Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 1, 9–16

FUNDAMENTALS OF MASS MEASUREMENTS

V. M. Mecea[*]

QCM Lab, Gäddvägen 16, 175 47 Järfälla, Sweden

The article makes a bridge between quartz crystal microbalance (QCM) and conventional beam balances revealing the role of the field in mass measurements. Thus, three fundamental principles for mass measurements are formulated and demonstrated: the field principle, the mass sensitivity principle and the general equivalence principle.

Keywords: *acceleration, beam balance, equivalence principle, general relativity, mega-gravity field, QCM*

Introduction

Measuring lengths and masses were probably the earliest challenges of mankind. Drawings showing beam balances with arms of equal length can be seen on a 3500 years old papyrus from ancient Egypt [1]. The accuracy of the mass measurements with mechanical beam balances was continuously improved ever since. During the 19th century these balances achieved the relative sensitivity (sensitivity/maximum load) of 10^{-9} [2].

In 1959 Sauerbrey [3] introduced a new method for mass measurements. Instead of measuring the tipping angle of a beam balance, or the displacement in case of a spring balance, he used the change in the frequency of a quartz resonator to measure the mass of a film adherently deposited on the quartz resonator surface. Thus it was possible to detect even 10^{-16} kg, while the commercial analytical microbalances can detect about 10^{-10} kg [4]. Since Sauerbrey demonstrated that mass can be measured using vibrations and frequency is related to the mass, several vibrating systems were developed to measure the mass [5, 6]. The mass measuring instrument introduced by Sauerbrey was named quartz crystal microbalance (QCM). It became a widely used instrument for small mass measurements in vacuum, gas and liquid phase [7–15]. Since 1980 QCM was used also with one face of the quartz resonator in contact with a liquid [16]. A few years later, Kanazawa and Gordon calculated the frequency change when one face of a quartz resonator is in contact with a liquid [10]. The equation derived by Kanazawa and Gordon, supported by dozens of experimental results, revealed that the frequency response of the QCM in contact with a liquid depends not only on the liquid density, but also on its viscosity. Thus, more and more QCM users came to the idea that QCM is not a real mass sensor and, therefore, it is more appropriate to use the name thickness shear mode (TSM) sensor [7] instead of QCM. On the other hand it was not clear why QCM is more sensitive than analytical microbalances and why the deposition must be adherent to the quartz resonator surface in order to measure its mass using the frequency change of the quartz resonator. These questions have limited the development of the QCM technique and a reliable interpretation of the experimental results.

The aim of the article is to provide an answer to these questions and to put some light on the more general problem of mass measurement, by formulating three fundamental principles for mass measurements.

Sensitivity analysis

Quartz crystal microbalance

Ever since quartz crystal resonators have been used for frequency control applications in radio-communication equipment, the effect of a foreign material deposited on their surfaces on the resonant frequency has been known. However a quantitative relationship was not established until 1959. The possibility of using quartz crystal resonators as quantitative mass measuring devices was first explored by Sauerbrey [3]. The decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator, having AT or BT cut, was found to be proportional to the added mass of the deposited film:

$$\Delta f = -\frac{f_q^2 M_f}{N\rho_q S} = -\frac{f_q^2 m_f}{N\rho_q} \qquad (1)$$

where f_q is the fundamental resonant frequency of the quartz, N is the frequency constant of the specific crystal cut (N_{AT}=1.67·10^5 Hz cm; N_{BT}=2.5·10^5 Hz cm),

* vasile.mecea@qcmlab.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

ρ_q=2.65 kg dm^{-3} is the quartz density and S is the surface area of the deposited film, the mass of which is M_f. When the deposited film covers the whole sensitive area of the quartz resonator it is easier to use the surface density $m_f=M_f/S$ to further calculate the film thickness $l_f=m_f/\rho_f$, where ρ_f is the density of the deposited film. A typical quartz crystal resonator is shown in Fig. 1.

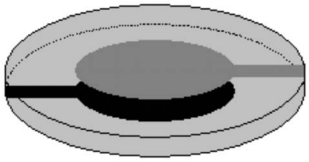

Fig. 1 A typical quartz crystal resonator used for mass measurements

The key-hole shaped electrodes on both major faces of the quartz resonator are vacuum deposited gold or silver films, about 150 nm in thickness. The mass-sensitive area is situated in the central part of the resonator, covering about the area where the two electrodes overlap.

Equation (1) shows that the QCM mass sensitivity $\Delta f/m_f$ is proportional to the square of the quartz resonator frequency.

There are also experimental data showing that on the surface of a quartz crystal resonator we have a mass sensitivity distribution that closely follows the vibration amplitude distribution. In Fig. 2 are shown experimental results published elsewhere [10, 11]. The recorded frequency change for deposited silver spots, having the same mass M_f, is proportional to the vibration amplitude at that point indicated by the voltage U. A 5 MHz, plano-convex, AT-cut resonator with 200 mm curvature radius was used. The diameter of the resonator was 14 mm. It had silver electrodes of different diameters on each side: 13 mm on the flat side and 6 mm on the convex side. To reveal the mass sensitivity distribution, small silver spots having the same thickness and a diameter of 0.6 mm were

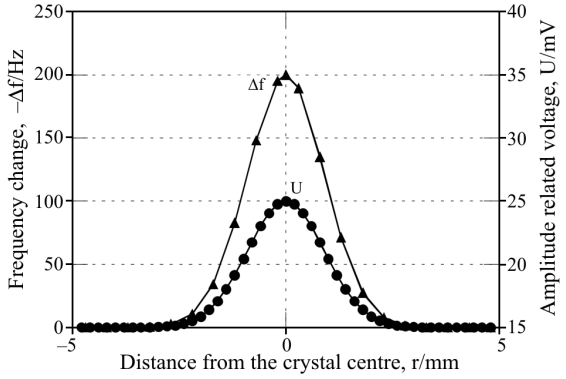

Fig. 2 Mass sensitivity related Δf and vibration amplitude related U distribution along one of the quartz resonator diameters

vacuum deposited along one of the crystal diameters, with 0.5 mm spacing between them. The amplitude distribution along the same diameter was revealed, by using the scanning probe method [15–17]. The voltage U is proportional to the vibration amplitude at each point along the chosen diameter. Similar results were reported in the literature [3, 18–23].

Both the mass sensitivity and amplitude distribution curves follow a Gaussian function [20].

The displacement of a point, vibrating with simple harmonic motion, may be described as

$$x=A\sin(\omega t)$$

where A is the vibrational amplitude at that point and $\omega=2\pi f$ is the angular frequency.

The acceleration of this motion is

$$a=-\omega^2 A\sin(\omega t)=-4\pi^2 f^2 A\sin(\omega t)$$

The maximum value of the acceleration at that point is $a_{max}=\omega^2 A$. On the crystal surface the highest vibration amplitude A_0 and the maximum acceleration $a_0=\omega^2 A_0$ is in the centre of the quartz resonator.

From Eq. (1) we conclude that the mass measuring sensitivity is proportional to the square of the quartz resonator frequency. From the experimental results shown in Fig. 2 we conclude that the mass measuring sensitivity of the QCM is proportional to the vibrating amplitude at that point. These two statements lead to the conclusion that the physical quantity which determines the mass measuring sensitivity at every point on the surface of a quartz crystal resonator is the acceleration of the crystal vibration at that point.

Earlier experimental results in gas and vacuum [18, 24, 25] indicated that the vibration amplitude at the centre of a quartz resonator is in the range from 10 to 200 nm.

In order to correlate the mass measuring sensitivity at the centre of the quartz crystal resonator with the corresponding acceleration at this point, we shall rely on the previous results obtained for amplitude measurements at the centre of a 5 MHz plano-plano AT-cut quartz resonator using scanning tunnelling microscopy [25]. Here it is stated that the maximum vibration amplitude at the centre of such a crystal is

$$A_0=CQV_d$$

where C=1.4·10^{-12} m V^{-1}, Q is the quality factor of the quartz resonator and V_d is the peak voltage applied on the quartz resonator electrodes.

A small silver spot with a diameter of 0.45 mm and thickness of 200 nm, measured with an adjacent film thickness monitor, having a mass M_f= 3.3399·10^{-10} kg was vacuum deposited in the centre of a 4951605 Hz plano-plano AT-cut quartz resonator. The frequency change Δf=96.925 Hz, the crystal in-

ductance L=73 mH and resistance R=15 Ω were measured with a Hewlet Packard network analyser model E 5100A, driving the crystal at P=100 μW. Calculating $Q=\omega L/R$=151411 and $V_d=\sqrt{2PR}$=0.0548 V we get A_0=11.61 nm. The maximum acceleration is $a_0=1.1238\cdot10^7$ m s^{-2}=$1.1456\cdot10^6$ g, where g=9.81 m s^{-2} is the gravitational acceleration. It shows that, at the centre of a quartz crystal resonator, acceleration is more than one million times higher than the gravitational acceleration. Using plano-convex quartz resonators with higher Q value and higher driving levels, this acceleration can be much higher. Thus a quartz crystal resonator can create a mega-gravity field on its surface.

In order to evaluate the minimum detectable mass in the centre of the quartz resonator we use the frequency shift Δf=96.925 Hz corresponding to the deposition of a silver spot with a mass $M_f=3.3399\cdot10^{-10}$ kg. The minimum detectable mass M_f^{min} depends also on the frequency stability $\Delta f/f$ which can be attained over the length of the mass measuring process. Previously reported results [26] showed an experimental frequency stability $\Delta f/f=\pm1.5\cdot10^{-9}$ and stated that even 1 pg cm^{-2} can be detected when temperature stability is better. This corresponds to a frequency stability $\Delta f/f=1.13\cdot10^{-11}$. In some special cases [27], using better temperature control and ultra-high vacuum we can rely on an even better frequency stability $\Delta f/f=5\cdot10^{-12}$. In this case $M_f^{min}=8.53\cdot10^{-17}$ kg. It is interesting to look at the product between the minimum detectable mass and the acceleration acting on that mass:

$$\Gamma=M_f^{min}\,a_0=8.53\cdot10^{-17}\text{ kg}\cdot1.1238\cdot10^7\text{ m s}^{-2}=9.5536\cdot10^{-10}\text{ N}\approx10^{-9}\text{ N}$$

Conventional microbalances

We can compare this result obtained in the case of the QCM with the case of the most sensitive balances we currently use in our laboratories: beam, cantilever, torsion or spring balances. Depending on their maximum allowable load, the minimum detectable mass is M_f^{min}=0.1 μg=10^{-10} kg. This sensitivity can only be attained in a vibration-free environment at a constant temperature.

All these balances have a common feature: the acceleration acting on the measured mass is just the gravitational acceleration g. In this case we have $\Gamma=M_f^{min}\,g=9.81\cdot10^{-10}\text{ N}\approx10^{-9}$ N.

Γ should not be interpreted as a universal constant. It is rather a proof that there is a connection between mass and acceleration. The magnitude of Γ refer to the same level of exigency towards the environmental conditions for both QCM and conventional balances. This idea was first discussed earlier [28].

Acceleration dependent mass sensitivity

On the surface of a quartz crystal resonator the acceleration of the shear vibration varies from zero to several million times the gravitational acceleration g over a distance of 2 to 3 mm from about the electrode edges to the electrode centre. In the same way the mass sensitivity varies too.

The effect of the gravitational acceleration on the cantilever, torsion and spring balances is obvious and will not be discussed here. However, a beam balance works as a comparator and it is interesting to look closer at this type of balance.

In case of a beam balance with arms of equal lengths, the equilibrium is attained when $M_Ag=M_Bg$, where M_A and M_B are the masses of the bodies laid on the pans A and B, respectively, and g is the gravitational acceleration. We will have equilibrium when $M_A=M_B$, whatever the value of the acceleration is. The two bodies will be in equilibrium both on Earth and Moon. However, the mass sensitivity is not the same on Earth and on the Moon. In the general case, at equilibrium we have $M_Aa=M_Ba$, where a is the magnitude of the acceleration at that point. This is illustrated in Fig. 3.

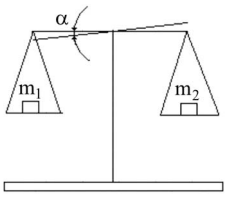

Fig. 3 Mass sensitivity of a beam balance

The balance sensitivity is measured by the tipping angle α, which corresponds to a small difference between the two masses. For small angles, α is proportional to the difference between the two forces acting on the two arms:

$$\alpha=k(M_A-M_B)a$$

where k is a constant which depends on the mechanical construction of the balance. When $M_A=M_B$ the tipping angle α will be zero (equilibrium) whatever the value of the acceleration. This is the typical situation for the use of a beam balance. However, if the two masses are not identical, the sensitivity illustrated by the angle α, will depend on the magnitude of the acceleration acting on the two bodies. If α=6° on Earth, it will be only 1° on the Moon. None of the balances we normally use in our laboratories (beam, cantilever, torsion or spring) can be used on a space laboratory orbiting around the Earth, because the gravitational acceleration is cancelled by the centrifugal acceleration. However, a QCM works excellent in outer space [15]. The mass

deposited on the surface of a quartz crystal resonator is subjected to an acceleration caused by the vibration of the quartz resonator.

The maximum value of the acceleration on the crystal surface can be increased by increasing the driving level in the crystal. However this will not increase the integral mass sensitivity of the crystal. The additional energy will be shared between quartz and the deposited film and the same fraction of vibration energy will be transferred to the film, whatever the driving level. This is clearly stated in the energy transfer model [15].

The value $\Gamma \approx 10^{-9}$ N corresponds to very stable conditions. For a QCM this means ultra-high vacuum, constant temperature, no temperature gradients and no stress inside the crystal resonator. For a laboratory balance this means constant temperature, no air convection and no external vibrations. These provide an additional acceleration, which will be vectorially added to the gravitational acceleration.

Acceleration as field intensity

Since Isaac Newton published 'Principia' in 1687 mankind has lived with two accelerations:

- gravitational acceleration
- inertial acceleration, as a second time-derivative of space.

Einstein made a big step forward by formulating 'The Equivalence Principle' in 1907. This states that the gravitational acceleration g=9.81 m s^{-2} is equivalent with the acceleration of a uniformly accelerating frame with $g=\mathrm{d}^2x/\mathrm{d}t^2$. There is no experiment which can distinguish that we are on Earth, under the influence of the gravitational acceleration g, or we are in a spaceship, moving with the velocity $v=gt$ in a space without stars, without planets, thus, without any gravity. As a consequence, a body has the same mass on Earth as on that spaceship.

There is a striking similarity between the gravitational law, formulated by Newton:

$$F = G\frac{Mm}{r^2}$$

where G=6.67·10^{-11} N m^2 kg^{-2} is the gravitational constant, and the force acting between two electric charges, defined by Coulomb's law:

$$F = \frac{1}{4\pi\varepsilon}\frac{Qq}{r^2}$$

In the case of electric charges, the intensity of the electric field created by the charge Q is defined as the ratio between force and the charge q:

$$E = \frac{1}{4\pi\varepsilon}\frac{Q}{r^2}$$

Thus, it is appropriate to define, in a similar manner, the intensity of the gravitational field created by the mass M, as the ratio between the gravitational force and the mass m. It is clear that this ratio is the acceleration.

$$a = G\frac{M}{r^2}$$

Sometimes, the gravitational acceleration is interpreted as 'gravitational field strength' [29]. In a similar way even the inertial acceleration, as the second time-derivative of space, can be interpreted as field intensity. When the value of this acceleration is constant, e.g. non-time-dependent, we have an inertial field in which intensity is not time dependent. When the value of the acceleration is time-dependent, we have a time-dependent inertial field. Thus, on the surface of a quartz crystal resonator, used in QCM measurements, a time-dependent inertial field with intensity $a=-\omega^2 A\sin(\omega t)$ is developed during crystal vibration. The maximum value of the intensity of this field, $a=-\omega^2 A$, is several million times higher than the intensity of the gravitational field on Earth, g. Thus, the field developed on the surface of a quartz resonator, used for QCM measurements, can be interpreted as a time-dependent, mega-gravity inertial field.

Experimental evidence for the presence of a mega-gravity inertial field on the surface of a quartz resonator

The experiments were performed using QCM lab equipment with a specially designed oscillator, which permits a high drive level of the quartz resonators up to 150 mA. Using automatic level control (ALC) the crystal current could be scanned between 1 and 100 mA at different rates.

6 MHz, AT-cut plano-convex quartz resonators (Maxtek P/N 103200 and P/N 103218), with gold electrodes and a diameter of 14 mm were used in the experiments.

The carbon-covered iron nanoparticles were deposited by a L-CVD (laser assisted chemical vapor deposition) system consisting of a vaporizing/sublimation chamber and a deposition chamber. An ArF excimer laser was used, operating at a wavelength of 193 nm, 50 Hz (nominal pulse duration: 15 ns [FWHM]) and a fluence of around 110 mJ cm^{-2}. The laser beam was focused with a cylindrical lens achieving a focusing area above the QCM crystal of 0.13 cm^2 located at around 2 mm above the crystal.

The precursor ferrocene was vaporized/sublimed at a temperature of 43°C and introduced into the deposition chamber by the carrier gas Ar. The gas mixture of ferrocene and argon traveled parallel with the laser beam for 10 cm before reaching the deposition zone. Total pressure in the system was 30 mbar (1 bar=10^5 Pa) with a linear gas velocity of 8 cm s^{-1}. The deposition time was 40 min.

In Fig. 4 is shown a quartz resonator coated with carbon nanoparticles for 40 min, while the crystal current was 90 mA.

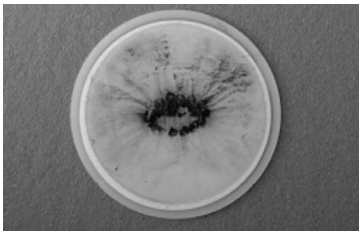

Fig. 4 A 6 MHz plano-convex, AT-cut quartz resonator coated with carbon nanoparticles for 40 min, while the crystal current was 90 mA

Although the laser beam was about 20 mm wide and the crystal was placed about 3 mm under the laser beam, the deposition was located only in the central part of the resonator where its vibration is located. This might be interpreted as sedimentation induced by the mega-gravity field of the shear vibrations in the centre of the crystal. The deposition also reveals some lines, radiating from the centre, with significant difference in thickness. Those locations where the carbon film is thinner are regions where the crystal vibration has an out-of-plane component. At these locations the acceleration of the vibrations normal to the crystal surface is high enough to expel the carbon nanoparticles, which accumulate at the nodal locations. This experimental result is in accordance with the calculations made by EerNisse *et al*. [30] for flexural vibrations associated with the normal shear vibrations of the AT-cut resonators. The fact that deposition is located mostly in the central part of the resonator might be interpreted as proof that shear vibrations induce sedimentation of the deposited carbon nanoparticles. It is a competition between sedimentation induced by shear vibrations and expelling induced by out-of-plane vibrations of the crystal. In Fig. 5 is shown a resonator coated with carbon nanoparticles while the crystal was placed 1 mm under the laser beam and the crystal current was 140 mA. It reveals two lobes, symmetrically positioned with respect to the centre of the crystal along the *x*-axis. The carbon-nanoparticles were also expelled because of the high acceleration. The amplitude of the out-of-plane vibrations in these regions is about 6% of the maximum amplitude of the shear vibration in the centre of the crystal [30]. The amplitude of the shear

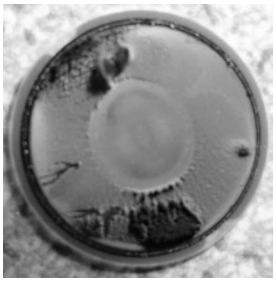

Fig. 5 A 6 MHz plano-convex, AT-cut quartz resonator coated with carbon-nanoparticles while the crystal current was 140 mA

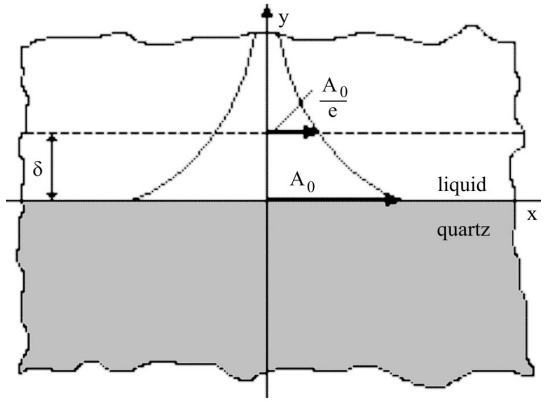

Fig. 6 Amplitude and acceleration decay at the quartz-liquid interface

vibration can be calculated using the equation established by Borowsky *et al*. [25]. In our case it is about 100 million times higher than the gravitational acceleration. Thus the acceleration of the out-of-plane vibrations in the region of the two lobes is about 6 million times higher than the gravitational acceleration. This acceleration develops a force, normal to the crystal surface, which exceeds the binding force of the carbon-nanoparticles to the gold electrodes. In Fig. 6 is shown a SEM picture of an area located at the edge of one of the two lobes. This reveals the expelling of the carbon nanoparticle agglomerates in the region with a high acceleration normal to the crystal surface.

The experimental results shown here reveal the complex situation on the surface of a shear vibrating quartz resonator used in QCM applications. The very high acceleration of the shear vibrations induces sedimentation of the C-nanoparticles, while the out-of-plane vibrations induce an expelling of the C-nanoparticles. In the early years of the QCM it was thought that AT-cut resonators exhibit a pure shear vibration. Later, compressional waves were detected in liquids and the explanation was based on the existing velocity gradients in the contacting liquid [31]. The two lobes shown in Fig. 5 reveal that compressional waves are also produced by the crystal itself. More recently [30] the possibility for flexural vibrations was evident. This is slightly evident even in Fig. 4.

Thus, by coating a quartz resonator with C-nanoparticles it was possible to reveal the effects of the mega-gravity field.

On the surface of a vibrating quartz crystal resonator we have a time-dependent inertial field, its maximum intensity being at the centre of the quartz resonator. The strong inertial field can be interpreted as a mega-gravity field. Although the intensity of this field varies between a maximum positive value and a maximum negative value, following the sinus function, its intensity is more than 90% of the maximum positive value during about 14% of the vibration period and is more than 90% of its maximum negative value during about 14% of the vibration period. This time is long enough to produce significant effects at the atomic and molecular level. Here the sedimentation of even atoms and the development of anomalous phenomena are possible. A mega-gravity field may be useful in many applications in metallurgy, solid state chemistry, polymer physics, materials processing or biochemistry.

Recently [32, 33], this mega-gravity field was used for the development of the so-called 'bond breaking spectroscopy' and it might explain the enhanced catalytic activity on vibrating catalysts [34, 35].

The inertial field developed at the surface of the QCM permits its use as a mass sensor in outer space on a space laboratory orbiting around the Earth although the gravitational acceleration is cancelled by the centrifugal acceleration [15].

The QCM is not only a mass sensor, but also an actuator, providing a mega-gravity field on its surface.

It does not matter what the vibrational mode of the quartz resonator is, in order that it can be used as a mass sensor [15, 36–38]. It does not matter also if we use quartz or other piezoelectric material for mass sensing [15, 39, 40]. The only important thing is to create a field that can act on the body whose mass we want to measure.

QCM response in a liquid

It was shown that the product Γ between the minimum detectable mass and the acceleration acting on that mass is a constant. This means that mass sensitivity is proportional to the acceleration acting on the measured body or, in other words that the mass sensitivity is proportional to the intensity of the field acting on the measured body. The concept of a field intensity dependent mass sensitivity can explain why the frequency of a shear vibrating quartz crystal resonator, in contact with a liquid, depends not only on the liquid density, but also on its viscosity.

The frequency change, when one face of a quartz crystal resonator is in contact with a liquid of density ρ_l and viscosity η_l, was first calculated by Kanazawa and Gordon [10, 41] and later using the energy transfer model [15].

$$\Delta f = -f_q^{3/2}\left(\frac{\rho_l \eta_l}{\pi \rho_q \mu_q}\right)^{1/2} \quad (2)$$

where ρ_q and μ_q are the quartz density and shear modulus, respectively.

When such a resonator is in contact with a liquid, and this is a common situation in many applications of the QCM, the vibration amplitude and also the acceleration decays exponentially from the crystal surface into the liquid, as shown in Fig. 7.

$$A(y)=A_0\exp(-y/\delta)$$

where $\delta=(\eta_l/\pi f_q \rho_l)^{1/2}$ is the penetration depth, defined as the distance into the liquid layer where the vibration amplitude has diminished *e* times. Here η_l and ρ_l is the liquid viscosity and density respectively and f_q is the quartz resonator frequency. A_0 is the maximum vibration amplitude at the centre of the crystal resonator.

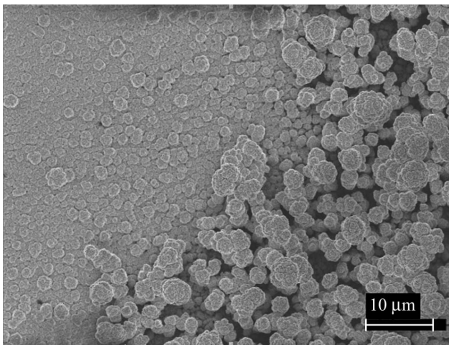

Fig. 7 SEM picture of an area situated at the edge of one of the two lobes on the surface of the quartz resonator coated with carbon-nanoparticles, while the crystal current was 140 mA

The larger the distance *y* from the quartz-liquid interface, the lower the vibration amplitude and acceleration. The field intensity varies in the same way too. A certain small volume of liquid situated at distance δ from the quartz liquid interface will produce a frequency change *e*-times smaller than the same volume of liquid situated in direct contact with the quartz surface. Because the mass sensitivity is field intensity dependent, it is obvious that the mass sensitivity depends on both the liquid density and viscosity. Liquid viscosity determines the amplitude and field intensity the decaying profile. It is a widespread opinion that QCM is not only sensitive to the mass of the contacting liquid, but also to the viscosity of this liquid [42]. This is true, but it is a second order effect. The prime effect is a field

intensity dependent mass sensitivity and the field intensity, as well as vibration amplitude, follows a function that includes both the liquid viscosity and density, as illustrated in Fig. 7. It is interesting to notice that in Eq. (2) we have the product between density and viscosity under square root. The two physical quantities cannot be separated. It should be a mechanism that is binding them together. This is the field intensity dependent mass sensitivity.

The film deposited on the quartz resonator surface must be adherent to the quartz resonator surface in order to have the same acceleration as the quartz resonator.

When the quartz resonator is in contact with a liquid, its roughness, or crevices can trap liquid molecules, which will vibrate with the same amplitude and acceleration as the quartz resonator surface. These trapped molecules will exhibit solid film behaviour, producing an additional frequency change [11, 43].

Fundamental principles of mass measurements

The equivalence principle, formulated by Einstein in 1907, states the equality of the gravitational acceleration and inertial acceleration of a uniformly accelerating frame. This is not only the basis for the theory of general relativity, but also has a direct consequence: if both a gravitational field and an inertial field are present at a point in space, then the total acceleration is $\vec{a}_t = \vec{a}_g + \vec{a}_i$, where $\vec{a}_g$ is the gravitational acceleration and $\vec{a}_i$ is the inertial acceleration.

At a certain point of a gravitational field $\vec{a}_g$ has the same magnitude and direction.

At a certain point of an inertial field $\vec{a}_i$ can have a time-independent or a time-dependent magnitude and direction.

Acceleration measures not only the rate of the velocity change or the rate of the direction change but also the intensity of the associated field.

It is not possible to penetrate into a body, to identify all the atoms and to add their masses in order to get the total mass of that body. One should use something that can act on a body from a distance, and this is the field. For a neutral body the field should be gravitational, inertial or a superposition of these fields. For an electrically loaded body the field can be electric or magnetic. In a mass spectrometer we need at least an electric field to measure the mass of the ions.

For mass measurements three fundamental principles can be formulated:

- The field principle: the mass of a body can only be measured by placing the body in a field. Acceleration acting on a body measures the field intensity.
- The mass sensitivity principle: the mass sensitivity of any balance is proportional to the intensity of the field acting on the measured body. ($\Gamma = M_{min}a$=const.)
- The general equivalence principle: the mass measured in a gravitational field or in a time-independent inertial field (a=const.) is undistinguishable from the mass measured in a time-dependent inertial field. When the field intensity is not time-dependent (a=const.), the mass is evaluated using a space related parameter (displacement, angle). When the field intensity is time-dependent [$a=-\omega^2 A\sin(\omega t)$], a time related parameter that is synchronous with the field intensity (frequency) must be used in order to evaluate the mass of the body.

Einstein's equivalence principle refer to the situation when a=const. When Sauerbrey introduced the QCM in 1959, in order to test the validity of his equation, he placed a quartz crystal resonator, which developed a time dependent inertial field [$a=-\omega^2 A\sin(\omega t)$], in the close vicinity of a mica substrate attached to a torsion microbalance in a vacuum deposition system. He measured the mass of the deposited films using both the time dependent inertial field developed by the quartz resonator and the time independent gravitational field that was acting on the torsion balance. Thus he provided the first experimental proof on the validity of the general equivalence principle.

The fact that the mass of a body can be measured using both a space related parameter (angle, displacement) and a time related parameter (frequency) reminds one of Einstein's general relativity which states that mass creates a curvature of the space-time.

Conclusions

QCM is not only a sensitive mass sensor but also an actuator generating a mega-gravity field on the surface of the quartz resonator. The very high mass sensitivity of the QCM is explained by the very high acceleration acting on the deposited film.

The product between the minimum detectable mass and the acceleration acting on that mass is a constant for both QCM and analytical microbalances when equivalent experimental conditions are used. For best experimental conditions this constant has a value of about 10^{-9} N.

Acceleration is a paramount condition for mass measurement. Therefore, in order to measure the mass of a body, we must place that body in a field.

The viscosity dependent frequency change of a quartz resonator in contact with a liquid is a second order effect resulting from the field intensity dependent mass sensitivity of the QCM.

Experiments with carbon nanoparticles revealed that AT-cut quartz crystal resonators do not exhibit a pure shear vibration. An out-of-plane, extensional vibration is associated to the shear vibration.

Acknowledgements

I thank Jan-Otto Carlsson, Mats Boman and Oscar Alm from the Ångström Laboratory, Department of Materials Chemistry, Uppsala University for their kind support in performing the measurements with carbon nanoparticles.

References

1 E. Robens and S. P. Garg, J. Therm. Anal. Cal., 71 (2003) 13.
2 Th. Gast, T. Brokate, E. Robens, Z. Alia and K. Pavey, J. Therm. Anal. Cal., 71 (2003) 19.
3 G. Sauerbrey, Z. Phys., 155 (1959) 206.
4 V. M. Mecea, Anal. Lett., 38 (2005) 753.
5 T. Brokate, Th. Gast, E. Robens and Z. Ali, J. Therm. Anal. Cal., 71 (2003) 25.
6 Z. Ali, K. Pavey and E. Robens, J. Therm. Anal. Cal., 71 (2003) 31.
7 D. S. Ballantine, R. M. White, S. J. Martin, A. J. Ricco, E. T. Zellers, G. C. Frye and H. Wohltjen, Acoustic Wave Sensors: Theory, Design and Physico-Chemical Applications, Academic Press, San Diego, CA 1997.
8 C. Lu and A. W. Czanderna, Eds Applications of Piezoelectric Quartz Crystal Microbalances, Elsevier: Amsterdam, Oxford, New York, Tokio 1984.
9 S. J. Martin, V. E. Granstaff and G. C. Frye, Anal. Chem., 63 (1991) 2272.
10 K. K. Kanazawa and J. G. Gordon, Anal. Chem., 57 (1985) 1770.
11 S. J. Martin, G. C. Frye, A. J. Ricco and S. D. Senturia, Anal. Chem., 65 (1993) 2910.
12 C. K. O'Sullivan and G. G. Guilbault, Biosens. Bioelectron., 14 (1999) 663.
13 M. Rodahl and B. Kasemo, Sens. Actuators, A 54 (1996) 448.
14 K. A. Marx, Biomacromolecules, 4 (2003) 1099.
15 V. M. Mecea, Sens. Actuators, A 40 (1994) 1.
16 P. L. Konash and G. J. Bastiaans, Anal. Chem., 52 (1980) 1929.
17 V. M. Mecea, J. Phys. Sci. Instrum., 22 (1989) 59.
18 G. Sauerbrey, Z. Phys., 178 (1964) 457.
19 R. M. Mueller and M. White, Rev. Sci. Instrum., 39 (1968) 291.
20 B. A. Martin and H. E. Hager, J. Appl. Phys., 65 (1989) 2630.
21 T. W. Schneider and S. J. Martin, Anal. Chem., 67 (1995) 3324.
22 D. A. Buttry and M. D. Ward, Chem. Rev., 92 (1992) 1355.
23 R. Lucklum and P. Hauptman, Faraday Discuss., 107 (1997) 123.
24 K. K. Kanazawa, Faraday Discuss., 107 (1997) 77.
25 B. Borowsky, B. L. Mason and J. Krim, J. Appl. Phys., 88 (2000) 4017.
26 A. W. Warner and C. D. Stockbridge, Vacuum Microbalance Technique, Behrndt, K. H. Ed. Plenum Press, New York 1963, Vol. 3, p. 55.
27 R. J. Vig and F. L. Walls, 1994 International Frequency Control Symposium, p. 506.
28 V. M. Mecea, J.-O. Carlsson and R. V. Bucur, Sens. Actuators, A, 53 (1996) 371.
29 J. Breithaupt, Understanding Physics for Advanced Levels, 3rd Edition, Stanley Thornes Publishers Ltd., 1995, p. 160.
30 E. P. EerNisse, E. Benes and M. Schmid, 2002 IEEE International Frequency Control Symposium and PDA Exibition, p. 2.
31 B. A. Martin and H. E. Hager, J. Appl. Phys., 65 (1989) 2627.
32 F. N. Dultsev, V. P. Ostanin and D. Klenerman, Langmuir, 16 (2000) 5036.
33 M. A. Cooper, F. N. Dultsev, T. Minson, P. V. Ostanin, C. Abell and D. Klenerman, Nature Biotechnology, 19 (2001) 833.
34 H. Nishiyama, N. Saito, M. Shima, Y. Watanabe and Y. Inoue, Faraday Discuss., 107 (1997) 425.
35 S. Kelling, T. Mitrealis, Y. Matsumoto, V. P. Ostanin and D. A. King, Faraday Discuss., 107 (1997) 435.
36 S. W. Wenzel and R. M. White, Appl. Phys. Lett., 54 (1989) 1976.
37 E. Benes, M. Gröschl, W. Burger and M. Schmidt, Sens. Actuators, A, 48 (1995) 1.
38 S. J. Martin, M. A. Butler, J. J. Spates, M. A. Mitchell and W. K. Schubert, J. Appl. Phys., 83 (1998) 4589.
39 R. P. O'Toole, S. G. Burns, G. J. Bastiaans and M. D. Porter, Anal. Chem., 64 (1992) 1289.
40 H. Fritze, H. L. Tuller, H. She and G. Borchard, Sens. Actuators, B, 76 (2001) 103.
41 K. K. Kanazawa and J. G. Gordon, Anal. Chim. Acta, 175 (1985) 99.
42 C. Henry, Anal. Chem., 68 (1996) 625A.
43 L. A. Theisen, S. J. Martin and A. R. Hillman, Anal. Chem., 76 (2004) 796.

OnlineFirst: June 27, 2006

DOI: 10.1007/s10973-006-7570-x