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Static Friction and Dynamics at the Nanoscale

Candidato: Dott. Massimo Rovatti

Relatore: Chiar.mo Prof. Sergio Valeri
Correlatore: Dott. Guido Paolicelli
Felix qui potuit rerum cognoscere causas.
Virgilio (Georgiche, II, 490)
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Introduction

Since prehistorical age, humankind had to deal with practical problems concerning the friction of bodies. This represents without any doubt one of the most intellectually interesting and applicability relevant idea up to our days. In this view, tribology is a new interdisciplinary science that involves physicists, engineers, chemists, biologists, having the ambitious goal to understand mechanisms which control the static and dynamic friction processes of two bodies in relative contact.

Thanks to the new extraordinary advances in technology, investigation of such phenomena from macroscale down to the nano and atomic scale has been performed enormous progresses in last decades. Supercomputing and extremely rapid outbreak of new apparata have brought to light the study of friction from both theoretical and experimental point of view.

The understanding of atom-atom interactions and computer-based modelling of complex systems have led to Molecular Dynamics simulations mimicking the dynamical behaviour of millions of atoms, as well as the exploitation of simpler mathematical models that are able to describe the essential physics involved in nonlinear sliding phenomena. Moreover, from the experimental point of view thanks to the recent proliferation of proximal probes, and in particular of tip-based microscopes (e.g. Atomic Force Microscopy, AFM), it is now possible to perform friction force measurements with atomic resolution in Ultra High Vacuum (UHV).

This thesis has the aim to present an experimental work focused on friction of nanoparticles deposited on different substrates, studied by a new and unconventional AFM-based approach. In the first chapter basic physical principles behind friction processes will be presented. In particular the problem of contact area rising from Amontons phenomenological laws will be focused. In the following sections it will be explored some configurations for contact in terms of classical Hertian model and, coming down to the nanoscale, the main forces acting between the sample and an AFM tip will be treated.

The second chapter is entirely dedicated to the utilized instrument, the Atomic Force Microscope, with particular emphasis on possible modes of operation: contact, non-contact and tapping.
Third and fourth chapters represent the core of this PhD thesis. Here in fact the physical system composed by spherical gold nanoparticles with different diameters deposited on Highly Oriented Pyrolitic Graphite (HOPG) and silicon covered by native oxide will be described in the context of the scientific open problem of friction force dependence on contact area. It is theoretically and experimentally well-known a superlubric behaviour when very clean conditions like Ultra High Vacuum (UHV) and incommensurability effects are verified, but it is nothing but trivial that also in air conditions gold nanoclusters, on graphite in particular, represent a system characterized by high mobility. In the third chapter the details of our developed AFM-based method to study the dissipated energy in tip-sample periodical interaction and, at the same time, to manipulate nanoclusters of 13, 24 and 42 nm of nominal diameter in tapping mode will be discussed. Intentionally increasing the oscillation amplitude, we are able to increase the energy given to the system, and so to reach and evaluate quantitatively a threshold of detachment, which we have found to be related to particle dimensions. A very sensitive calibration of all experimental parameters is required, but one the advantages of this approach resides in the fact that the dissipated energy is the only parameter which uniquely controls the depinning event.

In the fourth chapter several results and capabilities of this method will be shown, also compared with those obtained by standard friction force experiments in literature. We have found the existence of characteristic thresholds for the energy required to depin, and it will be discussed their dependence on the contact area and on the substrate. All measurements have been performed both in air and in nitrogen atmosphere, in order to understand the role of eventually present water layers and capillary forces on depinning events.

A separate section will concern with another aspect that we have analyzed: the dynamics of the sliding nanocluster and the influence of surface defects, in the case of graphite steps and of Focused Ion Beam-made grooves on silicon dioxide.

As last topic, we have discussed in details an analytical model describing the interaction between the AFM tip and the pushed nanoparticle as a function of the path followed by the scan, checking its applicability to our system in exam, with particular attention on measurements on silicon dioxide for its low roughness.
Chapter 1

Theory behind sliding friction

1.1 Historical notes

Sliding friction is one of the oldest problems that humans had to deal with since from origins and it has certainly huge practical significance. Some years ago it has been estimated [1] that monetary losses for United States due to ignorance of tribology aspects amount to 6% of the gross national product, corresponding to 420 billion of dollars.

The word *tribology* derives from Greek *tribos*, meaning rubbing. This word covers a large number of ancient and well-known topics such as the study of friction, lubricants and wear. It is the engineering aspect of friction that has the longest history. More than 400 000 years ago our hominid ancestors in Algeria, China and Java were making use of friction when they chipped stone tools. By 200 000 BC, Neanderthals achieved a clear mastery of friction, generating fire by rubbing wood on wood and by striking of flint stones. The second main practical use of friction in history, showing an understanding of sliding phenomena, concerned lubricants employment to minimize work required to move heavy objects, which dates back more than 4000 years.

The value of lubricants was appreciated at an early stage in the Sumerian and Egyptian cultures; a chariot from about 1400 BC was found in a tomb, called tomb of Yuua and Thuiu, with traces of the original lubricant remaining on the axle. At an ever earlier stage, lubricants had been used to reduce friction between sledges used to transport building plocks and the wooden logs or planks on which they are moved. Thus the use of grease, oil or mud as lubricant is dated as early as 2400 BC.

The first temptative of formalizing phenomenological friction laws is due to eclectic Leonardo da Vinci (1452-1519) between 15th and 16th century. His work was rediscovered in 1699 by French scientist Guillaume Amontons (1663-1705)
1.1 Historical notes

Figure 1.1: Guillaume Amontons shows at Luxembourg Gardens (Paris) an early optical telegraph experiment - Print.

in 17th century. Despite of his early deafness, he worked fruitfully on many fields of physics from thermodynamics to celestial mechanics (in a print in Fig.1.1 he’s showing an experiment involving an early optical telegraph), through the tribology of course. These formalizations of friction laws were considered with some scepticism until they were verified in 1781 by French physicist Charles-Augustin de Coulomb (1736-1806).

The theory of hydrodynamic lubrication is based on Navier-Stokes equations of motion for viscous fluids. Mr Beauchamp Tower, English inventor and railway engineer, in 1885 performed experiments to determine friction of car wheels and observed the generation of hydrodynamic pressure in bearings. Reynolds became intrigued with Tower’s result and showed that they could be well explained by applying the principles of fluid dynamics. In 1886 Reynolds published his classical work on theory of hydrodynamic lubrication, widely used in modern machinery design.

Hydrodynamic (or fluid) lubrication is only one of at least two possible configurations of lubrication; the English biologist Hardy clarified the situation introducing the term boundary lubrication in 1922. He found that very thin (∼ 10Å) absorbed layers were sufficient to cause very low friction sliding of two glass surfaces on each other. Therefore he concluded that under such conditions the lubrication depends only on chemical composition of the fluid, not on its viscosity,
and that a good lubricant was a fluid which was adsorbed by surfaces of solids. For example fatty acids have a polar head, that tends to bind relatively strongly to polar surfaces such as metal oxides, and a long hydrocarbon tail pointing away from surfaces. The sliding occurs at the plane where hydrocarbon tails meet.

More recently, advances in surface science and coatings have brought to light the new-generation solid lubricants. They are represented by materials like graphite, molibdenum disulfite, boron nitride, polytetrafluorethylene (PTFE), calcium fluoride, cerium fluoride and tungsten disulfide, that are able to prevent contact thanks to their lamellar structure, if they are present in form of dry powder between two sliding bodies. These kind of materials is particularly useful whenever standard lubricants application fails, like for example in extremely high pressures and temperatures.

In this chapter a description of phenomenological friction laws from original works by Amontons and Coulomb until the assumption of the difference between apparent and real contact area will be given. A general overlook on most relevant features of physical processes in terms of forces acting between two bodies in contact will be presented. The picture that friction can be calculated and measured in terms of dissipated energy as well of forces is the basic idea behind this PhD work.

1.2 Problem of contact area

Macroscopically, the key relations ruling the tribological behaviour are represented by well-known da Vinci-Amontons-Coulomb phenomenological laws [2] [3], stating that:

1. Friction is proportional to the applied load.
2. Friction is independent of the apparent contact area.
3. Friction is independent of sliding velocity.

It is intuitive thinking about friction as a surface phenomenon and it is an everyday experience that a car wheel during rain or in a fast bend having an high width (so a large contact area) is more stable than a sharp one. Thus there is a no-common sense in the second law, solved by Bowden and Tabor [4] in the mid-50’s with the assumption that the friction force is proportional to the real contact area $\Delta A$, through a constant for the system represented by the average frictional shear stress $\sigma_f$. Thus:

$$ F_f = \sigma_f \Delta A. $$
The second assumption is that $A$ is proportional to the applied normal force $F_N$ because of the surface roughness, so:

\[ A = \alpha F_N, \tag{1.2} \]

where $\alpha$ is a constant. With these assumptions we can write the relation that encloses all three phenomenological laws:

\[ F_f = \mu F_N, \tag{1.3} \]

with $\mu$ is the friction coefficient, independent of the load.

Thus we can conclude that if most real surface have roughness on many different length scales, then when a block is put on a substrate, the real contact area will not be the whole bottom surface ($A$) of the block, but the area of real contact ($\Delta A$), usually much smaller than $A$. Firstly, as the block is lowered towards the substrate, a single contact area (that is called junction) occurs; in this point the pressure becomes so high as to give rise to local plastic deformation. If the block is further lowered towards substrate surface more junctions (multiple contacts) appear until the real contact area $\Delta A$ is so large that the load $L = Mg$, with $M$ is the block mass, is balanced by the contact pressure integrated over $\Delta A$. If it is assumed that each junction is in a state of incipient plastic flow. It means that the plastic regime for the system is being triggered. Thus $Mg = \sigma_c \Delta A$, with $\sigma_c$ is the penetration hardness and it is the largest compressive stress that the material can tolerate without plastic yielding. Plastic deformations in crystalline materials are due to the motion of dislocations, that are widely distributed defects on the crystal. Dislocations are always pinned, e.g. by foreign impurities, but a minimum force is required to pull a dislocation over its pinning barrier, that usually are so high that thermal excitations over the barriers are negligible in the first approximation, and the yield stress is only weakly dependent on temperature.

### 1.3 Dynamics

The argumentation of Bowden and Tabor [4], that will be reported in the following, can provide a simple explanation for the origin of sliding friction in the case of clean surfaces. They assumed that the friction force is the force required to shear cold-welded junctions between solids.

We have seen that, in many practical cases, the real contact area can be estimated accurately by assuming that plastic deformation occurs at each junction and that all junctions are in a state of incipient plastic flow. So we can write:

\[ \Delta A = \frac{L}{\sigma_c}. \tag{1.4} \]
The force $F$ necessary to shear the junctions with a total contact area $\Delta A$ is

$$F = \tau_c \Delta A,$$

(1.5)

where $\tau_c$ represents the yield stress during shear. But $\Delta A = L/\sigma_c$, so

$$F = \left( \frac{\tau_c}{\sigma_c} \right) L.$$

(1.6)

Physically the ratio $(\tau_c/\sigma_c)$ is equal to $\mu$, the friction coefficient. This simply derivation highlights why friction force is proportional to the load and why it is independent of the surface area $A$ and of nature of roughness. It can provide also an explanation of why $\mu \sim 1$ for sliding on clean surfaces: this follows from the fact that $\tau_c$ and $\sigma_c$ have similar magnitude.

Usually for lubricated surfaces the mechanism discussed above is not applicable since it is known experimentally that while a boundary lubrication may reduce sliding friction by a factor of 10 [2], it may reduce also the metallic transfer, resulting from the formation of cold-welded junctions, by a factor of $10^4$ or more. Under these conditions the contribution of metallic junctions to friction force is very low; friction is entirely due to the force required to shear the lubricant film itself.

Practically all devices used for experiments of friction can be modelled as an interface in which friction forces are generated by a sliding body with finite mass $M$ and some elastic properties, that can be represented by a spring with elastic constant $k$ as shown in Fig.1.2. In the large part of friction experiments the spring has a free end that moves with a constant velocity $v$. There is no leak of generality assuming that velocity can also vary with time $v = v(t)$.

![Figure 1.2: A body of finite mass $M$ slides on a flat substrate. A spring of elastic constant $k$ is linked to the body; it has a free end, that moves with velocity $v$.](image)

Assuming that the spring is in its natural length at the beginning of sliding, the elastic force increases linearly with time while the body is stationary. When
spring force reaches a critical value $F_a$, the block starts to move. This value of the force $F_a$ is commonly called static friction force. In Fig.1.3 three different sliding regimes are reported for the spring force as a function of time. In the first case (a), after reached static friction force $F_a$, the motion is of steady type, with constant spring force value equal to $F_b$. Otherwise the motion of the block can be stick-slip like (b) or chaotic (c).

Figure 1.3: Sliding dynamics of the block in three different cases: (a) steady sliding; (b) periodic stick-slip; (c) chaotic motion.

Now, to understand the physics behind this sliding process it is necessary to map out the dynamical phase diagram to determine for example regions in $(k, v)$-plane where steady and stick-slip motion occur.

It is an experimental observation that stick-slip always disappears if the spring $k$ is stiff enough, or if the sliding velocity $v$ is high enough, as it is depicted in Fig.1.4.

Figure 1.4: General form of kinetic phase diagram. Below values $k^*$ and $v^*$ we have a region in which sliding motion is stick-slip like.

Assume that the block is rigid and that the free end of the spring moves with
velocity \( v \). Let us discuss the nature of the sliding, under the assumption that friction force \(-F_0(t)\) only depends on the instantaneous velocity \( \dot{x}(t) \) of the block.

Let \( x(t) \) be the position coordinate of the body at time \( t \). The equation of motion for the block has the form

\[
M \ddot{x} = k(\dot{x} - x) - F_0(\dot{x})
\]

(1.7)

Starting with steady state sliding and reducing the spring velocity \( v \), steady sliding is replaced by stick-slip motion when \( v \) is less than a critical value \( v' \). This critical value can be determined by linear instability analysis.

During steady sliding \( x = x_0 + vt \) which satisfies (1.7) if \( kx_0 + F_0(\dot{x}) = 0 \).

To determine when steady sliding becomes unstable, let us write

\[
x = x_0 + vt + \xi,
\]

(1.8)

where \( \xi(t) \) is a small perturbation. Substituting (1.8) in (1.7) and expanding \( F_0(v + \xi) \approx F_0(v) + F'_0(v)\xi \) gives

\[
M \ddot{\xi} = -k\xi - F'_0(v)\dot{\xi}.
\]

(1.9)

Assume that \( \xi(t) \sim e^{\kappa t} \). Substituting this in (1.9) gives

\[
\kappa^2 + \left[ F'_0(v) \right] \kappa + \left( \frac{k}{M} \right) = 0.
\]

(1.10)

This equation has two zeros. If the real parts of zeros are negative then the perturbation \( \xi(t) \) of steady motion will decay increasing the time; so the steady motion is stable with respect to small perturbations. If the real parts of zeros are positive, the steady state is unstable. Thus the curve \( v = v^*(k) \) in \((k, v)\)-plane separating steady from stick-slip motion is determined by \( \Re(\kappa) = 0 \), i.e. \( F'_0(v) = 0 \).

Note that this condition is independent of \( k \), so for all models where friction force only depends on instantaneous velocity of the block, the curve in \((k, v)\)-plane will be a vertical line. This conclusion is in contradiction with the experimental observation, for which is always proved that it is possible to eliminate stick-slip by using a stiff enough spring \( k \) (as depicted in Fig.1.4). However it follows naturally in models with static friction force increases monotonically with the time of stationary contact, for example because of the increasing in contact area with time, as it is proved in the following.

On the other hand, the condition \( F'_0(v) = 0 \) implies that for all models where \( F_0 \) increases with increasing sliding velocity, steady sliding will be stable for large enough \( v \). This is in accordance with experiments. The disappearing of stick-slip for large sliding velocities \( v \) is confirmed by everyday experience. For example, if a door is opened slowly, a loud “squeeze” noise (associated to stick-slip) usually
occurs, while if the door is opened fast enough, steady sliding occurs and no noise is generated.

Let us now demonstrate that if static friction force increases with time of stationary contact, steady sliding will occur if $k$ is large enough (1.4). Assume that the static friction force depends only on time of stationary contact, $F_0 = F_0(t)$, after the return to the pinned state. We assume that $F_0(t = 0)$ is the kinetic friction force at low sliding velocity just before stick, and that for $F_0(t)$ increases monotonically with time of stationary contact. For this demonstration we will refer to the Fig.1.5.

![Figure 1.5](image)

Figure 1.5: Solid line represents the variation of static friction force with respect to time of stationary contact. Dashed lines represents spring force for different sliding velocities: $v_1 > v^*$ but $v_3 < v_2 < v^*$.

Dashed lines show the increase of spring force $kvt$ as a function of the contact time for three different velocities. In the case (1) the spring force increases faster then the initial linear increase of static friction force. Thus no stick-slip motion and no stop of the block will occur. If the spring velocity $v$ is lower than the critical velocity $v^*$ (such in cases (2) and (3)), the spring force will be smaller than the static friction force, until $t$ reaches value $t_2$ (2) or $t_3$ (3), at which time slip motion starts. In these cases, stick-slip will occur.

There are at least three different mechanisms by which static friction force may increase with time of stationary contact:

1. The real contact area increases with stationary contact.

2. If surfaces are covered by fatty acid monolayers or other long-chain polymers, chain interdiffusion will lead to an increase of static friction force with time of stationary contact.

3. If a thin inorganic “contamination” layer occurs between surfaces, and if the lateral corrugation of the adsorbate-substrate interaction potential is weak,
the lubrication film may undergo dynamical phase transitions between a fluidized state during slip and a solid state during stick. The formation of solid state during stick is likely to be a nucleation process.

1.4 Hertzian model for contact

In this section we present a brief summary of some analytical approaches describing the contact between two bodies [5]. Hertz classic contact theory dates back to 1882 [6]. This approach assumes that adhesion and surface forces can be neglected. In a large number of experiments and of course also in Atomic Force Microscope, when a body (e.g. the tip) exerts a pressure on another one (e.g. a nanoparticle, a nanowire, etc.), there are several combinations of behaviours depending on the relative stiffness of the two bodies.

Tip on substrate: elastic sphere on rigid flat surface

This approach is commonly used for indentation of few angstroms or nanometers. In this case the sphere of radius $R$ has a deformation $\delta$ when it is pressed on surface under a force $F$ and a pressure $P(y^*)$. The contact area of the sphere is a circle of radius $a$ and $y$ represents the distance between the circle and the center of the sphere. Expressions relating contact radius and applied load are the following:

$$a = \left(\frac{3RF}{4E^*}\right)^{1/3}, \quad (1.11)$$

$$F = \frac{4}{3} E^* R^{1/2} \delta^{3/2}, \quad (1.12)$$

$$P(y^*) = \frac{3F \sqrt{1 - y^*^2}}{2\pi a^2}, \quad (1.13)$$

where $y^* = y/a$, and the reduced Young modulus $E^*$ is given by

$$\frac{1}{E^*} = \left(\frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i}\right). \quad (1.14)$$

$E$ and $E_i$ are the Young moduli, $\nu$ and $\nu_i$ are the Poisson ratios for surface and indenter respectively.

If we want to assume the indenter as a rigid body and the surface as an elastic medium, and if the indentation is larger than sphere radius, it is necessary to employ the Sneddon analysis [7] (see next cases).
Tip on substrate: rigid sphere on soft elastic surface

The force and the elastic surface deformation are given by the following numerically solvable transcendental equations:

\[ F = \frac{E^*}{2} \left[ (a^2 + R^2) \ln \left( \frac{R + a}{R - a} \right) - 2aR \right], \]  
(1.15)

\[ \delta = \frac{1}{2} a \ln \left( \frac{R + a}{R - a} \right). \]  
(1.16)

Tip on substrate: rigid cone on soft elastic surface

In the case of deep indentations, in which the tip can no longer be modelled as a sphere, pyramidal tips have been modelled as cones. This approach is useful when the indentation is deeper than 10 nm and in the case of softer than tip (e.g. in biological samples). Relations linking indentation \( \delta \), loading force \( F \) and diameter of contact area \( d \) are the following:

\[ F = \delta^2 \frac{\pi E}{2(1-\nu^2)} \tan(\alpha), \]  
(1.17)

\[ d = 2F \sqrt{\frac{2\pi}{\tan(\alpha)}} \frac{(1-\nu^2)}{E}, \]  
(1.18)

\[ \delta = \sqrt{\frac{kd}{\frac{\pi}{2}(1-\nu^2)\tan(\alpha)}}, \]  
(1.19)

where \( E \) and \( \nu \) are respectively Young modulus and Poisson ratio of the sample and \( \alpha \) is the opening angle of the cone.

When surface forces are negligible, Hertz and Sneddon analytical approaches can be used. Otherwise there are several theories that can be used such as: DMT (Derjaguin-Müller-Toporov), that includes only long-range forces (van der Waals) between bodies in contact region, or JKR (Johnson-Kendall-Roberts), that takes into account only short-range forces. All these theories assume no plastic deformation and no viscoelastic phenomena. To treat these conditions it can be possible to use finite elements approaches [8].

In all analytical methods surfaces are assumed to be ideally flat as well as frictionless. Realistically speaking, surfaces are rough at nanoscale and friction is inherent to all contacts. One of the most important question is: at which point does the discreteness of matter start to play an important role such that continuum mechanics can no longer be used? The existence of roughness makes calculations of real contact area much more difficult, because the contact occurs at several
points. First models and their improvements that were used in mid-60’s and mid-80’s assumed a rigid surface completely covered by an assembly of rods [9] and hemispherically asperities [10] to mimic real roughness. These approaches have a limited applicability to real life because they simplify the geometry of asperities, they assume a Gaussian distribution of asperities heights and they neglect interactions between adjacent asperities.

Some microscopic roughness measurements have shown a fractal structure from nanometer to millimeter scale in different surfaces. Majumdar and Bhushan [11] in early 90’s developed a model of contact between isotropic rough surfaces based on scale-independent fractal roughness parameters. They related the real contact area of an elastic deformation due to the load for a fractal dimension between one and two, using a power-law relation for the size distribution of contacts.

Another approach to the study of roughness including fractals was made by Persson in 2001 [12]. He developed a theory of contact mechanics between surfaces with randomly roughness, valid also for self-affine fractal surfaces. The intriguing property of self-affinity in fact allows that morphology does not change under different scales along different directions. Persson assumed the bodies to deform elastically under a certain yield stress and plastically above it. When an elastic medium is pressed on a substrate with roughness at different length scales, it will fill out the small cavities at the top of large asperities. However it will not do the same at the bottom of large cavities, where the load is smaller. Persson’s model works successfully showing the proportionality between real contact area and load. This theory does not include adhesion contribution but it is of course important in elastically soft objects.

Even considering the roughness at all length scales, surfaces are still being considered as a continuum down to atomic scales. Luan and Robbins [13] few years ago performed some molecular dynamics simulations to test when continuum mechanics breaks down or in other words whether Hertz theory of contact is still valid also at nanoscale. They found that continuum mechanics may underestimate the area of AFM contacts by up to 100% at small loads and the error decreases with increasing load and yield stresses may also be underestimated by a factor of 2 or more.

1.5 Tip-sample relevant forces

In this section it is our intention to briefly present an overview of relevant forces acting between AFM tip and sample, following the distinctions by Meyer et al. [14]. The ranges of interaction play a crucial role in force microscopy, since the total measured force is composed by each contribute coming from all different parts of tip and cantiever.
1.5 Tip-sample relevant forces

1.5.1 Short-range forces

Short-range forces have their origin in the overlap of electron wave functions and in the repulsion of ion cores. So the typical range of such forces is comparable to the extension of electron wave function, e.g. less than one nanometer. Short-range forces can be both attractive or repulsive; we have the first case if the overlap of wave functions reduces the total energy, e.g. in molecular binding. The latter case comes from Pauli principle that tends to avoid strong waves overlap, leading to repulsion.

Ionic repulsion acts over small distances, where the screening of ion cores by the electrons decays. When tip interacts with a surface, at least contributions of nearest neighbor atoms have to be taken into account and to describe short-range forces coming from pairwise atoms interactions model potentials like Lennard-Jones or Morse can be applied.

Attractive short-range forces are of the order of $0.5 \div 1 \text{ nN per each interacting atom}$ at tip-sample distances typical for STM experiments.

1.5.2 Dipole-dipole forces

Both so-called dispersion forces (London forces) and van der Waals forces are due to dipole-dipole interaction. The difference is that the first are due to induced dipole and an instantaneous dipole, while the latter is due to the interaction between two induced dipoles. Dispersive forces are always attractive, and they are present even for chemically inert noble gas atoms.

The decay for van der Waals forces at short distance goes as $F \sim 1/r^7$ if $r > 5 \text{ nm}$ and $F \sim 1/r^8$ if $r \approx 5 \text{ nm}$. In order to calculate these forces acting between two macroscopic bodies, Lifshits theory is required. It treats bodies as a continuum and it involves the Hamaker constant, which is characteristic of the materials. For a configuration composed by a spherical tip approaching to a semi-infinite body, the corresponding van der Waals force is

$$F_{vdW} = \frac{HR}{6D^2},$$

where $H$ is Hamaker constant, that is of the order of $10^{-19} \text{ J}$, $R$ the radius of the tip and $D$ the distance between tip and sample. If we assign to these variables typical values for vacuum AFM experiment $R = 30 \text{ nm}$ and $D = 0.5 \text{ nm}$, we obtain $F_{vdW} = 2 \text{ nN}$.

Lifshits theory points out that the medium eventually present between interacting tip and sample plays an absolutely relevant role. The force in fact depends is proportional to the products $(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)$ and $(n_1^2 - n_3^2)(n_2^2 - n_3^2)$, where $\epsilon_i$ and $n_i$ denote respectively dielectric constant and refractive index of the tip ($i = 1$), the sample ($i = 2$) and the medium in-between ($i = 3$).
1.5 Tip-sample relevant forces

1.5.3 Electrostatic forces

In the case of insulating tips and samples, localized charges can be present. Long-range electrostatic forces acts between these charges coming for example from sample surface preparation (e.g. ion sputtering) and their strength and distance dependence obey Coulomb’s law. Charges on surface can persist for hours or in vacuum for days. They can attract conductive tips and to evaluate forces a calculation of interaction between charges on sample and their mirror image on tip apex is needed.

In the case of both conducting tip and sample at different potentials, considering this system as a capacitor with distance-dependent capacitance \( C \), the electrostatic force is given by

\[
F_{el} = \frac{\partial C}{\partial z} (U_{bias} - U_{cpd})^2,
\]

(1.21)

where \( U_{bias} \) is the applied bias voltage between tip and sample and \( U_{cpd} \) is the contact potential difference due to different work functions of tip and sample. It is important to note that work functions are very sensitive to perturbations at the surface, so the irregular shape of the tip can give rise to patch charges, that are not completely compensated by bias voltage.

The derivative term \( \partial C/\partial z \) depends on the geometry of the probe, usually modelled as a sphere or a truncated cone. For small tip-sample distance (e.g. \( z = 0.5 \) nm), the electrostatic force is

\[
F_{el} = \pi \epsilon_0 \frac{R}{z} (U_{bias} - U_{cpd})^2.
\]

(1.22)

For a usual tip radius \( R \) of 20 nm and a potential difference \( (U_{bias} - U_{cpd}) = 1 \) V, the corresponding force is \( F_{el} = 0.5 \) nN. The distance dependence changes its form as the separation between tip and sample increases, from \(-z^{-1}\) to \(-z^{-2}\) until \( \ln(z/H) \), where \( H \) is an effective height \((z < H)\).

1.5.4 Magnetic forces

Magnetic dipoles located in a magnetic field give rise to magnetic forces. To evaluate the range of action of these force we have to calculate the total magnetostatic energy of tip-sample system with assumption of neglecting that the tip magnetization is influenced by sample magnetization and vice-versa:

\[
E = \frac{\mu_0}{2} \left[ \int \mathbf{M}_{tip} \cdot \mathbf{H}_{sample} dV + \int \mathbf{H}_{tip} \cdot \mathbf{M}_{sample} dV \right] = \mu_0 \int \mathbf{M}_{tip} \cdot \mathbf{H}_{sample} dV.
\]

(1.23)
1.5 Tip-sample relevant forces

The used system of coordinates \((x, y, z)\) is fixed to the surface of the sample but, to calculate the force on the tip, it is useful to introduce a new reference system \((x', y', z')\) linked to the tip, that is located in \(s = (s_x, s_y, s_z)\) in the coordinate system attached to sample. Thus

\[
E(s) = \mu_0 \int M_{\text{tip}}(x', y', z') \cdot H_{\text{sample}}[(x', y', z') + s]dV'.
\] (1.24)

The \(z\)-component of the force acting on tip is given by

\[
F_z(s) = -\mu_0 \int M_{\text{tip}}(x', y', z') \cdot \frac{\partial}{\partial s_z} H_{\text{sample}}[(x', y', z') + s]dV' \\
= -\mu_0 \int M_{\text{tip}}(x', y', z') \cdot \frac{\partial}{\partial z'} H_{\text{sample}}[(x', y', z') + s]dV'.
\] (1.25)

If the assumption of neglecting mutual tip-sample magnetization cannot be avoided, other terms in the expression of energy like exchange and anisotropy have to be considered. The range and the strength of interaction strongly depends on the particular tip-sample configuration.

1.5.5 Capillary forces

Microcontacts act as condensation nuclei so for AFM experiments in air conditions water vapor plays a crucial role. A meniscus will be formed if the radius of contact is less than the Kelvin radius, defined by

\[
r_K = \frac{1}{(\frac{1}{r_1} + \frac{1}{r_2})},
\] (1.26)

where \(r_1\) and \(r_2\) are meniscus radii of curvature. Kelvin radius is connected with partial pressure \(p\) by

\[
r_K = \frac{\gamma V}{RT \log(p/p_s)},
\] (1.27)

in which \(\gamma\) is surface tension, \(R\) the gas constant, \(T\) the temperature, \(V\) the molar volume and \(p_s\) the saturation vapor pressure. If we assign to these variables typical values such as \(\gamma = 0.074\) N/m at room temperature \(T = 20^\circ\) C and \(p/p_s = 0.9\), thus we obtain a radius \(r_K = 100\) nm.

If a meniscus is formed then a capillary force has to taken into account:

\[
F_{\text{cap}} = \frac{4\pi \gamma R \cos(\Theta)}{1 + D/[R(1 - \cos(\varphi))]},
\] (1.28)

where \(R\) is the curvature radius of the meniscus, \(\Theta\) the contact angle, \(D\) the distance between tip and sample and \(\varphi\) the angle of meniscus. For a tip of radius 100 nm we can obtain a force of \(10^{-8}\) N, so at least one order of magnitude greater than the corresponding van der Waals force.
Chapter 2

The Atomic Force Microscopy

In this chapter a brief and general description of basic features of Atomic Force Microscope is given. Some details on possible feedback systems will be presented in the second section, in which the differences between operational modes are pointed out. AFM represents the key tool of my PhD work. It will be used in fact in an unconventional way (see Chapter 3). With the new method developed in this thesis, AFM in tapping mode with amplitude modulation feedback can be exploited not simply as a microscope but as a manipulator for particles at nanoscale and measurements can be interpreted in terms of dissipated energy.

2.1 The instrument

The Atomic Force Microscope (AFM) was invented by Binnig in 1986 [15] and very shortly after in the same year, Binnig, Gerber and Quate [16] built up a working prototype. The basic idea of AFM is to exploit the interactions between very few atoms (in principle one atom) present on a tip apex with atoms on a surface and thus obtaining an image of the surface down to the atomic scale. Inspite of Scanning Tunneling Microscope (STM), invented by Binnig et al. in 1982 [17] in which a current flows from a probe to the surface in exam, AFM does not need an electrically conductive sample so it can image metals, semiconductors and of course insulators.

The other positive feature of AFM differently from STM is the capability to analyze surfaces both in vacuum, in air and in liquid conditions. This peculiar characteristics allows AFM to be an ideal tool for experiments on contacts (e.g. for mechanics applications) in real conditions of work at the micro and nano scales as well as imaging reaching the atomic resolution in Ultra High Vacuum (UHV) for very controlled flat samples. It can perform imaging with resolution down to the nanoscale virtually for any other kind of sample, from the biological sur-
2.1 The instrument

faces thanks to the capability to work in liquid environment, to flat or patterned substrates.

As Giessibl [18] pointed out, AFM took almost five years from its birth to reach the atomic resolution for inert surfaces [19] [20] and ten years for reactive surfaces [21].

Basically AFM is a force sensor, composed by a cantilever made by silicon with rectangular or triangular shape and at the apex a proper probe is present. The probe consists on a tetraedrical, conical or pyramidal tip (it depends on the fabrication process). Conical tips generally made by silicon dioxide etching are more sensitive and easy to damage but they present the advantage of being made conductive by silicon doping. Triangular and tetraedrical tips are made depositing a layer of silicon nitride on a etched groove on the surface of crystalline silicon. They are much more resistant but not ideal for imaging of samples with very rough surfaces or deep grooves.

The cantilever is normally mounted on a piezoelectric component, that provides movement in \((x, y)\)-plane and \(z\) direction. The principal idea is to detect forces between the tip apex and the surface of the sample measuring the deflection of the cantilever and through Hook’s law it is possible to get informations on forces. Deflection of cantilever is usually thanks to displacements on screen of a laser spot reflecting on the upper surface of cantilever.

![Figure 2.1: Schematic top view and side view of a microfabricated cantilever. The picture is not in scale.](image)

For a generic rectangular cantilever, shown in Fig.2.1, with dimensions \(w, t\) and \(L\), the corresponding spring constant \(k\) is given by [22]:

\[
k = \frac{Ywt^3}{4L^3},
\]

where \(Y\) is the Young’s modulus. The fundamental eigenfrequency \(f_0\) is given by
the relation [22]:
\[ f_0 = 0.162 \frac{t}{L^2} \sqrt{\frac{Y}{\rho}}, \] (2.2)

where \( \rho \) is the mass density of the cantilever material [18].

Usually the properties of interest for a particular cantilever are the stiffness \( k \), the proper frequency \( f_0 \), the quality factor \( Q \) and of course the chemical composition of the tip.

Early AFM’s have worked in static mode (see next section for details) in which the tip slides always in contact with the surface, so the cantilever stiffness should be less than the interatomic spring constants of atoms in solid [23], so typically \( k \leq 10 \) N/m. This assumption was thought valid also for dynamic mode, which is characterized by the continuous cantilever oscillation over the sample, but it turned out later that greater values for \( k \) can help to reduce noise and increase stability of the system.

Quality factor \( Q \) is an index of damping mechanisms acting on the cantilever, so it depends on experimental conditions of work (air, vacuum, liquid, etc.).

It is important to note that all modes of operation (e.g. static, dynamic) are not limited to mapping topography and surfaces properties; recording respective signals as a function of distance for example or of other parameters (e.g. tip-sample voltage), one can obtain force-distance curves, also known as force spectroscopy, particularly useful to understand the physics behind tip-sample interaction. In following sections a general overview on possible AFM operational modes will be given. For clarity, a self-explaining picture on force microscopy modes sorted with respect the feedback and tip-sample contact formation is reported in Fig.2.2.

\section*{2.2 Operational modes}

In the following sections brief descriptions of the two most used modes of operation for AFM are presented. For what concerns the static mode, basic features of contact measurements will be reported. For dynamic mode, non-contact and tapping setup with their feedback formalism will be presented in details.

\subsection*{2.2.1 Static mode: contact}

AFM is a force sensor by definition; the force acting between tip and sample \( F_{ts} \) is the signal used to perform an imaging of the surface. The tip is always in contact at a distance variable between few angstroms and one hundred of angstroms from the sample and the force felt by tip induces a deflection of cantilever, translated into a displacement of the laser spot on a screen. The cantilever deflection \( q \)
2.2 Operational modes

Figure 2.2: In this picture AFM operational modes are presented, sorted by detection and contact formation.

follows the Hook’s law:

\[ q = \frac{F_{ts}}{k}. \]  

(2.3)

Because of the continuous interaction between tip and surface, the cantilever must be much softer than the atomic bonds in both interacting solids. Since typical spring constants for solids are between 10 and 100 N/m, usually in contact mode the elastic constant for a cantilever is \( k = 0.01 \div 5 \text{ N/m} \).

It has been proved by Jarvis and co-workers [24] that atomic resolution with contact mode is possible but a very delicate apparatus is required. It is needed in fact UHV condition and an electromagnetic field to cancel the long-range (up to 100 nm) contribution of the force \( F_{ts} \), coming from van der Waals electrostatic and magnetic forces, or, as Ohnesorge and Binnig pointed out [20], by immersing tip and sample in liquid.

If the experimental setup is difficult, for contact mode the interpretation of measurements is relatively simple and direct: obtained images are map of heights \( z \) at \( (x, y, F_{ts} = \text{const}) \). The contact operational mode is not only essential to reach atomic resolved images but is also useful to study the mechanical response of sample (e.g. Friction Force Microscopy, FFM).

For the sliding tip there is an equilibrium of forces: the attractive long-range force between tip and sample is compensated by the repulsive short-range force at the contact and by the repulsive force coming from the bending of cantilever
2.2 Operational modes

(Fig.2.3).

Decreasing the tip-sample distance means increasing repulsive forces, so images of constant repulsive force are often identified with topography of the surface. For soft cantilevers the effect called "jump to contact" occurs: when the gradient of the increasing attractive force becomes larger than the cantilever spring constant, an instability occurs and the tip jumps to contact with surface. This effect gives rise to a hysteresis in deflection versus distance curve (see Fig.2.4).

Concerning atomic resolution, AFM in contact mode is able to image the lat-
2.2 Operational modes

...
Figure 2.5: Lateral force along a Cu (110) direction with typical atomic stick-slip behaviour. Two different spring constants were used: on Panel (a) $k_n = 0.01$ N/m and on Panel (b) $k_n = 24$ N/m. Reprinted figure with permission from [25]. Copyright 1999 by the American Physical Society.

Slope of lateral force versus distance curve during sticking, is composed by the torsional stiffness of cantilever $k_T$, the bending stiffness of the tip $k_{tip}$ and the lateral stiffness of the contact $k_{con}$, following the relation:

$$\frac{1}{k_{eff}} = \frac{1}{k_T} + \frac{1}{k_{tip}} + \frac{1}{k_{con}}$$

where, for a typical silicon tip, $k_{tip} = 84$ N/m. With $k_{con}$ it is possible to determine contact radius $a$:

$$a = \frac{k_{con}}{8G^*},$$

(2.4)

where the effective shear modulus is given by

$$\frac{1}{G^*} = \frac{2}{G_1} + \frac{2}{G_2} - \frac{\nu_1^2}{G_1} - \frac{\nu_2^2}{G_2}$$

(2.5)

in which $G_1$ and $G_2$ are shear moduli of the sample and the tip respectively, and $\nu_1$ and $\nu_2$ are their Poisson ratios. All these physical quantities can be calculated.
from elastic coefficients. Combining them with typical values for silicon (tip) we can evaluate a contact radius of few tens of nanometers so for atomic friction the description given by continuum contact mechanics collapses and an atomistic modelling is required.

### 2.2 Operational modes

#### 2.2.2 Dynamic mode: non-contact and tapping

There are few possible dynamic operational modes for AFM, including most commonly used ones like non-contact and tapping mode. By now non-contact approach is the only one that can reach true atomic resolution in UHV and images of surface with a quality comparable to STM images. Dynamic modes are characterized by a cantilever excited by a piezoactuator to oscillate at its mechanical eigenfrequency. The principal difference between non-contact and tapping mode is that in the first case we acquire the signal at constant oscillation amplitude and so the feedback is on the frequency (it is also called Frequency Modulation AFM, FM-AFM), while in the latter case the feedback is on the amplitude (Amplitude Modulation AFM, AM-AFM). While non-contact FM-AFM it is well-known to be used in UHV conditions to reach atomic resolution, tapping mode AM-AFM requires a medium, like gas or liquid, through which the cantilever can oscillate. Moreover, because of this capability to work also in liquid environment, AM-AFM is a needful instrument to image also biological samples.

A relevant technical detail has now to be pointed out. The laser spot displacement on the screen is linearly related to the true cantilever displacement only in first approximation. The AFM in fact do not measure variations along $z$-axe directly through cantilever bending due to interactions with substrate but a mechanism of feedback exists. Usually for tapping mode it works maintaining the amplitude of oscillation constant during the entire scan; when the tip feels a difference of height in the sample, a piezoelectric device moves in $z$ direction to keep constant the oscillation amplitude and so the displacement of piezo is directly related to height difference.

#### Modelling Non-contact AFM

Following the argumentation of Giessibl [18], in FM-AFM the main observable is the frequency of oscillation and an expression relating frequency shift to forces acting between and sample is extremely relevant.

We can start the derivation with a simply Hamiltonian approach. An oscillating cantilever with spring constant $k$ and effective mass $m^*$ can be modelled as an harmonic oscillator forced by a piezoactuator and weakly damped by internal friction mechanisms (not air or liquid because now we consider UHV). Let $q(t)$ the distance of the cantilever tip from the sample as a function of time. $q'(t)$ is the
2.2 Operational modes

deflection of cantilever; it oscillates with amplitude $A$. The closest point to the sample is $q = d$. Thus the Hamiltonian of the system tip on cantilever is:

$$H = \frac{p^2}{2m^*} + \frac{kq'^2}{2} + V_{ts}(q), \quad (2.6)$$

where

$$p = m^* \frac{dq'(t)}{dt}.$$ 

The unperturbed motion is given by

$$q'(t) = A \cos(2\pi f_0 t), \quad (2.7)$$

with the frequency $f_0$ expressed as

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m^*}}. \quad (2.8)$$

If the gradient of the force along $z$, $k_{ts} = -\partial F_{ts}/\partial z$, is constant during oscillation cycle, the frequency shift is given by

$$\Delta f = f_0 \frac{k_{ts}}{2k}. \quad (2.9)$$

In classic experiments of FM-AFM however, $k_{ts}$ can vary by orders of magnitude during each cycle, so a perturbative approach is needed. The first derivation is due to Giessibl in 1997 [27] with a canonical perturbation theory resulting (average on one oscillation cycle):

$$\Delta f = -\frac{f_0}{kA^2} \langle F_{ts}q' \rangle. \quad (2.10)$$

Applicability of the first-order perturbation theory depends on the magnitude of perturbation, e.g. on the ratio between $V_{ts}$ and the energy of oscillating cantilever $E$. In FM-AFM typically $E$ is larger than $V_{ts}$ by at least three orders of magnitude, so first-order perturbation theory yields results with excellent precision.

An alternative approach involving Newton’s equations of motion has been developed by Dürig in 1999 and also used by Meyer et al. [14]. The equation of motion describing the system is:

$$\mu^* q'' = -kq' + F_{ts}(q'), \quad (2.11)$$

where $\mu^*$ is the effective mass and $F_{ts}$ the force between tip and sample.
2.2 Operational modes

We assume that the cantilever motion is periodic. Thus we can express deflection $q'(t)$ as a Fourier series with fundamental frequency $f$:

$$ q'(t) = \sum_{m=0}^{+\infty} a_m \cos(2\pi mf t). \quad (2.12) $$

Inserting it in 2.11, we obtain

$$ \sum_{m=0}^{+\infty} a_m[-(2\pi mf)^2 \mu^* + k] \cos(2\pi mf t) = F_{ts}(q'). \quad (2.13) $$

Now we multiply by $\cos(2\pi ft \ell)$ and we integrate:

$$ a_m[-(2\pi mf)^2 \mu^* + k] \pi (1 + \delta_{m0}) = 2\pi f \int_0^{1/f} F_{ts}(q') \cos(2\pi mf t) dt, \quad (2.14) $$

where we have used the orthogonality of angular conditions:

$$ \int_0^{2\pi} \cos(mx) \cos(lx) dx = \pi \delta_{ml}(1 + \delta_{m0}). \quad (2.15) $$

If the perturbation is weak then

$$ q'(t) \approx A \cos(2\pi ft) \quad (2.16) $$

with $f = f_0 + \Delta f$, $f_0 = (1/2\pi) \sqrt{k/\mu^*}$, and

$$ |\Delta f| << f_0. \quad (2.17) $$

At first order, the frequency shift is given by the following relation:

$$ \Delta f = -\frac{f_0^2}{kA} \int_0^{1/f_0} F_{ts}(q') \cos(2\pi f_0 t) dt 
= -\frac{f_0}{kA^2} \langle F_{ts}q' \rangle. \quad (2.18) $$

This result is equal to 2.10, obtained with Hamilton-Jacobi approach.

Meyer et al. [14] pointed out that the evaluation of the right-hand integral can be performed assuming different force laws; if the distance between tip and sample is smaller compared with tip radius, long-range interactions are dominated by the spherical tip apex. In this case simple expressions for frequency shift by electrostatic interactions $\Delta f_V$ and by van der Waals interactions $\Delta f_{vdW}$ can be obtained:

$$ \frac{\Delta f_V}{f_0 kA} = -\frac{\pi \epsilon_0 R(V_{bias} - V_{cpd})^2}{(2\pi A)^{0.5} f_0}, \quad (2.19) $$
2.2 Operational modes

\[ \frac{\Delta f_{\text{vdW}}}{f_0} = \frac{HR}{6s(2sA)^{0.5}}, \]  
\[ (2.20) \]

where \( R \) is tip radius, \( V_{\text{bias}} \) the sample bias voltage, \( V_{\text{cpd}} \) the potential difference between tip and sample at the contact, \( s \) the separation between sample and the mesoscopic part of the tip at closest approach, \( \epsilon_0 \) the vacuum dielectric constant and \( H \) the Hamaker constant of the system. These relations point out a dependence by \( A^{3/2} \) for the frequency shift, therefore Giessibl introduces a reduced frequency shift \( \gamma_{\text{freq}} \):

\[ \gamma_{\text{freq}} = \frac{\Delta f}{f} kA^{3/2}, \]  
\[ (2.21) \]

that is particularly useful to compare results obtained with different experimental parameters.

Modelling Tapping AFM

To model tapping mode AM-AFM in terms of forced and dumped harmonic oscillator a similar approach is adopted. The equation of motion for the oscillating cantilever is exactly the same as that used for non-contact AFM seen in previous section. A modelling of oscillating cantilever in tapping mode in terms of dissipated power, approach used in this PhD work, following the argumentation of Anczykowski and co-workers [28] is given.

If we assume a dynamical system in equilibrium, the conservation law states that the average energy input must be equal to average energy output. In this view, we can apply this principle to AFM, assuming that the average power coming from an external driver (e.g. the piezoelectric actuator) to the oscillating cantilever (denoted \( P_{\text{in}} \)) is equal to the sum of the average power dissipated in tip-sample interaction (\( P_{\text{ts}} \)) and the average power dissipated by several internal friction mechanisms (\( P_0 \)):

\[ \bar{P}_{\text{in}} = \bar{P}_{\text{ts}} + P_0. \]  
\[ (2.22) \]

What we are interested in is the term denoted \( \bar{P}_{\text{ts}} \), that represents the physical observable to describe the system tip-surface. In order to calculate other two terms, to properly model dynamic system, a simplified model made by a spring and two dashpots represents a good approximation in this case (see Panel (a) Fig.2.6).

The spring, characterized by elastic constant \( k \), represents the only channel through which the power coming from oscillating driver, \( z_d(t) \), can reach the moving cantilever, \( z(t) \). The power is composed by the force exerted by external driver times the velocity of the driver:

\[ P_{\text{in}} = F_d(t) \dot{z}_d(t) = k[z(t) - z_d(t)] \dot{z}_d(t). \]  
\[ (2.23) \]
2.2 Operational modes

Assuming now sinusoidally steady states at first order for driven and response, we can write

\[ z_d(t) = A_d \cos(\omega t) \tag{2.24} \]
\[ z(t) = A \cos(\omega t - \varphi) \tag{2.25} \]

with \(0 \leq \varphi \leq \pi\) and where \(A_d\) and \(A\) are oscillation amplitudes of driving piezo and the cantilever respectively and \(\omega\) is the frequency. Now we can average the power over a period of oscillation \(T = 2\pi/\omega\):

\[
\bar{P}_{in} = \frac{1}{T} \int_0^T P_{in}(t) dt = \frac{1}{2} k \omega A_d A \sin(\varphi). \tag{2.26}
\]

Figure 2.6: A rheological model to describe dynamic AFM is given. In panel a) the cantilever is modelled as a spring with elastic constant \(k\) and damping factors due to internal friction mechanisms \(\alpha_1\) and due to the presence of air or another surrounding medium \(\alpha_2\) (predominant in ambient conditions AM-AFM) are present. In panel b) all damping mechanisms are summarized in factor \(\alpha\).
This relation gives the usual information that the dissipated power reaches a maximum when the phase shift $\varphi$ is equal to ninety degrees. The simple rheological model depicted in Fig.2.6 assumes that all damping mechanisms are well represented by coefficients $\alpha_1$ and $\alpha_2$. If we consider AFM in UHV conditions, the dominant damping is due to intrinsic friction, due for example to relative motion of the tip with respect to the cantilever base and the instantaneous dissipated power through this channel is

$$P_{01} = |F_{01}(t)\dot{z}(t)| = |\alpha_1 [\dot{z}(t) - \dot{z}_d(t)]\dot{z}(t)|.$$  \hspace{1cm} (2.27)

However if AFM is running in air conditions, an additional damping effect has to be considered. The damping due to the motion of cantilever in surrounding media is the dominant mechanism and the instantaneous dissipated power is given by

$$P_{02} = |F_{02}(t)\dot{z}(t)| = \alpha_2 \dot{z}^2(t).$$  \hspace{1cm} (2.28)

To obtain the the average power it is necessary to integrate equations (2.27) and (2.28) over an oscillation period $T$:

$$\bar{P}_{01} = \frac{1}{T} \int_0^T P_{01}(t)dt =$$

$$= \frac{1}{\pi} \frac{\alpha_1 \omega^2 A}{\alpha_1} \left\{ [A - A_d \cos(\varphi)] \arcsin \left[ \frac{A - A_d \cos(\varphi)}{\sqrt{A^2 + A_d^2 - 2AA_d \cos(\varphi)}} \right] + A_d \sin(\varphi) \right\}$$

$$+ A_d \sin(\varphi) \right\}$$  \hspace{1cm} (2.29)

$$\bar{P}_{02} = \frac{1}{T} \int_0^T P_{02}(t)dt = \frac{1}{2} \alpha_2 \omega^2 A^2$$  \hspace{1cm} (2.30)

Thanks to the aspect that large part of cantilevers has a quality factor of at least several hundreds, we can assume the oscillation amplitude $A$ much more greater than $A_d$, so we can reach for equation (2.29) a form similar to equation (2.30). Then it is possible to write a general expression for average dissipated power by friction:

$$\bar{P}_0 = \frac{1}{2} \alpha \omega^2 A^2$$  \hspace{1cm} (2.31)

with $\alpha = \alpha_1 + \alpha_2$ denotes the overall damping coefficient. We can correlate this factor with measurable physical quantities like cantilever quality factor $Q$, frequency $\omega_0$ and elastic constant $k$ through the following relation:

$$\alpha = \frac{k}{Q \omega_0}.$$  \hspace{1cm} (2.32)
2.2 Operational modes

Now we can substitute each term in equation (2.22) obtaining

\[ \bar{P}_{ts} = \bar{P}_{in} - \bar{P}_0 = \frac{1}{2} k \omega Q \left[ QA_d A \sin(\varphi) - A^2 \frac{\omega}{\omega_0} \right]. \]  \hspace{1cm} (2.33)

It is important to note that no assumptions have been made so far, with exception of sinusoidal steady states. Equation (2.33) is valid for several AFM dynamic modes. The correctness of this model and of the assumption of neglecting high harmonic contributions has been positively tested comparing the analytical behaviour of force and energy dissipation curves as a function of tip-sample separation with dedicated experimental tests and with numerical results obtained with standard force model [29] [30] [31]. Nowadays this approach is widely used to obtain quantitative information by Dynamic AFM like for example the force distribution maps [32].

In FM-AFM, dynamic mode in UHV conditions for example, Thus the oscillation frequency \( \omega \) changes due to tipsample interaction while at the same time the oscillation amplitude \( A \) is kept constant by adjusting the drive amplitude \( A_d \). By measuring these quantities one can apply equation (2.33) to determine the average power dissipation related to tipsample interaction.

In ambient conditions tapping mode (AM-AFM) the cantilever is excited by a piezoelectric actuator at fixed frequency \( \omega \) and with constant drive amplitude \( A_d \), when the phase shift \( \varphi \) and oscillation amplitude \( A \) can vary as the tip interacts with surface. In resonance conditions \( \omega = \omega_0 \), equation (2.33) can be further simplified, considering that the free oscillation amplitude (meaning the amplitude of cantilever oscillation far from the sample) \( A_0 = QA_d \):

\[ \bar{P}_{ts} = \frac{1}{2} \frac{k A \omega_0}{Q} [A_0 \sin(\varphi) - A]. \]  \hspace{1cm} (2.34)

In terms of dissipated energy per cycle in tip-sample interaction:

\[ \bar{E} = \frac{\pi k A}{Q} [A_0 \sin(\varphi) - A]. \]  \hspace{1cm} (2.35)

Equations (2.34) and (2.35) imply that if the oscillation amplitude \( A \) is kept constant by a feedback loop, like in common tapping mode, simultaneously acquired phase data can be interpreted in terms of energy dissipation.
Chapter 3

Understanding friction using nanoclusters

The fundamental comprehension of the origin of friction at atomic-scale is a formidable still open scientific problem and in recent years many efforts have been directed towards this direction. An in-depth knowledge of physical mechanisms of friction at several length scale is crucial for the optimization of materials and processes in a wide variety of technological applications. Friction for example is decisive for the lifetime of any equipment with mutually mobile parts, such as micro and nano devices (MEMS, NEMS, etc.).

In the following sections a description of the physical system that has been studied during this PhD work and the new experimental procedure adopted to investigate some friction properties at nanoscale will be given. In the last section we will spend few words about some technical aspects of the extremely delicate process of calibration.

3.1 Scientific problem: friction vs contact

A central question to be considered when an experiment or a simulation on friction problems is thought about is represented by the dependence of friction force $F_f$ on contact area $A_{contact}$, as Schwarz and co-workers pointed out [5] [33] [34].

Macroscopically, applicability of Amontons’ law $F_f = \mu F_l$, where $F_l$ is the external load and $\mu$ the friction coefficient, is well-known. Since $\mu$ is considered as a constant in good approximation, it follows that friction is independent on apparent contact area, as we have already seen in the Chapter 1. If however we perform a transition from macroscopic to microscopic world, two different scenarios are expected, depending on exact conditions of contact:
1. Clean surfaces down to atomic scale (no adsorbed third bodies). In these conditions, typical of Ultra High Vacuum (UHV) experiments, there are no molecules in the interface of the two sliding surfaces and so an effect called *structural lubricity* (originally called superlubricity) can occur. This particular phenomenon takes its origin from the reduction of shear stress $\tau_c = F_f/A_{\text{contact}}$ (referring to equation 1.5) on atomically flat surfaces due to a reduction of potential barrier between stable states caused by lattice mismatch.

This effect holds only under the hypothesis that the stiffness of sliding surfaces is high enough to consider them as rigid bodies. If this assumption cannot be applied then an energy dissipation through elastic deformations can occur.

2. Adsorbed layers between sliding bodies. In this case friction is expected to change dramatically and Amontons law is verified.

Looking in details these two points, a simple theoretical model to depict the friction scenario at the microscopic scales has been given by Müser and colleagues [35]. They have modelled interaction between two surfaces by an energy penalty that increases exponentially with the degree of surface overlap. The resulting static friction is proportional to the load, in accordance with Amontons laws. However, the friction coefficient between bare surfaces vanishes as the area of individual contacts grows, except in the rare case of *commensurate* surfaces. Moreover they have shown that introducing mobile molecules, like for example hydrocarbons, water and so on, into the interface between incommensurate or disordered surfaces yields a value of friction coefficient that is independent of contact size and load. This naturally leads to Amontons laws for any distribution of contacts.

In the model carried on by Müser the energy penalty $V_{ww}$ that two surfaces have to “pay” when they begin to overlap can be written as an integral over the contact area $A$, function of mean height $z_t$ and the lateral position $x_t$:

$$V_{ww}(x_t, z_t) = \epsilon \int d^2x e^{-\left[z_t + \delta z_t (x - x_t) - \delta z_b (x)\right]/\xi}, \quad (3.1)$$

where $\xi$ and $\epsilon$ represent the length and energy per unit area of the interaction. This integral depends only on $x_t$ and can be expressed as an effective shift in the mean wall separation by $\Delta z(x_t)$:

$$V_{ww}(x_t, z_t) = \epsilon A e^{-\left[z_t + \Delta z(x_t)\right]/\xi}, \quad (3.2)$$

It can be noted that because of the simple form of $V_{ww}$, the ratio of friction to normal load is independent of load. The static friction coefficient corresponds to
the maximum of this ratio, taken along the applied force direction:

\[ \mu_s = \max \left[ \frac{\partial}{\partial x_t} \Delta z(x_t) \right]. \] (3.3)

The effect of the contact area on the friction coefficient \( \mu_s \) is most easily seen by making a cumulant expansion of equation 3.1. Noting that \( \Delta z \) is proportional to the mean-squared difference between \( \delta z_t \) and \( \delta z_b \), only the contribution from the cross product contributes to the variation of \( \Delta z \) with respect to \( x_t \), yielding

\[ \mu_s \approx \max_{x_t} \frac{1}{\xi} \sum_k i k_x \delta \tilde{z}_b(k) \delta \tilde{z}^*_t(k) e^{ik \cdot x}, \] (3.4)

where \( \delta \tilde{z}_{b,t} \) are the 2-Fourier transforms of \( \delta z_{b,t} \).

Müser et al. pointed out that equation 3.4 implies that: (i) if the two surfaces are crystalline and commensurate, then \( \delta z_t \) and \( \delta z_b \) share a common periodicity. The corresponding Bragg peaks in their Fourier transforms lead to a friction coefficient \( \mu_s \) that is area-independent. (ii) If the surfaces are identical, all Bragg peaks contribute and \( \mu_s \) is largest; if the surfaces are not identical, \( \mu_s \) decreases exponentially with the length of common period. (iii) as a consequence of (ii), \( \mu_s \) vanishes completely for infinite incommensurate contacts. (iv) For two disordered but smooth surfaces \( \delta \tilde{z}_t(k) \) and \( \delta \tilde{z}_b(k) \) have rings of diffuse scattering that overlap. For interfaces with contact-area independent corrugation \( \langle \delta z^2 \rangle \), one can immediately conclude that \( \mu_s \propto A^{-1/2} \).

In order to incorporate also mobile atoms, eventually present between surfaces, into this quantitative model, authors presumed that wherever a mobile atom sits in the interface, the effective distance between the top and the bottom wall is reduced by the diameter \( d \) of the mobile atom, and for simplicity they assumed a direct wall-wall interaction screening by mobile layers, so interactions between mobile atoms can be neglected. With detailed molecular dynamics simulations, Müser and co-workers have shown that as long as the temperature is small compared to the energy barrier for diffusion between the surfaces, atoms will sit near local energy minima, usually corresponding to (+ +) configuration in the Fig. 3.1.
A relevant result from the authors is that if all atoms sit at (+ +) positions, the response to a lateral displacement is an opposing force that is linear in the normal load \(L\) and independent of the apparent area of contact. So mobile atoms in the interface lead to Amontons laws with a not-vanishing coefficient of friction, independent of surface area and load for any contact geometry.

In the last 20-30 years a large number of experiments focused on micro and nano aspects of friction have been carried out, thanks to the growth of several dedicated tools such as Surface Force Apparatus (SFA), Quartz Crystal Microbalance (QCM) and of course Friction Force Microscope (FFM), that is essentially an AFM modified to allow the detection of lateral forces. The latter approach is based on a nanocontact represented by a tip sliding on an arbitrarily rough surface.

Few years ago Dienwiebel and co-workers [36] provided an experimental evidence of structural lubricity of graphite, developing a novel friction force microscope, which allowed quantitative tracking of forces on the scanning tip in three directions, with a resolution in the lateral forces down to 15 pN. In fact in scanning probe microscopy experiments on graphite, it is known that thin, flat flakes of graphite, parallel to the natural lattice planes of graphite, are frequently transferred to the scanning tip, thus providing a multiatom contact. Their apparatus was composed by a dedicated friction force sensor, called Tribolever (see Fig.3.2), that combines low and symmetric spring constants in the two lateral directions with a high stiffness in the normal, in order to avoid “snap to contact”. They determined the lateral spring constants of the Tribolever to be \(k_{T ribo lever}^{x,y}\) equal to \(5.75 \pm 0.15\) N/m and the normal spring constant \(k_{T ribo lever}^{z}\) of \(26 \pm 1\) N/m. A tungsten tip was glued into the Tribolever using silver epoxy, such that it extended about 50 to 60 \(\mu\)m out of the device. The displacements of the Tribolever tip are monitored using four all-glass-fiber interferometers.

With Tribolever apparatus Dienwiebel and colleagues have performed FFM experiments on Highly Oriented Pyrolytic Graphite samples in nitrogen atmosphere. In contrast to a conventional AFM cantilever, with the Tribolever it is possible...
3.1 Scientific problem: friction vs contact

Figure 3.2: Schematic picture representing the microfabricated silicon force sensor, the Tribolover. It is composed by four glass fibers to detect three dimensional motion of the scanning tungsten tip, placed in the center. The visible pyramid acts as mirrors for interferometers. Reprinted figure with permission from [36]. Copyright 2004 by the American Physical Society.

to choose any sliding direction in the measurement. One forward scan line and the subsequent reverse scan line together form a closed hysteresis loop, that is often referred to as the “friction loop”. Authors have rotated the sample in small steps with respect to the tip and, for each orientation, they have measured the lateral forces at a range of constant normal forces between +25 nN and pull-off (typically -22 nN). Results are summarized in Fig.3.3.

In Panel (a) it is clearly visible atomic stick-slip behaviour in lateral force. The area enclosed in the complete loop corresponds to the energy dissipated irreversibly during the loop, and the area divided by twice the loop width is the average dissipative friction force, experienced by the tip, equal to 203 ± 20 pN. In Panel (b) the corresponding lateral force map in the sliding direction is reported.

Panels (c) and (d) show friction force measurements performed in the same conditions of Panels (a) and (b) but with a rotation of the sample equal to 12° clockwise around a normal axe. The rotation caused the average friction force to reduce by more than one order of magnitude to 15.2 ± 15 pN. It can be useful to note that this kind of variations are completely reversible. On Panel (d) in particular the ultra-low lateral force reflects a regular variations with the periodicity of graphite.

On Panels (e) and (f) authors have performed identical measurements with a rotation of the sample of 22° anticlockwise from the initial position. Particularly interesting are results shown on Fig.3.4.

In this picture the average friction forces are measured over a 100° range of substrate rotation angles. What is immediately clear is the presence of two narrow angular regions with high friction, separated by a wide angular interval with nearly
Figure 3.3: Friction loops (black, forward; grey, reverse) and lateral force images (forward), measured along the scanning direction at tip-surface orientation angles $\phi$ of 60° (a), (b); 72° (c), (d); 38° (e), (f). Normal force $F_N = 18$ nN (a – d) and 30.1 nN (e), (f). Grey scale 590 pN (b), 270 pN (d), 26 pN (f). Image size 3 nm × 3 nm. Reprinted figure with permission from [36]. Copyright 2004 by the American Physical Society.

Figure 3.4: Friction loops (black, forward; grey, reverse) and lateral force images (forward), measured along the scanning direction at tip-surface orientation angles $\phi$ of 60° (a), (b); 72° (c), (d); 38° (e), (f). Normal force $F_N = 18$ nN (a – d) and 30.1 nN (e), (f). Grey scale 590 pN (b), 270 pN (d), 26 pN (f). Image size 3 nm × 3 nm. Reprinted figure with permission from [36]. Copyright 2004 by the American Physical Society.
zero friction. The distance between the two friction peaks is $61^\circ \pm 2^\circ$, which corresponds well with the $60^\circ$ symmetry of individual atomic layers in the graphite lattice.

Dienwiebel and co-workers provided also strong arguments that the observed structural lubricity has taken place between the graphite substrate and a graphite flake, attached to the tip. The presence of a flake at the interface between the tip and the substrate can naturally explain the strong orientation dependence of the friction. In fact at the two orientations corresponding to the friction peaks, the flake and substrate lattices have been perfectly aligned, while they have been incommensurate for the intermediate angles. Unfortunately SEM images after FFM experiments were not able to confirm directly the presence of graphite layer on the tip (principally because of the rapid removal of the amorphous layer by electron beam), although high-resolution TEM measurements showed clearly that the tungsten tip had a radius of about 80 nm and was covered with a smooth amorphous layer of 7 nm thick tungsten oxide.

From the widths of peaks, authors have been able to estimate a flake diameter of 7 to 12 lattice spacings. In conclusion it can be assumed that excellent friction properties of graphite and more in general of diamond-like carbon coatings might be caused by superlubric graphite contacts. Nevertheless, for sufficiently large contacts, superlubricity might break down, as the two lattices are not perfectly rigid, and a network of misfit dislocations should form between the two, the motion of which will dissipate energy.

Therefore it is extremely evident that the main problem coming out from FFM approach is represented by the accurate determination of real contact area of the nanojunction (e.g. the tip) that can vary dramatically during the experiment, and also the reproducibility of measurements to ensure an adequate statistics of possible area-dependent effects. So far many studies (see for example [37] [38]) have been performed indirectly, determining $F_f$ through the measure of the applied load $F_l$, thanks to the elastic deformability of contact area as a function of load. In most works it has been found a strong no-linearity in relation $F_f$ versus $A_{\text{contact}}$, in contrast with macroscopic behaviour [39] [40].

Summarizing the above discussion, it is immediately visible how the precise determination, or more in general the control of the area at the contact is crucial to understand friction properties. While contacts in SFA experiments are too much large (typically ten thousands of squared microns), with FFM apparata it is possible to reach contacts of some tens of squared nanometers. However FFM does not allow to measure directly the true contact area of sliding and we need a specific contact geometry model. To try to solve these problems, a very promising approach consists in changing the point of view; instead of investigating tip-substrate systems, as in SFA or in FFM experiments, we can try to probe frictional properties of particle-substrate systems.
3.2 Physical system in exam

One way to realize this is depositing or growing nanoparticles on atomically flat surfaces and pushing them with an AFM tip, measuring friction and/or energy dissipation during translation. This approach presents some relevant advantages with respect to traditional friction force microscopy (as depicted in Fig.3.5):

Figure 3.5: Schematic representation of the analysed interface during FFM measurements (Panel a) and cluster manipulation (Panel b). In the first case usually only the substrate can be properly cleaned and characterized while the tip is amorphous and difficult to maintain in stable conditions. In the second case the contact region can be controlled on either side using well established deposition or growing techniques for both the cluster and the surface. The AFM tip is ideally disentangled from the physical system in exam [41].

1. The contact area is well defined and it usually does not change during the experiments as long as the particle is not plastically deformed (we are able to see this eventually present effect directly from the image). On the contrary, in FFM experiments we need to know exactly the shape of the tip and we require to make assumptions based on the specific contact model that we apply.

2. Depending simply on the size of nanocluster, it is possible to vary the contact area and so to study a wide range of contact configurations, from few squared nanometers to several hundreds of squared nanometers.
3. Also a large number of different combinations of materials for particle and substrate are possible.

Figure 3.6: SEM image (600 nm \times 600 nm) of gold nanoclusters of 13 nm of nominal diameter deposited on silicon substrate. Reprinted figure with permission from [42]. Copyright 2008 by IOP.

Figure 3.7: TEM image (115 000 X, 200 nm \times 140 nm) of gold nanoclusters of 24 nm of nominal diameter. Reprinted figure with permission from [3]. Copyright by Springer.

Following this point of view, during all experiments concerning this work of thesis we have employed gold spherical nanoclusters of nominal diameters of 13 \pm 2 nm, 24 \pm 3 nm and 42 \pm 4 nm, provided by a chemistry group from CNRS - Mulhouse (F) with whom we have collaborated. Clusters have been chemically synthesized in a colloidal suspension starting from an aqueous solution of tetra-chloroauric (III) acid hydrate (HAuCl$_4$, 3H$_2$O). The detailed procedure of synthesis can be found elsewhere [43]. The heights of clusters have been measured by
AFM, while lateral dimensions distribution has been checked by SEM and TEM images (see Fig.3.6 and Fig.3.7). These different measurements of shape parameters are consistent, so it is possible to conclude that clusters are almost spherical.

Particles have been deposited on clean silicon substrates (Si(100) with native oxide) and on High Oriented Pyrolitic Graphite (HOPG). Gold clusters composed by thousands of atoms represent an appealing system for their intrinsic physical properties; they are in fact physically and chemically inert and they represent a system characterized by a well-known high mobility, especially on HOPG, resulting from both theoretical and experimental works [44] [45].

Some technical details about the experimental procedure will be given in the following section.

### 3.3 Experimental procedure

The experimental key tool used for our measurements is the Atomic Force Microscope (AFM), that is able to push nanoparticles on the substrate thanks to its tip that has typical dimensions at the apex comparable to dimensions of the cluster. As we will see in details in the next chapter, some groups [46] [47] manipulate antimony islands evaporated on the surface of mica and graphite. This approach can lead to very clean and controlled conditions of the experiment and with such configuration is possible to measure in direct way the friction force. Nevertheless particles having an overall dimension comparable or smaller than the typical tip apex cannot be easily addressed because aligning the sliding path of the cluster to the torsional movement of the cantilever may result a very critical issue. Moreover with deposition techniques such as evaporation the shape of clusters is not well controlled thus the resulting distribution of sizes is spread in a wide range.

Recently Dietzel and colleagues [48] have performed very sensitive experiments of manipulation by contact mode AFM of antimony and gold nanoparticles deposited of freshly cleaved graphite. They have prepared clusters by thermal evaporation on HOPG cleaved under UHV conditions and they have optimized parameters of deposition to reach lateral dimensions for particles ranging from 50 nm up to few 100 nm. SEM and TEM images in fact confirmed that nanoparticles grew flat on the graphite substrate. One common aspect to all nanoparticle approaches, commonly used for mere positioning purpose or for nanofriction studies, is that the tip has always been positioned at the side of the nanoparticle during the pushing process. However, when pushing a nanoparticle from the side, it often occurs that the particle is moving perpendicular to the intended tip path. Then authors have tested an alternative manipulation technique based on positioning the tip on top of a nanoparticle (see Fig.3.8).

The relevant result obtained by Dietzel et al. is that the tip on top manip-
3.3 Experimental procedure

Figure 3.8: AFM used in contact mode to push the cluster by the side (Panel a) or to drag it with the tip placed on top of the cluster (Panel b). Friction force is measured from the torsional bending of the cantilever as in standard Friction Force Microscopy (FFM). Usually this method is applied to clusters having lateral size much larger with respect to the curvature radius of the tip.

ulation is mostly suitable for analyzing relatively small antimony nanoparticles \( A_{\text{contact}} < 10^5 \text{ nm}^2 \), but it may even fail completely for larger nanoparticles, since this mode relies on the condition that the tip remains stuck on top of the particle during pushing. Only if the tip-particle friction is higher than the friction between particle and substrate, this manipulation condition is fulfilled. On the other hand, pushing nanoparticles from the side allows a large range of particle sizes to be measured. While both approaches are basically suitable for small nanoparticles with lateral dimensions of few tens of nanometers, in their experiments only the tip on side mode allowed manipulating large nanoparticles with diameters in the range of microns. Moreover, measurements in contact mode have been shown very clearly the limits of this approach in terms of dimensions of manipulated particles.

We use AFM in an “unconventional” way, performing measurements of dissipated energy on a distribution of nanoclusters both in air and in controlled atmosphere (nitrogen flux, room temperature, relative humidity RH = 40%) with the microscope operating in tapping mode with amplitude modulation feedback (AM-AFM, Fig.3.9). The periodic tip-cluster interaction, typical of AM-AFM, is able, as it will be proved in this PhD work, to induce depinning events with particles having comparable dimensions with respect to tip apex and to produce smooth cluster movements along a precise direction. Nevertheless the connection of the corresponding energy dissipation signal to the friction forces acting on the system cluster-surface requires an elaborate modelling.

As we have seen in Chapter 2, dynamic AFM is widely used for imaging
3.3 Experimental procedure

Figure 3.9: Atomic Force Microscope with Amplitude Modulation feedback. The tip oscillates with a fixed peak to peak amplitude $2A$. Periodic interactions between tip and cluster induce depinning of particles having comparable dimensions with respect to tip apex and produce smooth cluster movements. With our method depinning and induced movements may be correlated to the energy dissipation signal reconstructed from phase shift measurements through relation 3.5.

on soft and hard materials both in air and liquid environment. In tapping operational mode the cantilever is driven by an oscillating piezo placed at the base of the beam. The frequency is held fixed at or close to the cantilever resonance, so the tip oscillation amplitude becomes relatively large and linearly depends on the amplitude of driver movement. Approaching the substrate, tip oscillations are damped because of the interaction with surface and the damping effect depends on the separation distance. Introducing a feedback loop, which acts on the separation between cantilever base and surface, and keeping reduced but constant the tip oscillation amplitude while scanning over the sample, a topographic map is obtained. The feedback is set in such a way that tip at the bottom of each oscillation cycle interacts with the substrate both in the attractive and eventually in repulsive regime. Even if this method is widely used on delicate samples also, during the imaging of loosely bonded nano-objects, unintended particle translations are often obtained because feedback activation requires always some interaction between tip and substrate. These movements are uncontrolled because the signal optimization is focused to obtain high quality images. Nevertheless if the interaction strength is carefully tuned, selected detachments and controlled movements of nanoclusters may be achieved.

We use a commercial atomic force microscope mod. ENVIROSCOPE by VEECO (see Fig.3.10) and cantilevers with nominal spring constants between 5 and 50 N/m.

Our experimental procedure is based firstly on a deposition of nanoparticles by droplet on freshly cleaved graphite and silicon dioxide. Then we select an area of about one squared microns and we perform an image of the resulting distribution with optimized AFM parameters (we call it imaging step in the following). We are
3.3 Experimental procedure

Figure 3.10: The instrument used for this PhD experiments: a commercial Atomic Force Microscope by VEECO (mod. ENVIROSCOPE). It composed by a chamber in which measurements in controlled atmosphere or in vacuum can be performed. The blue apparatus is the gauge controller. All the system is mounted on a special compressed-air table to insulate it from the ground.

interested in the evaluation of dissipated energy between tip and sample through the measurement of phase shift signal, according to equation 2.35, that we report here for clarity:

\[ E = \frac{\pi k A}{Q} \left[ A_0 \sin(\varphi) - A \right]. \]  

(3.5)

Details about the exact procedure to evaluate dissipated energy from measured parameters will be discussed further. Once we have detected a suitable area, with a sufficient number of well separated single clusters and no impurities, we perform an imaging with intentionally larger free oscillation amplitude \( A_0 \) (we will refer to this as manipulation step), giving energy to the system; if this energy is higher than a characteristic threshold of the system, gold nanoclusters detachments can occur.

Thanks to the equation 3.5, we have estimated the theoretical energy that we are able to provide to the system through interaction between tip and sample. As an example, in Fig.3.11 we have plotted the dissipated energy \( E \) as a function of \( A_0 \) and the phase shift \( \varphi \), setting all parameters with values that can be easily accessed with our apparatus.

In particular the first value of \( A_0 \) corresponds to the imaging step and the fi-
3.3 Experimental procedure

Figure 3.11: Plot of the function \( E = E(A_0, \varphi) \) for 13 nm gold nanoclusters on HOPG. For this particular experiment we have set all parameters with the following values: \( k = 5 \text{ N/m}, \; Q = 320, \; A = 13 \times 10^{-9} \text{ m} \). Free oscillation amplitude \( A_0 \) is varied from 18 and \( 24 \times 10^{-9} \text{ m} \), that are extremal values used for all measurements of 13 nm particles. Phase shift \( \varphi \) is varied from \( \pi/4 \) and \( (3/4)\pi \). The maximum energy that we are able to provide to the system is ranged between 20 and 43 eV. It is clear from the color scale that, increasing \( A_0 \), energy available for depinning increases too.

The maximum one is the highest value of oscillation amplitude that we have used for 13 nm nanoparticles manipulation. It is immediately clear from the picture that increasing free oscillation amplitude \( A_0 \), the energy that we give to the system increases too. Considering the maximum of energy (that corresponds to the condition \( \varphi = \pi/2 + 2k\pi \), with \( k \in \mathbb{Z} \)) we have evaluated a theoretical dissipation between 20 and 43 eV, that results compatible with typical values of gold/carbon thermal activation energy [49] [50] rescaled for our cluster dimensions, as we will see in the following chapter. The increasing of the available energy is related to two parameters. The first one is represented by the elastic constant \( k \), that we can vary by choosing different cantilevers at the beginning of the measurement (in this case as a consequence also quality factor \( Q \) will be changed). The other parameter is the oscillation amplitude, that can be varied continuously during the experiment, easily.

Coming back now to the experimental method, between two manipulation
3.3 Experimental procedure

Steps there is always an imaging step to check new positions of particles after movements. A typical set of imaging-manipulation alternation is reported in Fig.3.12. This sequence is repeated several times, slowly increasing the free oscillation amplitude, until all single particles have detached. We always acquire simultaneously the topographic signal and the phase signal and so we are able to evaluate, according to equation 3.5, the dissipated energy per cycle on each cluster.

![Figure 3.12: In this picture a typical sequence imaging-manipulation-imaging for 42 nm particles on HOPG is presented. In Panel a) it is represented an imaging of a one squared micron with four single particles, one double particle (on the graphite edge, in the left upper corner) and a cluster. The not spherical shape of particles reflects the shape of tip. In Panel b) particles named 1 and 2 are depinned and start to move excited by the tip (manipulation step). In Panel c) the following imaging step is presented, with the previous positions of 1 and 2 in white circles. We can find the particle 1 in a different position and we note that particle 2 has been pushed by the tip out of scan margins and so it is not longer visible. Reprinted figure with permission from [3]. Copyright by Springer.](image)

In our setup, the oscillating cantilever scans one line of the image typically in one second from the left side to the right side (trace). In the meanwhile the cantilever also goes forward in the up-down direction (slow scan direction, solid red arrow in Fig.3.13) of a minimum step of 2 nm, so the second line in the opposite direction (retrace) is not perfectly parallel to the trace; the result is a zig-zag pattern of scan (dash yellow arrow). The left-right direction is commonly called fast scan direction.

To understand in details the great importance of phase signal, we refer to Fig.3.14. In Panel a) it is reported a typical imaging step of an area equal to one squared micron with some single and double particles. This is a distribution of particles of 24 nm of nominal diameter on graphite. In Panel b) the associated phase image, acquired simultaneously with topographic image, is reported.

3.3 Experimental procedure

Figure 3.13: Deposition of 24 nm particles on graphite. This picture represents the AFM mode of scan; the blue arrow is oriented along the slow scan direction and the yellow arrow shows the resulting zig-zag pattern. The step of scan in the slow scan direction is at least 2 nm. Reprinted figure with permission from [3]. Copyright by Springer.

The phase shift measured on particles is slightly different from that measured on the surface, so there is not an high contrast for particles in the image. This phenomenon is due to the parameters setting, optimized for simple imaging purpose, which means minimum tip-sample interaction. In Panels c) and d) the same area is reported but it has been scanned with an intentionally large oscillation amplitude (manipulation step) and some detachments occur. The corresponding associated phase image shows an high contrast of the particles with respect to the substrate: this is an indication that different dissipation mechanisms occur on the clusters with respect to the graphite because of differences in material properties or peculiar characteristics of gold-graphite interfaces.

Now we like to briefly describe the particular mechanism that allows inducing and controlling nanoclusters movements with the AFM tip (readers are referred to [51] [52] for more details). Initially, a small increase of $A_0$ (in equation 3.5) corresponds to a dissipation localized on the cluster but the cluster itself remains stable. Further increasing $A_0$ the dissipation increases too and detachments events followed by small displacements may occur. Moreover, reducing $A_0$ stable imaging can be retrieved, while maintaining a large $A_0$ a series of pinning and depinning events is obtained.

From the analysis of statistics composed by a large number of events, made by hundreds of manipulation sequences, we have found that induced cluster movements are usually directed towards the slow scan direction (solid red arrow in Fig.3.13). Moreover we have identified two kinds of possible movements for clus-
3.3 Experimental procedure

Figure 3.14: An imaging step with topographic (Panel a)) and its associated phase (Panel b)) image are presented for a deposition of 24 nm particles on graphite. In Panels c) and d) is visible a manipulation step of the same area. What is immediately visible is the relevant difference of contrast in the two phase images: when we perform a simple imaging we give energy to the system just to support the feedback loop and the dissipation effects are not so different from clusters and substrate. Increasing the input energy to the system, the contrast in the phase image increases too, revealing the difference in the dissipation mechanism of the two materials (gold graphite). In the manipulation step few movements of particles are clearly visible. Reprinted figure with permission from [3]. Copyright by Springer.

ters. On one hand, after the detachment, the particle can jump for several nanometers covering a distance equal also to 20 times the typical AFM scan which is 2 nm. On the other hand, it can move with steps smaller or comparable to the AFM lines separation. In the latter case we are able to push and follow the moving cluster step by step, so that the overall movement appears as a continuum trajectory like in Fig.3.14 and Fig.3.15. Generally however we have observed that the largest part of movements belonged to step by step class.

The mechanism can be described as follow. The tip may pass over the particle several times before the depinning (principally it depends on the size of the particle and the step of cantilever progress [52]), so the topographic and phase shape of the cluster are perfectly visible until the detachment occurs. Then the particle moves (usually towards the slow scan direction) and if the jump is smaller
or comparable to the AFM lines separation, the same mechanism (partial imaging and detachment) is repeated during following scan lines. Finally the sum of all these little steps gives rise to a visible trace, like in Fig.3.15.

![Topographic image](image1.png) ![Phase image](image2.png)

Figure 3.15: A detailed trace of a moving particle in the topographic and in the phase image is reported. Especially on the left picture it is clearly visible the succession of steps by which the trajectories are composed. Reprinted figure with permission from [3]. Copyright by Springer.

**From phase signal to dissipated energy**

Now we come back to the problem of transforming the phase shift signal into an energy dissipation measurements according to equation 3.5, focusing our attention on each physical observable of the experiment. The parameter $k$ in the relation is the elastic constant of cantilever, calculated with the standard method developed by Sader et al. [53] for every cantilever that we have used. $Q$ is the cantilever quality factor, that has been regularly monitored during each measurement sequence. The oscillation amplitude in volts from the detector should be transformed in the real one in nanometers through a sensitive calibration, discussed in details in the following section.

The parameter $A$ in the equation 3.5 represents the reduced oscillation amplitude, usually called *Amplitude Setpoint*, which is optimized during the first imaging step to obtain a good image without perturbing the particles. It is keep fixed during all steps of the measurement. We have already seen that $A_0$ is the free
oscillation amplitude e.g. the cantilever oscillation amplitude measured far from
the surface. During every simple imaging step \( A_0 \) is keep fixed, while in a manip-
ulation step \( A_0 \) is carefully increased. Having measured and calibrated all these
parameters we are able to transform every phase image into an energy image, and
to evaluate quantitatively the dissipation on each cluster. As an example, Fig.3.16
represents the transformation of Panel d) of Fig.3.14. As one can see clearly in
this map the dissipated energy [eV] is higher (bright colors) on particles with re-
spect to the substrate. In particular sliding particles produce visible tracks (on
center and on bottom right corner) showing the higher and more uniform energy
dissipation signal.

Figure 3.16: A transformation of the manipulation step of Fig.3.14 (Panels c) an
d d)) into a dissipated energy image is presented. Yellow circles highlight depinning events. As
one can note, the higher dissipation occurs on particles. Reprinted figure with permission
from [3]. Copyright by Springer.

Looking in details the topography and the energy map of a single trajectory
(Fig.3.17) we are able to better understand the mechanism below cluster manipu-
lation.

From the topography image (on Panel a)) we can identify two regions: the
first one corresponds to the beginning of the scan, in which the particle is cor-
rectly imaged. In other words it remains pinned at least during three consecutive
scan line. Then the first detachment occurs (dashed line). Subsequently the parti-
3.4 Calibration method

We have seen in the previous section that it is possible to evaluate dissipated energy per cycle of oscillation starting from the measurement of phase shift signal and the oscillation amplitudes, according to equation 3.5. Thus is crucial the precise determination of all parameters, both measured and/or calculated, that are present in the relation. In particular it is important to convert the Amplitude Setpoint $A$ and the free amplitude oscillation $A_0$, that are recorded by the detector as a signal in Volt into the corresponding value in nanometer.

Figure 3.17: Topography (Panel a)) and energy dissipation image (Panel b)) in a typical manipulation step. The particle, initially pinned, starts its displacement (dashed line) and gives raise of a path up and right long about 250 nm. During all the trajectory the energy dissipation profile remains almost uniform and centered on values equal to that measured on the initial particle pinned position. Reprinted figure with permission from [3]. Copyright by Springer.

cle starts following a long path of about 250 nm up and right and it likely happens that along every scan line one (or more) detachment events occur. This trajectory identifies the second region. From the dissipation image (on Panel b)) we note that energy profile does not show any particular difference between the first and the second region. This leads to the conclusion that phase signal can give information about energy dissipation on the cluster in the pinned position and not on cluster sliding under dynamic friction. This behaviour is in agreement with the description consisting of a succession of pinning and depinning events discussed before.
The parameter $k$ represents the elastic constant of cantilever. It is calculated for each cantilever that we have used, adopting the standard method developed ten years ago by Sader et al. [53]. This approach is based on the evaluation of the length and the width of cantilever, easily measurable by optical microscope. The cantilever thickness enters in the calibration procedure in terms of drive frequency and quality factor $Q$.

To convert the signal in tension [V] into a length [nm] we need to evaluate the sensitivity coefficient, that we will call $\beta$, defined as

$$A = \beta V.$$  \hfill (3.6)

The coefficient $\beta$ is obtained from the slope of the experimental curve $V$ versus vertical position $z$, approaching the oscillating cantilever to the surface (for few details see the Fig.3.18 and its caption). For simplicity so far we have always referred to $A$ as Amplitude Setpoint, being it the analogue term of $V$ in nanometers. Thus coefficient $\beta$ is calculated trough 3.6.

![Figure 3.18: In this picture a standard curve Amplitude [V] versus $z$ displacement [nm] is presented. The size of the ramp in $z$ direction for this particular case is 40 nm. As $z$ increases, the tip approaches to the surface and the amplitude decreases linearly with the distance from the substrate. Parameter $\beta$ is the inverse of the angular coefficient of the linear fit (in green) of approaching region. For this calibration $\beta \approx 16 \times 10^{-9}$ m/V. It is interesting to note that, when the tip is close to the surface, the so-called jump to contact occurs, with a rapid increasing of curve slope.](image)
For free oscillation amplitude $A_0$ we use an absolutely analogue relation:

$$A_0 = \beta V_0,$$  

(3.7)

where $\beta$ is the same parameter evaluated before, and $V_0$ (free oscillation amplitude in Volt) is related to another adjustable quantity that is called *drive amplitude*, $V_d$. It corresponds to oscillation amplitude (in tension) of the forcing piezo. For the particular case represented in Fig.3.18, drive amplitude is equal to $57 \times 10^{-3}$ V. The relation between $V_0$ and $V_d$ is:

$$V_0 = \gamma V_d,$$  

(3.8)

with $\gamma$ a proper coefficient to be determined. Now we can insert relation 3.8 into 3.7, obtaining:

$$A_0 = \beta (\gamma V_d).$$  

(3.9)

The last step is to determine coefficient $\gamma$. It is easily evaluated as the angular coefficient of the curve $V_0$ versus $V_d$ in resonance conditions.

The parameter $A$ is carefully tuned during the first imaging step to reach an image of good quality, without induce nanoclusters depinning. Then it is kept fixed for all subsequent images and manipulations steps.

Free oscillation amplitude $A_0$ is linearly dependent on drive amplitude (in nanometers) $A_d$ and the proportional coefficient is evaluated before each single manipulations sequence. During every simple imaging step $A_0$ is kept fixed, while in a manipulation step we are able to increase $A_0$ increasing $A_d$. 
Chapter 4

Results and discussions

In Chapter 3 we have pointed out how phase shift signal in atomic force microscopy experiments with amplitude modulation feedback can be correlated to the energy dissipated in the interaction between the tip and a sample. In this PhD work sample is represented by a deposition of gold spherical nanoparticles of different nominal diameters on HOPG and on silicon substrate with native oxide. In first two sections of this chapter we would like to show main results of our measurements in air conditions, highlighting the differences between the two substrates. Results will be compared with those obtained in the international panorama, especially by the groups of Garcia and co-workers and Schwarz and co-workers in Spain, Germany and United States.

Moreover in a separate section we will present some results and considerations on measurements performed with same conditions (deposition, substrate, experimental procedure) but in controlled atmosphere, in particular in nitrogen flux. In the last section we would like to show few aspects strictly related to the dynamics of nanoparticles, like for example the role of edges of graphite, impurities, and so on the trajectory of a sliding cluster.

4.1 Detachment energy thresholds

Single cluster depinning

We have verified using different cantilevers and/or different combinations of oscillation amplitude $A$ and Amplitude Setpoint $A_0$ that the parameter which univocally controls detachments and the manipulation experiment is the energy dissipation signal on the cluster. Using this parameter it is possible to identify an energy threshold below which detachments do not occur, so it is a clear indicator of the energy threshold necessary to obtain the detachment. This is clearly shown in Fig 4.1.
4.1 Detachment energy thresholds

Figure 4.1: On Panel a) topographic image of a gold nanocluster deposited on a freshly cleaved HOPG graphite (the blue plane is a 10 nm cut off introduced for graphical reason). The measured height is in agreement with the nominal diameter of the deposited clusters while the shape strongly depends on tip dimensions. Corresponding energy dissipation signal is shown on Panel d). Panel b), the tip oscillation amplitude $A_0$ is increased at the beginning of the scan (bottom) by increasing the piezo amplitude oscillations (Amplitude Setpoint held fixed along the whole scan). The energy dissipation signal consequently increases (Panel c)), and the particle detachment is induced. After few scan lines $A_0$ is reduced to the optimized value for imaging. As a result, the particle movement is stopped and the scan continues as an usual image acquisition. On Panels c) and f) the same procedure is repeated while scanning the image from the top. The topographic images corresponding to Panels a), b), c) do not reveal the variation of tip oscillation amplitude. Simultaneous acquisition of the phase shift signal, that is transformed into energy dissipation per cycle according to equation 3.5, makes evident (Panels d), e) and f)) the energy dissipated into the substrate by the tip-cantilever system [41].
On Panel a) the topographic image of a gold nanocluster deposited on a freshly cleaved HOPG graphite is reported. The blue background represents a 10 nm cut-off plane introduced for graphical reason. The corresponding energy dissipation signal is shown on Panel d). On Panel b) the tip oscillation amplitude $A_0$ has been increased at the beginning of the scan (bottom) by increasing the piezo amplitude oscillations, while the Amplitude Setpoint is held fixed. As a consequence the dissipated energy increases (see Panel e)), and the particle detachment occurs. After few scan lines $A_0$ has been reduced to the optimized value for imaging purpose, and the particle movement is stopped. In Panels c) and f) the same procedure is repeated while scanning the image from the top. The topographic images which correspond to Panels a), b) and c) correctly do not reveal the variation of tip oscillation amplitude, while the simultaneous acquisition of the phase shift signal, transformed into energy dissipation per cycle by equation 3.5, makes evident the energy dissipated into the substrate by the tip-cantilever system (see Panels d), e) and f)).

The depinning energy threshold, as we will see further, correctly depends on the substrate and on the cluster size. Extracting physical informations from the detachment energies represents an important goal and, so far, the work that can be helpful in this context is represented by the detailed analysis of possible dissipation mechanisms between an oscillating tip and a flat surface in absence of plastic deformation, performed in 2006 by Garcia et al. [30] [54].

Authors have modelled and calculated analitically the energy dissipation per cycle due to surface energy hysteresis, long range interfacial hysteresis (Fig.4.2, [54]) or visco elasticity damping as a function of measurable and controllable parameters like the Amplitude Setpoint $A$ and the free amplitude oscillation $A_0$. Moving from weak interaction ($A \approx A_0$) to strong damping ($A << A_0$) the calculated curves predict the existence of a maximum, but the three mechanisms give rise to different behaviours as a function of the ratio $A/A_0$. In particular the two hysteresis mechanisms show a broad or even flat region of maximum dissipation while the profile corresponding to visco elastic damping has a pronounced maximum at a $A/A_0 = 0.5$.

Making a comparison between experimental results and these theoretical curves may help understanding the dominant dissipation channel for a particular physical system. As an example the authors have measured in air the dissipation between a silicon tip and a Si(100) surface passivated with native silicon dioxide founding a remarkable agreement with curves calculated considering both surface energy and long range interfacial hysteresis (see Fig.4.3, Panel b), [54]). They also measured the response of the same tip on a polystyrene and polybutadiene blend finding a complete agreement with a viscous damping dissipation mechanism (Fig.4.3, Panel c), [54]).

In agreement with these results we found, on the system composed by gold
4.1 Detachment energy thresholds

Figure 4.2: On Panel a) curves (simulations) of dissipation for different non-conservative interactions. Energy dissipation values are calculated per oscillation cycle. Triangles are for surface energy hysteresis, squares for a (non-contact) interfacial interaction, and the solid line is for viscoelasticity. Each curve has been normalized with respect to its respective maximum, equal to 9.2, 1.4 and 50 eV, respectively. On Panel b) derivatives with respect to the amplitude ratio of the curves shown in a) are presented. Reprinted figure with permission from [54]. Copyright 2006 by the American Physical Society.

Figure 4.3: Measured and simulated dynamic dissipation curves are reported. On Panel a) on a silicon surface when there is not mechanical contact between tip and surface. Parameters used: $A_0 = 6.6$ nm, $k = 2$ N/m. On Panel b) on silicon when there are surface energy hysteresis and long-range interfacial interactions. $A_0 = 32.5$ nm, $k = 2$ N/m. On Panel c) on a polystyrene (PS) region (cross in the inset) of polystyrene/polybutadiene blend, with $A_0 = 15$ nm. On Panels d), e), f) derivatives of the normalized energy-dissipation curves shown respectively in a), b), c) are reported. The insets show the energy-dissipation images taken on Si, Fig. 2(a) (attractive) and Fig. 2(b) (repulsive), and on a PS region (Fig. 2(c)). The steplike discontinuities observed in Fig. 2(b) mark the transition between attractive and repulsive interaction regimes. Reprinted figure with permission from [54]. Copyright 2006 by the American Physical Society.
4.1 Detachment energy thresholds

nano-cluster on HOPG graphite, that energy dissipation on clusters initially increases by decreasing \( A \) with fixed \( A_0 \). Then the process is limited by the occurrence of cluster detachment and movement which indeed behave as a new dissipation channel. In Fig.4.4 we report a typical profile of the experimental energy dissipation increase measured on cluster, to compare this behaviour with the curves predicted by Garcia et al. A direct and accurate comparison is difficult because the accessible range of \( A/A_0 \) is limited by the cluster depinning event, nevertheless the absence of an extended maximum plateau suggests that surface energy hysteresis associated with sample deformation gives a negligible contribution. A typical cluster manipulation obtained by varying \( A \) with fixed \( A_0 \) is presented on Fig.4.5.

Figure 4.4: Typical cluster manipulation obtained by varying \( A \) with fixed \( A_0 \). Panel a), topographic image of a gold nanocluster deposited on a freshly cleaved HOPG graphite. The corresponding energy dissipation signal is shown on Panel c). Panel b) and Panel d), the Amplitude Setpoint \( A \) is reduced at the beginning of the scan (bottom) while maintaining the oscillation amplitude \( A_0 \) fixed (\( A/A_0 = 0.5 \)). In this condition the particle detachment is induced, then after few scan lines \( A \) is increased to the optimized value for imaging and the particle movement is stopped. The scan continues as a normal image acquisition [41].

Starting from the relative weak interaction regime, characteristic of the imaging scan (Fig.4.5a), depinning and movements are induced when \( A/A_0 \) approaches the value of 0.5 (Fig.4.5b, bottom). Then the movement can be easily stopped by restoring the value of parameter \( A \) characteristic of the imaging scan (Fig.4.5b, up). This behaviour is completely equivalent to that one presented on Fig.4.1,
obtained by increasing $A_0$.

Figure 4.5: Typical cluster manipulation obtained by varying $A$ with fixed $A_0$. Panel a), topographic image of a gold nanocluster deposited on a freshly cleaved HOPG graphite. The corresponding energy dissipation signal is shown on Panel c). Panel b) and Panel d), the Amplitude Setpoint $A$ is reduced at the beginning of the scan (bottom) while maintaining the oscillation amplitude $A_0$ fixed ($A/A_0 = 0.5$). In this condition the particle detachment is induced, then after few scan lines $A$ is increased to the optimized value for imaging and the particle movement is stopped. The scan continues as a normal image acquisition [41].

The energy dissipation signal obtained from the phase shift measurement cannot capture directly the energy released to the cluster to initiate sliding, as we have already pointed out, rather it measures the dissipation on the system composed by cluster bonded on the surface until it remains stable. Then the analysis of the energy dissipation signal as a function of $A$ or $A_0$ may help understanding the initial damping mechanism but it also gives clear evidence of the existence of a threshold value for the energy dissipated by the tip on the cluster above which the sliding event becomes an active dissipation mechanism.
4.1 Detachment energy thresholds

Statistical analysis of depinning events

So far we have always discussed about single detachment energies but to obtain significant and more general results it is needed a large amount of data to perform a suitable statistical analysis. For this reason we have performed several measurements collecting approximately two hundreds of single cluster detachments for each particle dimension, exploring a total area of about ten squared microns for each particle size (13 nm, 24 nm, 42 nm) on graphite substrate and of about eight squared microns for each one on silicon dioxide [42] [51] [3]. From the statistical analysis of all data, the existence of well defined thresholds of detachment energy as function of the substrate and the particles dimensions is clearly evident. The results are presented in Fig.4.6, Panel a) and summarized in the Table 4.1.

<table>
<thead>
<tr>
<th>$eV \times 10^2$</th>
<th>13 nm</th>
<th>24 nm</th>
<th>42 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Graphite</strong></td>
<td>0.2 ± 0.1</td>
<td>0.6 ± 0.2</td>
<td>1.3 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4.1: In this table detachment energy thresholds found on HOPG are reported for all different diameters of particles.

Curves represent the fraction of detached single clusters normalized to the total number of particles. As one can see from Fig.4.6, the general behaviour of these curves is characterized by a rapid increasing, representing most of depinning events, and the achievement of a plateau, when all possible detachments have been occurred. The linear increase typically represents a random uniform probability so the detachment energy threshold can be conveniently located in the centre of this region, while its width on the $x$ axis corresponds to the maximum associated error.

In Fig.4.6 Panel b) analogue curves showing all data on silicon dioxide are presented, and in the Table 4.2 detachment energy thresholds are summerized.

<table>
<thead>
<tr>
<th>$eV \times 10^2$</th>
<th>13 nm</th>
<th>24 nm</th>
<th>42 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SiO$_2$</strong></td>
<td>30 ± 25</td>
<td>80 ± 50</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2: In this table detachment energy thresholds found on silicon dioxide are reported for all different diameters of particles tested.

Particles of 42 nm of nominal diameter on silicon have been tested but they were so strongly pinned to the substrate that it has not been possible to reach a statistically significant number of detachments, with our used tips.
4.1 Detachment energy thresholds

Figure 4.6: The picture represents fractions of depinning events normalized to the total number of single particles. In Panel a) detachment energy thresholds for 13 nm, 24 nm and 42 nm on graphite are presented. In Panel b) for 13 nm and 24 nm on silicon dioxide. The results are summarized in Tables 4.1 and 4.2.

Comparison with experiments in literature

Since we have noticed a dependence on the contact area of depinning energies, in order to make a comparison of resulting values, especially on graphite, with the literature, we have referred to theoretical and experimental works [50] [49] on gold nanocluster diffusion, because the thermal diffusion coefficient $D$, as Guerra and colleagues pointed out [50], is expressed as a function of the activation energy per contact atom $\Delta$, and it is described by the following relation:

$$D = Ae^{-\frac{Nc\Delta}{k_BT}},$$  \hspace{1cm} (4.1)
where $A \approx 0.04 \text{Å}^2/\text{ps}$, $N_c$ is the number of atoms in contact with the substrate, $k_B$ the Boltzmann constant and $T$ the temperature. They found a value of $\Delta$ equal to about 1.19 meV.

To compare this result we have to perform an estimate of $\Delta$ in our case, dividing the measured depinning energy $E$ by the number of atoms in contact with the substrate, according to

$$\Delta = \frac{E}{N_c}. \quad (4.2)$$

The evaluation of $N_c$ requires to make assumptions on our contact area. Since it is extremely difficult to identify the real contact area for our deposited nanoparticles, we have choose to consider the nominal contact area, so the projection on the substrate of the maximum area of the cluster. Thus with these assumptions, by the ratio between the nominal contact area and the area occupied typically by one gold atom, we have estimated a number of atoms in contact for our cluster of $N_c \approx 2200$ for 13 nm nanoparticles. Thus multiplying the value of $\Delta$ from Guerra et al. for our $N_c$ we obtain a total energy of 2.6 eV, instead of about 20 eV found by our measurements.

On the other hand, we have considered the experimental work from Bardotti et al. [49], in which gold clusters of 250 atoms have been deposited on graphite by laser vaporization in UHV, assuming the ramified shape of clusters, characteristic of this technique of deposition. Thus authors have been provided a value of 0.5 eV as total activation energy. To estimate a value per atom to compare with our energies, we have to make the assumption that all atoms in the experiment of Bardotti are in contact with the surface. This particular guess gives an energy per atom $\Delta \approx 2$ meV, about two times larger than the energy of Guerra et al.

To make a more realistic guess, we can assume that only the 50% of atoms (125 in this case) are in contact, reaching a value per atom $\Delta \approx 4$ meV, instead a value per atom from our measurements of $\Delta \approx 9$ meV. The result of this comparison with both works is that we obtain an higher depinning energy. This difference of course can be due to the presence of water layers eventually present on the substrate in air conditions. In fact, as it will be presented in the following, for analogue measurements in nitrogen atmosphere the detachment energy results the half of the value in air conditions. Moreover, taking into account the nominal contact area which is the maximum area that can be in contact with the substrate, we make an underestimation of energy $\Delta$, according to relation 4.2. Nevertheless the tip does not hit the particle perfectly on its top, because of several factors including relative dimensions of tip apex-cluster and a tilt of 12 degrees of the cantilever with respect to the substrate. So, as it is schematized in Fig.4.7, there will be some force components that do not contribute to the cluster motion but they are taken into account however in the measure of total dissipated energy.
4.1 Detachment energy thresholds

Figure 4.7: The repulsive force $F$ between two hard bodies is directed along the normal to the contact surface. Assuming a spherical shape for both the cluster and tip apex, this corresponds to the segment connecting the centers of the two spheres. Under these assumptions, the problem becomes intrinsically anisotropic with respect to the substrate normal and it will be sensitive to the two force components $[F_x, F_y]$ coplanar to the graphite surface. The effect of the cantilever tilting, particularly may slightly contribute as well.

Now coming back to our results, the increasing of dissipated energy is consistent with the variation of cluster size, and so with the increasing of nominal contact area, in both physical systems, HOPG and silicon dioxide.

As we have already pointed out, the contact area dependence of frictional forces in the nanometer regime is a topic of strong scientific interest and an argument of debate since the advent of the Friction Force Microscope (FFM).

The first systematic attempt to solve this problem analyzing cluster manipulation is represented by the work of Ritter and colleagues [33]. They have grown antimony nanoparticles on HOPG and on molybdenum disulfide ($\text{MoS}_2$) in Ultra High Vacuum conditions. They have performed delicate experiments on controlled translation of nanoparticles induced in ambient condition ([33], Fig.2, reported as Fig.4.8 in the following), using the same method we have discussed in the previous chapter, e.g. slowly increasing the amplitude oscillation $A_0$ while working with AFM in tapping mode with amplitude modulation feedback.

During manipulation, the power dissipated by tip-sample interaction has been measured and the threshold value which marks the transition to sliding has been recorded as a function of cluster dimension. Antimony nanoparticles grown both on HOPG and molybdenum disulfide have ramified and relatively flat shape. In this case particles height lies in a range from 20 nm to 35 nm and lateral dimension...
Figure 4.8: In this picture the manipulation procedure of antimony clusters on HOPG is illustrated. The image size is one squared micron and the height of particle \( a \) is 26 nm. On Panel a) imaging of the particle of interest \( a \) and the surrounding area. A white and a gray arrow indicate the path of the subsequent tip motion and the resulting dislocation of the particle, respectively. On Panel b) the topography after the manipulation is presented. Comparing this with previous panel, it is visible that particle \( a \) experienced a lateral translation of 83 nm and an in-plane rotation of 58°. For the following manipulation step, another contact point between the particle and the tip has been selected by authors (white arrow). On Panel c) the imaging resulting from the second manipulation step, revealing a translation of 211 nm and an in-plane rotation of 77°. The particle labeled as \( b \) has been accidentally translated during the imaging process. The contact area of this particle is slightly below 10 000 nm\(^2\) and thus in the range of very low energy dissipation. On Panel d) final result after the third manipulation step. In this latter case, the translational motion of 175 nm was accompanied only by a small in-plane rotation of about 3°. Reprinted figure with permission from [33]. Copyright 2005 by the American Physical Society.

from 120 nm and 400 nm. Thus the corresponding contact areas have been set between 104 and 11 \( \times \) 104 nm\(^2\). Since the lateral dimension of the particle is bigger than the typical radius of the tip apex (about 10 nm), an approximation of the effective contact area with the measured shape of the particle can be assumed.

The result shows unambiguously that the threshold value of the power dissipation necessary for translation of antimony nanoparticles for both HOPG and molybdenum disulfide substrates linearly depends on the contact area [33], in agreement with our results.

Different models have been discussed by Aruliah et al. [55] in connection with this experiment, showing that also a linear relation between friction force and
dissipated energy may exist but the hypothesis leading to that conclusion seems to be in contradiction with our guess expressed above and with recent results of Rao et al. [56]. Nevertheless the comparison of this result with FFM experiments requires to model the relationship between dissipated power and frictional forces. This step is nothing but trivial.

A significant step for the understanding of the system composed by antimony nanoparticles on HOPG has been recently obtained by D. Dietzel and colleagues [46]. Using AFM cluster manipulation in contact mode they found clear evidence of the linear dependence between contact area and sliding friction force in the nanoscale regime. The authors have shown about fifty dislocation events obtained on particles with contact areas between 22000 nm$^2$ and 310000 nm$^2$. They have used two different cantilevers and different samples, with identical preparation. The main data have been obtained performing both the deposition and the manipulation measurements in UHV conditions. Dislocation events have been divided in two distinct regimes ([46], Fig.3 a,b, reported as Fig.4.9).

Figure 4.9: On Panel a) data obtained in Ultra High Vacuum conditions are presented. They show the existence of two friction regimes for contact areas up to 90 000 nm$^2$. The first regime (black symbols) is composed by particles with substantial friction. In the second regime (red symbols) data of particles that exhibit virtually no measurable friction are presented. The square markers and circular markers represent measurements for two similarly prepared samples but with different cantilevers used. Triangular markers show a third set of measurements with focus on smaller islands. On Panel b) data plot featuring 39 not-vanishing friction events under UHV conditions for particle sizes up to 310 000 nm$^2$ are reported. Data can be well approximated by a linear fit (black solid lines) with no statistically significant offset. On Panel c) data obtained under ambient conditions for particles with contact areas between 21 000 nm$^2$ and 62 000 nm$^2$ are presented. Two different regimes of friction can once again be identified. The events featuring substantial friction follow an approximate linear dependency. Reprinted figure with permission from [46]. Copyright 2008 by the American Physical Society.

The largest part belongs to a class characterized by substantial frictional resistance behaviour, but about one quarter of the events shows almost no detectable
friction. These events have been found only for islands smaller than 90 000 nm². In the first case results suggest a linear dependence on contact area and so a constant shear stress τc equal to (1.04 ± 0.06) MPa, calculated by the relation 1.5, here reported for clarity:

$$\tau_c = \frac{F_l}{A}.$$ 

Since the normal force experienced by the particles is due to adhesion, which scales linearly with area, an area independent friction coefficient follows, reinforcing Amontons law also at the nanoscale.

The coexistence of “normal” and superlubric behaviour is explained by the authors in terms of competition of structural superlubricity between crystalline clusters and HOPG surface and the counter effect due to the presence of a small amounts of mobile molecules such us hydrocarbon or water molecules [35]. These particles can be trapped on the HOPG surface during the initial cleaning procedure and indeed, decreasing the accuracy of cleaning procedure, the ratio of superlubric to normal translations decreases too.

A complementary set of data, performed in ambient conditions, shows a similar linear behaviour with an increased shear stress τc equal to (40 ± 1) MPa ([46], Fig.4.9 Panel c) and few superlubric transitions (about 8%).

Nevertheless the direct comparison of our results with measurements performed by Dietzel and co-workers is difficult because of the different techniques that we have used highlight two separate aspects of the friction process. In our case sensitivity is on the threshold of depinning while in the other case measurements are sensitive to sliding friction. On the contrary a useful comparison can be established with results obtained by Ritter and collegues because they have been performed with the same technique in ambient condition, though on a slightly different physical system.

In the work of Ritter a guess has been made regarding the mechanism of damping for a sliding cluster. They assumed that hit cluster moves from a stable energy equilibrium position to the nearest one. This distance should be comparable to typical lattice constant (few angstroms). This model is not immediately applicable to our system because we did not work in vacuum conditions and we have used large amorphous clusters and so the displacement cannot be easily thought in terms of single atom jumps between two nearest energy minima.

For our experiments it seems to be more correct the description of Rao et al. [56], who assumed the dumped displacement is due to dynamic friction mechanisms. In this case, the fraction of energy utilised to overcome static friction respect to those stored in the initial cluster velocity remains unknown unless you may suppose this part being negligible or you are able to evaluate the dumping mechanisms.
4.1 Detachment energy thresholds

However we have taken as a reference the angular coefficient of the linear fit of antimony cluster detachments on HOPG ([33], Fig.4, here reported as Fig.4.10 for clarity) which has dimension of power divided by a surface area [nW/nm$^2$]. Then we have translated the power found by Ritter into energy according to the oscillation frequency used in the experiment ($\omega_0/2\pi = 172.9$ kHz) and we have compared these results with our findings on Table 4.3.

Figure 4.10: Plot of the minimum values of power dissipation needed for translation of different-sized antimony nanoparticles on HOPG (filled triangles) and MoS$_2$ (empty circles), respectively. The threshold values for both substrates are in the same range and scale linearly with the contact area of the translated particles. The straight lines represent linear fits of the measured data. Reprinted figure with permission from [33]. Copyright 2005 by the American Physical Society.

<table>
<thead>
<tr>
<th>[eV/nm$^2$]</th>
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<th>42 nm</th>
<th>Ritter et al. [33]</th>
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<td>graphite</td>
<td>0.15 ± 0.09</td>
<td>0.15 ± 0.07</td>
<td>0.09 ± 0.04</td>
<td>0.14 ± 0.01</td>
</tr>
</tbody>
</table>

Table 4.3: Comparison between the detachment energy threshold per unit area evaluated on the 13, 24 and 42 nm particles and the value corresponding to the linear fit of results by Ritter et al. [33].

The values corresponding to 13 and 24 nm particles is in perfect agreement with the result found by Ritter, while the value corresponding to 42 nm particles overlaps within the error bars. This result is consistent with the behaviour of antimony and gold clusters on HOPG which exhibits a large and similar thermal
4.1 Detachment energy thresholds

diffusion coefficient at room temperature. But, more important, the comparison of these values suggests a linear decrease of detachment energy with respect to the contact area for particles having a lateral dimensions in the tens nanometer scale.

These data confirm and at the same time extend by more than one order of magnitude with respect to the contact area the results obtained on antimony nanoclusters.

Finally, we must highlight, in accordance with the results of Dietzel, that also superlubric translations have been observed with a frequency of about 5%. These events, as shown in Fig.4.11, usually follow an “usual” movement phase. They suggest that this behaviour is due to random and momentary realization of a clean interface between an amorphous surface (cluster) and an ordered surface (graphite).

![Figure 4.11](image)

Figure 4.11: Manipulation sequence relative to 24 nm clusters on HOPG. Panel a) shows AFM directions of scan superimposed to initial topographic image. The cantilever tilting is pictured. On Panel b) represents the manipulation step in which detachments of two single clusters are visible, together with their trajectories. On Panel c) the subsequent topographic image is shown. The cluster on the right has left the scan area while the centered cluster now sits on upper right corner. Note the large jump at the end of its trajectory (about 120 nm long) and the deflection effect due to the presence of graphite edge.

At the end we would like to spend few words about the difference of about two orders of magnitude in the energy values that we have found for the two substrates HOPG and SiO$_2$. They could be explained by different mechanisms. On one hand, it is well known that gold nanoclusters grown in Ultra High Vacuum conditions on graphite are characterized by high mobility at different temperatures [49] [57] [58]. This aspect indicates that the interface between gold nanoparticles and HOPG is characterized by a relatively low surface energy. On the other hand the formation of capillary neck in the contact between cluster and surface cannot
be neglected in our experimental conditions. The silicon dioxide surface possess a more hydrophilic behaviour with respect to graphite, which means that stronger capillary forces can be build around nanoscale particles deposited on the SiO$_2$ surface. All these general properties are confirmed by our experimental results in which the contact is controlled down to the nanometer scale. Nevertheless a direct comparison of our experimental energy values with those obtained with different techniques (e.g. contact angle) or by numerical simulation requires further dedicated measurements and modelling.

4.2 Measurements in controlled atmosphere

In order to reach a better physical comprehension of the role of air conditions (e.g. humidity) on depinning events, we have performed several experiments in nitrogen atmosphere. We have followed exactly the same protocol described so far, focusing our attention on one dimension of gold nanoclusters, $42 \pm 4$ nm of nominal diameter. We have worked on graphite as an interesting substrate for its surface features (steps, flat terraces) and to investigate the role of eventually present water layers also on a well-known hydrophobic material.

The deposition by droplet has been made in air on freshly cleaved HOPG and then the sample has been dried reaching high vacuum (typically $10^{-5}$ Torr) in the AFM chamber using a scroll and a turbomolecular pump. After few minutes, the chamber has been filled with nitrogen (pureness 99.999%) until the pressure inside was equal or slightly higher than the atmosphere pressure in the room. This cleaning technique has been repeated three or four times before each sequence of measurements, to be sure about the pureness of nitrogen atmosphere.

We have followed two different procedures of data acquisition: the first one was based on the investigation on water layer influence on the single particle, measuring the dissipated energy in nitrogen and in air on the same cluster, acquiring continuously the signal. In these controlled conditions we have performed several scans with areas typically ranged between $500 \times 500$ nm$^2$ up to $1.3 \times 1.3$ $\mu$m$^2$, adopting the imaging-manipulation-imaging procedure, increasing step by step the oscillation amplitude. After few steps, when all possible detachments were occurred, we have refilled the chamber with air for half an hour, with the foresight to keep the tip in contact with the sample. In this way we have been able to acquire the image without interruptions.

With the chamber now filled with air at room pressure, we have identified the same area of the last sequence of measurements, with the same particles, and we have performed another sequence of increasing oscillation amplitude with the energies adopted before (see Fig.4.12 and 4.13 for few details). The interesting result is that nanoclusters that in nitrogen atmosphere run into depinning phenomenon,
in air conditions with the same maximum energies they remains stuck on the substrate. To reach detachments it is necessary to increase the energy given to the system. Reasonably the energy threshold for depinning in air conditions is equal to the value found for “standard” measurements of detachment energy described so far on graphite.

Figure 4.12: In this figure two topographic images of the same area (in this case for clarity $5 \times 5 \, \mu m^2$) of 42 nm clusters deposition on HOPG substrate. The image on the left has been performed in nitrogen atmosphere, the right one in air, acquiring the signal without interruptions. The direction of the slow scan (black arrow) is top-down. Both images are obtained setting parameters to give a total energy equal to about 40 eV to the system. In the nitrogen case three depinning events are reached (particles labeled as $a$, $b$ and $c$). Correctly, with this value of energy in air conditions no detachment occurred. In the right image it is visible (purple circle) a new particle, because of a little drift of the sample.

Figure 4.13: Zoom of sliding clusters labeled as $a$, $b$ and $c$ on Fig.4.12, Panel a). Nitrogen atmosphere, $E = 40$ eV.
This approach requires a very high control of the parameters to keep in a proper interaction the tip on the sample during the air filling, to maintain the same area of scan in nitrogen. However, because of the long time required from this kind of measurements, to reach an high number of results for depinning in controlled atmosphere, we have followed a different procedure, working for the following sequences always in nitrogen conditions, taking care of refill the chamber after cleaning procedure at every measurement.

The result is clearly visible on the Fig.4.14 and schematized on the Table 4.4:

\[
\begin{array}{c|c|c}
| \text{eV} & \text{Nitrogen} & \text{Air} \\
| E_{\text{threshold}} & 67 \pm 30 & 130 \pm 55 \\
\end{array}
\]

Table 4.4: Comparison between the detachment energy thresholds evaluated on 42 nm particles in nitrogen atmosphere and in air conditions on graphite.

The two found energy thresholds for depinning are obviously consistent within their maximum associated error but thanks to a large number of performed measurements and an high reached statistics, we can conclude that a difference in energy between the two examined conditions can be assumed. Nevertheless further sensitive experiments are required, but as a preliminary result we have an indication of graphite surface, well-known for its hydrophobical behaviour, is sensitive
to the atmosphere conditions (e.g. humidity) and the presence of water layers and capillary forces play a relevant role in detachment events at the nanoscale.

4.3 Dynamics on surfaces

Selection by dimensions

As we have seen in the previous sections, with the method developed during this work of PhD thesis it is possible to evaluate the minimum energy needed by the nanoparticle to reach its detachment but this delicate, well calibrated and quantitative procedure has a large class of capabilities. For example, starting from the assumption (experimentally confirmed) of linearity relation between energy and contact area, we are able to know in principle depinning energy thresholds for a wide range of dimensions of nanoclusters. Thus it is possible to perform a mass-selective manipulation, keeping fixed the energy transferred to the system on a given threshold and so depinning and moving only clusters that have characteristic detachment values equal or below this threshold.

To test this idea we have deposited a mixed solution of gold spherical nanoparticles of 24 nm and 42 nm of nominal diameter on graphite [51]. In Fig.4.15 we can see the initial topographic image.

![Figure 4.15: A mixed deposition of gold nanoclusters of 24 nm and 42 nm of nominal diameter on graphite (first imaging step). Few moving objects are visible, probably adsorbed molecules or weekly bonded particles.](image)

We have set all parameters of the scan like Amplitude Setpoint and Drive Amplitude to transfer to the system just energy required for 24 nm detachments (ma-
nipulation step), according to values presented in the first section of this chapter. The result is clearly shown in Fig. 4.16.

Figure 4.16: Imaging step subsequent of manipulation. In dashed white square the area of manipulation with energy typical of 24 nm depinning. For clarity we have slightly enlarged the area of topographic scan. All clusters remained pinned are 42 nm of diameter or multiple particles cluster.

Figure 4.17: Imaging step subsequent of manipulation. In dashed white square the area of manipulation with energy typical of 24 nm depinning. For clarity we have slightly enlarged the area of topographic scan. All clusters remained pinned are 42 nm of diameter or multiple particles cluster [51].
For clarity we have slightly enlarged the scan area for the following imaging step to see better the “border” effect, with all moved particles pushed along the boundaries of last scan. The result is that all particles remained pinned are effectively 42 nm of diameter and/or multiple particles clusters, probably already present in the solution.

All these measurements have high degrees of reproducibility but it is important to be careful on the searching of a suitable area of scan, without a large number of impurities due to room conditions and without too much clusters composed by several particles. To reach a significant statistics we have tried to manipulate few tens of clusters and all data, summarized in Fig.4.17, confirm the correctness of the initial idea regarding a manipulation sensitive to the mass of nanoparticles.

**Analytical model on dynamics**

Independently from the material of the substrate, what we have seen is that the moving nanocluster, interacting with an oscillating tip, always follows the slow scan direction. Nevertheless the tip can assume during the scan particular and difficultly controlled shape (see Fig.4.18) and it can generate the effect of inducing small deviations of particle trajectory.

![Interesting SEM image (80 000 X) of an used AFM silicon tip that has assumed a shape no more suitable for further measurements.](image)

A detailed analysis of the cluster movements induced by an AFM oscillating tip from the point of view of dynamics and interaction between tip and particle has been developed by Rao and colleagues from the University of Basel [52]. The
The relevant dimension parameter is the reduced radius \( R = R_1 + R_2 \).

The tip is approximated with a truncated cone terminated with an hemispherical apex, while the cluster is described by a complete sphere. The two possible geometrical configurations are described in Fig.4.19. Two conditions are avoided, involving the radii of the particle \( R_p \) and of the tip \( R_t \):

1. Panel a) of Fig.4.19
   \[ R_p > R_t[1 - \sin(\gamma)] \]

2. Panel b) of Fig.4.19
   \[ R_p < R_t[1 - \sin(\gamma)] \]

where \( \gamma \) is the angle of conical tip (in green on Fig.4.19).

If the first condition is verified, the nanoparticle interacts with the conical part of the tip and so:

\[
R_1 = R_t[1 + \sin(\gamma)] \tan(\gamma) + R_t \frac{1 - \sin \gamma}{\cos \gamma} \tag{4.3}
\]

and

\[ R_2 = R_p \cos(\gamma). \tag{4.4} \]

The relevant parameter in this kind of analysis is the effective reduced radius \( R = R_1 + R_2 \). Instead if the second condition is verified, the cluster interacts with
the *spherical* part of the tip and we have:

\[ R_1 = \frac{2\sqrt{R_1 R_p}}{1 + (R_p/R_t)} \]  \hspace{1cm} (4.5)

and

\[ R_2 = \frac{2\sqrt{R_1 R_p}}{1 + (R_t/R_p)}. \]  \hspace{1cm} (4.6)

The tip-particle interaction is based on a model that describes every single interaction between tip and sample in terms of a collision between two hard bodies so that an elementary cluster displacement occurs along the direction connecting the centers of tip apex and cluster, Fig. 4.20.

Moreover the elementary cluster movements (further called \( d \)) on the surface are supposed to be strongly damped by friction effects, as we have pointed out in previous section. Following these assumptions, the overall trajectory is calculated as the sum of different small displacements due to subsequent tip-cluster interactions and it turns out to depend on the AFM scan parameters as well as on tip and particle size.

![Figure 4.20: Typical scan movements of the AFM tip over the sample. On Panel a) a raster pattern scan; on Panel b) a zig-zag pattern scan. The direction of cluster trajectory is depicted on both panels. Note that we always refer the movements to the fast scan direction.](image-url)
The authors have made a distinction between two possible AFM scan movements, the *raster path* and the *zig-zag path* (visible on Panels a) and b) of Fig.4.20). They have described the direction of the sliding particle trace as a function of the reduced radius $R$ (see Fig.4.19) and the spacing $b$ between consecutive scan lines (Fig.4.20). It is interesting that the analytical relation and the corresponding conclusions are different in the two cases. In the case of raster pattern the trajectory results as a straight line which forms an angle $\alpha$ (in green on Fig.4.20) with respect to the fast scan direction and this parameter $\alpha$ depends only on the $R$ and $b$.

In the case of zig-zag pattern instead no preferred direction exists because the angle $\alpha$ depends also on the initial position of the moving cluster. In the limit of $b/R \to 0$ the angle $\alpha$ always approaches the value of ninety degrees. This implies that the cluster is moved in a direction normal to the fast scan.

Thus the analytical approach describing the trajectory deflection has been applied in our manipulation experiments performed in air and ambient conditions on gold spherical clusters (nominal diameter 24 nm) deposited on silicon dioxide. As seen before a substrate of SiO$_2$ is ideal for such measurements because of its low roughness.

The results show a good qualitative correspondence of the trajectory deflection $\alpha$ as a function of the parameter of scan step $b$ in the range between 2 nm and 20 nm ([52], Fig.5, reported for clarity in the following as Fig.4.21].

Figure 4.21: In this picture are presented experimental angles of deflection (open circles) and best fit (solid curve). Reprinted figure with permission from [52]. Copyright 2009 by IOP.
The comparison with our findings is very satisfying, noting that the parameters that we have set during the acquisition of Fig.4.1 correspond to the limit $b/R \to 0$. In this case, even if our system performs scan following a zig-zag pattern, the overall movement results normal to the fast scan direction.

Very recently Rao and co-workers have improved their analysis by simulation of cluster trajectories as a function of the sliding distance $d$ [56]. We have compared their results to our experimental data on nanoparticles of 42 nm deposited on silicon dioxide.

The simulated behaviour shows that an increasing of the friction force between particle and surface, corresponding to $d << b$, is translated into a more “regularity” of the trajectories. That regularity is measured from the deviation of each trajectory steps from the ideal one, and this quantity can also be extracted from the measured cluster pathways. From the direct comparison of the observed discontinuities with the simulated ones we may conclude that the typical sliding distance $d$ in this particular case is quite large, about 20 nm, with respect to the lattice constant of the substrate. This is not surprising because the actual silicon surface is covered by an amorphous native oxide layer.

At this point we have to note that if one could be able to know the initial velocity acquired by the particle during the interaction with the AFM tip, it could be possible to extract information on the friction forces damping the cluster during its motion. To overcome this drawback, the collision process between tip and particle should be better understood in the future both from experimental and theoretical point of view.

**Surface defects and texturing**

Another important aspect regarding the dynamics of a sliding nanoparticle pushed by an AFM tip in air conditions concerns the role of asperities of the substrate on its final trajectory. Analyzing several thousands of AFM images during this PhD work a large collection of possible events have been observed during manipulation steps. Thinking about the substrate, most important in this view is graphite because of the presence of edges well defined and easily measurable with typical heights from 1 nm (three or four atomic layers) up to 5-6 nm. Silicon dioxide on the contrary is characterized by a very low surface roughness, thus it represents an ideal substrate for example to study tip effects like different shape, influence of scan step dimensions and so on.

This is true for a particle sliding on a planar, flat surface like a terrace of graphite or simply silicon covered with native oxide. But what happens when the cluster experiences a superficial asperity on its way?

From the large number of events that we have collected, it has been observed two different behaviours. In the case of graphite, as clearly visible on Fig.4.22,
there is a high probability that a particle which meets a defect (typically a step) will follow it without overcoming. The typical heights of this kind of defects are ranged from few tenths of nanometer up to few nanometers, so they are at least one order of magnitude smaller than our particles. The particular behaviour described before can be of course reasonable in macroscopic world if we consider a step configurated as a lower level in which the particle slides and an higher level over the step. It is interesting the opposite case, depicted in Fig. 4.22, in which the step with an height equal to about 0.8 nm belongs to the configuration characterized by an higher level where the cluster resides and a lower level over the step.

Figure 4.22: In this picture a typical topographic image of a manipulation step of 24 nm particles on graphite is presented. Two single sliding clusters with their trajectories are clearly visible. The particle on the right exits from the scan area, while the left one at the end of a terrace meets a step of graphite. The profile next to the image represents the shape of the step and its height, equal to about 0.8 nm. Interesting is the fact that the terrace in which the particle slides is higher than the surface sample after the edge and nevertheless the cluster does not overcome the defect. The particle that resides on the edge does not depin.

These results on graphite defects are in perfect agreement with data obtained by Molecular Dynamics (MD) simulations performed by Yoon et al. [59]. They investigated the behaviour of gold nanoclusters composed by 38, 79, 140 and 586 atoms, respectively, on a graphite surface modelled with holes and steps, with periodic boundary conditions imposed in the two directions defining the basal plane. As first case they have studied linear ascending steps, with the cluster sitting on the lower terrace. At room temperature, over a time period of 240 ns, only two escape events for Au$_{38}$ has been observed and none for Au$_{140}$. However the mo-
bility along the step is high, especially for $\text{Au}_{140}$. Clusters made by tens of atoms underwent structural changes close to the step at different stages of constrained MD simulations. The main structural change is associated to the climbing process by the cluster over the defect. This changes occurred only on smaller clusters, whereas the larger $\text{Au}_{140}$ maintained their structure.

Moreover it has been found that descending steps, with clusters sitting on upper terrace, act as repulsive walls and the cluster motion is confined to the terrace. The origin of repulsion between particle and step is similar to what obtained for cluster-hole interaction: when the nanoparticle begins to overlap the step, from the upper terrace, it will lose contact area (and so attractive energy) associated with the top terrace. It is replaced by a smaller interaction energy with the more distant lower terraces. This results in an overall energy increasing and consequent repulsive forces directed away from the step, acting on the cluster located on the upper terrace.

In conclusion, a hole or an descending step will be precluded areas for clusters, because they act as repulsive Schwoebel-like barriers, so the probability to diffuse over these kind of defects is low. On the other hand, for an ascending step, at room temperature the cluster will remain trapped to the lower terrace in the vicinity of the step and it will diffuse along it, because calculated step energy barriers are higher than the center-of-mass kinetic energy of cluster. At higher temperatures, the nanoparticle will move away from the defect but always in the lower terrace.

If we consider now a textured silicon surface we will obtain a different result. This part of measurements has been performed during a period spent at the Departement für Physik, University of Basel (CH), in the group of Prof. Ernst Meyer and Dr. Enrico Gnecco.

We have prepared a $4 \times 4$ matrix of groove patterns using Focused Ion Beam (FIB) technique on silicon substrate covered by native oxide. Each pattern is $10 \times 10 \, \mu\text{m}^2$ and for manipulation measurements we have used 42 nm gold nanoparticles in air conditions. All patterns have pitch between 125 and 500 nm, depth equal to 5 and 20 nm, and fixed width of 50 nm, thus the dimensions of the grooves are comparable with clusters.

Even if we do not have an high number statistics of events, nevertheless, as visible in the Fig.4.23 Panels a) and b), a preliminary evidence is that the trajectories of nanoparticles are influenced by the presence of grooves but in a different way with respect to graphite edges.

Orienting by some different angles the grooves with respect to the slow scan axis, we have seen that a cluster pushed by the tip above a patterned area will follow the direction of the grooves just like on graphite steps but, in the observed events, the particles moved from one side to the other one, alternatively.

However many other experiments varying the angle between grooves and slow scan axis and testing different patterned surfaces (ripples, holes) to improve the
Figure 4.23: In this picture two topographic images of a manipulation step of 42 nm particles on silicon patterns are presented. The only difference between them is in the value of the pitch. On Panel a) pitch \( p = 250 \) nm and on Panel b) \( p = 150 \) nm. The depth and the width are 5 nm and 50 nm, respectively. In both images trajectories of a sliding cluster are visible and highlighted by arrows. As one can see, clusters on patterned surface globally follow the direction of the pattern, but alternate particle overcomings of the groove occur.

statistics of events are necessary.
Conclusions

Summarizing, in this PhD thesis we have presented a new and unconventional experimental approach to study quantitatively the friction behaviour of single contacts at the nanoscale, obtained by depositing well characterized nanoclusters on clean surfaces. We have opted for gold nanoparticles with spherical shape with nominal diameter of $13 \pm 2$ nm, $24 \pm 3$ nm and $42 \pm 4$ nm. They have been prepared by chemical synthesis [43] and deposited by droplet on freshly cleaved HOPG and on silicon with a layer of native oxide.

The clusters have been moved in a controlled way by using the atomic force microscope setup. Resulting information can be obtained analyzing the torsional bending of the cantilever (Friction Force Microscopy, FFM, see for example [37] [38] [39] [40]) or the energy dissipation in the interaction between tip and sample through the phase shift signal at the onset or during the cluster translation. Among these two possible AFM modes we have concentrated on the analysis of the energy dissipation signal which is obtained operating the system in tapping mode AFM with amplitude modulation feedback (AM-AFM).

We have shown in Chapters 3 and 4 that the periodic tip-cluster interaction, characteristic of AM-AFM, is able to induce depinning events and to produce smooth movements of particles having comparable or smaller dimensions with respect to tip apex [42] [51] [3]. Nevertheless the connection of the corresponding energy dissipation signal to the friction forces acting on the system cluster-on-surface is only indirect and it requires a specific model.

On the other hand, the use of AFM in contact mode to push nanoclusters can give a direct evaluation of the friction force corresponding to the induced cluster movement. Nevertheless, aligning the torsional bending of the cantilever to the sliding path of cluster having an overall dimension comparable or smaller than the typical tip apex may result a very critical issue.

The main advantage of using cluster manipulation as compared to FFM relies on the better control of the sliding interface. The AFM tip in fact is ideally disentangled from the physical system in exam because the contact region between the cluster and the substrate now represents the interface we are measuring on. So a wide range of well established cleaning and deposition techniques can be used to
prepare first the surface, and then depositing the overlayer in form of nanoclusters. In comparison, during FFM measurements, the tip, which is one of the interface side, is much more difficult to prepare and to maintain in stable conditions. Usually only the substrate can be properly cleaned and characterized before and after a FFM measurement.

During our experiments on gold nanoparticles in air conditions we have verified using different setup (different cantilevers and combinations of Amplitude Setpoint $A_0$ and free oscillation amplitude $A$) that the parameter able to univocally control detachments and the following manipulation is the energy dissipation signal on each cluster, evaluated from phase shift signal. Thus using this parameter it is possible to identify an energy threshold below which detachments do not occur, so it is a clear indicator of the energy threshold necessary to obtain the detachment. This energy threshold correctly depends on the substrate and on the cluster size.

Resulting depinning energies for each dimension of cluster and for each substrate are summarized in Tables 4.1 and 4.2 in Chapter 4. We note that particles of 42 nm of nominal diameter on silicon dioxide have been tested but they resulted too strongly pinned to the substrate, so a suitable statistics of depinning events has not been reached.

The interesting result is that the increasing of dissipated energy for each substrate is consistent with the variation of sizes of clusters, so with the increasing of nominal contact area. For what concerns the contact area dependence on friction forces, we have made a comparison between our measurements and results obtained by Ritter et al. [33] with AM-AFM experiments on similar systems (antimony clusters on HOPG and mica surfaces) and a similar behaviour is obtained (Table 4.3). Static friction and energy dissipation at the onset of movement decrease both linearly with the contact area, with the exception of few events where movements without apparent friction have occurred.

Experiments performed by Dietzel [46] in UHV conditions and in ambient environment produce similar results but an increase of frictionless translations has been noticed while working in UHV and very clean conditions. This observation supports the hypothesis that at these small contact areas the linear dependence of frictional force is due the presence of a small amounts of mobile molecules trapped at the interface.

Moreover, we would like to highlight that values of depinning energy on HOPG differ from those on silicon dioxide of about two orders of magnitude. This is in agreement with many results [49] [57] [58] of high mobility at different temperatures of nanoclusters grown in UHV on graphite. This aspect can indicate that the interface between gold nanoparticles and HOPG is characterized by a relatively low surface energy. On the other hand the formation of capillary neck in the contact between cluster and surface cannot be neglected in our experimental
conditions. The silicon dioxide surface is characterized by a more hydrophilic behaviour with respect to graphite, which means that stronger capillary forces can be build around nanoscale particles deposited on the SiO$_2$ surface. All these general properties are confirmed by our experimental results in which the contact is controlled down to the nanometer scale. Nevertheless as a future perspective a direct comparison of our experimental energy values with those obtained with different techniques or by numerical simulation requires dedicated measurements and modelling.

To better clarify the role of capillary forces in our system, also on substrates (like graphite) that are well-known for their hydrophobic behaviour, we have performed a large number of measurements in nitrogen atmosphere. We have focused our attention on 42 nm nanoparticles on HOPG. In the first part of these experiments we have been able to scan same areas before in nitrogen flux and immediately after in air conditions, without interrupting tip-sample interaction. The immediately visible result was that, keeping constant the energy given to the system, depinning events that were present in nitrogen did not occur in air. Reaching a suitable statistics of detachments in nitrogen, we have found an energy threshold for 42 nm particles on graphite well separated from that measured on the same system in air conditions (see Table 4.4). In particular we have obtained an energy threshold of $67 \pm 30$ eV. Following this point of view further sensitive experiments are required, but as a preliminary result we may conclude that the graphite surface, well-known for its hydrophobical behaviour, is sensitive to the atmosphere conditions (e.g. humidity) and the presence of water layers and capillary forces play a relevant role in detachment events and contacts at the nanoscale.

We have tested also the influence of defects present on the surface on the trajectory of the sliding particle. It has been observed that the cluster trace is always parallel to the slow scan direction, for both flat substrates like silicon covered with native oxide and graphite terraces. If on the contrary defects like steps or textured patterns (e.g. grooves, ripples, holes) are present, different situations can be achieved. Generally the role of a superficial defects is represented by a deviation of the sliding particle, but if on one hand a graphite step up to few nanometers of height is a formidable obstacle for a cluster also ten times larger, on the other hand a groove of depth 5 nm and width 50 nm can be relatively easily passed by a 42 nm particle. Our observations are completely in agreement with MD simulations performed by Yoon and colleagues [59], in which they have concluded that graphite defects like holes and descending step act as repulsive Schwoebel-like barriers at room temperature. Instead ascending steps are trapping areas for gold clusters, so their movements occur along the edge on the lower terrace. These preliminary results on this particular aspect of dynamics have been obtained in collaboration with the University of Basel (CH).

As future perspectives, thanks to the high reproducibility of our method, some
measurements of 13 nm and 24 nm on controlled atmosphere on graphite have to be performed, and, to make a comparison with theoretical works in literature, the influence of temperature in the activation energy could be experimentally investigated. At the end a new challenge could rise up: our experiments have provided three points in the curve dissipated energy versus contact area. Consistently with experimental and theoretical results, our data show a linear behaviour, but they could be fitted, with a lower level of confidence, also with a power-like curve. To clarify this intriguing behaviour, analogue measurements for other different dimensions of nanoclusters have to carried out in the future.
Publications and Conferences


Bibliography


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