Development and applications of sensors based on piezoelectric resonators

Ph. D. Thesis

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Abstract

Monitoring the physical properties of liquids is of high practical and economical interest in many fields such as the automotive, wine, aerospace, healthcare or pharmaceutical industry. In the case of the automotive industry, the on-board assessment of the lubricating oil properties is critical to determine its performance. In the wine industry, the in-line monitoring of a fermentation process through density measurements is crucial since the traditional procedure followed by winemakers for monitoring grape must fermentation is not automated, has not enough accuracy or has only been tested in discrete must samples. Furthermore, current experimental methods rely on benchtop instruments of high cost and dimensions. Nevertheless, the development of micro-electro-mechanical systems (MEMS) has enabled on-chip micrometer-scaled mechanical resonators offering a high integrability and ease of fabrication by available silicon technologies.

Piezoelectric resonators with in-plane vibration modes, flexural and torsional modes have already been tested. However, it is well-established that higher order out-of-plane modes present better quality factors at moderate frequencies. In this work we focus on the use of resonant microstructures as an interesting alternative for the determination of the rheological properties of liquids, density and viscosity.

The determination of these parameters through the measurement of the resonance frequency and the quality factor of a mechanical resonator, has already been reported. This approach presents several advantages with respect to traditional methods of rheological analysis: real-time measurements, in-line configuration, low liquid volumes, etc.

To determine from the measurements the resonance parameters, an interface circuit was implemented and included within a closed-loop scheme. The oscillator circuit constitutes a simple technique to track the resonant frequency. For this reason different oscillator circuits were tested: a Phase-Locked Loop (PLL) based on instrumentation, a more compact version based on discrete electronics and a PLL based on the integrated circuit 74HCT4046, showing similar resolution. Furthermore, different open-loop techniques were implemented, a low-cost interface circuit based on tran-
sient analysis and an impedance analyser, showing similar resolution.

Another key objective of this work is the assessment of a calibration method for piezoelectric MEMS resonators in simultaneous density and viscosity sensing. An advanced calibration model, based on a Taylor series of the hydrodynamic function, was established as a suitable method for determining the density and viscosity with the lowest calibration error.

In addition other applications were tested with similar resonators for the elasticity sensing of different materials and cigarette particle detection. These applications were also based on similar electronic circuits demonstrating the ability of these to be used in a large number of applications.
Resumen

La medida y el control de las propiedades físicas de los líquidos es de gran interés en diferentes campos como la industria del automóvil, vitivinícola, aeroespacial, sanitaria o farmacéutica. En el caso de la industria del automóvil, la evaluación en tiempo real de las propiedades del aceite lubricante de un motor es fundamental para determinar su rendimiento. En la industria del vino, el control en línea de un proceso de fermentación, a través de medidas de densidad, es crucial ya que el procedimiento tradicional seguido por los enólogos para controlar la fermentación del mosto de uva no se encuentra automatizado, no tiene suficiente precisión o solo ha sido probado en muestras discretas de mosto. Además, los métodos experimentales de análisis se basan en instrumentos de un elevado coste y dimensiones.

Por lo que uno de los objetivos de esta tesis es el desarrollo de microestructuras resonantes (MEMS) para la determinación de propiedades reológicas de diferentes líquidos como la densidad y la viscosidad. La determinación de estos parámetros se ha realizado a través de la medida de la frecuencia de resonancia y el factor de calidad de un resonador piezoelectrico. Este enfoque presenta varias ventajas con respecto a los métodos de análisis reológicos: mediciones en tiempo real, medidas en línea, bajos volúmenes de líquidos, etc.

Para determinar los parámetros de resonancia del resonador piezoelectrico, se ha diseñado un circuito interfaz capaz de reducir los efectos parásitos del resonador para posteriormente incluirlo en un circuito oscilador, ya que este nos permite monitorizar la frecuencia de resonancia en tiempo real y de una forma sencilla. Por esta razón se han analizado diferentes circuitos osciladores: un circuito de lazo de enganche de fase (PLL) basado en instrumentación, una versión más compacta basada en componentes discretos y un PLL basado en el circuito integrado 74HCT4046, mostrando todos ellos una resolución similar. Además se han estudiado diferentes circuitos para realizar medidas en lazo abierto: un circuito de bajo coste basado en análisis transitorio, otro para la medida de la respuesta en función de la frecuencia y un analizador de impedancias.
Otro objetivo clave de esta tesis es la evaluación de un método de calibración de resonadores piezoeléctricos con el objetivo de obtener de forma simultánea la densidad y la viscosidad. Un avanzado modelo de calibración, basado en un desarrollo en serie de Taylor de la función hidrodinámica, se ha establecido como un método adecuado para determinar la densidad y la viscosidad con el menor error de calibración.

Finalmente, se han estudiado otras aplicaciones como la medida de elasticidad de diferentes materiales y la detección de partículas procedentes de un cigarro. Estas aplicaciones también se basaron en circuitos electrónicos similares demostrando la capacidad de estos para ser utilizados en un gran número de aplicaciones.
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Chapter 1

Introduction

I have not failed. I’ve just found 10,000 ways that won’t work.

Thomas A. Edison

Summary: In this chapter, the fundamental theoretical concepts and technologies of interest for this dissertation are introduced. At the end, the state of the art is discussed and the main objectives are set.

1.1 Fundamentals of piezoelectric resonators

1.1.1 Introduction to piezoelectricity

In March 1880, the Curie brothers discover piezoelectricity. Microphones, quartz watches, and inkjet printers all rely on an unusual phenomenon known as the piezoelectric effect found in various crystals, ceramics, and even bone. It was discovered by none other than French physicist Pierre Curie, working with his older brother Jacques, who found that putting pressure on these materials created electricity [Ame14]. Over the next few decades, piezoelectricity was explored due to the great potential of the piezoelectric effect. The breakout of World War I marked the introduction of the first practical application for piezoelectric devices, which was the sonar device, creating an intense international developmental interest in piezoelectric devices. Over the next few decades, new piezoelectric materials and new applications for those materials were explored and developed [Nan].

In summary, the piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress.
The word piezoelectric is derived from the Greek *piezein*, which means to squeeze or press, and *piezo*, which is Greek for "push".

One of the unique characteristics of the piezoelectric effect is that it is reversible, meaning that materials exhibiting the direct and inverse piezoelectric effect (see figure 1.1). When piezoelectric material is placed under mechanical stress (direct), a shifting of the positive and negative charge in the material takes place, which then results in an external electrical field. When reversed (inverse), an outer electrical field either stretches or compresses the piezoelectric material [Moh]. Only materials formed by fixed ions ordered in some manner can present this behaviour, as it is based on the existence of changing electric dipoles within the material structure [Nan]. There are many materials, both natural and man-made, that exhibit a range of piezoelectric effects. Some naturally piezoelectric occurring materials include Berlineite (structurally identical to quartz), quartz, Rochelle salt, topaz, tourmaline, and bone. An example of man-made piezoelectric materials includes aluminium nitride (AIN) and lead zirconate titanate (PZT). These materials will be used in the resonators designed in this thesis since they present a greater sensitivity, a high dielectric constant, a high coupling and a high charge sensitivity compared to other materials.

![Figure 1.1: Schematic representation of direct and inverse piezoelectric effect](image)

**Figure 1.1:** Schematic representation of direct and inverse piezoelectric effect: (a) disk after polarization, (b) disk compressed, (c) disk stretched, (d) applied voltage with the same polarity as polarization voltage, (e) applied voltage with the opposite polarity as polarization voltage.

### 1.1.2 Applications of the piezoelectric effect

In the last decades, the development of modern microfabrication technologies along with piezoelectric materials have brought the appearance of complex microelectromechanical systems (MEMS) and piezoelectric resonators. One of the great potentials of MEMS is the integration of transducers, either actuators, which translate electrical signals into mechanical magnitudes, or sensors, which allows for reading mechanical magnitudes by conversion to the electrical domain. As long as the environment affects
its electromechanical response, a piezoelectric resonator can be used to measure physical properties or perturbations from the medium [Man15].

These resonators have been attracting intensive attention due to their advantages in low-cost fabrication, high sensitivity, low driving voltage and full integration [Fad04]. We can find applications of the piezoelectric effect in different fields such as:

- **High Voltage and Power Sources:**

  An example of applications in this area is the electric cigarette lighter, where pressing a button causes a spring-loaded hammer to hit a piezoelectric crystal, thereby producing a sufficiently high voltage that electric current flows across a small spark gap, heating and igniting the gas.

- **Frequency standard:**

  Several piezoelectric materials (e.g. quartz) can be used as frequency standards, as the vibration frequency of them is practically constant with almost no variations when they work as oscillators. The most known application is the use in quartz clocks, where the vibration of a crystal of quartz is used to measure the time (see section 2.3.1.1).

- **Actuators:**

  In this case, we take advantage of the inverse piezoelectric effect to control changes in the shape of the material produced by an electric field [Rui15; Tol17c]. A big change in the electric field causes a small change in the shape, so the sensibility of this kind of devices is very high. Some of the classical applications are fuel injectors, loud speakers and piezoelectric motors. In the case of the piezoelectric motors, very high voltages correspond to only tiny changes in the width of the crystal that can be manipulated with micrometer precision, making piezo crystals an important tool for positioning objects with extreme accuracy.

- **Sensors:**

  This thesis is based on piezoelectric sensors where a physical dimension, transformed into a force, acts on two opposing faces of the sensing element. MEMS resonators have been used in a large variety of industries such as: aerospace, automotive, biomedical, chemical optical displays, wireless and optical communications. In the literature we can find different examples of acoustic wave resonators [Rub07], ultrasonic transducers [Mar00], gyroscopes [Mad03], accelerometers [Bee00], filters [Ste07], energy harvesters [Hor06], micro
balances [Sök10], fluid sensors [Aye07; Jam05; Hoy98; Man15], ink injection [Pri03], energy harvesting [Bee06], optical switching [Gil99], resonators for frequency synthesis and filtering [Ngu07; Bee12], mass sensors [Lav04], pressure sensors [Eat97], inertial sensors such as accelerometers and gyroscopes [Bar01], atomic Force Microscopy (AFM) [Alg10], microphones [Sch03].

1.1.3 Actuation and detection of different vibration modes for piezoelectric sensors

Piezoelectric sensors present different shapes and structures such as cantilevers, bridges, membranes and plates, which are fully or partially anchored, usually onto a silicon substrate. Each resonator structure has its own displacement pattern. For example, the cantilever may vibrate in a flexural, torsional or lateral mode presenting several higher-order resonance frequencies [Qiu14].

There are several types of excitation techniques for these vibration modes, each having a corresponding detection method based on the same principle for the interrogation of the vibration [Elw89], such as: electrostatic excitation and capacitive detection [Mat02; Pou05; Kim07], piezoelectric excitation and detection [Jaa08] [Ros08; Pia06; TM04], magnetic excitation [Li03; Rei10; Xia08], electrothermal excitation [Seo08], photothermal excitation, piezoresistive detection [Cer12], and optical detection [Tam01; Zho03] are widely used in MEMS resonator applications [Ste91; Mad03].

The most popular used methods are based on electrostatic excitation and capacitive detection as well as on piezoelectric excitation and detection. In this work we have focused on piezoelectric excitation and detection since they present several advantages. For example, no counter electrode is necessary so that the gap size can be designed to any desired value. In this case, one of the layers forming the resonator must be made of a piezoelectric material. An electric field, generated through electrode layers above and below, produces mechanical strain within the piezoelectric, which is equivalent to a distributed force. Besides, the stress generated in the structure is transformed to electric charge that can be collected by the electrodes.

1.1.4 Mechanical model of a piezoelectric resonator

In this section, we will introduce the modelling of mechanical resonators and the main figures of merit: resonant or resonance frequency, $f_r$, and quality factor, $Q_{factor}$. As a starting point, we will consider a simple model of a mechanical resonator, as in figure 1.2, where $m$, $c_0$ and $k_0$ are the mass,
damping coefficient and spring constant of the resonator, respectively, $f$ is the external force acting on the resonator, and $x$ is the position of the mass [Qiu14]. For a linear harmonic vibration, which means the vibration amplitude is much smaller compared to the resonator dimensions, the mechanical performance of the resonator can be described by a second order differential equation (see equation 1.1).

$$m\ddot{x} + c_0\dot{x} + k_0x = f$$  \hspace{1cm} (1.1)

When operated in a fluid, the resonator will experience a drag force from the fluid, the external force $f$ can be separated into two contributions as in equation 1.2, where the first component is a hydrodynamic loading component due to the motion of the fluid around the beam, whereas the second term is a driving force that excites the beam. The driving force is usually a known function whereas the hydrodynamic loading can be obtained by deriving from measurement or solving for the flow field around the resonator (see section 4.3.2).

$$f = f_{\text{hydro}} + f_{\text{drive}}$$  \hspace{1cm} (1.2)

In previous studies [Fer03; Qiu14], $f_{\text{hydro}}$ was characterized by damping force and spring force terms as in equation 1.3, where $c_a$ is the fluidic damping coefficient and $k_a$ is the fluidic spring constant.

$$f_{\text{hydro}} = c_a\dot{x} + k_a x$$  \hspace{1cm} (1.3)

Substituting equations 1.2 and 1.3 into equation 1.1, we obtain an uncoupled equation for the structure as in equation 1.4, where $c$ ($c = c_0 + c_a$) and $k$ ($k = k_0 + k_a$) include the contributions from the resonator and the surrounding fluid.
\[ m\ddot{x} + c\dot{x} + kx = f_{\text{drive}} \]  

Finally, the main figures of merit, the resonance frequency \( f_r \) and the quality factor \( Q \) factor can be defined as in equations 1.5 and 1.6, where \( \Delta\omega \) is the resonance bandwidth at which the response amplitude equals 71% of the peak value.

\[
f_r = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \tag{1.5}
\]

\[
Q = \frac{\omega}{\Delta\omega} \tag{1.6}
\]

\[
\Delta\omega = \frac{c}{m} \tag{1.7}
\]

These figures of merit, are used in most applications since these change due to external environmental influences to the device. The \( Q \) factor is defined as the ratio of stored energy to the dissipated energy per cycle. The stored energy is proportional to the device mass, whereas the power losses are proportional to the surface area of the resonator, in the case of fluid dominated losses and out-of-plane vibration. In general, a high \( Q \) factor results in a sharper resonance peak and leads to a better detectable resolution as it will be observed in following chapters.

1.1.5 Circuit model of a piezoelectric resonator

In this section, a basic resonator model is described explaining the degradation of the quality factor in liquid media, one of the final applications of the resonators. Assuming linearity, a mechanical resonator can be described as a damped second-order system as it was explained in section 1.1.4 [Fer03]. The coupling of the electrical and mechanical domains allows the direct integration of the MEMS device into an electronic circuit. A piezoelectric resonator can be modelled as a two-port admittance network for the applied voltage and the output motional current. For this reason, the most convenient method of finding the equivalent circuit is through the admittance \( Y_p \), defining the actuation (\( \eta_a \)) and sensing (\( \eta_s \)) coupling coefficients, as in equation 1.8 [Ho08]. In this equation \( k_n \) represents the elastic constant, \( Q \) the quality factor and \( s \) the Laplace variable. For a complete modelling of the electrical behaviour of real piezoelectric resonators, a parallel capacitance (\( C_p \)) that accounts for the dielectric coupling between the electrodes must be considered.
\[ Y_p(s) = \frac{I(s)}{V(s)} = \frac{\omega_n^2 \eta_a \eta_s s}{\kappa_n(s^2 + \omega_n^2 s + \omega_n^2)} \] (1.8)

The resonator model is based on a two-port scheme: one for actuation and the other for sensing. The sensing port is connected to a low shunt resistor \( R_s \), which behaves as a low impedance path to ground. This way \( C_p \) does not produce a significance dielectric current. However, our results show that a capacitive crosstalk across the actuation and sensing ports, represented by \( C_{ft} \) in figure 1.3, may have a significant impact on the transfer function [Mul92] producing a feedthrough term in the current measured.

![Resonator model with two-port configuration.](image)

Figure 1.3: Resonator model with two-port configuration.

Equation 1.9 approximates the response when \( R_s \) is low enough to locate the pole at least two decades above the operation frequency and the pole effect can be neglected. As the immersion in liquid media degrades the quality factor of the resonator modes, the feedthrough term (the second one in equation 1.9) becomes significant in the response.

\[ \frac{V_{res}(s)}{V_{in}(s)} = Y_p(s)R_s + sC_{ft}R_s \] (1.9)

This resonator model was applied in the design of an interface circuit described in section 3.2.5.

1.2 State of the art

In this section, a brief introduction to the state of the art of piezoelectric resonators and their applications is presented.

Monitoring the physical properties of liquids is of high practical and economical interest in many fields such as the automotive, wine, aerospace, healthcare or pharmaceutical industry.
In the case of the automotive industry, the on-board assessment of the lubricating oil properties is critical to determine its performance [Lut97]. Contamination by diesel soot has a significant impact on engine wear, with most engine manufacturers opting for Exhaust Gas Recirculation (EGR) technology to decrease NOx emissions. Returning exhaust product to the diesel engine combustion chamber may accelerate the degradation of the lubricant oil, affecting its rheological properties [Geo07; Ald07; Lap14]. For this reason, a real time monitoring of the viscosity is a key parameter to decide the substitution of the lubricant since it provides valuable information of the oil condition [Ago05b; Ago05a].

In the wine industry, the in-line monitoring of the fermentation process through density measurements is crucial [JM16] since the traditional procedure followed by winemakers for monitoring grape must fermentation is not automated, has not enough accuracy or has only been tested in discrete must samples. The food industry represents a large source of applications of liquid monitoring, since quality and safety of food are topics of major concern nowadays [Cul01]. The possible uses of sensors for the physical properties of liquids also extends to biotechnology [Oli12; Alv10].

In the last years, the determination of the density and the viscosity of liquids, through the measurement of the resonance frequency and the quality factor of a mechanical resonator, is attracting great interest [Jak11; Duf14; McL07; Man14; Pfu15; Tol17d]. This approach presents several advantages with respect to traditional methods of rheological analysis: real-time measurements, in-line configuration, low liquid volumes, etc.

Initially, thickness shear mode (TSM) quartz resonators [Kei85] and surface acoustic wave (SAW) devices [Jak98] were used to measure physical properties of liquids. Nevertheless, these devices present two important issues. On one hand, resonance frequencies are typically in the MHz range, which may bring viscoelastic effects [Kun05]. On the other hand, and due to a pure shear force between the liquid and the resonator surface, changes in both the resonance frequency and quality factor depend on the density-viscosity product and therefore these parameters cannot be separated [Rod95].

Piezoelectric resonators with in-plane vibration modes have already been tested for density and viscosity monitoring. Nevertheless, the problem of not-independent response to density and viscosity remains [Man12; Rie09; Rei10].

More recently, research has been focused on suspended structures, such as cantilevers or plates with higher order out-of-plane modes since these present better quality factors at moderate frequencies [Wil07; Kuc14b].
In this case, the liquid loading is a combination of shear and pressure forces. Shear forces, present in the faces parallel to the vibration direction, were solved analytically by Stokes [Sto05]. Nonetheless, pressure forces, present in the faces normal to the vibration direction, cannot be obtained in closed-form. However, a model described by Sader achieved a reasonable accuracy for cantilevers of large aspect ratio [Sad98; Van07]. In addition, other semi-analytical forms, with generic functional forms and geometrical parameters based on experimental data, were also reported [Maa05; Duf14; Man15].

1.3 Motivation and objectives

The global objective of this thesis is to contribute to the development of low-cost electronic circuits for different piezoelectric resonators and applications. The motivation of this work is due to the great advantages of using a piezoelectric sensor of high sensitivity, portable, precise and economical that allows us to obtain the density and viscosity for different fluids and pressures, being able to work with very small volumes and obtaining measurements in real time. In this work different resonant microstructures, with in-plane and out-of-plane modes, will be compared and used for the determination of the rheological properties of liquids and gases. Furthermore, different electronic circuits were tested with similar resonators for the elasticity sensing of different materials and cigarette particle detection demonstrating the ability of these to be used in a large number of applications. It is important to highlight that in the realization of this work different fields of engineering have been manipulated, such as the design and fabrication of circuits, calibration processes, fabrication of resonators and different physical and chemical aspects for the final applications.

The main objectives of this work have been structured in different chapters as follow:

- Chapter 1. Introduction: briefly introduces the context of the research and describes the work objectives and strategy.

- Chapter 2. Resonator design, fabrication and characterization: the resonators are compared and described for a later use in different applications. The main aspects for the modelling of piezoelectric MEMS resonators and some design procedures are presented.

- Chapter 3. Electronic circuits: this chapter deals with the implementation of electronic circuits for driving piezoelectric MEMS resonators
and to determine from the measurements the resonance parameters of interest: resonance frequency and quality factor. In order to do that, two techniques are approached: open-loop measurements based on an impedance analyser, transient analysis, frequency response function and a interface circuit to compensate the parasitic effects, and the inclusion of the resonator in different oscillator circuits to track the resonance. Three types of oscillator circuits were tested, a Phase-Locked Loop (PLL) based on instrumentation, a more compact version based on discrete electronics and a PLL based on the integrated circuit 74HCT4046, showing similar resolution.

- Chapter 4. Calibration procedure for piezoelectric MEMS resonators: another objective of this work is the assessment of a calibration method for piezoelectric MEMS resonators in simultaneous density and viscosity sensing. An advanced calibration model, based on a Taylor series of the hydrodynamic function, was established as a suitable method for determining the density and viscosity with the lowest calibration error. In addition, we have studied other important aspects of the calibration such as: the liquids selected for the calibration, the number of coefficients used and the effect of the temperature in the coefficients and the calibration error.

- Chapter 5. Applications: this is the main chapter where the performance of the resonators, electronic circuits and calibration models is evaluated in different applications. For example for the monitoring of lubricant oil condition, the monitoring of a grape must fermentation, the gas damping effect of piezoelectric resonators, the detection of cigarette particles and for elasticity sensing. These applications were based on similar electronic circuits demonstrating the ability of these to be used in a large number of applications.
Chapter 2

Resonator design, fabrication and characterization

Summary: The resonators used in this work are compared and described for a later use in different applications. The main aspects for the modelling and characterization of piezoelectric MEMS resonators and some design procedures are presented.

2.1 Introduction

Resonant structures are an interesting option in the determination of the viscosity and density of liquids.

Some authors claim that a convenient approach is the use of structures with in-plane vibration modes, i.e. modes that involve a displacement parallel to the larger surface of the structure [Jak10]. Although, typically a pure in-plane shear interaction, in the resonator-liquid interface, does not allow an independent determination of the density and viscosity, higher quality factors in liquid have been reported, associated with lower hydrodynamic loading [Man12].

Previous reports also suggest the use of structures with out-of-plane movement to overcome this limitation since these present independent responses to density and viscosity, regardless of the thickness [Wil07]. Nevertheless, the most studied out-of-plane modes, such as flexural or
torsional modes are considered to have lower quality factors and may be less suitable for such application scenarios [Wag09; Man10].

However, it is well-established that a different family, such as the roof tile-shape modes, present better quality factors at moderate frequencies as it was demonstrated in latest reports [Wil07; Kuc14b; Kuc15]. As it will be observed in section 2.3.2, these roof tile-shape modes feature spatial areas with variable curvature leading to piezoelectrically induced surface charges of different sign [Kuc15]. These resonators present a top metallization with different striped electrodes that allow a selective excitation of the vibration modes and act as a filter for higher modes [SR10; RD13; RD16].

In section 2.3 different resonators with in-plane and out-of-plane vibration modes will be analysed and compared.

2.2 Setup and initial characterization of the resonators

Before the resonators are introduced, the setup and the initial characterization of the resonators are described. Two different preliminary techniques for investigation purposes are introduced: optical, which measure mechanical displacement, and electrical, which measure voltage or current generated in the devices.

2.2.1 Optical characterization

- Scanning laser vibrometer:

The resonance frequencies and modal shapes of the different vibration modes of the resonators presented in section 2.3 were measured with a scanning laser vibrometer Polytec MSV400 (see figure 2.1). While the device under test is electrically excited, a laser beam is pointed with the aid of a microscope onto the resonator, and scattered back through the microscope to the interferometric sensor. Due to the Doppler effect, the movement of the device results in the modulation, with the aid of decoders, of the frequency or the phase of the reflected light.

The system can scan a grid of points in a certain area of the device. At each point, when the laser is focused, the time-domain vibration signal is recorded by a data acquisition module (DAQ). After that, a software fast Fourier transform (FFT) algorithm may be applied to obtain frequency domain data. The amplitude and phase information at each point allows to create the pictures presented in this chapter.

Nevertheless, this instrument presents an important limitation since only out-of-plane vibration modes can be detected.
2.2. Setup and initial characterization of the resonators

Figure 2.1: Schematic of the experimental setup including the Doppler effect vibrometer and the probe station.

- Optical interferometer:

For this reason, the optical interferometer MEMSMap510, developed by Optonor, was used as a complementary characterization tool. A picture of the equipment is found in figure 2.2. The measuring principle technique can be described as full field speckle pattern-based interferometry. The full device under test is illuminated by an expanded laser beam, and the object is imaged by a microscopic zoom lens onto a charge-coupled device (CCD) array. The instrument takes advantage of the speckle pattern over a rough surface to detect the displacement of each point. A post-processing algorithm is used to calculate numerical amplitude and phase maps. With this optical system, a full 3D representation can be obtained, so every mode detected electrically can be identified [Man15]. This instrument was used for the measurements of in-plane vibration modes.
2.2.2 Electrical characterization

- Impedance analyser:

The electrical characterization of devices was performed by the impedance analyser Agilent 4294A (see 3.2.1). This instrument performs electrical measurements, allowing to characterize the behaviour of resonant structures, but without information of the vibration shape. For that, it applies voltage to the electrodes of the resonator at a single frequency. Simultaneously, the current flowing is recorded by a lock-in technique that gets its relative amplitude and phase. Frequency sweeps can be realized, in which successive measurements are performed at different frequency values over a configurable range.

In order to calculate the quality factor and resonance frequency of the different resonators presented in this work, the measured impedance spectrum was fitted to a modified Butterworth-Van-Dyke (BVD) equivalent circuit as in figure 2.3 [Arn00].
2.2. Setup and initial characterization of the resonators

The BVD equivalent circuit combines a parallel and series resonant circuit. The motional branch consists of $R$, $L$ and $C$. The capacitance $C$ represents the elasticity of the resonator, the inductance $L$ the initial mass and the resistance $R$ the energy losses due to the viscous effects and internal friction. The parallel capacitance $C_p$ represents the presence of parasitic contributions and predominates outside the resonance, while the components of the series branch (R-L-C) dominate close to the resonance. Finally, we must also consider the parallel resistance $R_p$, which originates when coming into contact with liquid media producing dielectric losses.

After processing the data, the values of the resonance frequency and the quality factor were obtained applying a method developed by Marshall and Brigham [Mar04]. As it was reported, Q factor and resonance frequency can be calculated from the impedance spectrum in the range of the mode peak through equations 2.1 and 2.2. Nevertheless, this approximation is only valid for low figures of merit, i.e. low Q factor values, as it will be observed in the results of section 3.2.2.

\[ Q = \frac{2f_r^2}{f_+^2 - f_-^2} \]  

(2.1)

being:

\[ f_r = \sqrt{\frac{f_+^2 + f_-^2}{2}} \]  

(2.2)

where $f_-$ and $f_+$ are the frequencies that maximize and minimize the susceptance (i.e. imaginary part of admittance), respectively (see figure 2.4) [Man10].
In a similar way, the resonant parameters can be also obtained with the equivalent RLC values by fitting the conductance of the circuit model to the experimental conductance spectrum around resonance through equations 2.3 and 2.4.

\[
  f_r = \frac{1}{2\pi\sqrt{LC}} \tag{2.3}
\]

\[
  Q = \frac{\omega L}{R} \tag{2.4}
\]

- Lock-in amplifier:

In addition, a digital lock-in amplifier Zurich HF2LI [Zur] was used for the initial characterization of the resonators [Kuc14a]. A lock-in amplifier is one of the most used tools in research laboratories since it is used to detect and measure small AC signals (in the order of nanovolts). Accurate measurements can be made even when the signal is obscured by noise sources with much higher values. Lock-in amplifiers use a known technique called phase-sensitive detection (PSD) to obtain the component of the signal at a specific reference frequency and phase. In this way the noise signals, which are not in the reference frequency, are rejected and do not affect the measurement. In this work, a lock-in amplifier was used in order to obtain an accurate measurement of the transfer function of the resonators along with the electronic circuits. The resonant parameters can be obtained with the same process described for the impedance analyser. Furthermore, this instrument can also be used as a PLL-based oscillator, providing a software-based voltage-controlled oscillator, proportional integral controller and phase detector blocks that enable to track the resonant parameters (see section 3.3.1).
2.3 Comparison of resonators

In this section the resonators will be described explaining some details about the design, characterization and fabrication process while they are analysed and compared in terms of error and density-viscosity resolution in next chapters. Nevertheless, the fabrication of some resonators was realized with the assistance of the group of Prof. Helmut Seidel at the Universität des Saarlandes (Saarbrücken, Germany) and the group of Prof. Ulrich Schmid at the Technische Universität Wien (Vienna, Austria).

2.3.1 In-plane vibration modes

2.3.1.1 Commercial tuning fork

One of the piezoelectric resonators used in this work is a commercially available millimetre-sized quartz tuning fork [Mom97], working at 32.7 kHz with an anti-phase in-plane vibration mode (see figure 2.5). The basic principle of tuning fork is well known by musicians: two tips or arms are connected at one side of the resonator, whose resonance frequency is defined by the properties of the material and its geometry. Although each tip can be considered individually, it is necessary to take into account the symmetry of the two tips since this reduces the number of possible modes with a high quality factor.

![Figure 2.5: Millimeter-size tuning fork resonator. (a) Picture of the resonator, (b) measured modal displacement with an optical interferometer.](image)

This resonator present different advantages such as its great frequency stability, small size, a high quality factor and a low-power consumption. Therefore, tuning forks have become a basic component in circuits where a stable frequency signal is required, such as real time clock circuits or digital electronics. Tuning forks have also been reported as sensors for measurement of various physiochemical properties of liquids such as density and viscosity [Was11].

Among the wide variety of tuning fork resonators that exist in the market, we will focus on a piezoelectric resonator from Fox Electronics [Ele12].
Nevertheless, this resonator is vacuum encapsulated in a metallic cylinder with two electrical terminals. For this reason, for the final application of the resonator in liquid media it is necessary to open it by compression or using a file to separate the encapsulate from the device.

In order to assure the full immersion of the resonator in the liquids under consideration, special cells were designed. In the case of the tuning fork, a simple test tube was used. The bottom of the test tube is removed and the tuning fork is inserted through the bottom aperture, while the two pins of the tuning fork remain outside for the electrical connection. Silicone is used to attach the base of the tuning fork to the test tube (see 2.6).

![Figure 2.6: Liquid cell for the tuning fork resonator.](image)

### 2.3.1.2 Extensional "20"

One of the extensional resonators used in this work is a state-of-the-art micron-sized AlN-based rectangular plate. This resonator was fabricated in the Universität des Saarlandes depositing AlN film as the piezoelectric actuator and it is a state-of-the-art micron-sized (1000x250x20 \( \mu \text{m}^3 \)) rectangular plate, actuated in the first extensional mode in the MHz range (see figure 2.7) [Man12]. In order to differentiate with the second extensional mode, this microresonator is labelled as "extensional 20" because of the thickness of the device.
2.3. Comparison of resonators

Figure 2.7: Micron-sized AlN-based rectangular plate, labelled as "extensional 20". (a) Picture of the resonator, (b) measured modal displacement with an optical interferometer.

In this case, the device is attached to a printed circuit board (PCB), and microsoldering is used to connect the resonator electrodes to the copper pads of the printing circuit board (PCB). Immersion is achieved by placing a drop of fluid on top of the device (see figure 2.8).

Figure 2.8: Liquid cell for the extensional 20.

2.3.1.3 Extensional "130"

The second extensional resonator is a relatively thick plate for in-plane vibration, actuated also in the first extensional mode [Tol14]. This resonator was fabricated in the Technische Universität Wien. Unlike the previous extensional 20, this thicker resonator will allow us to separate and obtain density and viscosity. This microresonator is applied in section 5.2 and has a top area of 3000x250 $\mu m^2$ and 130 $\mu m$ of thickness (see figure 2.9). It was labelled as "extensional 130" because of the thickness. This resonator was placed in a DIP package which was used also as a liquid cell.
2.3.2 Out-of-plane vibration modes

In this section, different out-of-plane vibration modes will be analysed and compared.

In a first stage, different roof tile-shaped vibration modes (see section 2.1), within micromachined self-actuated and self-sensing aluminium nitride (AlN)-based cantilever sensors, are described [RD13; Kuc14b]. In this case, different designs were implemented for the 1\(^{st}\), 2\(^{nd}\), 3\(^{rd}\) and 4\(^{th}\) order roof-tile shaped vibration mode.

Finally, a commercially available piezoelectric ceramic bi-morph element (PZT), is described for a later use in a tactile and sensing application.

2.3.2.1 12-mode and 14-mode

By optimizing the top electrode layout with several strips, flexural modes of different orders may be optimally excited [Kuc14b]. One of the devices used in this work features three top metal strips which preferentially allow for the excitation of modes with two and four nodal lines in the axial direction.

The vibration modes have been designated as 12-mode and 14-mode, according to the number of nodal lines in each direction [Lei69]. The resonator, fabricated in the Technische Universität Wien, is a cantilever-type microplate (2524x1274x20\(\mu\)m\(^3\)) and it is based on sputter-deposited piezoelectric aluminium nitride (AlN) film, serving as both actuator and sensing element [Kuc14b]. In this case, the top metallization has three striped electrodes that allow a selective excitation of the vibration modes and act as a filter for higher modes [SR10]. The resonator is excited by an antiparallel connection of the electrodes (+-) to obtain the desired modal vibrations, where two electrodes (+) were used as actuation ports and the other one (-) as sensing port. The resonators and the considered modes are
shown in figure 2.10. The sensing characteristics are compared for both modes under immersion in engine oil SAE 0W30 diluted with diesel fuel in section 5.2.

Figure 2.10: (a) Picture of the resonator. Modal shapes measured with a laser Doppler vibrometer: (b) 12-mode, (c) 14-mode.

In this device, the effect of the compressibility, described in section 1.2 can be neglected since the acoustic wavelength is approximately 4 times greater for the 14-mode and 10 times for the 12-mode than the mechanical wavelength in the beam [Van09b; Van09a]. The same happens with the resonators described in section 2.3.2.2 and 2.3.2.3. The possible effect of the spurious reflections was studied by performing several measurements in fluid cells of different geometries obtaining that the distance from the device surface to the top cover of the cell or the bottom surface of the DIP has no effect on the Q factor or the resonance frequency.

2.3.2.2 13-mode

In this section, an advanced design was implemented for the out-of-plane vibration resulting in a cantilever with optimized electrode layout featuring three nodal lines in axial direction, and 1 nodal line in the perpendicular direction (13-mode) [Pfu15]. The resonator is excited by an antiparallel connection of the electrodes (+-) to obtain the desired modal vibration, where one electrode (+) was used as actuation port and the other one (-) as sensing port.

The device has a length of $L = 1511 \, \mu m$, width of $W = 1268 \, \mu m$ and thickness of $T = 45 \, \mu m$. The resonator is packaged and wire bonded in a 24-pin dual inline package (DIP) containing different cantilevers and optional devices for the compensation of parasitic effects. The device
used is designated with a red line in figure 2.11. This resonator was also fabricated in the Technische Universität Wien.

Figure 2.11: (a) Micrograph of the cantilever resonator packaged and wire bonded in a DIP containing different cantilevers and optional devices. The device used is designated with a red line. (b) Modal shape measured with a laser Doppler vibrometer.

This device designed to resonate with the 2\textsuperscript{nd} order out-of-plane modal vibration (13-mode) was immersed in several test liquids and applied in the calibration process described in section 4.4.1.

2.3.2.3 15-mode and 05-mode

Two different kinds of resonators were designed and fabricated for the 4\textsuperscript{th} order roof-tile shaped vibration mode. The considered modal shapes and the fabricated resonators are shown in figure 2.12. Both with optimized electrode layout featuring five nodal lines in one direction, and 1 (cantilever) or 0 (free plate) nodal lines in the perpendicular direction. Considering Leissa’s nomenclature, the vibration modes are named as 15-mode and 05-mode, respectively [Lei69].

In order to have ideally the same resonance frequency, the ratio of the thickness to square of the width was held constant [Kuc14b]. The cantilever (15-mode) has a length of $L = 2524 \, \mu m$, width of $W = 1274 \, \mu m$ and thickness of $T = 20 \, \mu m$. The suspended micro-plate (05-mode) has a length of $L = 3000 \, \mu m$, width of $W = 900 \, \mu m$ and thickness of $T = 10 \, \mu m$. In section 5.4.3, other micro-plate with the same length and thickness but a different width ($1800 \, \mu m$), was also tested. The latter structure is anchored with five supports in the 05-mode nodal lines to resemble a free plate condition. Subsequently, this leads to an increased piezoelectric response compared to a single side clamped cantilever structure with the same geometry and quality factor [Pfu16].
The fabrication of the micro-plate resonator excited in the out-of-plane 05-mode was carried out by MEMSCAP, following the PiezoMUMPS process: a SOI wafer with 10 µm-thick device layer is covered with a 500 nm-thick aluminium nitride (AlN) piezoelectric film. The silicon is doped to serve as both bottom electrode and structural layer. As top electrode, a layer of aluminium (1 µm) is deposited.

In contrast, the micromachined cantilever operated in the 15-mode was fabricated in the Technische Universität Wien from a SOI wafer with a 20 µm-thick device layer. The cantilever thickness was chosen so that the vibration mode is observed at low frequencies, 600 kHz. In order to meet the restrictions of the fabrication process, minor modifications were introduced with respect to the optimal design, as lateral dimensions of the structure narrower than 2 µm are not allowed. Regarding the electrodes, a minimum spacing between adjacent metal areas of different sign, which is determined by lithographical resolution and limitations from the etching process, were taken into account. The electrodes are isolated from the conductive silicon beam with a SiO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4} bi-layer of thickness 250/80 nm. For actuating and sensing, an aluminium nitride (AlN) thin film with a thickness of 650 nm was sputter deposited between two chromium/gold thin films for bottom and top electrode, with equal thickness 50/450 nm [Kuc14c] [Kuc14a]. Furthermore, to prevent the interaction with the liquid, an aluminium
nitride thin film with a thickness of 650 nm was deposited. Figure 2.13, shows an schematic cross-sectional view on the MEMS resonator illustrating the electrode design and the plate support of the 15-mode. The 12-mode, 13-mode and 14-mode followed a similar fabrication scheme.

![Figure 2.13](image)

**Figure 2.13:** Schematic cross-sectional view on the MEMS resonator illustrating the electrode design and the plate support of the 15-mode.

In this case, the top metallization has four striped electrodes that allow a selective excitation of the vibration modes and act as a filter for higher modes [SR10]. The resonators are excited by an antiparallel connection of the electrodes (+--+) to obtain the desired modal vibrations. In this case, two top electrodes connected in parallel (+) were used as actuation ports and the other two (-) as sensing ports (see figure 2.12).

It should be noted that the fabricated devices have similar resonance frequency in vacuum, but different geometry and quality factor. In fact, the quality factor measured at 25°C in 2-Propanol was 71.7 for the 05-mode device (10 µm thick) and 116 for the 15-mode device (20 µm thick). This difference in the quality factor is attributed to the different thickness.

This resonators will be applied for the monitoring of lubricant oil dilution with diesel in section 5.2.2.1. As it will be observed, the error term and the density-viscosity resolution is slightly better for the 15-mode because it presents a higher Q factor at the same \( f_r \). For this reason, we considered that the thicker device (15-mode) is superior to the thinner one (05-mode).

**2.3.2.4 20-mode: piezoelectric ceramic bi-morph element (PZT)**

This piezoelectric bi-morph element is a commercially available low power electromechanical transducer capable of converting mechanical or acoustic energy to electrical energy [Pro]. When the element is stressed or subjected
to vibration, the minute movement causes one layer to be under tension while the other is under compression, since the two layers are polarised in opposite directions the opposite stresses in each layer will produce an electrical output or voltage. It is composed of two chemical elements lead and zirconium combined with the chemical compound titanate, also called PZT.

In this work the PZT device was used for sensing and tactile applications (see chapter 5). The device used resonates with an out-of-plane vibration mode, 20-mode [Lei69], and has a length of \( L = 15 \text{ mm} \), width of \( W = 1.5 \text{ mm} \) and thickness of \( T = 0.6 \text{ mm} \) (see figure 2.14).

![Figure 2.14: (a) Micrograph of the PZT device, (b) optically measured modal shape 20-mode with a laser Doppler vibrometer.](image-url)
Chapter 3

Electronic circuits

*Science is not only a disciple of reason but, also, one of romance and passion.*
Stephen Hawking

Summary:
This chapter deals with the implementation of electronic circuits for driving piezoelectric MEMS resonators, to be used as sensors. In this work, different techniques are addressed: open-loop measurements based on an impedance analyser, transient analysis, frequency response function and an interface circuit to compensate the parasitic effects, and the inclusion of the resonator in different oscillator circuits to track the resonance.

3.1 Introduction
One of the main objectives of this dissertation is to achieve a real time monitoring system for the determination of density and viscosity with a MEMS resonator. The use of resonators as sensors requires the determination of the resonant magnitudes, resonance frequency and quality factor, to be related to the liquid properties. In this work, the resonant parameters were measured by different open and closed-loop techniques. In a first stage, the resonators were measured with different open-loop techniques based on an impedance analyser, a low-cost circuit based on transient analysis, frequency response function and an interface circuit to compensate the parasitic effects.

Nevertheless, one of the main objectives is to achieve a real-time monitoring system. For this reason, the resonators, along with the interface
circuit designed to minimize parasitic effects, were included in the closed loop of an oscillator circuit. Initially, the oscillator was based on a Phase-Locked Loop (PLL) instrument allowing for an easy tracking based on the phase change introduced by the resonator. Moreover, an oscillator circuit based on discrete components was tested with the same resonator, showing a comparable resolution with respect to the mentioned PLL-based scheme. Finally, an oscillator based on the integrated circuit 74HCT4046 was also tested.

3.2 Open-loop measurements

Initially, the measurements were taken with an impedance analyser of high cost and dimensions. Although this is a powerful characterization tool, its use beyond the laboratory is often prohibitive. For applications requiring field or remote measurements, a compact, low-cost and precise enough approach is desirable [Nie09; Fer09]. Oscillators based on piezoelectric resonators may be a suitable choice as it is demonstrated in section 3.3, although their application with the low quality factors considered in this work is challenging [Fer07; Sch01].

In addition, measurements of the resonance frequency and the quality factor were also carried out with the development of a PC-based virtual instrument and low-cost electronic circuits. These techniques were applied to measure the response of the tuning fork and the extensional 20, previously described in section 2.3.1.1 and 2.3.1.2, actuated in three different environments: air, 2-Propanol and the viscosity standard by Paragon Scientific N35 [Sci].

With regard to the low-cost techniques, frequency response measurement and the transient analysis technique are compared in section 3.2.2 and 3.2.3 in terms of error and resolution. These circuits feature a transimpedance amplifier [Fer01], necessary to convert the current signal de-
livered by the resonator to a voltage signal that is sampled by a data acquisition board (DAQ) (see figure 3.1).

At the end of this section, we have also included an interface circuit to compensate the parasitic effects of resonators for a later use with the oscillator circuits.

### 3.2.1 Impedance analyser

Electrical impedance measurements were carried out to characterize the initial performance of different resonators in various liquid media over a wide range of viscosities. In this case the tuning fork, the extensional 20 and the 13-mode resonators were characterized with an impedance analyser.

In order to register the resonant parameters in different fluids, a high precision Agilent 4294A impedance analyser was employed (see section 2.2). The measurement setup with the impedance analyser is presented in figure 3.2.

![Impedance analyser 4294A](image)

**Figure 3.2: Measurement setup with the impedance analyser**

In order to calculate the resonance frequency and the quality factor (see results in table 5.1), the measured spectrum was fitted to a modified Butterworth-Van Dyke equivalent circuit, as it was described in section 2.2.2 (see figure 2.3) [Arn00].

The parameters $L$ and $C$ of the equivalent circuit are adjusted to minimize the difference between the calculated conductance and the experimental data for each frequency [Cas10a]. Although there exists a variation of the parameters $L$ and $C$, the value of the resonance frequency undergoes no or little deviation as it is a function of the product $LC$, and an increase in $L$ reduces $C$ and vice versa (see equation 2.3). For example, the error obtained from various consecutive measurements in the case of the tuning fork resonator for $L$ and $C$ were 2.24 and 2.26%, respectively. However, the error presented in the resonance frequency was 0.02%.
3.2.2 Frequency response function

This open-loop technique was applied for the tuning fork and for the extensional 20 with some minor modifications.

- Tuning Fork:

This technique is based on a frequency response function (FRF) (MUX A and MUX B closed in figure 3.3). The excitation is performed with a multi-tone signal which was created with LabVIEW, from National Instruments, and applied to the resonator through a data acquisition card (DAQ) [Pau10]. The DAQ board (USB 6211 from National Instruments [Daq]) was also used to read the voltage signal output of the transimpedance amplifier.

After processing the data with LabVIEW (see figure 3.4), the values of the resonance frequency and the quality factor were obtained applying a method developed by Marshall and Brigham [Mar04], previously described in section 2.2.2.

![Figure 3.3: Circuit diagram for the measurement of the resonance frequency and the quality factor with the tuning fork resonator.](image)

A remarkable difference in the value of the quality factor obtained in air using this technique and comparing it to the impedance analyser measurements can be observed in table 3.1. The origin of this discrepancy may be related to the fact that the approach of Marshall et al. handles only low figures of merit, i.e. low-Q values [Mar04]. For the cases of 2-Propanol and N35, where the model of Marshall is valid, it has been demonstrated that the estimated quality factor agrees with the impedance analyser measurement (see table 3.1).
3.2. Open-loop measurements

Figure 3.4: Frequency response function both in air and 2-Propanol for the tuning fork.

- Extensional 20:

The same technique was also applied for the extensional 20. Nevertheless, some modifications in the electronic circuits were introduced due to the higher resonance frequency of the resonator (see figure 3.5).

The extensional 20 resonates at a frequency (3.8 MHz) that cannot be generated with the DAQ card, previously used for the tuning fork resonator, whose maximum sampling rate is limited to 250 kS/s. For this reason a voltage-controlled oscillator (VCO) and a passive envelope detector were added to the system [Jak05; Rie07]. The envelope detector includes a diode (BAT43), a resistance (1 MΩ) and a capacitance (100 pF). The VCO input is supplied with a sawtooth waveform generated with the DAQ card at a much lower frequency [Nak94]. The sawtooth waveform frequency is related to the Q factor of the sensor. The biggest decay time constant for the extensional 20, measured in heptane fluid, is approximately 9 ms. It is clear that the period of the sawtooth waveform should be longer than the total decay time ($5\tau = 45\text{ms}$). In order to avoid problems with the oscillation decay we have used a sawtooth frequency of 1 Hz.

In order to assure that the oscillator output frequency falls within the resonance frequency, different parameters of the VCO have been modified. A frequency counter (Agilent 53131A) was employed to determine the open-loop Allan deviation of the VCO, obtaining a value of $1.338 \times 10^{-5}$ which is much lower than the width of the resonance peak for all the cases studied here, allowing to excite the resonator in a stable way [RP04].
The VCO utilized, based on integrated circuit 74HCT4046 [Pll], cannot deliver a sinusoidal waveform but a square wave signal instead. The purpose of the low pass active filter shown in the schematic of figure 3.5 is to filter out all the harmonics present in the square wave. The resulting waveform is mostly sinusoidal and suitable to excite the microresonator. Finally, the envelope detector tracks the maximum output voltage of the transimpedance amplifier [Fan11]. As can be seen in figure 3.6, the response of the envelope detector peaks at $V_{in-VCO} = 1.5V$ and helps to identify the resonance frequency value.

Figure 3.5: Circuit diagram for the measurement of the resonance frequency and the quality factor with the extensional 20.

Figure 3.6: Frequency response function in air for the extensional 20.
3.2. Open-loop measurements

3.2.3 Transient analysis

The second technique is based on a transient analysis [Rod96]. This technique was also applied for the tuning fork and the extensional bone.

- Tuning Fork:

In this case, the excitation is also performed with a multi-tone signal and measured with a DAQ. Nevertheless, the multiplexer A (MUX A) in figure 3.3 is controlled by a TTL signal generated by the DAQ board. This TTL signal switches the multiplexer every second triggering the DAQ samples during the exponential decay. In this case the DAQ board registers the output of the transimpedance amplifier. The response is finally fitted to an exponential decay in LabVIEW through equation 3.1.

\[
A(t) = A_0 e^{-t/\tau} \sin \omega t + \phi
\]  

(3.1)

This fitting allowed us to obtain the decay time constant and the quality factor through equation 3.2. The resonance frequency has also been calculated with LabVIEW, dividing the number of peaks detected by the measured time interval (see figure 3.7).

\[
Q = \frac{\tau \omega}{2}
\]  

(3.2)

Figure 3.7: Transient response in both air and 2-Propanol for the tuning fork.
- Extensional 20:

A similar technique was also applied for the extensional 20. Once the VCO input voltage of the integrated 74HCT4046 [PIII] that allows an efficient excitation of the resonator was obtained with the previous FRF technique, the transient analysis technique can be applied.

Figure 3.8: Signal timing: (a) signal control of the multiplexer, (b) transimpedance amplifier output, (c) logic comparator output, (d) envelope detector output.

In this circuit the multiplexer is also controlled by a TTL signal. Besides, in order to obtain the resonance frequency more accurately, a logic comparator was added to the system (AD8561). Its output is connected to the frequency counter included in the DAQ board. The relevant signals of the circuit are shown in figure 3.8 and the measured transient response in air is presented in figure 3.9.
3.2. Open-loop measurements

3.2.4 Comparison of the open-loop techniques

In table 3.1, the results obtained with the low-cost electronic circuits (see section 3.2.3 and 3.2.2) and the impedance analyser (3.2.1) in air, 2-Propanol and N35 are compared for the extensional 20 and tuning fork resonator. In order to obtain an accurate measurement of the resolution, each liquid was measured five times to yield the measurement error for each technique and resonator.

Table 3.1: Comparison of the different measurement techniques for both resonators.

<table>
<thead>
<tr>
<th></th>
<th>Tuning fork</th>
<th>Extensonal</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>2-Propanol</td>
<td>N35</td>
</tr>
<tr>
<td>Frequency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>976&lt;sup&gt;a&lt;/sup&gt;</td>
<td>75.5</td>
<td>19.5</td>
</tr>
<tr>
<td>ΔQ</td>
<td>3.07</td>
<td>17.62</td>
<td>26.67</td>
</tr>
<tr>
<td>f&lt;sub&gt;r&lt;/sub&gt;[Hz]</td>
<td>32776</td>
<td>29394</td>
<td>28308</td>
</tr>
<tr>
<td>∆f&lt;sub&gt;r&lt;/sub&gt;[%]</td>
<td>0.02</td>
<td>0.23</td>
<td>0.69</td>
</tr>
<tr>
<td>Transient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>13150</td>
<td>70.4</td>
<td>14.7</td>
</tr>
<tr>
<td>ΔQ</td>
<td>6.39</td>
<td>3.41</td>
<td>2.04</td>
</tr>
<tr>
<td>f&lt;sub&gt;r&lt;/sub&gt;[Hz]</td>
<td>32758</td>
<td>29298</td>
<td>28253</td>
</tr>
<tr>
<td>∆f&lt;sub&gt;r&lt;/sub&gt;[%]</td>
<td>0.02</td>
<td>0.11</td>
<td>0.34</td>
</tr>
</tbody>
</table>

<sup>a</sup> Discrepancy related to the fact that the approach of Marshall and Brigham (2004) handles only low figures of merit

<sup>b</sup> Noise present in DAQ board

The results in table 3.1 demonstrate that the transient response and
the frequency response techniques are an accurate method that can be used to determine both the quality factor and the resonance frequency in liquids without any compensation of the parasitic effects. In the case of the extensional 20 in N35 fluid it was hard to obtain an accurate measurement due to noise from the electronic circuit and the resolution limitation of the DAQ board.

Finally, the density and viscosity resolutions were estimated only for the case of the tuning fork resonator [Was11]. As can be seen in table 3.2, it is clear that the impedance analyser holds the lowest error in density and viscosity. For this reason, the impedance analyser technique was applied for the monitoring of lubricant oil and diesel fuel in section 5.2.1. However, with regard to the low-cost techniques, it can be observed that the frequency response technique outperforms the transient analysis technique in terms of the measurement error, being the error in the transient response approximately twice as much as in the frequency response for the viscosity value of the N35 fluid [Sci].

Table 3.2: Comparison of the different measurement techniques for the tuning fork resonator where $\rho_{\text{MEMS}}$ and $\mu_{\text{MEMS}}$ are the density and viscosity estimated with the MEMS resonator.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Frequency response</th>
<th>Transient response</th>
<th>Impedance analyser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_{\text{MEMS}}$</td>
<td>$\mu_{\text{MEMS}}$</td>
<td>$\rho_{\text{MEMS}}$</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.748 ± 0.025</td>
<td>2.08 ± 0.77</td>
<td>0.715 ± 0.065</td>
</tr>
<tr>
<td>N35</td>
<td>0.894 ± 0.074</td>
<td>42 ± 7.5</td>
<td>0.888 ± 0.11</td>
</tr>
</tbody>
</table>

### 3.2.5 Interface circuit to cancel parasitic effects

The simultaneous measurement of density and viscosity of liquids, through measurement of the resonance frequency and the quality factor of a mechanical resonator, may be challenging due to the low quality factors and parasitic effects present in liquid media [Fer01].

For this reason, an interface circuit based on resonators in two-port configuration and a parasitic compensating device was developed to cancel the parasitic effects. In previous publications different interface circuits, that could also fulfil the function of cancelling the parasitic effects of a resonator, were analysed [Aki03; Miy02]. However, the interface circuit presented in this work (see figure 3.10) was selected due to the efficiency and simplicity of the design [Qiu15; Man14].

In the two-port scheme, one of the electrodes was used for actuation (+) and the other for sensing (-) (see figures 2.12 and 3.10). However, our
results show that a capacitive crosstalk across the actuation and sensing ports has a significant contribution to the output current. This crosstalk, represented by the capacitance $C_{ft}$ in figure 3.10, causes a current ($i_{C_{ft}}$) approximately 10 times greater than the piezoelectric current ($i_{piezo}$) under liquid immersion.

Figure 3.10: (a) Schematics of the interface circuit. (b) Implemented interface circuit on a PCB.

To minimize this parasitic component, a compensating device was introduced [Kuc14a]. This compensating or dummy device duplicates the structure of the resonator, being basically an unreleased copy of the plate, to prevent its vibration. An approximately 1% of mismatch in capacitance between the cantilever and the dummy has been observed [Iva11].

The interface circuit, shown in figure 3.10, uses an instrumentation amplifier to subtract the dummy response ($v_{dum}$) from that of the resonator ($v_{res}$). In this work, two different instrumentation amplifiers with different bandwidth were tested: the AD8428 with a bandwidth of 3.5 MHz and the AD8129 with a bandwidth of 270MHz. As it can be observed in figure 3.10, the cancellation or compensation can be accurately tuned by implementing a variable resistance ($R_s$) at the input of the instrumentation amplifier.

Since the materials and dimensions in the dummy and resonator devices
are approximately the same, they are expected to show identical electrical behaviour with respect to their parasitic effects. The interface circuit response is then represented by equation 3.3, where $G_{amp}$ is the gain of the instrumentation amplifier, set by an external resistor.

$$G = \frac{V_{out}(s)}{V_{in}(s)} = G_{amp} \frac{V_{res}(s) - V_{dum}(s)}{V_{in}(s)} = G_{amp} R_y Y_p(s)$$ (3.3)

Figure 3.11: Open loop response of the interface circuit for the 14-mode in lubricant oil SAE 0W30 with and without the dummy compensation using the instrumentation amplifier AD8428. Vertical offsets were applied to the measurement without compensation for clarity purposes.

The application of the interface circuit results in a clear resonance, with low baseline and the necessary phase to meet the Barkhausen criterion for oscillation (see figure 3.11, 3.12 and 3.13). Although the impact of parasitic effects is minimized, a phase shift is still present at the output of the instrumentation amplifier, resulting from the differences in electrical performance between the dummy and the resonator device, the capacitive crosstalk and the bandwidth limitation of the amplifier. This phase shift results in a non zero phase (about $-25^\circ$ for the 14-mode with the AD8428, $-50^\circ$ for the 15-mode with the AD8428 and $-9^\circ$ for the 15-mode with the AD8129) at the resonance frequency which implies a shift in the oscillation frequency for the closed-loop measurements as it can be observed in the next section.

In addition, this interface circuit can be modified to work as an oscillator circuit. In order to meet the Barkhausen criterion, the interface circuit need
Figure 3.12: Open loop response of the interface circuit for the 15-mode in 2-Propanol with and without the dummy compensation using the instrumentation amplifier AD8428. Vertical offsets were applied to the measurement without compensation for clarity purposes.

Figure 3.13: Open loop response of the interface circuit for other 15-mode in 2-Propanol with and without the dummy compensation using the instrumentation amplifier AD8129. Vertical offsets were applied to the measurement without compensation for clarity purposes.
to modified introducing a higher gain in the instrumentation amplifier and closing the loop. In this case, the resistance that controls the amplifier (AD8428) is replaced by a capacitor. This component acts as a low-pass filter and introduces the maximum possible gain (G=2000). Nevertheless, in this case only the resonance frequency can be obtained when closing the loop, and therefore it is only valid for applications where the value of the quality factor is not required (see section 5.6.2).

3.3 Closed-loop measurements

The application of oscillator circuits, as an interface for piezoelectric sensors, is the most common method, since the resonator can oscillates in stable conditions by means of simple circuits. Furthermore, the analogue output signal can be easily processed in digital systems, obtaining a frequency proportional to the density or viscosity of the liquid in which the resonator is immersed. However, the Barkhausen criterion must be met, i.e. the loop gain reaches a modulus equal or greater than 1 and its phase equals 0°.

In addition, the implementation of an oscillator becomes challenging for MEMS under liquid immersion, as the response is dramatically degraded due to the hydrodynamic loading. Because of this, the interface circuit, previously described in section 3.2.5 to cancel the resonator parasitic signal, was designed with a phase shift as low as possible at the resonance frequency of the piezoelectric resonator and included in the scheme of different oscillator circuits designed in this section.

This section describes different oscillator circuits for tracking the resonant parameters of piezoelectric resonators: a PLL-based oscillator based on the HF2LI Lock-in Amplifier from Zurich instruments, an oscillator circuit based on discrete components with an automatic gain control and a PLL oscillator based on the integrated circuit 74HCT4046 [PLL].

3.3.1 PLL-based oscillator

Once the parasitic effects of the resonator are minimized with the interface circuit previously described in section 3.2.5, we included the resonator in an oscillator circuit scheme based on a phase locked-loop (PLL) instrument from Zurich instruments (see section 2.2.2). Thanks to the digital nature of the implemented PLL-based oscillator, the target phase can be set to any value. This way the PLL can be adjusted to work at different points of the phase curve, so that the oscillation frequency and the resonance frequency of the resonator are approximately equal (red solid line in figure 3.11 and 3.12 ).
The PLL instrument provides software-based voltage controlled oscillator (VCO), proportional-integral controller (PI) and phase detector (PD) blocks that form a control system able to track the resonance frequency, as illustrated in figure 3.14. The configuration parameters used for the 14-mode and 15-mode are shown in table 3.3, where $K_p$ is the proportional gain, $t_c$ the time constant of the PI controller and $BW$ is the bandwidth of the system, respectively.

<table>
<thead>
<tr>
<th>Phase detector</th>
<th>PI controller</th>
<th>Phase shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>$BW=200\text{Hz}$</td>
<td>$K_p=1.89\text{Hz/deg}$</td>
<td>14-mode= $-25^\circ$</td>
</tr>
<tr>
<td>24 dB/oct</td>
<td>$t_c=29.33\text{ms}$</td>
<td>15-mode= $-50^\circ$</td>
</tr>
</tbody>
</table>

To describe the spreads given for Q factor and $f_r$ we have used the Allan deviation for $f_r$ and the "mean square successive difference method" for Q factor [All81; Neu41; Wal86]. In this case, the Allan deviation of the output signal was evaluated by recording 1000 frequency samples. Furthermore, the Allan deviation of $f_r$ was evaluated for different values of the target phase using the 14-mode and the results are plotted in figure 3.15. It can be seen that the best stability is obtained for $-25^\circ$, as a result of the compensation of the phase shift introduced by the interface circuit.
Figure 3.15: Normalized Allan deviation obtained for the 14-mode with the resonator immersed in lubricant oil SAE 0W30 versus the tracked frequency with a gate time of 60 ms.

As this magnitude depends on the gate time used to determine each frequency sample, data series were recorded for different values. As it can be seen in figure 3.16, a gate time of around 60 ms offers the best stability.

Figure 3.16: Normalized Allan deviation obtained for the 14-mode with the resonator immersed in lubricant oil SAE 0W30 versus the gate time at the resonance frequency.
Nevertheless, an oscillation frequency different from the resonance frequency deteriorates the frequency resolution. For example, the oscillation frequency showed an Allan deviation, in lubricant oil SAE 0W30 for the 14-mode, of \(3.70 \times 10^{-8}\) without phase compensation, and \(3.17 \times 10^{-8}\) when the oscillation is forced to the resonance frequency.

The minimum Allan deviation value obtained \((3.17 \times 10^{-8})\) improves by two order of magnitude the value reported by Seo and Brand [Seo08] with a resonator featuring a quality factor value of around 100 in water \((2.3 \times 10^{-6})\) and by one order the frequency deviation reported by Manzaneque et al. \((2.32 \times 10^{-7})\) featuring a quality factor of 64 in isopropanol [Man14]. Furthermore, the reported Allan deviations of oscillators based on MEMS resonators in air are similar to ours: \(4.81 \times 10^{-7}\) by Pettine et al. [Pet13]; \(1.2 \times 10^{-8}\) by Seo and Brand [Seo08]; \(6.67 \times 10^{-8}\) by Park et al. [Par07].

### 3.3.2 Discrete oscillator circuit

The results shown in section 5.2.2 demonstrate the use of a PLL-based oscillator circuit to track \(f_r\) and Q factor of a piezoelectric MEMS resonator immersed in lubricant oil. In addition, an alternative oscillator, based on discrete components, was tested showing a comparable stability. The possibility of reducing the total size, cost and power consumption of the system makes the discrete oscillator a very interesting solution for any potential application scenario. The reasonably good value of the admittance peak amplitude, along with the low resonance frequency of the resonators, allowed for a great flexibility and simplicity in the design and selection of the electronic parts. A resonator-based oscillator consists of a positive feedback loop circuit. The Barkhausen criterion must be met, i.e. the loop gain reaches a modulus equal or greater than 1 and its phase equals 0º.

Figure 3.17 shows the complete circuit used to implement the discrete oscillator. After the previously described interface circuit (see figure 3.10), a variable-gain stage introduces the gain necessary to get an overall loop gain of 1 at the resonance frequency. At its output, a follower stage is introduced in order to avoid loading problems. A passive filter prevents higher modes from oscillating. Moreover, an automatic gain control (AGC) is implemented to regulate the output voltage amplitude. To do so, the output amplitude, estimated by a passive envelope detector, is compared to the control input \(v_{AGC}\) and the result is integrated. The obtained signal serves to control de loop gain, avoiding the saturation of the amplifiers.

The tracking of the circuit output parameters, the oscillation frequency \(f_{osc}\) and the gain \(G_{osc}\), was carried out with the lock-in amplifier from Zurich instruments previously described in section 2.2.2. However, in order to reduce the cost of the setup for monitoring the gas damping effect
of piezoelectric MEMS resonators (see section 5.4.2), a DAQ was used instead (USB6211 from National Instruments). In that case, the oscillation frequency is higher than the maximum sampling rate of the DAQ (250 kS/s). For this reason, it was necessary to introduce an envelope detector and a comparator for the measurement of $G_{osc}$ and $f_{osc}$, as we can see in figure 3.17.

As predicted by the open-loop response in figure 3.11, the oscillation frequency is slightly lower than the resonance frequency, producing a decrease in the measured frequency stability. In this case, two additional constant, $K_{ic}$ and $\varphi_{osc}$, which are not affected by the loading conditions of the resonator, are necessary to perform the conversion from the circuit output parameters $f_{osc}$ and $G_{osc}$ to $f_r$ and Q factor as described in the first step of the calibration process in section 4.2.

Following the same procedure as in section 3.3.1, the density and viscosity can be deduced with a calibration process (see section 4.3.2) from the resonant parameters in any liquid in which the resonator is immersed. As it is demonstrated in section 5.2.2.2, the performance of the discrete oscillator circuit is similar in terms of frequency stability to that achievable by using a PLL-based oscillator.
3.3. Closed-loop measurements

Figure 3.17: Discrete oscillator circuit including the interface circuit, gain stage, follower and AGC.

3.3.3 PLL 74HCT4046

This PLL (phase locked-loop) oscillator circuit, based on the integrated circuit 74HCT4046 [Pll], is a feedback system composed of a phase comparator (PC2), a low-pass filter (filter 1) and a voltage controlled oscillator (VCO). In addition, as it can be seen in figure 3.18, the output signal of
the VCO \( (f_{osc}) \) was adapted with a low-pass filter (filter 2) since the VCO generates a digital signal. In this way, the excitation of the resonator is carried out with a filtered sinusoidal signal obtaining a higher stability of the oscillation frequency.

![Figure 3.18: Schematic of PLL 74HCT4046 oscillator circuit including the interface circuit.](image)

This oscillator circuit allows us to obtain a reference signal \( (f_{ref}) \) which controls the frequency and phase of the oscillator. It is important to consider that it is a feedback system like any other since it is mathematically characterized with the same equations that apply to other conventional feedback systems. Nevertheless, in this circuit the feedback error signal is a phase error while that in conventional systems is a voltage or current error signal.

The basic principle of operation of this PLL can be explained as follows: If there is no signal applied to the system input \( (f_{in}) \), the voltage that controls the VCO block has a zero value and the VCO oscillates at a frequency known as free oscillation frequency. If a signal is applied to the system input \( (f_{in}) \), the phase comparator compares the phase and frequency of that signal with the reference signal of the VCO \( (f_{ref}) \) and generates an error voltage proportional to the phase difference of these signals. This error voltage is then filtered and applied to the control input of the VCO, which generates the oscillation frequency \( (f_{osc}) \) at its output. In this way, the oscillation frequency of the VCO is modified, thus reducing the phase and frequency difference between the input and output signal.
If the input frequency \( (f_{in}) \) to the PLL system is enough close to the output frequency \( (f_{osc}) \), the nature of the PLL feedback causes that the frequency output of the VCO synchronize with the signal input. Once these signals are "locked-loop", the frequency output of the VCO is identical to the input signal with a finite phase difference. This self-correcting capability of the system allows the PLL to modify the oscillation frequency as a function of the changes produced in the resonator medium such as variations in density, viscosity, mass, temperature, etc.

This oscillator circuit was applied for the detection of cigarette particles in section 5.5.2. In this case, the phase comparator (PC2) is designed with a zero phase shift, so that the Barkhausen criterion can be met since the interface circuit will produce also a phase shift around zero as it was demonstrated in section 3.2.5. Nevertheless, we will have the same issue that affects the discrete oscillator circuit, since there will be differences between the oscillation frequency and the resonance frequency of the resonator producing a decrease in the system resolution.

### 3.4 Temperature control unit

In addition, for the application of our system as a sensor, reference measurements of density and viscosity of different liquids were performed with a temperature control unit capable of setting a target temperature with deviations of \( \pm 0.05 \, ^\circ C \) [Tol15]. This temperature control unit was implemented for the density and viscosity measurements of lubricant oils at different temperatures. Figure 3.19 shows a cross-section of the thermal module. It is composed of a thermal circuit made of aluminium, an NTC (negative temperature coefficient), a Peltier device, a heatsink and a fan. The temperature control is implemented by means of a PID (proportional-integral-derivative) controller programmed in LabVIEW, whereas the Peltier device is driven with current supplied by a power stage that allows for a bidirectional current flow. Figure 3.20 shows an schematic of the electronic circuit.

However, it has been demonstrated that the impact of temperature fluctuations in the resolution of the sensor during the measurement process is minimal, thus obtaining a resolution in resonance frequency \( (\Delta f_r) \) of 8 mHz and 9 mHz for the 15-mode with and without the temperature control unit, respectively, when immersed in the reference liquid D5. For this reason, in some applications it is not necessary to use a temperature control since a NTC sensor can be used instead to know the temperature value of the fluid.
Figure 3.19: Schematic, cross-sectional view on the temperature control unit and the liquid cell. The cell was developed with a 3D printer and allows confinement and recirculation of the liquid. The resonator is packaged and wire bonded in a 24-pin DIP (dual inline package).

Figure 3.20: Schematic of the electronic circuit designed for the temperature control unit.
Chapter 4

Calibration procedure for piezoelectric MEMS resonators

Summary: This chapter deals with the calibration process required for determining density and viscosity of the fluid in which the resonator is immersed and other important aspects of the calibration such as: the liquids selected for the calibration, the number of coefficients used and the effect of the temperature in the coefficients and the calibration error.

4.1 Introduction

In order to estimate the density and viscosity values of the fluid in which the resonator is immersed, one of the main applications of this work (see chapter 5), a relationship between both quality factor and resonance frequency, against density and viscosity is required. Such study has been already reported for tuning fork resonators [Was11; Zha02; Kok84] and for extensional resonators [Cas10b; Duf14].

The main objective of this chapter is the assessment of a calibration method for piezoelectric MEMS resonators for simultaneous density and viscosity sensing. For this reason, different resonators were calibrated with
different calibration models and liquids since it is required for the final applications described in chapter 5.

In this work, the calibration procedure is carried out in two steps, each with adjustable parameters. In figure 4.1 is presented a summary of the whole calibration process.

Nevertheless, if the measurements are obtained with an impedance analyser it would only be necessary to perform the second step of the calibration process since $f_r$ and Q factor can be directly obtained through the adjustment of the impedance spectrum (see section 3.2.1).

![Figure 4.1: Steps to determine density and viscosity with the PLL-based and the discrete oscillator circuit.](image)

### 4.2 First step of the calibration process:

In the first step, the oscillator circuit outputs, oscillation frequency $f_{osc}$ and the circuit output gain $G_{osc}$, were transformed into the mechanical magnitudes of the resonator $f_r$ and Q factor applying the resonator model previously described in section 1.1.5, obtaining the expressions 4.1 and 4.2. The constant $K_{ic}$ and $\phi_{osc}$, which are not affected by the loading conditions of the resonator, were calculated by fitting the values of $f_r$, Q factor and the experimental data obtained for different liquids [Man14].

\[
f_r = \frac{f_{osc}}{\sqrt{1 - 2\pi K_{ic} \sin(\phi_{osc}) \frac{f_{osc}}{G_{osc}}}} \quad (4.1)
\]

\[
Q = \frac{f_{osc} f_r \tan(\phi_{osc})}{f_r^2 - f_{osc}^2} \quad (4.2)
\]

In the case of the PLL-based oscillator, due to the phase shift compensation provided by the instrument, the resonant frequency is obtained as the
4.3 Second step of the calibration process:

In the second step of the calibration process, the physical properties of the liquid in which the resonator is immersed, density and viscosity, were obtained from the figures of merit of the resonator, Q factor and $f_r$, previously obtained in the first step (see section 4.2). In this section, different calibration models of two, four, six and ten coefficients are compared for the later application in chapter 5.

4.3.1 Calibration model with two coefficients

In this section two different calibration model with two different coefficients are explained.

4.3.1.1 Waszczuk calibration model

The first model is used for the monitoring of lubricant oil condition and it was applied for the tuning-fork resonator (see section 2.3.1.1).

In this case, the resonance parameters, $f_r$ and Q factor, were obtained with an impedance analyser. Following the procedure reported by Waszczuk et al. [Was11] to solve the corresponding equations for both density and viscosity, we have estimated two different constants, $C_\mu$ and $C_\mu \rho$, through a calibration process. The procedure is as follow: Once the resonance parameters are known, the viscosity can be calculated through equations 4.4 and 4.5.

$$
\mu = C_\mu \frac{R_\mu^2}{f_r \rho}
$$

$$
R_\mu = \frac{k}{\omega_0 Q}
$$

Where $R_\mu$ represents the viscous damping coefficient of the tuning fork operating in liquid, $k$ the resonator spring constant and $\omega_0$ the angular
resonance frequency. Once the viscosity values are estimated, the density can be obtained through equation 4.6.

\[ \rho = \rho_0 - C_{\rho\mu} \sqrt{\frac{\mu \rho_0}{f_r}} \]  

(4.6)

Where \( \rho_0 \) is the initial density value that depends on the resonance frequency measured in liquid and on the tuning fork geometry and quartz density. Although the constant \( C_{\rho\mu} \) can be calculated on the basis of the tuning fork geometry and material parameters, it was also obtained along with the coefficient \( C_\mu \) in a calibration process (see figures 4.2 and 4.3).

In this case, the values of the calibration coefficients, \( C_\mu \) and \( C_{\rho\mu} \), were obtained using different viscosity standards [Sci] and liquids obtaining a value of \( 1.02 \times 10^{13} \) 1/m\(^4\) and 195.32 1/m, respectively, in the viscosity range of 0.5-56 mPa s. All the results obtained with this calibration model are described together with the application in section 5.2.1.

![Figure 4.2: Calibration curve of the tuning fork used to calculate the coefficient \( C_\mu \).](image)
4.3. Second step of the calibration process:

![Graph showing calibration curve](image)

Figure 4.3: Calibration curve of the tuning fork used to calculate the coefficient $C_{\rho \mu}$.

### 4.3.1.2 Matsiev calibration model

This calibration model was previously reported by Matsiev et al. [Mat99; Mat00]. The calibration coefficients ($d_1$ and $d_2$) were calculated using equations 4.7 and 4.8.

\[ Re\{Z_m(\omega_r)\} = R_m + d_2\sqrt{\mu\rho\omega_r} \]  
\[ Im\{Z_m(\omega_r)\} = \omega_r L_m - \frac{1}{\omega_r C_m} + \omega_r d_1 \rho + d_2\sqrt{\mu\rho\omega_r} \]  

where $\omega_r$ is the angular frequency; $\mu$ describes the dynamic viscosity; $\rho$ the density of the fluid; $R_m$, $L_m$ and $C_m$ the circuit equivalents of the unperturbed resonator; and $Re\{Z_m(\omega_r)\}$ and $Im\{Z_m(\omega_r)\}$ the real and imaginary parts of the motional impedance at the resonance frequency.

This calibration model is applied for the 13-mode resonator in section 4.4.1.1.

### 4.3.2 Calibration model with four and six coefficients

This calibration model adds additional terms to the damping modelling of the oscillatory fluid-structure interaction and it is intended to decrease the systematic deviation and the error.
In this model, the physical properties of the liquid in which the resonator is immersed, density and viscosity, were also obtained from the figures of merit of the resonator, Q factor and $f_r$. These are related to the mechanical properties of the resonators, i.e. resonator equivalent mass ($m$) and undamped resonance frequency in vacuum ($f_{o,vac}$), and the fluid conditions, i.e. distributed damping associated to the liquid ($g_1$) and the distributed equivalent added mass ($g_2$), both per unit length ($L$). A model allows the determination of these variables separately as in equations 4.9 and 4.10 [Cas10b; Maa05; You11b; Duf14; Tol17b; Tol17d].

$$f_r = \frac{f_{o,vac} \sqrt{1 - \frac{1}{2Q^2}}}{\sqrt{1 + \frac{Lg_2}{m}}}$$  \hspace{1cm} (4.9)$$

$$Q = \frac{2\pi \sqrt{1 + \frac{Lg_2}{m}}}{\frac{Lg_1}{m} f_{o,vac}}$$  \hspace{1cm} (4.10)$$

The parameters $g_1$ and $g_2$ represent the viscous damping and added mass due to the liquid and depend on the liquid properties, the resonator geometry and the operation frequency. They can be expressed in terms of the real and imaginary parts of a hydrodynamic function $\Gamma$ as in equations 4.11 and 4.12. Nevertheless, the dependence of the fluid damping and added mass on the viscosity and density of the fluid, as a closed-form analytical expression, is only available for simple geometries and particular cases [Lan87].

$$\Gamma_r = \frac{4}{\pi \rho b^2 g_2}$$  \hspace{1cm} (4.11)$$

$$\Gamma_i = \frac{4}{\pi \rho b^2} \frac{g_1}{\omega}$$  \hspace{1cm} (4.12)$$

In order to approximate the hydrodynamic function, a Taylor series expansion based on the Reynolds number, $Re = \rho \omega b^2 / 4\mu$, has been widely used (see equations 4.13 and 4.14) [Duf14; Tol17a].

$$\Gamma_r = A_0 + A_1 \frac{1}{\sqrt{Re}} + A_2 \frac{1}{Re}$$  \hspace{1cm} (4.13)$$

$$\Gamma_i = B_0 + B_1 \frac{1}{\sqrt{Re}} + B_2 \frac{1}{Re}$$  \hspace{1cm} (4.14)$$

Simplifying the previous equations, we could finally obtain the system of equations presented in equations 4.15 and 4.16, where the coefficients $a_i$ and $b_i$ are proportional to the coefficients $A_i$ and $B_i$. 

$$f_r = \frac{f_{o,vac} \sqrt{1 - \frac{1}{2Q^2}}}{\sqrt{1 + \frac{Lg_2}{m}}}$$  \hspace{1cm} (4.15)$$

$$Q = \frac{2\pi \sqrt{1 + \frac{Lg_2}{m}}}{\frac{Lg_1}{m} f_{o,vac}}$$  \hspace{1cm} (4.16)$$
4.3. Second step of the calibration process:

\[ g_2 = a_0 \rho + a_1 \frac{\sqrt{\rho \mu}}{f_r} + a_2 \mu \]  
(4.15)

\[ g_1 = b_0 \rho f_r + b_1 \sqrt{f_r \sqrt{\rho \mu}} + b_2 \mu \]  
(4.16)

In our case, since the width of the resonators is much larger than the thickness, it is possible to reduce the calibration model using only four coefficients obtaining the simplified system equations described in equations 4.17 and 4.18 [Duf12; Hei14; Hei15]. Since \( g_1 \) is associated with damping and \( g_2 \) with mass, it is straightforward to show that the expressions 4.7 and 4.8, previously described in section 4.3.1.2 are a particular case of 4.17 and 4.18, where \( b_2 = 0 \) and \( a_1 = b_1 \).

\[ g_2 = a_0 \rho + a_1 \frac{\sqrt{\rho \mu}}{f_r} \]  
(4.17)

\[ g_1 = b_1 \sqrt{f_r \sqrt{\rho \mu}} + b_2 \mu \]  
(4.18)

These equations were solved iteratively to obtain the values of the coefficients for each temperature that fit best to the experimental data. In order to solve the system of equations, the Levenberg-Marquardt algorithm [Lev44; Mar63] was used in Matlab [The].

Coefficients \( b_2 \) and \( a_0 \) are zero for an ideal zero-thickness plate moving in-plane [Duf14; Hei14]. Nevertheless, due to the relatively thick resonators used in this work they show non-zero values that allow to separate density and viscosity (see table 5.6).

- Error and sensor resolution:

Once the density and viscosity for each liquid is known, both the error associated with the calibration process and the resolution can be determined. The error terms, i.e. \( \varepsilon_\mu \) and \( \varepsilon_\rho \), are calculated as the deviation between the values of viscosity and density deduced from our calibration and the values measured with the commercial instrument. The reference values for density and viscosity were measured at controlled temperature with the commercial density-viscosity meter Anton Paar DMA4100 [Ant14b]. To estimate the resolution of the sensor, uncertainty propagation is applied to the measured fluctuations in \( f_r \) and Q factor by equations 4.19 and 4.20.

\[ \Delta \rho = \sqrt{\left( \frac{\partial \rho}{\partial f_r} \Delta f_r \right)^2 + \left( \frac{\partial \rho}{\partial Q} \Delta Q \right)^2} \]  
(4.19)
\[ \Delta \mu = \sqrt{\left( \left| \frac{\partial \mu}{\partial f_r} \right| \Delta f_r \right)^2 + \left( \left| \frac{\partial \mu}{\partial Q} \right| \Delta Q \right)^2} \tag{4.20} \]

Where \( \Delta \rho \) and \( \Delta \mu \) are the estimated resolutions for density and viscosity, respectively, and the partial derivatives are computed from equations 4.9, 4.10, 4.17 and 4.18.

### 4.3.3 Calibration model with ten coefficients

Finally, an advanced calibration model, based on a higher order Taylor series of the previously described hydrodynamic function, for determining the density and viscosity, was established. In this case, the calibration model presents ten coefficients, five for each part of the hydrodynamic function, in order to reduce the calibration error [Tol17b].

In order to approximate the hydrodynamic function previously described in equations 4.11 and 4.12, a Taylor series expansion based also on the Reynolds number was implemented as in equations 4.21 and 4.22.

\[ \Gamma_r = a_0 + a_1 \frac{1}{\sqrt{Re}} + a_2 \frac{1}{Re} + a_3 \frac{1}{Re^{3/2}} + a_4 \frac{1}{Re^2} \tag{4.21} \]

\[ \Gamma_i = b_0 + b_1 \frac{1}{\sqrt{Re}} + b_2 \frac{1}{Re} + b_3 \frac{1}{Re^{3/2}} + b_4 \frac{1}{Re^2} \tag{4.22} \]

Substituting in the previous equations the expression of the Reynolds number, \( Re = \frac{\rho \omega b^2}{4 \mu} \), we could finally obtain the system equations presented in equations 4.23 and 4.24. This model was also solved iteratively with a Levenberg-Marquardt algorithm to obtain the values of the coefficients, \( a_i \) and \( b_i \), that fit best to the experimental data.

\[ g_2 = a_0 \rho + a_1 \frac{\sqrt{\rho \mu}}{f_{r}} + a_2 \frac{\mu}{f_{r}} + a_3 \frac{\mu^{3/2}}{f_{r}^{3/2} \sqrt{\rho}} + a_4 \frac{\mu^2}{f_{r}^{2} \rho} \tag{4.23} \]

\[ g_1 = b_0 \rho f_{r} + b_1 \sqrt{f_{r} \sqrt{\rho \mu}} + b_2 \mu + b_3 \frac{\mu^{3/2}}{f_{r} \sqrt{\rho}} + b_4 \frac{\mu^2}{f_{r} \rho} \tag{4.24} \]

### 4.4 Other aspects to consider in the calibration procedure

In this section, the previously described calibration models are applied for different resonators, 13-mode and 15-mode, and calibration liquids in order to clarify other aspects that should be consider in the calibration procedure.
such as: the liquids selected for the calibration, the number of coefficients used and the effect of the temperature in the calibration error.

### 4.4.1 Calibration of the 13-mode with viscosity standards and other liquids

In this section, the 13-mode (see section 2.3.2.2) was calibrated with different test liquids and calibration models taking into account the number of coefficients for the calibration, the liquids selected for the calibration process, the temperature and the effect of the resonant frequency in vacuum.

Firstly, the main resonant parameters, $f_r$ and Q factor, were obtained with an impedance analyser. The electrical impedance measurements, obtained in a previous work [Pfu15], were fitted to a Butterworth-van Dyke equivalent circuit (see figure 2.3) [Man09] in order to estimate $f_r$ and Q factor (see table 4.1).

In this case, reference measurements of density and viscosity of different liquids were performed with a temperature control unit in a temperature range from 20 to 100 °C ± 0.5 °C. In order to carry out the density-viscosity measurements, we have used a laboratory density-viscosity meter Stabinger SVM3000 [Ant14c] which presents an accuracy of 0.0005 g mL$^{-1}$ and 0.35% for the density and viscosity, respectively. The liquids measured in this section comprise a range of 0.78-0.92 g mL$^{-1}$ and 1-286 mPa s for the density and viscosity, respectively. The liquids D5, N10, N35 and N100 are viscosity standards from Paragon Scientific [Sci]. The liquids DITA and PAO8 are synthetic oils. For the case of the PAO8, the number indicates the kinematic viscosity at 100 °C. In addition, an ester and olive oil were included in this study.

Table 4.1: Resonance parameters measured with the impedance analyser and viscosity-density values ($\mu$ and $\rho$) measured with the commercial density-viscosity meter in several liquids at different temperatures for the 13-mode.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Temperature</th>
<th>$f_r$ [Hz]</th>
<th>$Q$</th>
<th>$\mu$ [mPa s]</th>
<th>$\rho$ [g mL$^{-1}$]</th>
<th>$f_r$ [Hz]</th>
<th>$Q$</th>
<th>$\mu$ [mPa s]</th>
<th>$\rho$ [g mL$^{-1}$]</th>
<th>$f_r$ [Hz]</th>
<th>$Q$</th>
<th>$\mu$ [mPa s]</th>
<th>$\rho$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5</td>
<td>20 °C</td>
<td>424210</td>
<td>76.73</td>
<td>5.718</td>
<td>0.839</td>
<td>425990</td>
<td>101.90</td>
<td>3.345</td>
<td>0.825</td>
<td>430270</td>
<td>161.25</td>
<td>1.198</td>
<td>0.785</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>420754</td>
<td>43.87</td>
<td>18.004</td>
<td>0.851</td>
<td>423714</td>
<td>67.14</td>
<td>8.518</td>
<td>0.838</td>
<td>427140</td>
<td>96.62</td>
<td>4.527</td>
<td>0.809</td>
</tr>
<tr>
<td></td>
<td>100 °C</td>
<td>415519</td>
<td>22.36</td>
<td>73.834</td>
<td>0.858</td>
<td>420305</td>
<td>37.22</td>
<td>27.388</td>
<td>0.846</td>
<td>425470</td>
<td>97.12</td>
<td>4.527</td>
<td>0.809</td>
</tr>
<tr>
<td>N10</td>
<td>20 °C</td>
<td>408437</td>
<td>11.98</td>
<td>286.360</td>
<td>0.866</td>
<td>415711</td>
<td>19.91</td>
<td>86.800</td>
<td>0.854</td>
<td>425470</td>
<td>62.06</td>
<td>9.712</td>
<td>0.818</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>407705</td>
<td>20.79</td>
<td>81.355</td>
<td>0.913</td>
<td>412253</td>
<td>34.42</td>
<td>35.467</td>
<td>0.899</td>
<td>419330</td>
<td>68.11</td>
<td>7.301</td>
<td>0.860</td>
</tr>
<tr>
<td></td>
<td>100 °C</td>
<td>408735</td>
<td>23.94</td>
<td>58.632</td>
<td>0.912</td>
<td>411278</td>
<td>29.31</td>
<td>41.539</td>
<td>0.902</td>
<td>421410</td>
<td>71.82</td>
<td>7.907</td>
<td>0.863</td>
</tr>
<tr>
<td>N35</td>
<td>20 °C</td>
<td>417643</td>
<td>93.561</td>
<td>59.789</td>
<td>0.829</td>
<td>413117</td>
<td>37.33</td>
<td>23.505</td>
<td>0.898</td>
<td>419520</td>
<td>88.89</td>
<td>4.527</td>
<td>0.857</td>
</tr>
<tr>
<td></td>
<td>40 °C</td>
<td>406245</td>
<td>19.16</td>
<td>98.884</td>
<td>0.916</td>
<td>422425</td>
<td>31.47</td>
<td>37.146</td>
<td>0.816</td>
<td>432640</td>
<td>76.69</td>
<td>6.204</td>
<td>0.780</td>
</tr>
<tr>
<td>N100</td>
<td>20 °C</td>
<td>408735</td>
<td>23.94</td>
<td>58.632</td>
<td>0.912</td>
<td>411278</td>
<td>29.31</td>
<td>41.539</td>
<td>0.902</td>
<td>421410</td>
<td>71.82</td>
<td>7.907</td>
<td>0.863</td>
</tr>
<tr>
<td>Olive oil</td>
<td>20 °C</td>
<td>407705</td>
<td>20.79</td>
<td>81.355</td>
<td>0.913</td>
<td>412253</td>
<td>34.42</td>
<td>35.467</td>
<td>0.899</td>
<td>419330</td>
<td>68.11</td>
<td>7.301</td>
<td>0.860</td>
</tr>
<tr>
<td>DITA</td>
<td>20 °C</td>
<td>408735</td>
<td>23.94</td>
<td>58.632</td>
<td>0.912</td>
<td>411278</td>
<td>29.31</td>
<td>41.539</td>
<td>0.902</td>
<td>421410</td>
<td>71.82</td>
<td>7.907</td>
<td>0.863</td>
</tr>
<tr>
<td>PAO8</td>
<td>20 °C</td>
<td>417643</td>
<td>93.561</td>
<td>59.789</td>
<td>0.829</td>
<td>413117</td>
<td>37.33</td>
<td>23.505</td>
<td>0.898</td>
<td>419520</td>
<td>88.89</td>
<td>4.527</td>
<td>0.857</td>
</tr>
<tr>
<td>Ester oil</td>
<td>20 °C</td>
<td>407705</td>
<td>20.79</td>
<td>81.355</td>
<td>0.913</td>
<td>412253</td>
<td>34.42</td>
<td>35.467</td>
<td>0.899</td>
<td>419330</td>
<td>68.11</td>
<td>7.301</td>
<td>0.860</td>
</tr>
</tbody>
</table>
In the next sections, three different calibration models were compared in order to obtain the density and viscosity of the liquid in which the resonator is immersed. The first model is based on the previous work reported by Matsiev et al. where two coefficients were required to determine the density and viscosity (see section 4.3.1.2). However, the other two models are based on a Taylor series of the hydrodynamic function where four and six coefficients were used in the calibration (see section 4.3.2).

4.4.1.1 Calibration of the 13-mode using two coefficients

Firstly, the resonator was calibrated using the calibration model previously reported by Matsiev et al. (see section 4.3.1.2). The calibration coefficients \(d_1\) and \(d_2\) were calculated using equations 4.7 and 4.8 and the liquid N35 as reference.

As it can be seen in table 4.2, the error in the estimation of the density is around 1% whereas the viscosity error is around 23% at 100 °C when two coefficients are used. This deviation at higher temperatures suggests that the dependency of \(f_r\) and Q factor on the temperature affects the measurement accuracy [Han02; Sch14].

Table 4.2: Mean viscosity and density error \((\epsilon\mu, \epsilon\rho)\) compared with the values obtained with the commercial density-viscosity meter using all the liquids in the case of the four coefficients model.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>2</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration liquid</td>
<td>N35</td>
<td>All liquids</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>(\epsilon\mu) [%]</td>
<td>6.34</td>
<td>6.87</td>
</tr>
<tr>
<td>(\epsilon\rho) [%]</td>
<td>0.64</td>
<td>0.55</td>
</tr>
</tbody>
</table>

4.4.1.2 Calibration of the 13-mode using four coefficients

Secondly, the calibration model of four coefficients, previously described in section 4.3.2, was applied in order to decrease the systematic deviation and the error in viscosity at 100 °C. This procedure results in the density and viscosity values presented in figures 4.4, 4.5 and 4.6 at 20, 40 and 100 °C, respectively. In this procedure, all the available liquids were used in the calibration process with four coefficients, so the overdetermined system of equations was solved using the Levenberg-Marquardt algorithm.
4.4. Other aspects to consider in the calibration procedure

Figure 4.4: Viscosity and density values estimated from calibration models and measured with the density-viscosity meter at 20 ºC.

Figure 4.5: Viscosity and density values estimated from calibration models and measured with the density-viscosity meter at 40 ºC.
As it was described in section 4.4.1.1, for the calibration model with two coefficients, only the N35 was used as a calibration liquid for each temperature: 20, 40 and 100 °C. In that case, the mean viscosity error at 100 °C is around 23.4% whereas the density error is around 1%. However, in the calibration model with four coefficients, we used all the available liquids in the calibration process at each temperature, thus being able to reduce the viscosity error to a value around 7.2%, in the worst case scenario.

As it can be seen in table 4.2, the viscosity error increases with temperature, particularly for the calibration model with two coefficients. This is associated with the absence of coefficient $b_2$ which appears in the four coefficients model and which is proportional to the viscous damping. Furthermore, the high error observed at 100 °C may be also influenced by the temperature controller since a slight deviation of the temperature during the impedance measurement affect the $f_r$ and Q factor values and therefore the density and viscosity estimated with the calibration model. In order to make a fair comparison of the calibration error between the different calibration models, we used the N35 as calibration liquid in the four coefficients model. In order to solve the underdetermined system of equations, the Levenberg-Marquardt algorithm was also used in Matlab. The mean error at 100 °C was approximately the same as with the Matsiev model. Nevertheless, if we introduced the D5, N35 and N100 as calibration liquids, the error decreases, resulting in a viscosity error of about 9.2% at 100 °C (see table 4.3).
4.4. Other aspects to consider in the calibration procedure

According to the obtained results, we can conclude that the error depends not only on the calibration model or the number of coefficients but also on the liquids selected to determine the coefficients.

Table 4.3: Mean viscosity and density error ($\epsilon_\mu$, $\epsilon_\rho$) at 100 °C compared with the values obtained with the commercial density-viscosity meter using the N35 and D5-N35-N100 as calibration liquids.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients</td>
<td>2</td>
</tr>
<tr>
<td>Calibration liquid</td>
<td>N35</td>
</tr>
<tr>
<td>$\epsilon_\mu$ [%]</td>
<td>23.44</td>
</tr>
<tr>
<td>$\epsilon_\rho$ [%]</td>
<td>1.04</td>
</tr>
</tbody>
</table>

4.4.1.3 Calibration of the 13-mode using six coefficients

This calibration model arises from the previous equations 4.15 and 4.16, where the coefficients $a_2$ and $b_0$ are also considered. In this case, we used three calibration liquids, D5-N35-N100 in order to calculate the six coefficients. Nevertheless, the addition of two terms in the Taylor series does not reduce the mean error for the other validation liquids (see table 4.4).

Table 4.4: Mean viscosity and density error ($\epsilon_\mu$, $\epsilon_\rho$) at 100 °C compared with the values obtained with the commercial density-viscosity meter using the N35 and D5-N35-N100 as calibration liquids.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients</td>
<td>2</td>
</tr>
<tr>
<td>Calibration liquid</td>
<td>N35</td>
</tr>
<tr>
<td>$\epsilon_\mu$ [%]</td>
<td>23.44</td>
</tr>
<tr>
<td>$\epsilon_\rho$ [%]</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The main reason is that for the model of four coefficients there is a training or optimization of the coefficients, but there is only one possible solution for the model of six coefficients. However, if we use all the liquids in the calibration process, as we can see in table 4.5, the mean error in viscosity is lower when we use the model of six coefficients at 100 and 20 °C.
Table 4.5: Mean viscosity and density error ($\epsilon_{\mu}$, $\epsilon_{\rho}$) at 100 and 20 °C compared with the values obtained with the commercial density-viscosity meter using the N35 and all the calibration liquids.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>100</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Calibration liquid</td>
<td>N35</td>
<td>All liquids</td>
</tr>
<tr>
<td>$\epsilon_{\mu}$ [%]</td>
<td>23.44</td>
<td>7.21</td>
</tr>
<tr>
<td>$\epsilon_{\rho}$ [%]</td>
<td>1.04</td>
<td>0.44</td>
</tr>
</tbody>
</table>

4.4.1.4 Cross-validation for determining the optimal liquids for calibration

As it can be inferred from the results obtained in previous sections, there is a clear dependence between the selected liquids in the calibration process and the calibration error. In order to obtain the optimal liquids for the calibration process, a cross-validation function [Gol79; Luk06] was implemented in Matlab [The] using the model of four coefficients.

A cross-validation process, is any of various similar model validation techniques for assessing how the results of a statistical analysis will generalize to an independent data set [Koh95]. In a prediction problem, a model is usually given a dataset of known data on which training is run, and a dataset of unknown data against which the model is tested. The goal of cross-validation is to test the ability of the model to predict new data in order to flag problems like overfitting and to give an insight on how the model will generalize to an independent dataset [Sen10].

Table 4.6: Mean viscosity and density error ($\epsilon_{\mu}$, $\epsilon_{\rho}$) at 100 °C compared with the values obtained with the commercial density-viscosity meter using only one liquid in the calibration model of four coefficients.

<table>
<thead>
<tr>
<th>Calibration liquid</th>
<th>D5</th>
<th>N10</th>
<th>N35</th>
<th>N100</th>
<th>Olive oil</th>
<th>DITA</th>
<th>PAO8</th>
<th>Ester oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{\mu}$ [%]</td>
<td>13.83</td>
<td>8.10</td>
<td>19.27</td>
<td>8.27</td>
<td>8.51</td>
<td>13.65</td>
<td><strong>7.30</strong></td>
<td>7.41</td>
</tr>
<tr>
<td>$\epsilon_{\rho}$ [%]</td>
<td>1.20</td>
<td>0.82</td>
<td>0.74</td>
<td>0.61</td>
<td>0.72</td>
<td>2.13</td>
<td><strong>0.61</strong></td>
<td>0.68</td>
</tr>
</tbody>
</table>

This cross-validation process was used to estimate density and viscosity of different liquids using other as calibration liquids. As it can be observed in table 4.6, the optimal liquid to obtain the lowest mean calibration error is the PAO8, instead of the N35 used previously for the model with two coefficients. These results suggest that the error may be minimized if the calibration liquid is positioned near the middle of the density-viscosity range. In order to clarify the cross-validation process and the error analysis,
the density-viscosity error for each calibration liquid was estimated.

As it can be seen in figures 4.7 and 4.8, the validation liquids that are farthest from the calibration liquid show a higher error. Nevertheless, if we focus on the calibration error when the N35 is selected as calibration liquid, we can see that it leads to a higher error. One possible reason for this increase in the calibration error may be the temperature controller used, which has a resolution of ±0.5 °C compared with the ±0.02 °C of the commercial instrument. As indicated in the certificate of calibration of the viscosity standards, the N10 has approximately a sensitivity of 0.68 mPa s/°C around 20 °C. Therefore, if the temperature resolution is ±0.5 °C we can estimate an error of ±0.34 mPa s, which corresponds to 1.9% for the N10 at 20 °C. As this value is comparable to that previously obtained with the different calibration models, we can confirm that the temperature controller may affect the calibration error.

As it can be observed in figures 4.7 and 4.8, the results obtained with the cross-validation process do not follow a clear pattern. This may be associated with the contributions from different error sources such as: the commercial density-viscosity meter, the impedance measurements, the temperature controller and the calibration model which is based on an approximation to the hydrodynamic function.

![Figure 4.7: Density error at 100 °C compared with the values obtained with the commercial density-viscosity meter using only one liquid in the calibration model of four coefficients.](image-url)
Figure 4.8: Viscosity error at 100 °C compared with the values obtained with the commercial density-viscosity meter using only one liquid in the calibration model of four coefficients.

In addition, the same cross-validation process was performed, but using two liquids for the calibration model with four coefficients.

Table 4.7: Mean viscosity and density error ($\epsilon_{\mu}$, $\epsilon_{\rho}$) at 100 °C compared with the values obtained with the commercial density-viscosity meter using a combination of two liquids for the calibration model of four coefficients.

<table>
<thead>
<tr>
<th>$\epsilon_{\mu}$ [%]</th>
<th>D5</th>
<th>N10</th>
<th>N35</th>
<th>N100</th>
<th>Olive oil</th>
<th>DITA</th>
<th>PAO8</th>
<th>Ester oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{\rho}$ [%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>47.36</td>
<td>64.81</td>
<td>6.92</td>
<td>9.11</td>
<td>9.82</td>
<td>8.43</td>
<td>6.83</td>
<td></td>
</tr>
<tr>
<td>N10</td>
<td>1.08</td>
<td>65.19</td>
<td>5.75</td>
<td>8.46</td>
<td>9.42</td>
<td>6.18</td>
<td>5.73</td>
<td></td>
</tr>
<tr>
<td>N35</td>
<td>0.53</td>
<td>0.43</td>
<td>15.55</td>
<td>21.78</td>
<td>15.43</td>
<td>30.54</td>
<td>20.50</td>
<td></td>
</tr>
<tr>
<td>N100</td>
<td>0.66</td>
<td>0.57</td>
<td>0.57</td>
<td>16.21</td>
<td>27.16</td>
<td>5.98</td>
<td>5.86</td>
<td></td>
</tr>
<tr>
<td>Olive oil</td>
<td>0.44</td>
<td>0.39</td>
<td>0.38</td>
<td>1.24</td>
<td>22.65</td>
<td>10.40</td>
<td>28.96</td>
<td></td>
</tr>
<tr>
<td>DITA</td>
<td>1.18</td>
<td>1.17</td>
<td>1.46</td>
<td>4.70</td>
<td>6.14</td>
<td>11.10</td>
<td>32.40</td>
<td></td>
</tr>
<tr>
<td>PAO8</td>
<td>0.50</td>
<td>0.44</td>
<td>15.54</td>
<td>0.63</td>
<td>0.45</td>
<td>1.58</td>
<td>6.12</td>
<td></td>
</tr>
<tr>
<td>Ester oil</td>
<td>0.43</td>
<td>0.39</td>
<td>0.38</td>
<td>0.93</td>
<td>0.54</td>
<td>5.96</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7 shows the mean error obtained with all the possible combinations using two calibration liquids at 100 °C where the upper diagonal indicates the error in viscosity and the lower the error in density. As it can be seen, the combination of ester oil-N10 presents the lowest error in viscosity with a value of around 5.73%. Moreover, the liquids olive oil-N35 presents the lowest error in density with a value of around 0.38%. In order
to confirm the results of the cross-validation procedure, we carried out a sensitivity analysis of the resonant parameters to the liquid magnitudes using all the calibration liquids with the model of four coefficients at 20 °C [You11b; VB15].

Table 4.8: Sensitivities of $\rho$ and $\mu$ to $f_r$ and Q factor using all the calibration liquids with the model of four coefficients at 20 °C.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\frac{\partial \rho}{\partial f_r}$ [$\text{g s mL}^{-1}$]</th>
<th>$\frac{\partial \rho}{\partial Q}$ [$\text{g mL}^{-1}$]</th>
<th>$\frac{\partial \mu}{\partial f_r}$ [$\text{m Pas}^2$]</th>
<th>$\frac{\partial \mu}{\partial Q}$ [m Pas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5</td>
<td>$-6.16 \times 10^{-6}$</td>
<td>$1.65 \times 10^{-4}$</td>
<td>$1.81 \times 10^{-6}$</td>
<td>$-1.51 \times 10^{-1}$</td>
</tr>
<tr>
<td>N10</td>
<td>$-6.27 \times 10^{-6}$</td>
<td>$5.17 \times 10^{-4}$</td>
<td>$5.54 \times 10^{-6}$</td>
<td>$-8.35 \times 10^{-1}$</td>
</tr>
<tr>
<td>N35</td>
<td>$-6.40 \times 10^{-6}$</td>
<td>$2.10 \times 10^{-3}$</td>
<td>$2.55 \times 10^{-5}$</td>
<td>$-6.82$</td>
</tr>
<tr>
<td>N100</td>
<td>$-6.54 \times 10^{-6}$</td>
<td>$8.00 \times 10^{-3}$</td>
<td>$1.42 \times 10^{-4}$</td>
<td>$-5.17 \times 10^1$</td>
</tr>
<tr>
<td>Olive oil</td>
<td>$-6.76 \times 10^{-6}$</td>
<td>$2.53 \times 10^{-3}$</td>
<td>$1.86 \times 10^{-5}$</td>
<td>$-8.56$</td>
</tr>
<tr>
<td>DITA</td>
<td>$-6.74 \times 10^{-6}$</td>
<td>$1.88 \times 10^{-3}$</td>
<td>$1.25 \times 10^{-5}$</td>
<td>$-5.48$</td>
</tr>
<tr>
<td>PAO8</td>
<td>$-6.28 \times 10^{-6}$</td>
<td>$2.53 \times 10^{-3}$</td>
<td>$3.79 \times 10^{-5}$</td>
<td>$-9.24$</td>
</tr>
<tr>
<td>Ester oil</td>
<td>$-6.81 \times 10^{-6}$</td>
<td>$3.01 \times 10^{-3}$</td>
<td>$2.20 \times 10^{-5}$</td>
<td>$-1.11 \times 10^1$</td>
</tr>
</tbody>
</table>

As it can be observed in table 4.8, the viscosity was more sensitive to the Q factor variation. Therefore, a slight variation in the temperature during the measurement may increase the error in Q factor and therefore in the viscosity.

4.4.1.5 Calibration at different temperatures

Once the calibration coefficients are calculated at a given temperature, it is important to know the temperature range in which they can be considered valid and the resulting error. In order to verify this, we compared the coefficients obtained at different temperatures using all the liquids in the calibration process.

Table 4.9: Values of the coefficients obtained with the calibration models at different temperatures.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Temperature [°C]</th>
<th>$a_0$ [$m^2$]</th>
<th>$a_1$ [m]</th>
<th>$a_2$ [ ]</th>
<th>$b_0$ [$m^2$]</th>
<th>$b_1$ [m]</th>
<th>$b_2$ [ ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>20</td>
<td>0.23</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
<td>3.68</td>
<td>-20.29</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.23</td>
<td>2.60</td>
<td>-</td>
<td>-</td>
<td>3.57</td>
<td>-15.66</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.23</td>
<td>-3.17</td>
<td>-</td>
<td>-</td>
<td>4.02</td>
<td>-408.66</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.22</td>
<td>1.70</td>
<td>-22.04</td>
<td>$-1.223 \times 10^{-4}$</td>
<td>1.90</td>
<td>-9.93</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>0.23</td>
<td>1.05</td>
<td>17.13</td>
<td>$5.05 \times 10^{-4}$</td>
<td>1.49</td>
<td>30.37</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.24</td>
<td>-6.54</td>
<td>1106.90</td>
<td>$7.31 \times 10^{-4}$</td>
<td>1.18</td>
<td>103.13</td>
</tr>
</tbody>
</table>

As it can be seen in table 4.9, there is a difference of less than 10% in the coefficients when going from 20 to 40 °C. Nevertheless, when the
temperature increases up to 100 °C, the differences are greater, especially for the coefficients related to the higher order terms in the Taylor series.

The same can be applied to the model with six coefficients. In this case, the coefficient $a_0$ is approximately constant at different temperatures, while the rest of the coefficients change their value significantly. In order to confirm that, the density and viscosity values were estimated at 20 °C using the coefficients at 40 °C and compared with the measurements of the commercial density-viscosity meter at 20 °C, obtaining an error lower than 1 and 3% for the density and viscosity, respectively. As this error is similar to that previously obtained in the calibration using all the liquids at 20 °C, we can conclude that the coefficients calculated at 20 °C can be used to estimate the density and viscosity of liquids at temperatures of 40 °C and vice versa.

### 4.4.1.6 Effect of the resonant frequency in vacuum

Another important issue is the effect of the resonant frequency in vacuum, $f_{o,vac}$, in the calibration error since it is expected to depend on temperature [Han02; Hop07; Jin10]. As it can be observed in equations 4.9 and 4.10, $f_{o,vac}$ appears as an additional term in the expression of $f_r$ and Q factor. Therefore the term $f_{o,vac}$ could also introduce an error in the calibration process. For this reason, we have introduced $f_{o,vac}$ in the calibration model as another calibration coefficient. For the 13-mode, the value of $f_{o,vac}$ measured at 20 °C was around 711.78 kHz. In order to check the effect of $f_{o,vac}$, we used the model of four coefficients at 100 °C and the optimal liquids previously obtained with the cross-validation process in section 4.4.1.4, N10-ester oil, where the mean error in viscosity is minimal.

As it can be observed in figures 4.9 and 4.10, there is a minimum mean error at around 711 kHz for the density. Nevertheless, the effect of this coefficient in the calibration error is insignificant since the error produced by the possible variation of $f_{o,vac}$ with the temperature will be low compared with other error sources such as the temperature controller, the uncertainty in the impedance measurements or the calibration model. Something similar occurs when we introduce all the liquids in the calibration process at 20, 40 and 100 °C. Furthermore, the difference observed between $f_r$ in air and $f_{o,vac}$ is minimal, 710.26 and 711.78 kHz, respectively. Therefore, we can also conclude that it is not necessary an accurate measurement of $f_{o,vac}$ since the calibration error will be similar.
4.4. Other aspects to consider in the calibration procedure

Figure 4.9: Effect of the resonant frequency in vacuum in the density calibration error at different temperatures.

Figure 4.10: Effect of the resonant frequency in vacuum in the viscosity calibration error at different temperatures.

4.4.2 Calibration of the 15-mode with mixtures of lubricant oil with diesel

In this section, the 15-mode (see section 2.3.2.3) was calibrated with different mixtures of lubricant oil with diesel using an advanced calibration model of ten coefficients [Tol17b]. In this case, the number of coefficients for the
calibration and the effect of the temperature in the calibration error was studied.

The calibration process was implemented with seven mixtures of lubricant oil SAE 0W30 with diesel. The mixtures were labelled as F0, F2, F4, F6, F7, F8 and F10, where the number means the percentage of diesel in the lubricant oil SAE 0W30. These mixtures comprise a range between 0.8505-0.8071 g mL\(^{-1}\) and 89.66-7.55 mPa s for the density and viscosity, respectively. For the application of our system as a sensor, the reference measurements of density and viscosity of the different mixtures were performed with a temperature control unit capable of setting a target temperature with deviations of ±0.05 °C (see section 3.4).

Figure 4.11 shows the value of \(f_r\) and Q factor for the different mixtures (F0-F10) and temperatures (T1=25, T2=40, T3=55, T4=70 and T5=90 °C) obtained with the PLL-based oscillator circuit. As it can be observed, an almost linear increase occurs for \(f_r\) and Q factor when the temperature increases, since the density and viscosity decrease. These results show the potential to distinguish between the different mixtures of lubricant oil with diesel at different temperatures.

In addition, the resolution of \(f_r\) and Q factor were evaluated by recording 1000 samples (see section 3.3.1). As it can be seen in figure 4.12, the resolutions obtained were below 74 mHz for \(f_r\) and 0.1 for Q factor in the worst scenario, i.e. when the resonator was immersed in the pure lubricant.
4.4. Other aspects to consider in the calibration procedure

oil SAE 0W30 at 25 °C.

Figure 4.12: Q factor and $f_r$ resolution as a function of the measured Q factor of the 15-mode for the different mixtures of lubricant oil with diesel at different temperatures.

4.4.2.1 Calibration coefficients

Once the system of equations, describing an advanced calibration model, was presented in section 4.3.3, different particular cases of the model were studied with the aim of obtaining an optimal calibration model which presents an acceptable calibration error with the minimal number of coefficients. In this case, the coefficients for each calibration model were estimated using the seven mixtures of lubricant oil with diesel (F0-F10) at 25, 40, 55, 70 and 90 °C (T1-T5) as calibration fluids (see table 4.10).

With the aim of determining the density and viscosity of a fluid through a calibration process, it is important to know the temperature range in which the coefficients can be considered valid. In order to verify this, we compared the coefficients obtained at different temperatures using all the fluids in the calibration process. As it can be seen in table 4.10, the coefficient $a_0$ is approximately constant at different temperatures. Nevertheless, the rest of the coefficients change their value significantly when the temperature increases, being especially true for the coefficients related to the higher order terms in the Taylor series.
Table 4.10: Values of the coefficients obtained for each calibration model and temperature for the 15-mode. The crossed out cells indicate that the coefficients are assumed to be zero to vary the dimensionality of the calibration model. F0-F10 stands for all the mixtures F0, F2, F4, F6, F7, F8, F10. T1-T5 stands for all the temperatures T1, T2, T3, T4, and T5.

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Calibration fluids</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0 )</td>
<td>( b_1 )</td>
<td>( b_2 )</td>
<td>( b_3 )</td>
<td>( b_4 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 25ºC} )</td>
<td>( 0.109 )</td>
<td>( 0.62 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F0-F10 at 40ºC} )</td>
<td>( 0.110 )</td>
<td>( 0.53 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F0-F10 at 55ºC} )</td>
<td>( 0.111 )</td>
<td>( 0.32 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F0-F10 at 70ºC} )</td>
<td>( 0.111 )</td>
<td>( 0.32 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F0-F10 at 90ºC} )</td>
<td>( 0.110 )</td>
<td>( 0.73 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{F0 at T1-T5} )</td>
<td>( 0.111 )</td>
<td>( 0.39 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Calibration fluids</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0 )</td>
<td>( b_1 )</td>
<td>( b_2 )</td>
<td>( b_3 )</td>
<td>( b_4 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 25ºC} )</td>
<td>( 0.109 )</td>
<td>( 0.30 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 40ºC} )</td>
<td>( 0.107 )</td>
<td>( 1.85 )</td>
<td>-184</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 55ºC} )</td>
<td>( 0.107 )</td>
<td>( 5.66 )</td>
<td>-506</td>
<td>-782.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 70ºC} )</td>
<td>( 0.102 )</td>
<td>( 7.33 )</td>
<td>-125.0</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 90ºC} )</td>
<td>( 0.110 )</td>
<td>( 0.73 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0 at T1-T5} )</td>
<td>( 0.111 )</td>
<td>( 0.75 )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Calibration fluids</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b_0 )</td>
<td>( b_1 )</td>
<td>( b_2 )</td>
<td>( b_3 )</td>
<td>( b_4 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 25ºC} )</td>
<td>( 0.110 )</td>
<td>( 2.86 )</td>
<td>-685.6</td>
<td>6.29 ( \times 10^4 )</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 40ºC} )</td>
<td>( 0.107 )</td>
<td>( 2.53 )</td>
<td>-2.53</td>
<td>324.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 55ºC} )</td>
<td>( 0.123 )</td>
<td>( -5.06 )</td>
<td>631.9</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 70ºC} )</td>
<td>( 0.102 )</td>
<td>( -1.90 ) ( \times 10^{-3} )</td>
<td>1.76</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0-F10 at 90ºC} )</td>
<td>( 0.110 )</td>
<td>( -2.19 ) ( \times 10^{-3} )</td>
<td>13.56</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{F0 at T1-T5} )</td>
<td>( 0.112 )</td>
<td>( 1.55 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.4.2.2 Calibration error and sensor resolution

Once the calibration coefficients were calculated, the density and viscosity were estimated using different fluids at different temperatures in the calibration process. The mean error term was calculated as the deviation between the values of density and viscosity estimated from our calibration and those measured with a commercial density-viscosity meter, Anton Paar DMA4100M [Ant14b]. This error term was used as a key parameter to compare between the different calibration models and to determine which model is the most suitable.

As it can be observed in table 4.11, if the fluids (F0-F10) at 25 °C are selected as calibration fluids, the mean viscosity and density error increases with the number of coefficients. As it can be seen, if the number of coefficients increase, the calibration model fits better to the initial calibration fluids at 25 °C but increases the error for the rest of them. For example, the calibration error for the model of eight coefficients was around 123% and 0.91% for viscosity and density, respectively.

Table 4.11: Mean viscosity and density error ($\epsilon_\mu$, $\epsilon_\rho$) compared with the values obtained with the commercial density-viscosity meter.

<table>
<thead>
<tr>
<th>Calibration fluids</th>
<th>Coefficients</th>
<th>$\epsilon_\mu$ [%]</th>
<th>$\epsilon_\rho$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0-F10 at 25°C</td>
<td>4</td>
<td>16.43</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20.90</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>43.82</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>123.10</td>
<td>0.91</td>
</tr>
<tr>
<td>F0-F10 at 55°C</td>
<td>4</td>
<td>9.72</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>8.09</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.90</td>
<td>0.47</td>
</tr>
<tr>
<td>F0 at T1-T5</td>
<td>4</td>
<td>6.24</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>3.85</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.07</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.80</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.61</td>
<td>0.11</td>
</tr>
<tr>
<td>F0 and F6 at T1-T5</td>
<td>10</td>
<td>3.84</td>
<td>0.07</td>
</tr>
</tbody>
</table>

With the aim of decreasing the error, the fluids (F0-F10) at 55 °C were selected as calibration fluids since these are located at a midpoint of the density-viscosity range. In this case it can be observed that the errors decrease considerably if we compare with the previous case. Therefore, we could conclude that this is an acceptable approach to reduce the mean calibration error. In this case, the mean calibration error was around 9.72-6.9% and 0.23-0.47% for viscosity and density, respectively.
In order to reduce even more the calibration error, the measurements of the pure lubricant oil SAE 0W30 at different temperatures (F0 at T1-T5) were selected as calibration fluids. In this case, the mean calibration error was the lowest, being around 6.2-3.8% and 0.14-0.08% for viscosity and density, respectively. This occurs because the density-viscosity range considered in the calibration process comprises almost the total density-viscosity range of application. Besides, we can conclude that the simplified model of five coefficients it is simple and precise enough to determine the density and viscosity of the fluids with an acceptable calibration error.

Nevertheless, for the model calibration of ten coefficients the mean calibration error was higher. The main reason is that for the model of eight coefficients there is a training or optimization of the coefficients, but there is only one possible solution for the model of ten coefficients. This occurs because we only have five calibration fluids, each one at a different temperature, and the system solution is unique. However, if we also introduce the mixture 94% lubricant oil-6% diesel as a calibration fluid in the calibration process (F0 and F6 at T1-T5), the mean calibration error is lower since there is a training of the coefficients. In this case we obtained a calibration error around 3.84% and 0.07% for the density and viscosity, respectively.

According to the obtained results, we can conclude that the error depends not only on the calibration model or the number of coefficients but also on the fluids selected to determine the coefficients. This conclusion was also observed in the cross-validation process in section 4.4.1.4. In addition, these results show the potential of piezoelectric MEMS resonators to distinguish between different mixtures of lubricant oil contaminated with diesel at different temperatures.

In addition, the density and viscosity resolutions were obtained from uncertainty propagation from $f_r$ and Q factor resolutions obtained in section 4.4.2. As it can be observed in figure 4.13, the density and viscosity resolutions increase when Q factor increases [Tol16b]. The sensor resolution was in the range $2.4 \times 10^{-6}$-2.8 $\times 10^{-4}$ g mL$^{-1}$ and $2 \times 10^{-3}$-1.2 mPa s for the density and viscosity, respectively. The resolution and the calibration error obtained are better in density than in viscosity since the Q factor determined from the measurement of $G_{osc}$, presents a worse resolution than $f_r$. 
4.4. Other aspects to consider in the calibration procedure

Figure 4.13: Density and viscosity resolution as a function of the measured Q factor for the different mixtures of lubricant oil with diesel at different temperatures.

4.4.3 Summary of the calibration procedure

In order to clarify all the concepts, a summary with the most important aspects to consider in a calibration process is presented.

■ We could observed that the model of two coefficients is not precise enough for the estimation of the density-viscosity values at high temperatures because of the absence of the coefficient $b_2$ which is proportional to the viscous damping.

■ A cross-validation process demonstrate the importance of the liquids selected in order to reduce the calibration error.

■ The effect of $f_{o,vac}$ in the calibration error is insignificant since the error produced by the possible variation of this coefficient with the temperature will be low compared with other error sources such as the temperature controller, the uncertainty in the impedance measurements or the calibration model. Therefore, it is not necessary an accurate measurement of $f_{o,vac}$ since the calibration error will be similar.

■ It is important to know the temperature range in which the coefficients can be considered valid. For example, we observed that the coefficients calculated at 20 °C can be used to estimate the density and viscosity of liquids at temperatures of 40 °C and vice versa.
■ If the number of coefficients increase, the calibration model fits better to the initial calibration fluids but may increase the error for the rest of them.

■ Our results suggest that the error may be minimized if the calibration liquids are positioned near the middle of the density-viscosity range or if the density-viscosity range considered in the calibration process comprises almost the total density-viscosity range of application.

■ We could observed, that a simplified model of five coefficients it is simple and precise enough to determine the density and viscosity of fluids with an acceptable calibration error.

■ According to the obtained results, we can conclude that the error depends not only on the calibration model or the number of coefficients but also on the liquids selected to determine the coefficients.
Chapter 5

Applications

There are no such things as applied sciences, only applications of science.

Louis Pasteur

Summary: The performance of the resonators, electronic circuits and calibration models, previously described in chapters 2, 3 and 4, is evaluated in different applications. For example, for the monitoring of lubricant oil condition, the monitoring of a grape must fermentation, the gas damping effect of piezoelectric resonators, for the detection of cigarette particles and for elasticity sensing.

5.1 Introduction

5.2 Piezoelectric MEMS resonators for monitoring lubricating oils

Real time monitoring of the physical properties of liquids is of great concern in the automotive industry. For example, tracking the viscosity of lubricating oils is of great importance because they are exposed to dilution with diesel fuel as result of late-injection processes, which are essential for regenerating diesel particulate filters. For this application, different resonators were measured with the open-loop and closed-loop techniques previously described in section 3.2 and 3.3.
5.2.1 Open loop techniques

In this section the tuning fork resonator and the extensional 20, previously described in section 2.3.1.1 and 2.3.1.2, were employed to check their capability to assess oil dilution with diesel and biodiesel fuels using an impedance analyser.

- Calibration of the resonators:

Firstly, the tuning fork resonator and the extensional 20, were characterized with an impedance analyser (see section 3.2.1), using various liquids whose viscosity and density are known [Chr17]. The fluids D5, N10, S20 and N35 correspond to viscosity standards by Paragon Scientific [Sci]. The impedance measurements, were developed at room temperature (25°C) for both resonators obtaining the results presented in figure 5.1, 5.2 and table 5.1.

![Figure 5.1](image)

**Figure 5.1:** Conductance measurements for the tuning fork resonator obtained with the impedance analyser. Vertical offsets were applied for clarity purposes.
5.2. Piezoelectric MEMS resonators for monitoring lubricating oils

![Conductance vs Frequency Graph]

Figure 5.2: Conductance measurements for the extensional 20 obtained with the impedance analyser. Vertical offsets were applied for clarity purposes.

Table 5.1: Comparison of quality factor and resonance frequency for both resonators measured with the impedance analyser.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Tuning fork</th>
<th></th>
<th>Extensional mode</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q</td>
<td>( f_r ) [Hz]</td>
<td>Q</td>
<td>( f_r ) [Hz]</td>
</tr>
<tr>
<td>Heptane</td>
<td>163.76</td>
<td>29804.5</td>
<td>109.71</td>
<td>384693.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>133.87</td>
<td>29400.0</td>
<td>86.9</td>
<td>383704.56</td>
</tr>
<tr>
<td>Ethanol</td>
<td>86.18</td>
<td>29299.5</td>
<td>71.43</td>
<td>383025.16</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>70.45</td>
<td>29298.0</td>
<td>61.98</td>
<td>383211.88</td>
</tr>
<tr>
<td>D5</td>
<td>46.92</td>
<td>29033.9</td>
<td>53.66</td>
<td>381937.46</td>
</tr>
<tr>
<td>N10</td>
<td>26.68</td>
<td>28756.4</td>
<td>33.1</td>
<td>379794.23</td>
</tr>
<tr>
<td>S20</td>
<td>17.87</td>
<td>28460.0</td>
<td>24.95</td>
<td>378242.13</td>
</tr>
<tr>
<td>N35</td>
<td>14.75</td>
<td>28253.0</td>
<td>18.39</td>
<td>376338.90</td>
</tr>
</tbody>
</table>

In order to assure the viability of both resonators as density-viscosity sensors, we have calculated both the quality factor and the square root of the product of the density and the viscosity of the liquids. A reasonable linear correlation is found, what demonstrates the viability of both resonators even for high viscous liquids (see figure 5.3).
Figure 5.3: Quality factor of both resonators in various liquids.

Table 5.2: Comparison between the estimated and the reported values of density and viscosity for different liquids as deduced by means of the impedance measurements obtained in the tuning fork.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Estimated values with the tuning fork [25°C]</th>
<th>Reported values [25°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_{MEMS}$ [g mL$^{-1}$]</td>
<td>$\mu_{MEMS}$ [mPa s]</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.48</td>
<td>0.663</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.65</td>
<td>0.767</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.29</td>
<td>0.780</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>2.39</td>
<td>0.771</td>
</tr>
<tr>
<td>D5</td>
<td>5.19</td>
<td>0.818</td>
</tr>
<tr>
<td>N10</td>
<td>16.23</td>
<td>0.832</td>
</tr>
<tr>
<td>S20</td>
<td>37.07</td>
<td>0.836</td>
</tr>
<tr>
<td>N35</td>
<td>55.63</td>
<td>0.838</td>
</tr>
</tbody>
</table>

Secondly, the tuning fork resonator, was calibrated using the Waszczuk calibration model previously described in section 4.3.1.1 and the previous results obtained with the impedance analyser. In this case, the values of the calibration coefficients estimated for the tuning fork resonator $C_\mu$ and $C_{\rho\mu}$ were $1.02 \times 10^{13}$ $1/m^4$ and 195.32 $1/m$, respectively, in the viscosity range of 0.5-56 mPa s. Table 5.2 shows the estimated values of density $\rho_{MEMS}$ and viscosity $\mu_{MEMS}$ for the different liquids used. Theoretical values are also shown according to Wohlfarth [Chr17].
For the case of the extensional, assuming a hydrodynamic force determined by the Stokes’s second problem approximation, both quality factor and resonance frequency depend on the density-viscosity product, preventing the resolution of these variables separately [Duf14]. For the application of this resonator, the quality factor against the density-viscosity product was fitted to a second order function in the reference liquids, determining coefficients in equation 5.1, with the reported density and viscosity values. This approximation can then be used to determine viscosity from the measured quality factor in other liquids, if we assume a known density.

\[ aQ^2 + bQ + c = \frac{1}{\sqrt{\rho \mu}} \]  
(5.1)

- Application to lubricant oils:

The main goal is to apply these resonators to the analysis of the rheological properties of low-viscous automotive industrial fluids, such as lubricants and fuels. In the case of the lubricants, we paid attention to their dilution with diesel fuel. In this case, an automotive lubricant oil such as SAE 15W40 was used and a commercial diesel fuel supplied by Cepsa was blended with the mentioned lubricant. In the case of the fuels blends, it is of great importance to quantify the biodiesel content in biodiesel/diesel blends, since different contents will require a modification of diesel engine parameters for a clean and efficient combustion. To simulate different scenarios of biodiesel penetration, different diesel/biodiesel blends were prepared with biodiesel produced from animal fat, supplied by Stock del Valles S.L. Figure 5.4 shows a tuning fork resonator in contact with the lubricant oil SAE15W40.
Table 5.3 shows the values of density and viscosity, deduced with the previous calibration coefficients, for different diesel/biodiesel blends using the impedance analyser. The same can be seen in table 5.4 for the different lubricant/diesel mixtures prepared. Both tables indicate also the quality factor and resonance frequency for the two resonators under study. In the case of the extensional 20, the density has been assumed to be constant to allow the determination of viscosity from the measured quality factor. The results obtained in table 5.3 and 5.4 demonstrate that the impedance analyser technique is an accurate method that can be used to determine both the density and viscosity of diesel fuel and lubricant oils.

In this case, the measurements of the viscosity and density for lubricants and fuels, as specified in the ISO 3104, were developed at 40°C. Densities were measured by means of hydrometers submerged in a thermostatic bath at 40°C (Tamson TV2000) following the method established in the standard EN-ISO 3675. Viscosities were measured with modified Ostwald Cannon-Fenske type viscometers, using the same thermostatic bath at 40°C, following standard EN-ISO 3104 (see appendix A). As the viscosity increases, in both cases, there is a clear decrease of the quality factor that can be detected with the instrumentation.
Table 5.3: Density and viscosity values of blends of diesel and biodiesel fuels deduced by means of the measured frequency and quality factor with the impedance analyser. Measured values with laboratory instruments are also included.

<table>
<thead>
<tr>
<th>Blends</th>
<th>Tuning fork</th>
<th>Extensional</th>
<th>Estimated [40°C]</th>
<th>Measured [40°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tuning fork</td>
<td>Extensional</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$f_r$ (Hz)</td>
<td>$f_r$ (Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\rho_{MEMS}$ [mPa s]</td>
<td>$\mu_{MEMS}$ [g mL$^{-1}$]</td>
</tr>
<tr>
<td>Diesel</td>
<td>100</td>
<td>0</td>
<td>50.10 3829699</td>
<td>3.15 0.833</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>80</td>
<td>20</td>
<td>48.86 3821368</td>
<td>3.78 0.828</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>40</td>
<td>48.04 3815999</td>
<td>3.91 0.829</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>60</td>
<td>47.17 3809837</td>
<td>3.99 0.832</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>80</td>
<td>46.51 3814660</td>
<td>3.97 0.832</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>45.71 3808740</td>
<td>4.31 0.834</td>
</tr>
</tbody>
</table>

Table 5.4: Density and viscosity values of mixtures of lubricants and diesel fuel deduced by means of the measured frequency and quality factor with the impedance analyser. Measured values with laboratory instruments are also included.

<table>
<thead>
<tr>
<th>Blends</th>
<th>Tuning fork</th>
<th>Extensional</th>
<th>Estimated [40°C]</th>
<th>Measured [40°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tuning fork</td>
<td>Extensional</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$f_r$ (Hz)</td>
<td>$f_r$ (Hz)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\rho_{MEMS}$ [mPa s]</td>
<td>$\mu_{MEMS}$ [g mL$^{-1}$]</td>
</tr>
<tr>
<td>Diesel</td>
<td>0</td>
<td>100</td>
<td>12.71 3714548</td>
<td>75.39 0.903</td>
</tr>
<tr>
<td>Lubricant</td>
<td>2</td>
<td>98</td>
<td>13.13 3726633</td>
<td>69.78 0.873</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>96</td>
<td>13.26 3727707</td>
<td>64.51 0.864</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>94</td>
<td>13.4 3729945</td>
<td>63.41 0.853</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>92</td>
<td>14.18 3752444</td>
<td>58.56 0.839</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>90</td>
<td>14.71 3744971</td>
<td>42.36 0.862</td>
</tr>
</tbody>
</table>

5.2.2 Closed loop techniques

In this section different resonators were used for the monitoring of density and viscosity of liquids and its application to detect lubricant oil dilution with diesel fuel through closed-loop measurements.

5.2.2.1 15-mode and 05-mode for the monitoring of low-viscosity lubricant oil

Two devices designed to resonate in the 4$^{th}$ order roof tile-shaped vibration mode but with two different anchor schemes, 15-mode and 05-mode, previously described in section 2.3.2.3, were characterized in the lubricant oil SAE 2.5W.
Calibration using the model of four coefficients:

Firstly, the resonators were calibrated with viscosity standards using the model of four coefficients described in section 4.3.2. Table 5.5 shows the mean values of $f_r$ and Q factor, obtained with the PLL-based oscillator (see section 3.3.1).

Table 5.5: Comparison of quality factor and resonant frequency for both resonators in different viscosity standards at 25 °C.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>05-mode</th>
<th>15-mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_r$ [Hz]</td>
<td>Q</td>
</tr>
<tr>
<td>D5</td>
<td>549828</td>
<td>44.86</td>
</tr>
<tr>
<td>N10</td>
<td>543468</td>
<td>27.76</td>
</tr>
<tr>
<td>S20</td>
<td>539213</td>
<td>19.74</td>
</tr>
<tr>
<td>N35</td>
<td>534994</td>
<td>14.62</td>
</tr>
<tr>
<td>N100</td>
<td>525503</td>
<td>8.01</td>
</tr>
<tr>
<td>S200</td>
<td>516537</td>
<td>4.46</td>
</tr>
<tr>
<td>D500</td>
<td>509887</td>
<td>4.21</td>
</tr>
</tbody>
</table>

Due to the high sensitivity of the viscosity to the temperature, both $f_r$ and Q factor, may present small drifts. The random uncertainties obtained are below 193 mHz for $f_r$ and $4.1 \times 10^{-2}$ for Q factor. In addition, the best Allan deviation normalized values obtained, were $1.66 \times 10^{-8}$ and $1.38 \times 10^{-8}$ for the 05-mode and 15-mode, respectively. These values correspond to the uncertainty of $f_r$ in the liquid reference D5, with a value of 9 mHz and 8 mHz for the 05-mode and 15-mode, respectively.
5.2. Piezoelectric MEMS resonators for monitoring lubricating oils

Figure 5.6 shows how as quality factor increases, there is a clear improvement in the uncertainty of the resonant frequency ($\Delta f_r$) and the quality factor ($\Delta Q$) detected with the read-out electronics. For a better understanding, the Allan deviation of $f_r$ instead of the absolute value was plotted. Table 5.6 shows the optimal values calculated with the calibration model of four coefficients (see section 4.3.2).

![Figure 5.6: Resolution in Q factor and in $f_r$ ($\Delta Q$, Allan deviation $f_r$) as a function of the measured Q factor.](image)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>05-mode</th>
<th>15-mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>$a_1$</td>
<td>1.47</td>
<td>1.39</td>
</tr>
<tr>
<td>$b_1$</td>
<td>2.49</td>
<td>1.96</td>
</tr>
<tr>
<td>$b_2$</td>
<td>-2.53</td>
<td>6.00</td>
</tr>
</tbody>
</table>

Table 5.6: Values of the coefficients obtained in the calibration process.

Once the density and viscosity for each liquid is known (see figure 5.7 and table 5.7), both the error associated with the calibration process and the resolution can be determined. As our results show, the error associated with the calibration process for both resonators is comparable. The mean error of the viscosity is 4.04% and 7.2% for the 15-mode and 05-mode, respectively. While the mean error of the density is 0.2% and 0.13% for the 15-mode and 05-mode, respectively.
Figure 5.7: Viscosity and density values estimated from our resonators and measured with the density-viscosity meter DMA4100M.

Table 5.7: Density and viscosity values obtained with the viscometer Anton Paar DMA4100M ($\mu_{\text{viscometer}}$, $\rho_{\text{viscometer}}$) and estimated by our MEMS resonators ($\mu_{\text{MEMS}}$, $\rho_{\text{MEMS}}$) at 25 °C.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>$\mu_{\text{viscometer}}$ [mPa s]</th>
<th>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</th>
<th>$\mu_{\text{MEMS}}$ [mPa s]</th>
<th>$\rho_{\text{MEMS}}$ [g mL$^{-1}$]</th>
<th>$\mu_{\text{MEMS}}$ [mPa s]</th>
<th>$\rho_{\text{MEMS}}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5</td>
<td>4.71</td>
<td>0.8343</td>
<td>4.86</td>
<td>0.8326</td>
<td>4.73</td>
<td>0.8310</td>
</tr>
<tr>
<td>N10</td>
<td>13.79</td>
<td>0.8481</td>
<td>12.91</td>
<td>0.8488</td>
<td>14.38</td>
<td>0.8462</td>
</tr>
<tr>
<td>S20</td>
<td>30.16</td>
<td>0.8519</td>
<td>25.95</td>
<td>0.8525</td>
<td>27.08</td>
<td>0.8526</td>
</tr>
<tr>
<td>N35</td>
<td>55.36</td>
<td>0.8544</td>
<td>48.25</td>
<td>0.8569</td>
<td>53.54</td>
<td>0.8537</td>
</tr>
<tr>
<td>N100</td>
<td>217.50</td>
<td>0.8622</td>
<td>201.07</td>
<td>0.8616</td>
<td>207.58</td>
<td>0.8597</td>
</tr>
<tr>
<td>S200</td>
<td>395.92</td>
<td>0.8661</td>
<td>407.59</td>
<td>0.8645</td>
<td>423.19</td>
<td>0.8608</td>
</tr>
<tr>
<td>D500</td>
<td>495.08</td>
<td>0.8675</td>
<td>556.61</td>
<td>0.8690</td>
<td>546.04</td>
<td>0.8664</td>
</tr>
</tbody>
</table>

The density-viscosity resolutions were obtained from uncertainty propagation from $f_r$ and Q factor [Man14]. This procedure results in the resolutions and the error term for the viscosity and density of the different liquids, as illustrated in figures 5.8 and 5.9. The density resolution was in the range $1.5 \times 10^{-7} - 6.4 \times 10^{-4}$ g mL$^{-1}$ and $9 \times 10^{-7} - 9.4 \times 10^{-4}$ g mL$^{-1}$ for the 15-mode and 05-mode, respectively.

However, the viscosity resolution was in the range $1.3 \times 10^{-4} - 6.4$ mPa s and $5.9 \times 10^{-4} - 7.9$ mPa s for the 15-mode and 05-mode, respectively.
5.2. Piezoelectric MEMS resonators for monitoring lubricating oils

![Viscosity and density resolution graph](image1)

Figure 5.8: Viscosity and density resolution ($\Delta \mu$, $\Delta \rho$) for each fluid.

![Viscosity and density error graph](image2)

Figure 5.9: Viscosity and density error ($\varepsilon_{\mu}$, $\varepsilon_{\rho}$) as a function of the values obtained with the commercial density-viscosity meter.

As it can be observed, the resolution and the calibration error obtained are better in density than in viscosity. In addition, the error term and the density-viscosity resolution is slightly better for the 15-mode because it presents a higher $Q$ factor at the same $f_r$.

For this reason, we considered that the thicker device, 15-mode, is superior to the thinner one, 05-mode.
Application to lubricant oils using a PLL-based oscillator:

In order to check the consistency of the previous calibration, the density and viscosity values were estimated ($\mu_{\text{MEMS}}, \rho_{\text{MEMS}}$) for two different mixtures of lubricant oil: pure lubricant oil SAE 2.5W and a mixture with 2% diesel, designated as 100 and 98-2 in table 5.8.

As it can be observed in table 5.8, the 15-mode presents a higher quality factor due to a higher thickness, as it was discussed in section 2.3.2.3. It is therefore reasonable to assume that this is the reason for the better density-viscosity resolution of the 15-mode. The higher the quality factor, the lower its relative error, demonstrating the importance of having a resonator with a high quality factor.

As can be seen in table 5.8, a frequency shift of 158 Hz was detected due to the addition of the mixture with 2% diesel. Assuming a linear dependence in frequency versus diesel contamination, the measured frequency resolution of 13 mHz for the 15-mode in the mixture 98% lubricant oil-2% diesel, corresponds to a minimum amount of 1.65 ppm of diesel, that could be detected by monitoring $f_r$ and Q factor for the 15-mode.

Table 5.8: Comparison of Q factor, $f_r$, $\mu$ and $\rho$ for both resonators in different mixtures of lubricant oil.

<table>
<thead>
<tr>
<th></th>
<th>15-mode</th>
<th>05-mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>98-2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>98-2</td>
</tr>
<tr>
<td>$f_r$ [Hz]</td>
<td>593676</td>
<td>593834</td>
</tr>
<tr>
<td>$\Delta f_r$ [Hz]</td>
<td>$14 \times 10^{-3}$</td>
<td>$13 \times 10^{-3}$</td>
</tr>
<tr>
<td>Q</td>
<td>41.60</td>
<td>42.40</td>
</tr>
<tr>
<td>$\Delta Q$</td>
<td>$3.54 \times 10^{-3}$</td>
<td>$2.81 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\mu_{\text{viscometer}}$ [mPa s]</td>
<td>20.7</td>
<td>19.04</td>
</tr>
<tr>
<td>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</td>
<td>0.8299</td>
<td>0.8300</td>
</tr>
<tr>
<td>$\mu_{\text{MEMS}}$ [mPa s]</td>
<td>19.44</td>
<td>18.71</td>
</tr>
<tr>
<td>$\Delta\mu_{\text{MEMS}}$ [mPa s]</td>
<td>$3.82 \times 10^{-3}$</td>
<td>$3.71 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\rho_{\text{MEMS}}$ [g mL$^{-1}$]</td>
<td>0.8298</td>
<td>0.8301</td>
</tr>
<tr>
<td>$\Delta\rho_{\text{MEMS}}$ [g mL$^{-1}$]</td>
<td>$3.77 \times 10^{-6}$</td>
<td>$3.14 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Application to lubricant oils using a discrete oscillator circuit:

The previous results demonstrate the use of a PLL-based oscillator circuit to track $f_r$ and Q factor of a piezoelectric MEMS resonator immersed in lubricant oil. Finally, the alternative oscillator (see section 3.3.2), based on discrete components, was tested showing a comparable stability in a higher viscosity lubricant oil SAE 0W30 for the 15-mode (see table 5.9) but reducing the cost and dimensions of the setup.
5.2. Piezoelectric MEMS resonators for monitoring lubricating oils

Table 5.9: Values of resonance frequency, quality factor and their resolutions obtained with the PLL-based and the discrete oscillator circuit in pure lubricant oil SAE 0W30 for the 15-mode.

<table>
<thead>
<tr>
<th>Oscillator circuit</th>
<th>$f_r$ [kHz]</th>
<th>$\Delta f_r$ [mHz]</th>
<th>Q</th>
<th>$\Delta Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLL-based</td>
<td>572.075</td>
<td>74</td>
<td>21.73</td>
<td>0.0092</td>
</tr>
<tr>
<td>Discrete</td>
<td>571.655</td>
<td>153</td>
<td>21.79</td>
<td>0.012</td>
</tr>
</tbody>
</table>

5.2.2.2 12-mode, 14-mode and extensional 130 for the monitoring of high-viscosity lubricant oil

In this section, the 12-mode, 14-mode and the extensional 130 were calibrated (see section 2.3.2.1 and 2.3.1.3) with mixtures of lubricant oil SAE 0W30 (100-90%) and diesel (0-10%) at 25 °C.

The calibration was performed with the model of four coefficients, previously described in section 4.3.2, using the PLL-based oscillator (see section 3.3.1) and also the discrete oscillator circuit (see section 3.3.2).

In addition, to check the consistency of the procedure, the density and viscosity values were determined for a mixture not included in the calibration, in this case a mixture 93% lubricant-7% diesel.

- Calibration using the model of four coefficients:

Once the quality factor and resonance frequency are deduced with the PLL-based oscillator, the density and viscosity were obtained with the second step of the calibration process using again a model of adjustable coefficients.

Table 5.10 shows the optimal values of the coefficients calculated with the resonance parameters and the density and viscosity values measured with a commercial density-viscosity meter (see tables 5.11 and 5.12).

Table 5.10: Values of the coefficients obtained in the second calibration step for the 12-mode, 14-mode and extensional 130.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ [m$^2$]</th>
<th>$a_1$ [m]</th>
<th>$b_1$ [m]</th>
<th>$b_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-mode</td>
<td>0.19</td>
<td>3.08</td>
<td>3.21</td>
<td>-7.82</td>
</tr>
<tr>
<td>14-mode</td>
<td>0.19</td>
<td>1.38</td>
<td>2.09</td>
<td>-70.08</td>
</tr>
<tr>
<td>Extensional 130</td>
<td>0.19</td>
<td>5.31</td>
<td>5.05</td>
<td>340.49</td>
</tr>
</tbody>
</table>
Application to lubricant oils using a PLL-based oscillator:

The previous calibration coefficients were applied for the monitoring of different mixtures of lubricant oil with diesel. Following the same procedure as in previous sections, $f_r$ and Q factor (see table 5.11), were obtained through the PLL-based oscillator outputs (see section 3.3.1).

Figure 5.10: Density values estimated from the 12-mode, 14-mode, extensional 130 and commercial instrumentation.

Figure 5.11: Viscosity values estimated from the 12-mode, 14-mode, extensional 130 and commercial instrumentation.
Table 5.11: Comparison of quality factor and resonant frequency for both resonators in mixtures of lubricant oil SAE 0W30 (100-90%) with diesel (0-10%) at 25 °C.

<table>
<thead>
<tr>
<th>Lub-Die [% vol]</th>
<th>12-mode</th>
<th>14-mode</th>
<th>Extensional 130</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_r$ [Hz]</td>
<td>$\Delta f_r$ [Hz]</td>
<td>$Q$</td>
</tr>
<tr>
<td>100-0</td>
<td>51033</td>
<td>$1.06 \times 10^{-1}$</td>
<td>6.91</td>
</tr>
<tr>
<td>98-2</td>
<td>51235</td>
<td>$9.83 \times 10^{-2}$</td>
<td>7.16</td>
</tr>
<tr>
<td>96-4</td>
<td>51317</td>
<td>$9.51 \times 10^{-2}$</td>
<td>7.43</td>
</tr>
<tr>
<td>94-6</td>
<td>51489</td>
<td>$9.14 \times 10^{-2}$</td>
<td>7.66</td>
</tr>
<tr>
<td>93-7</td>
<td>51590</td>
<td>$8.72 \times 10^{-2}$</td>
<td>7.82</td>
</tr>
<tr>
<td>92-8</td>
<td>51644</td>
<td>$8.48 \times 10^{-2}$</td>
<td>7.89</td>
</tr>
<tr>
<td>90-10</td>
<td>51735</td>
<td>$8.39 \times 10^{-2}$</td>
<td>8.21</td>
</tr>
</tbody>
</table>
Table 5.12: Values of density and viscosity measured with the commercial density-viscosity-meter ($\rho_{\text{ref}}, \mu_{\text{ref}}$) and estimated by our system after the calibration procedure for lubricant-diesel mixtures ($\rho_{\text{est}}, \mu_{\text{est}}$) at 25 °C.

<table>
<thead>
<tr>
<th>Mixtures Reference values</th>
<th>12-mode</th>
<th>Extensional 130</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-0</td>
<td>89.87</td>
<td>0.8503</td>
</tr>
<tr>
<td></td>
<td>89.52</td>
<td>$4.76 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8518</td>
<td>$5.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>98-2</td>
<td>81.03</td>
<td>0.8501</td>
</tr>
<tr>
<td></td>
<td>82.07</td>
<td>$4.16 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8506</td>
<td>$4.60 \times 10^{-4}$</td>
</tr>
<tr>
<td>96-4</td>
<td>76.41</td>
<td>0.8499</td>
</tr>
<tr>
<td></td>
<td>75.09</td>
<td>$3.66 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8503</td>
<td>$4.24 \times 10^{-4}$</td>
</tr>
<tr>
<td>94-6</td>
<td>69.66</td>
<td>0.8496</td>
</tr>
<tr>
<td></td>
<td>69.78</td>
<td>$3.27 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8497</td>
<td>$3.93 \times 10^{-4}$</td>
</tr>
<tr>
<td>93-7</td>
<td>65.90</td>
<td>0.8495</td>
</tr>
<tr>
<td></td>
<td>66.42</td>
<td>$3.03 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8488</td>
<td>$3.73 \times 10^{-4}$</td>
</tr>
<tr>
<td>92-8</td>
<td>63.82</td>
<td>0.8494</td>
</tr>
<tr>
<td></td>
<td>65.03</td>
<td>$2.92 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8487</td>
<td>$3.63 \times 10^{-4}$</td>
</tr>
<tr>
<td>90-10</td>
<td>60.42</td>
<td>0.8491</td>
</tr>
<tr>
<td></td>
<td>59.23</td>
<td>$2.49 \times 10^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.8480</td>
<td>$3.26 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

By our system after the calibration procedure for lubricant-diesel mixtures ($^{15}l, {^{18}l}$) at 25 °C.
To estimate the resolution of the sensor, uncertainty propagation is applied to the measured fluctuations in $f_r$ and Q factor. This procedure results in the resolutions of density and viscosity of table 5.12.

In view of the results, the implemented density-viscosity sensors were able to determine both variables simultaneously in the ranges 0.8491-0.8503 g mL$^{-1}$ and 60.42-89.87 mPa s. Both variables were determined with a maximum error of 0.18% for density and 4.06% for the viscosity compared to a commercial instrumentation (see figures 5.10 and 5.11).

The resolution in density and viscosity is significantly different for both types of resonators. As can be seen in table 5.12, the best resolution was achieved by the 14-mode, reaching values of $3.92 \times 10^{-5}$ g mL$^{-1}$ for the density and $1.27 \times 10^{-1}$ mPa s for the viscosity in pure lubricant oil SAE 0W30.

Application to lubricant oils using a discrete oscillator circuit:

In addition, an alternative discrete oscillator previously described in section 3.3.2, was also tested. The reasonably good value of the admittance peak amplitude, along with the low resonance frequency of the 14-mode, allowed for a great flexibility and simplicity in the design.

Table 5.13: Values of resonance frequency, quality factor, viscosity and density obtained with the PLL-based and the discrete oscillator circuit in pure lubricant oil SAE 0W30.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$f_r$ [kHz]</th>
<th>$\Delta f_r$ [Hz]</th>
<th>Q</th>
<th>$\Delta Q$</th>
<th>$\mu_{est}$ [mPa s]</th>
<th>$\Delta \mu_{est}$ [mPa s]</th>
<th>$\rho_{est}$ [g mL$^{-1}$]</th>
<th>$\Delta \rho_{est}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLL-based</td>
<td>338.89</td>
<td>$1.07 \times 10^{-2}$</td>
<td>18.59</td>
<td>$9.48 \times 10^{-3}$</td>
<td>90.92</td>
<td>$1.27 \times 10^{-1}$</td>
<td>0.8508</td>
<td>$3.92 \times 10^{-5}$</td>
</tr>
<tr>
<td>Discrete</td>
<td>338.90</td>
<td>$19.7 \times 10^{-2}$</td>
<td>18.57</td>
<td>$1.28 \times 10^{-2}$</td>
<td>90.13</td>
<td>$1.71 \times 10^{-1}$</td>
<td>0.8511</td>
<td>$5.24 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The viscosity-density reference values are 89.87 mPa s and 0.8503 g mL$^{-1}$ (see section 5.12). Following the same procedure as in section 3.3.1, the density, viscosity and resolutions were deduced from the 14-mode response in pure lubricant oil SAE 0W30. The results in table 5.13 demonstrate that the performance of the discrete oscillator circuit is similar in terms of frequency stability to that achievable by using a PLL-based oscillator but reducing the size, cost and power consumption of the system. This was also checked with the previous measurement with the 15-mode in section 5.2.2.1.

In-line measurements of different mixtures of lubricant oil:
Our previous results demonstrate the application of both resonators as density-viscosity sensors while the liquid is confined inside the liquid cell. Besides, the behaviour of the 14-mode resonator in a real-time continuous-flow system has also been tested. In order to check the variation of density and viscosity in a dynamic system, the resonance frequency has been recorded while the fluid circulates and eventually changes from a pure lubricant oil SAE 2.5 W ($\mu = 20.7 \text{ mPa s}; \rho = 0.8299 \text{ g mL}^{-1}$) to another mixture with 98% Lubricant-2% Diesel ($\mu = 19.04 \text{ mPa s}; \rho = 0.830 \text{ g mL}^{-1}$). As it can be seen in figure 5.12, a frequency shift of 150 Hz has been detected due to the addition of 2% Diesel. In this case, the measured frequency resolution is 4 mHz instead of the 10.7 mHz obtained with the lubricant oil SAE 0W30, because of the lower viscosity. Based on this resolution and extrapolating the change in frequency for the addition of 2% diesel, we could estimate that the minimum detectable amount of diesel in lubricating oil is 0.5 ppm.

![Figure 5.12: Frequency shift measured in-line with the injection of a mixture 98% lubricant-2% diesel after pure lubricant oil SAE 2.5 W.](image)

This results demonstrate that the discrete oscillator circuit is able to track the resonance frequency of the 14-mode immersed in different mixtures of lubricant oil.
5.3 Piezoelectric MEMS resonators for monitoring grape must fermentation

The fermentation of grape must involves the interaction between yeasts, bacteria, fungi and viruses. A correct biochemical process is a necessary condition but not sufficient by itself to determine the final quality of the wine, whose assessment relies on a comprehensive analysis of its chemical components, as the basic flavour of wine depends on at least 20 compounds [Ron08]. Therefore, winemakers must carefully supervise the wine fermentation process to ensure a wine of the expected quality. One of the key parameters monitored during wine fermentation is the fermentation kinetics. This provides essential information about the steady transformation of grape must into wine due to the decrease of glucose and fructose that leads to the formation of ethanol, glycerol and carbon dioxide along with biomass, as a result of yeast metabolism [Bou99]. This process is traditionally monitored by enologists, who manually extract and analyse discrete samples at least twice a day using instruments such as the aerometer, spectrophotometer or colorimeter. They essentially determine the density and its rate of change since these parameters provide information about the evolution of the fermentation as a result of yeast metabolism.

In an industrial fermentation process, temperature fluctuations would influence to some extent the fermentation process and thus the density. Nevertheless, it is the variations that help enologists determine the current fermentation status, and whether or not corrective measures are required as it progresses. Besides, a variety of alternative procedures have been used for monitoring the grape must fermentation such as density determination based either on differential pressure measurements [El 88] or on the use of flexural oscillators [Kou91], monitoring of CO\textsubscript{2} released during the process due to the gradual loss of mass [El 88], determination of yeast cell population evolution by means of impedance techniques [Pér09] and turbidity measurements [Cre10], ultrasound measurements conducted to determine the propagation velocity in grape musts [Lam09; Res04], refractive techniques based on fibre optics [Qui09], optoelectronic device based on measurements of the refractive index [JM13; JM14; JM16] and an off-line monitoring based on a piezoelectric resonator [Tol16a].

Overall, these different approaches have not enough resolution or have only been tested in discrete must samples. In order to contribute to the automation and improvement of the wine fermentation process, we have used the 15-mode resonator, serving as a density sensor, resonantly excited in the 4\textsuperscript{th} order roof tile-shaped vibration mode (see section 2.3.2.3). Furthermore, the interface circuit and a PLL-based oscillator circuit, previously described
in section 3.2.5 and 3.3, were applied to track the resonance frequency and the quality factor of the microresonator.

5.3.1 Sensor calibration

The device was first calibrated with an artificial model solution of grape must and then applied for the in-line monitoring of real grape must fermentation. This calibration process was carried out in two steps, each with adjustable parameters using the model of four coefficients described in section 4.3.2.

In order to confirm that piezoelectric resonators are valid for the monitoring of grape must fermentation, two different sets of model solutions were used for pre-investigation purposes. The first set represents a normal fermentation (N1:N9) and the second represents a sluggish fermentation (S1:S9). A variety of reasons may be attributable to this kind of failed or sluggish fermentations, which occasionally occur: the lack of dissolved oxygen, an unbalanced ratio between sugar and nitrogen, a low fermentation temperature, an inadequate rehydration, a thermal shock of yeast, etc. [RG06].

These model solutions represent different stages of the corresponding fermentation process according to their particular mixture of glucose, fructose, ethanol and glycerol dissolved in water. The composition of the prepared model solutions for a normal and sluggish fermentation is shown in table 5.14 [JM14]. In the normal model solution, a decrease in fructose and glucose concentration from 110&100 g L\(^{-1}\) (N1) to 2&1 g L\(^{-1}\) (N9) occurs. Similarly, the glycerol and ethanol concentration are increasing from zero to 9 g L\(^{-1}\) and 14% v/v. In the sluggish fermentation the decrease in fructose and glucose concentration stops prematurely and settles around 57 and 21 g L\(^{-1}\). Along with this development the increase in the ethanol concentration stops and does not exceed the value of 8% v/v.

Figure 5.13 shows the mean values of \(f_r\) and Q factor when the resonator is immersed in the model solutions of grape must: normal and sluggish fermentation process. The measurements of \(f_r\) and Q factor were performed with a temperature control unit (see section 3.4) obtaining a resolution below 100 mHz for \(f_r\) and 0.7 for Q factor. Nevertheless, the impact of temperature fluctuations in the resolution of the sensor during the measurement process is minimal compared with the continuous evolution of the real grape must fermentation. As it can be seen in figure 5.13, the significant changes in the composition of the model solutions affects the \(f_r\) and the Q factor of the resonator [Tol16a]. The combination of unfermented sugars and less than expected ethanol concentration, resulted into a flat curve of \(f_r\) for the sluggish fermentation.
5.3. Piezoelectric MEMS resonators for monitoring grape must fermentation

Table 5.14: Composition of model solutions representing a fermentation process.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Fructose [g L(^{-1})]</th>
<th>Glucose [g L(^{-1})]</th>
<th>Glycerol [g L(^{-1})]</th>
<th>Ethanol [% v/v]</th>
<th>Solution</th>
<th>Fructose [g L(^{-1})]</th>
<th>Glucose [g L(^{-1})]</th>
<th>Glycerol [g L(^{-1})]</th>
<th>Ethanol [% v/v]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>110</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>S1</td>
<td>110</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N2</td>
<td>90</td>
<td>80</td>
<td>0</td>
<td>1</td>
<td>S2</td>
<td>90</td>
<td>80</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>N3</td>
<td>70</td>
<td>30</td>
<td>5</td>
<td>6</td>
<td>S3</td>
<td>80</td>
<td>60</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>N4</td>
<td>60</td>
<td>20</td>
<td>5</td>
<td>8</td>
<td>S4</td>
<td>70</td>
<td>30</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>N5</td>
<td>40</td>
<td>10</td>
<td>6</td>
<td>9</td>
<td>S5</td>
<td>66</td>
<td>27</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>N6</td>
<td>20</td>
<td>2</td>
<td>7</td>
<td>12</td>
<td>S6</td>
<td>64</td>
<td>26</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>N7</td>
<td>8</td>
<td>2</td>
<td>7</td>
<td>13</td>
<td>S7</td>
<td>62</td>
<td>24</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>N8</td>
<td>5</td>
<td>2</td>
<td>7</td>
<td>13</td>
<td>S8</td>
<td>58</td>
<td>22</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>N9</td>
<td>2</td>
<td>1</td>
<td>9</td>
<td>14</td>
<td>S9</td>
<td>57</td>
<td>21</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 5.13: Resonant frequency and quality factor of the resonator immersed in two model solutions of grape must at 20 °C.

The values of the coefficients obtained in the calibration process that fit best to the experimental data for the normal model solution are shown in table 5.15 [Tol16a]. These calibration coefficients are applied in the next section for the in-line monitoring of real grape must fermentation.

Table 5.15: Values of the coefficients obtained in the calibration process for the normal model solution.

<table>
<thead>
<tr>
<th>K(_{ic}) [s]</th>
<th>a(_0) [m(^2)]</th>
<th>a(_1) [m]</th>
<th>b(_1) [m]</th>
<th>b(_2) [(\cdot)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal model solution</td>
<td>(3.58 \times 10^{-10})</td>
<td>0.12</td>
<td>-20.99</td>
<td>2.11</td>
</tr>
</tbody>
</table>
The results of the estimated density values using our MEMS device are compared to those measured by the density-viscosity meter Anton Paar DMA4100M [Ant14b] at 20 °C in table 5.16. As it can be seen, an almost linear decrease in the density occurs for the normal model solution and a premature stop in the density decrease for the sluggish solution. These results show the potential to distinguish between ordinary and sluggish fermentations at an early stage of the fermentation process in artificial grape must. As we can observed, the mean error term for the sluggish fermentation was around 8.3% for the viscosity and 0.38% for the density. The resolutions obtained through uncertainty propagation (see section 4.3.2) for all the model solutions are below 500 µg mL\(^{-1}\) and 17 µPa s, for density and viscosity. The resolutions and the calibration errors obtained are better in density than in viscosity. This occurs because the Q factor, determined from the measurement of \(G_{osc}\) in the interface circuit, presents a worse resolution than the frequency measurement.

### 5.3.2 Monitoring grape must fermentation

In the previous section, the theoretical background for using the density and viscosity as valid parameters of the fermentation process was checked. In addition, the performance of the resonator was verified and validated with two model solutions of grape must. Nevertheless, our main goal is the monitoring of a real grape must fermentation process. For this reason, we applied the same procedure that was developed for the model solutions. In this case, through the measurements of \(f_{osc}\) and \(G_{osc}\) in the interface circuit and using the coefficients obtained for the normal model solution (see table 5.15), we were able to monitor the density and the viscosity during a fermentation process.

The performance and reliability of the sensor in a real grape must were validated by three different fermentation processes and carried out by different procedures. In the first process, designated as off-line, grape must samples were manually extracted from a commercial fermenter and measured with the resonator under static immersion. In the second set-up, denominated as in-line, a home-made fermenter was implemented. In this case, the grape must was automatically injected into the cell containing the resonator with a peristaltic pump. After each measurement, the sensor was cleaned with water. In both set-ups the measurements were made with the grape must in static conditions and verifying that the resonator characteristics were maintained after each measurement and cleaning step. However, in the third set-up, denominated as flow-through, there was a continuous flow of grape must through the liquid cell with the resonator. In this case, the sensor was not cleaned after each measurement as grape...
Table 5.16: Density and viscosity values estimated from our resonator (MEMS) and measured with the commercial density-viscosity meter (viscometer) at 20 °C for model solutions of grape must and the calibration error.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Normal fermentation</th>
<th>Sluggish fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscometer values</td>
<td>MEMS values</td>
</tr>
<tr>
<td></td>
<td>$\mu$ [mPa s]</td>
<td>$\rho$ [g mL$^{-1}$]</td>
</tr>
<tr>
<td>1</td>
<td>1.949</td>
<td>1.082</td>
</tr>
<tr>
<td>2</td>
<td>1.974</td>
<td>1.063</td>
</tr>
<tr>
<td>3</td>
<td>1.722</td>
<td>1.028</td>
</tr>
<tr>
<td>4</td>
<td>1.707</td>
<td>1.017</td>
</tr>
<tr>
<td>5</td>
<td>1.770</td>
<td>1.003</td>
</tr>
<tr>
<td>6</td>
<td>1.754</td>
<td>0.991</td>
</tr>
<tr>
<td>7</td>
<td>1.770</td>
<td>0.985</td>
</tr>
<tr>
<td>8</td>
<td>1.809</td>
<td>0.984</td>
</tr>
<tr>
<td>9</td>
<td>1.742</td>
<td>0.983</td>
</tr>
</tbody>
</table>

Mean error [%] 7.36 0.38 | Mean error [%] 8.3 0.38
must was continuously circulating.

5.3.2.1 Off-line monitoring of a grape must fermentation

Before the results are presented, a small summary with some guidelines about the fermentation of the grape must is introduced. Grape must was completed using 25% (w/v) of red grape skin from Cencibel variety. Afterwards, the must was inoculated with 0.2 g mL\(^{-1}\) of *Saccharomyces cerevisiae* strain (UCLM S325, Fould-Springer) previously rehydrated following the supplier’s guidelines.

A commercial cylindrical fermenter (mini-Bioreactor Applikon) was filled with 3 L of inoculated must and grape skins, where the temperature was controlled at 28 ºC. In this method, the fermentation monitoring was carried out by means of the extraction and analysis of 7 mL-samples every 5 h approximately during 6 days. After the extraction the samples were centrifuged for one minute at 1000 rpm (Universal 32R Hettich) and kept refrigerated until analysis. In this case, the resonator was immersed in grape must samples (see figure 5.14), cleaned with water and dried with \(N_2\) after each measurement. Once the measurements were completed, the samples were kept frozen at -20 ºC, in order to stop the evolution of the fermentation process.

![Figure 5.14: 15-mode resonator wire bonded in a 24-pin DIP (dual inline package) and immersed in a red grape must.](image-url)
Following the same procedure as in the previous section with the model solutions, the evolution of density and viscosity was measured, as shown in figure 5.15. As can be observed, the density follows the expected evolution for a normal fermentation [JM14] and viscosity values follow a rather similar trend. Both parameters decrease with the evolution of the fermentation since the ethanol concentration increases. The viscosity is not usually a measured variable in the monitoring of a fermentation. However, in our case it is obtained simultaneously with the density providing further information of the process. The error terms and resolutions were calculated as in section 5.3.1. The mean error term obtained was around 2.4% for the viscosity and 0.3% for the density being the viscosity resolution below 7 µPa s. In the case of the real grape must, the obtained density resolution was below 100 µg mL\(^{-1}\) instead of the 1200 µg mL\(^{-1}\) value obtained in some previous works using a high-resolution low-cost optoelectronic instrument [JM13; JM14]. By comparing to the measurements with the benchtop instrument, the errors obtained confirmed that the calibration process involving the normal model solutions is also valid for other liquids in a similar range of density and viscosity.

![Figure 5.15: Off-line monitoring of the density-viscosity values estimated from our resonator (MEMS) and measured with the commercial density-viscosity meter (viscometer) at 20 ºC.](image)

5.3.2.2 In-line monitoring of a grape must fermentation

In the second method, a home-made fermenter, with a volume of 3 L, and a flow cell for the resonator, were designed and implemented in a fluidic
circuit. The fermenter was immersed in a thermostatic bath at 29 °C and connected to a peristaltic pump, which enabled the recirculation of the grape must between the fermenter and the cell resonator (see figure 5.16).

![Figure 5.16: Schematic of the fermenter and external fluid circuit designed for the in-line monitoring of grape must fermentation process.](image)

Two filters, with a pore size of 500 and 100 µm, were introduced in the tube, sampling the grape must. These filters prevent the circulation of grape skin, clots or sediments through the flow cell. An air pump provides oxygen for the adequate yeast fermentation. The cell flow, fabricated with a 3D printer, enabled the input/output of the grape must and the housing of the electronic package enclosing the resonator. In addition, the cell has an aperture to evacuate the air that enters into the cell from the fermenter. The systematic procedure for the measurements is as follows. First of all, the grape must was injected in the flow cell with the peristaltic pump until its temperature reached 20 °C (around one minute). This temperature stabilization was assisted by a thermoelectric controller in contact with the resonator.
5.3. Piezoelectric MEMS resonators for monitoring grape must fermentation

Figure 5.17: In-line monitoring of the density-viscosity values estimated from our resonator (MEMS) and measured with the commercial density-viscosity meter (viscometer) at 20 °C.

The measurement of the circuit outputs, $f_{osc}$ and $G_{osc}$, was carried out following the same procedure as in the previous sections obtaining the density and viscosity values of figure 5.17. Once completed, the grape must was extracted and measured with the commercial density-viscosity meter. After that, the valves in figure 5.16 were switched to allow water injection into the cell, cleaning the resonator during one minute. In order to check that the cleaning process was successful and effective, the value of $f_r$ and Q factor was registered before and after each measurement in water, obtaining a value of $560000 \pm 10$ Hz and $140 \pm 2$, respectively. The mean error term obtained was around 2% for the viscosity and 0.6% for the density being the resolution below 1 µPa s and 88 µg mL$^{-1}$, respectively.

5.3.2.3 Flow-through monitoring of a grape must fermentation

Once the previous in-line set-up was proved as a valid configuration for the continuous monitoring, a third procedure, designated as flow-through, was carried out. In this scheme, all the measurements were taken in a continuous flow-through circulation of the grape must as the fermentation progresses, without cleaning the resonator with water. Unlike the previous procedures, the circuit outputs, $f_{osc}$ and $G_{osc}$, were registered every minute, and density and viscosity deduced with the same calibration constants as before. The measurements are summarized in figure 5.18.
In order to check the correct evolution of the process and resonator behaviour, different grape must samples were taken approximately every six hours and measured with the commercial density-viscosity meter. This final procedure presents two main advantages compared to the ones previously described. On the one hand, we developed a real time monitoring system allowing the detection of a sluggish fermentation or any other problem during the whole process span. On the other hand, all the measurements were carried out without any cleaning process. In the flow-through measurements, the mean error term was around 1.55% for the viscosity and 0.23% for the density, being the resolution around 20 µPa s and 1 mg mL⁻¹, respectively.

These values are similar to those of the off-line set-up, demonstrating the performance of piezoelectric resonators as sensors for a real in-line monitoring of a fermentation process. It is worth to remark that the density and viscosity resolutions were slightly better in the previous cases, probably due to the dynamics of the flow in the continuous flow-through of grape must and the eventual formation of air bubbles in the cell (see table 5.17).

However, the calibration error is slightly lower than those obtained for the other two measurement schemes. This error was determined from the difference between the data measured with the commercial instrument and those taken with the MEMS sensor every six hours. In addition, we have estimated the average error considering all the measurements obtained during the fermentation (one per minute). For that, we took the difference...
between the fitting curve plotted in figure 5.18, obtained with the values of the commercial instrument, and those estimated with the MEMS sensor, resulting an error of 4% for the viscosity and 0.7% for the density. This is similar to the values obtained in the two other fermentation processes and within the interval determined in the initial calibration (see table 5.16).

### 5.3.2.4 Temperature dependence

In the experiments described above, the temperature of the grape must was stabilized to 20 °C ± 0.05 °C, as a reference in the evolution of the process, to neutralize the temperature fluctuations outside the fermentation tank and their influence on the density and viscosity. Nevertheless, our sensor was validated for other temperatures of interest in the fermentation industry. Two grape must samples, representing the beginning and ending of the fermentation process, were analysed at 15 and 30 °C. The density and viscosity values were determined at these temperatures with our MEMS sensor, with the same calibration of previous sections, and compared with the commercial density-viscosity meter, obtaining an error lower than 1 and 2% for the density and viscosity, respectively. As this error is similar to that previously obtained in the calibration at 20 °C, we can conclude that the sensor responds accurately to the changes in density or viscosity caused by changes in temperature, in this range. The density values obtained at 15 or 30 °C can be used to extrapolate the density to a reference temperature of 20 °C [vin14], the common reference in winemaking, obtaining a mean density error of 0.5% with respect to the value directly measured at this temperature. These low errors demonstrate the possibility to replace the temperature control unit by a basic temperature monitoring system, where the density at 20 °C can be inferred at any stage of the process from its value at a different temperature.
5.4 Gas damping effect of piezoelectric MEMS resonators

Real time monitoring of the physical properties of gases is an important subject in different markets such as aerospace, healthcare or pharmaceutical industry. Microelectromechanical systems have been widely employed in gas sensors, pressure sensors and flow meters [Sen17; Amp17]. Resonant microstructures may be a precise and compact solution for tracking other physical properties of gases such as viscosity and density [Nie11; Liu11].

In this section, the 05-mode resonator (see section 2.3.2.3) was characterized to study how various factors, such as pressure, gas composition, the resonator geometry or the order of the vibrational mode, influence the resonant frequency and quality factor of micro resonators. The resonator has a dimensions of $3000 \times 900 \times 10 \, \mu m^3$. In addition, other micro-plate resonator, with the same length and thickness, but different width ($1800 \, \mu m$), was also studied and characterized. In order to determine the resonant parameters of interest, a closed-loop scheme was applied (see section 3.3).

Depending on gas species different gas damping effects in the molecular, viscous and transitional flow regimes were observed. In general, when the resonator is operated in high vacuum, only intrinsic energy losses are relevant (intrinsic). These can be divided into the thermoelastic damping of the structure (thermoelastic), anchor losses (anchor) and energy losses due to coating films (coating). However, when the resonator vibrates in a gaseous medium in normal atmosphere, external losses are the main energy loss source (gas). These comprises viscous losses (viscous), acoustic losses (acoustic) and squeeze film losses (squeeze). The energy dissipated per cycle in a resonator can be expressed as the sum of the energy dissipated of the previous mechanisms [Lu09] as in equation 5.2. In this work, the effects of ambient pressure, the nature of the surrounding gas, resonator geometry and higher mode operation, were evaluated and compared systematically for different resonators.

$$Q_{total}^{-1} = \left( Q_{viscous}^{-1} + Q_{acoustic}^{-1} + Q_{squeeze}^{-1} \right) Q_{gas}^{-1} + \left( Q_{anchor}^{-1} + Q_{thermoelastic}^{-1} + Q_{coating}^{-1} \right) Q_{int}^{-1} + Q_{other}^{-1}$$

(5.2)

5.4.1 Measurement setup

The resonator along with the interface circuit (see section 3.2.5), were placed in a custom-built vacuum chamber. The rest of the oscillator circuit was located outside the vacuum chamber and connected with coaxial cables (see
In order to sample the output parameters of the oscillator circuit, a data acquisition board (DAQ USB6211) was employed. This is controlled with a PC-based virtual instrument where a calibration process was carried out to determine the resonance parameters of interest, $f_r$ and $Q$ factor. A schematic diagram of the measurement setup is showed in figure 5.19.

![Figure 5.19: Schematic diagram of the measurement setup used to characterize the 05-mode in the vacuum chamber with the oscillator circuit.](image)

The vacuum chamber is equipped with a turbo molecular pump and a rotary vane pump. The combination of both pumps allows us to modify the pressure from atmospheric pressure (950 mbar) to medium vacuum (0.1 mbar). In order to avoid the environment air leak into the chamber, the maximum pressure was set to 950 mbar, which is slightly lower than normal atmospheric pressure (around 1000 mbar).
In order to determine the resonator performance, different gases were introduced in the chamber at specific pressure values. The gases, Air, \( N_2 \), Ar, \( CO_2 \) and He, were chosen for their significantly different properties. The density and viscosity theoretical values as a function of the pressure are presented in figure 5.20 [E.W]. As it can be observed, He and \( CO_2 \) present the lowest and highest density values, respectively. In order to check the performance of the sensor, Air and \( N_2 \) were also measured in the chamber. Although they present similar density and viscosity values, we could observed differences in the resonant parameters of the resonator. Moreover, Ar, which presents a density value between \( CO_2 \) and \( N_2 \)-Air, but the highest viscosity, was also introduced in the chamber. As it can be seen in figure 5.20, the viscosity remains almost constant for each gas. The total measured range was \( 1.13 \times 10^{-4} - 1.69 \text{ mg mL}^{-1} \) and \( 14.93 - 22.55 \mu \text{Pa s} \) for the density and viscosity, respectively.

### 5.4.2 Measurements with the low-cost oscillator circuit

The monitoring of the resonance frequency and the quality factor of a mechanical resonator is challenging due to the parasitic effects present in gas media. For this reason, the interface circuit, previously described in section 3.2.5, to subtract the dummy response from that of the resonator, was used. In this case the interface circuit was designed with the AD8129 instrumentation amplifier in order to reduce the phase shift produce at the resonance frequency. As it can be observed in figure 5.21, this results in a clear resonance, with low baseline and the necessary phase to meet...
the Barkhausen criterion, needed condition for the implementation of the oscillator circuit.

![Graph showing open loop response for the 05-mode measured in a liquid test (2-Propanol) after cancelling the parasitic effects.](image)

**Figure 5.21:** Open loop response for the 05-mode measured in a liquid test (2-Propanol) after cancelling the parasitic effects.

Once the parasitic effects of the resonator were minimized with the interface circuit, we included the device in an oscillator circuit scheme. In this case the discrete oscillator circuit, described in section 3.3.2, was applied. In this case, the oscillation frequency (1.107 MHz) is higher than the maximum sampling rate of the DAQ used for this application (250 kS/s). For this reason it was necessary to use the envelope detector and the comparator for the measurement of $G_{osc}$ and $f_{osc}$, respectively. The measurements obtained with the oscillator circuit are showed in figure 5.22.

Once the values of $f_{osc}$ and $G_{osc}$ were obtained, these were transformed into the key parameters of the resonator, $f_r$ and Q factor, following the procedure previously reported in section 4.2. The calibration constant $K_{ic}$ was obtained by fitting the measurements of the oscillator circuit, $f_{osc}$ and $G_{osc}$, with the measurements obtained in $N_2$ at different pressures with an impedance analyser.
The resonance frequency and quality factor were characterized as a function of the ambient pressure (see figure 5.23). As it can be observed, when vibrating in vacuum, the gas damping on the resonator is minimized and a high Q factor value can be achieved. Increasing the pressure by starting from vacuum conditions results in a slight shift in the resonance frequency but a dramatic reduction in the Q factor. These results indicate
that \( f_r \) and Q factor decreases as the density and viscosity of the gas increases. These results confirm that, by measuring these parameters, the viscosity and density of the fluid can be determined since gases that have similar density-viscosity values, as the \( N_2 \) and Air, can be clearly distinguished with the measurements of the oscillator circuit. In these measurements, different gas damping regions can be identified [Mer03]. In this case, when the pressure was below 0.1 mbar, no differences in the resonance parameters could be observed; so the Q factor below this pressure is assumed to be the intrinsic energy losses since the gas damping is negligible. Nevertheless, this region could be also disguised with the molecular region. In this region, damping is caused by independent collisions of non-interacting gas molecules with the vibrating surface of the resonator. The second region, from 1 to 100 mbar, can be identified as the transition regime. In this case, the gas is neither non-interacting nor continuous. Finally, from 100 to 950 mbar, the viscous regime can be observed. In this region the gas acts as a continuous viscous fluid with a square root of the pressure dependence [Blo92].

In order to check the performance of the oscillator circuit, the 05-mode was also measured with an impedance analyser obtaining approximately the same resonance parameters (see figure 5.31). Therefore, we could conclude that the oscillator circuit employed in this work is also a suitable alternative for the monitoring of the gas damping effect of piezoelectric resonators. Finally, the resolution of \( f_r \) and Q factor were evaluated by recording 30 samples of \( f_{osc} \) and \( G_{osc} \) every 500 ms with the DAQ. As it can be seen in figure 5.24 and 5.25, the resolutions obtained were below 0.5 Hz for \( f_r \) and 4 for Q factor in the worst scenario, i.e. when the resonator presents the lowest Q factor at atmosphere pressure (950 mbar).
Figure 5.24: Frequency resolution ($\Delta f_r$) obtained with the DAQ for the 05-mode at 25 ºC.

Figure 5.25: Q factor resolution ($\Delta Q$) obtained with the DAQ for the 05-mode at 25 ºC.
5.4.3 Measurements with the impedance analyser

Once the 05-mode was measured with the oscillator circuit, different resonators, included in the same chip and DIP package, and vibration modes, were analysed with an impedance analyser (see figure 5.26). In this case the resonant parameters, were directly obtained without any calibration process. In this case, the measured impedance spectrum of the piezoelectric film was fitted to a modified Butterworth-Van-Dyke equivalent circuit (see section 2.2.2) [Arn00]. The equivalent RLC values were obtained by fitting the conductance of the circuit model to the experimental conductance spectrum around resonance.

In this section, two different resonators with different geometries are analysed. The first one, is the previously measured 05-mode with a dimension of 3000x900x10 $\mu m^3$. For this resonator, the 02-mode and 04-mode can be also measured with the impedance analyser. The second microplate resonator has a dimension of 3000x1800x10 $\mu m^3$. These resonators are compared according to their vibration modes. The main objective of this comparison is to investigate the hydrodynamic loading in detail by exploring how factors, such as ambient pressure, the nature of the surrounding gas, the resonator geometry and higher vibration modes, affect the resonance parameters of piezoelectric resonators.
02-mode:

The first mode analysed was the 02-mode. This mode presents the lowest resonant frequencies, approximately 128.85 kHz and 35.6 kHz for the resonators with a width of 900 µm and 1800 µm, respectively. As it can be observed in figure 5.27 and 5.28, the evolution of the resonant frequency with the pressure is the expected, since the highest density gases presents the lowest $f_r$ and Q factor values. For example, He presents the highest $f_r$ and Q factor values and CO$_2$ the lowest values. In this case, for the widest resonator, the molecular regime is below 0.1 mbar and the transition regime comprises the range from 0.1 to 10 mbar. However, for the narrowest resonator, when the ambient pressure was lower than 1 mbar no differences in the resonant parameters could be observed. So the results at 0.1 mbar are assumed as the intrinsic losses of the resonator.

Figure 5.27: Measurement of Q factor and $f_r$ for the 02-mode. Resonator 3000x900x10 µm$^3$. 
Afterwards, the 04-mode was measured (see figures 5.29 and 5.30). For slim structures, viscous losses are dominant, with a $1/\sqrt{\rho \mu}$ dependence, which can be simplified to $1/\sqrt{p}$ for a single gas with a given viscosity, where $p$ is the pressure [Blo92; Bhi04]. For this reason, Q factor increases as the pressure decreases, but this tendency in lower pressure is limited by intrinsic damping effects occurring in the mechanical structure, reaching its maximum value at 0.1 mbar. Incompressible flow is expected for the first resonant modes. Although, the resonant mode is the same (04-mode), the resonance frequency of the narrowest resonator is four times bigger than the widest resonator. Therefore, we could observed a different evolution of the resonant parameters because the contribution of acoustic effects are significant for the narrowest but not for the widest resonator.
Figure 5.29: Measurement of Q factor and $f_r$ for the 04-mode. Resonator 3000x900x10 $\mu m^3$.

Figure 5.30: Measurement of Q factor and $f_r$ for the 04-mode. Resonator 3000x1800x10 $\mu m^3$.

- 05-mode:

Finally, the 05-mode was also measured with the impedance analyser (see figures 5.31 and 5.32). In this case, can be clearly observed that as the resonance mode number increases and therefore the resonance frequency, the acoustic wavelength reduces. For this reason, the contribution of acoustic effects on the energy loss cannot be neglected any more in comparison
with viscous effects. Because of that, big differences between both resonators can be distinguished. For the narrowest resonator, Ar presents the lowest Q factor. However, for the widest resonator, CO$_2$ presents the lowest Q factor. Furthermore, the evolution of $f_r$ is completely different for both resonators because of acoustic effects.

**Figure 5.31**: Measurement of Q factor and $f_r$ for the 05-mode. Resonator 3000x900x10 $\mu m^3$.

**Figure 5.32**: Measurement of Q factor and $f_r$ for the 05-mode. Resonator 3000x1800x10 $\mu m^3$.

These results demonstrate the performance of both resonators in different gases (Air, $N_2$, Ar, CO$_2$ and He) and pressures (0.1-950 mbar) by
developing and applying specific experimental setup. Furthermore, by measuring the resonant parameters, the viscosity and density of the fluid can be determined since gases that have similar density-viscosity values as the \( N_2 \) and air, can be clearly distinguished with the measurements of the discrete oscillator circuit and the impedance analyser.

5.5 Piezoelectric MEMS resonators for cigarette particle detection

Nanoparticles (NPs) are used in an increasing amount of industries. For this reason, many studies have been reported about the adverse effects to human health of different nanoparticles which can penetrate the human organism easily via the respiratory tract due to their small size [DS16; Pin16; Ram11]. For this reason, there is a great need to detect and control these particles. In such case, it is necessary to have a low-cost system capable of detecting these particles in real-time. Several research groups developed various types of microelectromechanical systems as mass-sensitive sensors [Was13a; Was13b; Bea10; Sch13].

In this work, the sensor working principle is based on the resonance frequency shift induced by additional collected masses of particles on the resonator surface [Was13a; Ber17]. In this case, the resonator used, 05-mode (see section 2.3.2.3), was exposed to cigarette particles in a sealed chamber, to test the sensor sensitivity obtained from mass-loading effects.

The detection of the resonance frequency can be performed using several methods [Sta04; Was13a] (see section 1.1.3). In this case, a phase-locked loop (PLL) circuit, based on the integrated circuit 74HCT4046 (see section 3.3.3), is applied for tracking the resonance frequency of the resonator. In addition, the interface circuit is also applied to cancel the resonator parasitics (see section 3.2.5). To demonstrate the functionality of the system, the 05-mode is characterized with different techniques in open-loop and closed-loop. For these measurements, a low-cost commercial instrument [Dig], capable of tracking the resonance frequency of the PLL and to perform sweep frequency measurements for the open-loop technique, is used.

5.5.1 Open-loop measurements

Initially, the 05-mode was analysed with an open-loop technique based on the frequency response function (see section 3.2.2). This technique was performed with a low-cost commercial instrument, *Digilent instrument Analog Discovery 2* [Dig], capable of performing sweep frequency measurements. This instrument is connected to a PC in order to calculate
the resonance frequency and quality factor of the resonator (see section 2.2.2) since these parameters have a main influence on the sensitivity and efficiency of the mass concentration sensing principle. An schematic of the setup is presented in figure 5.33.

![Schematic of the open-loop setup with the digilent instrument.](image)

Figure 5.33: Schematic of the open-loop setup with the digilent instrument.

In a first step, the performance of the resonator was checked by collecting cigarette particles on the surface resonator during 15 minutes and measuring the frequency shift produced.

![Open loop response of the interface circuit for the 05-mode before and after the deposition of cigarette particles.](image)

Figure 5.34: Open loop response of the interface circuit for the 05-mode before and after the deposition of cigarette particles.
As it can be observed in figure 5.34, a frequency shift of around 10 kHz was detected after collecting the particles. Nevertheless, a phase shift of around -15° is observed due to differences between the dummy and resonator, and the bandwidth limitation of the instrumentation amplifier. However, this resonance curve is adequate for the later implementation of the PLL circuit.

Once the behaviour of the resonator and system was tested, two similar experiments for the detection of cigarette particles were performed. The main objective was to check the deposition rate of the cigarette particles and the reproducibility of the measurements. In this case, we carried out a frequency sweep every minute. After that, the resonance parameters were determined with the procedure described in section 2.2.2. The frequency resolution measured of the resonator was ±70 Hz, a low value compared with other results presented in this thesis. Nevertheless, we should take into consideration that the resolution of the commercial instrument is low and the measurement process is not fast enough.

In figures 5.35 and 5.36, the open-loop measurements, showing the evolution of the resonance parameters with the deposition of cigarette particles, are presented. As expected from the previous results, the resonance frequency and quality factor decreased due to a higher concentration of particles on the surface resonator. More deposited cigarette particles result in higher frequency shifts. As we can observed, an almost linear decrease occurs for the resonance frequency and quality factor obtaining a decrease for \( f_r \) of around 617 and 632 Hz/min.

![Figure 5.35: Open loop measurements showing the evolution of the resonant parameters with the deposition of cigarette particles.](image-url)
5.5. Piezoelectric MEMS resonators for cigarette particle detection

5.5.2 Closed-loop measurements

In the previous section, we could check that the open-loop technique has a low resolution. In addition, this technique requires a high time measurement and therefore cannot be considered a real-time monitoring system. For this reason, we have developed a low-cost PLL circuit based on the integrated circuit 74HCT4046 (see section 5.5.2).

Figure 5.36: Open loop measurements showing the evolution of the resonant parameters with the deposition of cigarette particles.

Figure 5.37: Schematic of the closed-loop setup with the PLL 74HCT4046.
Nevertheless, the implementation of an oscillator is challenging due to the hydrodynamic loading and parasitic effects of the resonator. For this reason, the previous interface circuit was also included in the system. In this setup, the PLL circuit was combined with the resonator and the previous interface circuit as a closed-loop system. A schematic of closed-loop setup is presented in figure 5.37.

The main electronic component used in the developed closed-loop system is the integrated circuit 74HCT4046. Basically, this circuit is a feedback loop where a voltage controlled oscillator (VCO) can be automatically synchronized with the signal coming from the resonance of the 05-mode. The integrated circuit consists of three main elements connected in a feedback loop: a phase detector, a filter, and a VCO, as illustrated in the block diagram of figure 3.18. [Hsi96; Li12]. For further information, see section 3.3.3.

In order to obtain the resonance parameters, $f_r$ and Q factor, it was necessary to perform the first step of the calibration process (see section 4.2) using the previous results obtained with the open-loop setup. In this case the commercial instrument, Digilent, was able to obtain the circuit outputs, $f_{osc}$ and $G_{osc}$, with a rate of 5 samples/s obtaining therefore a higher frequency resolution of 1 Hz.

In this case, two different experiments were carried out with the closed-loop setup. In the first experiment (see figure 5.38), particles were collected as in the previous section obtaining a decrease for $f_r$ of around 621 Hz/min.

![Figure 5.38: Closed loop measurements showing the evolution of the resonant parameters with the deposition of cigarette particles.](image)

$f_r = -621.5x + 1.168 \cdot 10^5$ [Hz]

$Q = -0.58x + 184.8$
In the second experiment, the sensitivity and response of the system was checked. In order to do that, we opened and closed the sealed chamber to check the response of the system. As it can be observed in figure 5.39, several peaks in the resonance curves were detected. In addition, we could checked that the deposition of particles was higher, with a decrease for $f_r$ of around 1690 Hz/min, since in this case two cigarettes were introduced at the same time in the sealed chamber.

![Graph showing resonance curves](image)

Figure 5.39: Closed loop measurements showing the evolution of the resonant parameters with the deposition of cigarette particles.

Figures 5.40 and 5.41 show a sensor top-view photograph developed with a scanning electron microscope (SEM). The SEM images show the resonator covered by particles of different sizes and shape. The previous measurements show that these particles can be detected in real-time with a low-cost oscillator circuit.
Figure 5.40: Micrograph of the 05-mode resonator and the dummy device with scanning electron microscope (SEM) after the deposition of cigarette particles.

Figure 5.41: Micrograph of different cigarette particles deposited on the surface of the resonator.
5.5.3 Estimation of added mass

Once the performance of the resonator was tested with different open-loop and closed-loop techniques, the mass of the deposited cigarette particles, $\Delta m_{cig}$, can be calculated through equation 5.3 [Was14; Ber17].

$$\Delta m_{cig} \approx \frac{2m_{can}}{f_{can}} \Delta f_{cig} \tag{5.3}$$

Where $\Delta f_{cig}$, $f_{can}$, $m_{can}$ are the resonance frequency shift after particle deposition, resonator frequency, and mass, respectively. This expression is under assumption that the spring constant of the cantilever is kept the same and that the deposition of particles is uniform. The 05-mode resonator has a weight of $m_{can} = 62.91 \, \mu g$ and a resonance frequency in air of $f_{can} = 1108 \, kHz$. The added mass was estimated for the open-loop measurement presented in figure 5.36. In this case, a frequency shift, $\Delta f_{cig}$, of around 10 kHz was detected after collecting particles for 15 min, obtaining a value of $\Delta m_{cig} = 1.14 \, \mu g$. Moreover, the mass-loading sensitivity of the sensor ($\Delta f_{cig}/\Delta m_{cig}$) was calculated obtaining a value of 8.8 Hz/ng. This sensitivity value is similar to other reported in the literature. For example, Hutomo et al. reported a value of 0.15 Hz/ng for a cantilever sensor of reduced dimensions with a lower resonance frequency [Was14].

In conclusion, the development of a closed-loop setup based on the integrated circuit 74HCT4046 has been demonstrated. The system is capable of tracking the resonance frequency and quality factor of a micro-plate resonator, oscillating in a high order vibrational mode (05-mode), with a sensitivity of 8.8 Hz/ng. In this case, the mass-loading effect tests were proven by collecting particles from a cigarette. Nevertheless, the results obtained in this application, will be helpful for further applications such as for the detection of nanoparticles in workplace environment.

5.6 Piezoelectric MEMS resonators for tactile and elasticity sensing

In this work, a new application was tested to estimate the elasticity of different materials. In this case, the PZT resonator, previously described in section 2.3.2.4, was selected to work as a tactile sensor for elasticity sensing.

Tactile sensing might be the one of the most complex sensing modality compared to sight, hearing, smell, and taste, as it is not a simple transduction of one physical property into a bioelectric signal [Lee99]. Typically with tactile sensors, the contact force as well as the position, shape, and
elasticty properties of the object can be obtained [Uch02] through different transduction techniques such as: capacitive, piezoresistive, thermoresistive, inductive, piezoelectric and magnetic principles [Tiw12]. Considerable promising results have been reported for sample discrimination or deformation prediction in different fields such as in robotic systems [You11a] or bio-engineering [Mur04; Oma04]. For example, it can be used as an identification parameter for diagnosis of tissue diseases or defects detection in non-destructive testing [Sam07].

On the other hand, the Atomic Force Microscopy (AFM) technique, which uses a micro cantilever with a tip to sense the information of the sample including the force, roughness, and elasticity, can be regarded as a micro tactile sensor [Bin86; Zho14]. Nevertheless, in AFM, the interaction force between the tip and sample is obtained by detecting the deformation of the cantilever using a laser diode [Mon10; Bhu94].

In this work, we propose a tactile sensor to measure the elasticity of different materials but using low-cost electronic circuits. In this case, when the sensor tip touches the sample, the elasticity of the sample was derived by tracking the contact resonance frequency of the cantilever-sample system. This method offers an effective and non-destructive solution for tactile sensing.

5.6.1 Materials and setup

The PZT was characterized with an impedance analyser and a vibrometer to check the different out-of-plane vibration modes. In this case, the first (10-mode) and second (20-mode) order vibration modes were studied since they are located at a lower frequency and therefore they are suitable for the inclusion in an oscillator circuit.

As it can be seen in table 5.18, the quality factor is relatively low ($Q \approx 20$) compare with other resonators previously described in this work. Nevertheless, the conductance peak ($\Delta G$) of the 20-mode is superior. This will be very useful for the simplicity in the design of the oscillator circuit and for the later measurements.

Table 5.18: Comparison of resonance frequency, quality factor and conductance of the PZT for different vibration modes.

<table>
<thead>
<tr>
<th>Device</th>
<th>Mode</th>
<th>$f_r$ [Hz]</th>
<th>Q</th>
<th>$\Delta G$ [$\mu S$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT</td>
<td>10-mode</td>
<td>1191</td>
<td>15.85</td>
<td>0.954</td>
</tr>
<tr>
<td></td>
<td>20-mode</td>
<td>7190</td>
<td>20.27</td>
<td>20.2</td>
</tr>
</tbody>
</table>
In the previous measurements with the impedance analyser the PZT was free-clamped. However, in order to perform the elasticity measurements, it is necessary to design a base that fixes the cantilever at one end. This base has been designed with a 3D-printer where the PZT is introduced and glued with epoxy in order to reduce possible vibrations. Subsequently the base is fixed with four screws to a platform which is controlled by six stepping motors that allow the movement in any direction: three high-precision piezoelectric motors that allow a maximum displacement of 20 µm and three other motors that allow a greater range of movement of 5 mm (see figure 5.42).

![Figure 5.42: Schematic of the setup for the elasticity measurements.](image)

After analysing the vibration modes, the 20-mode was selected for this application since it presents the highest Q factor and conductance peak. This mode was measured with a vibrometer (see section 2.2.1), applying different excitation signals, in order to measure the maximum displacement in the tip (see table 5.19), being this tip the interface between the PZT and the material sample to measure. In addition, two PZT with different tips were measured. The PZT named as PZT 1 has an aluminium tip, while the PZT 2 has a tungsten tip (see figure 5.43). Once the PZT and tip were glued, we could observed an increase of the resonance frequency (see table 5.19). This occurs because the length of the PZT is reduced since it is introduced and glued inside the 3D-printer base. As we can observed, the PZT 2 presents a higher resonance frequency and displacement compared to the PZT 1 since the size and mass of the tip is smaller.
Table 5.19: Measurement of the resonant frequency and displacement for both PZT.

<table>
<thead>
<tr>
<th>Device</th>
<th>Mode</th>
<th>$f_r$ [kHz]</th>
<th>Voltage [V]</th>
<th>PZT displacement [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT 1</td>
<td>20-mode</td>
<td>11</td>
<td>0.1</td>
<td>38.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>77.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>650</td>
</tr>
<tr>
<td>PZT 2</td>
<td>20-mode</td>
<td>11.5</td>
<td>1</td>
<td>437</td>
</tr>
</tbody>
</table>

Figure 5.43: Picture of the different tips fixed to the PZT. (a) PZT 1: aluminium tip; (b) PZT 2: tungsten tip.

5.6.2 PZT measurements

The measurements of the different samples were performed with similar electronic circuits in open-loop and closed-loop.

- **Open-loop measurements:**

  Firstly, the behaviour of the PZT was tested by making measurements in open-loop with the interface circuit (see section 3.2.5). In order to perform these measurements, a lock-in amplifier (see section 2.2.2) was used to excite and collect the signal from the interface circuit. The main objective of the interface circuit is to reduce the parasitic effects of the PZT in order to obtain an appropriate resonance curve for the later closed-loop measurements (see section 3.3.1). In order to perform these measurements,
the platform and PZT were manually moved to apply an indeterminate force on a sample of polylactic acid material, commonly know as PLA (see table 5.20. Three measurements were performed by moving the platform 10 µm in z-axis direction. As can be seen in figure 5.44, a higher force or displacement is equivalent to an increase of the resonance frequency, indicating that this method is valid for elasticity sensing. This displacement of 20 µm produced approximately an increase in the resonance frequency of 176 Hz.

![Figure 5.44: Open-loop measurements of the PZT in contact with PLA with a displacement of 10 µm between measurements.](image)

- Closed-loop measurements:

Once the behaviour of the PZT and the measurement setup were verified, different closed-loop measurements were performed using a modified version of the interface circuit and a frequency meter to obtain the value of the resonance frequency. In order to meet the Barkhausen criterion, the interface circuit was modified introducing a higher gain in the instrumentation amplifier and closing the loop. In this case, the resistance that controls the gain of the instrumentation amplifier (AD8428) was replaced by a capacitor. This component acts as a low-pass filter and introduces the maximum gain (G=2000) of the instrumentation amplifier.

In order to control the piezoelectric motors of the platform, a virtual instrument (VI) was designed in LabView. This samples data from the frequency counter (Agilent 53220a) and the motors position, or what is the same, the platform position. In this case, 1000 measurement points were
obtained in the 20 µm range of the platform taking measurements every 0.8 s.

In table 5.20, the analysed materials are shown from lowest to highest elasticity: PDMS, a rubber, ABS, nylon, PLA and aluminium. As can be seen in table, the PDMS and the rubber present a similar elasticity. The same occurs for the ABS, Nylon and PLA samples. However, it is possible to observe small differences in the resonance frequency for both PZT (see figures 5.45 and 5.46).

Table 5.20: Materials measured with the PZT.

<table>
<thead>
<tr>
<th>Material</th>
<th>E [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS (Polydimethylsiloxane)</td>
<td>0.003</td>
</tr>
<tr>
<td>Rubber</td>
<td>0.007</td>
</tr>
<tr>
<td>ABS (Acrylonitrile Butadiene Styrene)</td>
<td>2.3</td>
</tr>
<tr>
<td>Nylon (Synthetic polymers based on polyamides)</td>
<td>3</td>
</tr>
<tr>
<td>PLA (Polylactic acid)</td>
<td>3.5</td>
</tr>
<tr>
<td>Aluminium</td>
<td>69</td>
</tr>
</tbody>
</table>

As it can be seen in figures 5.45 and 5.46 a higher force or displacement, is equivalent to increasing the resonance frequency, as was also verified with the open-loop measurements. In addition, the resonance frequency changes accordingly with the elasticity of the sample, indicating that the resonance frequency could be used as a valid parameter for elasticity sensing. As the results suggest, it would be necessary to implement a force control capable of monitoring the force applied on the sample. Nevertheless, in this work an alternative solution was tested by taking the point where the PZT tip makes contact with the sample, and therefore the resonance frequency increases, as a reference. This way we will have a reference point which will allows us to compare the frequency measurements of different materials and to estimate the force applied.

The procedure performed to obtain the elasticity of the samples can be summarised as follows. Firstly, the resonator is excited and brought into contact with the sample with a tip approaching process. After that, the resonator tip contacts the sample, the position of the platform is derived and the resonance frequency is tracked with the oscillator circuit.

As it can be observed in the measurements performed with the PZT 2, there is no difference in the resonance frequency at the beginning of the measurement (see figure 5.46). This may be due to the fact that the tungsten tip is not correctly fixed to the PZT 2. In other words, the elasticity of the
epoxy glue, that fixed the tip with the PZT 2, is being analysed instead. Once that range of approximately 4 µm is exceeded, the tip remains fixed to the PZT 2, being able to observe differences in the resonance frequency. For example, a higher resonance frequency was obtained for the PLA due to its higher elasticity. On the contrary, almost no differences were observed for the PDMS and rubber due to low elasticity of these materials compared with the PZT device. As indicated in previous studies on AFM, to get a high detection sensitivity, stiff or flexible cantilevers are required for testing on samples of high or low elasticity [Tur01].

Figure 5.45: Closed-loop frequency measurements for the PZT 1.
5.6.3 PZT calibration

The main objective of this application is to obtain the elasticity of different materials. For this reason, it is necessary to perform a calibration process that correlates the resonance frequency of the PZT with the force applied on the material and the elasticity. To do this, the stiffness constant (K) of the PZT 2 was measured using a commercial force sensor [Fsg]. With this force sensor, we were able to obtain a linear relationship between its output voltage and the force applied by the PZT when the platform is moved. In figure 5.48 is presented the measurement performed in static, or what is the same without exciting the device.
According to the datasheet of the force sensor, this presents a sensitivity of 7.2 mV/V/N, as the force sensor is supplied with a voltage of 10 V, we obtain a conversion factor of 72 mV/N. With this conversion factor we can finally obtain the value of the stiffness constant (K). Table 5.21 shows the average value of K and the deviation obtained with three different measurements. As it can be seen, an average value of 1565 ± 138 N/m was obtained, similar to the value of 1520 N/m reported in the datasheet.
Table 5.21: Stiffness constant for the PZT 2 in static.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Voltage/Displacement [mV/µm]</th>
<th>K [N/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static</td>
<td>0.112 ± 0.01</td>
<td>1565 ± 138</td>
</tr>
</tbody>
</table>

5.6.4 Elasticity sensing

In this section, the performance of the tactile sensor for elasticity sensing is carefully examined.

Once the calibration of the PZT 2 was performed, the elasticity of the different materials were obtained through the Hertz contact theory [Joh82; Mac12] and following a procedure previously reported by Fu et al. [Fu15]. In a previous step, the elasticity of the PZT 2 (E) and the moment of inertia (I) were calculated through equations 5.4 and 5.5.

\[
E = \frac{4Kl^3}{wt^3} \quad (5.4)
\]

\[
I = \frac{wt^3}{12} \quad (5.5)
\]

Where K is the stiffness constant previously obtained with a value of 1565 N/m. In this case, the length of the PZT is shorter due to the anchor in the base, being now of 12x1.5x0.6 mm$^3$. Using this data we could obtained an elasticity value (E) for the PZT of 33.3 GPa.

In order to estimate the elasticity of the samples, it is necessary to calculate the constants \(C_c\) and \(k_t\) defined in equations 5.6 and 5.7. Once the elasticity of the resonator is known, and taking into account that the density of the PZT (\(\rho\)) is 7500 kg/m$^3$, it was possible to estimate the constant \(C_c\) obtaining a value of 0.0498 s$^{1/2}$.

\[
C_c = L\sqrt{2\pi} \sqrt[4]{\frac{\rho A}{EI}} \quad (5.6)
\]

The constant \(C_c\) depends on the dimensions and properties of the cantilever. As these data, present different error sources, such as the dimensions or the density value of the PZT, the constant \(C_c\) was calibrated to reduce the final error. In this case, four different positions of the platform (7, 11, 15 and 18 µm) and the corresponding values of resonance frequency, force and elasticity for the ABS, nylon and PLA, were taken as a reference in equations 5.7 and 5.8 (see table 5.22).
5.6. Piezoelectric MEMS resonators for tactile and elasticity sensing

\[ k_t = \frac{k_c (C_c \sqrt{f_n})^3}{3} \frac{\cos(C_c \sqrt{f_n}) \cosh(C_c \sqrt{f_n}) + 1}{\sinh(C_c \sqrt{f_n}) \cos(C_c \sqrt{f_n}) - \sin(C_c \sqrt{f_n}) \cosh(C_c \sqrt{f_n})} \]

\[ E_s = \frac{(1 - \nu_s^2) E_t \sqrt{k_t^3 / 6RF}}{E_t - (1 - \nu_s^2) \sqrt{k_t^3 / 6RF}} \]

(5.7)  

(5.8)

Where \( E_t \) represents the elasticity of the tungsten tip with a value of 450 GPa, \( R \) is the radius of the tip with a value of 10 \( \mu \)m, \( \nu_s \) is the Poisson’s coefficient with a value of 0.35, \( k_c \) is the cantilever stiffness constant previously named as \( K \), \( f_n \) is the measured resonance frequency and \( F \) is the applied force. With all these data and using equations 5.7 and 5.8 it was possible to calibrate the constant \( C_c \) obtaining a value of 0.0458 \( s^{1/2} \). Once this constant \( C_c \) is known, the PZT device can be used to estimate the elasticity of different materials.

Table 5.22: Materials analysed to obtain the stiffness constant with the PZT 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Position [( \mu )m]</th>
<th>Force [mN]</th>
<th>Frequency [Hz]</th>
<th>( E_{\text{ref}} ) [GPa]</th>
<th>( E_{\text{est}} ) [GPa]</th>
<th>Error [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>7</td>
<td>10</td>
<td>12465</td>
<td>2.3</td>
<td>2.73 ( \pm ) 0.129</td>
<td>18.62</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>17.5</td>
<td>13038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>24</td>
<td>13302</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>30</td>
<td>13430</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon</td>
<td>7</td>
<td>10</td>
<td>12474</td>
<td>3</td>
<td>2.79 ( \pm ) 0.077</td>
<td>6.92</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>17.5</td>
<td>13040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>24</td>
<td>13364</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>30</td>
<td>13528</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA</td>
<td>7</td>
<td>10</td>
<td>12828</td>
<td>3.5</td>
<td>3.5 ( \pm ) 0.022</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>17.5</td>
<td>13381</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>24</td>
<td>13778</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>30</td>
<td>14034</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As it can be seen in table 5.22 the elasticity of the different materials were obtained with an average error of 18.62, 6.92 and 0.03 % for the ABS, nylon and PLA, respectively. As it can be observed, the error for the ABS is higher, this may be due to the fact that the elasticity value taken as a reference (2.3 GPa) is lower than the real value of the sample since other materials present a lower error.

In conclusion, the proposed resonator was tested for elasticity sensing, using low-cost electronic circuits, and obtaining an excellent performance.
For this reason, the PZT resonator can be considered an effective and non-destructive solution for elasticity sensing and sample characterization. Furthermore, sample information such as the position, orientation, and surface topography could further be obtained by using a scanning testing.

Nevertheless, further investigations are needed in order to confirm the results and performance of this application.
Chapter 6

Conclusions and future research

We live in a society exquisitely dependent on science and technology, in which hardly anyone knows anything about science and technology.

Carl Sagan

This doctoral thesis has dealt with sensing the density and viscosity of different liquids such as: viscosity standards, solvents, lubricant oils, diesel and grape must. Other applications for monitoring the gas damping of piezoelectric resonators, for mass-sensitive particle detection and for elasticity measurements were also tested. Specifically, the use of piezoelectric interfacing has been demonstrated as a good alternative to obtain a compact sensor. Aiming a rather broad analysis of the topic, several aspects have been addressed; from the basic design and characterization of piezoelectric resonators, to the implementation of electronic circuits and calibration processes.

6.1 Outline

The results reported in this thesis demonstrate that piezoelectrically excited MEMS resonators, carefully combined with a well-balanced electronic interface, promise to be a good alternative for liquid, gas or particle monitoring purposes, especially when a compact design of the sensing unit is requested.

In next paragraphs, a brief summary with the main conclusions for each application is presented.
Piezoelectric MEMS resonators for monitoring lubricating oils:

In this application different resonators were measured with different open-loop and closed-loop techniques.

On the one hand, two different resonators, tuning fork and "extensional 20", were characterized with different open-loop techniques in liquids with a broad range of densities and viscosities showing a resolution in the worst case of 14 mPa s and 0.11 g mL\(^{-1}\). Furthermore, we demonstrated the performance of both resonators in oils and diesel mixtures as well as in diesel/biodiesel blends.

On the other hand, different roof tile-shaped modes and the "extensional 130" were analysed with different closed-loop techniques in fluids having viscosities up to 500 mPa s. In addition, different calibration models were studied in order to reduce the calibration error. A simplified calibration model of five coefficients, based on a Taylor series of the hydrodynamic function, was proved as valid method for determining the density and viscosity of liquids. Furthermore, the effect on the calibration error was also studied taking into consideration different effects such as: the liquids selected for the calibration, the number of coefficients used and the effect of the temperature. Our results show a resolution in the worst case of 7.9 mPa s and 9.4 \(\times 10^{-4}\) g mL\(^{-1}\) using the liquid D500 with the PLL-based oscillator and the 05-mode resonator.

Piezoelectric MEMS resonators for monitoring grape must fermentation:

In this application, a piezoelectric resonator, 15-mode, was tested for the monitoring of a grape must fermentation process. In order to measure the density and the viscosity in a real grape must, a calibration procedure of the resonator was performed using model solutions of artificial grape must and a commercial density-viscosity meter. Furthermore, an in-line flow-through monitoring of a grape must fermentation was carried out. Our results demonstrate the high performance of MEMS resonators to detect the decrease in sugar and the increase in ethanol concentrations during the grape must fermentation with a resolution in the worst case of 1 \(\times 10^{-3}\) g mL\(^{-1}\) and 0.02 mPa s for the density and viscosity, respectively.

Gas damping effect of piezoelectric MEMS resonators:

This application presents a novel approach for monitoring the gas damping effect of piezoelectric MEMS resonators. In this case, two resonators with different geometries and vibration modes were analysed with an
impedance analyser. We could observe that as the resonant mode number increases and therefore the resonant frequency, the acoustic wavelength in the fluid reduces and becomes comparable to the structural wavelength. For this reason, the contribution of acoustic effects on the energy loss cannot be neglected any more in comparison with viscous effects.

- Piezoelectric MEMS resonators for cigarette particle detection:

In this application, the performance of a closed-loop setup, based on the integrated circuit 74HCT4046, was tested for the detection of cigarette particles. The system is capable of tracking the resonance frequency and quality factor of a micro-plate resonator, oscillating in a high order vibrational mode (05-mode), with a sensitivity of 8.8 Hz/ng. The results obtained in this application, will be helpful for further applications such as for the detection of nanoparticles in workplace environment.

- Piezoelectric MEMS resonators for elasticity sensing:

In this case, a PZT resonator was tested for elasticity sensing, using low-cost electronic circuits, and obtaining an excellent performance. For this reason, the PZT resonator can be considered an effective and non-destructive solution for elasticity sensing and sample characterization. In this case, the elasticity of the the ABS, nylon and PLA were obtained with an average error of 18.62, 6.92 and 0.03 %, respectively.

### 6.2 Future research

Throughout this thesis we have shown that there is a vast body of ongoing research in different fields. There are still many possible applications that can be studied with similar resonators and electronic circuits. Nevertheless, research requires a continuous effort to reach positive results and this is not always possible due to time constraints. Therefore, in this section, a brief summary, with possible future research, was introduced.

- Piezoelectric resonators:

It is clear that it would be interesting to design new piezoelectric resonators with different vibration modes and higher quality factor in order to improve the system resolution. However, other practical option would be to design resonators which lower parasitics in liquid media. In this way, a better resolution and simplicity in circuit design would also be achieved.
Electronic circuits:

Regarding the electronic circuits, a possible future objective would be to compare the oscillator based on the integrated circuit 74HCT4046 with other oscillator circuits in liquid media. The main advantage of this circuit is that it is no necessary a high-cost instrument such as the lock-in amplifier in the PLL-based oscillator or an automatic gain control in the discrete oscillator circuit.

Calibration process:

About the calibration process it would also be interesting to observe how the model of four coefficients fits to in-plane resonators of reduced thickness. Since this model was tested with the "extensional 130" but not with the "extensional 20".

Applications:

In this section, there is a vast range of possibilities. Some new applications have already been tested with good results such as the thickness monitoring of a layer material during a sputtering process. However, there is a huge number of applications, as it was described in the introduction, which could be analysed with the resonators and circuits described in this thesis obtaining fruitful results.
Appendices
Appendix A

Sensors for rheological properties

In this section, a brief introduction to the traditional measurement methods for density and viscosity sensing is introduced.

A.1 Introduction

The utility of rheological properties for liquid monitoring was documented in the introduction chapter. In this chapter, the traditional measurement methods for density and viscosity sensing are presented. Nevertheless, these methods tend to be bulky and costly and rely on the movement of macroscopic parts and complex reading mechanisms that prevents them from being implemented by microsystems. Because of that, a low-cost device, of limited dimensions capable of measuring density and viscosity in real-time, was designed in this thesis.

A.2 Density sensors

The density, has been determined by Archimedes principle-based hydrometers since time immemorial [HB14] (see figure A.1). These instruments, although useful for quick non exigent measurements, lack of a desirable characteristic basic in many applications: they are not automated and it is required a large liquid volume . In this work, these hydrometers were submerged in a thermostatic bath (Tamson TV2000) following the method established in the standard EN-ISO 3675 (see figure A.2).
Appendix A. Sensors for rheological properties

Figure A.1: Hydrometer sensor for density measurements.

Figure A.2: Thermostatic bath Tamson TV2000.

Other type is the U-tube density meter, based on the vibratory behaviour of a tube filled with the liquid under test. Nevertheless, U-tube density meters are still restricted to laboratory or industrial usage, due to the elevated cost and instrument volume. In this thesis, the density meter Anton Paar DMA4100 [Ant14a] was used for density measurements of liquids (see figure A.3).
Viscometers are used to measure viscosity in most circumstances. They work for fluids whose viscosity does not change under varying flow conditions. Viscometers usually work by comparing a stationary object and a fluid flow, or vice versa. The measure of the resistance is taken by measuring the drag resistance during relative motion through the fluid. There are several types of viscometers available, some for use in laboratories and others used as portable viscosity testers [Vis; Man15].

The simplest viscometers are those that rely on gravity as driving force. For instance, U-tube or Ostwald viscometers are laboratory instruments that contain a glass capillary through which the liquid is forced by its own weight. The time that takes for a certain amount of liquid to pass is correlated to the kinematic viscosity (see figure A.4). These viscometers were also used in this work along with the thermostatic bath (see figure A.2).
In falling ball viscometers, a solid sphere is allowed to descend through a vertical or inclined tube filled with liquid [Ant14b]. The time taken for the falling sphere, whose density and radius are known, to move between two markings is measured, and then users can calculate viscosity. They work on principles derived from Stokes’ Law, which gives drag force on a sphere (see figure A.5 and A.3).

Another version that uses the same principle is the falling piston viscometer [Nor14] (see figure A.6). These operate on similar principles as the falling sphere viscometers, except that they measure resistance to a piston moving through a fluid. These devices are very long-lasting and simple to operate, and require little maintenance. For this reason, they are very popular in industry.
A.3. Viscosity sensors

On the other hand, there are viscometers based on forced movement, be it oscillatory or rotatory. As example of the former, oscillating piston viscometers consist of a metal piston immersed in the liquid that is forced to move longitudinally by the magnetic field generated by an external coil. The amplitude of the piston oscillations is used to calculate the viscosity. Rotational viscometers measure the resistance of fluids to torque (see figure A.7).

Other rotational instruments are the electromagnetically spinning (EMS) viscometer [Kyo14], based on the optical measurement of the rotational speed of a metallic ball forced electromagnetically, and the Stabinger viscometer [Ant14c] (see figure A.8). In this instrument, the liquid is confined inside a closed cylindrical cavity that rotates at constant speed. This rotor speed can be correlated with the liquid viscosity.
Other type is the "bubble" viscometer. This measure the time it takes for bubbles to rise through a liquid. These viscometers are most often used for resins or varnishes. These viscometers are fast and very useful for measuring viscosity in the field (see figure A.9).

Finally, rheometers are used when the viscosity changes with flow conditions, i.e. for non-newtonian fluids (see figure A.10).
Appendix B

Liquids and their density-viscosity values

In this section, we have summarised the density and viscosity values of the liquids analysed in this thesis such as solvents, viscosity standards, lubricant oils and grape must. These density-viscosity values were obtained with the commercial density and viscosity sensors previously described in appendix A.

Table B.1: Summary table with density-viscosity values of solvents and other liquids.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Temperature [°C]</th>
<th>μviscometer [mPa s]</th>
<th>ρviscometer [g mL⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>25</td>
<td>0.38</td>
<td>0.679</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td>0.54</td>
<td>0.792</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>1.04</td>
<td>0.785</td>
</tr>
<tr>
<td>2-Propanol</td>
<td></td>
<td>1.96</td>
<td>0.781</td>
</tr>
<tr>
<td>DITA</td>
<td>20</td>
<td>58.632</td>
<td>0.912</td>
</tr>
<tr>
<td>PAO8</td>
<td></td>
<td>93.561</td>
<td>0.829</td>
</tr>
<tr>
<td>Olive oil</td>
<td></td>
<td>81.355</td>
<td>0.913</td>
</tr>
<tr>
<td>Ester oil</td>
<td></td>
<td>98.884</td>
<td>0.916</td>
</tr>
<tr>
<td>DITA</td>
<td>40</td>
<td>41.539</td>
<td>0.902</td>
</tr>
<tr>
<td>PAO8</td>
<td></td>
<td>23.505</td>
<td>0.898</td>
</tr>
<tr>
<td>Olive oil</td>
<td></td>
<td>35.467</td>
<td>0.899</td>
</tr>
<tr>
<td>Ester oil</td>
<td></td>
<td>37.146</td>
<td>0.816</td>
</tr>
<tr>
<td>DITA</td>
<td>100</td>
<td>7.907</td>
<td>0.863</td>
</tr>
<tr>
<td>PAO8</td>
<td></td>
<td>4.527</td>
<td>0.857</td>
</tr>
<tr>
<td>Olive oil</td>
<td></td>
<td>7.301</td>
<td>0.860</td>
</tr>
<tr>
<td>Ester oil</td>
<td></td>
<td>6.204</td>
<td>0.780</td>
</tr>
</tbody>
</table>
Table B.2: Summary table with density-viscosity values of the viscosity standards at different temperatures.

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Temperature [°C]</th>
<th>$\mu_{\text{viscometer}}$ [mPa s]</th>
<th>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5</td>
<td>20</td>
<td>5.718</td>
<td>0.839</td>
</tr>
<tr>
<td>N10</td>
<td></td>
<td>18.004</td>
<td>0.851</td>
</tr>
<tr>
<td>N35</td>
<td></td>
<td>73.834</td>
<td>0.858</td>
</tr>
<tr>
<td>N100</td>
<td></td>
<td>286.360</td>
<td>0.866</td>
</tr>
<tr>
<td>D5</td>
<td>25</td>
<td>4.71</td>
<td>0.8343</td>
</tr>
<tr>
<td>N10</td>
<td></td>
<td>13.79</td>
<td>0.8481</td>
</tr>
<tr>
<td>N35</td>
<td></td>
<td>30.16</td>
<td>0.8519</td>
</tr>
<tr>
<td>N100</td>
<td></td>
<td>55.36</td>
<td>0.8544</td>
</tr>
<tr>
<td>S200</td>
<td></td>
<td>217.50</td>
<td>0.8622</td>
</tr>
<tr>
<td>D500</td>
<td></td>
<td>395.92</td>
<td>0.8661</td>
</tr>
<tr>
<td>D5</td>
<td>40</td>
<td>3.345</td>
<td>0.825</td>
</tr>
<tr>
<td>N10</td>
<td></td>
<td>8.518</td>
<td>0.838</td>
</tr>
<tr>
<td>N35</td>
<td></td>
<td>27.388</td>
<td>0.846</td>
</tr>
<tr>
<td>N100</td>
<td></td>
<td>86.800</td>
<td>0.854</td>
</tr>
<tr>
<td>D5</td>
<td>100</td>
<td>1.198</td>
<td>0.785</td>
</tr>
<tr>
<td>N10</td>
<td></td>
<td>2.143</td>
<td>0.799</td>
</tr>
<tr>
<td>N35</td>
<td></td>
<td>4.527</td>
<td>0.809</td>
</tr>
<tr>
<td>N100</td>
<td></td>
<td>9.712</td>
<td>0.818</td>
</tr>
</tbody>
</table>

Table B.3: Summary table with density-viscosity values of lubricant oils and diesel fuel.

<table>
<thead>
<tr>
<th>Diesel [%vol]</th>
<th>Biodiesel [%vol]</th>
<th>Temperature [°C]</th>
<th>$\mu_{\text{viscometer}}$ [mPa s]</th>
<th>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td></td>
<td>2.87</td>
<td>0.834</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td></td>
<td>3.18</td>
<td>0.840</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td></td>
<td>3.46</td>
<td>0.846</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td></td>
<td>3.95</td>
<td>0.852</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td></td>
<td>4.45</td>
<td>0.857</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td></td>
<td>4.81</td>
<td>0.864</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diesel [%vol]</th>
<th>Lubricant SAE 15W40 [%vol]</th>
<th>Temperature [°C]</th>
<th>$\mu_{\text{viscometer}}$ [mPa s]</th>
<th>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td></td>
<td>71.95</td>
<td>0.862</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td></td>
<td>65.41</td>
<td>0.861</td>
</tr>
<tr>
<td>4</td>
<td>96</td>
<td></td>
<td>60.72</td>
<td>0.860</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td></td>
<td>55.20</td>
<td>0.859</td>
</tr>
<tr>
<td>8</td>
<td>92</td>
<td></td>
<td>50.54</td>
<td>0.858</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td></td>
<td>47.78</td>
<td>0.857</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Diesel [%vol]</th>
<th>Lubricant SAE 2.5W [%vol]</th>
<th>Temperature [°C]</th>
<th>$\mu_{\text{viscometer}}$ [mPa s]</th>
<th>$\rho_{\text{viscometer}}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td></td>
<td>20.7</td>
<td>0.8299</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td></td>
<td>19.04</td>
<td>0.8300</td>
</tr>
</tbody>
</table>
Table B.4: Summary table with density-viscosity values of lubricant oils and diesel fuel.

<table>
<thead>
<tr>
<th>Diesel [%vol]</th>
<th>Lubricant SAE 0W30 [%vol]</th>
<th>Temperature [°C]</th>
<th>$\mu_{viscometer}$ [mPa s]</th>
<th>$\rho_{viscometer}$ [g mL$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>89.660</td>
<td>0.8505</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>25</td>
<td>81.769</td>
<td>0.8502</td>
</tr>
<tr>
<td>4</td>
<td>96</td>
<td>40</td>
<td>75.205</td>
<td>0.8499</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td>40</td>
<td>68.933</td>
<td>0.8497</td>
</tr>
<tr>
<td>7</td>
<td>93</td>
<td>40</td>
<td>66.531</td>
<td>0.8496</td>
</tr>
<tr>
<td>8</td>
<td>92</td>
<td>40</td>
<td>63.876</td>
<td>0.8495</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>40</td>
<td>59.167</td>
<td>0.8493</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>45</td>
<td>45.419</td>
<td>0.8408</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>45</td>
<td>41.838</td>
<td>0.8405</td>
</tr>
<tr>
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Table B.5: Summary table with density-viscosity values for model solutions of grape must.

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Appendix C

Scientific production

C.1 Publications in peer-reviewed journals


### C.2 Contributions to international conferences


Bibliography


