

Forces at Atomic Scale

There are four known fundamental forces in nature:

- Strong (F_S) and the Weak (F_W) Interactions

very short ranged (protons, neutrons and other elementary particles).

- Gravitational Force (F_G)

long ranged (motion of planets, moons and satellites)

- Electromagnetic Interaction (F_{EM})

dominant of atoms and molecules

about forty orders of magnitude stronger than gravitational

less important on a microscopic scale

1- Important forces between atoms and molecules

i- Ionic Bonds

Coulombic forces which are a result of the electron transfer.

Example: in lithium fluoride the lithium transfers its 2s-electron to the fluorine 2p-state.

The shells of the atoms are filled up, but the lithium has a net positive charge and the fluorine a net negative charge.

These ions attract each other by Coulombic interaction which stabilizes the ionic crystal in the rocksalt structure.

ii- Covalent Bonds

The standard example for a covalent bond is the hydrogen atom. When the wave function overlap is considerable, the electrons of the hydrogen atoms will be indistinguishable. The total energy will be decreased by the “exchange energy”, which causes the attractive force. The characteristic property of covalent bonds is a concentration of the electron charge density between the two nuclei.

The force is strongly directed and falls off within a few Å.

iii- Metallic Adhesive Forces

Strong metallic bonds are observed when the atoms are condensed in a crystal. They originate from the free valency electron sea which holds together the ionic cores.

A similar effect is observed when two metallic surfaces approach each other. The electron clouds have the tendency to spread out, in order to minimize the surface energy.

Thus a strong exponentially decreasing, attractive interaction is observed.

iv- Van der Waals Forces

Van der Waals forces exist between all kind of atoms or molecules and can be divided into three groups:

- Dipole-dipole force: Molecules having permanent dipoles will interact by dipole-dipole interaction.
- Dipole-induced dipole forces: The field of a permanent dipole induces a dipole in a non-polar atom or molecule.
- Dispersion forces:

Due to charge fluctuations of the atoms there is an instantaneous displacement of the center of positive charge against the center of negative charge.

Therefore non-polar atoms (e.g. neon) or molecules attract each other.

The attractive van der Waals force between the atoms is proportional to $1/r^7$, where r is the distance between the atoms. The van der Waals forces are effective from a distance of a few Å to several hundreds of Å. Due to the finite velocity of light the dispersion forces are retarded for distances >100 Å, which leads to a different power law index ($\approx 1/r^8$).

2- Important forces between probing tip and sample

i- Van der Waals Forces

For distances above a few Å to hundreds of Å, van der Waals forces are significant.

Can be used to measure topography with a resolution of a few nm.

The interaction between different geometries:

- against plane
- sphere against plane
- crossed cylinders

Calculated by integration, assuming additivity, simple power laws result and the Hamaker constants specific for the materials can be defined. For example, the force between a sphere and a plane is $F(D) = -AR/6D^2$ where R is the radius, D the distance between the top of sphere and the plane and A the Hamaker constant.

ii- Magnetic Forces

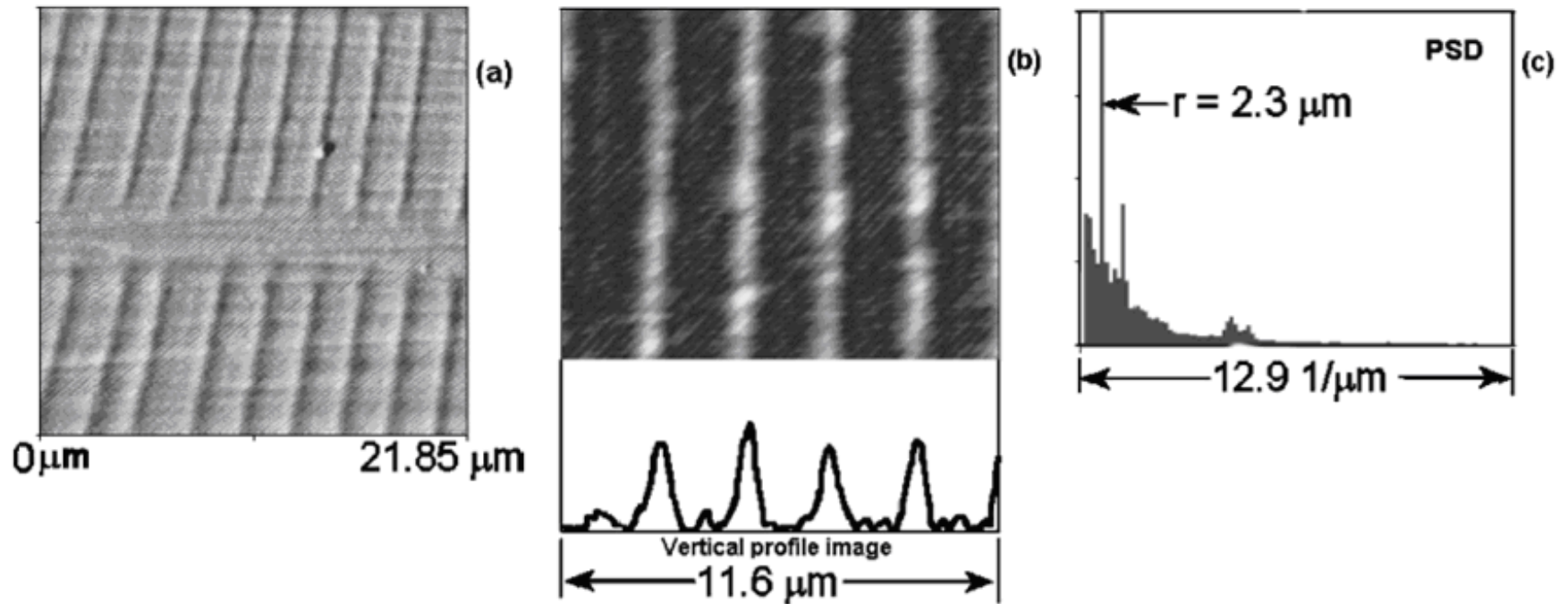


Figure 1- (a) MFM data collected using a Pt-coated tip from a region of a hard disk in which $\sim 2.3\text{ }\mu\text{m}$ transitions were written. (b) Vertical profile image indicated by the horizontal continuous line and (c) the corresponding power spectrum density (PSD).

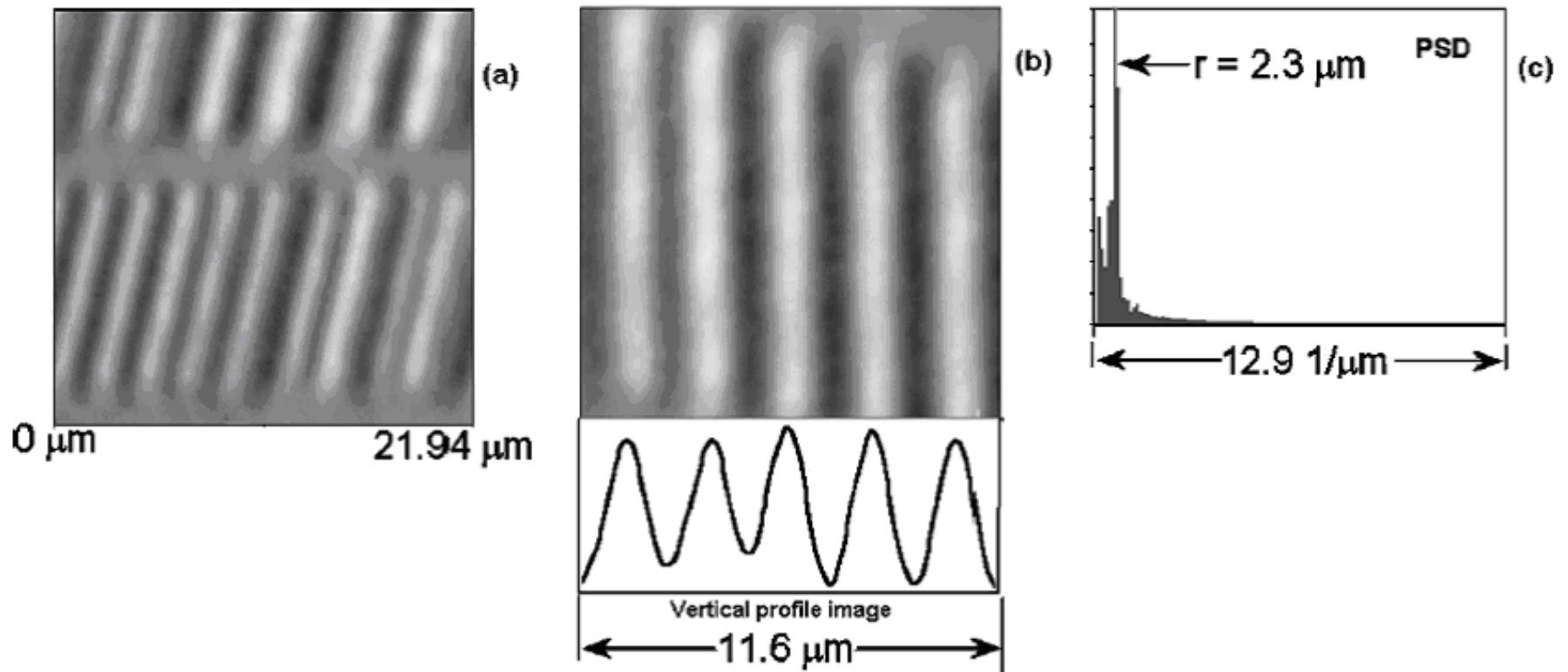


Figure 2- (a) MFM data collected using a Co-coated tip from a region of a hard disk in which $\sim 2.3\ \mu\text{m}$ transitions were written. (b) Vertical profile image and (c) the corresponding power spectrum density.

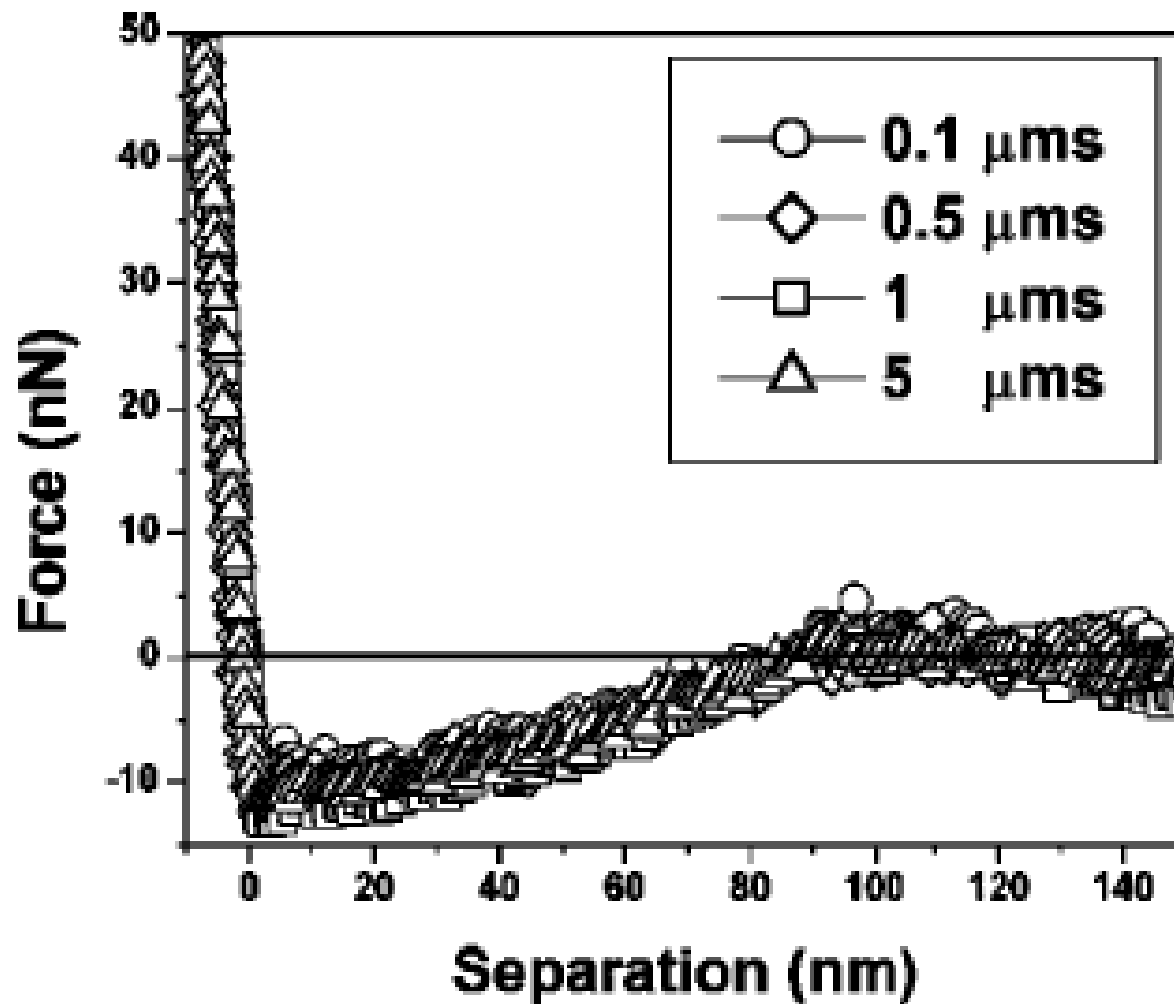


Figure 9- Force vs separation curve measured using a Co-coated tip for a Co51 film on a silicon substrate.

Paramagnetic Interaction

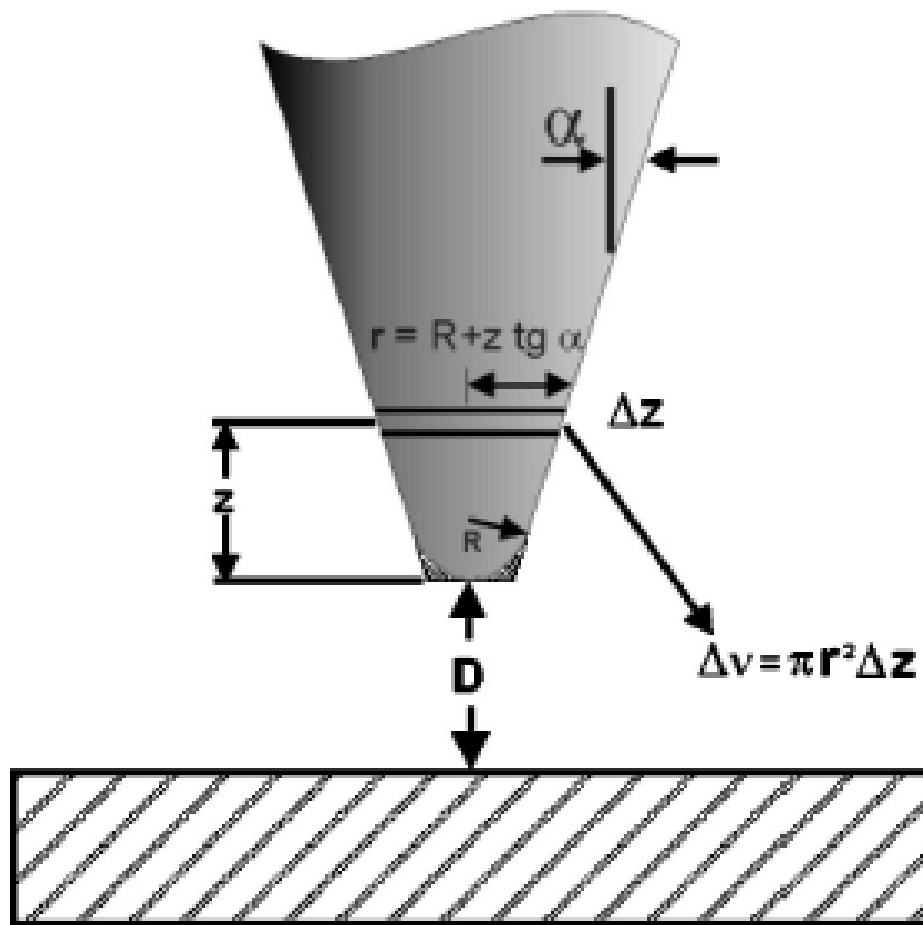


Figure 10- Schematic diagram of the tip and magnetic substrate paramagnetic interaction associated with the exchange of a region on the top of the magnetic substrate with magnetic permeability μ_0 by a Pt-coated tip with magnetic permeability $\chi = 4\pi \times 21 \times 10^{-6}$.

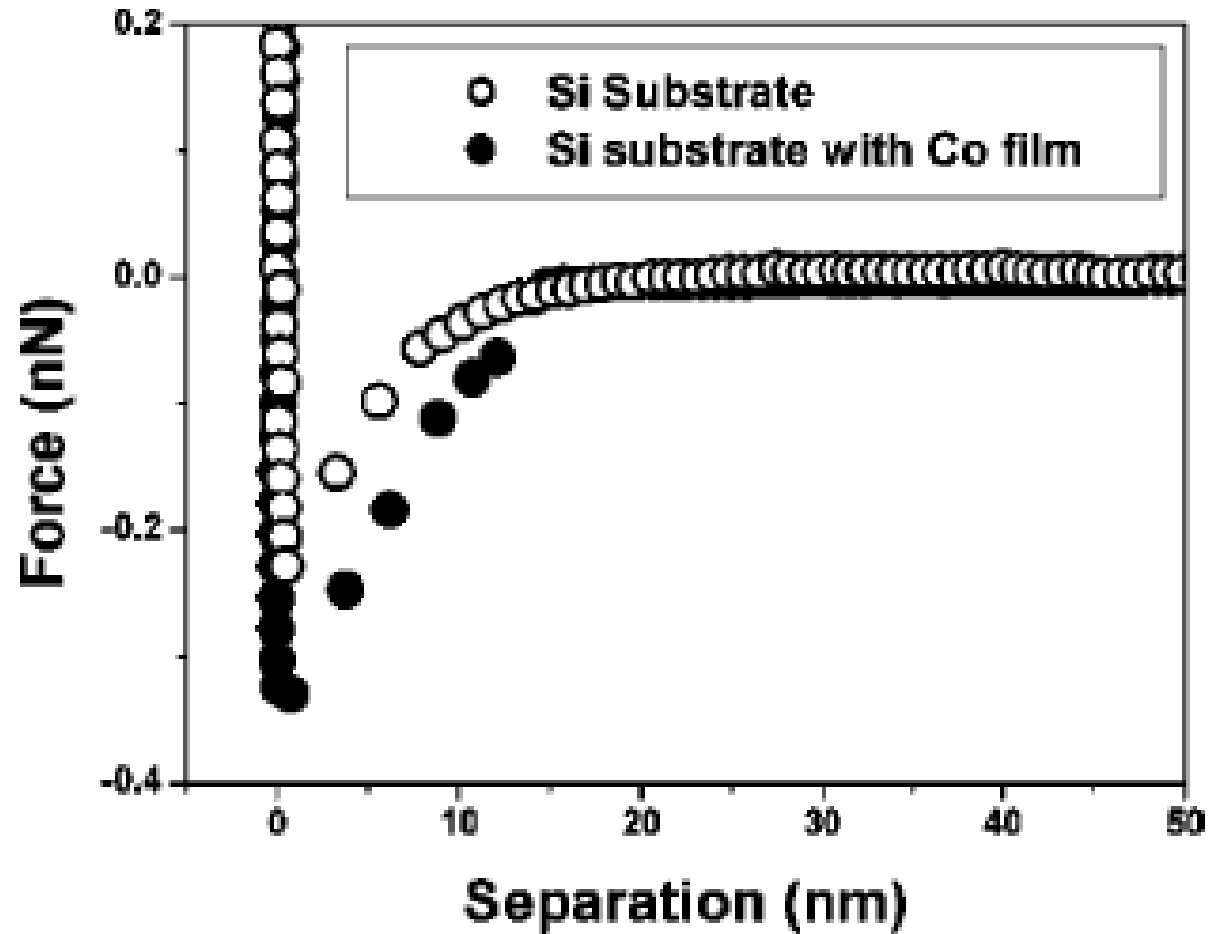


Figure 8- Force vs separation curve measured using a Pt-coated tip for a Si substrate (open circle) and for a Co51 film on a Si substrate (closed circle).

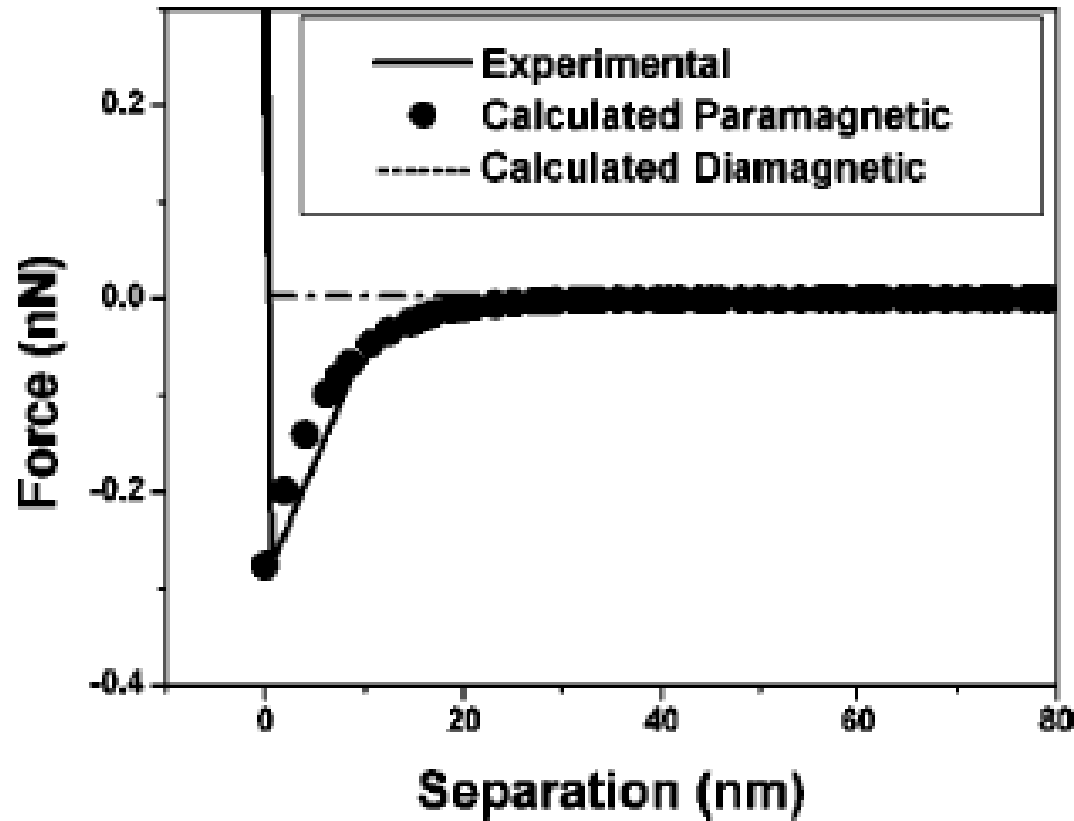


Figure 11- Difference (solid line) between the magnetic force curves in Fig. 8 measured using a $\text{Co}_x(\text{SiO}_2)_{1-x}$ magnetic substrate (closed circle) and a nonmagnetic substrate (open circle). Force calculated (closed circle) using Eq. (2) for $B(D = 0) = 0.055$ T, tip radius 250 nm and $\chi = 4\pi \times 21 \times 10^{-6}$; diamagnetic force (dash-dotted line).

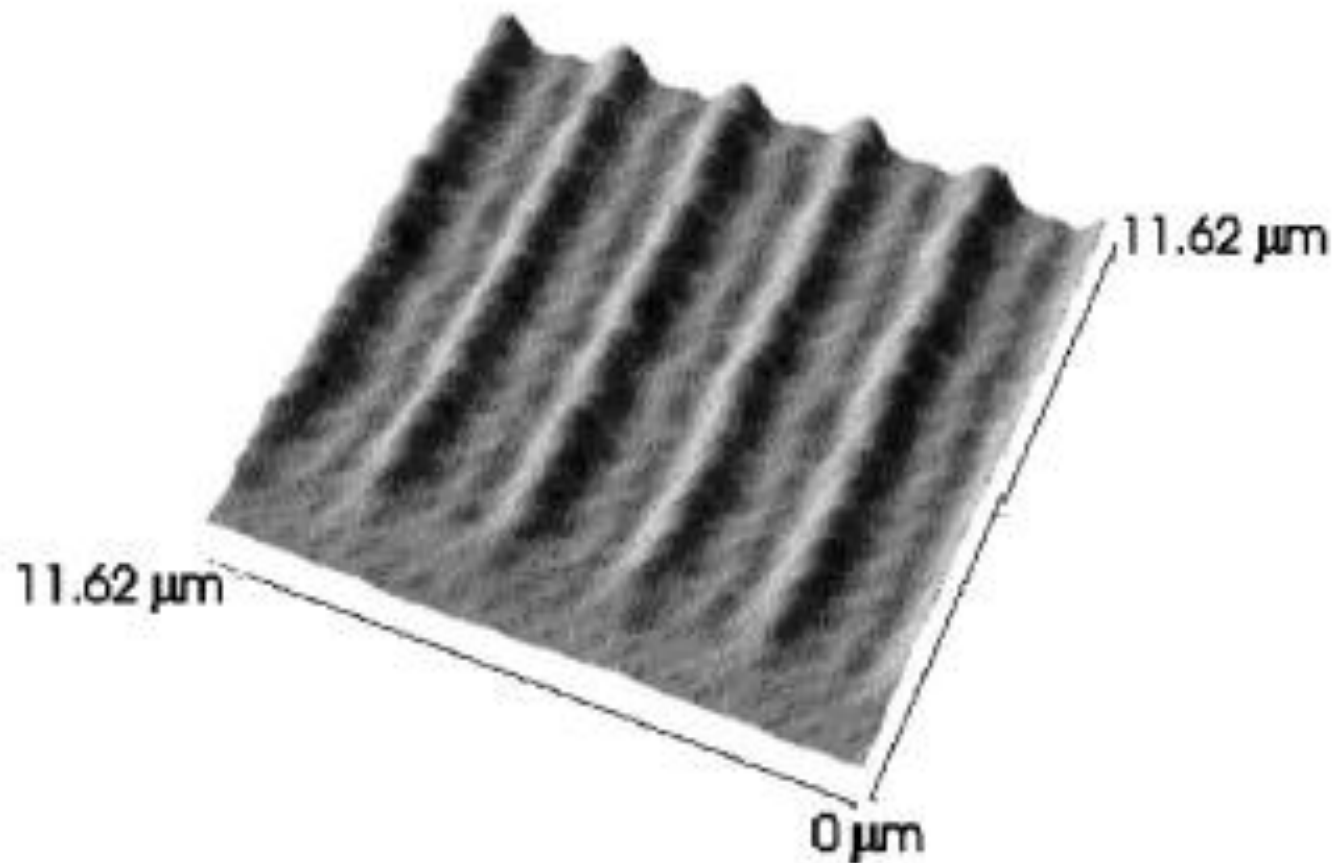


Figure 12- Reconstructed image of data shown in Fig. 1(b) collected by a Pt-coated tip, which corresponds only to the harmonics of the fundamental spatial frequency indicated in the PSD.

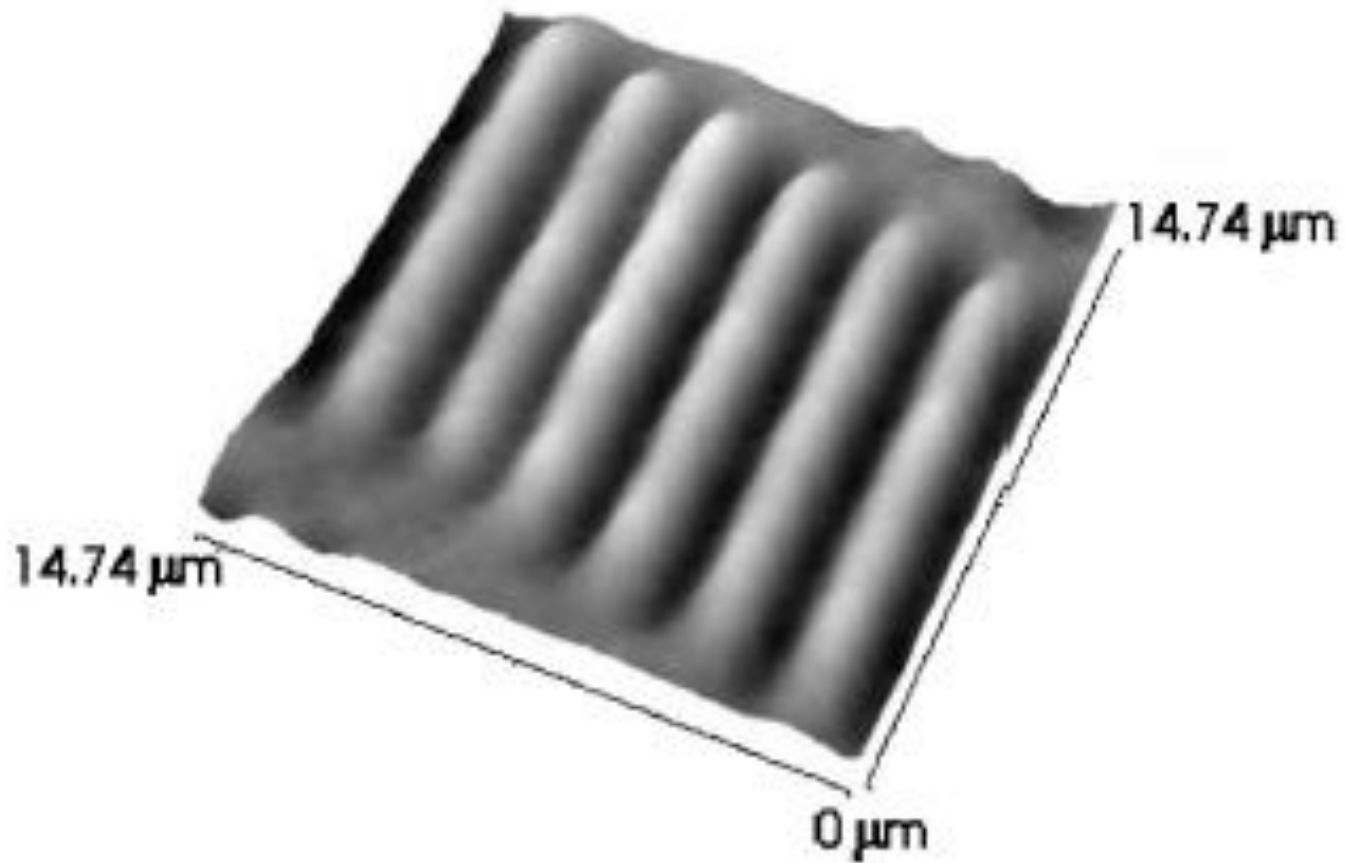


Figure 13-. Reconstructed image of data shown in Fig. 2(b) collected by a Co-coated tip displayed for comparison.

Model of tip-surface interaction

The expression derived for the diamagnetic interaction is given in the Appendix. The calculated values of the force acting on the tip for $B(D \approx 0) \approx 0.055$ T is shown in Fig. 11 by the dashed line and its maximum value at the film surface is $\sim 10^{-14}$ N. This force is three orders of magnitude smaller than the minimum detectable force previously estimated as 0.01 nN.

We then assume a paramagnetic interaction between the tip and substrate. In order to verify this hypothesis we calculated the MFM force acting on the tip during its immersion in the magnetic field of the film for Pt-coated tips with a magnetic susceptibility of $\chi = 4\pi \times 21 \times 10^{-6}$. A schematic diagram of tip immersion in the region is depicted in Fig. 10. The elemental volume (dV) of the trapezoidal tip immersed in the substrate magnetic field is given by $dV = \pi(R + z \tan \alpha) dz$ and the change in magnetic energy in immersion of the tip with a magnetic susceptibility χ in the stray field of the substrate is calculated by integrating the energy over the tip immersed volume in the magnetic field.

Recently a similar expression was derived for electric interaction between the tip and substrate. The force is obtained by the gradient of the energy expression, i.e., $F_z = (-\partial\Delta W)/\partial z$, where

$$\Delta W = \int \frac{B_z^2(z)}{\mu_0} \mu(R + z \tan \alpha)^2 \left(1 - \frac{1}{1+x}\right) dz$$

To compare the experiments with calculations, we fit the force versus separation curves to the gradient in Eq. 1. The best results of fitting the force versus separation curve measured for Co77 films is shown in Fig. 11 by the dotted line. The maximum calculated value for force F acting on the tip for $|\bar{B}(D=0)| \approx 0.055 \text{ T}$ and $R = \sim 25 \text{ nm}$ is 0.1 nN and this value is four orders of magnitude larger than the calculated diamagnetic force so a paramagnetic tip/substrate tip is very likely to be responsible for the imaging effect. Figure 11 also shows that the model fits the measured curves for reasonable values of the magnetic field $B \approx 0.055 \text{ T}$ at the film interface.

The diamagnetic interaction is given by Faraday's law. The current induced by immersion of the Pt-coated tip into the substrate magnetic field results in an induced tip magnetic moment which has opposite orientation relative to that of the substrate's magnetic field direction. In the analysis of the platinum tip response we treat the cantilever tip as a medium with resistivity ρ and the tip approaches the sample surface along the axis perpendicular to the sample plane. A schematic diagram of tip immersion in the region is depicted in Fig. 10, where z is the integration variable of trapezoidal volume and D is the distance between the surface and the end of the tip. Since the cantilever vibrates at resonance frequency ω_0 we assume that the current induced on the tip has the same frequency dependence. If the emf induced in the

elemental ring is given by Faraday's law $\oint \vec{E} \cdot d\vec{l} = \int \dot{\vec{B}} \cdot d\vec{s}$, i.e., $E_\phi = (\dot{B}_z r)/2$ where \vec{E} is the electric field, then the elemental magnetic moment is written as $\Delta M(z, D) = \pi(R + z \tan \alpha)^3 [\dot{B}_z(z, D)] / (3\rho)$. The magnetic energy involved in immersion of the tip in the \vec{B} region is given by $\Delta W = \frac{1}{2} \int d\vec{M} \cdot \vec{B}(z)$. Force is obtained by the gradient of the energy expression, i.e., $F_z = (-\partial \Delta W) / \partial z$, where

$$\Delta W = \int \pi \omega_0 B_z^2(z) \frac{(R + z \tan \alpha)^3}{3\rho} dz. \quad (\text{A1})$$

We tried to fit the force versus separation curves with the gradient of the above equation and the results are shown in Fig. 11 by the dashed line.

iii- Electrostatic Forces

iv- Capillary Forces

It is well known that microcontacts act as nuclei of condensation. In air water vapor plays the dominant role. If the radius of curvature of the microcontact is below a certain critical radius a meniscus will be formed. This critical radius is defined approximately by the size of the Kelvin radius $r_K = 1/(1/r_1 + 1/r_2)$ where r_1 and r_2 are the radii of curvature of the meniscus. The Kelvin radius is connected with the partial pressure p_s by the equation:

$$r_K = \frac{\gamma V}{RT \log(p / p_s)}$$

where γ is the surface tension, R the gas constant, T the temperature, V the mol volume and p_s the saturation vapor pressure. The surface tension γ of water is 0.074 N/m ($T = 20^\circ\text{C}$) which gives the parameter $\gamma V/RT = 5.4 \text{ \AA}$. Therefore we obtain for $p/p_s = 0.9$ a Kelvin radius of 100 \AA . A simple estimation is given by the equation:

$$F = \frac{4\pi r \gamma \cos \Theta}{1 + D / (R(1 - \cos \phi))}$$

where R is the radius of curvature, Θ the contact angle, D the distance between tip and sample and ϕ the angle of the meniscus. The maximum force is given by $F_{\max} = 4\pi r \gamma \cos \Theta$. For a tip radius of 1000 \AA we obtain a force $F_{\max} = 93 \times 10^{-9} \text{ N}$, which is a rather high value for typical forces in AFM.

v- Short-Range Forces

Magnetic, electrostatic, van der Waals and capillary forces have in common that they are quite long ranged.

To get real atomic resolution the size should be comparable to the atomic dimensions. For distances below a few Å the tip and sample are in contact. It is assumed that the force microscope follows closely the contours of the total charge density.

On the atomic scale several effects seem to contribute to the image contrast.

a- Pauli repulsion and ionic repulsion

These forces play an important role and hinder the tip from penetrating the sample, and give a simple explanation for the observed atomic corrugation, which arises from the variations of total charge density.

Repulsive forces have two origins:

- First, the strong overlap of the two electron clouds leads to incomplete screening of nuclear charges, which causes a Coulombic repulsion.
- Second, according to the Pauli exclusion principle, two electrons having the same quantum numbers cannot occupy the same place. Thus the electrons can only overlap when the energy of one electron is increased, which yields the repulsive force.

The repulsion forces are very short ranged ($\approx \text{\AA}$) and can be described by a power law $F = \text{const}/r^n$ or by an exponential function, where n is greater than 8.

b- Physisorption and chemisorption

Bonds can be formed between tip and sample. In some materials this will give an additional attractive force which varies on an atomic scale.

c- Metallic adhesion

This short ranged interaction has been studied in the most detail so far by force microscopy. This interaction becomes important when two metals come so close to each other that their individual electron wave functions overlap and electron exchange becomes important.

Quantum mechanical effect and leads to an attraction which is exponentially dependent on distance.

d- Friction

The component of the force parallel to the surface, called frictional force, can be quite large. It has been shown by *Mate et al.* [*Phys. Rev. Lett.* **59**, 1942 (1987)] that these frictional forces vary on an atomic scale.

e- Elasticity

Elastic deformations can play an important role in the image contrast. The theory of *Tomanek et al.* [*Phys. Rev. Lett.* **63**, 876 (1989)] predicts that variations in the local elasticity can be observed by AFM on layered materials, such as intercalated graphite.

f- Plastic deformation

Landman et al. [*Science* **248**, 454 (1990)] studied the tip sample interaction in AFM- and STM-type geometries by molecular dynamics calculations". Their simulations show strong plastic deformations for some metal-metal and silicon-silicon arrangements, often accompanied by complete collapse of the original tip and sample surface geometries. These results indicate that there are limits on suitable tip materials in applications to specific sample materials.

Interação de troca (exchange interaction)

A interação de troca é um efeito Quântico onde a energia é dada pelo modelo de Heisenberg e esta relacionada à superposição da distribuição de carga dos átomos i e j .

Energia de troca não tem análogo clássico, mas é uma energia de origem eletrostática definida como J , energia coulombiana do sistema quando os spins estão alinhados paralelos ou anti-paralelos.

Devido ao princípio de exclusão de Pauli a direção relativa dos dois spins não pode mudar sem mudar a distribuição de carga.

Mudança da energia coulombiana pode ser escrita como:

$U = -2JS_i \cdot S_j$ como se existisse um acoplamento entre as direções dos spins S_i e S_j .

Se os spins são paralelos, a parte espacial da função de onda tem que ser anti-simétrica em relação à troca dos dois elétrons, se os spins são paralelos a parte espacial da função de onda é simétrica, $U = 2\mu H_{\text{eff}}$.