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Introduction

The use of quartz crystal resonators in various fields of chemistry, biochemistry, and microbiology has grown tremendously during recent years. Although the early use of a quartz crystal microbalance (QCM) is dated back to the fifties when its mass sensitivity was invented in connection with vacuum coating,[1] the present interest is mainly due to the applications in the liquid phase. Though it was long thought to be too strongly damped by liquid, Nomura et al.[2] and Konash et al.[3] showed in 1981 that a quartz crystal resonator could oscillate when immersed in a liquid phase. The main applications have been and still are simply based on weighing the mass deposited on or removed from the surface. On the other hand, it was rather early realized that additional information from the material on the surface of the resonator could be obtained by recording also energy losses in the oscillation. This can be done by measuring the impedance of the crystal coated with a thin layer of material or immersed in the fluid to be studied. The purpose of this article is to give a new approach to the theory of the quartz crystal microbalance (QCM) or thickness-shear mode (TSM) resonator loaded with different material layers on its surface and immersed in liquid. The results from the prior theoretical research have been compiled in a recent publication by Bandey et al.,[4] where nearly all experimentally feasible combinations of material layers on the quartz resonator were discussed and the corresponding mathematical relations were given.

Even though comprehensive articles on the influence of medium and viscoelasticity have been published, the essential influence of medium on the mass sensitivity as given by the celebrated Sauerbrey equation has not been properly taken into account. Also, the important role of acoustic impedance has been emphasized only in a few works. As a matter of fact, it is shown in this work that acoustic impedance is actually a quantity which can be independently evaluated by solving a nonlinear first order differential equation without resorting to the complicated theory of acoustic vibrations in condensed matter.

Theory

The system to be studied is a quartz crystal resonator composed of a thin quartz disk with a very thin metal film on both sides, and one or more layers of materials evenly distributed on one side of the resonator. The surface of the resonator is assumed to be smooth, and in addition, there is no slip between the movement of the resonator surface and the contacting material. The mode of oscillation of the AT cut quartz crystal is the thickness-shear
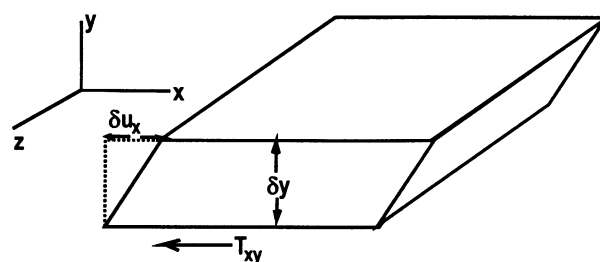

Figure 1. Infinitesimally thin material layer subjected to the shear stress T_{xy}.

mode (TSM), meaning that its surface undergoes lateral movements. We start by taking an infinitesimally thin slab of material (Figure 1), which is subjected to a shear stress to the x-direction in the xz-plane. Because of the geometry of the system, the problem can be handled one-dimensionally. The lateral movement δu_x of the adjacent layer divided by the thickness δy defines the strain S

$$S = \frac{\partial u_x}{\partial y} \qquad (1)$$

This strain is induced by the shear stress T_{xy} on the slab. For small strain we have a linear correspondence between strain and stress, corresponding to the Hooke's law

$$T = GS \qquad (2)$$

Here G is the shear modulus of the material. The subscript xy has been dropped because of the simple one-dimensional system.

In the present case, the motion is forced oscillatory movement with an angular frequency ω, and we can separate the time and space variables

$$T = T_0(y)e^{j\omega t}; \quad u_x = u_0(y)e^{j\omega t}; \quad S = S_0 e^{j\omega t}, \quad j = \sqrt{-1} \qquad (3)$$

Here u_x is the particle velocity in the x-direction. In the general case, the material may be assumed to be viscoelastic; strain is then lagging behind the applied stress, energy losses are introduced, and the shear modulus G in eq 2 becomes complex-valued. Its real part G' is called the storage modulus, and the imaginary part G'' is called the loss modulus. The inverse of G is the complex shear compliance of the material and is denoted by $J = J' - jJ''$.

Using the definitions of the quantities and Newton's second law, a coupled system of differential equations can be derived[5]

$$\frac{dT_0}{dy} = j\omega\rho u_0$$

$$\frac{du_0}{dy} = j\omega G^{-1} T_0 \qquad (4)$$

Here ρ is the density of the material. The basic assumption is that there is no slipping at the interfaces; that is, both the stress amplitude T_0 and velocity amplitude u_0 are assumed to be continuous functions even when crossing

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(5) Ristic, V. M. *Principles of acoustic devices;* John Wiley & Sons: New York, 1983; p 14.

the phase interfaces. This pair of equations can be solved for T_0 and u_0, but as a matter of fact, we do not need either of them for calculating the impedance of the quartz crystal resonator. The acoustic impedance is defined as the ratio of stress to the phase velocity v of the acoustic wave

$$Z = -\frac{T}{v} \qquad (5)$$

The negative sign is due to a convention. Another expression in terms of density and shear modulus can also be derived:

$$Z = \rho v = \sqrt{\rho G} \qquad (6)$$

In the case of oscillatory movement, the shear modulus becomes complex-valued and we have defined the complex shear acoustic impedance Z, which is a frequency-dependent property of the material. This is called the bulk acoustic impedance in order to distinguish it from the local acoustic impedance, which is a function of the coordinate y.

In analogy with the definition in eq 5, we define the local (shear) acoustic impedance ζ as the ratio of T_0 to u_0:

$$\zeta = -\frac{T_0}{u_0} \qquad (7)$$

By differentiating eq 7, we obtain

$$\frac{d\zeta}{dy} = -\frac{d(T_0/u_0)}{dy} = -\frac{1}{u_0}\frac{dT_0}{dy} + \frac{T_0}{u_0^2}\frac{du_0}{dy} =$$
$$-j\omega\rho + j\omega G^{-1}\zeta^2 \quad (8)$$

The independent variable y is now changed in eq 8:

$$\tilde{m} = j\omega m; \quad m = \int_0^y \rho(s)\,ds \qquad (9)$$

Here m is nothing else but the cumulative mass distribution in the layer calculated for a unit area or areal mass density. The new variable $\tilde{m}$ has the dimensions of acoustic impedance and could be called the acoustic mass impedance. Taking into account eq 6, we obtain from eq 8 the fundamental equation of local acoustic impedance in stratified thin films:

$$\frac{d\zeta}{d\tilde{m}} = \left(\frac{\zeta}{Z}\right)^2 - 1 \qquad (10)$$

In the general case, the impedance Z depends on the distance from the surface and it has discontinuities at the interfaces of strata. It is assumed that T_0 and u_0 are continuous functions, which means that their ratio ζ is also continuous. Only its derivatives are then discontinuous at the interfaces.

Equation 10 is known in the theory of differential equations as a Riccati differential equation, which is deceptively simple but analytically soluble only in few special cases. However, if Z is constant, eq 10 is easily soluble. One solution is a constant value of ζ:

$$\zeta = \pm Z \qquad (11)$$

A positive sign is chosen because of the conventions in eqs 5 and 7. The second solution is obtained by integration:

$$\int_{\zeta_1}^{\zeta}\frac{d\zeta}{(\zeta/Z)^2 - 1} = -Z\operatorname{arctanh}\frac{\zeta}{Z} + Z\operatorname{arctanh}\frac{\zeta_1}{Z} = \tilde{m} -$$
$$\tilde{m}_1 = j\omega(m - m_1) \quad (12)$$

In the general case, if we assume that ζ_1 corresponds to the value of the local acoustic impedance at the film–liquid interface, ζ_0 is that at the resonator–film interface, and m_f is the total areal mass density of the film, we obtain

$$\zeta_0 = Z\tanh\left(\frac{j\omega m_f}{Z} + \operatorname{arctanh}\frac{\zeta_1}{Z}\right) = \frac{\zeta_1 + jZ\tan\dfrac{\omega m_f}{Z}}{1 + j\zeta_1 Z^{-1}\tan\dfrac{\omega m_f}{Z}} \qquad (13)$$

There is a well-known functional relationship between ζ_0 and the electrical ac impedance of the resonator close to the resonance frequency, and consequently ζ_0 is an indirectly measurable quantity.[6] In the following we shall denote the real and imaginary parts of ζ_0 by ζ' and ζ'', respectively.

Kanazawa and Gordon[7] were the first to show the influence of liquid immersion on the resonance frequency of a quartz resonator. The same result is obtained from the Riccati equation in two ways. We may assume that local acoustic impedance is constant everywhere in liquid, in which case we take the constant solution of eq 11. Another possibility is that we allow m_f in eq 13 to tend to infinity, corresponding to a semi-infinite layer, and keep $\zeta_1 = 0$. In both cases, we get $\zeta_0 = Z = Z_l$. For Newtonian liquids we have $G_l = j\omega\eta_l$, where η_l is viscosity, and thus the impedance is

$$\zeta_0 = Z_l = (j\omega\rho_l\eta_l)^{1/2} \qquad (14)$$

Now we assume that there is a thin layer of some material on the resonator surface which is immersed in liquid with bulk acoustic impedance Z_l. The local acoustic impedance at the surface of the resonator is obtained from eq 13 by putting $\zeta_1 = Z_l$. However, a better insight into the system and also the basis for approximations is obtained by using the Taylor expansion with $\tilde{m}$ as the variable. Taking only the first term, we obtain for the local acoustic impedance at the resonator surface

$$\zeta_0 \approx Z_l - j\omega m_f \frac{d\zeta}{d\tilde{m}}\Big|_{\tilde{m}=j\omega m_f} \qquad (15)$$

Mathematically speaking, the point of expansion is assumed to be infinitesimally close to but not exactly at the interface in order to avoid discontinuities. The derivative in expansion 15 is most conveniently obtained directly from the Riccati equation (eq 10):

$$\zeta_0 \approx Z_l + j\omega m_f\left(1 - \frac{\rho_l G_l}{\rho_f G_f}\right) \qquad (16)$$

where the subscripts l and f refer to liquid and film, respectively. This expression can be separated into real and imaginary parts. If we assume that the liquid is Newtonian and use shear compliance instead of shear modulus, that is, $G_f^{-1} = J'_f - jJ''_f$, we have

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$$\Delta\zeta' = Re(\zeta_0 - Z_l) \approx \omega m_f \frac{\rho_l}{\rho_f} Im\left(\frac{G_l}{G_f}\right) = \omega^2 m_f \frac{\rho_l \eta_l}{\rho_f} J'_f \quad (17)$$

$$\Delta\zeta'' = Im(\zeta_0 - Z_l) \approx \omega m_f \left[1 - \frac{\rho_l}{\rho_f} Re\left(\frac{G_l}{G_f}\right)\right] =$$
$$\omega m_f \left(1 - \frac{\omega \rho_l \eta_l}{\rho_f} J'_f\right) \quad (18)$$

Equation 18 leads to the *medium-corrected form* of the celebrated *Sauerbrey equation*:

$$\frac{\Delta f_s}{f_s} = -\frac{\Delta\zeta''}{\omega \rho_q d_q} = -\frac{m_f}{\rho_q d_q}\left[1 - \frac{\rho_l}{\rho_f} Re\left(\frac{G_l}{G_f}\right)\right] =$$
$$-\frac{m_f}{\rho_q d_q}\left(1 - \frac{\omega \rho_l \eta_l}{\rho_f} J'_f\right) \quad (19)$$

In this expression f_s is the series resonance frequency of the resonator, Δf_s is its change due to the layer on the surface of the resonator, ρ_q is the density of quartz, and d_q is the thickness of the resonator. In fact, the well-known form of the Sauerbrey equation is obtained by setting the density of the medium ρ_l to zero in eq 19. The Sauerbrey equation is a limiting law applicable for low values of loading, but in the original form it is strictly valid only in a vacuum, although in many practical cases the correction is negligible. As we see from eq 19, the magnitude of the correction depends both on the properties of the liquid and the imaginary part of the shear compliance of the film material. Very soft viscoelastic materials such as protein films in an aqueous medium need large corrections, typically up to 50% (unpublished results), whereas for elastic films the corrections are completely negligible.

The real part $\Delta\zeta'$ gives information on the real part of the shear compliance J'. Actually, from eqs 17 and 18 we may eliminate the areal mass density:

$$\frac{\Delta\zeta''}{\Delta\zeta'} = |Z_l|^{-2}\frac{\rho_f}{J'_f} - \frac{J''_f}{J'_f} = |Z_l|^{-2}\frac{\rho_f}{J'_f} - \tan\delta \quad (20)$$

Here δ is the loss angle of the film material, which for reasonably solid materials is below 70°, giving $\tan\delta < 2.7$. Because the density of the film can be often estimated fairly accurately, we have here a method for the crude estimation of the real part of shear compliance without knowing the mass of the layer. However, if accurate estimates are needed, one should be aware of the approximate character of eq 20 because only the first order term in the Taylor expansion was taken into account and, in addition, the accurate value of the loss angle is generally unknown.

Conclusions

Although the Sauerbrey equation is commonly used for estimating mass changes when the resonator is immersed in liquid, the combined effect of the viscoelasticity of the film and the viscosity−density product of the liquid has not been previously taken into account. The correction to the areal mass density given explicitly by eq 19 is apparently very small for elastic films with a low value of shear compliance, but it should be taken into account for soft viscoelastic materials. Equation 19 shows also that there is no first order correction for the viscoelasticity of the film if the measurement is done in air, contrary to some commonly expressed views. These facts, which are often misunderstood, are readily derived from the Riccati equation (eq 10). This fundamental equation of local acoustic impedance gives impetus also to other interesting methods which will be the subject of further publications.