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Diethelm Johannsmann

The Quartz Crystal Microbalance in Soft Matter Research

Fundamentals and Modeling

 Springer

Diethelm Johannsmann
Institute of Physical Chemistry
Clausthal University of Technology
Clausthal-Zellerfeld
Germany

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Dedicated to my family

Preface

If we date the birth of the quartz crystal microbalance (QCM) to Günter Sauerbrey's paper from 1959 [1] the QCM is now more than 50-years old. Its use in vacuum is routine to the extent that the fact is not usually mentioned in the scientific literature. The QCM flew to Mars in 1997 [2, 3] and there are at least four books covering it in detail. Why one more book?

Starting in the 1980s, the QCM got its second wind after it was immersed into liquids and after it was realized that the QCM is a surface-analytical tool with capabilities much beyond gravimetry. The advanced QCMs supply the bandwidth of the resonance in addition its frequency (where the "dissipation factor" of the QCM-D is equivalent to bandwidth), and they do so on a number of different overtones. This added information has opened the door to non-gravimetric applications of the QCM. "Non-gravimetric" sounds as if it was not known what—exactly—was measured. That may have been true at some instances in the beginning, but it is not true today. The QCM is a surface-acoustic-wave-based analytical instrument and the behavior of surface acoustic waves in complex media is not a mystery.

The widespread use of the QCM in liquids since 1990 was mainly driven by the novel instrumentation, but there also was a widespread interest in soft matter at interfaces. Typical samples were polymer brushes, supported lipid bilayers, polyelectrolyte multilayers, adsorbed proteins, cell cultures, and functional polymer films in a wider sense. The evolution of the QCM was paralleled by similar instrumental progress in optics (surface plasmon resonance spectroscopy, advanced ellipsometry, to name examples), by the long and multifaceted evolution of scanning force microscopy, and by improved electrochemical instrumentation. These instruments and the research done with them form the context of the QCM and the book therefore occasionally makes comparisons and indicates, where combinations can be of use.

The QCM is simple, basically, but to set up one's own instrument requires somewhat of a physics background. One needs a basic understanding of electrical circuits and one needs to pay attention to the construction of the crystal holder. If one is without such skills (or without the time to revive them), one can embark on QCM-based research with one of the commercial instruments. One may plug, play, and see what happens. This progress in the hardware means, among other things, that ever more users apply this technique to ever more diverse samples. As always,

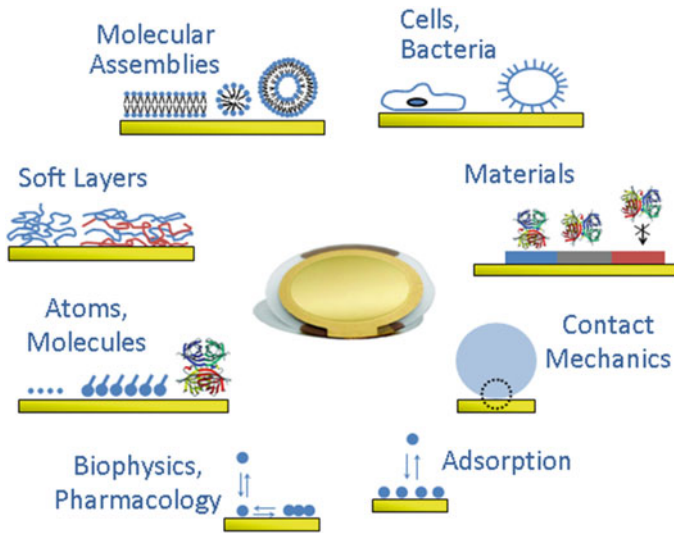


Fig. 1 Various applications of the QCM

plugging and playing is one thing, not having to worry about the instrument is another. The advanced QCMs open up new research opportunities, but there is a danger of not sufficiently appreciating the different sources of artifacts.

This book provides a detailed description of the background behind the technique and the data analysis methods, in a format that can be understood and appreciated by users with backgrounds ranging from biology to engineering and at a sufficient level of detail that it is educational. The analysis of acoustic shear waves builds on a number of fundamental concepts of physics, which many users of the technique do not usually come across. Short discussions of background material (viscoelasticity and contact mechanics, in particular) have therefore been included.

The author's thinking about the QCM is guided by what he calls the "small load approximation" (SLA). The SLA states that the frequency shift is proportional to the amplitude of the periodic stress at the resonator surface. A recent appraisal of the SLA can be found in Ref. [4]. The SLA is as old as acoustic sensing (meaning: older than the QCM) and it was not called small load approximation previously. The approximation needs a name and "small load approximation" is the best one the author could think of. The SLA was made the guiding principle for modeling. Of course choosing such a unique perspective has its pros and cons. It gives the book a clear structure. It (hopefully) simplifies the presentation of the more advanced topics. At the same time, it makes some of the familiar and time-honored results look unfamiliar. The Sauerbrey equation has suffered this fate. It is derived in the middle of the book (Sect. 8.1). Had the Sauerbrey relation been the main topic of the book, the formal machinery leading to the SLA and from there to the Sauerbrey result would have been too much of a good thing. With the SLA at

hand, the discussion can move on from the Sauerbrey case to viscoelastic films, bubbles, slip, multilayers, proteins, and contact mechanics (Fig. 1). With the machinery established, it all falls in place.

The mathematics was kept at such a level that undergraduate students in any of the science disciplines should be able to follow every single step. The physics of the QCM in many respects makes for an interesting bit of science education. Numerous aspects have counterparts in optical spectroscopy, electrical engineering, quantum mechanics, rheology, or mechanics. Familiarizing oneself with the QCM, one renews old acquaintances and that in itself can be an enjoyable exercise.

The book is self-contained. At least this was the intention. As far as the QCM itself is concerned, all proofs are outlined step-by-step. Some derivations, where the mathematical machinery serves as proof only and contains little physical insight, have been moved to the appendices. The appendices also contain background information. The book walks on a somewhat narrow line with regard to anisotropy. Anisotropy is essential. Quartz would not be piezoelectric if it was isotropic. Yet, if anisotropy had been covered in its full beauty, this would have hidden some of the simpler concepts. In order to avoid the discussion of anisotropy, the parallel-plate model is often pushed to the foreground. Within the parallel-plate model, all tensor properties (just about all properties of a crystal other than density) reduce to complex numbers, which are called the “relevant tensor component.” The “relevant component” is meant to be evaluated after the respective tensor has been transformed to the coordinate system of AT-cut quartz. The algebra leading to these tensor components is not needed and it is therefore not reproduced. Good books on the matter are Refs. [5] and [6]. The algebra does not hold any unsolved problems; anisotropy is well understood. Not coincidentally, the early masterpiece on anisotropy, the “Lehrbuch der Kristallphysik” by W. Voigt (first published in 1910), contains a thorough discussion of piezoelectricity. Voigt coined the term “tensor.” Tensor algebra is not a black art, it is merely a matter of not letting oneself be intimidated by large equation systems.

With regard to the fundamentals, the book has to start somewhere. For example, while the reader is reminded of what complex numbers are, there is no detailed introduction to their properties. Readers not familiar with complex numbers will need to exercise the basic operations. Similarly, Taylor-expansions are often applied. The respective formula is then cited but not proven. Furthermore, resonances and waves are introduced only briefly. Resonances and waves are explained with much didactic zeal in the textbooks of physics; there is no point in trying to do better here.

The number of papers *making use* of the QCM is so large that it is futile trying to reference even a significant fraction. The book is brief on applications for a second simple reason, which is limited expertise. The QCM has become a standard tool in diverse areas of soft matter research and the life sciences. The book touches on selected applications only. Along similar lines: The QCM is a member of a wider class of acoustic sensors. Other acoustic sensors are mentioned, but the focus is on the QCM.

Much knowledge has been gained already and giving due credit to all previous workers is a difficult task. This shall not be an excuse not to try. However, the following remarks should not be understood as a historical account. While writing the book, the author discovered work, which he had not been remotely aware of. It is fair to assume that there is more work waiting for rediscovery. The author covers his own work in more depth than the work of others because this is what he knows best. Please do not misunderstand this as a lack of appreciation for the achievements of others.

Below is a list of datable accomplishments deserving a special mention:

- Starting with the early days of acoustic sensing, the book by Mason from 1948 certainly is a hallmark [7]. It contains many of the modern concepts. That includes the electromechanical analogy, equivalent circuits, the small load approximation, and an acute emphasis on the fact that the viscoelastic parameters of soft materials depend on frequency.
- What is called the tensor form of the small load approximation here (Sect. 6.1), was derived by Pechhold in 1959 and published under the title *Zur Behandlung von Anregungs- und Störungsproblemen bei akustischen Resonatoren* [8]. As the title says, Pechhold chose to publish in German (but so did Sauerbrey). The paper is not cited well; it is not even listed in the Web of Science. Its outcome is of fundamental relevance to the physics of all resonant acoustic sensors.
- Central to acoustic sensing of course is Günter Sauerbrey's paper from 1959 [1]. Sauerbrey is open about the fact that the influence of added mass onto the resonance frequency was known to many in the field. People used to tune resonators by marking the resonator surface with a pencil. There actually is a second brief paper from 1959 proposing the use of piezoelectric crystals for microweighing [9]. Sauerbrey put the idea into a concise form.
- As far as instrumentation is concerned, the QCM-D from Q-Sense has certainly made a remarkable contribution to the field. It has made the technique available to a broad community. It should be remembered, though, that the "QCM-D principle" is equivalent to impedance analysis. Knowing this context is worthwhile.

A recent book on the QCM and related piezoelectric sensors, edited by Janshoff and Steinem, appeared in 2007 [10]. The book has a rather wide scope; it covers diverse applications in-depth. An earlier book, edited by Arnau, covers similar content, but has more of an emphasis on acoustics, instrumentation, and modeling [11]. Still earlier, the books by Thompson and Stone [12], and by Balantine et al. [13] as well as volume 107 of the *Faraday Discussions* [14] collect knowledge about the advanced QCM and related techniques at a time, when this methodology was picking up momentum.

A book often quoted with regard to the classical QCM (operated in air or vacuum) is the one edited by Lu and Czanderna [15]. Still further back in time, the book chapter by Stockbridge gives an overview of the QCM applied in vacuum [16]. Quartz crystals in general are treated in-depth by Bottom [17] and by Salt [18]. Bottom is interested in resonators more than in sensors. He approaches the

subject from the perspective of the practitioner, but still covers physical background (including anisotropy). The book by Rosenbaum [19] complements Bottom's book. Rosenbaum is more detailed with regard to theory and modeling than Bottom. The tutorial by Vig covers quartz resonators in time and frequency control [20]. There are a number of excellent reviews covering specific applications and topics, referenced further below in the respective context. For the newest developments, the literature surveys by Cooper and co-workers are a good source [21–23]. Cooper et al. are brief on technology and modeling; they are mostly interested in the growing range of applications.

A few remarks on notation:

- The formal machinery heavily builds on complex numbers and complex amplitudes. Complex numbers and amplitudes of complex time-harmonic functions were given a tilde (\sim) and a hat ($\hat{}$), respectively (example: $\tilde{u}(t) = \hat{u} \exp(i\omega t)$). If one and the same letter is used with and without a tilde, the letter without tilde denotes the real part. The imaginary part then is small and was neglected. The prime ($'$) and the double prime ($''$) denote the real and the imaginary part of a complex quantity. What is often called the “modulus” of a complex quantity, $|\tilde{z}|$, is called “absolute value” here. This is intended to avoid confusion with the shear modulus.
- Bold letters denote vectors.
- The components of piezoelectric tensors relevant to the AT-cut carry the index “26”. The text does not elaborate on tensor algebra. With regard to the index 26, we just follow the practice in other sources [19].
- In cases where variables have different meanings in the literature, they were mostly given an index, rather than risking confusion. For example, G is the shear modulus in rheology, and is the conductance in electricity. The electrical conductance is called G_{el} here, even though this makes the equations look clumsy. A few variables *do* have more than one meaning (D , n , ϵ). In these cases the context hopefully clarifies the variable's meaning.
- When inserting numbers into equations, the chosen values mostly pertain to the crystals used in the author's laboratory. These are AT-cut crystals ($Z_q = 8.8 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$) with a fundamental frequency of $f_0 = 5 \text{ MHz}$. Less important than f_0 is the size. The author mostly uses 1-inch crystals. These have an active area around 30 mm^2 .

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