

Effects of finite crystal size in the quartz crystal microbalance with dissipation measurement system: Implications for data analysis

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A quartz crystal microbalance with dissipation, or QCM-D, allows the properties of a loaded quartz oscillator—resonance frequency and dissipation $[1/(\text{the quality factor})]$ —to be monitored on several overtones. The frequency and the dissipation factor of the loaded oscillator are functions of the physical properties (such as thickness, density, viscosity, elasticity, roughness) of the media loading the resonator (e.g., a liquid, a thin polymer film, a phospholipid bilayer, etc.) and the frequency at which the measurement was performed. In this contribution, it is shown that the frequencies measured with the QCM-D instrument on the first, third, fifth, and seventh overtones do not agree with those expected of an ideal, infinite crystal. Therefore, the results of QCM-D measurements cannot be directly compared with theoretical models that require the resonance frequency of an unloaded crystal to be used as one of the input parameters. A phenomenological procedure for dealing with this problem is proposed. © 2004 American Institute of Physics.

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I. INTRODUCTION

Recently, the quartz crystal microbalance with dissipation (QCM-D) has emerged as a tool to study ultrathin bio-organic films in aqueous environments.^{1–4} The QCM-D instrument employs a standard setup in which a piezoelectric quartz crystal driven to oscillate in a thickness-shear mode at its resonance frequency serves as a frequency-determining element of an electronic oscillator circuit. The decay constant of the oscillations is measured by periodically disconnecting the crystal from the driving circuit and following the decay of the oscillations.^{1,5} It describes the extent to which the oscillator dissipates energy, and is related to the width of the resonance peak. (Another way to measure the resonance frequency and quality of resonance is to passively record the complete impedance spectrum of the resonator with a network analyzer.^{6,7} This method provides a direct measure of the resonance peak width.)

The usefulness of the QCM(-D) technique rests in the fact that the resonance frequency, as well as the quality of resonance, depend on the environment in which the crystal is placed. In a typical experiment, one “loads” the crystal by depositing a layer on the crystal surface and/or immersing the crystal in a liquid reservoir. The resonance frequency of the loaded crystal is then measured. The difference between this frequency and the resonance frequency of the unloaded crystal—referred to as the “frequency shift”—contains information about mechanical properties of the deposited layer and/or the surrounding liquid: its mass, thickness, density,

viscosity, elasticity, etc. However, these properties cannot be calculated from the frequency shift directly; a model needs to be developed which relates them to the frequency shift. Thus, interpretation of QCM(-D) data relies on the use of models.

The starting point of any model is the resonance frequency of an unloaded crystal. In the simplest case, the crystal is assumed to be an infinite elastic plate that oscillates in the direction parallel to its surface. If the oscillations are assumed to propagate only in the direction perpendicular to the surface of the crystal, the series resonance frequency of such a plate in vacuum is given by⁸

$$f_{Rn} = \frac{n}{2h_q} \sqrt{\frac{\mu_{qn}}{\rho_q}}, \quad (1)$$

$$\mu_{qn} = \mu_q + \frac{\epsilon^2}{\kappa} - \frac{8\epsilon^2}{\pi^2 n^2 \kappa},$$

where n is the overtone order (odd), h_q is the crystal thickness, ρ_q the density of quartz, and μ_{qn} is the elastic modulus of quartz, in the calculation of which the piezoelectric stiffening effect was taken into account.^{8,9} μ_q is the appropriate stiffness coefficient (2.93×10^{10} N/m²), ϵ is the appropriate piezoelectric stress coefficient (-9.24×10^{-2} C/m²), and κ is the effective (clamped) dielectric constant (3.982×10^{-11} F/m; values given for AT-cut quartz^{5,8,10,11}). For $n = 1$, the quantity given by Eq. (1) is typically referred to as the fundamental f_0 . The dissipation in the ideal crystal is assumed to be negligible.¹²

The case of a crystal loaded with a thin elastic overlayer, oscillating in vacuum, can be modeled based on similar

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assumptions.¹³ This approach predicts that the frequency shift ΔF (the difference between the resonance frequency of a loaded crystal and the resonance frequency of a bare crystal in vacuum) is proportional to the mass per unit area of the overlayer. This is referred to as the Sauerbrey relationship.¹³ Its success can be attested to by the near-ubiquitous use of quartz resonators as film thickness measurement monitors in vacuum-deposition systems (where film density is known). This point is discussed in more detail in Reed *et al.*⁶ and Johannsmann *et al.*⁷

In the case of a crystal immersed in liquid, derivation based on the same set of assumptions yields the expression for the resonance frequency F_{ln} in terms of the density ρ_1 and viscosity η_1 of the liquid:^{6,14}

$$F_{\text{ln}} = f_{Rn} - \frac{1}{2\pi\rho_q h_q} \sqrt{\rho_l \eta_l \pi f_{Rn}}. \quad (2)$$

Similarly, for the dissipation (represented in terms of the so-called dissipation factor $D_n = (\pi \tau f_{Rn})^{-1}$, where τ is the decay time constant of the oscillations¹):

$$D_{\text{ln}} = \frac{1}{\rho_q h_q} \sqrt{\frac{\rho_l \eta_l}{\pi f_{Rn}}} \quad (3)$$

(the equations are given in the form in which they appear in Voinova *et al.*¹⁵)

The ability to predict the behavior of the crystal in fluid using the above equations depends, among other things, on the knowledge of the resonance frequency of the unloaded crystal f_{Rn} . Precise knowledge of it becomes even more important when the resonance frequency and dissipation factor of a crystal loaded with a thin viscoelastic layer are modeled: Survey of the literature indicates that the frequency shifts due to thin viscoelastic layers studied (lipid bilayers,¹⁶ protein^{3,17} and polymer^{7,18} layers, vesicles^{16,19–21}) are in the range of tens to hundreds of hertz (this refers to the difference between the frequency of the unloaded crystal in liquid and the frequency of the crystal loaded with the thin viscoelastic layer in the same liquid—the value normally cited in QCM-D literature). Thus, an error in the value of f_{Rn} of 100 Hz [in 5 MHz, or $(2 \times 10^{-3})\%$] can effectively absorb the effect due to the viscoelastic properties of the layer. The predictions of the above equations do not agree with the experimental data in simple liquids to such a degree yet.⁵

Furthermore, due to the large number of parameters that enter models that describe viscoelastic layers (layer density, thickness, viscosity, and shear elastic modulus),^{7,15} measurements on several overtones become indispensable⁷ (though not necessarily sufficient²²). If a measurement needed to be performed on one overtone only, or if a simple linear relationship between the resonance frequency and the overtone order was obeyed, f_{Rn} could be treated as an adjustable parameter. But since it is known that on the lower-order overtones ($n < 9$) available in the QCM-D system the relationship is not linear,^{7,8} the dependence of f_{Rn} on the overtone order needs to be known with great precision as well. (Note that the areal mass of the layer is not expected to be as sensitive to the errors in the resonance frequency as the viscoelastic properties. There are two reasons for this. First,

mass is frequency-independent and is treated as such in the models. Therefore, when predictions of a model are compared with experimental results, the dependence of f_{Rn} on the overtone order will be absorbed into the frequency-dependent viscoelastic term, and lead to erroneous values of the shear modulus and viscosity. Second, errors in areal mass are expected to be of order $\delta f/f$, where δf is the difference between the frequency used in the calculations and the actual frequency; for δf of 50 kHz, this amounts to 1% in the case of a 5 MHz crystal. On the other hand, viscoelastic terms contain higher powers of f , magnifying the effect of discrepancies.)

In this contribution, we examine the basic assumptions which are used in the derivation of the existing models. Specifically, we show that significant (\sim kHz) discrepancies between the predictions of, e.g., Eq. (1) and the frequencies actually measured on various overtones are observed. We assert that a possible reason for these discrepancies is the finite crystal size, and suggest an empirical correction procedure.

II. RESULTS AND DISCUSSION

We begin by examining the relationship between the frequencies measured with the QCM-D instrument on various overtones. In Fig. 1(a), the frequencies measured with various crystals in air, scaled by the overtone order, are plotted as a function of the overtone order. The resulting plots are clearly incompatible with the predictions of Eq. (1) (Fig. 1(a), gray line/open circles). As the example tabulated in Table I shows, the differences between the measured frequencies and those calculated using Eq. (1) are on the order of several kilohertz.

The observed behavior of the crystal on low-order overtones ($n=3, 5$, and 7) agrees better with the expression derived for the case of a *finite* circular crystal:²³

$$f_{Rnmk} = \sqrt{\frac{\mu_{qn}}{\rho} \left(\frac{n^2}{4h^2} + \frac{pX_{mk}^2}{4\pi^2 a^2} \right)}, \quad (4)$$

where a is the radius of the crystal covered by the electrodes, X_{mk} is the k th root of the Bessel function of a first kind of order m , and p is a fitting parameter. μ_{qn} is given by the same expression as in Eq. (1). This expression was obtained by solving the relevant equations for a circular plate oscillating in three dimensions, as opposed to the one-dimensional case which leads to Eq. (1). The fundamental is given by $n=1, m=0, k=1$, where m and k are overtone orders related to waves propagating in the plane of the crystal.²³ The need for empirical fitting parameters in expressions of this kind has been pointed out by Mason in his book.¹¹ Equation (4) was used to fit the data collected in air with the crystal thickness h and p as fitting parameters (Table II). The results of the fits, shown in Fig. 1(a), exhibit a much better agreement with the data acquired on the three overtones (cf. Tables I and II). The data acquired on the fundamental is not considered.²⁴

The frequency at which measurements were performed enters the models that describe the frequency shift due to loading with a viscoelastic layer in the same fashion as it

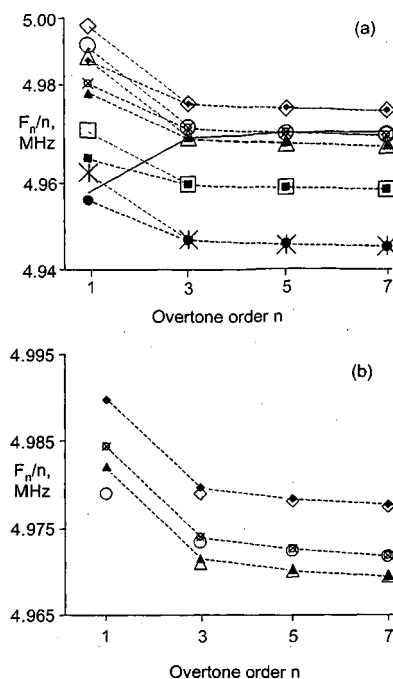


FIG. 1. The resonance frequencies observed with the QCM-D instrument on various overtones do not obey Eq. (1). (a) The absolute frequency of several 5 MHz crystals measured on various overtones with a QCM-D instrument in air (black dashed lines), with filled circles (crystal #6), filled squares (#30), filled triangles (#66), filled diamonds (#60), small open circles and small crosses (#67, two measurements)) is compared with the one calculated using Eq. (1) (black line) and using Eq. (4). The data was fit to Eq. (4) using h (the crystal thickness) and p (adjustable parameter) as fitting parameters. The results of the fitting are plotted with large open symbols of the same shape as those representing the experimental data (with the exceptions of large crosses for the crystal #6) connected by gray dashed lines. Values of the fitting parameters and fitting errors are summarized in Table II. (b) The absolute frequency of several 5 MHz crystals—#60, 66 and 67 [two measurements; symbols used as the same as in (a)]—measured on various overtones with a QCM-D instrument in air is compared with the values of f_n/n obtained using Eq. (5) (open symbols of the same shape for each crystal). Average values of f_n 's for several crystals are listed in Table III. All frequencies are scaled by the overtone order.

enters the Kanazawa-Gordon relationship [Eqs. (2) and (3)]. Thus, a direct consequence of our finding is that any algorithm which relies on the use of Eq. (1) to compare the frequencies observed on the low-order overtones with theoretical predictions will lead to erroneous or unreliable results

TABLE II. Fitting parameters h (crystal thickness) and p used to fit the data shown in Fig. 1(a) with Eq. (4), along with the error in the frequency (calculated—observed) in hertz.

Crystal ^a	h , μm	p	Fitting errors, Hz ^b		
			3	5	7
6	337.5	0.047	32	150	117
30	336.6	0.041	34	157	123
60	335.4	0.051	34	158	124
66	335.9	0.052	36	165	129
67	335.8	0.053	37	173	136
67	335.8	0.052	38	177	139

^aThe radius of the crystals was taken as 7 mm.

^bFitting errors were calculated on each of the three overtones as the absolute value of the difference between the observed and the calculated frequency.

for the viscoelastic properties of the layers. There are two more instances in which the precise knowledge of the resonance frequency of the unloaded crystal is required. In the perturbation analysis of Johannsmann *et al.*,^{7,25} δf in the $\delta f/f$ expression is the difference between the frequency of the crystal loaded with the thin film in liquid and the frequency of the unloaded, bare crystal in vacuum. Similarly, in the models of Daikhin and Urbakh,²⁶ subtracting the frequency of the rough bare crystal in liquid from the crystal loaded with the film in the same liquid (as is normally done when interpreting QCM-D data) will necessarily introduce errors into the analysis.

The fit between Eq. (4) and the experimental data is sufficiently satisfactory to propose that finite crystal size contributes to the observed behavior of the crystals. Yet, the errors that are observed (Table II) are still too large for this approach to be useful when trying to predict the resonance frequency of the unloaded crystal for use in the comparison of the QCM-D data with the models. Therefore another approach is proposed: Measurements on different overtones should be treated independently, without any assumptions with respect to the behavior of $f_{Rn}(n)$. In practice, this can be achieved in a number of ways. Frequencies can be measured on each overtone in air or in vacuum and used in place of f_{Rn} 's. Caution must be exercised, however, with respect to inharmonic resonances (spurs),²³ which may result in the frequencies measured in air being unreliable. For example, we

TABLE I. Frequencies and dissipations for one of the crystals measured in air and in liquid. Typical behavior is shown with the particular example of crystal 67.

Condition	Frequency (MHz)				Dissipation ($\times 10^{-6}$)			
	$n=1$	$n=3$	$n=5$	$n=7$	$n=1$	$n=3$	$n=5$	$n=7$
Eq. (1) ^a	4.958 547	14.914 809	24.863 230	34.810 533				
Air ^b	4.984 499	14.921 988	24.863 231	34.803 295	18.29	6.68	4.81	7.13
Air	4.984 507	14.921 923	24.863 055	34.803 075	21.36	7.04	5.34	6.31
Liquid	4.978 997	14.919 109	24.860 705	34.800 780	350.53	170.35	132.43	113.02
f_n^c	4.979 677	14.920 287	24.862 226	34.802 578		16 ^d	13	12

^aThe crystal thickness was adjusted in order for the frequency calculated on the 5th overtone to coincide with the measured one. This occurred at a particular value of crystal thickness h of $3.358\,971\,5 \times 10^{-4}$ cm.

^bValues from two experiments performed with this crystal in air (involving separate mountings) are tabulated.

^cValues calculated from the frequencies measured in liquid (line above) using Eq. (5), to be compared with those measured in air.

^dThe dissipation values tabulated in this line are differences $D_{\text{ln,measured}} - D_{\text{ln,calculated}}$ for the particular experiment (line above). For average values, see Table III.

TABLE III. Average values of the f_n/n , calculated according to Eq. (5), for different crystals (the data for some of which is plotted in (Fig. 1), together with the corresponding values of $(D_{\text{ln,measured}} - D_{\text{ln,calculated}})$.

Crystal	$f_3/3$ (Hz)	$f_5/5$ (Hz)	$f_7/7$ (Hz)	$d_3^b \times 10^{-6}$	$d_5 \times 10^{-6}$	$d_7 \times 10^{-6}$
60(6) ^a	4 979 029±112	4 978 110±121	4 977 511±131	13±3	15±5	15±8
66 (5)	4 971 014±30	4 970 046±29	4 969 421±29	9.9±0.3	8.7±0.4	6.5±0.2
67 (7)	4 973 390±23	4 972 406±24	4 971 757±24			
67 (1)	4 978 893	4 977 970	4 977 365	12.7±0.7	9.9±0.8	8.0±0.9
67 (1)	4 974 389	4 972 950	4 972 156			
68 (4)	4 978 232±19	4 977 237±16	4 976 584±14	11.2±1	19±6	8±2
207 (3)	4 974 481±11	4 973 556±10	4 972 952±10	12±2	10±1	9±0.5
237 (3)	4 968 230±28	4 967 345±26	4 966 757±27	10±1	10±2	8.2±07
237 (1)	4 959 023	4 958 101	4 957 458			

^aThe number of measurements used to calculate the average values is given in brackets. Each measurement represents a separate mounting of the crystal.

^b $d_n = (D_{\text{ln,measured}} - D_{\text{ln,calculated}})$ —that is, the difference between the dissipation factor observed in liquid and that calculated using the appropriate value of f_n substituted instead of f_{Rn} into Eq. (3).

found that the difference between the frequency measured in air and that measured in buffer did not correspond to that predicted by the Kanazawa-Gordon relationship [Eq. (2)]. Differences of up to -2.5 kHz were observed, ruling out the possibility that the disagreement was due to the difference between the viscosity and density of a buffer and that of water. In contrast to that observation, the differences between frequencies measured in various liquids of known viscosity and density corresponded reasonably well to those predicted by Eq. (2).²⁷

In the absence of reliable measurements of the frequencies of the unloaded crystals in air or in vacuum, Eq. (2) can be solved individually on each overtone for the resonance frequency (to distinguish it from the f_{Rn} given by Eq. (1), it is referred to as f_n below):

$$f_n = \left(\frac{a + \sqrt{a^2 + 4F_{\text{ln}}}}{2} \right)^2, \quad (5)$$

$$a = \frac{\sqrt{\pi \rho_l \eta_l}}{2\pi \rho_q h_q},$$

where F_{ln} is the resonance frequency of the crystal in buffer, $\rho_q = 2648 \text{ kg/m}^3$, $h_q = 3.37 \times 10^{-4} \text{ m}$, $\rho_l = 997.046 \text{ kg/m}^3$, $\eta_l = 8.97 \times 10^{-4} \text{ Ns/m}^2$ (the physically relevant solution was taken). Three distinct values are obtained, f_3 , f_5 , and f_7 . These were found to *qualitatively* reproduce the behavior of the frequencies measured in air [Fig. 1(b), Tables I and III], indicating lack of unexpected hydrodynamic effects (compression waves, hydrodynamic instabilities, etc) and justifying the application of the Kanazawa-Gordon relationship [Eq. (2)] to determine f_n 's. It is proposed that the values of f_n 's obtained in this manner be used instead of f_{Rn} when comparing QCM-D results with the physical models.

Quantitatively, the agreement between the frequencies measured in air and those calculated from Eq. (5) was extremely poor (Table I). Differences of up to 2 kHz were observed on the 3rd overtone. This discrepancy is attributed to the problems associated with the inharmonic resonances (spurs) discussed above.

Most of the models currently used to describe the frequency of the loaded quartz oscillators had been derived with

the assumption of the ideal oscillator in mind—i.e., the dissipation of the unloaded crystal was assumed to be zero.¹² It was therefore of interest to test whether substituting f_n 's calculated from Eq. (5) into Eq. (3) leads to the correct values of the dissipation in liquid, D_{ln} . Typically, the error in the calculated D_{ln} [calculated as $(D_{\text{ln,measured}} - D_{\text{ln,calculated}})/D_{\text{ln,measured}} \times 100$] was 7% for $n=3$, 9% for $n=5$, and 8% for $n=7$ (Tables I and III). For comparison, the dissipation measured in air was typically $\approx 6\%$ of that measured in liquid—i.e., of the same order of magnitude as the discrepancy between the calculated and the measured values of the dissipation factor in liquid. Yet this discrepancy can not be confidently assigned to the dissipation in air, since the measured values of the dissipation factor in air deviated by between 4% and 80% from $D_{\text{ln,measured}} - D_{\text{ln,calculated}}$ for liquid, indicating that another effect is playing a role. It should be kept in mind, however, that both the value of the dissipation factor measured in air and the value of the difference $(D_{\text{ln,measured}} - D_{\text{ln,calculated}})$ for liquid are very small numbers.

The variations in the calculated values of f_n between experiments involving separate mountings were found to be moderate for most crystals, although one of the crystals (#60) exhibited significantly larger variability (Table III). These variations can be attributed to a combination of the effect of mounting and variation in the viscosity and density of the various buffers used in the experiments. Two crystals exhibited extreme deviations for some of the measurements: For example, for crystal #237, f_n 's calculated from one of the experiments deviated by $\sim 9.3 \times n$ kHz from the average of the frequencies calculated from three other experiments. Similarly, for crystal #67, in one instance a difference of $\sim 5.6 \times n$ kHz was found between f_n 's calculated from one of the measurements and an average of those calculated from seven other measurements; In another instance—a difference of $1 \times n$ kHz for $n=3$, $0.5 \times n$ kHz for $n=5$ and $0.4 \times n$ kHz for $n=7$ (see Table III). Such extreme deviations are attributed to catastrophic events, such as crystal chipping, aging, or, perhaps, poor mounting.

Further improvements of the proposed method can be thought by using expressions more complicated than the Kanazawa-Gordon relationship to extract the “base”

frequencies—such as those including the effects of surface roughness, or expressions which explicitly treat the losses in the unloaded oscillator. These will be the subject of separate publication(s).

III. CONCLUSIONS

Interpretation of QCM data in terms of viscoelastic properties of thin films adsorbed on the crystal surface requires (i) measurements on several frequencies (overtones) and (ii) precise knowledge of the resonance frequency of the unloaded crystal. Examination of the frequency and dissipation factor values measured with the QCM-D instrument in air leads to the conclusion that the frequencies measured on overtones $n=1, 3, 5$, and 7 do not agree with those expected of an ideal, infinite crystal. Strong evidence that finite size effects contribute to this behavior is presented. It is proposed that measurements performed on different overtones should be treated independently of each other in the data analysis. A particular implementation of this procedure is discussed in detail.

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APPENDIX: EXPERIMENTAL PROCEDURES

QCM-D measurements were performed with a QE301 (electronics unit)/QAFC301 (axial flow chamber)/QSoft 301 (software version) instrument from Q-Sense AB (Göteborg, Sweden).¹ AT-cut 5 MHz quartz crystals with gold electrodes (crystals #6, 16, 30, 60, 66, 67, 68) and crystals coated with a layer of silica on top of the gold (crystals #207, 237), were purchased from Q-Sense. Crystals 60, 66, 67, and 68 were sputter-coated with a 20 nm TiO₂ layer with a Leybold dc-magnetron Z600 sputtering plant as described previously.²⁸

Immediately prior to each experiment, crystals were cleaned by first incubating them in a 2% aqueous solution of sodium dodecyl sulfate (Sigma, Buchs, Switzerland) for 30 min, rinsing with ultrapure water, and subjecting them to 30 min of UV/Ozone treatment in a model 135500 UV Cleaner from Boekel Industries Inc. (Feasterville, Pennsylvania) which was preheated for 30 min.

Measurements in air were performed for 3–5 h, with both valves in the closed position and the tubing sealed with plastic stoppers (supplied with the instrument) and parafilm.

An average of the frequency and dissipation factor values on each overtone was taken over a time period of ~ 2 hrs (where the signal was most stable).

For measurements performed in liquid, the chamber was filled with a buffer and the instrument was allowed to equilibrate (while collecting data) until the drift in the frequency had settled out to $\sim < 2 \times n$ Hz/h, where n is the overtone order. The “drift-free signal” was collected for a further 10–30 min. The average of the frequency (dissipation factor) over this time period was used in the calculations. All measurements were performed at 25 °C.

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