Dissipative and Electrostatic Force Spectroscopy of InAs Quantum Dots by Non-contact Atomic Force Microscopy

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To my wife and my son.

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Abstract

This thesis is devoted to the studies of self-assembled InAs quantum dots (QD) by lowtemperature Atomic Force Microscopy (AFM) in frequency modulation mode. Several spectroscopic methods are developed to investigate single electron charging from a two-dimensional electron gas (2DEG) to an individual InAs QD. Furthermore, a new technique to measure the absolute tip-sample capacitance is also demonstrated. The main observables are the electrostatic force between the metal-coated AFM tip and sample as well as the sample-induced energy dissipation, and therefore no tunneling current has to be collected at the AFM tip.

Measurements were performed by recording simultaneously the shift in the resonant frequency and the Q-factor degradation of the oscillating cantilever either as a function of tip-sample voltage or distance. The signature of single electron charging was detected as an abrupt change in the frequency shift as well as corresponding peaks in the dissipation. The main experimental features in the force agree well with the semi-classical theory of Coulomb blockade by considering the free energy of the system. The observed dissipation peaks can be understood as a back-action effect on the oscillating cantilever beam due to the fluctuation in time of electrons tunneling back and forth between the 2DEG and the QD.

It was also possible to extract the absolute value of the tip-sample capacitance, as a consequence of the spectroscopic analysis of the electrostic force as a function of tip-sample distance for different values of the applied voltage. At the same time, the contact potential difference and the residual non-capacitive force could also be determined as a function of tip-sample distance.

Résumé

Cette thèse a pour objet l'étude de boites quantiques (BQ) auto-assemblées d'InAs par la technique de Microscopie à Force Atomique (AFM) à basse temperature et dans le mode de modulation de fréquence. Différentes méthodes de spectroscopie sont développées dans le but d'étudier l'effet de chargement par un électron unique d'une BQ individuelle à partir d'un gaz d'électron bi-dimensionel. Les principales observables sont d'une part la force électrostatique entre la pointe AFM métallisée et l'échantillon, et d'autre part l'énergie dissipée induite par l'échantillon.

Les mesures sont effectuées en enregistrant simultanément le décalage de la fréquence de résonance et la dégradation du facteur de qualité d'une poutre oscillante en fonction soit de la différence de potentiel, soit de la distance pointe-échantillon. La signature du chargement d'un électron unique est détectée comme un changement soudain du décalage en fréquence ainsi que par un pic correspondant de dissipation. De telles caractéristiques expérimentales observées dans la force sont en accord avec la théorie semi-classique du blocage de Coulomb en considérant l'énergie libre du système. Les pics de dissipation observés peuvent être compris comme un effet de rétro-action sur la pointe AFM, dont l'origine est la fluctuation dans le temps du chargement par effet tunnel des électrons entre la BQ et le gaz d'électron bi-dimensionel.

Il fut également possible d'extraire la valeur absolue de la capacité pointe-échantillon, comme conséquence de l'analyse spéctroscopique de la force électrostatique en fonction de la distance pointe-échantillon pour différent potentiel appliqué. La différence de potentiel de contact et la force résiduelle purent aussi être déterminée en fonction de la distance.

Statement of Originality

The author claims the following aspects of the thesis constitute original scholarship and an advancement of knowledge. So far, one of these findings has been published.

- The processing of several frequency-shift versus distance curves for different applied bias voltage enables the determination of the absolute tip-sample capacitance as well as the contact potential difference and the residual non-capacitive force as a function of tip-sample distance. [R. Stomp, Y. Miyahara, D. Weiner and P. Grutter, submitted to *Appl. Phys. Lett.*]
- The detection of a single electron charging event from a 2-dimensional electron gas to a self-assembled quantum dot at liquid Helium temperature has been experimentally observed through the measurement of the frequency shift versus voltage curve, also called Electrostatic Force Spectroscopy. Each charging event is demonstrated by an abrupt change in the resonance frequency of the oscillating AFM cantilever. [R. Stomp, Y. Miyahara, S. Schaer, Q. Sun, H. Guo, P. Grutter, S. Studenikin, P. Poole, A. Sachrajda, *Phys. Rev. Lett.*, **94**, 056802 (2005)]
- Highly non-linear terms in the force such as a step function can lead to different behaviors in the frequency shift of the cantilever depending on the tipamplitude.
- The experimental observation of energy dissipation peaks correlated with the charging of an individual quantum dot at liquid Helium temperature was achieved. Such peaks could be explained as originating from the fluctuation in time of the interaction force due to the stochastic nature of electron tunneling in and out of the QD. [in preparation]

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1

Introduction

Single electron charging and tunneling are two fundamental phenomena that govern the transport properties of a wide range of nanoscale systems from artificially confined nanostructures such as quantum dots down to single atoms and molecules. The last two decades or so have seen a tremendous rise in the ability to control electron transport in mesoscopic or low dimensional systems [4, 5] thanks in part to the advanced development of epitaxial growth techniques of semiconductor heterostructures, which can produce atomically smooth interfaces to confine electrons in one, two or three dimensions. In particular, research on semiconductor quantum dots (QD) exhibiting quantum effects [6] suggest to use them as building blocks for quantum information processes scheme by either using the electron-spin [7] or any electron state in the dot as carrier of quantum information to obtain what is called a quantum bit (or qubit) [8, 9]. These quantum dots are lithographically defined by microfabricated electrodes drawn on top of a 2-dimensional electron gas (2DEG), and therefore exhibits rather large dimensions (100 nm or larger).

On the other hand, much less work has been performed on the transport properties of *self-assembled quantum dots* (SAQD). The main challenge in the experimental investigation of such dots lies in the ability to probe them *individually*, because of their small size and random distribution on a sample surface, which makes it difficult to draw sub-micron electrodes close to them. In that respect, **Atomic Force** **Microscopy** (AFM) can prove to be not only a valuable tool to image individual QD, but also a local movable gate and a local electrometer to detect charge down to a single electron. This is the main goal of this thesis, which consists in bringing together the now mature technique of scanning probe microscopy with the emerging field of self-assembled quantum systems.

In this introductory chapter, an overview of quantum dots properties and applications will be first given, followed by a review of some recent advances in probing the transport properties of such dots by several techniques. Lastly, the motivation and originality of using atomic force microscopy for performing spectroscopic analysis will be put into context.

1.1 Overview of Quantum Dot Physics

Usual bulk materials exhibit transport properties that can be understood in terms of macroscopic or statistical quantities, as well as from the periodicity of the lattice. In this case, the actual size and geometry of the sample does not really matter: it is assumed infinite in all dimensions. On the other hand, man-made nanostructures such as two-dimensional electron gas (2DEG), nanowires and quantum dots (QD) have in common that at least one of their dimensions become comparable (or smaller) in size to the Fermi wavelength of the electrons in the dot so that it is no longer possible to neglect some quantum mechanical effects. In such a case, the wave-like nature of particles becomes increasingly relevant, and coherent transport becomes a more appropriate description of low-dimentional systems. This is the domain of mesoscopic physics where quantities such as conductance or resistance are quantized and energy levels are discrete.

A QD is an excellent example of a mesoscopic system, since electrons are confined in all three dimensions. QDs are therefore often referred to as a zero-dimensional objects. Their actual sizes can range from several angstroms to a tenth of a micron, which determines an important QD parameter, namely the capacitance, C, between the dot and its environment (e.g. especially the leads). At this scale, the capacitances encountered are so small that the energy required to charge a structure with even a single electron is such that $e^2/2C \gg kT$ has to be always satisfied. Therefore, depending on the temperature and the geometrical size of the dot and the leads, charge transfer into and out of the structure can be inhibited by this inequality, which is known as Coulomb blockade. The 3D confining potential present in a QD is also responsible for allowing electrons only on discrete energy levels and many physical properties, such as the splitting of energy levels under electric and magnetic fields, spin-orbit coupling, and so on are conceptually similar to those which can be found in ordinary atoms, that's why QDs are also often called "artificial atoms" [10].

In terms of their applications, QDs seem very promising since their optical and electronic properties can be tailored in many different ways by changing their size or the material from which they are made. A non-exhaustive list of applications already implemented or being pursued is: more efficient lasers with lower threshold current [11, 12, 13], single photon source [14, 15], logic and memory devices [16], and solid state quantum computing [9]. Such a variety of applications is also reflected in the fabrication of QDs themselves, where both a top-down or a bottom-up approach are explored, which produce different types of QD for different kinds of applications. The top-down approach consists of drawing sub-micron electrodes on top of a 2DEG so that the electrostatic potential applied to the electrodes confine electrons underneath. Such QD are lithographically defined, where electrons are confined laterally, in the plane of the 2DEG. These QD structures, often referred to as *lateral QD*, have the advantage of being quite easily scalable and permit a large number of electrodes to change precisely the electrostatic environment of the dot. The drawback is that the overall dot size is rather big, at least 100nm, because of the size of the electrodes, therefore the charging energy is small with respect to the thermal energy, which means that typical experiments have to be carried out in the sub-kelvin temperature range.

In order to achieve higher temperatures or even room-temperature quantum dot devices, the self-assembled (or bottom-up) approach is often preferred since it can more easily reduce the dimension of QDs down to a few nanometers or less, which means a larger charging energy. Several self-assembling methods are being explored, which can be categorized into either colloidal and nanocrystal quantum dots on the one hand or semiconductor quantum dots on the other. The first category of selfassembling method can produce very small dots, such as CdSe nanocrystals [17], Aumetal nanoparticles, for instance, which can exhibit a very large charging energy as well as photoluminescence and optical properties. Such techniques are mostly found in chemistry labs, and these methods have already been passed on to the industry which can now propose a commercial variety of nanoparticule QDs [18]. The second category of self-assembled QDs comes mainly from physics labs that work on the growth of semiconductors in Ultra-High Vacuum (UHV) conditions. The advantage of using semiconductor material is that it can be easily integrated with some other semiconductor devices, and because the Fermi wavelength, which depends on the carrier density, is rather large in semiconductor compared to metal, it is possible to work with intermediate size dot (about 40 nm) in contrast to both very small metal nanocrystal and the large lithographycally-defined QD. The method of producing such self-assembled QDs can be achieved with different epitaxial growth techniques, where atomic layers of material can be added one by one. For the purpose of our discussion, we will describe here the fabrication of samples investigated in this thesis. This current method relies on the accumulation/relaxation of elastic energy within a thin, two-dimensional layer having a small lattice mismatch with the underlying lattice. Above a critical thickness, the 2D layer (or wetting layer) becomes unstable and the nucleation of three-dimensional, coherently strained islands spontaneously form from the wetting layer. In this way, the whole wafer surface is uniformly covered by QD,

(a) Coulomb blockade (b) Double barrier junction Tunneling -Ne barrier C_{l} , R_{tl} $\Delta E + e^2 / C$ Source Drain (c) Conductance peak ⊳ N+1 N< $\Delta E + e^2 / C$ e^2/C el B Source Source Drain Drain $\mu_{dot}(N+1)$ $\mu_{dot}(N)$

whose overall size and distribution can vary depending on the growth parameters [19].

Figure 1.1: Coulomb oscillations in a quantum dot in the linear regime. (a) Current is blockaded when no level in the quantum dot is aligned with respect to the difference of potential V_B . (b) Equivalent circuit representation of the double barrier junction, with an effective tunneling resistance and capacitance. (c) When a QD energy level sits between the difference of potential of the two leads, a constant flow of electrons can tunnel in and out of the dot but only one at a time: each time an electron tunnels on the dot the charging energy has to be overcome. Adapted from [5].

The most common and straightforward way to study the transport properties of QDs or any nanostructure, consists in measuring their conductance. Unlike bulk systems, conductance is restricted to some special conditions imposed by the dot size and geometry. Figure 1.1 illustrates schematically the physical picture of Coulomb oscillations, that is the succession of conductance peaks separated by domains where no current flows (see figure 1.2 for an experimental I - V curve). Experimentally, two leads have to be attached to the QD via tunnel barriers as depicted on figure 1.1(b). If the source-drain bias V_B lies between the Coulomb blockade gap no current can flow: figure 1.1(a). As voltage is ramped up, electrostatic energy builds up until it

reaches the value $\Delta E + e^2/C$ for which one and only one electron can tunnel in from the source to the dot, now changing the dot electrostatic energy and electrochemical potential μ from $\mu_{dot}(N)$ to $\mu_{dot}(N+1)$, so that we can define the addition energy (energy required to add an electron to the QD) as:

$$E_{add}(N) = \mu_{dot}(N+1) - \mu_{dot}(N) = \Delta E + \frac{e^2}{C}$$
(1.1)

where ΔE corresponds to the energy level spacing in the QD and e^2/C is called the charging energy. When an electron has tunneled in, the dot's electrostatic energy suddenly changes by e^2/C , and the electron in the highest occupied state is able to tunnel off to the drain, leaving again the dot in the state $\mu_{dot}(N)$ so that another electron from the source can tunnel in. This repeated process permits one to collect enough tunneling electrons so that a conductance peak is observed. Figure 1.2 is an example of an experimental spectrum obtained for such a configuration on a selfassembled QD. This simple picture of a two probe measurement can be further refined by introducing a gate voltage that can change the dot energy through electrostatic coupling and therefore shift QD energy levels with respect to the source-drain bias.

Due to their very small size, the challenge of characterizing and using the properties of self-assembled QDs consists mainly in having direct access to just a single one of them so as to locally modify its environment by external fields. This was the main motivation for this work wherein the use of AFM is considered a key technique. The next sections will therefore expose briefly the state-of-the-art techniques used so far for investigating QD and the motivations for using the AFM as a spectroscopic tool in the electrostatic regime.

1.2 Recent Advances in Charge Detection

In the literature, the majority of transport experiments on quantum dots have been performed on lateral QD, i.e. built from a top-down approach, and several good re-



Figure 1.2: Scanning Tunneling Spectroscopy of single InAs nanocrystal quantum dot on gold substrate. The tunneling barrier between the nanocrystal and gold is produced by a self-assembled monolayer of Di-Thiol. Adapted from reference Banin *et al* [1]

views can be found [10, 20]. Research on self-assembled dots, i.e. built by a bottom-up approach, because it is quite new, has focused mainly on the growing techniques to produce them so as to tailor their optical and electronic properties for various applications. Charaterisation of SAQD is done mainly by optical spectroscopy or transport properties on a large ensemble of such dots. Here we would like to focus on the shift from a dot-ensemble characterisation to an individual SAQD characterisation. It will nonetheless be very instructive to comment on very recent and astonishing results obtained on lateral QD, since such an achievement should one day be applied to SAQD.

In regard to transport experiments on SAQD, original work was performed by using capacitance spectroscopy, i.e. recording capacitance versus voltage curves (C - V spectra), to directly probe energy levels, charging energy, and electron-electron interaction [21, 22] in a large ensemble of QDs. This technique is very useful when the charging energy is important or of the same order of magnitude as the energy level spacing, since by being sensitive to a capacitance change, one has direct access to the charge per unit voltage. Another great advantage of this technique is that it is not more complicated to perform a magnetotransport experiment by applying a magnetic field [23], or study the dynamics of electron tunneling by varying the applied bias frequency [24]. The main drawback of this technique is that it averages the signal over a large ensemble of QD due to the macroscopic size of the electrodes.

That is why in the recent past the success of C-V spectroscopy created the need to carry out transport measurements on individual SAQD to get a better understanding of, and more control over the electronic state in such a device. Due to its high versatility, SPM has often been preferred for performing spectroscopy of individual nanostructures. In particular, Scanning Tunneling Spectroscopy (STS) enables the measurement of tunneling current flowing in the double barrier tunneling junction (DBTJ) formed by the tip, some nanostructures, and the back electrode, which was already presented schematically in figure 1.1(b). A typical example of an I - Vcharacteristic obtained for such a configuration on an InAs nanocrystal is presented in figure 1.2 and clear features can be observed which give valuable information on the charging energy and energy levels of an individual nanocrystal [1, 25]. Such direct transport measurements can therefore reveal many properties of any device in-between the DBTJ, even wave function mapping [26], but are still limited to substrates with adequate conductivity.

A more direct and intuitive solution, but quite challenging in practice, to carry out transport measurement on individual SAQD, is to fabricate nanolithographically-



Figure 1.3: (A to H) Evolution of SGM features with tip voltage. In all images, dashed lines show the location of the nanotube and contacts. Concentric rings are seen as electrons are removed from the dot as the tip approaches. (I) Charge occupancy of dot inferred from image at Vtip = 150 mV. The tip can either increase or decrease the occupancy of the dot, depending on its position, as it screens the dot from its electrostatic environment. Adapted from Woodside and McEuen [2].

defined electrodes on the sample with the possibility of having some dots lying in between them. Such achievement was reported very recently by Jung at al on InAs SAQD, who could observe Coulomb blockade oscillation in a lateral transport configuration [27]. This technique is however not suited for measurements on a routine basis as it requires intensive nanofabrication time, particularly if one aims to gather statistical information on the transport properties for different dot sizes and distributions. From a different perspective, the ability to perform transport measurements with such electrodes can be further refined by bringing a small tip from a Scanning Probe Microscope (SPM) in order to build a three-probes measurement similar to a transistor. In this case, it becomes possible to image directly quantum phenomena such as Coulomb blockade oscillations around a QD [2, 28], where the SPM tip acts as a local gate, locally modifying the dot electrostatic environment, hence the name of Scanning Gate Microscopy (SGM). The result obtained on a carbon nanotube contacted at both end by an electrode is illustrated in figure 1.3. These rather spectacular results obtained by such methods rely nonetheless very much on the ability to fabricate sub-micron electrodes, which can be a severe limitation, especially when the method is used on self-assembled nanostructures where there is no real control over where the structures of interest will grow with respect to the leads. Moreover, the coupling between the lead and a single molecule or nanostructure is far from trivial, since at this scale the leads themselves can have some complicated quantum behaviour as some recent work has reported [29]. From this point of view, it would be interesting to study the effect of the leads independently so as to separately study their effect on the SAQD.

Turning now to some recent achievements on *lateral QD*, we would like to address the issue of single-shot read out of electron tunneling in a QD. Apart from the interest of electron dynamics, the importance of single-shot read out techniques [30, 7] should enable ultimately the realization of qubit readout [8, 9], a necessary preliminary step towards building solid-state quantum computers.

So far and at large, most experimental set-ups rely on measuring a current that flows directly through the nanostructure to deduce its properties by current-voltage characteristics. This is referred to as a traditional transport experiment. Such a technique offers many advantages but no real control over a single electron can be achieved since the measured current always corresponds to a statistical average of the charge over time, and the tunneling current collected in such experiments typically corresponds to 10^{10} electrons to obtain a current of 1pA in one second (typical time used to record an I-V curve for instance). Therefore, if one wants to follow the dynamics of electrons in such a device, or the state of one electron in particular, experiments have to be designed with ac-current in the GHz regime and a very large measurement bandwidth [30]. Some complementary approaches can also be implemented for detecting single charge, which consists in using a Quantum Point Contact (QPC) or a Single Electron Transistor (SET) in the close proximity of a QD device and probing the charge state through its electrostatic coupling with the QPC or SET. A QPC is quite easy to build since it only consists of a small geometrical constriction that allows only discrete values, multiples of the quantum of conductance: $G_0 = 2e^2/h$, in the direction of the constricted channel. The SET on the other hand is slightly more complicated since it is a three-probes measurement, like a normal transistor, but for which the channel region is made of a small conductive island embedded in an insulator region between the source and the drain.

Very recently, single-shot read-out of spin qubits via spin to charge conversion, that is, charge in the dot remains constant only for spin-up state and changes by one for spin-down state, was first observed at the Delft University of Technology [7]. In this case, the ability to measure the presence or absence of a single electron was crucial. The average value over many single electron events would average out the spin information. Figure 1.4 illustrates the experimental details of the device where

1 Introduction



Figure 1.4: Scanning electron micrograph of a lateral QD and example of a Quantum Point Contact as a charge detector to probe the QD charging state. The QD is represented schematically as the dash circle. Note the constriction defined between electrodes R and Q that creates the QPC. Adapted from Elzerman et al [7]

the QPC is defined between electrodes R and Q and serves as a charge detector. If the amount of charge present in the dot changes, then the electrostatic potential of electrode R also changes, thus modifying the constriction defining the QPC and therefore the current *I*. In this case, and contrary to conventional transport measurement, no current directly flows inside the QD but only on the side to measure the value of the QPC that is capacitively coupled to gate R. Even though this thesis will not deal with QPC and lithographically defined QD, such work done on lateral QD sets a good background to highlight the aim behind this work: to use the electrostatic coupling between an AFM tip and a SAQD in order to probe the charge state of the dot. Such a configuration will offer new advantages, since in this case, the probing tool is mobile and the electrostatic coupling can be changed at will by simply changing the tip-sample distance. On the other hand, improvement toward higher resonance frequency cantilever [31, 32, 33] will be necessary if one is to reach single-shot measurement.

1.3 AFM as a Spectroscopic Tool

Not many years after the invention of the Scanning Tunneling Microscope (STM), Binnig et al [34] applied the same principle to image a surface with a very small tip attached to a flexible cantilever sensitive to various kinds of forces. This gave rise to the large family of Scanning Force Microscopes whose domain of applications are almost ubiquitous in the field of surface science.

The advantage of AFM is that not only can one image the topography of the surface, with the ultimate resolution of imaging real-space atoms on non-conducting surfaces [35], but very interestingly, one can also make all kinds of force images (electrostatic, magnetic, etc.) that give other relevant information about the sample properties apart from its topography. This is the primary goal of AFM: to record images of a surface at various conditions and with different choices of operation modes. A second use of AFM for sample characterisation is to perform force spectroscopies on a very local scale. Several spectra are obtained by sweeping either the tip-sample distance z, or the tip-sample voltage V, for a given and fixed x - y position above the sample. Applied to semiconductor surfaces, Electrostatic Force Microscopy (EFM) has been used for electrical imaging and characterisation using a conductive tip. Different modes of EFM are Kelvin Probe Force Microscopy (KPFM) [36], Scanning Capacitance Microscopy (SCM) [37, 38], and Scanning Spreading Resistance Microscopy (SSRM) [39]. In each case, the goal is to map a particular electric property of the sample from the measured electrostatic force, such as the contact potential difference, the change in sample capacitance or the carrier distribution in a semiconductor device.

It is also possible to use the AFM tip in a more invasive way to directly inject charges by either applying a voltage pulse between the AFM tip and the sample at very close tip-sample separation (below 5 nm) [40] or by a direct contact electrification [41]. Detection of the amount of charge deposited can be done by electrostatic force imaging or by monitoring either the amplitude [42] or frequency [43] of the cantilever response at a given height. Original investigation on carrier injection and recombination was performed by Schoenenberger and Alvarado [44], followed by several works on charge injection for Co nanoclusters on an insulator [45], SiO₂ insulator surfaces [46], an isolated metallic dot attached to the apex of an AFM tip [47, 42] and in individual silicon nanoparticles [48]. The study of the kinetic roughening of charge spreading was also reported in a silicon nanocrystal network [49]. These works have encouraged research toward the ultimate goal of detecting a single electron. Recently, the observation of single-electron tunneling events between a metal probe and the localized states of an insulator surface was achieved in UHV at room temperature [43]. Electrostatic force spectroscopy has also been applied to detect near-surface localized states [50].

So far, the techniques described above still lack appropriate control and reproducibility if one aims at single electron manipulation as was achieve for example in the previous section on single shot read out with lateral QD. One necessary requirement will be to use the AFM tip as both a local gate and an electrometer so as to inject and detect a single electron on demand. Moreover a weakly disturbing measuring scheme has to be thought of in order to detect the presence or absence of an electron in confined structures, even more so when the aim is to read-out their quantum information. In such a case, the detection of a single charge through a weak capacitive coupling made between the AFM tip and the SAQD can prove to be an important step toward that goal. Electrostatic force spectroscopy with a conductive AFM tip will be our main tool to detect single electron charging in individual selfassembled quantum dot. The QD will be gated by applying a voltage between the tip and a buried back electrode. The basic idea behind this approach is to try to combine the capability and achievements of capacitance spectroscopy with the high spacial resolution of AFM.

1.4 Outline

The rest of this thesis will present research into the local electronic properties of SAQD using Atomic Force Microscopy and concentrate on the detection of single charge events using simultaneously electrostatic force and dissipation information. The structure of this thesis is described as follows: an overall review of the operation of the AFM in the non-contact mode and at liquid helium temperature will be presented in chapter 2, while chapter 3 will review the spectroscopic methods to investigate tip-sample interaction and as a consequence will expose a new method of determining absolute tip-sample capacitance. These chapters should set the appropriate background for the final and most important chapters. Chapter 4 and 5 will present the main experimental results of Coulomb blockade in quantum dots as well as the dissipative processes occurring between a single electron and a mechanical oscillator. Finally, chapter 6 will conclude and give a brief outline of the open questions and possible directions for future work.

2

Review of Low Temperature Non-Contact AFM

Conducting experiments at low-temperature, below 5K, offers many advantages as well as challenges. For instance, one can improve substantially the signal-to-noise ratio of the instrumentation and its overall stability. But most importantly, in the particular field of man-made nanostructures, lowering the temperature also means reducing the thermal noise to a level for which quantum phenomena can be observed. This last aspect has been fostering home-built, and improving existing commercial AFMs around the world with different applications in view. As a matter of fact, the AFM used for this study has already been used successfully for imaging magnetic vortices and the reader is referred to the articles [51, 52] and Ph.D. thesis of Mark Roseman [53] for a detailed description of the construction of such an AFM. In this chapter, focus will be made on the changes and improvements of the existing AFM. Furthermore, a review of the theoretical description of the AFM, in the noncontact mode as well as in the presence of electrostatic interactions, will be presented in order to set up the required instrumentation background for the rest of this thesis.

2.1 AFM at Cryogenic Temperature

2.1.1 The Challenges of Low-Temperature Experiments

Sometimes depending on the applications in view, only the sample stage has to be cooled down. While this configuration offers the flexibility of having the microscope remain at room temperature, it often exhibits a temperature gradient between the tip and sample or at different part of the sample that can actually create mechanical instabilities as well as drift. This particular SPM configuration is appropriate for instance for freezing molecules so as to limit their thermal motion, but doesn't improve the measured signal-to-noise ratio (since the measuring probe is still subject to room-temperature thermal noise) and usually does not agree well with careful spectroscopic investigations.

In general, it is more recommended to cool down the whole microscope when, as will be the case in this thesis, the aim is to investigate quantum phenomena in semiconductor heterostuctures. In such case, a factor of hundred can be gained in the signal-to-noise ratio of the AFM signal, because of higher value of the Q-factor and lower temperature of the cantilever itself and its surroundings. This improvement in the detecting signal is of great concern when very low signal has to be measured such as the force originating from a single electron. Moreover, the overall stability of the microscope at low temperature is also very helpful to perform spectroscopic analysis since the tip has to maintain its pre-set position without drifting over several minutes. On the other hand, the cooling procedure is more challenging and demanding on the microscope design. Here is listed some of the problems encountered:

- Different thermal contraction of the materials can result in unwanted stress in different parts of the microscope, resulting in misalignment of the optical detection system or misfunctionment of the inertial motors.
- Inaccessibility of the microscope in the cryostat as well as a geometrical constraint fixed by the Dewar tank opening.
- A good thermal anchoring of the wires entering the microscope so as to minimize heat exchange and reach the lowest possible temperature close to the cooling liquid (in our case 4.5K in a liquid helium environment of 4.2K).

- Mechanical and electrical noise arising from vibrational coupling to the outside of the microscope, via the wires, boiling helium, acoustic noise, vibration of the building, etc.
- Formation of ice and frozen nitrogen that can stick to the inertial motor for fine positioning and reduce the range of motion or stop the movement.

Most of these problems were already well taken into account by the previous Ph.D. student when the microscope was originally designed and assembled. In particular, a good vibration-isolation bellows from which the microscope hangs reduces the mechanical vibrations with the outside world (with a low vertical oscillation resonance frequency of 4Hz). The cylindrical symmetry of the design also prevents most of the time misalignment of the optical fiber with the cantilever and a good compensation for the shrinking of the microscope at 4.5K. Nevertheless, even with all this great care, improvements are always possible, especially in terms of the reliability of routine experiments and the improvement of the signal-to-noise ratio. Therefore, a number of modifications and improvements needed to be implemented at the beginning of this project and are summarized as follows:

1. Design and assembly of a new inertial motor for both *in situ* sample and optical fiber coarse positioning (see figure 2.1). Piezoelectric actuators were glued directly onto the main body of the microscope instead of the moving hexagon that carried either the piezotube or optical fiber chuck. This enabled optimal adjustement of the force applied on each actuator for optimal friction between the saphirre plate and the alumina, and does not depend on the position of the hexagon with respect to the saphirre ball (where the force is applied by tightening the screws). Macor was preferred as a lighter material (i.e. easier to move against gravity) for the replacement of the existing stainless steel hexagonal piece that carried the piezo-tube. Each piezoelectric actuator unit consists



Figure 2.1: Schematic drawing of the coarse positioning module. The plate that closes the module and onto which a force is applied is not shown for clarity.

of four PZT stacks (instead of two). In this case, the power developed by the six actuator units was enough to move the hexagon against gravity in a reliable way.

- 2. Re-cabling of the wires going inside the microscope chamber after passing through a newly designed heat sink (see figure 2.2). This stage makes it easier to replace or add wires in case of bad contact or short-circuit.
- 3. Replacement of a 50/50 optical fiber coupler by a 90/10 coupler in order to decrease the noise from optical feedback going to the laser diode. Indeed with such a coupler, the actual optical feedback that return inside the laser is only 9% instead of 25% previously obtained. This change improved the signal-to-noise ratio of the interferometric signal, since it was then possible to carry out the experiment with higher optical output power from the laser with a similar value of the optical noise (measured by the photo-detector, to a value of 2.8 mV_{rms}) and ultimately improve the frequency shift signal from 0.11 Hz to 0.08


Figure 2.2: Upper electrical connectors and heat sink, which exhibits a cylindrical symmetry. The connector housing can accomodate up to 48 connector pins distributed over two rows.



Figure 2.3: Schematic drawing of the heat stage made from Copper. Sample is glued on top. The two ship resistors are wired in parallel and buried inside the groove with Stycast glue suitable for low-temperature applications. The temperature is monitored with a PID controler from Lakeshore.

Hz resolution in a 120 Hz bandwidth for a tip amplitude of 5 nm.

4. Fabrication of a sample holder stage that can accurately heat the sample at room temperature up to 200 °C (see figure 2.3). Heating is achieved by applying a constant voltage to two ship resistors (for a more uniform heating) connected in parallel for a resistance equivalent of 500 Ω . We observed that the imaging conditions were greatly improved by heating the sample surface at 130 °C for 90 minutes so as to efficiently evaporate the water layer. With such heat stage it also becomes possible to carry temperature control experiments at liquid helium by inserting a 1 to 10 attenuator in the resistance path.

The last two points were not directly linked to the improvement of the microscope reliability, but rather to the improvement of the signal-to-noise ratio, as well as to better imaging conditions, since in most experiments a water layer on the surface forms into ice at low temperature and prevents the tip from approaching close enough to the surface (or image at a higher set-point). The amount of time required to implement these modifications, even though not directly linked to the actual physical experiments, was nevertheless very fruitful for latter applications since it gave the necessary reliability and sensitivity required to pursue the goals fixed in the Ph.D. degree.

2.1.2 Principle of Operation

A block diagram describing the main components of the cryogenic AFM is illustrated in figure 2.4. The tip oscillations are detected via an optical fiber that brings the laser beam from a photo-diode directly above the cantilever, thus creating a Fabry-Perot cavity between the fiber end and the back-coated side of the cantilever. From the interference pattern, one can deduce the tip oscillation amplitude and its overall motion with a very good accuracy (typical z-motion can be detected below one angstrom [54]). Due to its thermal motion, the AFM cantilever is self-oscillated at its mechanical resonance frequency, and then monitored by a positive feedback circuit that includes an automatic gain controller (AGC) and a phase lock loop (PLL) (now commercially available from Nanosurf [55]). The PLL measures the detuning of the original resonant frequency, or frequency shift Δf , caused by the tip-sample interaction, while the AGC regulates the tip amplitude response so as to keep it constant by monitoring the voltage applied to the excitation bimorph. This control enables the measurement of the dissipation in the cantilever oscillation simultaneously with the frequency shift measurement Δf . The tip-sample distance is monitored by the feedback controller and relies on the set-point given by the user which corresponds



Figure 2.4: Sketch of the AFM design for non-contact mode operation, and block diagram of the electronics. Note the two feedback loops necessary (in gray) to both regulates the tip-amplitude and tip-sample distance.

to a pre-fixed value of the frequency shift (usually few Hz). Usually in non-contact mode, it is preferable for the tip to always stay in the attractive regime of the interaction potential, and can be easily enhanced by applying a constant bias voltage V_B , at least when the tip is first approached towards the sample. When performing force spectroscopies, the feedback is frozen at a constant tip-sample distance while varying the applied voltage.

2.2 Review of Dynamic Force Microscopy

2.2.1 Versatility of Use of the AFM in Various Modes

It has now become almost impossible to keep track of all of the names given to SPM techniques, which depend very much on the type of applications in view. However, all these AFM related techniques share to some degree the same common platform of

feedback regulation, and therefore it is possible to present an overview of the three mains modes of operation of an AFM:

- 1. Contact Mode: the tip always stays in contact with the surface, and the force is measured optically by the deflection of a usually very soft cantilever. This is the simplest mode to operate. By being able to detect the torsion motion of the cantilever, one can also be sensitive to shear force.
- 2. Tapping Mode (or amplitude modulation): the tip is oscillated close to the resonant frequency of the cantilever and touches the surface only periodically and therefore enters occasionally into the repulsive regime of the interaction potential. In this case, the lateral shear force is minimized. The feedback regulation relies here on a change of the amplitude or phase from the free amplitude oscillation while keeping the driving frequency constant. This can be achieved with the use of a lock-in amplifier that records the amplitude and phase of the signal [56].
- 3. Non-contact Mode (or frequency modulation): the tip is oscillated at the resonance frequency of the cantilever but never touches (or taps) the surface and therefore always stays in the attractive regime. The signal is usually detected from the change in the resonance frequency when interaction occurs while keeping the amplitude constant. The electronics is slightly more complicated than the previous modes and relies on a frequency counter (now commercially available as a Phase Lock Loop) and an automatic gain controller to maintain the amplitude constant.

The last two modes by either amplitude modulation (AM) or frequency modulation (FM) detection are usually classified as dynamic mode AFM since they share many similarities, but their applications remain often quite different. Both modes have very

similar sensitivity in terms of their force gradient resolution, but the response time to a given excitation can change dramatically between AM and FM modes depending on the value of the *Q*-factor, which can change by several order of magnitude if the AFM set-up is in air or in vaccum. In particular, FM detection mode is more suited for high vacuum applications due to its fast response [57]. This fact is linked with the measurement bandwidth that, contrary to AM detection, is not dependent on the value of the *Q*-factor while the AFM sensitivity is (see section 2.2.3). It also remains sensitive to long-range forces when the tip is rather far from the sample, hence its name of "non-contact" mode. This is why Magnetic Force Microscopy (MFM) and Electrostatic Force Microscopy (EFM) are operated in FM-mode detection.

2.2.2 A Micro Electro-Mechanical Oscillator

In the following sections, we will consider the coupling between a mechanical oscillator with the electrostatic force of a polarized sample, which in some sense can be viewed as a micro-electromechanical system (MEMS or NEMS) so that some parallel can be drawn for the interested reader. It is good to start here by recalling the equation of motion of a forced, damped oscillator:

$$m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + kz = F_0\cos(\omega t) + F_{int}(d+z,t)$$
(2.1)

where the resonance frequency of the cantilever is $\omega_0 = 2\pi f = \sqrt{k/m}$ and the friction coefficient $\gamma = m\omega_0/Q$ which correspond to an effective damping or drag of the cantilever motion. Q is called the quality factor and gives a measure of how fast the cantilever relaxes to equilibrium. The right-hand side of (2.1) corresponds to the conservative interacting force between tip and sample $F_{int} = -\nabla V_{int}(z(t))$ and the driving force, with a magnetude F_0 and frequency ω which imposes its own frequency for the steady state solution that can be written as:

$$z(t) = A\cos(\omega t + \phi) \tag{2.2}$$

We labeled A the amplitude response of the cantilever and ϕ the phase of the signal. We can note that equation (2.1) is general, since most typical forces can be included in the term F_{int} and is often solved numerically by finite difference method when dealing with more complicated non-linear problems. In this section we stay in the linear, harmonic regime for clarity, and later we will focus our attention on the special case of electrostatic force.



Figure 2.5: Equivalent representations of the tip-cantilever motion and definition of the z-axis. A_d and A correspond to the bimorph and cantilever amplitude respectively. The right hand side image illustrates the rheological model of viscous damping between tip and sample. In first order approximation, an effective damping $\gamma = \gamma_1 + \gamma_2$ can be introduced, where γ_1 is the intrinsic damping and γ_2 , surface induced damping.

When there is no interaction, the steady-state solution for A and ϕ can be written in the following form:

$$A = \frac{F_0/m}{\sqrt{(\omega_0^2 - \omega^2)^2 + \frac{\omega_0^2 \omega^2}{Q^2}}}$$
(2.3)

$$\tan(\phi) = \frac{\gamma\omega}{k - m\omega^2} \tag{2.4}$$

To illustrate the behavior of the above equation, a typical experimental resonance curve that has a Lorentzian shape is shown on figure 2.6 and was recorded as the driving frequency was swept close to the natural resonance frequency of the cantilever.



Figure 2.6: Experimental resonance curves of amplitude and phase of the cantilever motion.

When tip-sample interactions occur, the force $F_{int}(z)$ will be responsible for a shift in the resonance frequency of the cantilever and can be understood by expanding $F_{int}(z)$ as a Taylor series around the equilibrium position $z_0 = 0$ of the oscillating tip: $F_{int}(d + z) = F_{int}(d) + z \frac{\partial F_{int}(d)}{\partial z}$. The higher-order terms of this expansion are usually neglected if one stays in the harmonic regime (i.e. only linear terms in z(t)). Moreover, the static deflection of the cantilever $F_{int}(d)$ is also neglected, which is a good approximation when the cantilever stiffness k is sufficiently high. This last assumption is usually well satisfied in non-contact mode AFM since typical spring constant are around 40 N/m. After all of these approximations, the equation of motion can be simplified in the following form:

$$m\frac{d^2z}{dt^2} + \frac{m\omega_0}{Q}\frac{dz}{dt} + \left(k - \frac{\partial F_{int}(d)}{\partial z}\right)z = F_0\cos(\omega t) + F_{int}(d)$$
(2.5)

It is then natural to call $k' = k - \partial F_{int}(d) / \partial z$ a new effective spring stiffness so that

the resonance frequency of the cantilever is shifted by the amount:

$$\omega_{0}^{'} = \omega_{0} \sqrt{1 - \frac{1}{k} \frac{\partial F_{int}(d)}{\partial z}} \cong \omega_{0} \left(1 - \frac{1}{2k} \frac{\partial F_{int}(d)}{\partial z} \right)$$
(2.6)

The experimental observable is the frequency shift and is noted as [57]:

$$\Delta f = -\frac{f_0}{2k} \frac{\partial F_{int}}{\partial z} \tag{2.7}$$

The new excited ampltitude will also be modified by this force gradient according to:

$$A = \frac{F_0/m}{\sqrt{(\frac{k'}{m} - \omega^2)^2 + \frac{\omega_0^2 \omega^2}{Q^2}}}$$
(2.8)

Therefore in dynamic mode, the distance-feedback regulator is not directly sensitive to the force itself but rather to its gradient via the frequency shift.

In fact, an implicit assumption in the above analysis was that the force gradient is constant over the whole z range of the tip-motion. In other words, equation (2.7) is valid only when the oscillation amplitude are small with respect to the decay length of the interaction force F_{int} . When this is not the case anymore (for long range forces and/or small tip-sample separation), a more refined calculation by first order perturbation theory using the Hamilton-Jacobi approach, but still remaining in the harmonic motion of the tip, gives the following expression that relates interaction force to the measured frequency shift [58]:

$$\Delta f(z) = \frac{f_0^2}{kA} \int_0^{1/f_0} F_{int} \left[z + A \cos(\omega_0 t) \right] \cos(\omega_0 t) dt$$
(2.9)

This more complicated and convoluted expression is valid for *all amplitudes* and expresses the fact that the interaction force has to be averaged over an oscillation period, which is of particulary importance when the decay length of the force is large with respect to the tip amplitude.

To illustrate the importance of the possible discrepancy between the two expressions (2.7) and (2.9), the same raw experimental data of a frequency shift versus



Figure 2.7: Comparison of equations (2.7) and (2.9) in the processing of the same experimental data of the frequency shift, gold tip over a gold substrate with an applied bias of -2.5V

distance curve has been processed using both expressions and plotted on figure 2.7. In this case, it seems evident that at shorter distance, one has to take into account the effect of the amplitude for the averaging of the force. Throughout this thesis, expression (2.9) will be preferred, especially due to the fact that we will deal with long-range electrostatic force at rather close distance. A numerical treatement of equation (2.9) will be necessary to accurately recover the interaction force from the frequency shift and will be explained in detail in the next chapter.

2.2.3 Noise Consideration

Before stating what are the main noise limitation sources of our measurement, it is informative to express the minimum detectable force intrinsic to any AFM measurement. This limitation is set by the thermal motion of the cantilever beam, since any force smaller than this thermal vibration would clearly be not detectable. From a statistical point of view, the cantilever is in equilibrium with a reservoir (i.e. its environment) that acts as a thermal bath. From the equipartition theorem, and since the cantilever motion has only one degree of freedom, we can equate thermal energy and cantilever oscillation energy so that:

$$\frac{1}{2}k_BT = \frac{1}{2}k\left\langle z_{th}^2(\omega)\right\rangle \tag{2.10}$$

where $k_B T$ is the thermal energy and $\langle z_{th}^2(\omega) \rangle$ the mean thermal motion of the cantilever, which can be obtained from the product of the thermal white noise drive of an oscillator, namely $F_{th}(\omega) = \sqrt{4m\omega_0 kT/Q}$, times the transfer function of the harmonic oscillator:

$$\left\langle z_{th}^{2}(\omega) \right\rangle = \frac{4k_{B}T\omega_{0}}{mQ\left(\frac{\omega^{2}\omega_{0}^{2}}{Q^{2}} + (\omega_{0}^{2} - \omega^{2})^{2}\right)}$$
(2.11)

This last equation tells us how the thermal fluctuations are distributed in the frequency domain and clearly, the higher the Q-factor, the more concentrated are the thermal fluctuations around the resonance frequency ω_0 . A detailed analysis of the signal to noise ratio is given in references [57, 59] and the minimum detectable force and minimum frequency shift can be written as:

$$\delta F_{min} = \sqrt{\frac{4kk_BTB}{\omega_0 Q}} \tag{2.12}$$

$$\Delta\omega_{min} = \sqrt{\frac{\omega_0 k_B T B}{k Q \langle z_{osc}^2 \rangle}} \tag{2.13}$$

where B is the measurement bandwidth and $\langle z_{osc}^2 \rangle$ is the mean square amplitude of the driven cantilever. From equation (2.12) we can notice that by diminishing the operating temperature and increasing the Q factor (by going to high vaccum), one can win at least one order of magnetude in the signal-to-noise ratio. It is also interesting to compute here what are the typical values of equations (2.13) and (2.12) for our system at different operating temperatures, assuming values for k = 40 N/m, $f_0 = 170$ kHz and value for Q ranging from 5000 at room temperature up to at least 50,000 at liquid Helium temperature. The value presented in table 2.1 are calculated

Table 2.1: Minimum detectable force and frequency shift calculated	ed at v	various te	mperatures
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Temperature (K)	300	77	4.5
$\delta F_{min}/\sqrt{B} [{\rm fN}/(\sqrt{{\rm Hz}})]$	11.1	2.82	0.41
$\Delta f_{min}/\sqrt{B} [\mathrm{mHz}/\sqrt{\mathrm{Hz}}]$	6.7	1.7	0.2

and correspond to the minimum force detectable *if the microscope was thermally limited.* Experimentally, this is not the case for our measurement bandwidth of 120 Hz, and the main source of limitation in our set-up comes from the laser shot-noise (for a more detailed description of this, see [53]), which gives a frequency resolution of 4 mHz/ $\sqrt{\text{Hz}}$ at 4.5 K. Fortunately, one does not have to be thermally limited in order to observe interesting phenomena. In fact, as will be demonstrated later in this chapter, we concluded that an optimal tip-sample geometry would more efficiently increase the signal of interest over the background noise than a more complete and tedious pursuit of diminishing the microscope noise sources.

2.2.4 Dissipative Mechanism

So far, we have been considering only conservative force without damping taken into account, even thought the general equation 2.1 introduces a generic damping of the cantilever included in the term γ . In reality, complicated dissipative mechanisms can be observed whose origins are not always well-understood [60]. Figure 2.5 in the previous section illustrates the difference between intrinsic damping γ_1 , always present due to the motion of the cantilever beam with respect to its base, and sampleinduced damping γ_2 , originating from the tip-sample interaction. In this section, we will explain the general form of dissipation through viscous damping, later in section 2.3.4, electric dissipation will also be discussed.

The general formulation of dissipation is often linked with the so called dissipation-

fluctuation theorem (DFT) which states that a change or fluctuation in a system will be dissipated as the system returns to equilibrium. For a small perturbation the response is linear and in this frame-work, the damping coefficient γ is related to the autocorrelation function of the fluctuating force F_{fluct} (due to brownian motion) by the relation:

$$\gamma = \frac{1}{2kT} \int_{-\infty}^{+\infty} \langle F_{fluct}(0) F_{fluct}(\tau) \rangle \, d\tau \tag{2.14}$$

This statistical approch is however not always straightforward to relate to an experimental observable measured with an SPM set-up. This problem of relating an experimental observable such as excitation amplitude (or feedback gain), with the actual power dissipated has recently been tackled successfully for both tapping mode [61] and non-contact mode AFM [62].

To account for the measured dissipation, we must distinguish between intrinsic dissipation noted $\langle P_0 \rangle$, and the dissipation originating from the tip-sample interaction, noted $\langle P_{int} \rangle$ so that the total average dissipation is:

$$\langle P_{tot} \rangle = \langle P_0 \rangle + \langle P_{int} \rangle \tag{2.15}$$

This total dissipation corresponds to the average power fed into the cantilever by an external driver so as to sustain the oscillation motion of the tip with the steady-state amplitude A. Since this driving force is coupled to the cantilever motion by Hooke's law, the average power delivered to the oscillating tip is:

$$\langle P_{tot} \rangle = \frac{1}{T} \int_0^T k[z(t) - z_d(t)] \dot{z}(t) dt = \frac{1}{2} k \omega A_d A \sin \phi \qquad (2.16)$$

Where $z_d(t) = A_d \cos(\omega t)$ is the oscillatory motion of the bimorph actuator (or any excitation mechanism that brings the cantilever into motion). In practice, the phenomenological approach of considering dissipation as a viscous damping (i.e. $F_{diss} = \gamma \dot{z}(t)$) is very effective for describing a large variety of phenomena. The rheological model

depicted on figure 2.2.2 is often used, so that we can write in this line:

$$\langle P_0 \rangle = \frac{1}{2} \gamma \omega^2 A^2 \tag{2.17}$$

In the above calculation we made the assumption that both intrinsic (γ_1) and extrinsic (γ_2) damping follow the same behavior so that $\gamma = \gamma_1 + \gamma_2$ in first order approximation [62]. Experimentally, we are interested in the dissipation originating from the tip-sample interaction, therefore the observable of interest for us is:

$$\langle P_{int} \rangle = \langle P_{tot} \rangle - \langle P_0 \rangle = \frac{1}{2} \frac{kA^2\omega}{Q} \left[\frac{QA_d \sin\phi}{A} - \frac{\omega}{\omega_0} \right]$$
 (2.18)

Where we have made use of the definition of $\gamma = k/(Q\omega_0)$. In fact for the derivation of equation (2.18) we had no other assumption that the signal was sinusoidal (i.e. in the linear harmonic regime) which means it is fairly general and can be applied to different AFM modes. Experimentally, we only need to record the ratio of amplitude or gain, A_d/A to calculate the actual dissipation and in practice $\sin \phi = 1$ because on resonance ϕ is very close to $\pi/2$. We will later use this equation to compare the measured signal fed into the system with the effective power dissipated.

2.3 Electrostatic Considerations

The AFM has the ability to sense any type of interacting forces between tip and sample. Therefore if we apply a difference of potential between two conducting materials, we will be able to probe electrostatic forces and be sensitive to the electric properties of the sample. This is what we call Electrostatic Force Microscopy (EFM). In terms of imaging techniques, the role of EFM is to probe the electrostatic contribution originating from the sample and eventually distinguish it from the actual sample topography. Some corollary techniques have emerged from EFM, such as Kelvin Probe Force Microscopy (KPFM) and Scanning Capacitance Microscopy (SCM), which are able to map the change in the sample work function and sample capacitance respectively. All of these techniques can provide much useful information, in particular in semiconductor heterostructures where electrical properties depend on many parameters such as carrier density, depletion regions, contact potential difference, etc. In this section, we will give an overview of the information obtained by introducing a voltage between tip and sample.

2.3.1 Capacitive Force

In principle, electrostatic force can be either attractive or repulsive depending on the charge, but when we consider two conductive surfaces connected together by a battery that provides a bias voltage V_B , there is always a build up of charge on both sides of the surfaces with opposite sign so that the overall charge is zero and the resulting capacitive force always attractive. This is typically what any EFM is sensitive to: an attractive force that will depend on the exact geometry of the tip-sample capacitance:

$$F = -\frac{1}{2} \frac{\partial C}{\partial z} V_B^2 \tag{2.19}$$

This force always exhibits a parabolic behavior whose radius of curvature is determined by the capacitance gradient. Depending on the system and the demanded accuracy, three typical models can be chosen as described in figure 2.8 to calculate the tip-sample capacitance.

These models are only intended to give a first order estimate of what actually happens, any given tip can be rather complicated and depend from experiment to experiment. Figure 2.9 gives examples of three real AFM tips not yet coated and made from single crystal silicon. We can clearly distinguish different facets that will depend on the manufacturing techniques. Moreover the tip always approaches the sample with a slight tilt angle, increasing the effect of one side only of the tip. All these subtleties can not easily be rendered in simple analytical model.

It is nonetheless useful to recall here analytical expressions for cases (a) and (b) in



Figure 2.8: Three possible models for describing tip-sample capacitance: (a) Parallel plate model (b) Sphere-Plane model (c) Parabolic tip that can be simulated with finite difference modeling

figure 2.8. For two parallel plates of area S separated by a distance d with a dielectric constant ϵ_0 , we have a simple expression for the capacitance:

$$C = \epsilon_0 \frac{S}{d} \tag{2.20}$$

If a layer of thickness t sits between the tip and sample with a permittivity ϵ_r , then the above equation is changed to:

$$C = \epsilon_0 \frac{S}{d + t/\epsilon_r} \tag{2.21}$$

The capacitance of a sphere-plane configuration is given by the more complicated formula [63]:

$$C = 4\pi\epsilon_0 R \sum_{n=1}^{\infty} \frac{\sinh(\alpha)}{\sinh(n\alpha)}$$
(2.22)

with

$$\alpha = \ln\left[1 + \frac{d}{R} + \sqrt{\frac{d^2}{R^2} + \frac{2d}{R}}\right]$$
(2.23)

We will use these equations in the following chapters since they can fairly reliably give a good account of the main physics observed experimentally. A last example that can help visualize how the electrostatic potential drops between the conductive tip and sample is given with some finite difference modeling [64]. A square mesh



Figure 2.9: Scanning Electron Micrograph of typical real AFM tips: (a) Overview of a Micromasch tip, (b) top view of a nanosensors tip and (c) side view of a nanosensors tip.

of equal spacing is built around a given geometry (here a parabolic tip and sample with a buried dot). To solve the electrostatic potential in all space we need to solve the 2D-Poisson equation in cylindrical coordinate (because of the assumed cylindrical symmetry) given by:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\Phi}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2\Phi}{\partial\theta^2} = -\frac{\rho}{\epsilon}$$
(2.24)

It is then solved numerically on each grid point using an iterative method. An example of such results is given in figure 2.10.

2.3.2 Contact Potential and Localized Charges

It is very often assumed that when no voltage between tip and sample is applied, no electrostatic interaction occurs. Experimentally this is not so because there exists always a difference in work function of the two materials that creates an effective non-zero electrostatic potential when connected together, and that we will refer to as the *contact potential difference* (CPD). Typical order of magnitude for CPD is a few hundreds of a mV. This is true even for a symmetric configuration such as a gold



Figure 2.10: Finite difference modeling of a conductive tip and a buried pyramidal dot. Black lines outline where the surface and dot lies. Left image: electrostatic potential; right image: electric field. Note the change in the equipotential as it enters a material of different permittivity.

tip on a gold substrate. This discrepancy arises from the fact that the exact value of the contact potential depends on the detailed structure of the surface tip and sample, such as charged dipole, work function anisotropies [65], etc. On top of this effects of the CPD, can arise additional perturbation to the general parabolic background of capacitive forces due to localized charges, trapped in a confining potential. Such charges create another electric field between the tip and the sample which contributes to an additional term in the measured force. A fixed charge on the sample induces an image charge of opposite sign on the AFM tip. This image charge on the tip then interacts electrostatically with the sample, effectively modifying the applied voltage experienced by the sample as well as inducing a local change in the effective contact potential difference.

2.3.3 Kelvin Probe

Since CPD change and localized charges are important, particularly in regards to semiconductor or dielectric materials where charge can easily get trapped, an imaging technique has emerged to dynamically compensate the value of CPD while scanning the surface, called Kelvin Probe Force Microscopy (KPFM). On top of the main mode of operation depicted in section 2.2.1, can be added yet another regulation loop that will measure changes in work function. In order to do so, a small accomponent $V_{ac} = \tilde{V}_{ac} \sin(\Omega t)$ is added to the dc-applied voltage so that the total bias is: $V_B = V_{dc} + V_{ac}$. The electrostatic force given by equation 2.19 will now reflect this change by writting:

$$F = -\frac{1}{2} \frac{\partial C}{\partial z} (V_{dc} + V_{ac} - V_{cpd})^2$$
(2.25)

This expression still exhibits a parabolic behavior but with the maximum now defined by $V_B = V_{cpd}$. When equation 2.25 is fully developed, we end up with an DCcomponent of the force, as well as two periodic one at Ω and 2Ω . It is therefore easier to write the total force $F = F_{DC} + F_{\Omega} \sin(\Omega t) + F_{2\Omega} \cos(2\Omega t)$ where each term is expressed as follow:

$$F_{DC} = -\frac{1}{2} \frac{\partial C}{\partial z} \left[\left(V_{dc} - V_{cpd} \right)^2 + \frac{1}{2} \tilde{V}_{ac}^2 \right]$$
(2.26)

$$F_{\Omega} = -\frac{\partial C}{\partial z} \left(V_{dc} - V_{cpd} \right) \tag{2.27}$$

$$F_{2\Omega} = \frac{1}{4} \frac{\partial C}{\partial z} \tilde{V}_{ac}^2 \tag{2.28}$$

By keeping track of $F_{2\Omega}$ with a lock-in amplifier, one can follow the signal that is purely electrostatic and distinguishes it from the difference of potential $V_B - V_{cpd}$. In KPFM, V_B is kept identical to V_{cpd} and is used as the feedback signal. The ac component of the voltage serves as measuring force change around V_{dc} and tries to cancel the Ω contribution of the force F_{Ω} . Experimentally, a lock-in amplifier is used to track the amplitude change of equation 2.27 and a feedback controller try to nullify it by changing V_B , which is achieved when $V_B = V_{cpd}$.

To illustrate the relevance of KPFM even for pure topographical imaging, two images are shown in figure 2.11 when the KPFM loop is either on (left image) or



Figure 2.11: Topographical 4 x 4 μ m scan image when Kelvin probe feedback is on (left) compared to a conductive-AFM image (right) of the same gold surface. Be aware of the slight lateral drift between the two images, a better topographical contrast is demonstrated when the Kelvin feedback loop is on.

off (right image). From this experimental data, topographical features appearing on both images can be compared which demonstrates the better contrast obtained when the KPFM loop is turned on. This fact was actually recently stated in an article on true height determination in AFM by Sadewasser *et al* [66]. In the pratical implementation of KPFM, there is however not a wide consensus so far on what kind of modulating frequency Ω to choose in order to get the best signal. Some authors use $\Omega = \omega$ ([47, 67]), while some others use $\Omega = \omega/2$ ([68]), where ω is still the resonance frequency of the cantilever. The motivation behind these choices is to take advantage of the high resolution on resonance of the frequency (and its higher resonance modes) as well as having a better separation of the topograpy from the electrostatic forces. On the other hand it can easily create some difficulties in particular if parametric amplification is not well taken into account [69]. It is also possible to use a very slow modulating frequency (few 100 Hz to 2kHz) that is appropriately chosen so as to be small compared to the bandwidth of the FM demodulator and large with respect to the bandwidth of the z feedback (so as not to track the ac-component of the voltage in the topography image). The induced modulation of the frequency shift is measured with a lock-in amplifier and then sent to the feedback controller that regulates the bias applied to the sample. This last method was actually used during this thesis, in particular to obtain images on figure 2.11 with a typical value for $\tilde{V}_{ac} = 1V$.

2.3.4 Displacement Current and Joule Dissipation

A very general type of dissipation that is typically encountered when one applies a current through a resistor is what is called Joule Dissipation and is usually expressed as $P = V_B I = R I^2$ where P is the output power dissipated in Watt, R and I are the resistance and current through that resistance. In AFM, we also can account for those phenomena when a voltage is applied between the tip and the sample. Moreover in dynamic mode, since the tip is oscillated near the surface, an induced ac-current or displacement current is generated in the sample due to the change in the tip-sample capacitance C as the tip moves forward and backward at the excited frequency of the cantilever, $z(t) = A \cos(\omega t + \phi)$. This displacement current can be written as:

$$i_d = \dot{q}(t) = \frac{\partial C}{\partial t} V_B = \frac{\partial C}{\partial z} \frac{\partial z}{\partial t} V_B$$
(2.29)

And therefore, the Joule dissipation induced by i_d is given by:

$$P = Ri_d^2 = \gamma_J \dot{z}^2(t) \tag{2.30}$$

$$\gamma_J = R \left(\frac{\partial C}{\partial z}\right)^2 V_B^2 \tag{2.31}$$

where R is the effective resistance in the current path and γ_J corresponds to an effective damping coefficient. This instantaneous dissipation has to be averaged out over one period of oscillation which gives:

$$\langle P \rangle = \frac{1}{2} R A^2 \omega^2 V_B^2 \left(\frac{\partial C}{\partial z}\right)^2$$
 (2.32)

It is this last formula that can be more easily compared with experimental observations.

2.3.5 Why use High Aspect Ratio Tips?

Since the electrostatic force is long range, not only does the tip apex play a role but also the cone-like tip shape and even to some extent the cantilever. This case is very different from STM for instance where the signal of interest, the tunneling current, decays fast enough that one doesn't have to worry about the contribution of the tip that is not at the apex: only the few last atoms play most of the role in detecting the signal. The drawback of probing electrostatic forces is that one has to take into account the whole geometry of the tip because each part of the tip gives a nonnegligible contribution to the overall force. On the other hand, only the contribution from the very end of the tip attracts our curiosity since it interacts most strongly with the sample and has the best spatial resolution, while the rest of the tip and cantilever reveals a more generic background that is most of the time of no interest.

Then, for what tip geometry can we optimize the signal of interest? The above intuitive argument can now be well quantified by calculating the ratio of the apex and cone contribution to the measured electrostatic force assuming a given geometry. To do so we use the analytical expression given by Hudlet *et al* [70] where the cone contribution can be written as:

$$F_{cone} = \frac{\pi\epsilon_0 V^2}{\left(\ln\tan(\theta/2)^2 \ln\frac{H}{d}\right)}$$
(2.33)

where the two parameters H and θ are the cone height and cone angle respectively. The apex contribution of the tip for a sphere-plane geometry is given by:

$$F_{apex} = \pi \epsilon_0 R^2 \frac{(1 - \sin(\theta))}{d \left[d + R(1 - \sin(\theta)) \right]} V^2$$
(2.34)

where R is the effective tip-radius of the apex of the tip. Figure 2.12 represents some calculated value of the ratio F_{apex}/F_{cone} for different value of the cone angle θ and



Figure 2.12: Relative contribution of the tip-apex with respect to the side of the tip as a function of cone angle. The higher the aspect ratio, the greater the contribution of the electrostatic force coming from the end of the tip

tip-sample distance d (the cone height was kept constant at $H = 15\mu$ m). This graph clearly demonstrates the substantial increase in the signal coming from the tip apex if the cone angle is reduced, that is to say higher aspect ratio of the tip, at short tip-sample distance (less than 10nm let say). Such a tip should significantly increase the lateral resolution of EFM images as well as be more sensitive in general to the electrostatic contribution of the signal situated directly under the tip location. 3

Spectroscopic Methods in AFM

This chapter will describe the relevant information that can be obtained from spectroscopic curves with a conductive AFM, and should provide the necessary background to better understand the experimental results of chapter 4. Four main modes of spectroscopy will be distinguished: Current-Voltage curves (I - V), Frequency shift-Distance curves $(\Delta f - z)$, Frequency shift-Voltage curves $(\Delta f - V)$ and Dissipation-Distance curves (DS). From the measure of the frequency shift, a method to calculate the corresponding force will be exposed, which is a preliminary and necessary step for quantitative interpretation of the spectra. The combination of the voltage and distance dependencies of the interaction force will permit us to propose a new method for measuring the absolute tip-sample capacitance.

3.1 Current-Voltage Spectroscopy

3.1.1 Tunneling Junction

Tunneling is a typical quantum mechanical effect that occurs when an insulating material is inserted between two conducting materials preventing electrons from moving freely from one side of the barrier to the another. Depending on the barrier height and thickness, some electrons can nevertheless tunnel through this insulating region, giving rise to a transmission coefficient. A tunneling barrier can therefore be pictured as a capacitor but with some "leakage", and its equivalent circuit representation is in fact a resistor and a capacitor in parallel. Tunneling junctions are very important components of most mesoscopic devices for they permit a better control over the flow of carriers entering or leaving a structure as well as a more or less strong capacitive coupling. For instance, the Coulomb blockade phenomenon is a direct consequence of electron tunneling, since it ensures that there is no continuous change of the charge but rather discrete events of electrons tunneling.

Inside the barrier, the electron wave function decays exponentially and the transmitted wave function is usually only a small fraction of the incoming one. The transmission coefficient can be calculated as the ratio of the amplitude of these two wave functions so that [71]:

$$T(E) \approx \frac{16E(V_0 - E)}{V_0^2} e^{-2\beta d}$$
 (3.1)

where V_0 and d are the barrier height and thickness respectively, and E the incoming electron energy with the wave-vector $\beta = \sqrt{2m(V_0 - E)}/\hbar$. This simplified formula is valid for $\beta d \gg 1$. Experimentally, the measured observable is the current that flows through the device and is usually calculated from the following equation:

$$I \propto \int T(E)f(E)\rho(E)dE$$
(3.2)

where f(E) is the Fermi distribution function and $\rho(E)$ is the density of state of the sample.

The efficiency of the tunneling barrier depends on the tunneling resistance of the junction R_t and should be compared to the quantum of resistance $R_Q = h/e^2 \approx 25.8 \text{k}\Omega$: if $R_t >> R_Q$, there is a good localization of the wave functions on each side of the barrier and tunneling occurs as a stochastic process with a tunneling rate Γ at zero temperature defined by [72]:

$$\Gamma(n, n+1) = \frac{-1}{e^2 R_t} \frac{\Delta F(n, n+1)}{1 - \exp\left[\Delta F(n, n+1)/kT\right]}$$
(3.3)

where $\Delta F(n, n + 1)$ is the free energy change that accompanies the tunneling. This last equation determines the characteristic time for tunneling events to occur and all of the geometrical details of the barrier are included inside the term R_t .

3.1.2 Experimental I - V Curves

In a typical transport measurement on a quantum dot, two tunneling junctions are required, one for each lead, the so-called double barrier tunneling junction (DBTJ). In regard to SPM techniques, original work on the local measurement of I - V curves corresponds to the domain of STM, where the tunneling current is recorded as a function of tip-sample voltage and is referred to as Scanning Tunneling Spectroscopy (STS) as mentioned already in chapter 1. In principle, if an AFM tip is coated with some metallic material, there is obviously no objection for performing a similar type of spectroscopy with an AFM even though two main points of caution must be noted:

- 1. STS has the advantage of having a finite tip-sample distance (constant gap) while performing the spectroscopy, therefore leaving the tip with the exact tip-shape before and after the spectroscopy. If the experiment is not carried out in UHV conditions or with an adequate preparation chamber for tip/sample cleaning (as it is the case in our AFM set-up), a native oxide layer usually prevent the tip from approaching close enough to collect tunneling current without having a mechanical contact. It is therefore required to make a mechanical contact between tip and sample while performing I V curves with an AFM and such mechanical contact will depends on the load applied. This in turn necessitates a good knowledge on the tip-shape geometry, and depending on the load and applied voltage one can easily deteriorate the tip.
- 2. The tunneling barrier itself between tip and sample is not well defined, and it often requires the addition of one more dielectric layer for a suitable isolation

of the tip and the structures under study.



Figure 3.1: (a) Non-linear I - V curve obtained when the AFM tip was in contact with an individual InAs QD (b) derivation of (a). A gap of conductance is clearly observed. (Insert) Drawing of the DBTJ: upon application of a voltage V between tip and back electrode, a current I is measured.

Regardless of these difficulties, a series of experiments were carried out with a commercial AFM tip coated with 20 nm PtIr on a gold sample first, and then at low temperature on a self-assembled QD sample. A home-made I - V convertor was used to measure the current flowing from the sample, which was first tested on a simple gold surface to exhibit the expected linear I - V dependence and deduce the value of a test-resistance inserted in the current path. One of the typical non-linear I - V curves

that could be obtained above a QD sample is shown on figure 3.1. We supposed that the tunneling barrier between the tip and the QD comes essentially from the native oxide layer that covers the sample since sample fabrication and preparation were not done *in situ*.



Figure 3.2: Scanning Electron Micrograph of an AFM tip after a series of I - V curves. The PtIr coating at the apex of the tip is clearly destroyed thus rendering interpretation of the results difficult.

Unfortunately in such a configuration, the mechanical contact of the tip on the sample is not reliable and for some voltages, the destruction of the conductive layer of the tip could be observed as is clearly shown on the SEM images of the tip in figure 3.2 after I - V curves were taken. The electric field strength is too large for such a short distance between the tip and the back-electrode, which would require the tip to sit above the sample at a further distance. These rather inconclusive results from the direct measurement of the current with a conductive AFM tip are in fact a strong indication that careful I-V characteristics are better controlled with an STM in UHV where the sample itself as well as the tip can both be well prepared *in situ*. Since no convincing and reproducible experimental results could be obtained from this method, we then preferred to focus our attention on *non-contact* methods to investigate QD properties. That's why the following sections will deal with spectroscopic curves obtained from a conducting AFM in the dynamic or non-contact mode.

3.2 Numerical Conversion of the Force

Even though spectroscopy by non-contact AFM can more easily secure the tip in comparison with other modes, the original raw data, which is the change in the resonance frequency of the cantilever, is however not straightforward to interpret since this frequency shift doesn't correspond to a direct physical observable. The conversion of frequency shift into force is a necessary first step before rendering quantitative interpretations possible. To determine the actual interaction force from the observed frequency shift, equation (2.9) described in the previous chapter must be inverted. It can be performed analytically for cases where the amplitude of oscillation is far smaller or greater than all characteristic length scales of the interaction forces. In practice however, where the measured force contains a large spectrum of length scale, with a short and long range component, it is more advisable to use numerical computation in order to obtain accurate values. This has been done by several authors using various mathematical techniques [73, 74]. More recently, Sader et al [75] developed an accurate and simple formula. During the course of this thesis, the two different methods proposed by Giessibl [74] and Sader [75] have been tested. There is of course a good agreement between the two methods which gives the same quantitative value of the force for a given set of frequency shift data, but in terms of minimizing the noise originating from the deconvolution procedure, Sader's formula offers the best results and will therefore be used for the rest of the thesis. In this case the inverted force can be deduced from the frequency shift and is written as follow [75]:

$$F(z) = 2k \int_{z}^{\infty} \left(1 + \frac{a^{1/2}}{8\sqrt{\pi(t-z)}} \right) \Omega(t) - \frac{a^{3/2}}{\sqrt{2(t-z)}} \frac{d\Omega}{dt} dt$$
(3.4)

where $\Omega(z) = \Delta f(z)/f_0$ is the ratio of the frequency shift over the resonance frequency. A computer program can be used from here to calculate the interaction force from the experimental data points, equally spaced and stored as a row-vector (this is not strictly necessary but makes the program easier to write). Two loops are necessary: one for calculating the argument of the integral between z_i and z_{i+1} , and one for summing the overall integral from z_0 to z_{i+1} ; z_0 being the first point recorded experimentally and corresponding to "infinity", at least if the tip is retracted far enough from the sample (typically several hundred of nm for our case).

The result of the above conversion procedure is demonstrated on figure 3.3 for several experimental $\Delta f - z$ curves taken at different applied biases.

3.3 Voltage-Dependence on the Force

When the tip-sample voltage is varied, the electrostatic interaction will change according to equation (2.19), that is, to the square of the voltage. This parabolic behavior in a F - V curve will translate into different decay lengths of the force in a F - z curve whose origin corresponds to the capacitance gradient. Thus, there is in fact two equivalent ways of investigating tip-sample interactions by either a distancedependence or a voltage-dependence of the interaction force. In terms of converting the force from the measured frequency shift, it is unfortunately impossible to obtain directly the F - V from a $\Delta f - V$ curve since the knowledge of the decay length of the force is required. In order to deduce quantitative F - V curves, it is necessary to first record different $\Delta f - z$ curves for different bias voltages.

An example of such reconstructed F - V curve is illustrated in figure 3.4 where we can clearly see that each data point is well fitted by a parabola up to the last 10 nm above the surface. The discrepancy below 10 nm in this particular set of data could imply that the simple equation (2.19) describing the capacitive force is no longer valid. The superposition of short-range and voltage-independent forces such as van der Waals and chemical bond forces, to the general electrostatic interaction is also a plausible explanation. It is nevertheless very informative to extract different kind of information from both F - z and F - V curves, as it can readily allow a distinction between contributions of the interaction force that does depend on voltage from the



Figure 3.3: Numerical conversion of the force from the frequency shift measured at different biases. Experimental data taken for a gold tip on a gold sample.



Figure 3.4: Reconstruction of the F - V curves from the $\Delta f - z$ curves at different voltages of the gold tip and sample. Solid figures are experimental data points and dash lines are parabolic fits at a constant height.

ones that do not. This last point will form the main motivation to determine the quantitative tip-sample capacitance.

3.4 Tip-Sample Capacitance Measurement

This section focuses on a new measurement technique used to deduce absolute tipsample capacitance from force distance spectroscopy. This technique has the advantage of being conceptually simple, and therefore quite general, and does not require the addition of more electronic device to the SPM setup. If we actually look at some recent achievements of AFM used to investigate local electrical properties of nanometer-scale devices, we can distinguish three typical applications in which the capacitance plays a crucial role in determining the amount of induced charges on both tip and sample. In all cases an electrically conductive AFM tip is positioned in the proximity of the device of interest and can be used either for: (i) the detection of electrical charges (electrometer) [44, 42], (ii) the control of the electric field (local gating) [76, 28] or (iii) for both [2]. In the former case, the electric charge in the device is measured through the measurement of the electrostatic force and in the latter case, the local electric field in the device is modulated by the bias voltage of the AFM tip. The quantitative interpretation of the results often requires a reliable measurement of the tip-sample capacitance.

As a corollary of the method exposed here, one can also gain more knowledge when dealing with separation of forces in force-spectroscopy [77]. The mapping of the electrostatic force as a function of both distance and voltage can help suppress its manifestations in a more rigorous way when weaker or shorter range forces are investigated (chemical bond force, van der Waals forces, etc.).

Since the method described above was intented as a proof of principle, it was therefore tested on a very simple system: a gold-coated commercial AFM tip over a Au(111) surface. The sample was prepared by Au evaporation onto a mica substrate with a thickness of 100 nm and successive annealing for 1h at 400 $^{\circ}$ C which ensured large grain formation of gold. Figure 3.5 corresponds to two AFM images of the Au surface where several flat terraces can be clearly identified. Since the tip-sample voltage was not completely compensated, the brighter spot on the images correspond to a larger electrostatic force and seem to be correlated with some sharper features on the surface.

3.4.1 Principle of the Method

One of the main limitations in measuring quantitative and accurate values of capacitance comes from the presence of rather large and unavoidable stray capacitances, usually several orders of magnitude larger than the tip-sample capacitance, and originating from cables and impedance mismatches at electrical junctions for instance



Figure 3.5: NC-AFM images of a gold sample taken at 77 K: left image is a 3 by 3 micron scan and right image is a zoom in of a 1 by 1 micron scan. Some flat terraces can be clearly identified. The applied bias was close to V_{CPD}

in any type of AC capacitance bridge [78] or RF resonance sensor [79]. This makes it very difficult to obtain quantitative values of the tip-sample capacitance. As an alternative approach, Martin *et al* demonstrated already in 1988 a high-resolution capacitance gradient measurement by force microscopy [59]. In this case, the stray capacitance does not contribute to the measured force. The subsequent deduction of the tip-sample capacitance then relied on the fitting of some particular tip geometry and was not always reliable. But in essence, the advantage of such method is that the capacitance is deduced from the measure of the capacitive force, which interacts only between the microscopic tip and the sample. Therefore, such measurements are really local and free from typical stray capacitances present in conventional capacitance measurement techniques previously mentioned.

In the present method, we also rely on measuring the electrostatic force to get the absolute value of the tip-sample capacitance, thanks in part to the ability to deconvolute directly the force from the frequency shift. In order to do so, we construct a 2D data array of the electrostatic force measured for different sample voltages and tip-sample distances. In conventional SPM, the total force is composed of three main contributions:

$$F_{\rm tot} = F_{\rm chem} + F_{\rm vdW} + F_{\rm elec} \tag{3.5}$$

which corresponds to the chemical, van der Waals and electrostatic forces, respectively. For the sake of clarity, we will rewrite this equation in the following form:

$$F_{\text{tot}}(z, V) = -\frac{1}{2} \frac{\partial C}{\partial z} (V_{\text{bias}} - V_{\text{CPD}})^2 + F_{\text{other}}$$
(3.6)

where we focus on the electrostatic force, which is the main contribution when a bias is applied. The rest of the interaction is included in the term, F_{other} . Since equation (3.6) depends on both voltage and distance, it is therefore necessary to measure the electrostatic force as function of both z and V_B in order to fully recover the exact value of $\partial C/\partial z$. Also because the term F_{other} is not well defined but always present in any measured interaction force, it is impossible to simply fit a F - z curve at a particular voltage with equation (3.6) to obtain the right value for $\partial C/\partial z$. The overall measured interaction force which is a superposition of capacitive and other forces, still exhibits a parabolic behavior whose radius of curvature is determined by the value of the capacitance gradient for a given z_0 . The part of the force that is not capacitive in origin will give an offset of the whole parabolic curve along the y axis. By measuring the force, it is therefore possible to deduce $\frac{\partial C}{\partial z}|_{z_0}$, V_{CPD} and F_{other} by measuring the total force and fit the reconstructed parabola. If we assume second order polynomial fit of the form: $F(z_0, V) = aV^2 + bV + c$ we can then deduce the value of the three parameters in equation (3.6) at a given z_0 , that is to say:

$$\frac{\partial C}{\partial z} = 2a \tag{3.7}$$

$$V_{cpd} = -b/2a \tag{3.8}$$

$$F_{other} = c - b^2/4a \tag{3.9}$$

In this case, V_{cpd} corresponds to the shift of the parabola with respect to the Voltageaxis and F_{other} to the shift with respect to the frequency shift-axis. At this point, we may generalize the simple idea stated above to build a 2D data array of the gap distance z and applied bias V dependence of the total force. Each force-distance spectrum was measured for a different applied voltage so that we can construct the following type of force-matrix:

$$V_1 \quad V_2 \quad \dots \quad V_m$$

$$z_1 \left(\begin{array}{ccccc} F_{11} & F_{12} & \dots & F_{1m} \\ F_{21} & F_{22} & \dots & F_{2m} \\ \dots & \dots & \dots & \dots \\ r_{n1} & F_{n2} & \dots & F_{nm} \end{array} \right)$$

Where each column corresponds to a F - z curve taken at a fixed voltage V_i and each row corresponds to a fixed tip-sample distance z_i . For clarity, we represented a typical example of this matrix in figure 3.6 for some experimental data set. For each column the force increases as the distance decreases, whereas each line exhibits the expected parabolic behavior $(V - V_{CPD})^2$.



Figure 3.6: 3D representation of the force-matrix from the experimental data points of the F - z curves for different tip-sample bias. The voltage ranges from -2.5V to +2.5V.

Once the force-matrix is built, it is then necessary to fit each row for all the values

of z to extract the 3 parameters according to equations (3.7), (3.8) and (3.9). It is important to note here that the sampling rate of the z scale has to be the same for all of the FS curves in order to be able to reconstruct the parabola as shown on figure (3.4). Finally, a last numerical integration is needed to deduce the absolute capacitance from the experimental values of the capacitance gradient. Ideally, the integration would be performed from infinity (or where $\partial C/\partial z$ goes to zero) but we noticed that above 40 nm $\partial C/\partial z$ is well described by a simple parallel plate capacitance model, i.e. $C = \epsilon_0 S/z$. The error due to this approximation could be reduced by measuring Δf to larger z, limited only by instrumental constraints such as the overall range accessible with the piezotube for instance. This allow us to extrapolate analytically $\partial C/\partial z$ to distance beyond those accessible. We can then compute analytically the value of the capacitance from the last experimental data point to infinity and then start the numerical integration from this calculated value.

3.4.2 Experimental Results

Figures 3.7 and 3.8 illustrate the results for one set of data, i.e. one force-matrix, obtained between a 100 nm gold-coated tip over a gold sample. As described above, the capacitance plotted on figure 3.7 is deduced from a simple integration of the capacitance gradient shown in the insert that corresponds to the capacitance gradient. All of these data were consistently reproduced for different tip locations or with different tips on the same sample. The main difference would be the absolute value of the capacitance (for instance, an overall higher value for fatter tips), which is very much dependent on the tip geometry and that can change even during one experiment, but the general trend always remained the same. It is worth mentioning here that we observed a monotonic decrease of the contact potential difference as a function of gap distance. This could be due to a rearrangement of the charged domains of the tip as depicted by the patch charges model of Burnham *et al* [65]. As the electrostatic
interaction increases when approaching the tip toward the sample, this would give rise to a change in the overall value of the measured work function of the tip, ϕ_{tip} . This phenomenon observed in our experimental conditions, i.e. metallic tip against a metallic substrate, helps us to better understand the need for the above procedure. Since V_{CPD} changes with distance, it becomes all the more important to take this effect into account in order to deduce the non-electrostatic contribution of the force and the capacitance gradient. A simple subtraction of the electrostatic force assuming a constant V_{CPD} would not therefore be appropriate.



Figure 3.7: Experimental determination of the tip-sample capacitance plotted on a log-log plot. Two analytical models are necessary to give an good account of the capacitance behavior over the whole range of investigation. (Insert) capacitance gradient used to deduce the capacitance when integrated.

In terms of capacitance measurements, figure 3.7 exhibits a behavior previously reported [38] but with no absolute reference and for a non-isolated tip-sample system (including the stray capacitance from a resonator for instance [79]). At a long



Figure 3.8: Experimental determination of (a) the change of CPD and (b) the residual force.

distance, for a value of z > 40 nm, the normal parallel plates behavior is recovered, agreeing well with the fact that the exact tip geometry matters much less when it is far away from the surface, the only fitting parameter being the surface area assumed for the plate. In this particular set of data, we calculated a surface area, which is the only fitting parameter, to be on the order of 10^{-14} m². This value may seem high, but one has to keep in mind that this is an effective area that should actually include the overall contribution from the side of the tip and even from the cantilever. Since it was impossible to fit the whole experiment with only one analytical model, at short distance, a small logarithmic growth is observed that could be well described by the sphere-plane model (equation 2.22) with an effective tip radius of curvature of R = 85nm, which agrees well with typical SEM images of such commercial tips.

In figure 3.8, we plotted some other relevant information obtained from the fitting of the parabolic capacitive force, which are the contact potential difference and residual force as a function of tip-sample distance. Change in V_{CPD} as a function of distance has rarely been reported [80], even though there is no fundamental reasons why it should remain constant. This distance dependence could be the results of charge domain rearrangement or the patch charge model [65]. On the other hand, the residual force displayed in figure 3.8(b) is of no surprise since at such distance van der Waals force can play a significant role, as well as non-capacitive electrostatic force originating from fixed charges or different charge domains. In the attempt to distinghish contribution from different forces to the overall measured force, the method presented here can be of great help to substract in a very rigorous manner the capacitive electrostatic force.

Before concluding this section, it is important to state here the accuracy of such a measurement. First of all, since the measurement of the different experimental $\Delta f - z$ curves is rather long, of the order of several minutes, it is not very relevant to deal here with a measurement bandwidth since it would always be very small. Turning now to equation (3.6) we can deduce that the measured capacitance depends on the two main acquiring channels, namely the force F and the distance z, by a simple multiplication (we assume that the applied voltage V does not have a significant error with respect to z and F):

$$C(z,F) = \frac{-2Fz}{(V - V_{\rm CPD})^2} + constant$$
(3.10)

which basically gives a relative error for C of the form:

$$\frac{\Delta C}{C} = \sqrt{\left(\frac{\Delta F}{F}\right)^2 + \left(\frac{\Delta z}{z}\right)^2} \tag{3.11}$$

From this simple argument, we can work out each relative error for F and z and deduced the absolute error for C. We noticed we have at least one order of magnitude less error in the distance z than in the force F, which was measured to be $\Delta F = 3$ pN. This fact can easily be understood by the fact we have to deconvolute the force from the frequency shift which generate some noise. Therefore for our particular experiment, the accuracy of our capacitance measurement from equation 3.11 is $\Delta C = 0.03$ aF and is mainly limited by the force resolution and deconvolution procedure. The fitting procedure, which is better than 99%, does not really alter this value nor does the numerical integration, which has an error much less than the one arising from the deconvolution of the force.

3.5 Dissipation Spectroscopy

We now turn to a less conventional method of spectroscopy, which records the energy dissipated by the tip as it interacts with the sample as a function of either the gap distance or applied bias, and that we call dissipation spectroscopy (DS). In a semiconductor, dissipation can also be sensitive to the dopant concentration [81]. This channel of information is directly accessible in any frequency-modulation AFM and was already illustrated in figure 2.4 of the last chapter. This second feedback loop assured by the Automatic Gain Controller (AGC) enables to respond to a change in the tip-sample interaction by varying the gain that regulates the driving signal. It was assumed that the cantilever is damped due to the tip-sample interaction that is velocity dependent. In this case, the voltage applied to the bimorph to drive the cantilever with a constant amplitude is recorded and can be readily converted in a power dissipated or energy loss per cantilever cycle using equation (2.18), as explained in chapter 2. In this way, we can relate the excitation amplitude with the actual power dissipated.

This measure of damping is in fact a measure of the friction that occurs between the tip and the sample. In our case, this friction does not originate because of a physical contact, but is rather mediated by the interaction field and it is thus referred to as *non-contact friction*. Original work on local electric dissipation was initiated by Denk and Pohl in 1991, who were able to measure the damping of the cantilever oscillation that was attributed to Joule dissipation of charge carriers in a semiconductor (see section 2.3.4). This field of study has since then been the object of several experimental investigations [82, 83, 84], and in particular to account quantitatively for the electrostatic origin of the dissipation [60, 81, 85], but the detailed mechanisms still remain unclear. In this section we present measurements of non-contact friction between two closely spaced metallic surfaces at different temperatures.

As shown on figure 3.9 several DS curves were recorded for different tip-sample voltages and at a temperature of 77 K. Theses experimental curves were obtained at the same time as the $\Delta f - z$ curves previously analysed in section 3.4.2. In this case the tip was coated with a 100 nm thick layer of Au on top of a 10 nm layer of Ti for better adhesion. The higher the applied bias, the longer the decay length of the DS curve and an insert representing a zoom region on a log-log plot exhibits the power law behavior of these curves. A simple exponential decay of the form $A_1 \exp(-z/z_0)$ could fit the data over the whole z-range. For clarity only DS curves for negative voltages are shown. Similar behavior was also observed for positively bias voltages but doesn't add more information to the discussion. When processing the data to convert the measured excitation voltage in dissipation, we used the method exposed in chapter 2 (section 2.2.4) so that we just recall here the formula for the mean power dissipated:

$$\langle P_{int}(d)\rangle = \frac{\pi k A^2 f(d)}{4Q} \left[\frac{R(d)}{R_0} - \frac{f(d)}{f_0}\right]$$
(3.12)

where f(d) is the measured frequency shift at distance d from the surface, R(d) is the gain factor given by the AGC and R_0 is a constant corresponding to the gain when there is no interaction.

Assuming an exponential decay term for the damping coefficient $\gamma = \gamma_0 \exp(-z/z_0)$, each curves could very well be fitted over the whole range of investigation. For this fitting we assumed an empirical law written for the dissipative force and instantaneous



Figure 3.9: Dissipation-distance curves recorded for different applied voltages at 77K. The insert corresponds to a log-log plot of the last 35 nm to zoom in the region at shorter distance. Each curve was fitted with an exponential decay function. Only when the tip is not tapping the surface can the exponential fit be good.

power as:

$$F_{diss}(z, \dot{z}, d) = \gamma_0 e^{(-z/z_0)} \dot{z}$$
(3.13)

$$P(t) = \gamma_0 e^{(-z/z_0)} \dot{z}^2 \tag{3.14}$$

here, γ_0 and z_0 are constants. From this empirical definition and assuming a harmonic motion $z(t) = A \cos \omega t$, the average power dissipated can also be worked out to be [84]:

$$\langle P(d) \rangle = I_1 A^2 \omega^2 \gamma_0 e^{(-d/z_0)} \tag{3.15}$$

where I_1 is the modified Bessel function of first order and A the tip amplitude. Even though we have shown that our experimental data for the electric dissipation could be well fitted with an exponential decay we don't know the physical origin of this exponential dependence on the damping coefficient γ . Moreover, the voltage dependence of the dissipation is not taken into account in such a simple description.

What was more surprising than this first set of data, are some other experimental results also taken on a Au surface at 77 K but with a thinner Pt coating of 20 nm deposited by sputtering on top of a 10 nm Ti layer. This particular set of data exhibits some extraordinary type of DS curves presented on figure 3.10 for a large voltage span. In this case, no exponential decay term was observed but rather a clear bump moving to different z when voltage V_B is changed.



Figure 3.10: Dissipation-distance curves recorded for different applied voltages between Pt tip and gold sample at 77K. Each curve is given an offset of 5fW for clarity. Arrows indicate a bump or peak in the curve that moves as function of voltage. Note that no bump is observed at 1 V which is the closest value to CPD.

In order to account for this phenomenon, an attempt was made to include the results obtained from the method described previously in section 3.4.2, and to inves-

tigate the effect of the change in contact potential (CPD) as a function of distance onto the electric dissipation by Joule mechanism. Since the experimental value for V_{CPD} as well as $\partial C/\partial z$ were measured simultaneously to the one for the dissipation shown on figure 3.10, a quantitative approach is possible. The average power generated by the induced current of the oscillating AFM tip was already calculated in section 2.3.4 and the result is recalled here:

$$\langle P \rangle = \frac{1}{2} R A^2 \omega^2 (V_B - V_{CPD})^2 \left(\frac{\partial C}{\partial z}\right)^2 \tag{3.16}$$

The only fitting parameter is the effective resistance R in the induced current path, all of the other parameters can be measured experimentally as a function of distance. In particular, we do not have to assume any special geometry for the tip-sample capacitance gradient since its value has been measured experimentally. In fact, even when assuming a very high value for the resistance $R = 100 \text{ M}\Omega$, the overall value of the dissipation was still below the one measured by several orders of magnetude. This fact is not new since it was already reported, such as in reference [60]. What is new from the above approach is that it was indeed possible to reproduce a small bump in the dissipation curve that is voltage dependent. This bump originates around $V_B = V_{CPD}$ because in equation 3.16, the term $(V_B - V_{CPD})$ changes sign, thus decreasing to zero and then increasing again. The overall results for such a curve are illustrated in figure 3.11 for different values of the applied voltages V_B , chosen in the vicinity of the measured V_{CPD} , which was found in this case to vary between 0.4 V up to 1.2 V. We can notice that the shape of the bump is very broad. This approach can not therefore account, even qualitatively, for the observed bump in figure 3.10, since in this case bumps appear when V_B is actually far from V_{CPD} and are not as broad as the one calculated from equation (3.16).

Even though the results displayed in figure 3.9 and 3.10 were both measured at the same temperature of 77 K over the same Au sample, two distinctive behaviors



Figure 3.11: Calculated Joule dissipation, equation (3.16), using experimental value for V_{CPD} and $\partial C/\partial z$. (Insert) display of experimental data of V_{CPD} used in the calculation.

of the electric dissipation could be observed, and a clear voltage dependence was demonstrated in both cases. The main difference between experiments was the AFM tip, which was coated with a much thinner coating on the second experiment. This leads us to say that the larger the tip (due to a fat coating for instance), the stronger the electric dissipation and therefore some detailed structures can be easily smeared out. Only when the tip exhibits a better aspect ratio, and also a higher electrostatic resolution, were we able to probe an extraordinary type of dissipation with some bump features. To corroborate this assumption, the measured capacitance for the tips in this two type of experiments show that the tip with the larger coating exhibits (not surprisingly) the larger value of the capacitance at a given gap distance. An improvement of the tip shape and aspect-ratio would not only improve the resolution of electrostatic force measurement (as described in section 2.3.5 for instance) but also the electric dissipation itself and to some extend the measurement of weak forces at the nanometer scale.



Figure 3.12: Dissipation-distance curves as a function of applied bias over a Au surface at 4.5K. Each curve is given an offset of 5fW for clarity.

A last experimental investigation of dissipation spectroscopy at a lower temperature of 4.5 K is presented in figure 3.12. In this case, neither an exponential decay nor some bump at a given z were observed but rather an almost completely flat curve with for some value of the voltage a clear drop (or negative value) for the dissipation just before the onset when the tip starts tapping the surface resulting in a very steep increase of the power dissipated. This effect seems even more puzzling than the previous results since the power dissipated by the tip normally always increases to a higher value when the tip approaches toward the sample.

This last section on dissipation spectroscopy over such a simple system as a metallic tip on a gold substrate left us with more questions than answers. This is probably why the dissipation channel available in a non-contact AFM is not often used as a major channel of quantitative information. The importance of the tip geometry seems nevertheless an important factor that needs to be investigated in the future in greater details than in the present study. However, we will again have the opportunity to come back to discuss the dissipation channel when dealing with the charging event of a single electron in chapter 5.

3.6 Summary

In summary, we described in this chapter all the different tools available to the conductive AFM in the frequency-modulation and contact mode in order to perform several types of current and force spectroscopies. Both tip-sample distance and tipsample voltage are two important parameters to take into account in particular when dealing with the electrostatic force which exhibits a strong distance as well as voltage dependence. As a consequence of this analysis, a simple method to measure the absolute tip-sample capacitance, the contact potential difference and the residual non-capacitive force as a function of tip-sample distance was achieved, which can be of great value when trying to separate each force component or when the absolute value of the capacitance is an important parameter. On the other hand, the attempt to understand dissipation spectroscopy on gold offered several challenges and a compilation of more systematic studies would be necessary.

 $\mathbf{4}$

Single Electron Effects in Quantum Dots

After a review of the different force spectroscopies that can be carried out with a conductive AFM, our attention will now focus on some particular type of semiconductor samples to study their electronic properties. A description of the Coulomb blockade theory will be given before presenting and comparing experimental results of single electron detections in an individual quantum dot.

4.1 Semiconductor Heterostructures

Neither a good conductor nor an insulator, the main originality of semiconductor material comes from the fact that its energy levels are gathered into two distinct band structures in between which lies its chemical potential. The lower band in energy, or Valence band, is almost full of electrons and can only conduct charge by the movement of empty states or holes. On the contrary the upper or conduction band is almost devoid of electrons, whose number is described by the Fermi-Dirac statistics, thus depending on temperature as well as the width of the gap between valence and conduction bands. In a more quantitative way, if we define by $D_c(E)$ and $D_v(E)$ the density of state in the conduction and valence band respectively, the number of electrons per unit volume in the conduction bands n(T) will be [86]:

$$n(T) = \int_{E_c}^{\infty} D_c(E) \frac{1}{1 + e^{(E - E_F)/kT}} dE$$
(4.1)

where E_c is the bottom of the conduction band and E_F is the Fermi energy. There is a similar equation for the hole density, p(T), and the relationship between these two quantities, called the *mass action law*, can be written as:

$$np = n_i^2 \tag{4.2}$$

where n_i^2 is the intrinsic carrier density, a constant for each material at a given temperature. Unlike metals or insulators, the number of carriers, either electrons or holes, can be modified over several orders of magnitude, which makes semiconductor very useful for a wide span of applications both in electronics and optoelectronics. These conduction and optical properties can be tuned by changing the doping concentration, thus increasing the number of charge carriers. Some highly degenerated semiconductors, i.e. with a very high doping concentration, can even exhibit metalliclike properties at room temperature. But to fully take advantage of semiconductor, one wants to control the number of charge carriers by using external controllable parameters such as temperature, the effect of an applied electric field or by illumination in order to create electron-hole pairs.

Semiconductor	Lattice constant	Band gap	Carrier Density	Relative
Symbol	(Å)	(eV)	$n_i \ (m^{-3})$	Permittivity
Ge	5.64	0.66	$2x10^{19}$	16
Si	5.43	1.12	$2x10^{16}$	11.9
InP	5.86	1.35	$\propto 10^{14}$	12.4
InAs	6.05	0.36	$\propto 10^{21}$	14.6
GaAs	5.65	1.52	$\propto 10^{13}$	13.1

Table 4.1: Room temperature properties of various semiconductors.

A characteristic length scale that has to be taken into account when dealing with a semiconductor is the so-called Debye-Huckel length, l_D , that defines the screen-



Figure 4.1: Semiconductor band bending at the interface AlGaAs/GaAs, thus creating an quantum well at that interface. After the junction is made, the Fermi energy of the two semiconductors are aligned.

ing length of surface charges (or penetration depth of the electric field) inside the semiconductor and can be written as follows:

$$l_D = \sqrt{\frac{\epsilon_0 \epsilon_r kT}{4\pi^2 e^2 n}} \tag{4.3}$$

Therefore, unlike metal that can always completely screen charges underneath its surface, there is a characteristic length underneath the semiconductor surface that will determine how well the carriers respond to an electric field, thus also modifying their band structures close to the surface, which is known as a band bending effect. Such an effect, whose results give rise to a quantum well at the heterojunction, is illustrated in figure 4.1.

Even though there exits some pure element semiconductor materials, such as Ge and Si, there is a large variety of compound semiconductors whose special properties can be more easily tailored. In particular, the width of the band gap, ranging from socalled narrow to wide gap, is very useful for tuning the wavelength of photo-emission from the recombination of electron-hole pairs. In the periodic table of elements,



Figure 4.2: Schematic representation of two semiconductor samples with one or two layers of QD. Note the 2DEG at the heterojunction between InP and InGaAs. These samples are fabricated at the Institute of Microstructural Studies in Ottawa by P. Poole *et al.*

several semiconductor types are defined: the mostly encountered one are the III-V semiconductors, such as GaAs, InP and so on, and the II-VI type semiconductors such as for instance ZnTe and CdSe. Apart from these binary combinations, some three compound semiconductors can also be produced, such as InGaAs. Each resulting semiconductor exhibits different properties that will depend on its lattice constant, band gap, electron and hole mobilities, etc... some of which are gathered in table 4.1. Typical band gap for bulk InP and InAs at room temperature are $1.35 \ eV$ and $0.36 \ eV$ respectively compared to a $8 \ eV$ band gap for a good insulator such as SiO₂.

One of the many advantages of having such a large variety of semiconductors is that by forming several heterojunctions between semiconductors of different band gaps, one can easily modify the conduction properties of such new device and in particular, electrons can be confined in one or more dimensions giving rise to quantum wells (QW), wires or dots. This is what we refer to as semiconductor heterostructures.

To best illustrate our discussion let us now look at two samples that were used for

our experimental investigations and that are schematically presented in figure 4.2. In this case, each layer corresponds to the epitaxial growth of a different semiconductor, the matching of the different lattice constant is therefore important if one wants to grow atomically flat surfaces. At each interface between semiconductors of different band gap, a modification of the energy band will result, thus creating for the charge carriers some artificial barriers or wells at that interface. This is what precisely happens at the InP and InGaAs interface: a two-dimensional gas (2DEG) is formed due to the difference of band gap. This 2DEG or quantum well confines electrons in the horizontal plane parallel to the surface and therefore can act as an electron reservoir or back-electrode from which electrons can tunnel in or out. These techniques to produce heterostructures with barriers and wells of different thicknesses and heights are often referred to "band gap engineering".

If we now look at the interface between InP and InAs, the difference between the lattice constant of these two materials, close but not identical (see table 4.1) permits the formation of spontaneously self-assembled QD due to the results of a slight surface strain (in this case of 3.1%). This bottom-up approach of QD fabrication is very useful if one wants to cover a whole wafer with such semiconductor QDs. All of these recipes to produce self-assembled nanostructures require the use of UHV systems that can slowly grow atomically flat layers of semiconductors such as Molecular Beam Epitaxy (MBE) or Chemical Beam Epitaxy (CBE). After this brief description of the fabrication and basic properties of QD samples that we will investigate, it is useful to turn to the description of Coulomb blockade in such structures, as well as to have a good estimate of the tunneling rate between QW and QD.

4.2 Quantum Well to Quantum Dot Tunneling

For the purpose of our later experimental study of QD, one important parameter is the tunneling transfer of carriers from a quantum well or 2DEG (electron reservoir in our case) to a QD. This problem can be investigated theoretically using the transitionprobability of Bardeen [87], that is, an extention of Fermi's Golden rule for the case where initial and final states of the transition are not in the same confining structure. The advantage offered by such computation of the tunneling rate is two-fold:

- In the domain of QD lasers (which is also a serious application for the InAs QD that we studied), it is important to have an efficient QW to QD tunneling so as to inject rapidly carriers that will be able to recombine and produce light emission.
- On the other hand, for the study of single charge detection, we rather prefer a small capacitance between QW and QD, which usually translate in slower tunneling rate. The trade-off is that it still has to be large enough to be detectable with AFM probe for instance.

In both of this cases, a possible way to tune the tunneling rate to a more appropriate value if needed, would be to change the distance t between QW and QD during the growth of such samples.

Figure 4.3 illustrates the potential profile along the perpendicular direction to the surface and defines the relevant parameters such as the barrier, QW and QD potentials noted as V_b , V_w and V_d respectively, as well as the different layer thicknesses, w, t and d for the QW, tunnel barrier and QD respectively.

The approach that we will review here is attractive since it permits the calculation of the tunneling probability from a two-dimensional QW to a zero-dimensional QD in terms of the initial and final states in the QW and QD respectively, via a transfer Hamiltonian. If we consider the Hamilonian for the QW-QD system we have:

$$H = -\frac{\hbar^2}{2m^*} \nabla^2 + V_w(z) + V_d(\mathbf{r})$$
(4.4)

where $V_w(z) = V_w$ inside the well and V_b outside it, as shown on figure 4.3, and $m^* = 0.067m_e$ is the effective mass for the electron. Similarly, $V_d(\mathbf{r}) = V_d$ for \mathbf{r} in



Figure 4.3: Potential profile in real space of a quantum well coupled to a QD separated by a barrier layer and characterised by a potential height V_b and thickness t. Adapted from [3].

the dot and V_b outside it. It is also necessary to know the wave function and energy levels both in QD and QW that can be obtained by solving the time-independent Schrödinger equation:

$$H_w \Psi_w = E_w \Psi_w \tag{4.5}$$

with the QW Hamilonian written as:

$$H_w = -\frac{\hbar^2}{2m^*}\nabla^2 + V_w(z) \tag{4.6}$$

And a similar expression exists for the QD. For the QW, the quantization of the energy levels occur only in the z-direction and can be calculated by solving the following transcendent equations for even and odd parity states respectively [88]:

$$k_z \tan(k_z w/2) - \kappa_z = 0 \tag{4.7}$$

$$k_z \cot(k_z w/2) + \kappa_z = 0 \tag{4.8}$$

where $k_z = \sqrt{2m^* E_{lz}}/\hbar$, and $\kappa_z = \sqrt{2m^* (V - E_{lz})}/\hbar$, are the wave vectors in the z direction outside and inside the barrier region, respectively. Here we noted the energy quantization, E_{lz} , along z, where l is the quantum number for that direction. These

equations can be solved numerically by using the Newton-Raphson iteration method for instance to find the zeros of equations (4.7) and (4.8) corresponding to the energy level in the QW. Similarly for the QD, the quantization of energy level can be worked out in the z-direction with quantum number q, noted E_{qz} , whereas for the in-plane energy level, assuming a cylindrical symmetry we have [89]:

$$E_d = \frac{\hbar^2}{2m^*} \left(\frac{Z_{mn}}{a}\right)^2 + E_{qz} \tag{4.9}$$

where a is the dot radius and Z_{mn} the nth zero of the Bessel function so that $J_m(Z_{mn}) = 0.$

The transfer Hamiltonian is defined as $H - H_w$, so that the transition rate for tunneling to occur from the QW to the QD is [72]:

$$\Gamma = \frac{4\pi}{\hbar} \sum_{w,d} |\langle \Psi_d | H - H_w | \Psi_w \rangle |^2 (f_w - f_d) \delta(E_d - E_w)$$
(4.10)

where a spin factor of 2 has been introduced, and f_w and f_d are the Fermi function for the occupation probability of states in the well and the dot respectively. Note that the summation has to be made over the quantum numbers $w = (k_x, k_y, l)$ and d = (m, n, q) if we assume the simple cylindrical geometry described above for the well and dot. It is also useful to remark that the transfer Hamiltonian vanishes everywhere except in the region where the dot is, with a constant value equal to $V_d - V_b$. Equation (4.10) is rather awkward to compute but can still be calculated analytically and the method that we use in this section is well described in the paper from Chuang *ct al* [3].

By choosing the relevant parameters corresponding to the sample characteristics it becomes possible to calculate the tunneling rate. These parameters were obtained from a numerical band diagram calculation, carried out by G. Aers *et al* at the National Reseach Council in Ottawa and was obtained from a self-consistent solution of the Schrödinger and Poison equations in similar semiconductor heterostructures as

Table 4.2: Parameters obtained	from a band diagram	calculation and used in	the calculation of the
tunneling rate from QW to QD	and corresponding to	the three semiconducto	r layers of figure 4.3.

Parameters	QW	QD	Barrier
Height (eV)	-0.05	-0.1	0.2
Thickness (nm)	10	8	20

described in the previous section. Table 4.2 gathers the relevant parameters necessary for the calculation of equation (4.10). Here, the barrier height in electron-Volt is given with respect to the Fermi level. For the calculation of the data shown in figure 4.4, the barrier thickness was changed by a step of 5 nm and the overall data could be well fit with an exponential growth function as expected. From the values obtained with such parameter, we immediately notice that the tunneling rate is indeed very fast for a barrier thickness of 20 nm, in the GHz regime, ensuring that tunneling events are much faster that the typical resonance frequency of the cantilever, in the kHz regime, that will serve later as our detector. Even with a barrier thickness of 30 nm, the tunneling rate would still be in the MHz regime, which is fast enough for the detection of enough electron tunneling events in the time (or frequency) window set by the cantilever resonance frequency (typically about hundred kHz). In this case, the advantage of having a thicker tunneling barrier of 30 nm for instance, would allow a smaller overall QD-back-electrode capacitance, which could lead to a better energy resolution and broader span of investigation, as will be explained in the next section.

4.3 Single Electron Box: Theoretical Description

4.3.1 General Considerations

We shall first recall here what are the two necessary conditions in order to observe single electron effects that are linked with Coulomb blockade phenomena:



Figure 4.4: Coherent electron tunneling time from the quantum well ground state to the quantum dot ground state. Solid line: exponential growth fit to the calculated points.

- 1. The energy required to inject a single electron into a nanostructure (i.e. the charging energy, E_C) must exceed the thermal energy, otherwise we would not be able to distinguish the injection of a single electron from thermal fluctuations. This conditions is written as: $E_C = e^2/2C >> kT$.
- 2. The tunneling resistance R_t must be larger than the quantum resistance h/e^2 . This condition is necessary to suppress the fluctuations in the electron number N and assure that the electron wave function is well localised on the QD. This condition writes: $R_t >> h/e^2 = 25.8 \text{ k}\Omega$. Another way of stating this condition is by defining the coupling between the leads and a nanostructure: the stronger the coupling, the smaller will be the effect of single electron tunneling because of the smear out of the wave function in the QD.

Once these conditions are fulfilled in a single electron device, it becomes possible to control the motion of just a single electron. Experimentally, such a device consists



Figure 4.5: (a) Schematic diagram of the different coupling between a QD and the gate and backelectrodes. (b) Equivalent electric circuit where the charge on the dot is assumed to be q = -Ne, C_{tip} and C_{sub} are the tip-QD and QD-2DEG capacitance respectively. The dash square corresponds to the quantum dot.

usually of quantum dots having at least one tunneling junction with an electrode. The most basic electron box device would therefore consist of a single QD coupled electrostatically on one hand to a gate electrode and on the other hand to a backelectrode by a tunneling barrier. Of course, many more electrodes can in principle be added (if not sometimes for practical experimental difficulties). The next step would be for instance a so-called Single Electron Transistor (SET) composed of a nano-island electrostatically coupled to a gate electrode and sandwiched between two tunneling barriers to source and drain.

For the sake of clarity with our later experimental discussion, we presented in figure 4.5, the actual set-up used for performing measurement on an individual QD, which illustrates a single electron box where the conductive AFM tip plays the role of the gate electrode and the two-dimensional electron gas (2DEG) serves as the back-electrode. We use the equivalent circuit representation for the conceptual (and simplified) understanding of the effect of a QD that sits in-between two electrodes. Following the notation in figure 4.5, we can write the total charge on the dot as a function of the induced polarized charges on each of the capacitor plates, that is:

$$q = -Ne = q_{sub} - q_{tip} \tag{4.11}$$

where by definition: $q_{sub} = C_{sub}V_{sub}$ and $q_{tip} = C_{tip}V_{tip}$. The applied bias V_B drops between the tip and back-electrode in such a way that $V_B = V_{sub} + V_{tip}$, or in terms of the capacitance:

$$V_B = \frac{q_{sub}}{C_{sub}} + \frac{q_{tip}}{C_{tip}} \tag{4.12}$$

From the expression of equations (4.11) and (4.12), we can more conveniently write the values of the voltage across the tip-QD and QD-back-electrode in the following way:

$$V_{tip} = \frac{C_{sub}V_B - q}{C_{sub} + C_{tip}} \tag{4.13}$$

$$V_{sub} = \frac{C_{tip}V_B + q}{C_{sub} + C_{tip}} \tag{4.14}$$

These general considerations that are applicable for a variety of systems coupled to some tunneling junctions will then be used for determining the exact conditions on the bias voltage to observe Coulomb blockade phenomena in a single electron box.

4.3.2 Coulomb Blockade Phenomena

Briefly presented in the introductory chapter, Coulomb blockade phenomena will now be discussed more quantitatively to account for the charging of a single electron box (or quantum dot). The view presented here is somewhat simpler than the general description of conduction peaks illustrated in figure 1.1 because there is *no tunneling barrier* between the conductive AFM tip and the QD due to the large vacuum gap. In this case, no current is collected at the tip (in contrast to Scanning Tunneling Spectroscopy) and once the QD is charged it remains in this state for a given voltage window. To understand more rigorously why electron number can sometimes be blockaded inside a nanostructure for a certain voltage window, we first have to derive the free energy of the system. With the notations used so far in figure 4.5, the total charging energy of the quantum dot, which is the sum of the charging energy for each capacitance, can be expressed as function of accessible quantities like the capacitances, the total applied bias V_B and charge q, according to [90]:

$$U = \frac{q_{sub}^2}{2C_{sub}} + \frac{q_{tip}^2}{2C_{tip}}$$
(4.15)

$$= \frac{q^2}{2C_{\Sigma}} + \frac{1}{2} \frac{C_{sub} C_{tip}}{C_{\Sigma}} V_B^2$$
(4.16)

where $C_{\Sigma} = C_{sub} + C_{tip}$. This last equation (4.16) has a familiar expression since the first term corresponds to the QD charging energy (with a total capacitance C_{Σ}), whereas the second term is the equivalent expression for two capacitors connected in series.

So far, we have been dealing only with the electrostatic energy of the capacitances. It is however equally important to take into account the work done by the generator, W, in order to keep a constant applied bias V_B when bringing the charge in the dot from 0 to N and that can be expressed as [90]:

$$W = \int_0^{q_{tip}} V_B dQ = q_{tip} V_B = \frac{C_{sub} C_{tip}}{C_{\Sigma}} V_B^2 - q \frac{C_{tip}}{C_{\Sigma}} V_B$$
(4.17)

We now have all the necessary ingredients to account for the free energy, G, of the system defined by:

$$G = U - W = \frac{q^2}{2C_{\Sigma}} + qV_B \frac{C_{tip}}{C_{\Sigma}} - \frac{1}{2} \frac{C_{sub}C_{tip}}{C_{\Sigma}} V_B^2$$
(4.18)

From this expression of the free energy, we can work out the conditions to maintain the electron in the QD by stating that the final state has to be energetically favorable, that is $\Delta G(N, N+1) = G(N+1) - G(N) > 0$, or if we substitute directly into equation (4.18) we get:

$$\Delta G(N, N+1) = \frac{e}{2C_{\Sigma}}(2N+1) - \frac{C_{tip}}{C_{\Sigma}}eV_B < 0$$
(4.19)

The same argument holds for $\Delta G(N-1, N) = G(N-1) - G(N) > 0$, which finally gives an upper and lower boundary for the applied bias V_B so that:

$$V_B^- = \frac{e}{C_{tip}} \left(N - \frac{1}{2} \right) < V_B < V_B^+ = \frac{e}{C_{tip}} \left(N + \frac{1}{2} \right)$$
(4.20)

which means that the electron number in the QD is fixed to N in this range of voltage, or in other words, the current is blockaded as long as V_B stays in this voltage range that we call $\Delta = V_B^+ - V_B^-$. From the inequality (4.20) we can notice right away that the difference in voltage between two neighboring blockaded regions is constant (i.e. independent of N) and equal to $\Delta = e/C_{tip}$. Typical value for Δ is about 1 V. This effect is referred to as Coulomb blockade. In a more practical way, we usually define the function Int(x) that gives the nearest integer to x so that the inequality (4.20) can be more conveniently expressed as:

$$q = -Ne = -eInt\left(\frac{C_{tip}V_B}{e} + \frac{1}{2}\right)$$
(4.21)

this equation simply states that the charge has to be quantized with integer number of e. It is nonetheless interesting to note that expression (4.21) only depends on the tip capacitance and the total applied bias.

4.3.3 Single Electron Effect on the Force and Frequency Shift Derivation of the Total Electrostatic Force

The next question that may arouse our curiosity is: what would be the force due to a single electron detected by an AFM probe? Thanks to the calculations derived above (equation 4.18), it is not difficult to deduce the actual total electrostatic force F arising from the change in the tip capacitance, since:

$$F = -\frac{\partial G}{\partial z} = -\frac{\partial G}{\partial C_{tip}} \frac{\partial C_{tip}}{\partial z}$$
(4.22)

From this definition of the interaction force from the free energy, we can now express the electrostatic force acting between the AFM tip and the back-electrode in the presence of a charge in the QD as:

$$F = \frac{1}{C_{\Sigma}^2} \frac{\partial C_{tip}}{\partial z} \left(\frac{q^2}{2} - C_{sub} q V_B + \frac{1}{2} C_{sub}^2 V_B^2 \right)$$
(4.23)

$$=\frac{1}{2}\frac{\partial C_{serie}}{\partial z}\left(V_B - \frac{q}{C_{sub}}\right)^2\tag{4.24}$$

where $C_{serie} = C_{sub}C_{tip}/(C_{sub} + C_{tip})$ is the equivalent capacitance of C_{sub} and C_{tip} put in series. It is good to first remark from equation (4.24) that if q = 0, we recover the generic parabolic curve which is a typical behavior of the capacitive force between two metallic bodies already discussed in section 2.3.1. From equation (4.23) we can separate three components that have different origins: (i) the first term, proportional to q^2 , corresponds to the interaction between the charge in the QD and its image charge on the tip; (ii) the third term, proportional to V_B^2 , accounts for the interaction between the polarized charges in the tip (q_{tip}) and the back-electrode (q_{sub}) ; (iii) the second term linearly proportional to both q and V_B , reveals the actual interaction between the polarized charge in the tip and the charge in the QD, and therefore permits the measurement of the charge in the QD.

In order to represent equation (4.23) graphically, we need to put some numbers for the value of the two main capacitances and the simplest model of parallel plates capacitors can be used here. Referring to section 2.3.1 and using the notation on figure 4.5 we can write:

$$C_{tip} = \frac{\epsilon_0 S}{z}$$
 and $C_{sub} = \frac{\epsilon_0 \epsilon_r S}{d}$ (4.25)

where S is the effective surface area of the parallel plate, d the width of the tunnel barrier (or QD-back-electrode distance) and ϵ_r the relative permittivity of InP in our case. Substituting into equation (4.23), we end up for the electrostatic force:

$$F = -\frac{1}{(z+d/\epsilon_r)^2} \left(\frac{d^2 q^2}{\epsilon_0 \epsilon_r^2 S} - \frac{dq V_B}{\epsilon_r} + \frac{\epsilon_0 S V_B^2}{2} \right)$$
(4.26)

It then becomes possible to compute quantitative values for each of the three terms of the force. In particular, an effective diameter disk of 17 mm is assumed for S, which also corresponds to an area of 227 nm^2 . This value is to be compared with the effective area of the dot. From this calculation, it comes out that the first term, proportional to q^2 is always smaller by two and three orders of magnitude with respect to the next two terms, thus rendering the effect of the image charge of the dot on the tip experimentally difficult to resolve. Not surprisingly, it is the third term corresponding to the constant capacitive background, proportional to V_B^2 , that is predominant with some effect from the second term when some charging of the QD occurs. These effects are illustrated in Figure 4.6 where the generic parabolic background set the overall behavior for the electrostatic force with some deviation happening in the form of a sharp jump when the condition 4.21 is fulfilled. For a later comparison with experimental results where the frequency shift is the experimentally accessible observable, we also added in figure 4.6 the corresponding frequency shift, assuming the calculated force using the convolution procedure described by equation (2.9). Although the step-like structures on the force translate into broader increase in Δf because of the averaging effect of the amplitude, the onset of the increase still match the step in the force-voltage curve.

Since some clear jumps appears in figure 4.6 it is interesting to work out from equation (4.23) the step height in the force, $\Delta F = F(N+1) - F(N)$, that is, the difference in force before and after the electron number goes from N to N + 1:

$$\Delta F = \frac{e^2}{C_{\Sigma}^2} \frac{\partial C_{tip}}{\partial z} \left(N + \frac{1}{2} - \frac{C_{sub} V_B}{e} \right)$$
(4.27)

$$= \frac{e}{C_{\Sigma}^{2}} \frac{\partial C_{tip}}{\partial z} V_{B} (C_{tip} - C_{sub})$$
(4.28)

It is worth noting that since equation (4.28) is linearly proportional to V_B , the height in force will increase as the applied bias is increased, thus more clearly demonstrating QD charging at a higher voltage. There is nonetheless a trade-off, since a very large



Figure 4.6: Calculated electrostatic force and corresponding frequency shift as a function of voltage and for some given tip height z_0 ranging from 25 to 35 nm. The calculation of the frequency shift were derived assuming a tip-amplitude of 5nm.

difference of potential between tip and sample creates locally a very high field strength at the apex of the tip, therefore challenging the overall tip stability as well as possible field ionisation of the tip coating. That is why typical experimental $\Delta f - V$ curves never exceed a difference of potential of five volts.

Effect of the Tip-Amplitude on the Measured Frequency Shift

Before concluding this rather long section on Coulomb blockade phenomena and its manifestation in the overall electrostatic force, a last important remark concerning the effect of the tip-amplitude has to be pointed out here. The convolution procedure, described by equation (2.9), that arises because of the finite size effect of the tipamplitude with respect to the decay length of the interaction force is most of the time of no consequence on the overall shape of the frequency shift curve obtained experimentally. This is not the case when the predicted force curve reveals some step like structures as already shown on figure 4.6. This highly non-linear feature when averaged over on oscillation cycle of the cantilever motion can exhibit some quite unusual structures depending on the tip-amplitude.

To illustrate this point, the frequency shift calculated from equation (2.9) and assuming the *same* original force curve is plotted for four different values of the tipamplitude in figure 4.7. On such graphic, the original step like structures in the force translate in quite different frequency shift curve depending on the tip-amplitude. The tip-amplitude becomes therefore a very crucial parameter and a typical length scale in determining experimentally the effect of Coulomb blockade phenomena. This effect is basically caused by the averaging effect of the tip oscillation: the larger the tipamplitude, the larger the distance the effective force is averaged on. It is therefore of no surprise to see in figure 4.7 (d) a rather smooth curve where the effect of the Coulomb blockade jump is actually quite small and appears only as a small bump in the frequency shift. This observation can be of practical importance in optimizing



Figure 4.7: Frequency shift versus voltage curves obtained for different tip height as well as tipamplitude, assuming a force of the same type as shown on figure 4.6. The range for the tip-height, from 25 to 35nm, and the color code is the same as on figure 4.6. Depending on the tip-amplitude, A, the abrupt step in the force curve will translate is a very sharp peak for A=1nm or a rather smooth curve with just a small bump for A=10nm.

single electron detection with an FM-mode AFM apparatus. On one hand, the overall signal-to-noise ratio decreases as $A^{3/2}$, but as shown in this section, the effect of a single electron filling of a QD on the other hand can be dramatically enhanced with very small tip-amplitude.

4.4 Experimental Investigation of Single Electron Effect

4.4.1 General Sample Considerations

Now that we have clarified the effect of Coulomb blockade phenomena observable in the force through the electrostatic coupling between a conductive AFM tip and a QD, we can more confidently confront theory and experiments. We will present in this section the experimental results on a sample that includes one layer of selfassembled QD as illustrated previously in figure 4.2 in section 4.1. The actual detailed description of the set-up has already been illustrated in figure 4.5 where the difference of potential, V_B , is applied between the AFM tip and the 2DEG that serves as the buried back-electrode, as well as an electron reservoir for electrons to tunnel to the QD. This simple two electrodes configuration, where the AFM tip acts as a mobile gate is very convenient if one wants to have access to a large variety of individual QD that are uniformly distributed on the surface. The other advantage is that prior to the spectroscopic analysis, AFM images can be recorded, thus assuring access to a single QD, as well as the possibility to characterise its geometry. Moreover, since we use the AFM in the non-contact mode, deteriorations of neither the QD nor the tip can occur after the localization of the QD on the surface by imaging or while performing the spectroscopic curves.

First, we can show some AFM images of the self-assembled QD taken under the same experimental conditions as the later spectroscopy data. Figure 4.8 shows two different topographical images of the QD. The lateral resolution is not among the best



Figure 4.8: Non-contact AFM images of self-assembled QD taken at 4.5 K. Left: 2 microns scan, right: 180 nm scan.

achievable with a non-contact AFM for two reasons: (i) the metal coating sputtered onto the tip renders the apex of the tip broader and makes the tip very sensitive to electrostatic force which usually means poorer lateral resolution; (ii) because of the quite high aspect-ratio of the QD on the surface, it makes it more difficult to decrease the frequency shift set-point for higher resolution (i.e. increase the force gradient by bringing the tip closer to the sample) since this generates instability when the tip passes above the QD.

Regardless of this resolution, we can nonetheless differentiate very well each QD individually and localize them precisely on the surface which was the principle aim of topographical imaging. In particular for our study, it was important for instance to have a low density QD coverage so as to avoid confusion between side effects of neighboring dots. With such a sample that had a measured density of a few QD per micron-square, it was easier to locate individual as well as isolated QD.

4.4.2 Electrostatic Force Spectroscopy

Once the clear identification of a single QD has been made by regular non-contact imaging, we position the tip above the QD to perform the spectroscopic curves at



Figure 4.9: Energy band diagram of the AFM-QD-2DEG set-up described previously in figure 4.5. The applied voltage acts as a lever arm between AFM tip and 2DEG. (a) Tunneling events are blockaded as long as the charging energy E_c is not overcome. (b) When E_c falls below the Fermi level of the QW an electron can tunnel in the dot.

a given x - y position. While the spectroscopic mode is on, the feedback control that regulates the tip-sample distance is frozen so that each $\Delta f - V_B$ curve is taken at a constant gap, z_0 , of usually 10 nm or more. This rather large gap assures that tunneling events between the tip and QD are negligible and the electrostatic force is the dominant interaction. This is why hereafter we will refer to this type of spectroscopy as *Electrostatic Force Spectroscopy* (EFS) since the main contributing interaction is electrostatic. The changing of V_B acts as a lever arm for the voltage drop across the vacuum gap (V_{tip}) and the tunnel barrier (V_{sub}), thus shifting QD energy levels with respect to the 2DEG as illustrated on figure 4.9. When the charging energy E_c is overcome by the amount of voltage $V_{sub} = E_c/e$ an electron can tunnel in the dot. This charging event corresponds to a sudden change in the electrostatic force probed by the AFM tip and corresponds to the second term in equation 4.23 where q passes from Ne to (N + 1)e.

The experimental evidence of such an event detected on top of the overall back-



Figure 4.10: Resonant frequency shift (black), Δf , and dissipation energy (red) of the AFM cantilever as a function of tip-sample bias voltage. The arrows point to the sudden increase in Δf , revealing single electron charging events of the QD. The insert shows the magnified spectrum around the minimum to put into evidence smaller features noted as A- and A+. Here, a fitted parabola around the minimum is subtracted to the EFS.

ground capacitive force is given in figure 4.10, where some step-like structures deviating from the generic parabola are observed. Each jump is attributed to the sequential charging of the QD by a single electron tunneling from the 2DEG to the dot. It was therefore possible in this experiment to control the charge state of the QD by a step of one electron. The corresponding peaks from the dissipation channel help to corroborate the effect since it happens for the same applied bias. A more general discussion of these dissipative peaks is postponed to chapter 5. No features as those mentioned above were observed on the sample without the QD.

Returning to the EFS curve, we can observe a number of similarities as well as deviations from the calculated curves shown in figure 4.6. In particular, the height of the jump increases for higher voltage as expected by equation (4.28). In fact, the two Coulomb blockade events noted A- and A+ are so small that it was necessary to subtract a fitted parabola around the minimum in order to bring some evidence of their existence as shown in the insert of figure 4.10. A second expected behavior of the jumps is their (almost) symmetric position with respect to the minimum of the parabola. This fact is actually linked to the spacing in voltage, $\Delta = e/C_{tip}$, that is supposed to be more or less constant. A more careful look at figure 4.10 reveals however that this spacing between two neighboring jumps is not exactly the same as well as the fact that jump C appears sharper than expected. The most plausible explanation for this is that the oscillation amplitude decreased around the jumps due to feedback error, which was mainly due to the absence of integral gain in the AGC. A decrease in amplitude leads to an increase in the closest tip-QD distance, which results in the shift of the jumps to higher bias voltage as well as sharper jump for smaller amplitude. This unwanted (but avoidable) effect prevent us from having a more detailed analysis of the spectra, in particular possible internal energy level of the QD for which the resolution between neighbouring jumps is very important.

It is nevertheless possible to draw some quantitative information from the position of the jumps as well as to check the consistency with the theory described above. Since the overall shape of the spectra depends on the gap distance z_0 , we plotted in figure 4.11 a series of EFS taken over a QD at various z_0 . As expected from the theory, the jumps shift to lower bias voltage as the distance becomes smaller, due to a larger C_{tip} when the tip is approached. The insert (b) in figure 4.11 shows that the spacing between the jumps B- and B+ is linearly dependent on the tip-QD distance. This indicates that $C_{tip} \approx 1/z_0$ and implies that the parallel plate capacitor model works well in this distance range. Assuming that the spacing between jumps B- and B+ is equal to 3Δ , C_{tip} is found to range between 0.064 to 0.094 aF. This very small value of the tip-sample capacitance can teach us two things:



Figure 4.11: (a) Electrostatic Force Spectra as a function of tip-QD distance, z_0 . The numbers on the right-hand side is the tip-QD distance obtained from a linear fitting. (b) Spacing of the jumps B- and B+ versus tip-QD distance.

- 1. Such a small value would not be possible in a typical STS experiment since the associated tunneling rate would be far less than the smallest detectable current of about 1 pA. This fact points to one major advantage of the charge detection through electrostatic force, namely that EFS can be sensitive to even a single electron tunneling event while STS measures a statistical average of the current that corresponds to a large number of such events.
- 2. We can now compare this value of $C_{tip} \approx 0.08$ aF to the one we could obtain from the detailed analysis of the tip-sample capacitance in chapter 3, which is of the order of 10 aF in more or less the same condition. This large discrepancy (two orders of magnitude) reveals the clear distinction between on one hand the geometrical tip-sample capacitance and on the other hand the so-called "Coulomb blockade capacitance" that corresponds to the very end of the tip


Figure 4.12: (a) Schematic representation the different capacitances in play between tip and sample. (b) Equivalent circuit representation that takes into account the stray capacitance.

that interacts most strongly with the QD. In other words, there is a rather large *stray capacitance*, between the rest of the tip (in particular its sides) and the substrate around the QD, that also contribute to the overall electrostatic interaction but not to the CB phenomena.

This last point is best illustrated in figure 4.12 where we can note that a large portion of the tip does not directly contribute to the interaction with the QD, but to its surrounding, thus also diminishing the lateral resolution of the AFM when probing the electrostatic force. This is because of the low aspect ratio of the tip with respect to a small nanostructure such as a QD, typical coated tip radius are about 80 nm while QD are usually smaller than 40 nm. This problem was already mentioned in section 2.3.5 where the use of a high-aspect tip with a small cone angle would greatly enhance the relevant contribution in the electrostatic interaction that has a more direct effect with the QD sitting just underneath the tip.

Unfortunately it was impossible so far to display the value of the electrostatic force directly but rather the frequency shift of the cantilever. This information is contained in the force-distance spectroscopy that is analysed in the next section.

4.4.3 Force-Distance Spectroscopy

We now turn our attention to the information obtained from the $\Delta f - z$ curves and the subsequent F - z curves after the appropriate processing. As discussed in chapter 3, the only way to recover a quantitative value of the interaction force is by measuring its z dependence since non-contact AFM is first of all sensitive to the gradient of the interaction force. This is readily presented in figure 4.13 where clear jumps in the frequency shift and the corresponding jump in the force are observed in both the approach curve as well as when the tip is retracted. The most striking features observed in this set of experimental data are the "hysteresis loops" around the third Coulomb blockade jumps (corresponding to jumps C in figure 4.10) between the approach and retraction curves. A second point that does not agree with the theory exposed in section 4.3.3 is the presence of a "double jump" in the approach curve that has only a single jump counterpart in the retract curve. These two puzzling effects have not found satisfactory explanation so far and are left as open questions.

In theory, the informations contained in the EFS spectra and the force-distance curves are equivalent, but to extract the quantitative value of the jumps height for instance, it can only be done on such curves as the one presented in figure 4.13. From the value of the calculated force we can extract the jump height, ΔF , for the corresponding single electron filling of the QD, already denoted as jump *B* and *C* in figure 4.10 and whose measured values are: $\Delta F_B = 9$ pN and $\Delta F_C = 41$ pN. We can now compare these values with what can be calculated from equation (4.28) that determines the jump height from the expression of the electrostatic force. Assuming similar parameters as the one used when figure 4.6 were computed and using the experimental input values of *z* at which the jumps occur as well as the applied voltage of -4 V, we find that $F_B^{calc} = 2.5$ pN for jump B and $F_B^{calc} = 15$ pN for jump C.



Figure 4.13: Frequency shift-Distance and Force-Distance curves at 4.5 K above the same QD as in figure 4.10. Both approach and retract curves are shown on the same graph. Inserts are a zoom in the region where some hysteresis were observed. Here a bias voltage of -4 V is applied.

This rather large discrepancy between experimental and calculated value is not too surprinsing since in this particular set of data the amplitude controller relied on the proportional gain, P, rather that a PI gain (including the integral gain), which causes the tip amplitude to deviate substantially from its set-point value when jump occur. This lag from the AGC gain to respond appropriately tends to therefore increase arbitrary the actual effect coming from a sudden and abrupt change in the resonance frequency of the cantilever. This small artifact does not nevertheless discredit the actual effect of CB filling of the QD, since the actual onset of the jump is indeed caused by the tunneling of electron, but rather prevent a full quantitative treatment of the jump height.

4.5 Summary

This chapter has shown that single electron detection with an AFM at liquid Helium temperature was achievable. For this to be possible, no need to collect a tunneling current or measure a conductance was required but rather a clear signature was observed in an abrupt shift of the cantilever resonance frequency. The mechanism of tunneling between a 2-dimensional electron gas and a semiconductor QD was explained and correspond to the underlying mechanism for single electron detection. The signature in the frequency shift can in turn be related to the actual electrostatic force, which depending on the value of the applied bias voltage, can exhibit sharp jump of several picoNewtons as soon as the Coulomb blockade condition is satisfied. The rather complicated relationship between force and frequency shift have been studied in detail and the effect of such highly non-linear term as the jump in the force translates in different jump shapes for the frequency shift depending on the tip-amplitude. This is due to the averaging nature of the motion of the oscillating tip around the value of the voltage for which the jump from N electron to N + 1 electron occur. All these observed features could be well described by a simple theory based on consideration

of the free energy of the QD-back-electrode system and therefore leave opportunity to improve several important parameters such as the tunneling rate, optimal capacitances and optimal tip shape through the adequate design and fabrication of the sample and tip geometry.

 $\mathbf{5}$

Dissipative Processes between a Mechanical Oscillator and a Quantum System

5.1 Introduction

In the last chapter of this thesis, we will focus on describing as well as on quantitatively understanding the dissipative aspect originating from the coupling between a quantum dot and an oscillating AFM cantilever. The information of such dissipative processes is obtained mainly from the measurement of the Q-factor degradation (or gain), which can be converted to energy dissipated per oscillation cycle and corresponds to the amount of energy required to feed into the system by the driving actuator to keep the amplitude of the oscillation constant.

When measuring the frequency shift of the cantilever, it is the in-phase component of the interaction force with respect to the driving force that is recorded, which corresponds to the conservative part of the interaction. By measuring the out-of-phase component of the tip-sample force, we can access to non-conservative component of the interaction, or dissipation. Expressed in a mathematical form, according to the general theory of NC-AFM, the frequency shift and gain factor can be expressed as [91]:

$$\Delta f \cong \frac{f_0^2}{kA} \int_0^{1/f_0} F_{ts}[z(t)] \cos(2\pi f_0 t) dt$$
(5.1)

$$g \cong \frac{1}{Q} + \frac{2f_0}{kA} \int_0^{1/f_0} F_{ts}[z(t)] \sin(2\pi f_0 t) dt$$
(5.2)

These two simplified equations are obtained with the assumption that the frequency

shift caused by the tip-sample interaction is quite small with respect to the resonance frequency of the cantilever, which is always satisfied in our experimental conditions. Equations (5.1) and (5.2) tell us that by measuring the interaction force, F_{ts} , one can acquire independently the conservative as well as non-conservative component of the interaction. This chapter will try to demonstrate that the information obtained from the dissipation channel, available in any AFM in frequency-modulation mode, can give valuable insight into the dynamics and out-of-equilibrium aspects of single-electron tunneling inside a nanostructure.

Note that since we operate the AFM in non-contact mode, and always from a relatively large distance to the sample (above 10nm), we can rule out the possibility of adhesion hysteresis mechanism during the approach and retraction cycle accounting for the energy dissipation. Therefore, our main interest and following the original work of Gauthier and Tsukada [92, 93], is to address the issue of dissipation from the point of view of a *stochastic* behavior of the system, i.e. electron tunneling to the quantum dot in our case. The two different time scales of our system, namely the tunneling rate between the 2DEG and the QD, and the resonance frequency of the cantilever, f_0 , requires to considered the force experienced by the tip as an average value over many tunneling events.

This investigation of dissipative phenomena between the AFM tip and our QD sample will enable us to give a more general and complete picture of the Coulomb blockade regime already described in the previous chapter. More experimental results will be added, obtained under similar conditions as before, as well as with a so-called Quantum Dot Molecule (QDM), which consits of 2 stacks of QD layers with a tunneling barrier in between. This type of sample will permit us to address some important questions about the possible coupling between two superimposed QDs.



Figure 5.1: Dissipation measurement obtained over a QD at 4.5K (red). Several peaks are clearly observed, the one indicated by the arrows corresponds to Coulomb blockade charging events. The corresponding frequency shift curve is also shown for reference and only two symmetric jumps are clearly distinguishable.

5.2 Dissipation Spectroscopy Measurements

Since the previous chapters have given detailed descriptions of the QD sample structures and properties (see figure 4.2 for instance), we can now focus directly on the main piece of experimental data obtained at liquid Helium temperature and over an individual QD. This first section will focus on a single stack QD sample, that is, the same one has already investigated in chapter 4 by Electrostatic Force Spectroscopy (EFS).

Figure 5.1 shows the dissipation versus voltage curve taken over a QD. The peaks corresponding to Coulomb blockade charging of the QD are indicated by arrows and will be the main point of focus for our later discussion. Since the measured gain at resonance is directly related to the energy dissipated by the cantilever motion (intrinsic dissipation) and the dissipation originating from the tip-sample interaction, we presented the experimental data in figure 5.1 as energy dissipated per cycle. The relation between the Q-factor and the actual power dissipated per cycle is simply given by:

$$P = \frac{kA^2f_0}{2Q} \tag{5.3}$$

with the usual notation: f_0 is the resonance frequency of the cantilever with a stiffness k and amplitude A. The typical order of magnitude of such spectra of about 0.1 eV/cycle is similar to values obtained by Hoffmann *et al* when measuring atomic scale dissipation in the non-contact regime [94].

Only the largest peaks in the dissipation have a easily detectable jump counterpart in the frequency shift curve that was acquired simultaneously. This fact points to dissipation measurement as a more reliable and sensitive channel of information for the type of spectroscopy presented here. Indeed, the richness of the information shown in the dissipation curve far exceeds the one obtained in the frequency shift. To some extent, the dissipation channel seems to look like the derivative of the frequency shift, but this impression does not hold after careful data processing, which does not reveal as many features as the original raw data of the dissipation. In that sense, it seems that the force sensitivity to dissipative interactions, in particular when tunneling could occur, always out-performed the force sensitivity to conservative interaction recorded in the frequency shift, which corroborates the finding of Fukuna *et al* of a higher sensitivity obtained with a dissipation force modulation method [95].

The most striking features of these dissipation peaks are their height and width that depend on the electron number, N, entering or leaving the QD as the voltage is swept between -3 and 2V, with a small tip-sample capacitance modulation of a hundred kHz due to the oscillating AFM tip. Dissipation peaks increase for larger electron number, N, or equivalently for higher value of the sample voltage.

Several other peaks may also be distinguished, but as yet are still not fully understood. In particular, the two symmetric peaks that point downward, i.e. with a negative value for the dissipation, cannot be explained by just using Coulomb blockade phenomena.

5.3 Interpretation of the Spectra

In this section, we will try to account for the above observed peaks in the dissipation spectroscopy that correspond to single electron charging of the QD when the Coulomb blockade condition is satisfied, i.e. for $V_{jump} = \frac{e}{C_{tip}}(N + 1/2)$ with N an integer. At first, we will focus on explaining the underlying mechanism responsible for the observed dissipation peaks by carefully analysing the possible delay time that arises because of the *time dependency of the force* acting on the tip and that is explained extensively in reference [96]. Such treatment focused mainly on atomic instabilities that result from bistable potential energy surface [97] but can be applied for any type of transition state such as a change in the electron number in our quantum dot.

In a second part, we will give an analytical solution for the Q-degradation as a function of voltage, in the limits of small perturbation of the position of the QD energy level by the applied voltage modulated by the tip oscillation. Both approaches can be considered as the back action of the tunneling electrons to the motion of the oscillating AFM tip.

5.3.1 Understanding the Origin of Dissipation

In the previous chapter, we explained how Coulomb blockade phenomena manifested itself in sharp jumps in the force and smoother jumps in the frequency shift depending on the tip-amplitude. One thing that has to be kept in mind regarding that theory is that it was implicitly implied that the switching between a state of N electrons to a state of N + 1 electrons occurred *instantaneously* as soon as $V_B = V_{jump}$. This assumption was satisfactory to explain the abrupt shift in the resonance frequency of the cantilever, but it cannot be assumed anymore when trying to explain the corresponding dissipative peaks observed experimentally at that same value of the applied bias voltage.

If we now consider that there is a certain time dependence of the force originating from the tunneling of electrons to the QD or a fluctuation in time of such force, we can understand that this fluctuation can affect the motion of the tip differently upon approach (from -A to +A) or retraction (from +A to -A) over one oscillation cycle. This hysteresis is what precisely creates dissipation. Such a fluctuating force in time has basically its origin in the change of the electronic state of the QD from state 0 (where there is N electrons) to state 1 (where there is N+1 electrons) and *vicc-versa*. To be more specific, let's look at this transition probability for the QD to go from state 0 to 1 according to the so called "master equation":

$$\frac{dP_0(t)}{dt} = -P_0(t)W_{01} + P_1(t)W_{10}$$
(5.4)

$$\frac{dP_1(t)}{dt} = P_0(t)W_{01} - P_1(t)W_{1A}$$
(5.5)

where W_{01} is the transition probability to go from state 0 to state 1 which in terms of standard statistical physics can be written as:

$$W_{01} = \Gamma f(E) = \frac{\Gamma}{1 + e^{E/kT}}$$
(5.6)

$$W_{10} = \Gamma(1 - f(E)) = \frac{\Gamma e^{E/kT}}{1 + e^{E/kT}}$$
(5.7)

Here we called Γ the tunneling rate for electron to tunnel on and off the QD, f(E)the Fermi-Dirac function and E the energy associated with adding one electron to the QD, also called *addition energy*. If we call $E_c = e^2/2C$ the charging energy of the QD is then:

$$E = 2E_c \left(\frac{j}{2} - N\right) + \Delta E \tag{5.8}$$

In equation (5.8) we have introduced the energy level spacing ΔE that will depend on the internal structure of the dot. Note here that the electron number $N = C_{tip}V_B/e$ is no longer an integer but can vary continuously with the applied bias V_B . On the other hand j is an integer that corresponds to different transition states: for j = 1, the electron number goes from 0 to 1, for j = 2, electron number goes from 1 to 2 and so on. The solution of equation (5.4) is well-known and if we assume that at t = 0, $P_0(0) = 1$, we obtain:

$$P_0(t) = e^{-\Gamma t} \left(1 + \int_0^t W_{10} e^{\Gamma \tau} d\tau \right)$$
 (5.9)

This equation will tell us how the transition probability evolves over time as the tip oscillates according to: $z(t) = z_0 + A\cos(\omega t)$. It is good to keep in mind that the tip oscillation will change the value of the tip capacitance since (for a parallel plate configuration) $C_{tip} = \epsilon S/(z(t))$, and therefore the level position of the energy E will also be subject to a small variation, oscillating at the same frequency ω . From this consideration, we can deduce that $P_0(t)$ is a periodic function in time, of period $2\pi/\omega$, oscillating between state 0 and 1.

From the above description of the transition probability which accounts for the switching behavior of the QD from N electron state to N + 1 electron state, we can deduce the origin of damping in our system. The main parameters are the tunneling rate Γ , the cantilever resonance frequency f_0 and the tip capacitance C_{tip} . The temperature dependence is taken into account through the Fermi function.

Now let's look at figure 5.2, where we plotted the transition probability, $P_0(t)$, calculated from equation (5.9) as a function of time. For reference, the oscillatory motion of the tip, z(t), is also shown in order to more clearly identify the small delay between the switching from state 0 when the tip is at position -A to state 1 when the tip is at the position A. These graphs were calculated for a temperature of 5K, a tip amplitude of 5 nm at a distance $z_0 = 15$ nm and for the critical value of the applied



Figure 5.2: Origin of the dissipation. (a) Transition probability for different values of Γ as a function of time and for $V_B = V_{jump}$ for two periods and calculated from equation (5.9). (b) Tip motion around its mean position z_0 . Note the delay between z(t) and $P_0(t)$ that arises for slower tunneling rates. (c) Transition probability as a function of tip-position: the slower the tunneling rate, the larger the hysteris over one oscillation cycle. All graphs were calculated assuming a temperature of 5 K.

voltage, $V_B = V_{jump}$, that is when the tip is oscillating around the voltage for which the Coulomb blockade condition is fulfilled and an electron can tunnel into the dot. This can be referred to as resonant tunneling. As a matter of fact, if the switching behavior was *instantaneous* (or the value of Γ infinitely large), the probability would simply appear as a perfectly square function switching instantaneously from state 0 to state 1 exactly when the tip passes through $z = z_0$.

If we now plot the transition probability as a function of the tip excursion around its mean position z_0 , we can reproduce a hysteresis curve where the value of the probability is different upon the path followed by the tip whether it is going from -Ato +A or from +A to -A. We presented these calculated curves as a function of the tunneling rate Γ , which mainly tell us that the faster the electron is allowed to tunnel back and forth in the QD as the tip oscillates close to the critical voltage V_{jump} , the smaller will be the hysteresis curve.

The switching behavior of the QD state that we observed in the transition probability is also reflected in the measured interaction force between the AFM tip and the dot. The value of the electrostatic force in each state, noted as $F_A(z)$ and $F_B(z)$ when q = Ne or q = (N + 1)e respectively, will be weighted by the transition probability $P_0(t)$ and $P_1(t)$ according to [97]:

$$F_{ts}(z,t) = P_0(t)F_A(z) + [1 - P_0(t)]F_B(z)$$
(5.10)

where F_{ts} is the force due to tip-sample interaction. For the electrostatic force we use the analytical equation (4.24) derived in chapter 4. Note that in equation (5.10) the transition between state A and B is not anymore instantaneous as was previously assumed in equation (4.21) and that the time dependency is included in the time dependent probability $P_0(t)$.

This section has helped us understand rather qualitatively the origin of damping when tunneling occurs. The next section will prove more useful to compare our experimental data quantitatively with theory, even though several approximations will have to be made.

5.3.2 Analytical Dissipation-Voltage Curve

So far, we have described the origin of damping as the consequence of the time delay between the position of the oscillator and the effective response of the system, which in our case depends very much on the tunneling rate of the electron to the QD. A somehow similar approach can now be considered where we picture damping as the absorption of energy from the oscillator by an effective "bath" produced by the QD. This approach is legitimate if the coupling between the AFM tip and the QD is weak so that the QD response can be considered linear with respect to the motion of the oscillator [98]. Such a treatment has been applied successfully to the study of dissipation in quantum nano-electromechanic system by Clerk and Bennett [98, 99].

Recalling our previous definition of dissipation, we can always write the damping force, which is out-of-phase with the cantilever's motion, as:

$$F_{damp}(t) = -m \int \gamma(t - t') \dot{x}(t') dt \qquad (5.11)$$

In the linear regime, we can express the damping coefficient $\gamma(\omega)$ in Fourier space as a function of the linear response coefficient $\lambda(\omega)$ in the following manner [99]:

$$\gamma(\omega) = B^2 \left(-\frac{\mathrm{Im}\lambda(\omega)}{m\omega} \right)$$
(5.12)

where B is the coupling strength between the AFM oscillator and the QD and in our simple system can be approximate as $B \cong 2E_c N/z$, where z is the distance between the tip and the dot. Equation (5.12) allows us to calculate the damping. In order to do so, we can use the equation for the transition probability from the previous section, that is (5.4) to (5.7) to describe the charge state of the dot. But instead of trying so solve these equation exactly, which in the previous section required to solve them numerically, we assume that the position of the energy level in the QD are subject to a small variation following the tip resonance frequency ω :

$$E \to E + \delta e^{-i\omega t} \tag{5.13}$$

so that the transition probability will change accordingly to:

$$P_1(t) \to P_1(t) + \lambda(\omega)\delta e^{-i\omega t}$$
 (5.14)

From such approximation, and using the coupled equations (5.4) and (5.5) we can work out the imaginary part of $\lambda(\omega)$ to be:

$$-\frac{\mathrm{Im}\lambda(\omega)}{\omega} = \frac{\Gamma}{\omega^2 + \Gamma^2} \left(-\frac{f(E)}{dE}\right)$$
(5.15)

If we go to the regime where the tunneling rate is much faster than the cantilever resonance frequency, we can take the limit $\omega \to 0$ in equation (5.15), which finally gives us:

$$\frac{1}{Q} = \frac{\omega_0}{k} \gamma(0) = 4f(E)(1 - f(E))N^2 \left(\frac{E_c}{kz^2}\right) \left(\frac{E_c}{k_BT}\right) \left(\frac{\omega_0}{\Gamma}\right)$$
(5.16)

From equation (5.16), it is possible to compute the value of the dissipation for several transitions in order to compare it with our experimental results shown in figure 5.1. The main unknown parameters are the charging energy, E_c , and the tunneling rate Γ since all other parameters are either known as the experimental conditions (cantilever stiffness, k, and resonance frequency, ω_0) or obtained already from the EFS data in chapter 4 such as C_{tip} , which determines the spacing between two subsequent peaks. It is also good to note that in equation (5.16), 1/Q is inversely proportional to Γ and the slower the tunneling rate the higher the value of the dissipation, which corroborate the argument already discussed in the previous section.

We plotted some theoretical curves of the dissipation in figure 5.3 as a function of sample voltage for several temperatures that can be compared with the dissipation



Figure 5.3: Theoretical prediction of the effect of temperature on the energy dissipated, calculated from equation (5.16) with a charging energy of $E_c = 5.3$ meV.

peaks indicated by arrows in figure 5.1. The spacing between two adjacent peaks is determined by C_{tip} (included in the value of N in expression (5.16)) in the same way than in the force, as seen in chapter 4. We used for the calculation a charging energy of $E_c = 5.3$ meV and a tunneling rate $\Gamma = 6 \times 10^6 \text{s}^{-1}$. Such value for the charging energy for an *individual* QD, is comparable to the mean value of 23 meV obtained from capacitance spectroscopy data on a large ensemble of InAs SAQD [22].

From the overall shape of the dissipation peaks, we observe a similar trend between the theory and our experimental data, in particular the increase in dissipation peak height as the voltage is increased. On the other hand, some deviations can be noted in regard to the exact peak shape. In figure 5.3, in order to obtain the same order of magnitude in dissipation than the one obtained in the experimental data, it was necessary to use a rather slow tunneling rate but still around 50 times faster than the cantilever resonance frequency of 113 kHz. Unfortunately, since it is impossible to know *independently* and with a good accuracy the value of the tunneling rate, it follows that the charging energy cannot be deduced with certainty.

Moreover, in the above calculation the value of the tip-amplitude was not taken into account. From the results obtained in the frequency shift data we already recognized that the tip amplitude is an important parameter to determine the overall shape of the jump in the EFS. Concretely, we know from the experimental conditions that, because of small AGC error (only a P-gain, instead of a PI-gain as discussed in section 4.4.3) the value of the tip-amplitude dropped more for the largest peaks (at -2.2 V and 1.7 V) than for the peaks at -1.1 V and 0.9 V, resulting in a even sharper peak than theoretically expected. It is therefore reasonable to assume that the smaller the tip-amplitude, the sharper the dissipation peaks will be. That's why we anticipate that the averaging effect of the oscillator motion on the measured interaction should play an important role in determining the exact width and height of the dissipation peaks, and a better agreement between theory and experiment should certainly be possible.

5.4 Quantum Dot Molecules

One of the advantages of growing self-assembled semiconductor QD layers by Chemical Beam (CBE) or Molecular Beam Epitaxy (MBE) is that it does not require much more work to deposit one or several layers of QD. The basic idea for having QD multilayers lies mainly in having more efficient laser [100, 11], that should have higher gain, lower threshold current and higher thermal stability compared with conventional laser as well as with laser made with other quantum structures. This is due to the atomic-like density of state of the QD [12, 13]. Furthermore, in terms of transport properties, the possible interaction of two superimposed QD one on top of the other is very interesting since the two wave functions of each QD can overlap and give rise to more complex structures known as a Quantum Dot Molecule (QDM).

Because it is easier to start with a simple system, so far all experimental evidences for the charging of an individual QD presented are carried out on a single layer of QD. We would like to present here the same type of electrostatic force and dissipation spectroscopy over two layers of self-assembled QD, grown on top of each other with a thin layer of material used as the tunneling barrier. Such schematic examples were already well described in chapter 4 and displayed in figure 4.2(b) for reference. Before moving on to the next section, it is worth mentioning that in QDM sample, two QDs in different stacks are more likely to be aligned because of the small protrusion made by a QD in the first layer, which then serves as an privileged nucleation site for subsequent QD growth. Cross-sectional STM study of multilayer QD [101, 102, 103] tend to corroborate this preference of subsequent QD layers to grow on top of buried QD.

5.4.1 Dissipation Images

It is worth spending some time now with the kind of images that can be obtained on the surface of such layers of QD since several channel of information can be used either simultaneously, such as a dissipation and topography channel for a given voltage, or using the KPFM feedback loop.

Six different AFM images are shown in figure 5.4 from the same QDM sample. A first set of three images (a,b,c) were taken with the sample voltage very close to V_{cpd} , which gives the best topography images but a very poor dissipation image. Only some blurry spot seem to correspond to the underlying dot clearly distinguishable in the topography. If the images are now taken with a sample voltage of 2V (d,e,f), the dissipation contrast is enhanced, and some clear correspondence between dissipation and topography can be made. For clarity both images of the topography taken at $V = V_{cpd}$ and V = 2V are shown, the poor image resolution for V = 2V is as expected since the average electrostatic interaction is increased and tends to decrease the lateral resolution.

The most interesting observation that can be made from images 5.4 (d) and (f) is that not every QD on the topography image does have a dissipation counter-part in the dissipation image. This leads us to state that some dots are more "active" in terms of their dissipation contrast than others. One possibility that could be inferred from such a statement is that the dissipation contrast on the images is actually a measure of how well the surface QD is coupled to either the underneath (buried) QD or the 2DEG itself. We already know from the previous section that the tunneling rate, Γ , is an important parameter in determining the amount of dissipation contrast, especially on resonance when the Coulomb blockade condition is satisfied to allow some electrons to tunnel into the QD. The faster the tunneling rate, the smaller the dissipation. One consequence of this could be that if a buried QD lies in between the 2DEG and the surface dot, it could act as a "scatterer" and therefore would decrease the effective tunneling rate that corresponds to the charging of the surface dot. QDs with dissipation contrast in figure 5.4(c) would therefore correspond to dots that has a buried QD underneath them (or better coupled to), while dots with very little contrast would correspond to a surface dot sitting directly on top of the 2DEG.

Of course, to corroborate such a hypothesis, a detailed description of the coupling between 2 QDs would be necessary, and the knowledge of each tunneling rate (between 2DEG and a buried dot or between the buried dot and the surface dot, ...) are key parameters that would need to be determined.

5.4.2 Dissipation and Force Spectroscopy

This last section will deal with some experimental investigations of two superimposed stacks of QD layers in what we referred to as Quantum Dot Molecule (QDM) and



Figure 5.4: Topography, dissipation and KPFM images of the surface dot which has buried dots underneath. Only by applying a large sample voltage can we clearly identify QDs with dissipation contrast. Note that not all dots exhibit dissipation contrast (arrows).



Figure 5.5: Dissipation-voltage curve recorded at liquid Helium temperature for two dots which exhibit different contrast on figure 5.4 indicated by arrows. Similar spectrum obtained on bare InP is also shown for comparison. (Insert) Corresponding frequency shift data acquired simultaneously, note the small offset of the EFS on bare InP with respect to the EFS on QDs due to the contact potential difference.

address the possible coupling between them. Already in the previous section, we showed some evidence in the AFM images of topography and dissipation that not all surface QD exhibit clear dissipation contrast, and this effect does not depend on the dot shape but rather might depend on the surface-dot/buried-dot coupling.

The dissipation contrast obtained in figure 5.4 can be further investigated by recording spectra at different sample positions. In figure 5.5, three different spectra are shown, which were taken on a QD that exhibits dissipation contrast (called QD1), another QD with no clear contrast on image 5.4(d) (called QD2) and for reference, a last spectra obtained for bare InP. Note that in this experiment we used a softer cantilever of 15 N/m with a resonance frequency of 78 kHz, that's why the

overall value of the recorded frequency shift could be as high as 700 Hz. From such data it becomes clear that, especially for positive bias voltage, different behavior of the dissipation curve can greatly enhance the dissipation contrast for different QDs. On the other hand there is no ambiguity to distinguish spectra obtained on a surface QD from the one obtained on bare InP, which could never exceed a value for the dissipation of 0.04 eV/cycle. This last remark points out to the surprisingly high value of the dissipation of the QDs, since it could get as high as 0.6 eV/cycle. This value has to be compared for instance with the spectra shown in figure 5.1 for the single stack QD sample, where the highest value for the dissipation never exceed 0.1 eV/cycle.

In fact, it was possible in rare cases to record other types of spectra than shown thus far, with dissipation value of the same order of magnitude as those obtained previously on a single stack QD sample. Such a spectrum is shown in figure 5.6 where both frequency shift and dissipation curves were recorded simultaneously. Some clear peaks in the dissipation can be identified, but with very different shapes at positive or negative biases. Only one jump in the frequency shift was observed, and here again there is no symmetry in the voltage with respect to $V_B = V_{cpd}$. An important point to mention is that the noise level in the frequency shift is surprisingly high and does not correspond to the base noise level of the microscope: it is only when performing such EFS that the frequency shift noise would increase, it is therefore sample-induced. For comparison, the EFS shown in the insert of figure 5.5 has a much better signal-to-noise ratio under similar conditions. It is also worth noting that the noise level in the frequency shift increased even more after the jump in the frequency shift occurred at about $V_B = -2.6$ V, and surprisingly enough, the level of dissipation suddenly saturates. This type of spectroscopic curves were reproducible over the same QD but were seldom seen again on other QD.

Unfortunately, the exact conditions to obtain such spectra could not be clearly



Figure 5.6: Electrostatic Force Spectroscopy and Dissipation over a QDM at liquid Helium temperature. Note the increase in the noise level after a sharp jump is observed in the frequency shift at around -2.6 V.

identified since only a few QD would exhibit this type of behavior. Most spectra would look rather like the one shown on figure 5.5. In summary, the following types of dissipative and electrostatic force spectroscopy curves were observed on QDM samples:

- 1. Spectra taken over surface QD would most of the time be similar to the one shown on figure 5.5 with a very strong dissipation contrast and a parabolic-type behavior with the expected signal-to-noise ratio for the frequency shift. No clear features in the EFS could be identified.
- 2. Infrequently, depending on the surface QD (and possibly whether there is a well-aligned buried QD underneath or not), some spectra such as shown in figure 5.6 could be observed where the level of dissipation is similar as the one for a single stack QD sample, but with peaks of different shape. In such case, a very

unusually high noise level in the frequency shift is observed, and the overall spectra appears asymmetric with a jump only for negative value of the bias voltage.

3. For spectroscopic curves obtained on bare InP, the dissipation level would be low and more or less constant as a function of voltage. The EFS would look like the expected parabola with the expected microscope signal-to-noise ratio.

5.5 Summary

In this chapter, we have shown that the dissipation channel available in FM-AFM can indeed be a source of valuable information while performing spectroscopic investigations of QD, in particular to study out-of-equilibrium phenomena such as the tunneling event of a single electron to a quantum dot. Not only can dissipation spectroscopy corroborate similar features observed by electrostatic force spectroscopy, but it also proved to be an effective tool for studying the complex back-action mechanism that single tunneling events can have on a macroscopic AFM oscillator. In term of the observed dissipation contrast, the sensitivity given by the energy dissipation, in particular when tunneling could occur, always out-performed the corresponding observed features in the frequency shift, corroborating the finding of Fukuma *et al* of higher sensitivity obtained with a dissipation force modulation method [95].

The main source of dissipation was identified, namely: the time-dependence of the interaction force due to the stochastic process of electron tunneling, that can affect differently the tip between approach and retraction. On the other hand, the exact shape of the observed dissipation peaks remain somehow elusive in our attempt to fit the experimental data with some theoretical model but should be improved if the tip-amplitude is taken into account.

Our last attempt to understand two superimposed quantum dots, in a so-called

"quantum dot molecule" configuration, mainly encourages the pursuit of such investigation since interesting features in the dissipation could be observed for which we could only speculate that is due to the coupling between surface and buried dots. More work need to be done both experimentally and theoretically for a better understanding of such interesting nanostructures.

6

Conclusion and Outlook

6.1 Conclusion

Throughout this thesis, several spectroscopic methods with a low-temperature electrostatic force microscope in the non-contact regime have proved to be an effective tool to investigate local electrical properties of nanometer-scale devices. In particular, the possibility to position the AFM probe in the vicinity of a nanostructure allows one to control its electrostatic environment for local gating by modulating the applied bias voltage, as well as for electric charge detection by measuring the electrostatic force between tip and sample.

These technique has been applied to study Coulomb blockade phenomena in selfassembled InAs quantum dots in order to induce and control their sequential single electron charging. The originality of the experimental work that has been presented here relied on measuring the electrostatic force between the AFM tip and a back electrode or electron reservoir (a 2-dimensional electron gas) as a function of voltage. In this so-called Electrostatic Force Spectroscopy, no current has to flow to the tip. The signal detected is a long-range capacitive force, whose coupling to the QD can be changed at will by simply changing the tip-sample distance. The measurement relies more on measuring a change in a capacitance rather than a current. In this way, it is possible to detect jumps in the recorded force at some specific voltage which satisfies the Coulomb blockade phenomena, that is the energy required to overcome the confining potential of the QD. Each of these jumps was attributed to a single electron either entering or leaving the dot, which can be regarded as a controlled electron trap at the nanometer scale.

By acquiring two types of spectroscopies, i.e electrostatic force as a function of tip-sample voltage and distance, and upon the right data processing it also became possible to determine the value of the absolute tip-sample capacitance. Such knowledge can be of crucial importance for quantitative interpretation of the tip effect on the electrostatic environment of a nanostructure since the tip-sample capacitance determines the strength of the electrostatic interaction as well as the value of the voltage for which charging of the quantum dot can occur. Two other pieces of relevant information can also be extracted from the above analysis, namely the contact potential difference and the residual non-capacitive force, which can open the way to a more careful force separation treatment and interpretation of short-range forces when the long-range and almost ubiquitous capacitive force is present, yet undesirable.

At each step of the thesis, the dissipation channel was investigated and proved to be a somewhat unexpected source of important information for studying out-ofequilibrium phenomena such as the tunneling event of a single electron to a quantum dot. Even though the theoretical treatment of the dissipation didn't fully explained the observed experimental data, it opened a hopeful perspective and new opportunities for the study of dynamics of tunneling in individual QD as well as the possibility to extract such an important parameter as the charging energy of a self-assembled QD.

6.2 Future Directions

In regards to future work, electrostatic force spectroscopy combined with dissipation spectroscopy holds a lot of promises for the study of self-assembled quantum dots or



Figure 6.1: AFM images of direct lithography patterning of Au lines on InP substrate by NC-AFM deposition. Adapted from Pumarol *et al* [104].

nanostructures, since it is a local, non-contact, weakly perturbating method. Because of the long range nature of the electrostatic force, it is reasonable to assume that the methods exposed in this thesis could be applied even to buried structures.

From another perspective, it has proved so far quite challenging to attach leads to so small self-assembled nanostructures. In this domain, the NC-AFM itself could be used as the mean to deposit directly conductive wires as the work by Pumarol *et al* [104] anticipates. In that regard, Figure 6.1 illustrates the capability of direct metal lithography by NC-AFM. In such an eventuality, EFS could be performed before and after a wire has been deposited in order to study the invasive effect of such wire on the QD (such as strain, band bending, etc...) leading to a possible rearrangement of the QD energy levels and a better understanding of the effects of probing leads to a small nanostructure. Finally, the AFM tip could be used as a third probe terminal in a single electron transistor configuration. The advantage of using the AFM tip as a local movable gate with a variable capacitive coupling can be further refined by using full metal high-aspect ratio tips. Such tips should improve the lateral electrostatic resolution as well as reduce the tip-sample capacitance enough to allow probing of higher values of the electron number N, that is more jumps in the force. It is indeed important to have several jumps to more clearly investigate the shift of the energy levels in an externally applied magnetic field, while the charging energy should not be affected by the field.

Lastly, since the dissipation channel revealed many interesting phenomena related to the dynamics of tunneling, further experimental as well as theoretical investigation of the effects of temperature and tip amplitude on the peak shape should hopefully bring new insights and discoveries.

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