Urban Climate 24 (2018) 264–275

Contents lists available at ScienceDirect

Urban Climate

journal homepage: www.elsevier.com/locate/uclim

The theory of acoustic sensors application in air quality control

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ARTICLE INFO

Keywords:
Air quality control
QCM-D
Theoretical modeling
Complex fluids

ABSTRACT

Acoustic sensors based on piezoelectric resonators are widely used in the real-time monitoring of mass and in situ analysis of air composition, for example in environmental, health care and air quality control (AQC) applications, both indoor and outdoor. Recent advances in the QCM techniques include the possibility of measuring changes in resonance frequency, Δf, and the dissipation, ΔD (so-called QCM-D sensors). Another field of application is measurements of different overtones, which can provide additional information about the system. The sensing layers in QCM devices are often polymer- or supported membrane-based, both of which are soft (viscoelastic) materials. Viscoelasticity of adsorbed layers must thus be taken into account for adequate interpretation of QCM data.

This publication describes theoretical results, including analytical formulae for the resonance frequency shift and the dissipation of QCM-D, for two viscoelastic layers deposited onto resonator surface, as well as calculations for higher harmonics. In particular, the corrections in Δf and ΔD due to the softness of the top layer, considered as a bulk, are written explicitly in terms of the layer's material parameters. The results can be useful for quantitative analysis of measured characteristics of QCM in AQC, environmental monitoring and biosensor applications.

1. Introduction

The quartz crystal microbalance (QCM resonator) is an important analytical tool for precise gravimetrical measurements and characterization of thin films adsorbed on surfaces in both gaseous and liquid environments (Sekler and Wobmann, 2003; Johannsmann, 2014; Kumar et al., 2015; Zampetti et al., 2008; Pantalei et al., 2007; Ding et al., 2004; Graf et al., 2010; Öztürk et al., 2016; Johannsmann, 2008; Moorthy and Babu, 2005). Due to its high sensitivity, it was suggested that this acoustic sensor device would be able to monitor contamination levels even in ultra-clean and vacuum environments, e.g. microscopic dust particles and organic residue onboard space missions and in cleanrooms (Sekler and Wobmann, 2003).

Volatile compounds, dust, aerosols and microdroplets are most common types of air pollutants. Sensor detection of these components is thus an important part of AQC. Applications of QCM as a gas sensor include detection of volatile substances in the air (Kumar et al., 2015; Zampetti et al., 2008; Pantalei et al., 2007; Öztürk et al., 2016), pollutant control (Ding et al., 2004; Graf et al., 2010), carbon black emissions (Graf et al., 2010), aerosol analysis (Moorthy and Babu, 2005), ozone level control (Muller et al., 2011), as well as measurements of atmospheric dust and water vapour in space exploration missions (Battaglia et al., 2004; Esposito et al., 2011; Palomba et al., 2002) and stratospheric sampling (Hering, 1987). New advanced nanomaterials were suggested to improve the sensitivity of QCM in gas sensing and AQC measurements (Kumar et al., 2015; Ding et al., 2004; Öztürk et al., 2016; Wang et al., 2009). A multichannel-based QCM for the electronic nose with enhanced sensory properties have been reported elsewhere (Zampetti et al., 2008; Pantalei et al., 2007). In biosensor's QCM applications, recent trends demonstrate the possibility to detect small fragments of DNA (Höök et al., 2001) and small target analytes, such as airborne viruses (Lee et al., 2008) and organic

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https://doi.org/10.1016/j.uclim.2018.04.002
Received 23 October 2017; Received in revised form 30 January 2018; Accepted 6 April 2018

dust (Eduard and Halstensen, 2009; Gao et al., 2006; Hara and Zhang, 2012). Readers can find an exhaustive review of QCM's soft matter applications in a recent book by Johannsmann (Johannsmann, 2014). In most cases, the system under analysis is a two-layer material, with one layer typically being very thin (adsorbed film or coating layer), and the other one being a bulk (for example, vapors or water solution with various components). However, in some experimental situations the top layer should be considered as a viscoelastic bulk media rather than pure viscous liquid. Present paper investigates the latter case. Main result of the current work is the calculated correction due to the top layer viscoelasticity coming to the predicted response of the QCM. Bulk pure Newtonian liquid coating a viscoelastic film is a special case of the general theory developed here.

Gravimetrical QCM operation is based on the experimentally established linear relation between a mass firmly attached to the crystal surface and the resonance frequency shift. The high sensitivity of the device (< 1 ng/cm^2) allows for extremely high-resolution measurements: it can resolve very small frequency changes (a few Hz), in the ~1–70 MHz resonance frequency range, up to the 13th overtone.

When QCM operates in the air, the alteration of its resonance frequency f_0 due to the presence of a thin layer, composed of air components, is proportional to the film surface mass $M = \rho \cdot h$ (Sauerbrey, 1959), a product of the film thickness h and its density ρ,

$$\Delta f = -f_0 \frac{M}{m_q}. \tag{1}$$

An example of a system where this relation is valid is a thin rigid film of microparticles, mineral dust, polymers or (bio)organic molecules firmly coupled to the quartz plate surface. The Sauerbrey relation (1) for a mass-loaded quartz crystal resonator in vacuum states a principle of microbalance, while the mass sensitivity of microbalance is given by the coefficient $C_{QCM} = f_0/(\rho_q h_q)$, where $\rho_q h_q = m_q$is the mass density of the quartz crystal plate of thickness h_q (Kanazawa and Gordon, 1985; Martin et al., 1991; Rodahl and Kasemo, 1996; Rodahl et al., 1995; Lucklum and Hauptmann, 2006). The resonance frequency of an oscillating quartz crystal plate is a function of plate thickness h_q, quartz density ρ_q, and elastic modulus C_{66} (for AT-cut quartz plate):

$$f_0 = \frac{1}{2h_q}\sqrt{\frac{C_{66}}{\rho_q}}. \tag{2}$$

The QCM allows researchers to discriminate between volatile components in vapors and gases as the former bind only to receptive polymer coatings on the resonator surface. For gaseous phases or in the air, the gravimetrical measurements performed with QCM-based sensors provide high-precision experimental data for surface mass detection for the thin rigid layer.

In pure viscous (Newtonian) bulk medium (index “L”), the QCM resonance frequency shift is given by the Kanazawa and Gordon relation (Kanazawa and Gordon, 1985):

$$\Delta f \approx -\frac{1}{2\pi m_q}\sqrt{\frac{\rho_L \eta_L \omega}{2}}. \tag{3}$$

In adsorption from bulk liquid phase, the viscosity η and density ρ of an adsorbed (fluid) film also contributes to the output of the resonator (Voinova et al., 1997), diminishing the resonance frequency shift:

$$\Delta f \approx -\frac{1}{2\pi m_q}\left\{\sqrt{\frac{\rho_L \eta_L \omega}{2}} + M\omega\left(1 - \frac{\rho_L \eta_L}{\rho \eta}\right)\right\}. \tag{4}$$

This formula provides clear evidence of a viscous coupling between layers which is the physical reason behind the decrease in mass response of QCM (Voinova et al., 1997; Voinova et al., 1999). This phenomenon has been called the “missing mass” effect (Voinova et al., 2002).

Viscoelasticity of the adsorbed film may essentially influence measured characteristics (Martin et al., 1991; Rodahl and Kasemo, 1996; Rodahl et al., 1995; Lucklum and Hauptmann, 2006; Voinova et al., 1997; Voinova et al., 1999; Voinova et al., 2002; Martin et al., 2000; Johannsmann et al., 1992; Kanazawa et al., 2008). For example, it was shown (Lucklum and Hauptmann, 2006) that the swelling of polymer coatings due to analyte adsorption may not only change the thickness, but also viscoelastic parameters of the coating. In the linear approximation, resonance frequency shift is independent of the thin film's viscous, elastic or viscoelastic properties. However, in perturbative analysis, one can find the correction to the Sauerbrey formula (the additive term appears which scales as h^3) (Johannsmann, 2014; Johannsmann, 2008; Martin et al., 1991; Lucklum and Hauptmann, 2006; Voinova et al., 1999; Kanazawa et al., 2008; Feng and Xian-He, 2013; Johannsmann, 1999). For viscoelastic solid film (Voinova et al., 1999) characterized by a viscoelastic ratio value χ, we found:

$$\Delta f \approx -f_0 \frac{M}{m_q}\left\{1 + \frac{2h^2\chi}{3\delta^2(1+\chi^2)}\right\}. \tag{5}$$

For rigid film (Johannsmann et al., 1992) one can find from (5):

$$\Delta f \approx -f_0 \frac{M}{m_q}\{1 + h^2\rho\omega^2/3\mu\}, \tag{6}$$

where ρ and μ are film's material parameters (density and modulus of elasticity, respectively) and h is the film thickness.

Results (5)–(6) are valid only for vacuum or air environments. When the film is loaded by liquid instead of air, the viscous