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On Theory of Acoustic Sensors in the Air Quality Control

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COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir

European Network on New Sensing Technologies for Air-Pollution Control and Environmental Sustainability

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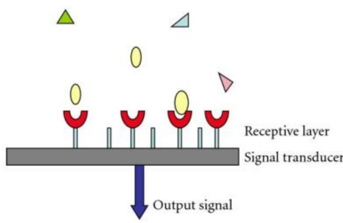
Challenges in Air Quality Control: Acoustic Sensors

Real-time monitoring of gas /air composition

Possibility *in situ* measurements with high precision

How to discriminate between components?

Biosensors solution:



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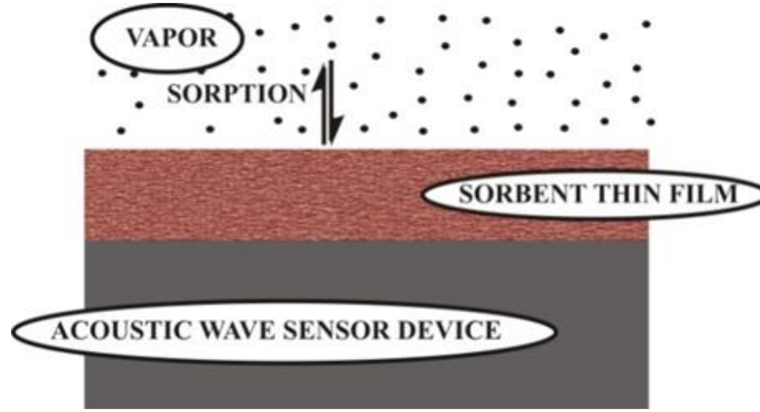
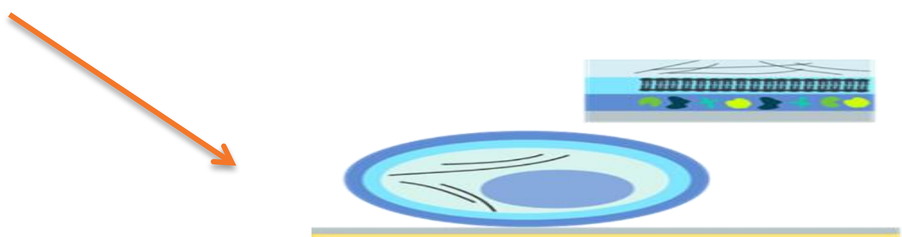


QCM as a chemical gas and vapor sensor
(picture compiled from Grate JW review, with permission)

Other than gaseous components of urban air:

Dust, microparticles and nanoparticles (NPs), aerosols and liquid microdroplets (including bacteria and other contaminants)



Acoustic sensors for real-time monitoring of gas composition

- Acoustic sensors based on piezoelectric resonator systems are widely used for the real time monitoring of mass and *in situ* analysis of gas composition .

- Selected examples are environmental **in-door, health care and out-door air quality control applications**, in particular, **the detection of explosives, pollutants or toxic compounds.**

- The quartz crystal microbalance (QCM) and the surface acoustic wave (SAW)-based sensors belong to the leading group due to their considerable advantages.

- These piezoelectric resonators of BAW (bulk acoustic waves) and SAW- type, respectively, are considered now as high resolution analytical tools allowing researchers to discriminate between volatile components in vapours and gases (or air) **due to selective polymer coating on the resonator surface**.

- In gas phases or in the air, the gravimetrical measurements performed with the QCM or SAW-based sensors provide the experimental data with high precision for the detection of surface mass for the thin adsorbed layer rigidly attached to the surface of the oscillator.

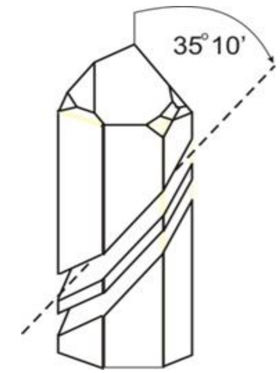
- The new challenge is the analysis of dust, liquid droplets and aerosols which can be a component of the urban air, which is a common situation for both in-door and out-door air conditions.

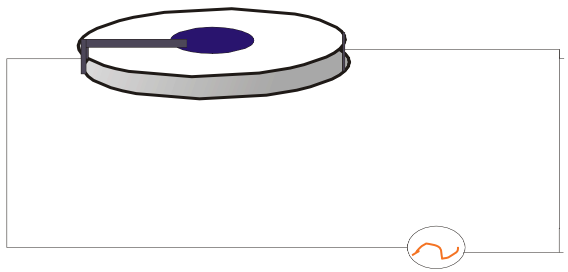
- The losses of energy of the oscillators due to the interfacial friction, slip or viscosity can influence the measured characteristics.

Acoustic Sensors:

BAW (Quartz Crystal Microbalance (QCM)

SAW (Surface Acoustic Waves) type

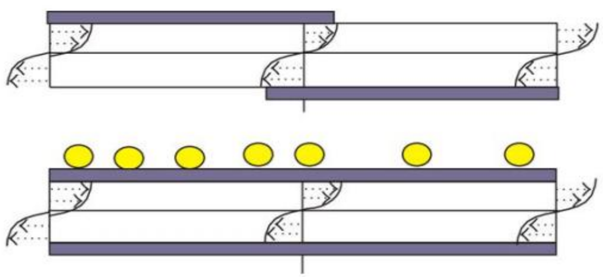




Resonance frequency of the quartz disc

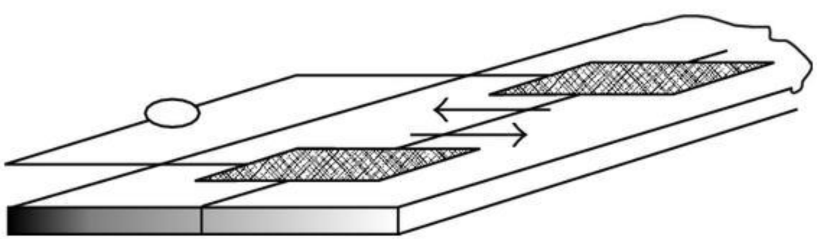
$$f_0 = \frac{n}{2h_q}\sqrt{\frac{C_{66}}{\rho_q}}$$

$$n = 1,3,5..$$



Fundamental resonance frequency of the quartz disc

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



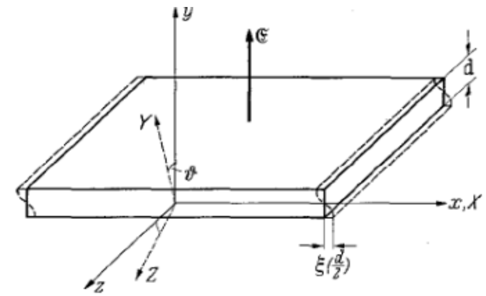
$$C_{66} = 2.947 \times 10^{10} N / m^2$$

$$\rho_q = 2648 kg / m^3$$

SAW sensor (schematic)

Sauerbrey relation:

$$\Delta f \;/\; f_0 = -\Delta M \;/\; m_q$$



$$\Delta f = f - f_0 = -(\frac{2 f_0^{\;2}}{\rho_q V_0})\Delta M = -C \cdot \Delta M$$

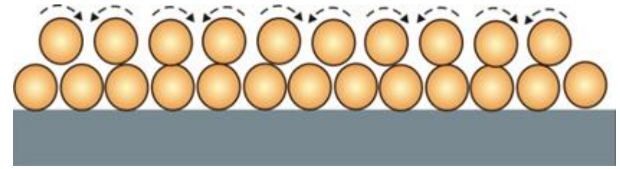
$$m_q = h_q \rho_q$$

C - mass sensitivity
of the microbalance

Validity of Sauerbrey relation:

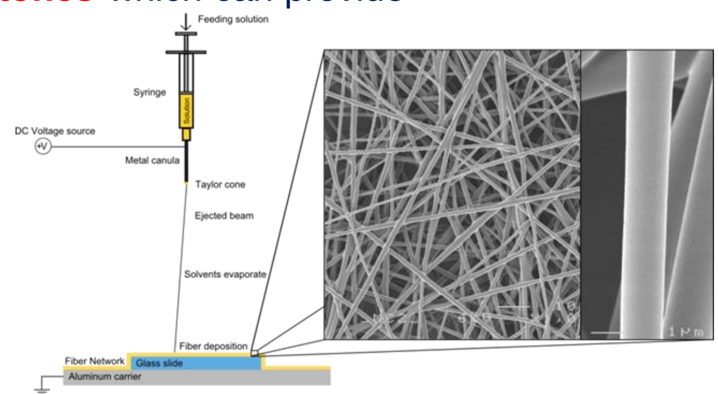
Thin films
Rigid films
No slip (rigidly adsorbed)
Very small mass adsorbed
Evenly distributed mass

QCM-D: *in situ* measurements, Real time monitoring of adsorbed mass



The new experimental challenge in IAQ is the analysis of **(respirable) dust, liquid droplets and aerosols which can be a component of the urban air**, which is a common situation for both in-door and out-door air conditions. Especially important IAQ for the industrial emissions, including carbon emission, dioxin, heavy metals, acid gases. Also applied to urban areas inside commercial or public buildings, traffic zones, airports, etc.

- Theoretical challnges: losses of energy of the oscillators due to the interfacial friction, slip or viscosity can influence the measured characteristics.
- Recent advances in QCM technique include the possibility of measurements of **change in the resonance frequency and the dissipation simultaneously**, with the so-called QCM-D sensors.
- Another help is the possibility of **measurements on different overtones** which can provide the additional information about the system.
- New solutions in **surface design of the sensor surface**: nanofibrous polymer coatings



Picture: courtesy C Zanden, C-T Wang, A Hossein, J Liu and M V Voinova

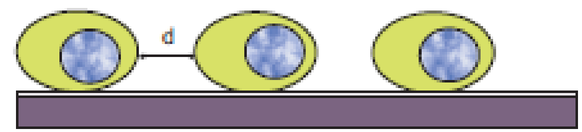
QCM-D measurements in Air Quality Control

Problem statement: how the resonance frequency shift Δf and the dissipation D of the QCM-D sensor depends not only on (1) mass but also on

(2)viscosity or (3) viscoelasticity of the adsorbed material?Overtone dependence?

$$\Delta f = -\sqrt{n}\frac{\sqrt{\pi\rho_2\eta_2 f_0}}{2\pi m_q}\{A-(a-1)B\} - n\frac{h_1\rho_1 f_0}{m_q}\left\{1-\frac{\rho_2\eta_2}{\rho_1\eta_1}\frac{\chi_1\chi_2+n^2}{\chi_1^2+n^2}\right\}$$

$$\Delta D = \frac{1}{\sqrt{n}m_q}\sqrt{\frac{\rho_2\eta_2}{\pi f_0}}\{B+(a-1)A\} + n\frac{h_1\rho_2\eta_2}{\pi\eta_1 f_0 m_q}\frac{\chi_1}{\chi_1^2+n^2}$$



(2)

$$\Delta f = -\sqrt{n}\frac{\sqrt{\pi\rho_2\eta_2 f_0}}{2\pi m_q} - n\frac{h_1\rho_1 f_0}{m_q}$$

$$\Delta D = \frac{1}{\sqrt{n}m_q}\sqrt{\frac{\rho_2\eta_2}{\pi f_0}} + n\frac{2\pi h_1\rho_2 f_0}{m_q\mu_1}.$$

(3)

$$\Delta f = -\sqrt{n}\frac{\sqrt{\pi\rho_2\eta_2 f_0}}{2\pi m_q} - n\frac{h_1\rho_1 f_0}{m_q}\left\{1-\frac{\rho_2\eta_2}{\rho_1\eta_1}\frac{4n^2\pi^2 f_0^2\eta_1^2}{\mu_1^2+4n^2\pi^2 f_0^2\eta_1^2}\right\}$$

$$\Delta D = \frac{1}{\sqrt{n}m_q}\sqrt{\frac{\rho_2\eta_2}{\pi f_0}} + n\frac{4\pi h_1\rho_2\eta_2 f_0}{m_q}\frac{\mu_1}{\mu_1^2+4n^2\pi^2 f_0^2}$$

References on QCM (and QCM-D) as an analytical tool for the gas /vapor analysis/ air quality control applications

- M.Rodahl and B.Kasemo. Rev.Sci.Instruments, 1996. (QCM-D, water vapor measurements).
- D. Johannsmann. Modeling of QCM data_Tutorial.
- J.Krim. Nanotribology. http://www.physics.ncsu.edu/nanotribology/
- *Damping of a Crystal Oscillator by an Adsorbed Monolayer and its Relation to Interfacial Viscosity,* J. Krim and A. Widom, Physical Review B 38, 12184-12189 (1988)

  Piezoelectric Sensors, Steinem C. and Janshoff A. (eds.) Vol. 5. Springer Verlag, pp. 425-447.
- Xianfeng Wang, et al. A high sensitive humidity sensors based on a nanofibrous membrane coated quartz crystal microbalance. Nanotechnology, 21 (2009) 055502
- B.Ding et al., Electrospun nanofibrous membrane coated quartz crystal microbalance as gas sensor for NH3 detection. Sens.Actuators B 101 (2004) 373.
- L. Daikhin et al., Quartz crystal impedance response of nonhomogenous composite. Anal.Chem. 2011.
- M.Cassiede, J.-L.Daridon, J.H.Pailol, J.Pauly, Electrical behavior of a quartz crystal resonator immersed in a pressurized fluid (gas or liquid). J.Appl.Physics 109 (2011) 077501.
- G.S.Korotchenkov. Handbook of the gas sensors materials: properties, advantages and shortcoming for applications. Springer, 2013.
- M.Voinova, and M. Jonson. The Quartz Crystal Microbalance. Chapter 9. In: Chemical sensors. Comprehensive sensor technologies. V.4: Solid-state devices.(Ed. G.Korotcenkov). Momentum Press, LLC, New York, 2011.
- Voinova M. "On Mass Loading and Dissipation Measured with Acoustic Wave Sensors: A Review", *Journal of Sensors,* ***2009*** (2009), ID 943125.
- L.McKenna, M.I.Newton, G.McHale, R.Lucklum and J.Schroeder. Compressional acoustic wave generation in microdroplets of water in contact with quartz crystal resonators. J. Appl.Phys. 89 (2001) 676.

CONCLUSIONS

Further development of the rigorous theoretical models in parallel with numerical calculations and computer simulations is needed for the quantitative characterization of vapours' content for both in-door and out-door **real-time monitoring** by acoustic sensors (specifically, by the QCM-D sensors) and for the correct interpretation of the results of ***in-situ*** measurements of air (vapour) components.

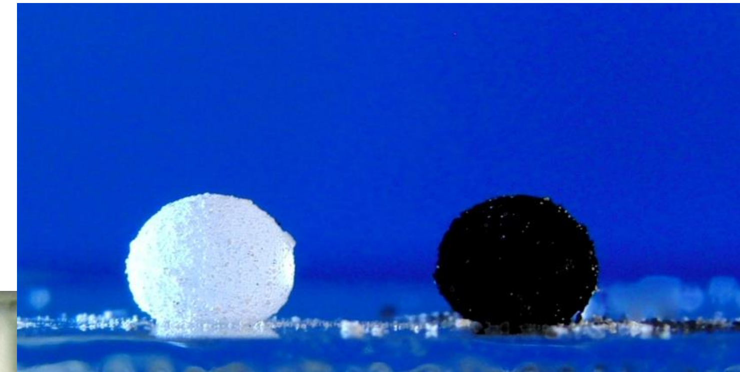
New challenges:

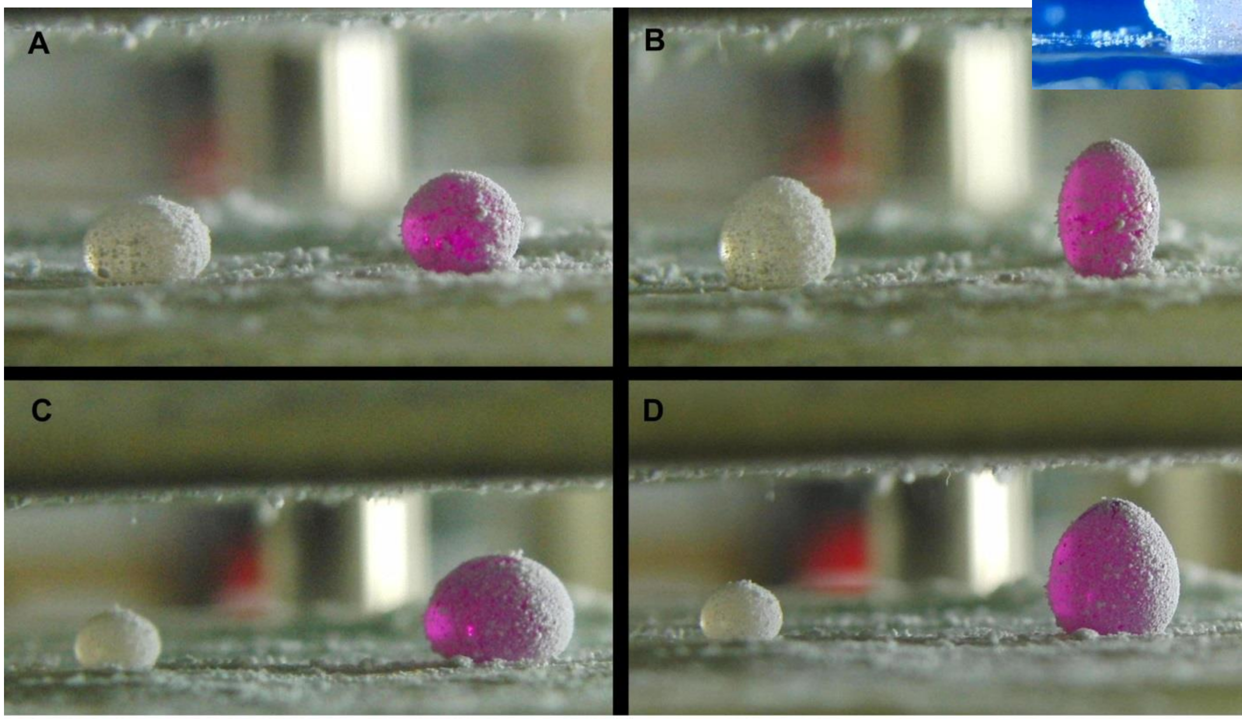
The new architecture design (MESA-shaped or nanofibrous membranes with higher surface area for gas adsorption) of the sensors surface should be taken into account.

Research directions as WGs R&I NEEDS for Action TD1105:

- Theoretical modeling of aerosols, liquid droplets and micro/nanoparticles or dust by means of acoustic sensors of BAW (QCM) or SAW-type including the tribology and nanotrobology aspects (the effects of friction by means of analysis of the dissipation monitored simultaneously with the changes in the resonance frequency of the acoustic resonators) and the effects of viscosity (viscoelasticity) in the detected microdroplets. QCM-D sensors allow researchers to measure the mass and mechanical properties of the adsorbed layers with high precision.

Liquid Marbles: New Model Systems





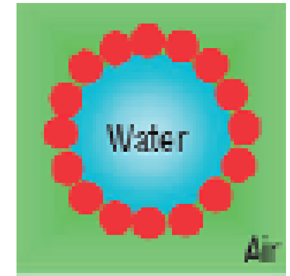
Beautiful picture of powder-coated liquid marbles: carbon black (right on up insertion) and hydrophobic powder coated liquid droplets (A); actuation (B-D)

(courtesy of the first author of the paper **Bormashenko et al.,** ***Langmuir*** **(2011))**

Picture source reference : **E. Bormashenko, Y.Bormashenko, R. Pogreb, O. Gendelman,** ***Langmuir*** **2011, 27(1), 7–10**

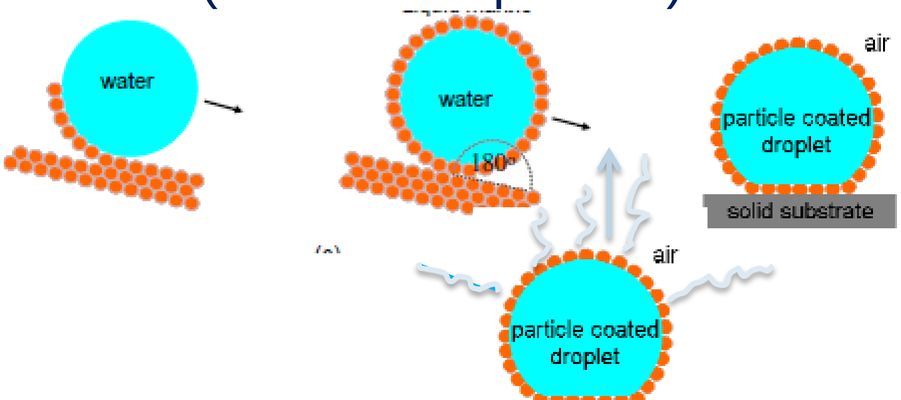
Liquid Marbles:

liquid + fine powder (dust, NPs) = small particles - encapsulated droplets



- Liquid Marbles: schematics of formation [1]:

  (water in air powder)



References:

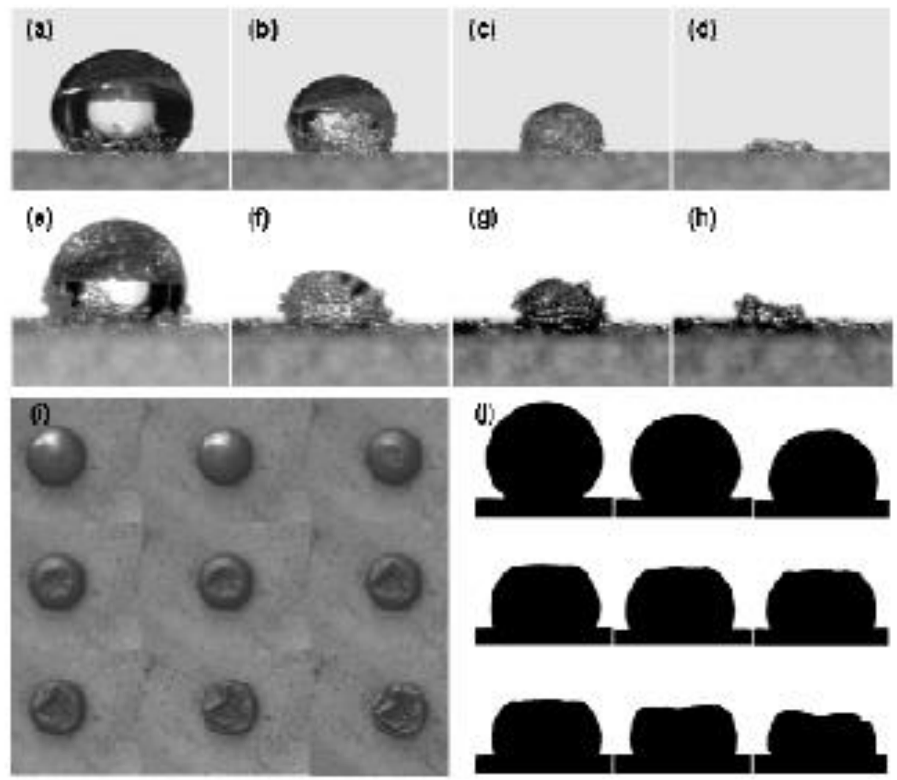
[1]. McHale and Newton, *Soft Matter* 7(12) (2011) 5473

[2]. Aussillous, Quéré, *Nature* 411 (2001) 924.

[3]. Bormashenko, and co-authors, *Langmuir*, 25 (4) (2009) 1893.

[4]. Binks , Murakami, *Nature Maters*. 5 (2006) 865.

[5]. Dandan, Erbil, *Langmuir*, 25 (2009) 8362



Evaporation of liquid marbles
Picture source: Ref. [5]