distance curves obtained at zero bias differ before and after charging. The effect of charging is roughly equivalent to applying a bias ΔV_H to the cantilever. The observations are well understood by considering the cantilever dynamics taking into account the electrostatic and nonelectrostatic interactions. Numerical calculations of how the oscillation amplitude of the fundamental resonant mode changes with bias and tip-sample separation is shown as solid curves in Fig. 5.6. Measurement results and simulation results of the tip-sample interaction indicate that, in the repulsive mode, the amplitude distance curves are single valued for tip-sample separations below the free oscillation amplitude. For drive frequencies below the zero-bias resonant frequency, peaking of the amplitude can be observed if the tip-sample separation is greater than the free oscillation amplitude. For stable operation of MFEFS, this parameter range must be avoided and amplitude set point of topographic feedback must be chosen below 90 percent of free oscillation amplitude. For drive frequencies above zero bias resonant frequency, there is no peaking that may potentially result in bistabilities. However, in this parameter range, coupling of the electrostatic interactions to the topography feedback are more pronounced. There are advantages of the MFEFS technique to force or amplitude versus distance measurements. In MFEFS, the tip is never brought into hard contact with the sample, therefore both the sample and the tip structures are preserved. In conventional force versus distance measurements, instrument drifts are not independently compensated; however, MFEFS inherently stabilizes the tip-sample separation. Bias sweeps in a conventional force versus distance measurement requires complicated data analysis, whereas MFEFS data directly give a hysteresis voltage that can be related to charging through characterization of the tip shape. Ideally, MFEFS measurements can be done rapidly (about $Q^2/f^2 \approx 1$ ms per

bias point), therefore, spatial drifts of instrumentation can have less effect on measurements.

5.4 Spectroscopy of Carbon Nano Tubes

In these section we present the spectroscopic results that are taken from the carbon nanotube film on highly doped silicon substrate with this technique. But different from the original technique here we bias the sample at a frequency different from the modes of the cantilever beam, namely second mode frequency. We use second mode frequency to stabilize the system and image the topography at 335 kHz and small electrical signal is applied at 25 kHz. The reason behind this configuration is to prevent the coupling of the topography signal to the electrical signal. First we take the image of the carbon nanotubes as seen in Fig.5.8. Then we choose different points either on silicon substrate and or on carbon nano tubes and perform the spectroscopy experiments. To achieve the repetability and reliability of the experiment we perform spectroscopy on a point several times. Below in Fig. 5.9 the representative data taken on silicon and the carbon nano tubes can be seen. We can clearly differentiate two different surface from their spectroscopy data. The spectroscopy data for silicon clearly linear in bias sweep like a conductor because of the high doping ratio. Also we can identify work function of the surface. As for the data of carbon nano tubes; it differentiates among different points, probably the film contain different types of carbon nano tubes in many different lengths. Besides these factors the metal catalyzer that is used to grow the tubes still remains in the film. The table below shows the work function data of different point for silicon and carbon nano tubes.

Table 5.1: Work function values taken from the spectroscopy experiments of the different points on either silicon or carbon nano tubes(CNT)

	1st point	2nd point	3rd point	4th point	5th point
Si	0.2355 V	0.2389 V	0.0838 V	0.0831 V	0.1998 V
CNT	0.0264 V	0.0504 V	0.0961 V	0.1555 V	0.0086 V

5.5 Conclusion

The MFEFS technique we presented here can be applied using a standard AFM system using a standard metal coated cantilever in ambient conditions. For conductive substrates and samples without a cap layer, a thin barrier coating on the tip can be applied to improve stability. The technique can be regarded as a technique that is similar to scanning tunneling spectroscopy (STS) used in scanning tunneling microscopy studies. However, it can be used to study trap levels on partially insulating samples where STS can not be applied.

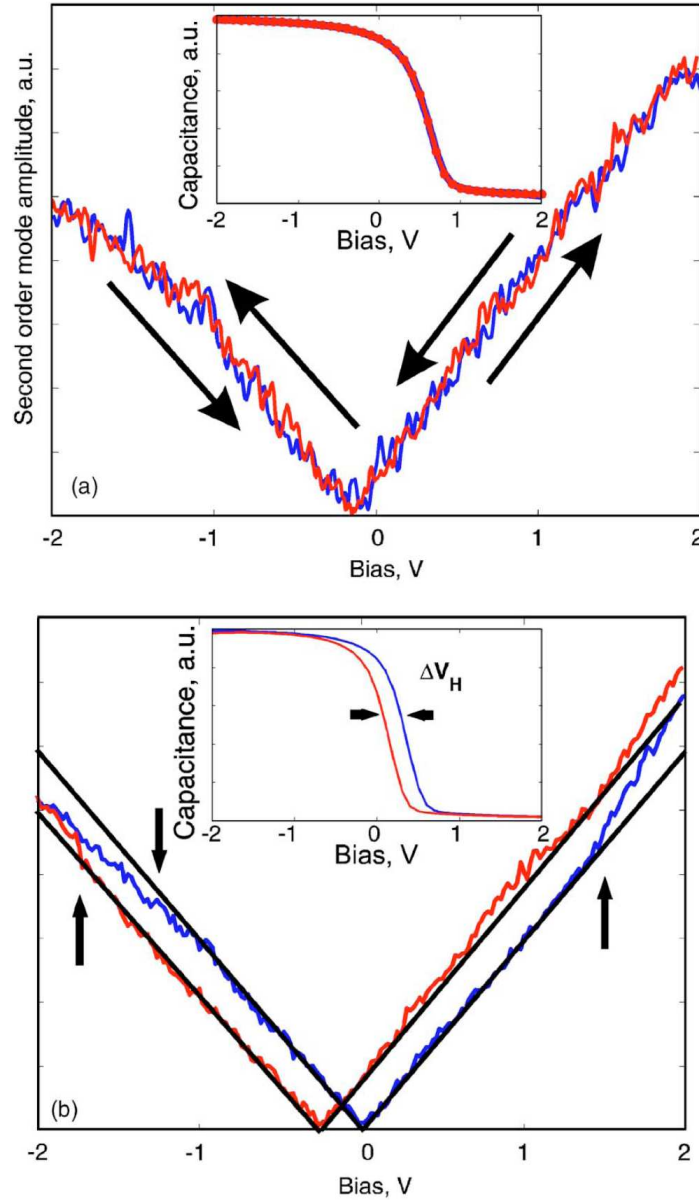


Figure 5.5: Electrostatic excitation of the second order mode during a voltage sweep on a clean silicon surface. The arrows denote voltage sweep directions. No hysteresis can be observed. (b) Electrostatic excitation of the second order mode during a voltage sweep on silicon nitride layer with silicon nanocrystals embedded. Significant hysteresis is observable, indicating charging of nanocrystals. The arrows denote onset of charging and discharging events. The insets show capacitance-voltage traces of macroscopic capacitors fabricated using silicon nitride films without and with nanocrystals.

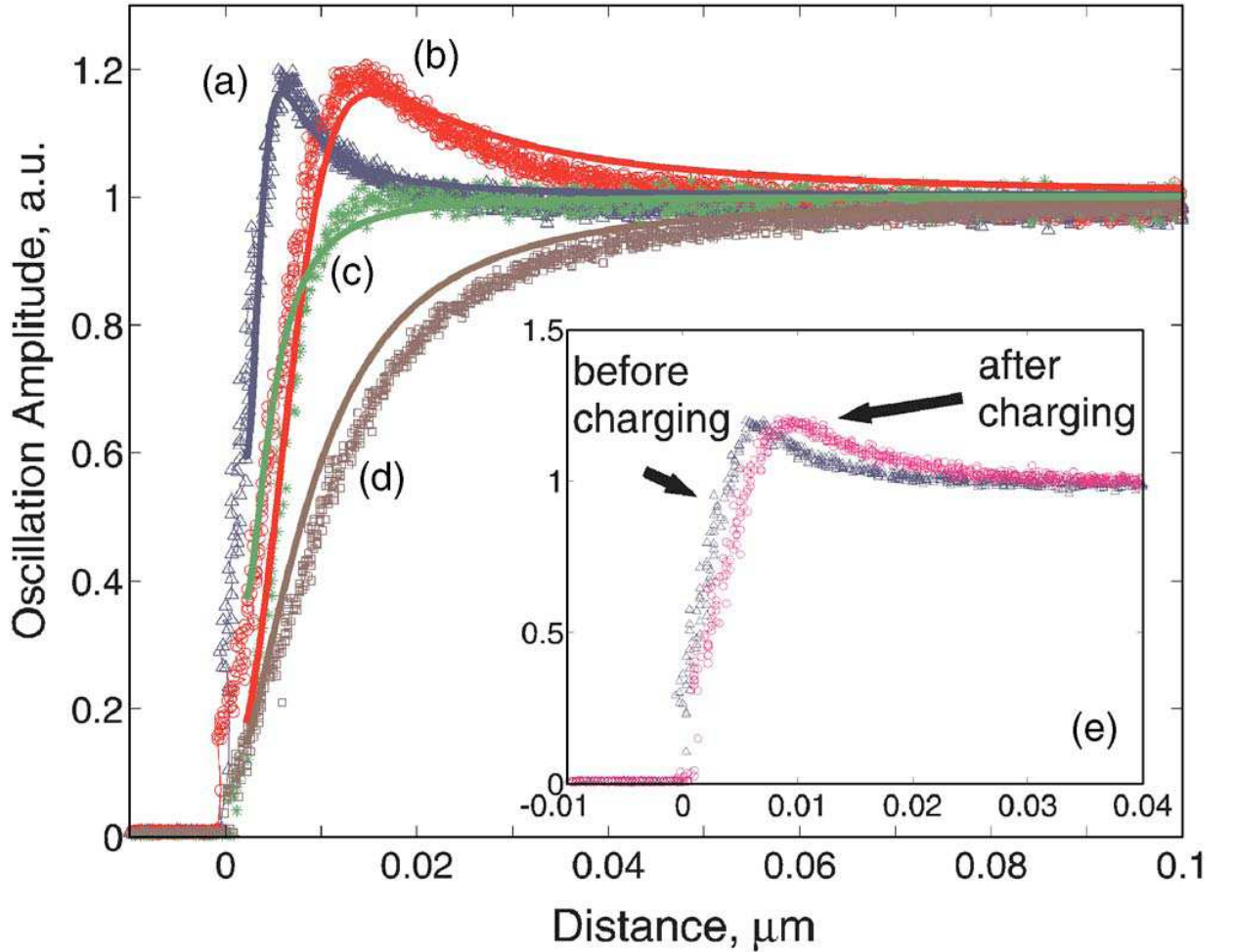


Figure 5.6: Oscillation amplitude vs tip-sample separation. When the cantilever is driven below its resonance frequency, peaking of the oscillation amplitude is observed (a) for 0 V bias and (b) for 2 V bias. If the drive frequency is above the resonance frequency, no such peaking occurs as seen in (c) for 0 V bias and (d) for 2 V bias. Representative theoretical fits obtained by using the same set of parameters and by only changing the bias parameter are shown as solid curves. (e) The inset shows amplitude vs tip-sample separation scans obtained at 0 V bias before and after charging the film by contacting with a 2 V biased tip. Shift of the curve and broadening of the peak after charging indicate a local surface potential shift.

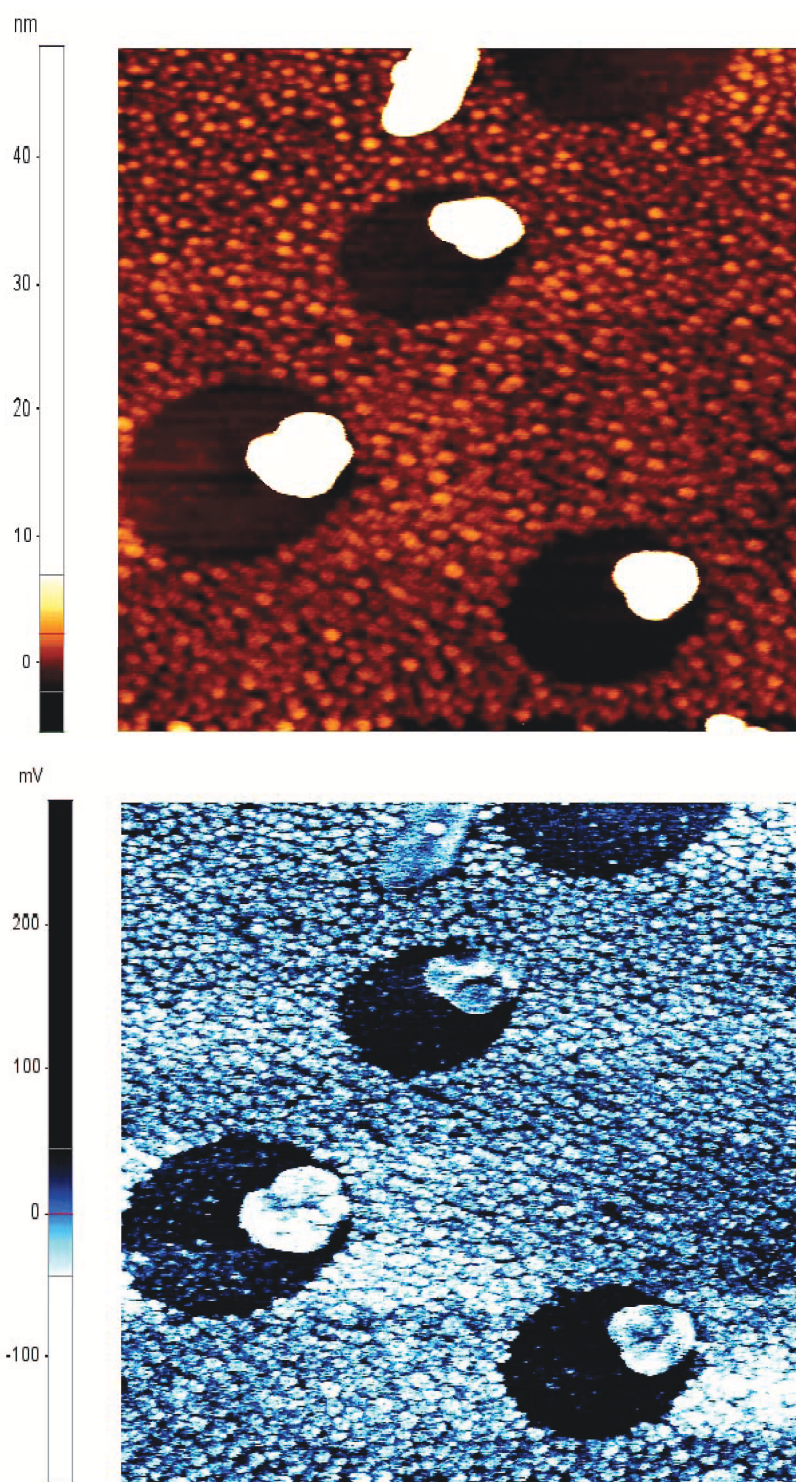


Figure 5.7: These are taken from the silver nanoparticles on Si substrate. above is the topography and the below is the electrostatic image of the particles. Topography and the Electrostatic image recorded simultaneously

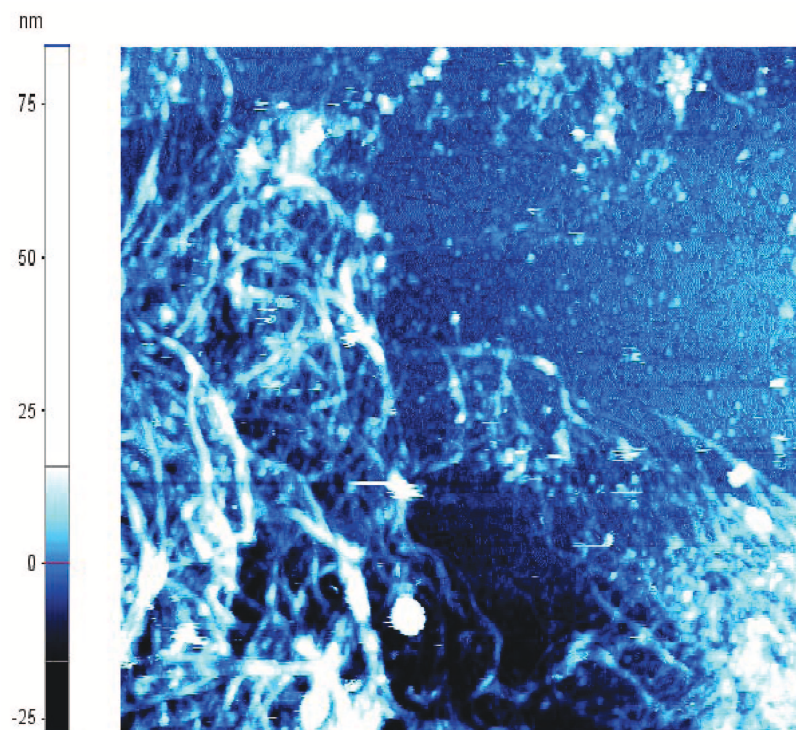


Figure 5.8: Topography image of the carbon nano tubes on silicon substrate.

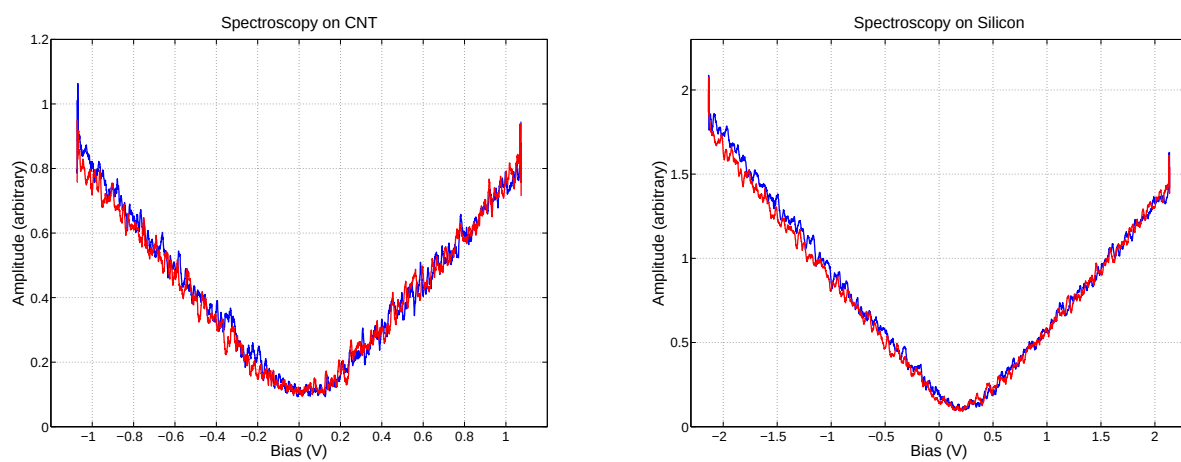


Figure 5.9: Representative spectroscopy datas taken on carbon nano tubes(CNT) and on silicon substrate

Chapter 6

Resonant Heterodyne Force Imaging

6.1 Introduction

Measurement and imaging of material dependent non-linear tip-sample interactions in atomic force microscopy (AFM)[17] provide information about the structure of the sample at the nano-scale. Short and long range forces can be best measured in the tapping-mode, where the tip is oscillated near the sample and interacts with the sample over the oscillation period in a non-linear way. In the conventional tapping mode, a single oscillation mode of the cantilever is used to resonantly detect the fundamental frequency component of the time varying interaction force, which is observed in the perturbations of the amplitude and phase of the oscillation.[31] This selective measurement filters out higher harmonics of the interaction force and results in loss of information. Material contrast is generally observed in dissipation related phase changes of the mechanical oscillation.[32, 34] Although excitation of the higher frequency harmonics can be strongly related to material elasticity, they are not detected in conventional tapping mode AFM.[26] The main reason for this is, for an arbitrary rectangular cantilever, higher order mode frequencies are not integer multiples of the fundamental mode frequency,

and harmonic forces can not be resonantly detected.[35, 39] Several authors have addressed the problem of measuring the complete tip-sample interaction during tapping using specialized modifications to the cantilever or the scanning probe electronics.[40, 27] Multi-frequency excitation of the cantilever simultaneously at the two flexural resonances has also been demonstrated to give complementary material contrast [41, 42]

6.2 Numerical Investigation of Resonant Heterodyne Force Imaging

Before going into details of experiment and measurements, we will first investigate the idea of the resonant heterodyne force detection with the aid of the model interaction forces and the numerical procedure we mentioned in chapter 4. We will also briefly compare an important measurement data with simulations.

As we mentioned, our numerical model can predict all the key issues of conventional amplitude and phase distance relationships between tip and the sample configuration in dynamic mode. While adjusting the imaging parameters for proper operation of dynamic mode, the most important issue is the bistability, meaning that; with certain set amplitudes, system has two stable solutions. Conventionally these two solutions are called attractive and repulsive branches of the interaction. Fig.6.1 shows the extreme case of bistability that is calculated with simulation.

The idea of Heterodyne Force Detection is first used in ultrasonic force microscopy by O. V. Kolosov *et al.* [54]. They excite the cantilever far from the resonance and introduce the local oscillator signal to the system by shaking the sample with a piezoelectric actuator. Non linear multiplication of the signals at the tip of the cantilever yields new frequencies at sum and difference frequencies of drive and local oscillator signals. By filtering high frequency component, they detected the converted signal at low frequencies. Both the local oscillator signal and converted frequency is very different from the resonances of the cantilever.

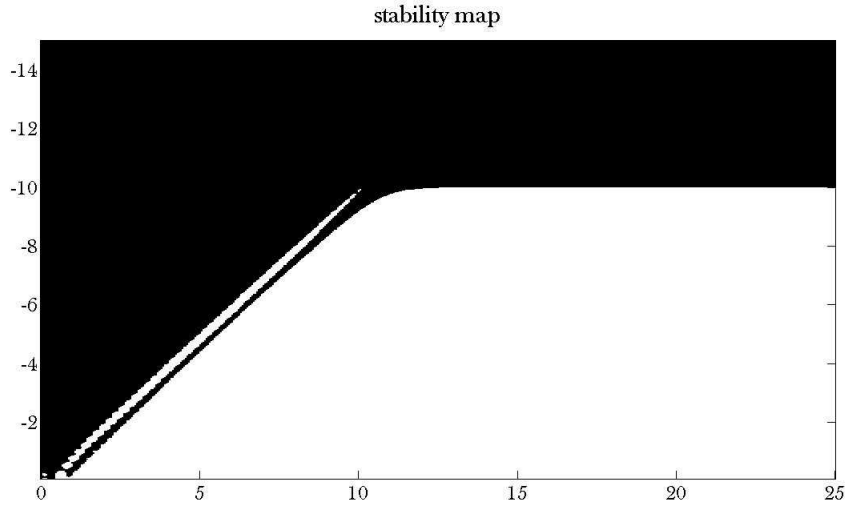


Figure 6.1: Stability map for the interaction amplitude with respect to distance. In figure repulsive branch is seen as the separated part from the wide white region which is attractive branch

As the process suggests, this procedure is the idea of the heterodyne mixing in electronics. Although this technique can give material dependant images, has some very severe drawbacks. Since they use off resonance signals and very high amplitudes, materials on the surface can easily be damaged, even working with hard samples.

As the name of our technique suggests, we have taken advantage of mechanical resonances of the cantilever for heterodyne mixing and conversion of material dependant signals. For realizing the idea we apply local oscillator signal at frequencies of differences between first mode and integer multiples of fundamental mode frequency to convert the relevant signals to the first mode frequency. Similarly by applying local oscillator signal at first mode frequency of the cantilever, we can convert the relevant signal to the differences of first mode and integer multiples fundamental mode frequency. These two schemes are called up-conversion and down-conversion. Also we introduce local oscillator signal at very low amplitudes, where we can think of the procedure as perturbation of conventional

dynamic mode imaging. This scheme also makes easier to control the tip sample separation stabilization. Our measurement technique can also avoid possible damage of the sample material while imaging. Consequently, soft materials, even biological samples can be imaged with resonant heterodyne force technique non-destructively.

Since the amplitude of the local oscillator is small, we can treat it as a perturbation to the imaging mode amplitude, and this will be the same for the simulations. We will focus on one of the schemes which is up-conversion. In order to calculate these converted signal outputs, we first calculate the amplitude distance data for imaging mode frequency only. Since we consider local oscillator signal as perturbation, we calculate the force signal in time by adding local oscillator signal, with very small amplitude ($1nm$), to the normal amplitude data which we obtain from amplitude distance simulation. Also we consider oscillations of cantilever for both signal as sinusoids. Then, we calculate the frequency spectrum of this force signal and extract the amplitude of the force for desired frequency. Assuming first mode and fundamental mode are independent, we calculate amplitudes by multiplying desired force amplitude with second mode transfer function. With this procedure we can analyze any frequency component of interaction with respect to both time and distance. You can see the flow chart of this procedure in Fig. 6.2.

For briefly comparing the experiment with the simulation, we consider the tip sample separation dependent amplitude of up-converted signal for different local oscillator frequencies. You can see this experimental data in Fig6.3. As the difference signal amplitude of first and integer multiples of fundamental mode frequency (the form of which is $f_1 - nf_0$) decreases, the force amplitude of the first mode decreases. With the simulation we calculated the same configuration, which you can see in Fig.6.4. It is obvious that this simulation result predicts the decreasing of the first mode amplitude, but at small tip sample separations amplitude does not follow the measured curve. We think that this is a consequence of not considering the decreasing of quality factor, as tip approaches to the sample. In the force model, we can introduce this effect by considering viscoelastic damping. Eq.6.1 shows the modified model where η is viscoelastic constant of the

sample. For calculating time dependency of the quality factor we first calculated dissipated power and elaborated the relationship between dissipated power and phase distance data. Finally we end up with a time dependent quality factor. Fig.6.5 shows the flow chart of the calculations.

$$F_{\eta}(z) = \begin{cases} -HR/[6(z_s + z)^2] & D \geq a_0 \\ -HR/6a_0^2 + \frac{4}{3}E^*\sqrt{R}(a_0 - z_s - z)^{3/2} - \eta(a_0 - z_s - z)^{1/2}\dot{D} & D < a_0 \end{cases} \quad (6.1)$$

By adding the time dependent quality factor parameter, we repeat the calculation for the first mode amplitude in the up-conversion scheme. With this correction, we can predict the shape of the measured curve Fig6.6. Also this simplistic model and numerical approach can predict the shift of the amplitude signal for different local oscillator frequencies.

An alternative interpretation of the behaviour in the measured curve is switching of the system between attractive and repulsive branches. It is possible that nonlinear multiplication happens only when the system goes into repulsive branch. We see that for certain parameters of interaction, system goes into the repulsive at large separations, after amplitude starts to decrease. Then, when separation is small, system jumps to the attractive again. This event can be seen in the stability map, amplitude and phase distance curves we calculated with our simulation in Fig6.7 . With this amplitude distance relationship, we repeat above mentioned calculations and obtain results of distance dependent amplitudes of second mode frequency as local oscillator frequency changes. Resulting graphs can be seen in Fig.6.8. As we can see, the calculation results give the same trends as in measurement results.

6.3 Description and implementation of the new technique

In this section, the highly non-linear tip-sample interaction is used to convert the frequency components of the interaction force, generated during tapping, to a frequency that can be resonantly measured. Both up-conversion and down-conversion schemes can be implemented. One of the flexural modes is used in tapping mode imaging, while a sinusoidal mechanical signal is applied at the difference frequency of the force component to be measured and the mode frequency to be used for harmonic detection. The frequency-converted force components are then resonantly detected using a lock-in amplifier. Frequency conversion efficiency is also related to the mechanical properties of the sample, therefore the conversion process itself also results in material contrast.

In the experiments, different commercial AFM systems (PSIA XE100 retrofitted with a home-made vibrating sample holder and an Asylum MFP 3D system fitted with an external circuit for multi-frequency excitation) are used. One of the flexural modes is used in tapping mode by the AFM controller and the AC deflection of the other flexural mode is detected using an RF lock-in amplifier (model SR844). Commercial rectangular AFM cantilevers are used. Typical measured mode resonant frequencies are $f_0=68$ to 80 KHz, $f_1=410$ to 500 KHz and nominal spring constants are $k_0=2.7$ N/m, $k_1 = (f_1/f_0)^2 k_0=99.3$ N/m. Typical quality factors of the fundamental and first-order flexural modes are determined to be $Q_0 \simeq 200$ and $Q_1 \simeq 500$. Supplier specified tip radius is $R = 15$ nm. Nominal thermomechanical force noise floors $F_{th} = (4kk_B T/\omega_0 Q)^{1/2}$ are 2×10^{-14} and 3.5×10^{-14} N for the fundamental and first-order modes respectively. Deflection detection noise floor of the AFM systems are $x_{min} \sim 2 \times 10^{-13}$ m/ $\sqrt{Hz}$ and resonant force measurements are Brownian motion limited. In up-conversion experiments, the fundamental mode is driven with an amplitude $A_0 \simeq 10$ nm at a frequency $f'_0 = f_0 \pm \Delta f$, and a local oscillator vibration with amplitude $A_{LO} \simeq 1$ nm is applied either by vibrating the tip or the sample at a frequency f_{LO} . The result of the conversion by heterodyne mixing is monitored at f_1 . Repulsive or attractive branches of the tip-sample interaction can be chosen by selecting a

sufficiently large positive or negative frequency offset Δf . [43] The resonant excitation of first order mode amplitudes A_1 with heterodyne mixing, as a function of the tip-sample separation z_{ts} are plotted in Figures 6.9 (b, c, d, e and f) for $f_{LO} = f_1 - n f'_0$, where $n=1, 2, 3, 4, 6$. The up-conversion process is seen to depend on local oscillator amplitude A_{LO} (Fig. 6.9(g)) and frequency f_{LO} (Fig. 6.9(h)). In the down-conversion process, the first-order flexural mode is used in tapping and lever vibration is monitored at a f'_0 . Since the fundamental mode spring constant k_0 is smaller compared to the higher order mode spring constant k_1 , resonant frequency shift of the fundamental mode is more pronounced (Fig. 6.9(i)). For resonant detection of down-converted signal, f_{LO} was carefully chosen to coincide the down-converted signal, with the shifted fundamental mode resonance frequency f'_0 (Fig. 6.9(j)). However, non-resonant detection of down-converted signal is also possible, at the expense of increased A_{LO} (Fig. 6.9(k)). In all cases, in order to avoid jumping between attractive and repulsive regimes, A_{LO} must be kept adequately small. For certain set of parameters, instabilities are observed for very large A_{LO} (5 nm) and in some cases increased stability was observed with increasing A_{LO} , possibly due to dithering effects. [44] The noise spectrum of the phase signal was observed before measurements to ensure stability.

In order to understand the conversion of force harmonics with resonant heterodyne mixing, we use numerical analysis. As we mentioned earlier the cantilever dynamics can be modeled using lumped independent harmonic oscillators for different flexural modes. The resonant frequency shift of the cantilever mode is given by [45]

$$\delta f(z_{ts}) = \frac{f^2}{kA} \int_0^{1/f} F_{ts}(z_{ts} + A \cos(2\pi ft)) \cos(2\pi ft) dt \quad (6.2)$$

where F_{ts} is the tip-sample interaction force, A is the amplitude of oscillation, k is the lumped spring constant and f is the resonant frequency. When the cantilever is driven by a fixed amplitude sinusoidal force $F_d(t) = F_d \cos(2\pi f_d t)$ at frequency f_d , the complex oscillation amplitude $\tilde{A}$ can be calculated through

$$\tilde{A}(\omega) = h(\omega) F_d = \Sigma_n \frac{F_d}{k_n} \frac{1}{(1 - \omega^2/\omega_{r,n}^2) + i\omega/\omega_{r,n} Q_n} \quad (6.3)$$

where $\omega = \omega_d = 2\pi f_d$ is the drive frequency, F_d is the driving force amplitude, Q_n

is the effective quality factor and $\omega_{r,n} = 2\pi(f_n + \delta f_n)$ is the resonance frequency of the mode n , perturbed by the tip-sample interaction. The nonlinear tip-sample interaction can be modeled using a piecewise description [43]. In this description the interaction force $F(z_{ts})$ can be described in terms of tip and sample elastic moduli and tip radius as a function of tip-sample separation z_{ts} . For the sake of simplicity the non-conservative effects are ignored. We have introduced the simulation procedur in previous section. Here we will consider some points more explicitly to a full comparison of experiment and calculations. For $A_0 \simeq 10$ nm and $A_{LO} < 1$ nm, and assuming that the resulting oscillations at frequencies other than f_{LO} and f_0 are also smaller than 1 nm, the time-dependent tip-sample separation $z_{ts}(t)$ can be approximated as

$$z_{ts}(t) = z_0 + A_{LO} \cos(2\pi f_{LO}t) + A_0 \cos(2\pi f_0t) \quad (6.4)$$

where z_0 is the average tip-sample separation. Using this time dependent tip sample separation $z_{ts}(t)$, a time dependent interaction force $F(t)$ can be calculated. The component of $F(t)$ at frequency ω can be calculated by $F_\omega = \int F(t) \exp(-i\omega t) dt$ and the amplitude of oscillation of the cantilever at frequency ω can be then calculated through the response of the cantilever. In order to calculate the oscillation amplitude for the tapping mode at a given tip-sample separation, Eqs. 6.2 and 6.3 are solved iteratively for $\tilde{A}$ for a given set of parameters. The amplitude and phase of the oscillation can then be calculated from $\tilde{A}$. In order to account for the heterodyne mixing effects, we make the approximation that $A_{LO}, A_1 \ll A_0$, which means, we can consider A_1 as a perturbation to the system. Using the tip-sample interaction model and lumped cantilever dynamics, A_0 versus z_0 and A_1 versus z_0 are calculated as shown in Figure 6.10(a) where curves are plotted for silicon (Si) and polystyrene (PS) surfaces. In order to observe the effect of dissipation, curves are replotted with Q-factors of 200 and 150 under the influence of the same driving force. In tapping mode, the AFM system fixes the oscillation amplitude. Therefore, to compare material contrast observed in different channels, we label the equilibrium points as 1 $\doteq$ (PS, Q=200), 2 $\doteq$ (PS, Q=150) ,3 $\doteq$ (Si, Q=200) and 4 $\doteq$ (PS,Q=150) respectively. Conventional phase contrast of the tapping mode is seen to depend strongly on dissipation only as

seen in Fig. 6.10(b), since (1,3) and (2,4) have similar phase and only Q change results in contrast. However, during heterodyne conversion, the peak force (Fig. 6.10(d)), converted forces with heterodyne mixing (Fig. 6.10(c, e)) shows stronger elasticity dependent contrast since (3,4) and (1,2) have similar values and contrast is mainly due to changes in elasticity. An interesting observation is that the down-conversion force contrast mechanism changes from $(1,3) \rightarrow (2,4)$ to $(3,4) \rightarrow (1,2)$ by increasing A_{LO} . Without the LO excitation, DC forces provide similar contrast to the phase contrast. This observation suggests that heterodyne mixing effects allow a type of force modulation microscopy in tapping mode if proper care is given to characterize the strength of the injected LO signal. However, reversal of contrast makes interpretation of this contrast mechanism more difficult. Comparing figures 6.9 and 6.10 we see that the up-conversion and down-conversion processes can be understood well by the described theoretical approach. For example, Figs. 6.9(b, c, d, e and f) can be compared with Fig. 6.10(g), where excitation of higher harmonics as a function of the tapping mode amplitude is plotted. It is observed both in experiment and theory that higher harmonics are more efficiently generated and converted for smaller deviations from the free amplitude. Also comparing Figs. 6.9(g) with Fig. 6.10(e), it is seen that increases in A_{LO} result in increasing up-conversion/down-conversion signals.

In order to demonstrate that the material dependent contrast can be imaged using the up-conversion/down-conversion processes, images were obtained on PMMA patterns on Silicon (Figs. 6.11(a, b, c and d)) and on plasmid DNA strands on silicon (Figs. 6.11(e, f, g and h)). On large PMMA patterns on Silicon, in the attractive regime, up-conversion contrast is observed even when there is no significant phase contrast. In a up-conversion process, the lower mode is used for tapping. Since the spring constant k_0 of the lower flexural mode is small, with a blunt tip it is more likely to operate in the overall attractive regime. In the attractive regime, simulations show reduced generation of heterodyne mixing component. The results of simulations are seen to be parallel with observations. Therefore, in order to observe the contrast, considerably larger (few nm) A_{LO} was used. Multiple harmonic components can be used for imaging attractive forces as shown in Figs. 6.11(a, b, c and d)). For the sample with DNA strands on silicon,

down-conversion imaging was demonstrated, where the second flexural mode is used in tapping. In this case, repulsive mode is easier to obtain. Elasticity dependent down-conversion contrast can be observed for double strand DNA samples, demonstrating the strength of the technique for imaging fragile samples. It was also observed that increasing A_{LO} or using a much lower amplitude set-point results in destruction of isolated DNA strands. This is also in accordance with Fig. 6.10d, where it is seen that peak interaction forces approach micronewtons for large A_{LO} . This shows that the technique is applicable for molecular imaging but care must be given to keep the peak forces low. It must be also noted that, resonant frequency shift of the lower mode proceeds in the same direction of resonant heterodyne force conversion when elasticity of the sample changes. This further enhances the contrast on elasticity. Another information channel is the phase of the parametrically converted force signal. The phase channel also gives complementary information on dissipation and elasticity.

6.4 Conclusion

The method presented here can be applied using a standard rectangular cantilever and a standard AFM system with a vibrating sample holder or an AFM system that allows access to the lever dither piezo by external electronics. In multi-frequency cantilever excitation, the oscillation amplitudes are determined by the lever transfer function, and imaging the fifth harmonic of the force was seen to be most convenient using the up-conversion process, due to enhanced intermediate frequency excitation. Further optimization of the cantilever properties can be done to operate the technique with lower interaction forces. Elasticity dependent contrast on molecular level can be observed using a standard cantilever.

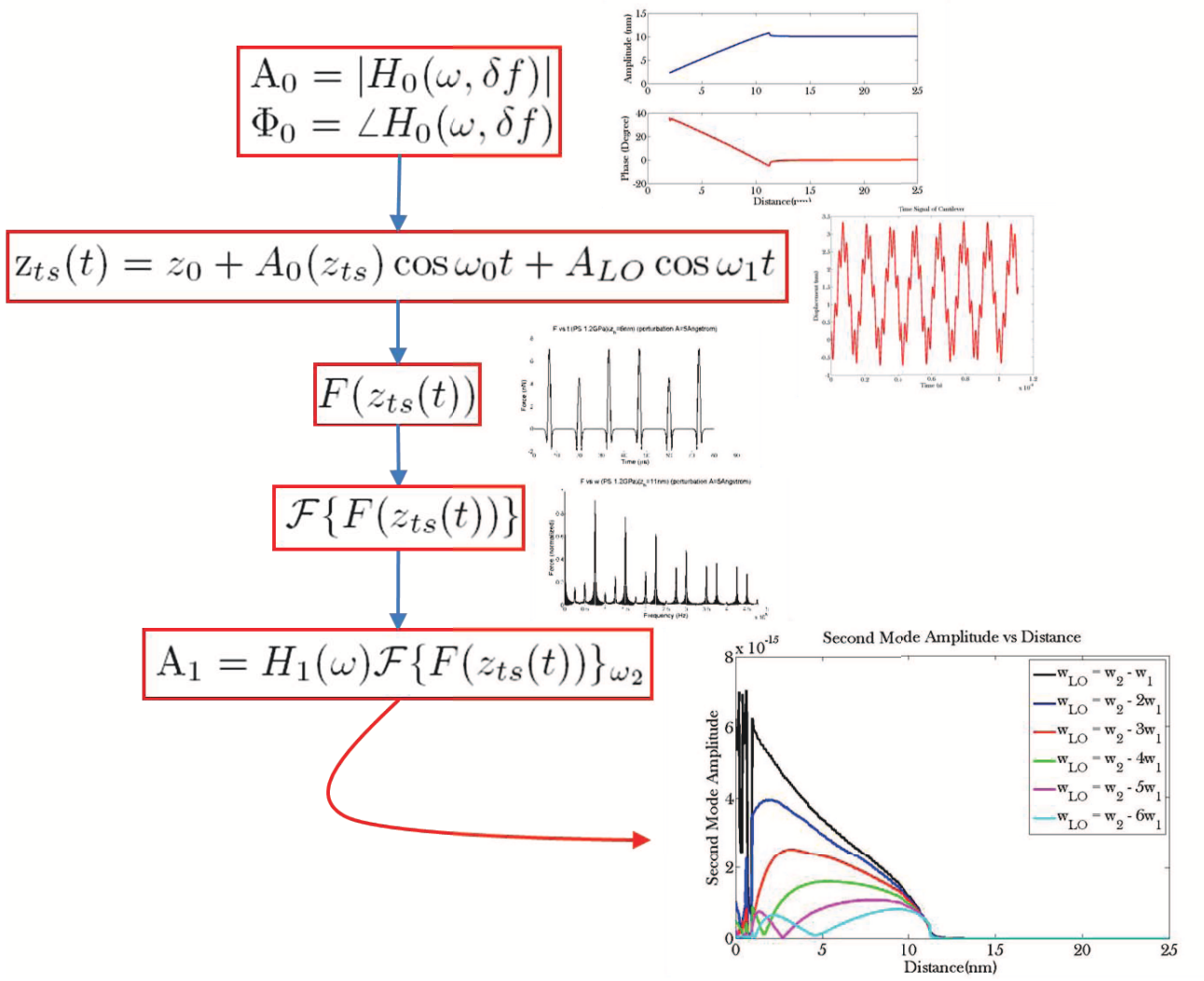


Figure 6.2: Calculation flow chart of amplitude of frequency components of interaction

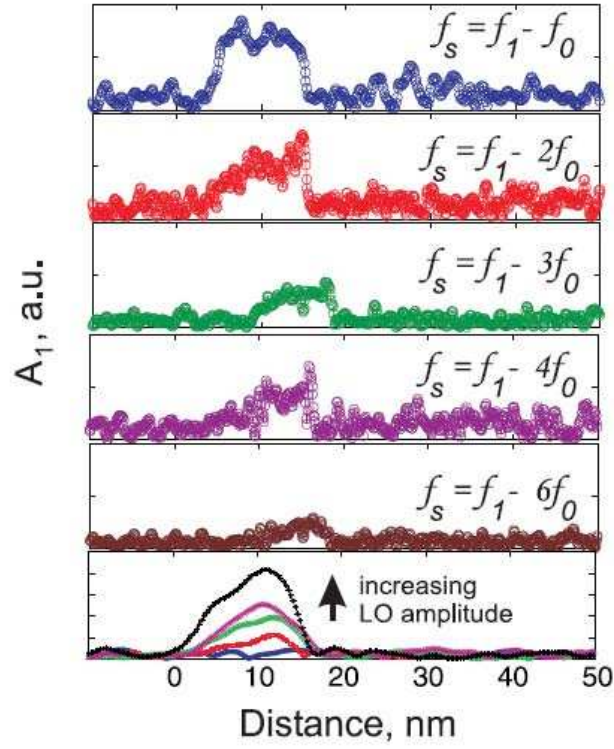


Figure 6.3: Experimental data of tip sample separation dependent amplitude of up-converted signal for different local oscillator frequencies

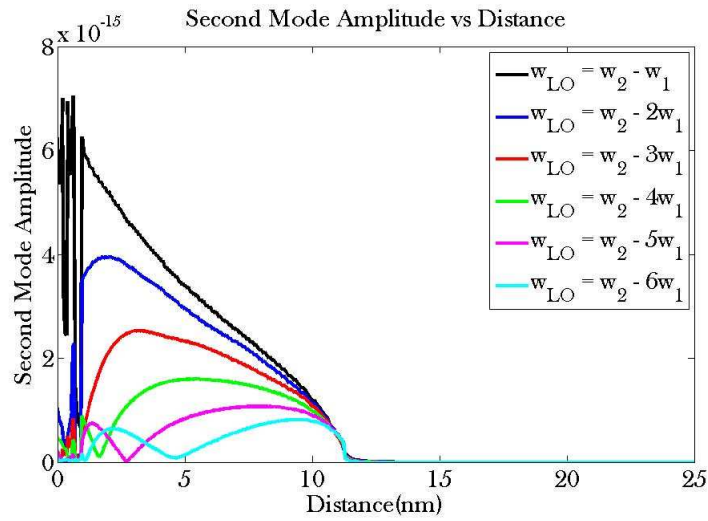


Figure 6.4: Calculated data of tip sample separation dependent amplitude of up-converted signal for different local oscillator frequencies

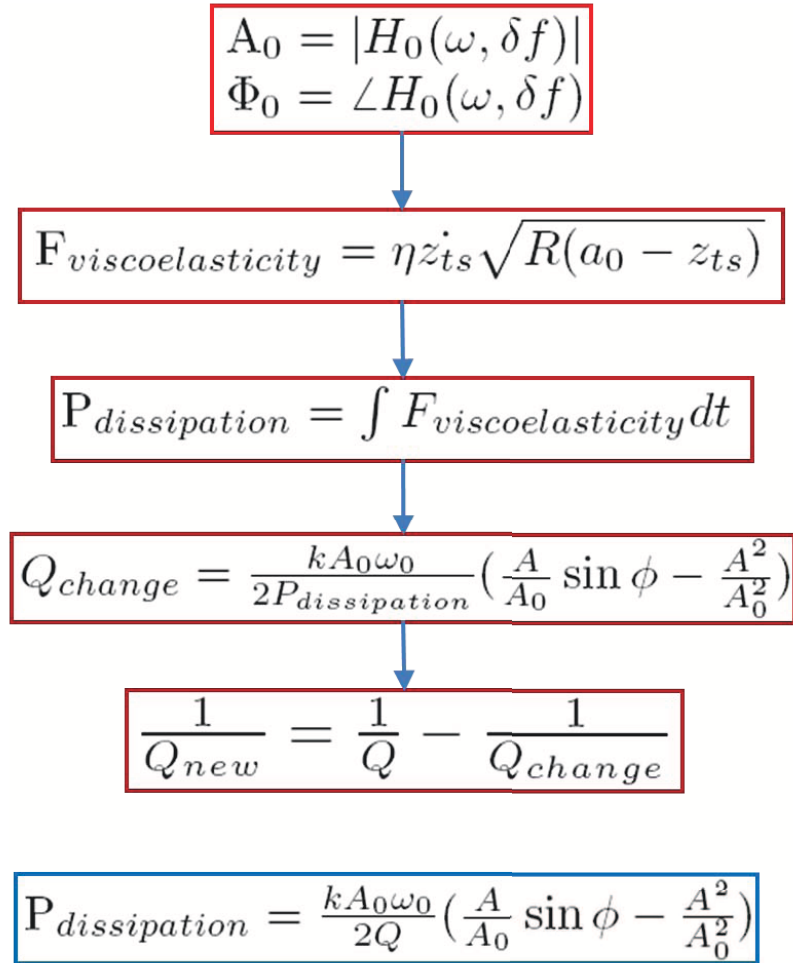


Figure 6.5: Flow chart of time dependent quality factor calculation

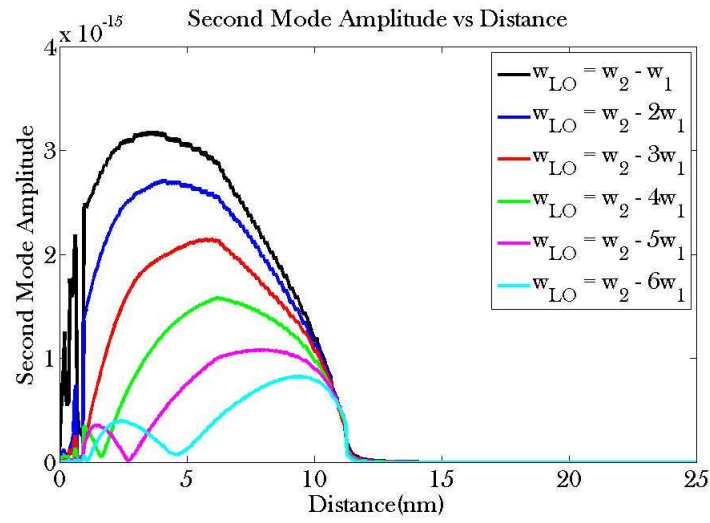


Figure 6.6: 'Time dependant quality factor' corrected simulation result for tip sample separation dependant amplitude of up converted signal for different local oscillator frequencies

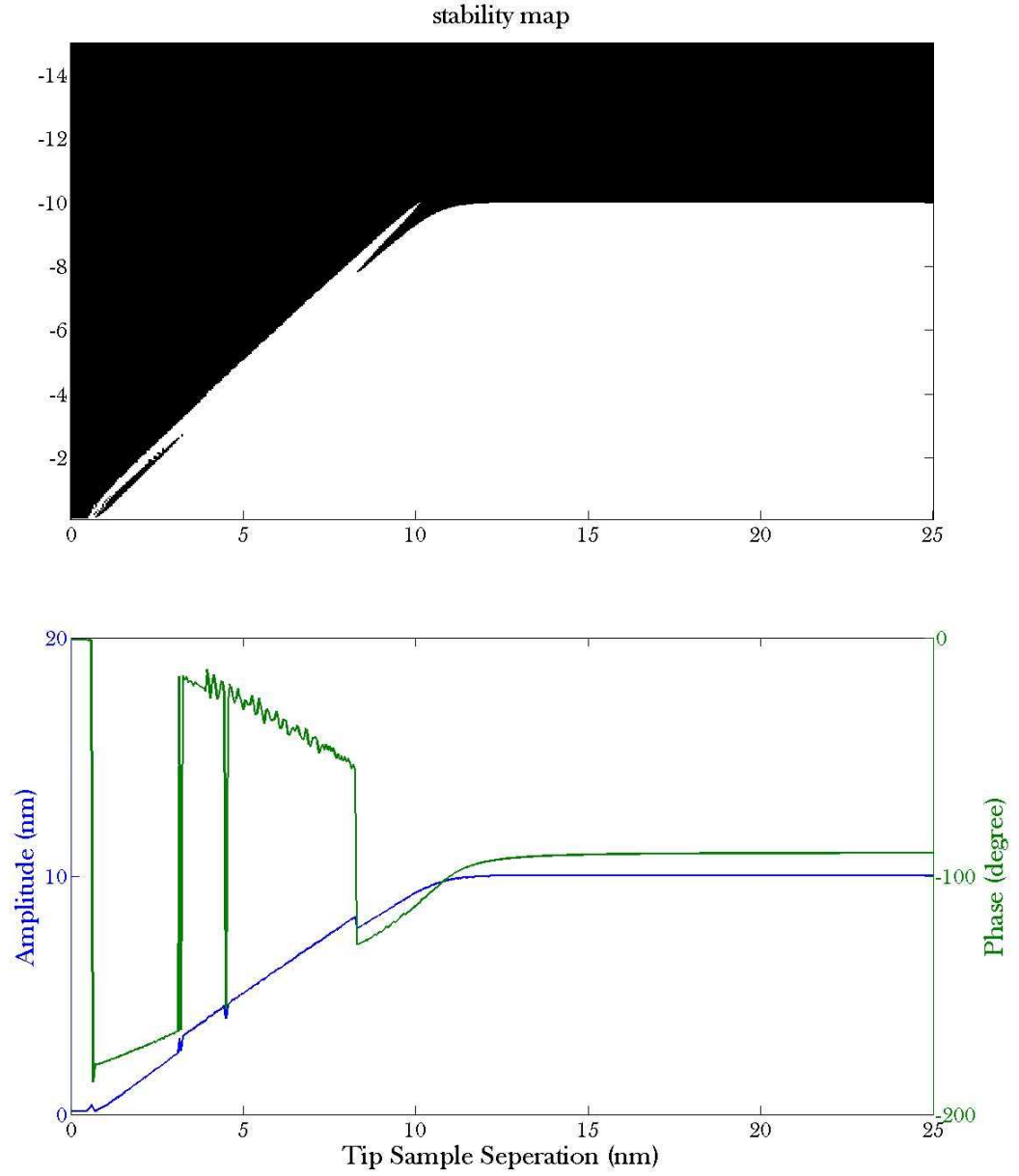


Figure 6.7: The stability map, amplitude and phase distance curves that shows the switching behaviour of the system between attractive and repulsive branches.

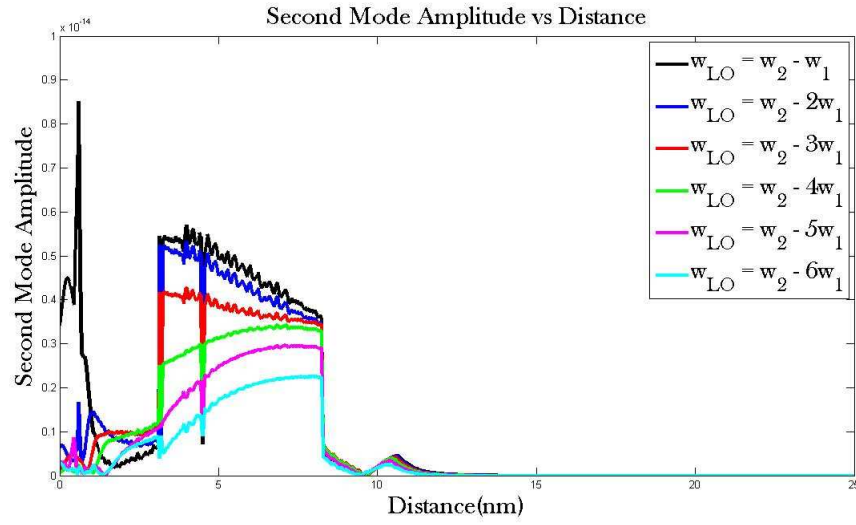


Figure 6.8: Calculated data of tip sample separation dependent amplitude of up-converted signal for different local oscillator frequencies with the switching behaviour of the system between attractive and repulsive regime

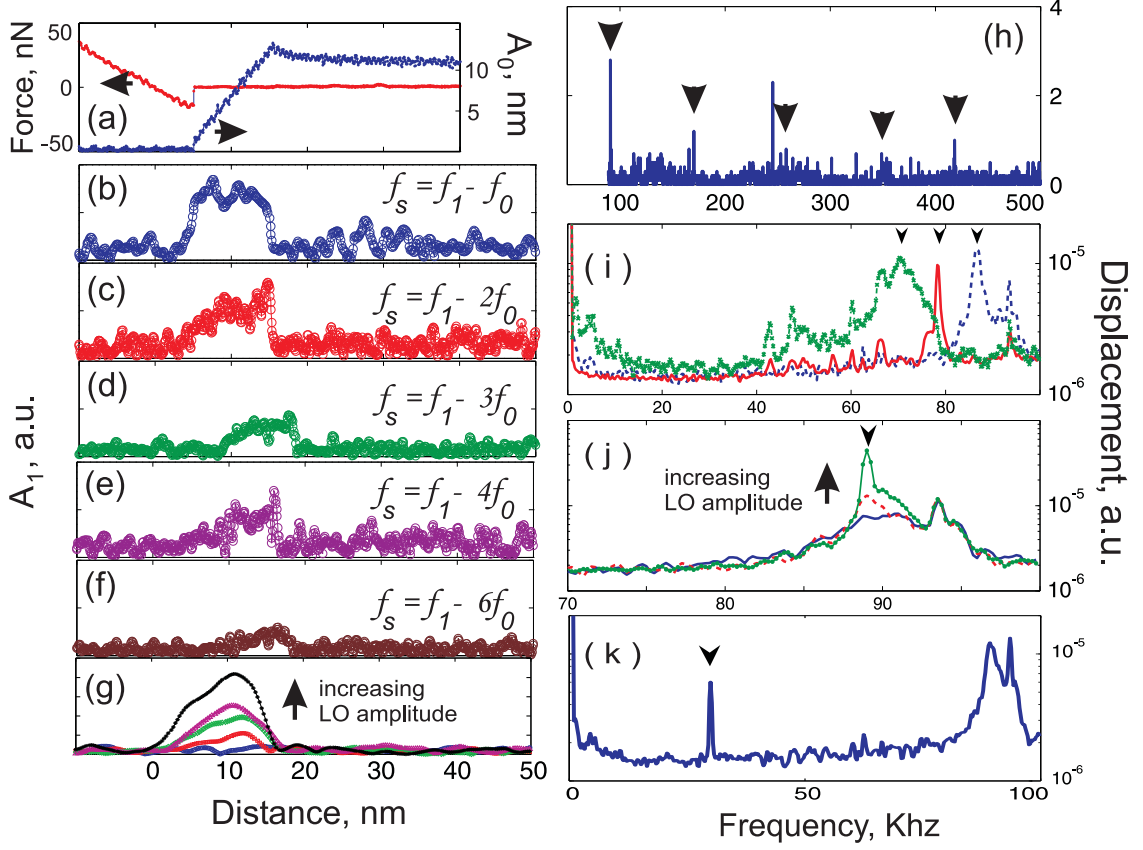


Figure 6.9: Excitation of the second order mode through resonant heterodyne mixing as a function of tip-sample separation. a) Typical Force-Distance and Amplitude-Distance curves acquired simultaneously with the up-conversion measurements. Second-order mode amplitude A_1 when b) $f_{LO} = f_1 - f_0$, c) $f_{LO} = f_1 - 2f_0$, d) $f_{LO} = f_1 - 3f_0$, e) $f_{LO} = f_1 - 4f_0$ and f) $f_{LO} = f_1 - 6f_0$. (Measurement bandwidth is 1 KHz.) g) Up-converted amplitude A_1 increases with increasing LO amplitude A_{LO} . (Measurement bandwidth is 100 Hz.) h) A_1 versus f_{LO} plot shows that up-conversion takes place at $f_{LO} = f_1 - nf_0$ (arrows). i) Perturbation of the dynamic properties of the fundamental mode as observed in the noise spectrum of the cantilever when the second mode is tapping in attractive (left arrow) and repulsive modes (right arrow). When the cantilever is lifted from the surface by a few micrometers, Brownian noise spectrum of the unperturbed cantilever can be observed (middle arrow). j) Down-converted amplitude A_0 at the shifted fundamental mode resonance frequency, during tapping with higher order flexural mode. As A_{LO} is increased down-converted signal amplitude increases. k) Down converted signal to 30 KHz (Non-resonant).

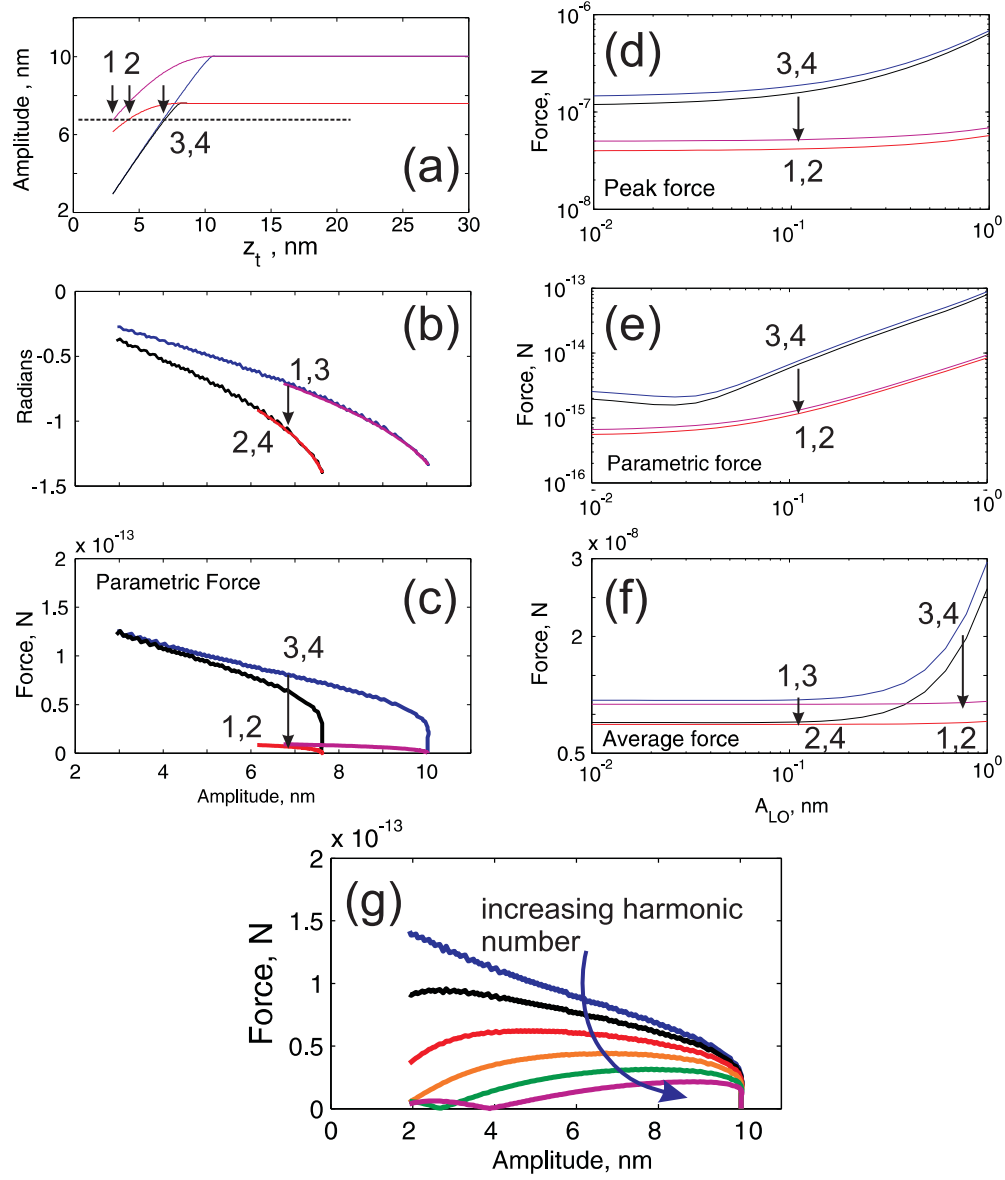


Figure 6.10: Simulation results for up-conversion process in pure repulsive regime. a) Amplitude vs z_{ts} for Si and Polystyrene samples for $Q_0=200$ and 150. b) Phase vs A_0 c) Up-converted force amplitude for $f_{LO} = f_1 - f'_0$ vs A_0 . d) Peak force vs A_{LO} . e) Up-converted signal vs. A_{LO} f) Average DC Force vs A_{LO} . g) Up-converted force vs A_0 for $f_{LO} = f_1 - n f'_0$ for $n=1, 2, 3, 4, 5, 6$.

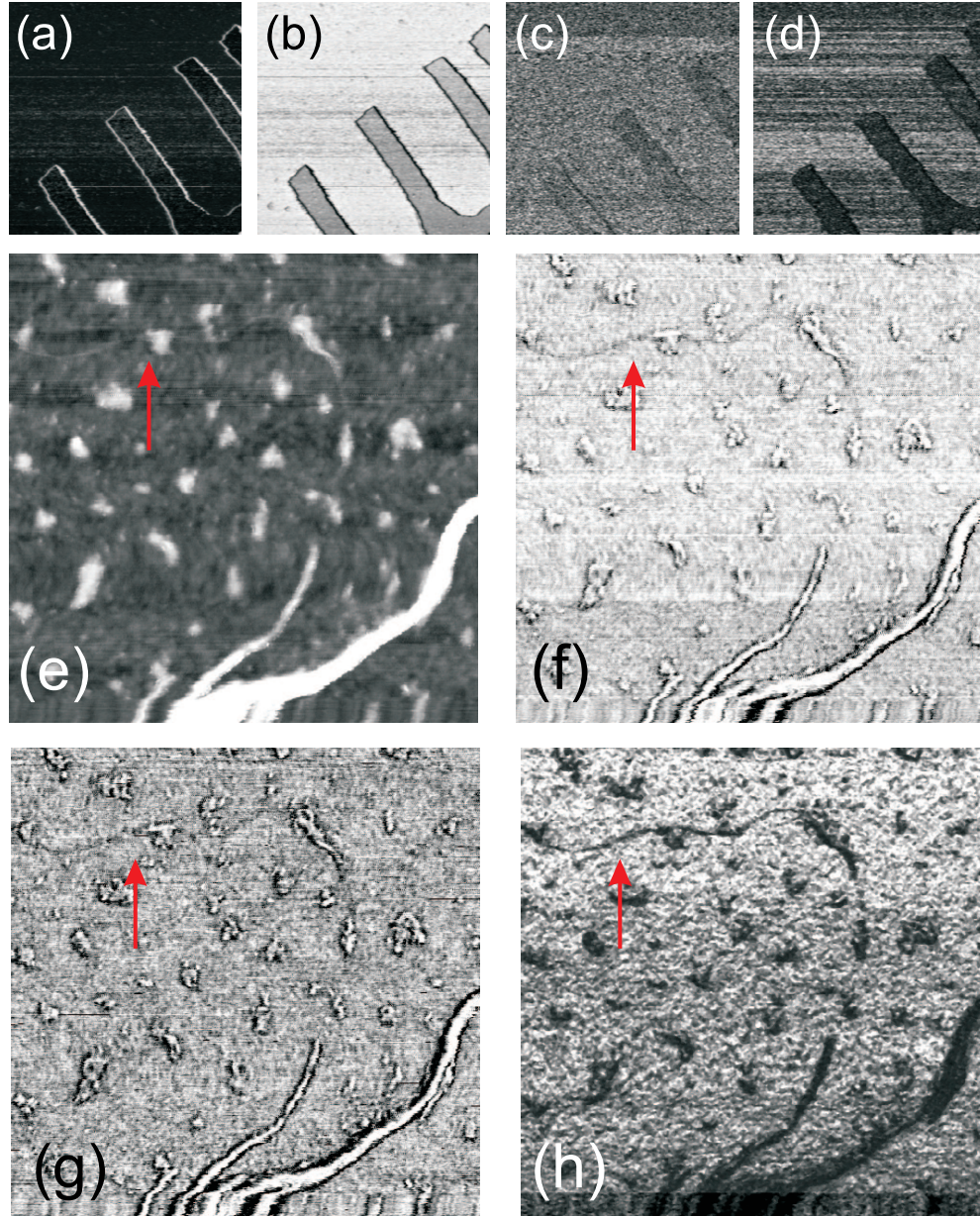


Figure 6.11: Material contrast observed through up-conversion in the attractive regime. a) Phase contrast image of PMMA patterns on silicon. Up-converted force detected at the first-order mode frequency when sample is oscillated at b) $f_{LO} = f_1 - f_0$ c) $f_{LO} = f_1 - 2f_0$ d) $f_{LO} = f_1 - 3f_0$. Images acquired with 0.5 Hz per line. Material contrast observed through down-conversion in the repulsive regime. Images of plasmid DNA on silicon: e) Topographic (full scale 10 nm) f) Phase (full scale 30°) g) DC Force (full scale 0.5 nN) and h) PDC signal at 90 KHz. Double strand (arrow), curled particles and bundles of DNA can be discerned. Images acquired with 1.5 Hz per line, $1 \mu m$ image width.

Chapter 7

Conclusion

As we mentioned, in the course of AFM system development, besides the topography imaging, acquiring additional information about the other properties of the samples (such as stiffness, electrical or magnetic properties etc) has been desired. In this thesis, we presented and demonstrated two novel techniques that can achieve this goal.

The first one is multifrequency electrostatic force spectroscopy(MFEFS) that can be thought as an extension of multifrequency AFM to a spectroscopy technique, similar to capacitance spectroscopy. In the application of this technique, basically the fundamental mode of the cantilever is used to stabilize the average tip-sample separation, and the second order mode is used to resonantly measure electrostatic forces. We have demonstrated the technique by observing charging hysteresis of silicon nanocrystals in a silicon nitride matrix on silicon. The technique, to some extent, is similar to scanning tunneling spectroscopy (STS) used in scanning tunneling microscopy studies. However, it can be used to study trap levels on partially insulating samples, where STS can not be applied.

With the resonant heterodyne force imaging, we have shown that the highly non-linear tip-sample interaction is elucidated to convert the frequency components of the interaction force occurring in the course of tapping to a frequency that

can be resonantly measured. We can implement two different schemes namely; up-conversion (UC) and down-conversion (DC). In UC scheme one of the flexural modes is used in tapping mode imaging while a sinusoidal mechanical signal is applied at the difference frequency of the force component to be measured and the mode frequency to be used for harmonic detection. We have detected the frequency-converted force components resonantly using a lock-in amplifier. Efficiency of frequency conversion is also related to the mechanical properties of the sample, consequently the conversion process itself also results in material contrast.

One of the remarkable aspect of these two techniques is that; both can be applied under ambient conditions with commercial AFM systems. In this thesis, presented techniques have only applied to detect two different properties of samples, but we can device different setups that can detect three or more properties. Even, combination of these two techniques can be proposed. Besides, in resonant heterodyne force imaging we detect only two frequencies. Since, with the nonlinear tip sample interactions, many different frequency components of force, that can be coupled to different interactions, arise; we can detect all these frequencies simultaneously. Consequently, these two techniques are indeed novel techniques and are open to further development.

Appendix A

Amplitude and Phase distance curve simulator code 1

THIS CODE DOES NOT CONSIDER BISTABILITY

```
clear all;
clc;
Et=130e9;
Es=1e9;
R=20e-9;
H=6.4e-20;
gg=0.031;
f0=75e3;%natural resonance frequency
A0=10e-9;%Amplitude of oscillation
freqoffset=+200;
z0=30e-9:-0.01e-9:0.1e-9;
wd=2*pi*(f0+freqoffset);
w0=2*pi*f0;
k0=2.5;%N/m
f0=w0/2/pi;
```

```

Q=220;

for jj=1:length(z0)
    dff(jj)=dfreqmatA(Et,Es,H,gg,R,A0,k0,f0,z0(jj));
    if dff(jj)>f0
        dff(jj)=f0;
    end;
end;

subplot(3,1,1);
plot(z0/1e-9,dff);grid on;title('Frequency shift of cantilever');hold on;
Amp0=A0;
hw1=1/k0./((1-wd.^2./w0.^2)+sqrt(-1)*wd./w0/Q);
F=Amp0/abs(hw1) %1 nNewton
dz=F*abs(hw1);
F00=F;%here we calculate the force amplitude needed to oscillate the
%lever with desired amplitude when far away from the sample
w00=w0+dff;%calculate new resonance frequency of lever during
%tip-sample interaction
hw2=1/k0./((1-wd.^2./w00.^2)+sqrt(-1)*wd./w00/Q);
A3=abs(hw2)*F00;
myphase=angle(hw2);
subplot(3,1,2);
plot(z0/1e-9,A3/1e-9,'b. ');grid on;
title('Amplitude of oscillation');hold on;
subplot(3,1,3);
plot(z0/1e-9,myphase/pi*180);grid on;title('Phase of oscillation');hold on;\

```

Appendix B

Amplitude and Phase distance curve simulator code 2

IN THIS CODE WE CONSIDER BISTABILITY AND ALSO COSTRUCT A
STABILITY MAP

```
clear all;
clc;
Et=130e9;
Es=1.2e9;
R=50e-9;
H=6.4e-20;
gg=0.031;
V=0;
f0=75e3;
k0=3;%N/m
A0=10e-9;
Amax=A0;
z0=25e-9:-0.2e-9:2e-9;
AA=0.1e-9:0.02e-9:Amax*2;
wd=2*pi*(f0);%-350);
```



```

[x,y]=meshgrid(AA,z0);
zb=max(z0):-0.05e-9:min(z0);
Ab=min(AA):2e-11:max(AA);
[x2,y2]=meshgrid(Ab,zb);

zz=(A3-AA4);
z2=interp2(x,y,zz,x2,y2,'cubic');

myph2=interp2(x,y,myphase,x2,y2,'cubic');

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

Aeq=zeros(size(zb));
Pheq=Aeq;
for jj=1:length(zb)
    for kk=length(Ab):-1:1
        if (sign(z2(jj,kk))== -1)
            Aeq(jj)=Ab(kk);
            Pheq(jj)=myph2(jj,kk);
        end;
    end;
end;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

subplot(3,1,1);
plot(zb/1e-9,Aeq/1e-9,'r');title('Amplitude , nm');hold on;
subplot(3,1,2);
plot(zb/1e-9,Pheq*180/pi,'r');title('Phase');hold on;
subplot(3,1,3);
imagesc(zb/1e-9,-Ab/1e-9,sign(z2));colormap(gray);title('stability map');
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

THIS IS THE SUBROUTINE THAT CALCULATES THE FREQUENCY SHIFTS

```

function [dF] = dfreqmat(Et,Es,H,gg,R,A0,k0,f0,z0,V);
%Function freq calculates the frequency shift by integrating F.*cos(w.*t)
Tper=1/f0;
dt=0.005*Tper;
t = 0:dt:Tper;
w0=2*pi*f0;
z = z0 + A0*cos(w0.*t);
Ht=15e-6;
t0=15/180*pi;
nu=0.3;
Eeq=1./((1-nu^2)/Et+(1-nu^2)/Es);
a0=sqrt(H/2/pi/gg);

i1=find(z>a0);

F=-H*R/6/a0^2+4/3*Eeq*sqrt(R)*(abs(a0-z)).^(3/2);
F(i1)=-H*R/6./z(i1).^2;

Fe=pi*8.82e-12*V.*V/(log(tan(t0/2)))^2.*(log(1+Ht./z)...
-Ht*(z-R/(tan(t0))^2)./z./(Ht+z));
F = F-Fe; %burada bazi normalizasyon sabitleri var
y = F.*cos(w0.*t);
dF=-f0*f0/k0/A0*sum(dt*y);

```

Bibliography

- [1] G.Binnig, H. Rohrer, C. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57(1982).
- [2] U.Drig, J.K.Gimzewski, and D.W.Pohl. Phys. Rev. Lett. **57**, 2403(1986).
- [3] G.Binnig, Atomic Force Microscope and Method for Imaging Surfaces with Atomic Resolution, US Patent No. 4,724,318, (1986).
- [4] U.Hartmann, J. Appl. Phys. **64**, 1561 (1988).
- [5] D.Baselt and J.Baldeschwieler, J. Vac. Sci. Technol. B10, 2316(1992).
- [6] R.Chatterjee, G.A.Hallock, and M.L.Gartman, Rev. Sci. Instrum. **66**, 457(1995).
- [7] Cristian Staii, Nicholas J. Pinto, and Alan T. Johnson, Jr. AIP Conf. Proc. **723**, 129 (2004).
- [8] U. Ch. Fischer and D. W. Pohl, Phys. Rev. Lett. **62**, 458 (1989).
- [9] C. T. Gibson *et al.* Nanotechnology 16 (2005)
- [10] Cleveland J P, Manne S, Bocek D and Hansma P K 1993 Rev. Sci. Instrum. **64** 4035
- [11] Sader J E, Chon J W M and Mulvaney P 1999 Rev. Sci. Instrum. **70** 39679
- [12] C.T. Gibson, G.S. Watson, S. Myhra, Nanotechnology 7 (1996).
- [13] H. Hertz, J. Reine Angew. Math. **92** (1882) 156.

- [14] K.L. Johnson, K. Kendall, A.D. Roberts, Proc. R. Soc. London A 324 (1971) 301.
- [15] B.V. Derjaguin, V.M. Muller, Y.P. Toporov, J. Colloid Interf. Sci. **53** (1975) 314.
- [16] Y. Song, B. Bhushan J. Phys.: Condens. Matter 20 (2008) 225012.
- [17] G. Binnig, C. F. Quate, and C. Gerber, Phys. Rev. Lett. 56, **930** (1986).
- [18] T. S. Jespersen and J. Nygard, Nano Lett. 5, **1838** (2005).
- [19] M. Bockrath, N. Markovic, A. Shepard, and M. Tinkham, Nano Lett. 2, 187 (2002).
- [20] R. M. Nyffenegger, R. M. Penner, and R. Schierle, Appl. Phys. Lett. 71, 13 (1997).
- [21] A. K. Sinensky and A. M. Belcher, Nat. Nanotechnol. 2, 653 (2007).
- [22] D. C. Coffey and D. S. Ginger, Nat. Mater. 5, 735 (2006).
- [23] A. Dâna and Y. Yamamoto, Nanotechnology 16, S125 (2005).
- [24] E. Bussmann and C. C. Williams, Appl. Phys. Lett. 88, 263108 (2006).
- [25] R. W. Stark, N. Naujoks, and A. Stemmer, Nanotechnology 18, 065502 (2007).
- [26] R. W. Stark and W. M. Heckl, Surf. Sci. 457, 219 (2000).
- [27] O. Sahin, C. F. Quate, O. Solgaard, and A. Atalar, Phys. Rev. B 69, 165416 (2004).
- [28] D. Ziegler, J. Reichen, N. Naujoks, and A. Stemmer, Nanotechnology 18, 225505 (2007).
- [29] D. M. Schaadt, E. T. Yu, S. Sankar, and A. E. Berkowitz, Appl. Phys. Lett. 74, 472 (1999).

- [30] Y. Azuma, M. Kanehara, T. Teranishi, and Y. Majima, Phys. Rev. Lett. 96, 016108 (2006).
- [31] Y. Martin, C. C. Williams, and H. K. Wickramasinghe, J. Appl. Phys. 61, 4723 (1987).
- [32] J. Tamayo and R. Garcia, Appl. Phys. Lett. 73, 2926 (1998).
- [33] J. P. Cleveland, B. Anczykowski, A. E. Schmid, and V. B. Elings, Appl. Phys. Lett. 72, 2613 (1998).
- [34] R. W. Stark, T. Drobek, and W. M. Heckl, Appl. Phys. Lett. 74, 3296 (1999).
- [35] R. W. Stark and W. M. Heckl, Rev. Sci. Instrum. 74, 5111 (2003).
- [36] S. Crittenden, A. Raman, and R. Reifenberger, Phys. Rev. B 72, 235422 (2005).
- [37] M. Stark, R. W. Stark, W. M. Heckl, and R. Guckenberger, Appl. Phys. Lett. 77, 3293 (2000).
- [38] M. Balantekin and A. Atalar, Appl. Phys. Lett. 87, 243513 (2005).
- [39] M. Balantekin and A. Atalar, Phys. Rev. B 71, 125416 (2005).
- [40] M. Stark, R. W. Stark, W. M. Heckl, and R. Guckenberger, Proc. Natl. Acad. Sci. U.S.A. 99, 8473 (2002).
- [41] N. F. Martinez, S. Patil, J. R. Lozano, and R. Garcia, Appl. Phys. Lett. 89, 153115 (2006).
- [42] J. R. Lozano and R. Garcia, Phys. Rev. Lett. 100, 076102 (2008).
- [43] R. Garcia and A. San Paulo, Phys. Rev. B 60, 4961 (1999).
- [44] O. Morgul, Phys. Lett. A 262, 144 (1999).
- [45] F. J. Giessibl, Appl. Phys. Lett. 78, 123 (2001).

- [46] Follows from equality of power delivered to the cantilever mode by position dependent driving forces
- [47] J.A. Turner and J.S. Wiehn, *Nanotechnology* 12, (2001) 322330
- [48] E. Bonaccorso, F. Schnfeld and H.J. Butt, *Phys. Rev.B.* 74,085413,(2006)
- [49] B.M. Law and F. Rieutord, *Phys. Rev. B.* 66, 035402, (2002)
- [50] H.-J. Butt, B. Cappella, M. Kappl, *Surface Science Reports* 59 (2005)
- [51] K.S. Birdi, *SCANNING PROBE MICROSCOPES: Applications in Science and Technology* (2003 CRC Press, LLC)
- [52] B. Bhushan H. Fuchs *Applied Scanning Probe Methods II: Scanning Probe Microscopy Techniques* (Springer-Verlag Berlin Heidelberg 2006)
- [53] B. Bhushan H. Fuchs S. Kawata *Applied Scanning Probe Methods V: Scanning Probe Microscopy Techniques* (Springer-Verlag Berlin Heidelberg 2007)
- [54] M. T. Cuberes, H. E. Assender, G. A. D. Briggs and O. V. Kolosov, *J. Phys. D: Appl. Phys.* 33 23472355, (2000)