DESIGN AND VALIDATION OF A QUARTZ-CRYSTAL RESONATOR NANOTRIBOMETER

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31/07/2014

Besançon (FRANCE)
ABSTRACT

Design and validation of a quartz-crystal resonator nanotribometer.

This report presents the design and construction of a Nanotribometer using the bibliography provided and integrating new ideas to increase the field of research in the future. It initially shows a brief summary of the functioning and the history of the Quartz Crystal Microbalance (QCM). This, at first, was used only for studies on the change of mass deposited on the surface of the resonator from the displacement of the resonance frequency. Then, in 1986 by Krim and Widom, the QCM was used for studies of friction where, taking into account the variation of frequency, also took into account the variation of the quality factor (Q-factor). This quality factor is directly proportional to the energy dissipation between the surface of the resonator and micro-objects deposited.

After explaining the basic operation of the QCM and its history, presents existing models to date to evaluate and better understand the behavior of friction in different cases of the samples. Is observed in models where there is a sufficiently large contact surface, the frequency shift is negative. However, if the surface is small, the displacement of the frequency is positive.

The goal is to build a Nanotribometer able to study the friction from the interaction of micro-objects placed on the surface of the resonator. With the help of the literature and the experts in the various fields were designed and purchased various items to build the equipment. One can imagine that will be required a resonator (quartz crystal), a device capable of exciting and analyze the response of the latter (Network Analyzer), the micro-objects (polystyrene micro-spheres), a system for the vacuum to reduce the influence of the air in response, a system for capturing images and a magnification, and finally a structure
capable to assemble all the latter.

Finally, in order to verify that this Nanotribometer meets the requirements have been carried out a number of different tests of the devices and it is observed that everything works properly and that the objective has been met within budget and time available for the project.
ACKNOWLEDGMENTS

First and foremost, I wanted to thank the whole team of the Department of Micro Nano Sciences & Systèmes (MN2S), to the École Nationale Supérieure de Mécanique et des Microtechniques (ENSMM) of Besançon and to the FEMTO-ST Institute.

I would like to take the opportunity to thank my supervisor Dr. Philippe STEMPFLE for all the support, guidance and confidence given to me during the course of the project. I also want to say that it has been a pleasure to work beside him, since he has made my job easier as a scholarship holder.

I also want to thank especially to Dr. Jean-Michel FRIEDT who helped me with the realization of the results, with the choice of the network analyzer and assemble the equipment.

I wish also to express my sincere gratitude to all those who’ve been helping throughout the project, to Dr. Anne DOMATTI for constant support along the whole project, the intern and also best friend Verónica COLLADO CIPRÉS for her constant patience with me and correcting the memory and Dr. Nicholas MARTIN that with his kindness and sympathy helped me to make the vacuum system.

I would also like to mention my gratitude to Xavier VACHERET for the construction of different supports designed, to Jean-Marc COTE for the assembling of some parts, to Joel ABADIE and to Brahim TAMADAZTE for involvement in the system of the camera and magnification, to my friends Juan MURIAS TORRECILLA to make rendering and Andrés MEANA FERNANDEZ, along with Gilles BOURBON, did the deposition of gold on quartz crystals.

And last, but not least, to all other friends and especially to my family that has always been in the moments that I needed.

Thank you all.
REMERCIEMENTS

D'abord, je voulais remercier toute l'équipe du département de Micro Nano Sciences & Systèmes (MN2S), à l'École Nationale Supérieure de Mécanique et des Microtechniques (ENSMM) de Besançon et à l’Institut FEMTO-ST.

Je voudrais profiter de cette occasion pour remercier mon tuteur Dr. Philippe STEMPFLE pour tout le soutien, l’orientation et la confiance qui m’a été donné au cours du projet. Je tiens également à dire que c’était un plaisir de travailler à vos côtés car il a facilité mon travail de stagiaire.

De plus j’aimerais remercier tout particulièrement le Dr. Jean-Michel FRIEDT qui m’a aidé à la mise en œuvre des résultats, au choix de l’analyseur de réseau et à assembler l’équipe.

Je voudrais aussi exprimer ma gratitude à tout ceux qui m’ont aidé tout au long du projet, la Dr. Anne DOMATTI pour le soutien constant tout au long du stage, la stagiaire et aussi ma meilleure amie Verónica COLLADO CIPRÉS pour sa patience constante avec moi et la correction de le mémoire et le Dr. Nicolas Martin qui avec sa gentillesse et sa sympathie m’a aidé à construire le système sous vide.

Je tiens également à mentionner ma gratitude à Xavier VACHERET pour la construction de différents supports, à Jean-Marc COTE pour le montage de certaines pièces, à Joel ABADIE et à Brahim TAMADAZTE pour leur implication dans le système de la caméra vidéo et le grossissement, à mes amis Juan MURIAS TORRECILLA qui m’a aidé faire les rendus et Andrés MEANA FERNANDEZ, qui avec Gilles BOURBON, ont fait le dépôt d’or sur les cristaux de quartz.

Pour terminer, à tous les autres amis et spécialement à ma famille qui a toujours été avec moi quand j’en avais besoin.

Merci beaucoup à tous.
AGRAÏMENTS

En primer lloc volia agrair a tot l’equip del Departament Micro Nano Sciences & Systèmes (MN2S), a l’École Nationale Supérieure de Mécanique et des Microtechniques (ENSMM) de Besançon i a l’institut FEMTO-ST.

M’agradaria aprofitar l’avinentesa per donar les gràcies al meu tutor Dr. Philippe STEMP-FLE per a tot el suport, orientació i confiança que m’ha donat durant el llarg de tot el projecte. També vull aprofitar a dir que ha sigut un plaer treballar al seu costat, ja que ha fet més fàcil la meva tasca com a becari.

També vull donar les gràcies especialment al Dr. Jean-Michel FRIEDT que m’ha ajudat en la realització dels resultats, en l’elecció de l’analitzador de xarxes i del muntatge de l’equip.

Voldria també expressar la meva gratitud per a totes aquelles persones que m’han anat ajudant al llarg del projecte, a la Dra. Anne DOMATTI pel constant recolzament al llarg de tot el període de pràctiques, a la també becària i millor amiga Verónica COLLADO CIPRÉS per la seva constant paciència amb mi i la correcció de la memòria i al Dr. Nicolas MARTIN que amb la seva gentilsa i simpatia em va ajudar en el sistema per fer el buit.

També voldria mencionar la meva gratitud a Xavier VACHERET per a la construcció dels diferents suports dissenyats, a Jean-Marc COTE per a l’assemblatge d’algunes peces, a Joël ABADIE i a Brahim TAMADAZTE per a la implicació en el sistema de la càmera de vídeo i la magnificació, als meus amics Juan MURIAS TORRECILLA per a fer els renders i Andrés MEANA FERNANDEZ, que juntament amb Gilles BOURBON, em van fer les deposicions d’or sobre els cristalls de quars.

Per acabar, i per això no menys important, a tota la resta d’amics i a la meva família que sempre ha estat allà en els moments que més ho necessitava.

Moltes gràcies a tots vosaltres.
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Chapter 1

INTRODUCTION

1.1 QUARTZ CRYSTAL MICROBALANCE

A Quartz Crystal Microbalance (QCM) is a surface-sensitive oscillating piezoelectric that can accurately measure mass uptake (it can easily detect mass changes on the order of micrograms) and energy dissipation from an adsorbed layer [1]. It has been used as a nanoweighing device in a non-destructive way for many decades due to the high sensibility of its resonant frequency (typically ranging from 5 to 10 MHz). One QCM is low cost and needs relatively low maintenance in terms of operation. A QCM is comprised of two main components, a precisely cut wafer of quartz (the functional component) and two conducting electrodes (Au, Pt, etc.) that are deposited on the top and bottom portions of the quartz wafer.

Figure 1.1.1: Schematic of a Quartz Crystal Oscillator
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When a voltage is applied to a material like quartz (piezoelectric) it will mechanically deform according to the crystal’s orientation respectively to the applied voltage, so it is very important the way the crystal quartz is cut. The most common crystal cut is AT-cut, which is oriented at $35^\circ 10'$ from the normal direction cf: figure 1.1.2b. The AT-cut QCM is optimized for frequency stability and low temperature coefficient at room temperature and it also allows a perfectly transverse shear [2]. When an alternating voltage is applied the quartz oscillates at its fundamental frequency in a transverse shear mode with a very high quality factor (Q), of around $10^5$. The quality factor or "Q-factor" is the ratio of frequency and bandwidth. In the following section it will be better defined, as well as its importance for this project.

![Figure 1.1.2: (a): QCM oscillates in transverse shear (b): AT-cut of a quartz crystal [3]](image)

When the QCM shear standing waves are created, if the thickness is an odd integer of the half wavelength of the induced wave, the fundamental frequency $f_0$ is given by:

$$f_0 = \frac{v_q}{\lambda} = \frac{v_q}{2t} \quad (1.1.1)$$

where $v_q$ is the speed of wave propagation in quartz, $\lambda$ is the wavelength, and $t$ is the thickness of the quartz. [4]
In 1880s, the Curie brothers discovered the piezoelectric effect in quartz crystals via a pressure effect. This is the signal transduction mechanism of the QCM technique [5]. After that, Lord Rayleigh showed a change in the inertia of a vibrating crystal which altered its resonant frequency $f_0$ [6]. Sauerbrey determined in 1959 a quantitative analysis that related the change in quartz oscillation frequency to the mass deposited on the QCM electrodes. The "microbalance", alias for the QCM, has its origins in this model. Sauerbrey found a relation between the mass and the frequency shift:

$$\Delta f = -2 \frac{(m_f/A)}{\rho q v q} f_0^2$$  \hspace{1cm} (1.1.2)

This equation represents the change in the frequency due to the absorbed mass per unit area on one side of the crystal, where $\rho_q (2.651 \text{ g/cm}^2)$ is the mass density of quartz, $A$ is the electrode area and $m_f$ is the mass of the film. This equation is valid as long as the attached film is non-dissipative (no slip) and the film is sufficiently thin ($m_f \ll m_q$) [7].

Then, in the 1980’s, a new theoretic field emerged, involving friction studies at atomic length and time scales [8]. This new field is called nanotribology and in 1986 the researchers Krim and Widom developed a model to quantify the friction between the QCM electrode and the sliding "decoupled" particles. They modeled the QCM as a driven mass-spring system with damping [9].

An unloaded QCM oscillating near to or at resonance frequency can be modeled as a Butterworth-Van Dyke (BVD) equivalent electrical circuit cf. figure 1.1.4. The BVD circuit is an approximation of the more rigorous Mason equivalent circuit [4]. The term $C_0$ is the "shunt" capacitance. It is a combination of the parasitic capacitance that arises from external sources, such as mounting, and the static capacitance between electrodes on both sides of the quartz. The right side of figure 1.1.4 (a) refers to the "acoustic" or "motion" branch.
and is composed of three parameters: inductance, capacitance and resistance ($L_1$, $C_1$, and $R_1$ respectively). These terms arise from electric coupling due to the shear mechanical displacement resulting from oscillation.

![Electrical equivalent circuit model for QCM (unloaded and loaded) by Butterworth-Van Dyke](image)

Figure 1.1.4: Electrical equivalent circuit modeled for QCM (unloaded and loaded) by Butterworth-Van Dyke

When a QCM is loaded by external means (film deposition, liquid loading, microspheres, etc.), the system experiences an additional impedance to its motion. This component is shown in Figure 1.1.4 (b) as an inductance ($L_2$) and a resistance ($R_2$).

The admittance (ratio between current flow and applied voltage) for an unloaded QCM is related to the frequency by the following equation:

$$Y(f) = i\omega C_0 + \frac{1}{Z_a}$$ \hspace{1cm} (1.1.3)

where $Z_a$ is the "acoustic" impedance:

$$Z_a = R_1 + i\omega L_1 + \frac{1}{i\omega C_1}$$ \hspace{1cm} (1.1.4)

When the QCM is loaded (cf: figure 1.1.4), the equation (1.1.4) becomes:

$$Z_a = R_1 + i\omega L_1 + \frac{1}{i\omega C_1} + Z_e$$ \hspace{1cm} (1.1.5)

where $Z_e$ is the electrical load impedance and is written as

$$Z_e = R_2 + i\omega L_2$$ \hspace{1cm} (1.1.6)
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The electrical load impedance is directly proportional to the load impedance $Z_L$ that results from the contact between the load material and the QCM surface. The load impedance $Z_L$ is defined by the ratio of the shear stress of the loading material and the shear velocity of the load at the QCM boundary.

$$Z_L = \frac{\sigma_{xy}}{v_x} \mid_{y=0} \quad (1.1.7)$$

where $\sigma_{xy}$ is the shear stress in the load material from the oscillation of the QCM and $v_x$ is the shear velocity of the load particles.

When $| Z_L | < | Z_q |$, the electrical load’s impedance can be calculated as:

$$Z_e = \frac{N \pi}{4K^2 \omega_0 C_0} \left( \frac{Z_L}{Z_q} \right) \quad (1.1.8)$$

where $N$ is the overtone order (1, 3, 5, ...), $\omega_0 = 2\pi f_0$ is the resonant frequency of the QCM, $K^2$ is the AT-cut quartz electromechanical coupling factor ($7,74 \cdot 10^{-3}$) and $Z_q$ is the shear wave’s impedance of quartz. The latter can be written as $Z_q = \sqrt{\mu_q \rho_q}$, where $\mu_q$ is the shear modulus of quartz ($2,947 \cdot 10^{11} \text{g/cm}^2 \text{s}^2$) and $\rho_q$ is the quartz density ($2,651 \text{g/cm}^3$).

It is important to note that $Z_L$ is a complex quantity. Its real component $\text{Re}(Z_L)$ represents the mechanical power dissipation and corresponds to the stress component in phase with the particle velocity. The imaginary component, $\text{Im}(Z_L)$, is the stress component which is $90^0$ out of phase from the particle velocity. It corresponds to the mechanical energy stored in the surface. The load components are:

$$R_2 = \frac{N \pi}{4K^2 \omega_0 C_0} \frac{\text{Re}(Z_L)}{Z_q} \quad (1.1.9)$$

$$L_2 = \frac{N \pi}{4K^2 \omega_0^2 C_0} \frac{\text{Im}(Z_L)}{Z_q} \quad (1.1.10)$$

Changes in $L_2$ lead to changes in $f$. The change in frequency $\Delta f$ can be approximated as:

$$\Delta f = \frac{-L_2 f_0}{2L_1} \quad (1.1.11)$$

Considering the expressions for the unloaded acoustic components $L_1, C_1, R_1$:
CHAPTER 1. INTRODUCTION

\[ L_1 = \frac{(N\pi)^2}{8K^2\omega_0^2 C_0} \]  

(1.1.12)

\[ C_1 = \frac{8K^2C_0}{(N\pi)^2} \]  

(1.1.13)

\[ R_1 = \frac{(N\pi)^2 \eta_q}{8K^2C_0 \mu_q} \]  

(1.1.14)

where \( \eta_q \) is the viscosity of quartz. \( C_0 \), in this case, is purely the capacitance between the electrodes. It can be calculated as \( C_0 = \varepsilon_q A_0 \), where \( \varepsilon_q \) is the permittivity of quartz, \( A_0 \) is the electrode active region and \( h_q \) is the thickness of quartz. This way the frequency shift can be obtained for one side of the QCM in terms of the load impedance \( Z_L \):

\[ \Delta f = -\frac{f_0}{N\pi} \frac{\text{Im}(Z_L)}{Z_q} \]  

(1.1.15)

In the 1990’s there was an explosive growth in the application of the QCM technique to study a wide range of molecular systems at the solution-surface interface, mainly in bio-polymer and biochemical systems. One of the recent QCM applications is the creation of protein and nucleic acid biosensors, where QCM is suited to the study of layer-by-layer film deposition. This technique is based on the alternation of polymer layers containing proteins and polymer layers containing DNA (nano-architecture). One of the future technical applications of QCM is centered in areas such as drug discovery [10].

1.2 IMPORTANCE OF MICRO- AND NANO-FRICTION

Friction has always been a present phenomenon since the beginning of material existence. Leonardo da Vinci, 500 years ago, deduced the laws that govern the sliding of a rectangular block over a planar surface. In 1699, Guillaume Amontons made the first known publication of classic friction laws. He observed that (1) the friction force is proportional to the normal load, where the coefficient of friction is the ratio between the frictional force and the load, and (2) the friction force is independent of the apparent area of contact. Then, in the 18th century, Charles-Augustin de Coulomb showed that the friction force is independent of velocity for ordinary sliding speeds, although the coefficient of friction depends on whether
the force is applied to an object at rest ($\mu_S$) or already moving ($\mu_d$). Tabor Bowden and coworkers studied molecular adhesion and found that friction is independent of apparent macroscopic contact area. In fact, it is proportional to the real contact area. In the 1970’s, Tabor and Jacob Israelachvili developed the Surface Forces Apparatus (SFA) for atomic-scale friction measurements, which definitively exhibited friction in total absence of wear. Tabor, in 1991, concluded that friction in the absence of wear is due to strains building up in the sliding contact region. These strains are released in the form of atomic vibrations, such as phonons, as it was suggested by Tomlinson in 1929 [11].

Some studies conclude that improved attention to friction and wear would save developed countries up to 1.6% of their gross national product. For example, it would mean over $100 billion annual savings only in the US [12].

What is surprising is how little is known, even now, about the fundamental origins of friction and wear. Friction and wear are surface and inter-facial phenomena which occur at several buried contacts, which are not only extremely difficult to characterize, but also continuously evolving as the microscopic irregularities of the sliding surfaces touch and push into one another.

As previously mentioned, in the late 1980’s there was a new interest in some areas of tribology. Experimental devices, such as QCM, Surface Forces Apparatus (SFA) and Lateral Force Microscope (LFM) could now record friction in geometries involving a single contacting interface. Tribology issues of particular importance include [11]:

- Understanding the tribochemical reactions which occur in a sliding contact and the energy dissipation mechanisms associated to it.
- Characterization of the micro-structural and mechanical properties of the contact regions between the sliding materials.
- Combining the information from the atomic scale to that observed at the macroscopic scale.
- Development of realistic material interaction models for computer simulations of special interest to tribological applications.
- Development of realistic laboratory test set-ups.

The micro-electro-mechanical systems (MEMS) have recently become an important area of technology. MEMS combine mechanical and electrical functions at very small scales. These
systems represent a rapidly developing area of technology with a great economic potential. MEMS also offer considerable opportunities to broaden the field of materials science to a larger scale. Micro-fabricated elements enable the fabrication of atomic force microscopes and scanning tunneling microscopes. These advances have revolutionized surface science and tribology.

Some MEMS devices may be subjected to a very high number of fatigue cycles during their service lifetime due to their high operating frequencies. It is also worth noting that many commercial accelerometers and pressure sensors have experienced extremely high numbers (>10^8) of cycles, apparently without suffering from fatigue failures. The high surface area to volume ratio of MEMS devices implies that tribological effects are likely to be important factors in determining their performance. Therefore, the miniaturization of MEMS makes it necessary to study lubrication properties and frictional behavior at the nano-scale.

Experiments with surface micro-machined accelerometers and micro-motors suggest that surface adhesion due to charge build-up or moisture adsorption is a critical issue that results in stiction and hysteresis. The use of a wet etch as the release step for surface micro-machined devices can be difficulted by the introduction of capillary forces between elements that prevent their separation. Results from some devices running at high rotational speeds on unlubricated sliding contacts have indicated that wear processes are very important in both allowing the bearing surfaces to be worn in with a low friction operation and subsequently contributing to failure.

Attempts are being made to modify micro-machined surfaces and to apply low friction coatings in order to promote better tribological characteristics. Currently, there is a great need to improve the understanding in this area if reliable and durable devices are to be
created [13].

An important consideration to keep in mind is the size of micro-objects. This is due to the fact that intermolecular (Van der Waals) and capillary forces become increasingly important as one approaches small length scales cf: figure 1.2.2.

![Figure 1.2.2: Forces at different scales](image)

The concept of transporting micro- and nano-objects has been of interest to the scientific community since the beginning of nano-technology. It is necessary to understand the friction effect during the transport and manipulation of nano- and micro-devices. Mastering this control can lead to many advances that span from drug delivery in nano-biotechnology, micro-particle sorting and grouping by mass to particle monitoring for toxicological studies, as well as many other favorable applications from multiple disciplines [4].
Chapter 2

QCM FOR TRIBOLOGY

2.1 INTRODUCTION

The QCM had been primarily employed for micro-weighting and time standard purposes. It was first used for friction measurements in 1986-88 by Widom and Krim. They modeled the QCM as a driven mass-spring system with damping. QCM has atomic length scales, short time scales (slip times of the order of nano-seconds) and low shear stress (from $10^3$ to $10^7 \text{ N/mm}^2$). Atomic thin films adsorbed on the QCM electrodes produce shifts in both the frequency and the quality factor Q. These two parameters are an indicative of the degree to which the films are able to track the oscillatory motion of the underlying substrate. In this case, friction is well characterized by the "viscous friction law"[8, 14]:

$$F_f = \frac{\rho \nu A_c}{\tau}$$

(2.1.1)

where $\tau$ is the slip time, $\nu$ is the average sliding velocity of the absorbed film, $\rho$ is the mass per unit area of the adsorbate and $A_c$ is the contact area. It defines the friction coefficient as:

$$\mu_f = \frac{\rho}{\tau}$$

(2.1.2)

Slip times measured by QCM are closely linked to energy transfer at an interface and vibrational properties of adsorbed molecules. The characteristic slip times are determined via the relation:
\[ \Delta \frac{1}{Q} = 4\pi \tau \Delta f \]  \hspace{1cm} (2.1.3)

The QCM slip time is frequently written in terms of phonon \((\tau_{ph})\) and electron-hole \((\tau_{eh})\) contributions according to \(\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{eh}}\).

When the thin films are adsorbed on the electrodes, the extra mass these provide lowers the resonance frequency of the microbalance. Also, the resonance is broadened by friction energy dissipation due to relative motion of the adsorbed layer and the microbalance. By measuring the shift in frequency and the broadening of the resonance (evidenced by a decrease in the micro-balance’s vibration amplitude), the sliding friction of the layer with respect to the metal substrate can be deduced. The friction can only be measured if it is sufficiently low, so as to result in significant sliding. For this reason, QCM measurements of sliding friction tend to be carried out on systems exhibiting very low friction, such as rare-gas adsorbed on noble metals. For other systems which exhibit higher friction (chemically bonded layers), the slippage of adsorbed monolayers on the surface of the QCM is too small to obtain a measurable broadening [11].

This technique was innovated by using impedance calculations (Krim and Widom). It was shown that if the shear stress between the substrate and the film is below \(10^3 \, N/mm^2\), the layer will sufficiently slip to be detectable by the QCM through frequency. The dissipation due to the relative motion of the adsorbed layer and the microbalance is related to the quality factor \(Q\) in the following way:

\[ Q = \frac{2\pi \text{Total energy in one cycle}}{\text{Energy lost in one cycle}} \]  \hspace{1cm} (2.1.4)

It is of importance to notice that QCM’s frequency and Q-value are severely affected by temperature, ambient gas pressure (importance to use a vacuum system) and stresses generated by the deposited film [15].

Any mass that is bounded to the surface will tend to oscillate with the same lateral displacement and frequency as the underlying crystal. If it does so elastically, there is no energy loss in the process. If on the other hand there is energy loss, the process is referred to as inelastic. [10]

A limitation for many nano-tribological devices is their contact speed. For an Atomic Force Microscope (AFM) or a Surface Forces Apparatus (SFA) nanometer resolution is achieved. However, top lateral speed mounts up only to \(10 \, \mu m/s\). Oppositely, the QCM’s surface can...
easily reach speeds of tens of cm/s or even few m/s with higher frequency oscillators. The STM-QCM situation was the first QCM-probe technique used to study friction. Since then, a number of probes have been used using the QCM. Krim et al., in 1998, used various gases (N2, He and H2O) adsorbed on liquid He and cooled Pb electrodes to observe the change in slip-time at the superconductive transition. All of this make the QCM a unique tool to enhance in nano-tribology [1].

The sample in contact with the QCM can be described by an equivalent mechanical model containing elements like a mass, a spring or a dashpot [16].

When loading with a mass, a small sphere rigidly attached to the crystal is considered. If the spheres are small enough, they can be treated like a Sauerbrey film. The frequency shift of the composite resonator is:

\[ \Delta f = -f_0 \frac{m_f}{m_q} \]  

(2.1.5)

where \( m_f \) is the areal mass density of the spheres and \( m_q \) the areal mass density of the crystal.

Loading a mass in series with a spring, it might occur that the object takes part in the oscillation to some extent. A typical object of this kind would be a small (<10 \( \mu \text{m} \)) sphere. In this case the frequency shift becomes:

\[ \Delta f = -f_f \frac{N_S \omega m_S}{A \pi Z_q} \frac{1}{1 - \frac{\omega^2}{\omega_S^2}} \]  

(2.1.6)

where \( Z_q \) is the load impedance of the quartz. In the limits of \( \omega_S^2 \gg \omega \) and \( \omega_S^2 \ll \omega \) the equation (2.1.6) reproduces the Sauerbrey equation.

The model used to interpret nano-tribological experiments with the QCM, consists in loading a mass in series with a dashpot. The drag coefficient of the dashpot (\( \xi_S \)) is considered a parameter independent of frequency. Within this model, the sphere slides in a liquid-like way. The drag force in creep depends linearly on sliding speed. The slip time can be written as:

\[ \tau_S = \frac{m_S}{\xi_S} \]  

(2.1.7)

Also, the frequency shift:
\[
\Delta \tilde{f} = -f_f \frac{N_S}{A \pi Z_q} \omega m_s \frac{1 - i \omega \tau_S}{1 + \omega^2 \tau_S^2}
\]  \hspace{1cm} (2.1.8)

The tilde denotes a complex frequency shift (\(\Delta \tilde{f}\)), where \(\Delta \tilde{f} = \Delta f + i \Delta \Gamma\). The imaginary part \(\Delta \Gamma\) is the shift of the half bandwidth at half maximum. The slip time is inferred from the ratio between \(\Delta \Gamma\) and \(\Delta f\), being written as equation (2.1.7):

\[
\tau_S = \frac{1}{\omega} \left(\frac{\Delta \Gamma}{\Delta f}\right)
\]  \hspace{1cm} (2.1.9)

Finally, the QCM can be loaded with a spring and a dashpot. The extension of the previous models to a sphere coupled to the plate via a spring and a dashpot is unambiguous. The coupling can be achieved either via a Voigt circuit (cf: figure 2.1.1a) or a Maxwell circuit (cf: figure 2.1.1b).

Voigt-type (viscoelastic solids) coupling is used for multi-asperity contacts. The load-bearing asperities correspond to springs but there is also interfacial drag (for example, across capillary bridges) acting in parallel to the elastic contacts. This model predicts a positive frequency shift.

For Maxwell-type (viscoelastic liquids) coupling, the situation is more complicated. The shift of frequency is also positive. A relaxation time (\(\tau_R\)) is introduced and the n-scaling depends on this value. In the limit \((\omega \tau_R \gg 1)\), \(n^{-1}\) scaling is found. In this case, the relaxation time is much longer than the period of oscillation and the Maxwell element behaves elastically. If the relaxation time is short \((\omega \tau_R \ll 1)\), the frequency shift is still positive but scales linearly with \(n\).
2.2 DIFFERENT MODELS TO ANALYZE THE QCM RESPONSE

Lynch, in 2011, in order to study micro-objects that slide on a QCM surface, compiled elaborated models describing the layer’s interface behavior for different cases. As previously mentioned in the chapter 1, the relationship between mass and the frequency shift is given by Sauerbrey’s relation:

\[
\Delta f = \frac{-2}{\rho_q v_q} \left( \frac{m_f}{A} \right) f_0^2
\]  

(2.2.1)

It is interesting to recall that this model relates the change in QCM’s adsorbed mass to a change in the thickness of the quartz. This equation is valid when dealing with thin rigidly attached monolayer depositions. However, when slip occurs on the surface, equation 2.2.1 is no longer valid in means of measuring mass, due to the additional effects of the particles slipping on the surface of the QCM. In this section different models considering slip between the surface and the micro-particles will be described.

2.2.1 KRIM AND WIDOM [9]

Krim and Widom, in the 1986, developed a method to quantify the friction between the QCM electrode and the sliding (not attached) particles.

They modeled the QCM as a driven mass-spring system with damping. In this system the mechanical impedance is:

\[
Z_m = \frac{F}{v} = R_m - iX_m = R_m - i \left( \omega M_m - \frac{1}{\omega C_m} \right)
\]  

(2.2.2)
where $R_m$, $M_m$, $C_m$ and $\omega$ are the mechanical resistance, mass, compliance ($1/(\text{spring constant } k)$) and frequency respectively. $X_m$ is the mechanical reactance of the system and is proportional to its inertial components and $R_m$ is proportional to the energy dissipation (lost by friction) of the system. In Sauerbrey’s model, the resistive term of the equation 2.2.2 would be zero. Instead, for systems where sliding takes place and the films begin to decouple, the resistive term is greater than zero. To find the dissipation excess per mass unit for a short relaxation time $\omega \tau_R \ll 1$ and for a 2D adsorbed gas film, the equation below can be used:

$$\omega \tau = \frac{R_2^*}{X_2^*}$$  \hspace{1cm} (2.2.3)

where $\tau$ is the characteristic slip time: The time it takes for an adsorbed film to be static once slipping has begun. The following results for the components of the added 2D adsorbed film on one side of the QCM were found:

$$R_2^* = \frac{\rho_2 \omega^2 \tau}{1 + (\omega \tau)^2}$$  \hspace{1cm} (2.2.4)

with $\rho_2$ the mass per unit area of the 2D adsorbed layer ($g/cm^2$)

$$X_2^* = \frac{\rho_2 \omega}{1 + (\omega \tau)^2}$$  \hspace{1cm} (2.2.5)

Stockbridge [17] described the following equations:

$$\Delta \left( \frac{1}{Q} \right) = \frac{2R^*}{\omega \rho_q t_q}$$  \hspace{1cm} (2.2.6)

$$\Delta \omega = \frac{X^*}{\rho_q t_q}$$  \hspace{1cm} (2.2.7)

where $Q$ is the quality factor or change in dissipation of the system and $t_q$ is the thickness of quartz. Using these equations, Krim and Widom found the most important relation in their work, an expression of slip time in terms of changes in frequency and the Q-factor.

$$\Delta \left( \frac{1}{Q} \right) = 4\pi \tau \Delta f$$  \hspace{1cm} (2.2.8)
and,

$$\Delta f = \frac{\Delta f_{\text{film}}}{1 + (\omega \tau)} \quad (2.2.9)$$

In this expression, $\Delta f_{\text{film}}$ is the frequency shift with mass loading (without slip) and is found by Sauerbrey’s relation.

In addition, in 1993 together with Sokoloff, the authors found that plotting $\ln(\tau)$ vs. $\ln(X)$ the friction law (Coulomb, Viscous Friction, Mindlin) can be determined from the slope of the line created. $X$ is the amplitude of particle slippage.

### 2.2.2 DYBWAD [18]

Dybwad carried out an experiment where he put a single gold micro-sphere in the center of a QCM. He observed a positive frequency shift, which is contradictory to Sauerbrey’s equation. He also modeled the QCM as a mechanical system and explained his result by modeling the single micro-sphere in the QCM as a coupled mechanic oscillator.

![Dybwad model](image)

Figure 2.2.2: Dybwad model

To justify the positive shift, he proved this with a single particle lightly coupled to the QCM’s surface. In the figure 2.2.2 M is the mass associated with the QCM, m is the mass of the micro-sphere deposited on one side of the QCM, k is the spring constant of the sphere, which is also referred to as the attachment parameter (that describes the bond strength between the sphere and the QCM’s surface) and K is the spring constant associated with the QCM.

Dybwad arrived to an expression for the frequency $\omega$ as a function of the attachment parameter $k$: 

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$
\[ 2\omega^2 = \left( \frac{K}{M} + \frac{k}{M} + \frac{k}{m} \right) \pm \sqrt{\left( \frac{K}{M} + \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{K}{M} \frac{k}{m}} \quad (2.2.10) \]

If this equation is plotted, the idealized behavior of the coupled system is obtained. This is shown in figure 2.2.3 where there are two regimes: the strong and the weak. In the strong region (large \( k \) values) frequency becomes negative, according to the equation equation (2.2.1). In the weak coupling (when the sphere is loosely attached and there are low \( k \) values) the plot shows positive shifts in frequency. This is a result of the bond not being strong enough for the micro-sphere to track the motion of the QCM’s surface, so that the resonator can not detect its mass. However, it can sense the added stiffness of the micro-sphere and electrode bond.

This model has been previously used in cases where the QCM and the micro-objects are approximated to equivalent mechanical models. Dybwad demonstrated the equivalent model of a mass attached to a spring series. The resulting expression is the equation equation (2.1.6), seen in the previous section.
2.2.3 FLANIGAN [19]

In the year 2000, Flanigan et al. obtained calibrations between the frequency changes and the corresponding contact area of a viscoelastic gel cap pressed against the crystal surface.

\[ \Delta f = -f_0 K \left( \frac{A}{A_0} \right) \frac{\left| G \right|}{\rho_g \mu_q} \left( \frac{\sin \left( \delta/2 \right)}{A_0} \right) \sqrt{\left| G \right| \rho_g \mu_q} \]  

(2.2.11)

where \( \rho_g \) is the density of the gel cap, \( \left| G \right| \) is the magnitude of the complex shear modulus of the gel, \( \delta \) is the phase angle, \( A \) is the active area (the area of the gel in direct contact with the QCM), \( A_0 \) is the area of the entire electrode and \( K \left( \frac{A}{A_0} \right) \) is the sensitivity factor. This last value is \( K \left( 1 \right) = 1 \) and \( K \left( 0 \right) \approx 2 \).

Figure 2.2.4: Flanigan model

Their overall goal was to show a QCM can be used to measure JKR mechanics contact model is an extension of the Hertz contact. Hertz assume an elastic interaction with no energy lost from the contact and JKR consider inelastic interactions in the contact. Flanigan et al. found a linear relationship between the resonant frequency of QCM and the gel/electrode contact area:

![Plot of a linear relationship between frequency shift and contact area of the viscoelastic gel cap](image)

Figure 2.2.5: Plot of a linear relationship between frequency shift and contact area of the viscoelastic gel cap [19]
2.2.4 LASCHITSCH AND JOHANNSMANN [20]

They indicate if the contact radius \( r_c \) is smaller than the wavelength of sound \( \lambda \), the wave field inside the micro-sphere may be approximated as spherical. Knowing the form of wave emitted into the sphere allows a first evaluation of the frequency shift in this case. Punctual contacts are due to the roughness between a sphere and the surface of the quartz. The figure 2.2.6 shows the punctual contact on the electrode surface.

![Figure 2.2.6: (a): Punctual contact due to the roughness (b): Laschitsch and Johannsmann model](image)

This model assumes that the true contacting asperities of the load is uniform throughout the apparent contact.

To obtain information regarding the dissipation they introduce a complex frequency shift:

\[
\Delta f^* = \Delta f + i \Delta \Gamma
\]  

(2.2.12)

where \( \Delta \Gamma \) is the shift in bandwidth and is directly proportional to energy dissipation \( D \) (as Q-value that it is related with the bandwidth). Then, for a small loads (SLA), the frequency and bandwidth shifts are:

\[
\Delta f = \frac{f_0 K}{r_e^2 \pi \omega Z_q} r_c
\]  

(2.2.13)

\[
\Delta \Gamma = \frac{f_0 K}{r_e^2 \pi Z_q \omega} r_c^2 k
\]  

(2.2.14)

where \( K \) is the elastic modulus for the sphere, \( r_e \) is the radius of the entire electrode, \( r_c \) is the radius of the contacting asperity or the "true" contact radius, \( k \) is the wave number.
and $Z_q$ is the impedance of quartz ($Z_q = \sqrt{\mu_q \rho_q}$). Also, the authors found that in the limit $\omega \gg \omega_s$ the frequency and bandwidth shift as:

$$\Delta f = \frac{f_0}{\pi Z_q \omega} \kappa$$  \hspace{1cm} (2.2.15)$$

$$\Delta \Gamma = \frac{f_0}{\pi Z_q} \gamma$$  \hspace{1cm} (2.2.16)$$

where $\kappa$ is the elastic constant between the single sphere and QCM electrode and $\gamma$ is the damping coefficient for the sphere. The latter can be written as $\gamma = \xi / m_s$, where $\xi$ is the drag coefficient and $m_s$ the mass of the loading sphere. These equations are in accordance with Dybwad model and leads to positive shift in frequency.

Finally, as a summary of the models already seen, there is a table showing the different models with a each picture and the shift in frequency (positive or negative):

<table>
<thead>
<tr>
<th>Model</th>
<th>Load geometry</th>
<th>Frequency shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sauerbrey</td>
<td><img src="image" alt="Sauerbrey Load Geometry" /></td>
<td>$\Delta f &lt; 0$</td>
</tr>
<tr>
<td>Krim and Widom</td>
<td><img src="image" alt="Krim and Widom Load Geometry" /></td>
<td>$\Delta f &lt; 0$</td>
</tr>
<tr>
<td>Dybwad</td>
<td><img src="image" alt="Dybwad Load Geometry" /></td>
<td>$\Delta f &gt; 0$</td>
</tr>
<tr>
<td>Flanigan</td>
<td><img src="image" alt="Flanigan Load Geometry" /></td>
<td>$\Delta f &lt; 0$</td>
</tr>
<tr>
<td>Laschitsch and Johannsmann</td>
<td><img src="image" alt="Laschitsch and Johannsmann Load Geometry" /></td>
<td>$\Delta f &gt; 0$</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of QCM frequency shift for different load geometries

This table outlines the effect loading a QCM with different cases of geometry. Sauerbrey, Krim and Widom, and Flanigan models have geometries that result in a negative shift
from resonance. Generally large contacts result in negative shifts in frequency whereas small contacts result in positive shifts from resonance, like Dybwad and Laschitsch and Johannsmann cases.

And last, the friction force can be found by the slip time \((\tau)\) using this follow equation:

\[
\frac{F_F}{A} = \frac{\rho \nu}{\tau}
\]  

(2.2.17)

This slip time \((\tau)\) can be obtained from the equation 2.2.8 means the frequency and Q-value shifts.
Chapter 3

DESIGN OF THE
NANOTRIBOMETER

3.1 OBJECTIVE

In order to get the displacement $\Delta f$ and $\Delta Q$ in real time, and then study the frictional behavior using the models shown in the previous section, a nanotribometer have to be design and validate. The final equipment should enable to study the friction-induced dissipation between micro-objects deposited on the resonator quartz crystal surface which is, or not, coated by various kinds of monolayers and distributions.

The most important goal is to shake the resonator to obtain slip behavior in the interface between the resonator and the micro-particles. Also important is to see and understand the shift values when it is shaking. As well, it is necessary to check what is the model that there are and see the sample movement in long periods. Each model implies a different treatment of the results, therefore It is important to differentiate them. A vacuum system is essential, as mentioned in section 2.1, the ambient air pressure is a source of energy dissipation like a viscoelastic material. From certain values of pressure, the effect of the air in the quartz is negligible. Experts working in the field of frequency control say that this value is from $10^{-2}mbar$. For this reason is required use a vacuum structure that provides less pressure than $10^{-2}mbar$.

All of this work has been made in a period of six month and a budget of 25.000 euros. This required do the purchases in different companies quickly and safely. So it was contacted
with various experts in each sector and they helped in making a good choice of material to buy.

### 3.2 COMPONENTS

Many components are necessary. One of the most important is the Network Analyzer (NA) that will be used to analyze, with very good accuracy, and to make the vibration. Quartz crystals (AT-cut) and micro-particles (polystyrene microspheres) are also essential. Then, a system of micro-imaging will be used to observe the samples. The latter consists of a high-resolution camera with variable magnification. To make the vacuum and achieve the required $10^{-2} \text{mbar}$, has bought a pump (capable of reaching up to $4 \cdot 10^{-4} \text{mbar}$) together with different valves and a pressure gauge. Finally, it was designed and built (in the manufacturing department of FEMTO-ST) a structure to assemble the above items. The supports created for the crystals allow to vary the position of these in various axes in order to be able to focus properly the sample and also make the transfer experiment. The following points explain the characteristics of each of the components and their usefulness.

#### 3.2.1 NETWORK ANALYZER

A network analyzer (NA) is an instrument that measures the network parameters of electrical networks. Today, the more common measure of network analyzers is the s-parameter because reflection and transmission of electrical networks are easy to measure at high frequencies. There are two basic types of NA: scalar network analyzer (SNA), that measures amplitude properties only, and vector network analyzer (VNA), that measures both amplitude and phase properties. Three prominent VNA manufacturers are Agilent, Anritsu, and Rohde & Schwarz.

R&S®ZNC Vector Network Analyzer was chosen to excite vibrations to resonator and induce the slip on the monolayers. It is enabled to get the resonant frequency of the crystal and analyze the response of $\Delta f$ and $\Delta Q$. 
CHAPTER 3. DESIGN OF THE NANOTRIBOMETER

The analyzer features excellent temperature (0.01 dB/°C) and long-term stability, which ensures reliable measurements over several days without having to recalibrate the unit. It operates in a range from 9 kHz to 3 GHz by the frequency and from -50 dBm to +13 dBm by the power, that provides to work with crystals with different frequency of resonant (other thicknesses). The analyzer’s maximum IF bandwidth of 300 kHz, together with its fast synthesizers, yields a sweep time as short as 11 ms for 401 points. Also, the R&S®ZNC VNA can do a swept-harmonic measurement and with this one can study the different levels that exist in the interfacial surfaces (molecules bonding, etc.). This Network Analyzer with a large, high-resolution 12.1" screen and a touchscreen user interface It costs 13,536,00 euros.

3.2.2 VACUUM SYSTEM

All of these components were purchased from Kurt J. Lesker® Company:

It is necessary a pump that should achieve more of $10^{-2} \text{mbar}$ in vacuum. The RZ6 is part of the VACUUBRAND® XS series of rotary vane vacuum pumps. the ultimate vacuum reaches up to $4 \cdot 10^{-4} \text{mbar}$ and it have a max flow of $5.7 \text{m}^3/\text{h}$ (50 Hz). This pump cost 1,130 euros.

Figure 3.2.2: RZ6 VACUUBRAND® XD pump
A bellows sealed angle valve (stainless steel) and a air valve (aluminium) were purchased. The first can work up to $10^{-9}\text{ mbar}$ with a leak flow of $2\cdot10^{-9}\text{cm}^3/\text{s}$ and the second one have $10^{-7}\text{cm}^3/\text{s}$ of leak. Vacuum gauge with integrated controller and display also was bought. This one have a range from $1.33\cdot10^{-4}$ to $1333\text{mbar}$. Finally it was necessary a flanged KODIAL glass view-port (to see the sample), two reducer nipples, centering rings and the cast clamps of aluminium. All these cost 724,57 euros (shipping costs included).

In order to check if this equipment is able to achieve the required levels, proceeds in two essays. The first is to see if the pressure reaches the limit pressure value and the second to know the time (if the pump is stopped and the angle valve is turned) which one can to take measures before to achieve this value.
When the pump starts cf: figure 3.2.4a it have to wait 3 minutes and 35 seconds to achieve in the system $10^{-2} \text{mbar}$. After 14 minutes, it was possible to reach up to $4.9 \times 10^{-3} \text{mbar}$. Then the pump was stopped and the valve was turned cf: figure 3.2.4b. Leaks make the system back to atmospheric pressure, therefore, is observed that one has 32 seconds before reaching the limit to take measures.

Figure 3.2.4: (a): Vacuum test Pump ON (b): Vacuum test Pump OFF
3.2.3 AT-CUT QUARTZ CRYSTAL

Pure quartz crystals were purchased from The Roditi International Corporation Ltd. The characteristics of these blank crystals are the resonance frequency range from 5025 to 5035 kHz, a diameter of 13.97 mm and a crystal AT-cut (35°15’ from the normal direction). 50 quartz crystals (with shipping included) cost 147.12 euros.

These blank crystals of quartz have been added two gold electrodes, one on each side. To do this, it was necessary to make a first coating of chromium (20 nm) to ensure adhesion of gold in the quartz. Then it proceeded to the coating of 200 nm of gold. The metal coating process is carried out using a sputtering machine (Pulvé Plassys MP500) in the Cleaning Room of Centrale de Technologie MIMENTO. This machine consists of two electrodes and creates a plasma by metal scouring, which is later deposited on the wafers. The process flow followed is described below:

1. **Vacuum setting** to get $1,2 \times 10^{-5} \text{mbar}$ and remove all the oxygen.

2. **Cleaning with argon** at a pressure of $10^{-3} \text{mbar}$.

3. **Creation of plasma** by a voltage of 200V during 2 minutes to clean and activate the crystal surfaces.

4. **Scouring of the chromium target** during 3 minutes.

5. **Rotation of the substrate holder** during 1 minute (two revolutions) at $7 \times 10^{-3} \text{mbar}$ and 1 A.

6. **Scouring of the gold target** during 2 minutes.

7. **Rotation of the substrate holder** during 8 minute (16 revolutions) at $7 \times 10^{-3} \text{mbar}$ and 0.3 A.

8. **Setting of the normal pressure** and turn over the crystals.

9. **Repeat** all the points previously exposed for the opposite faces.
The provided crystals present a great roughness of about 1 µm of the arithmetic average of the roughness (Ra). Nevertheless, it is possible to change by means of a polishing. Latter is important since it allows to obtain different levels of roughness and to be able to do studies with each of them. In the ANNEX you can find different photos of the crystal surface where one can see this surface irregularities.

Figure 3.2.6: Crystal roughness
3.2.4 MICRO-OBJECTS

In this project micro-spheres of polystyrene have been chosen to study the micro friction, which are of growing interest due to their medical and textile applications. The low weight of the micro-spheres avoids the effect of gravity and also study the friction behavior of the order of $\mu N$. One of the problems presented by the polystyrene micro-beads is the electrostatic force. To solve this, they can be functionalizable so it creates a protective layer of molecules around the micro-sphere. The crystal surface can also be functionalizable and so allow study the effect of hydrophobic coating on the adhesion and friction of patterned surfaces.

![Micro-spheres of polystyrene](image)

Polystyrene micro-sphere, with different sizes (1µm, 10µm, 45µm and 90µm), was purchased from to Polysciences Europe GmbH with a price of 420 euros. The reason why different sizes were chosen was to have several areas of contact. For example with a small diameter one can obtain a punctual contact area, while the larger diameter can obtain a greater contact area. Even one can get to study the behavior with a mixture of sizes of micro-spheres.

3.2.5 MICRO-IMAGING

In order to see the micro-spheres it is necessary have a micro-imaging equipment. The shape of the distribution and density of the micro-particles have an important influence of the resonator response. Each distribution have a theoretical model that provides a method to know better the frictional behavior. A camera and a magnification are essential, not only to choose the model, also to take images and observe the evolution in time of the sample, or micro-particle.
CHAPTER 3. DESIGN OF THE NANOTRIBOMETER

3.2.5.1 CAMERA

The camera that it is needed for this application should have a good resolution to see clearly the micro-particles. It has seen in the bibliography that the samples don’t change a lot of in a short periods of time. Therefore we don’t need a fast camera. The characteristics of the bought camera (AVT GUPPY PRO F-125B) are the following ones:

- Monochrome Camera
- Resolution: 1292 (H) x 964 (V) pxs
- Frequency: 30 images/s
- C-mount
- Fire Wire 1394b

![Figure 3.2.8: AVT GUPPY PRO F-125B](image)

A PCI card, with a compatible 1394b port, and a cable (IEEE-1394b) are required to read the camera signal, therefore these also were bought. These components were bought at a price of 635,56 euros in STEMMER® IMAGING.

3.2.5.2 MAGNIFICATION

To increase the depth of view and study in detail the samples magnification lenses were purchased also in STEMMER® IMAGING. First it is necessary a C-mount module to add the camera at the magnification. Then a camera tube to modify magnification to the camera optimizing chip coverage and performance. After camera tube is added a manual zoom and a lower lens module to modify the field of view and working distance.
CHAPTER 3. DESIGN OF THE NANOTRIBOMETER

<table>
<thead>
<tr>
<th>PART</th>
<th>ARTICLE</th>
<th>PRICE (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-mount</td>
<td>QIOPTIQ C/CS MOUNT</td>
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</tr>
<tr>
<td>Camera tube</td>
<td>CVO QIOPTIQ 0.8X 120FL CAMERA TUBE</td>
<td>254.04</td>
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<tr>
<td>Zoom</td>
<td>QIOPTIQ 12.5:1 ZOOM MANUAL DETENTS</td>
<td>1777.41</td>
</tr>
<tr>
<td>Lower lens</td>
<td>QIOPTIQ LOWER LENS 2.0X 100FL</td>
<td>193.14</td>
</tr>
</tbody>
</table>

Table 3.1: Magnification components

All of these plus the shipping costs amount to a total of 2304.48 euros. Finally with the elements chosen it is possible to obtain a working distance of 95 mm and a field of view of 11 x 8 mm (minimum) to 0.87 x 0.65 mm (maximum).

![Figure 3.2.9: Magnification system](image)

3.2.6 STRUCTURE

To hold the quartz crystals and to make the vacuum it is necessary to have a structure that allows the assembly of all the components outlined above. It has been expected that within the vacuum chamber there’s the quartz crystal and therefore it should to get the electrical signal. For this purpose, six holes were made for future connections and acquired SMA connectors (hermetically sealed bulkheads SMA female to SMA female adapter) to get the signal. Obviously it is also indispensable to think about an exit in the base for the sucked air and obtain the vacuum. Noteworthy that it is used two quartz crystals, one will
be to study the frictional behavior and another as auxiliary to make the transfer experiment. The transfer experiment consists in make fall the micro-spheres from one vertical crystal (auxiliary) to another horizontal (principal), in such a way one can study the effect of load addition in real-time. This is the only way to make a deposition when we’re working in a vacuum. Figure 3.2.10 shows from images how the transfer experiment works.

![Figure 3.2.10: Transfer experiment](image)

To hold the horizontal quartz is used a "cold weld HC-40 header" and a standard holder for the vertical one. Also is designed and created the two electrical circuits in a layer of 2 mm epoxy. In order to fix these holders, two supports (one for the auxiliary and another for the principal) were designed in AU4G (duraluminium). These last allow to modify the position of the crystals, vertically for the principal to improve the focus of the camera and the auxiliary horizontally to position it over the other and make the transfer experiment. The supports were made into the manufacturing department of FEMTO-ST.
CHAPTER 3. DESIGN OF THE NANOTRIBOMETER

Figure 3.2.11: Enclosure and supports for the quartz crystals

To create the enclosure is used a glass cylinder in order to observe the interior during the study and let the light come into allowing to see the samples with the camera. As mentioned in the previous section a view-port is installed on top to put the magnification and the camera.

It has also been necessary to buy different accessories for make the experiments and to attach all elements. These are: a micro-pipette (20 ml), a pipette support, 500 standard tips for micro-pipettes, one bottle of 1-octadecanethiol (96%) to make future functionalizations, a stand tripod (185 mm), a stand rod, five universal c-clamps and five pliers jaws. All these last ones were purchased in VWR International with a price of 304,58 euros.

Figure 3.2.12: Nanotribometer
To conclude this section, is shown below a summary table with the products purchased and their corresponding prices.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>PRICE (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R&amp;S®/ZNC Vector Network Analyzer</td>
<td>13,536.00</td>
</tr>
<tr>
<td>Vacuum systems</td>
<td>1854.57</td>
</tr>
<tr>
<td>AT-cut Quartz Crystals</td>
<td>147.12</td>
</tr>
<tr>
<td>Micro-Spheres of polystyrene</td>
<td>420.00</td>
</tr>
<tr>
<td>AVT Guppy PRO F-125B Camera</td>
<td>635.56</td>
</tr>
<tr>
<td>Magnification</td>
<td>2304.48</td>
</tr>
<tr>
<td>Structure (VWR International)</td>
<td>304.58</td>
</tr>
</tbody>
</table>

Table 3.2: Prices of the components

The total amount is 19,202.31 euros. Therefore, the sum of the costs is lower than the budget of 25,000 euros.
Chapter 4

EXPERIMENT SET-UP

In this section will be explained how one have to make a set-up and achieve good results. First of all is explained how to proceed to make samples dispositions in liquid medium. Then if one needs vacuum, it will be explained some details to be considered. Finally, how to obtain the frequency response using the Network Analyzer.

4.1 DISPOSITION OF THE SAMPLES

Samples can be delivered directly to the QCR electrode surface via micro-pipette (liquid medium). Depending on the amount of liquid of sample will be obtained a higher or lower proportion of micro-spheres. Also it depends on the size of the microspheres, for example in the bottle of 1 \( \mu \text{m} \) spheres there is a concentration of \( 4,55\cdot10^{10} \text{ particles/ml} \) against \( 6,24\cdot10^{4} \text{ particles/ml} \) if is the bottle of the \( 90 \mu \text{m} \).

To make the disposition on the auxiliary quartz is necessary to have it horizontally. Since then, one can rotate the vertical circuit and start the transfer experiment. Remember that this serves to make the study of addition of particles in real time and allows one to make disposition under vacuum.

As well as the procedure and the velocity to dry the sample has a lot of importance in the final distribution of the layer. For example, drying with heater or under vacuum (fast dry) allow obtain a pseudo-continuous distribution of the layer and drying in atmospheric air (slow dry) imply to have a continuous layer distribution of the particles.
CHAPTER 4. EXPERIMENT SET-UP

4.2 GET THE VACUUM

Achieving to work under vacuum allows study the response of the crystal without the air interaction (as a viscoelastic fluid). The following figure shows the pneumatic circuit scheme where can define all components of the vacuum system.
4.3 GET THE FREQUENCY RESPONSE

Frequency and Quality responses are the most important data that allow to understand the behavior between the micro-particles and the resonator. In this point is explained how to connect the cables, see the results and then saved them.
4.3.1 CALIBRATION AND CONNECTION

In order to have a good response is necessary to calibrate the electric circuit. For this, the cable has to be connected in the Port 1 (as the image following).

With the other end of the cable in the air and without moving, is started like the following procedure:

- Press the "CAL" button in the hardkeys panel.
• Select "Start...(Manual)" on the touchscreen.

• Select "Refl Norm Open" to calibrate the signal reflection of the Port 1. Then touch "Next".
• Check that everything is the same as the image and select "Start".

• Select "Open (m)" on the left of the screen and wait until it show the following symbol:

• Then can touch "Apply" and finish the calibration.
Finally when the calibration is finished it only have to connect the cable to the resonator and start the measurements.

### 4.3.2 SEE THE RESPONSE

After calibrating and connection of the resonator in to the Network Analyzer one can see on the screen the resonance frequency response. To do this it is necessary configure the frequency range in which one want to work and scale the image.

**CENTER**

- For the centering the frequency range, press the "CENTER" button in the panel.
  With this can position the selected value as the center of the screen.

![Stimulus Panel](image)

- Write the value of the resonator frequency (from 5 to 10 normally) and press "M/µ".
  Automatically the value of the center frequency will be the value written.

**SCALE**

- To scale the image, press the "SCALE" button in the panel.
Normally the values proposed in the image are enough to clearly see the response. If you do not see it, it is necessary to also change the following settings.

SPAN

- It is used for to indicate the frequency range that should appear on the screen. Press "SPAN" in the hardkeys panel and write the range and write the range, then press the "k/m" button to put the units in kHz.

POWER/BW/AVG

- The power and the bandwidth are also factors that influence in the plot of the response. Press "POWER-BW-AVG" in the panel. The power and the bandwidth recommended are the values in the following images (-10dB and 100Hz respectively).
CHAPTER 4. EXPERIMENT SET-UP

If you do not know the exact center of the resonance frequency can be found using the markers.

MARKER

• Press the "MARKER" button and, using the turning knob in the panel, place the screen marker at the peak of frequency. Then the value of the frequency of the marker will change in the "Mkr1 Stimulus" box.

• To put this new value in the center of the screen, it is necessary to touch "Marker Search" and select "Center = Marker".
Finally one can also record the trace in a temporal memory and show at the same time the trace recorded and the trace in real time. This can be useful to see the change in the frequency and Q factor when adding or removing loads the resonator.

**TRACE/CONFIG**

- Press "TRACE CONFIG" button in the panel.

- Select "All Mem All Data" and then in the tab of "All Data to Mem" touch "Show all mem".
Logically the NA has many more features but I leave the user to explore it.

4.3.3 SAVE RESULTS

If you want to save the data that are shown on the screen only should to follow four steps:

- Press the "FILE" button in the hardkeys panel.

- Select the "Trace Data" tab.
Then touch "s1p Active Trace...".

It just need to select the folder, put a name the file and click on "Save".

One can recover these files using a USB key looking the destination folder by pressing the "Windows" button on the panel.
Chapter 5

TESTS AND RESULTS

After the design and construction of the apparatus it is required some tests to verify that one can actually use as Nanotribometer. It is proceed as described in the previous section and the graphics are drawn from the data.

To verify the correct operation of Network Analyzer it was used a quartz crystal of about 10 MHz, different than it was purchased.

Three samples were prepared with different densities and distributions from polystyrene microspheres 45 $\mu$m. In this way it was possible to obtain a clear difference between the displacement of the frequency and quality factor among the three samples.

The first one was evaporated with atmospheric air and while the crystal was being excited by the Network Analyzer. From these procedures a dense monolayer with a continuous distribution was obtained. As one can expect, the displacement of $f$ and $Q$ is remarkably high compared with the other cases.

Figure 5.0.1: Continuous distribution
The second sample was evaporated using a heat source (heater) and without excitation of the quartz crystal. This gives a more irregular distribution and less density.

Finally, the last sample is less dense and fully discrete distribution. The latter was prepared from the transfer experiment, where the particles are located randomly on the main quartz electrode.

The comparative results between the three samples (under vacuum) is shown in Figure 5.0.4. You can see that the third sample (less dense) hardly has a frequency shift and change in Q-factor high compared to the other two. You can also see that the displacement of the three frequencies is positive, this is typical when there is slippage between a microsphere and the quartz crystal. The latter explains that clearly the sample no slides as a single element, but do separately each of the micro-spheres.
For the quartz, is verified the frequency response of the crystal without micro-spheres (at atmospheric pressure) is the corresponding that indicated by the manufacturer. It is observed that is slightly lower (4.989.303 Hz) than it is indicated to 5.025.000 Hz, this is due to the deposition of gold to create the electrodes, as the model of Sauerbrey describes.

As seen in the figure 3.2.6 the quartz crystals purchased have a roughness of approximately 1µm. This characteristic makes the behavior between micro-objects that are in contact with the surface of the crystal is completely different to the behavior if the surface is polished. To compare these results were been used micro-spheres of 90µm diameter and two quartz crystals with different surface roughness. A crystal is the one with the roughness of 1µm and the other is a 6 MHz crystal polished. Below it can see what is the difference of the frequency shift and Q factor between the two crystals of different roughness. The study was conducted under the same conditions for both crystals. It was deposited 10µl of the aqueous solution with micro-spheres and it was reached to 7 mTorr under vacuum to avoid the air effect.
With the load of the 90µm micro-spheres one obtains a shift positive of the resonance frequency. In the first case (polished crystal) there is a positive shift of 318 Hz from the initial resonance frequency. Also one can observe that the Q-factor is decreased. However, in the unpolished case there is a smaller shift of 100 Hz from the initial resonance. This may explain the fact that the surface has a high surface roughness makes the micro-spheres attach and avoid slipping due to irregularities of this.

It can see then, that the roughness plays a very important factor when studying the sliding between two micro-objects.
FUTURE WORK

Evaporation as was seen is an important factor in attaining distributions of monolayers. In the literature it has been noted that is very usual to use flow of dry air or nitrogen to dry the samples. In addition, using nitrogen gas one can calibrate the quartz crystal from his slip times that are known and evaluated to Krim and Widom.

It has also been said that the quartz crystals are highly sensitive to changes in pressure and temperature. To control the pressure is used a vacuum system. However, to control the temperature it would be necessary use a sensor with a source of heat-cold to keep a constant temperature in the resonator.

In the vacuum system always exists small leak flows and therefore one can not work for long without pumping. To increase this time there are several solutions. One is to use a secondary camera right next to the main chamber and avoid faster pressure losses. An other is the pumping to a lower level by using a more powerful pump. Without increasing the time but optimizing the use of the bomb and taking measurements while it is stopped, would be install an automatic control to stop and turn on the pump, thus only would begin to work from the limit value (10 \textit{mbar}) and stops another value defined.

The micro-objects selected have been the polystyrene micro-spheres. Logically the nanotribometer designed is able to assess many other materials and in different states (solid, liquid or gas).

Also the surfaces, as well as the micro-particles such as the crystal, can be functionalized and thus to study the hydrophobic behavior, etc. It is also possible to change the piezoelectric substrate and not to use always the gold electrode as study surface.
CHAPTER 6. FUTURE WORK

From elaborate and long studies would be interesting to observe the changes in the frequency and the quality factor and perform a comparative with the time. In the same way and with the Network Analyzer option, do studies at different levels of harmonics and differentiate the behaviors of different existent scales.
Chapter 7

CONCLUSIONS

In this project it has seen the importance of the Network Analyzer. Without it could not be excite the resonator neither obtain results of the resonant frequency and the quality factor. In addition, the ZNC Vector Network Analyzer from Rohde & Schwarz can work at different levels of harmonics and to assess the behaviors that appear in the upper and lower levels of scales. The wide range of frequencies and power that can work is useful for the future if crystals with different thicknesses are used and consequently one have to work with a other resonant frequency. We conclude therefore that the Network Analyzer selected can do a lot of functions and gives a great flexibility to the user.

To observe the sample, due to the slow movement of the distribution of the micro-particles over the quartz crystal surfaces, it is not necessary a high frequency per second of images. Therefore, it is not essential a fast camera, but yes a good resolution to observe in detail the particles if needed.

Must be said, the apparatus designed and built allows use it with good results as nanotribometer. Also, of course, can be used as a microbalance, primary use for the quartz crystal through the Sauerbrey model. Another application for our nanotribometer would be like a QCM-D (Quartz Crystal Microbalance with Dissipation Monitoring) where it is used in the determination of film thickness in a liquid environment (Such as the thickness of an adsorbed protein layer).

To finish, note that the specifications, that the nanotribometer designed had to meet, have been successfully completed and also has been able to perform experiments to validate it. In addition to complying with the specifications, the project has been able to conduct and conclude within six months and fulfilling initial budget of 25.000 €.
Bibliography


BIBLIOGRAPHY


[22] www.rohde-schwarz.com

[23] www.lesker.com


[26] www.stemmer-imaging.co.uk

[27] www.vwr.com
Chapter 8

ANNEX
CHAPTER 8. ANNEX

8.1 CAD MODEL

8.1.1 DRAWINGS
Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz
Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz

Base support QCM 2

MATERIAU : DURAL

BASE SUPPORT QCM 2

TITRE : Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz

MÉTHODE : Utilisation d'un résonateur à quartz

TOLERANCES : +/- 0,1 mm

STANDARDS : ISO 9001

SÉRIE : QCM 2

ÉDITATION : Édition de studiante SolidWorks.

SAUF INDICATION CONTRAIRE : LES COTES SONT EN MILLIMETRES

ÉTAT DE SURFACE : T

LIGNE : 2 : 1

HOJA 1 DE 1

A4
Embase pour un HC-40 Low Profile Cold Weld Crystal Base

Conception et réalisation d’un nanotribomètre utilisant un résonateur à quartz

Circuit Quartz 1

Sólo para uso académico.

Edición de estudiante de SolidWorks.
Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz

Circuit Quartz 2
**MATERIAL:**

- Eyelet: 30/70 Copper Clad Kovar
- Glass: 7052 or Equal, Natural
- Leads: ASTM F-15 Alloy, Kovar
- Mount: Nickel

**PLATING:**

1. **Option:** RoHS Compliant ElectroleSS
   Nickel Plate of 100 Microinches
   Minimum Final Plate
2. **Option:** RoHS Compliant ElectroleSS
   Nickel Plate of 100 Microinches
   Minimum Followed by a RoHS
   Compliant Lead Free Solder
   Coat, on Leads Only
3. **Option:** RoHS Compliant ElectroleSS
   Nickel Plate of 100 Microinches
   Minimum Followed by a Gold
   Flash of .99999 Pure 24 Karat Gold
   Up to a Max. of 8 Microinches.
Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz

Edgard

INSTITUT FEMTO-ST
ENSM- Dpt MN2S
26 chemin de l'Épitauche
25030 BESANCON Cedex

N.º DE DIBUJO
ESCALA: 2:1 HOJA 1 DE 1
A4
LAITON

Sólo para uso académico.

Philippe

SAUF INDICATION CONTRAIRE : LES COTES SONT EN MILLIMETRES

ÉTAT DE SURFACE : TOLÉRANCES : +/- 0,1 mm

LINÉAIRES : ANGULAIRES :

Édition de estudiante de SolidWorks.

DATETUTEUR

SERVICE COMMUN MÉCANIQUE
Conception et réalisation d'un nanotribomètre utilisant un résonateur à quartz

Support QCM 2

Tuteur: Philippe
Date: 14/05/2014
Materiau: DURAL

Support QCM 2

Sólo para uso académico.
Concepción y realización de un nanotribómetro utilizando un resonador a cuarzo

RÓTULO | UBIC X | UBIC Y | TAMAÑO
--- | --- | --- | ---
B1 | -19,09 | -64,09 | Ø 5 × 5
| | | M6 - 6H Ø 6
B2 | -19,09 | -25,91 | Ø 5 × 5
| | | M6 - 6H Ø 6
B3 | 19,09 | -64,09 | Ø 5 × 5
| | | M6 - 6H Ø 6
B4 | 19,09 | -25,91 | Ø 5 × 5
| | | M6 - 6H Ø 6
C1 | 9,05 | 64,37 | Ø 8 × 12
| | | ø 16 × 8
C2 | 39,12 | 51,91 | Ø 8 × 12
| | | ø 16 × 8
C3 | 51,91 | 39,12 | Ø 8 × 12
| | | ø 16 × 8
C4 | 64,37 | -9,05 | Ø 8 × 12
| | | ø 16 × 8
C5 | 64,37 | 9,05 | Ø 8 × 12
| | | ø 16 × 8
C6 | -9,05 | 64,37 | Ø 8 × 12
| | | ø 16 × 8

Edición de estudiante de SolidWorks. Sólo para uso académico.
8.1.2 RENDERS
8.2 PHOTOS

8.2.1 COMPONENTS

Figure 8.2.1: Support of the auxiliary crystal

Figure 8.2.2: Support of the principal crystal
Figure 8.2.3: Base of the principal crystal

Figure 8.2.4: Base of the enclosure
Figure 8.2.5: Enclosure

Figure 8.2.6: Blank crystals
Figure 8.2.7: Matrices to make the depositions

Figure 8.2.8: Quartz crystals with gold electrodes
Figure 8.2.9: Roughness of quartz crystals purchased

Figure 8.2.10: Supports and electrical circuits
Figure 8.2.11: Top view of the main crystal

Figure 8.2.12: Vacuum system
8.2.2 SAMPLES

Figure 8.2.13: Evaporation of a sample to atmospheric air and with vibration

Figure 8.2.14: Sample dried under vacuum