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

COST Action TD1105

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New Sensing Technologies for Air Quality Monitoring

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THEORETICAL MODELING of QCM-D and SH-SAW SENSORS in ENVIRONMENTAL APPLICATIONS

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Function in the Action (WG2 Member)

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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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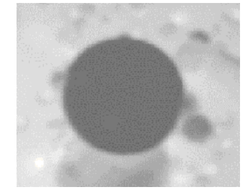
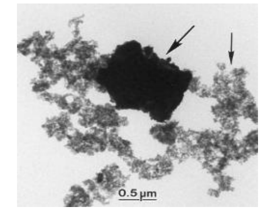
Background: functionalized QCM-D and SAW sensors multiple applications

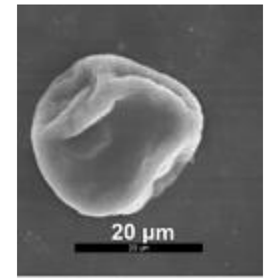
- **Gravimetry of air pollutants**, VOC precise measurements, toxic additives in gas and vapours, mineral and organic dust and microparticles in industrial, safety/military applications and
- out- and in-door AQC monitoring.
- E-nose /E-tongue components, in arrays.

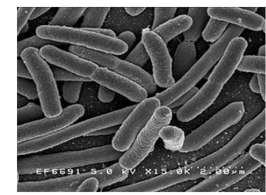
- **Biosensors and immunosensors** in liquid environments, water and food quality control, bacterial toxins and viruses detection, medical and biomedical analysis

- Mechanical parameters measurements (density, elasticity, viscoelasticity) of thin films (solid and soft coatings, polymers and adsorbed proteins among others)

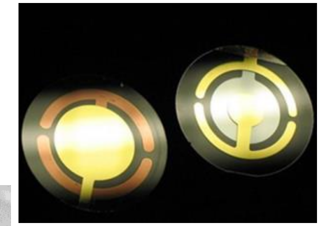


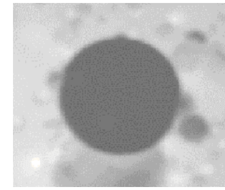


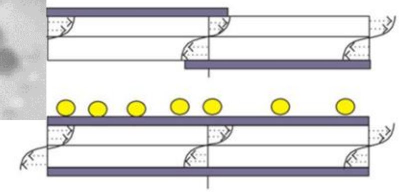




$$\Delta f = f - f_0 = -\left(\frac{2 f_0^{\,2}}{\rho_q V}\right)\Delta M = -C \cdot \Delta M$$







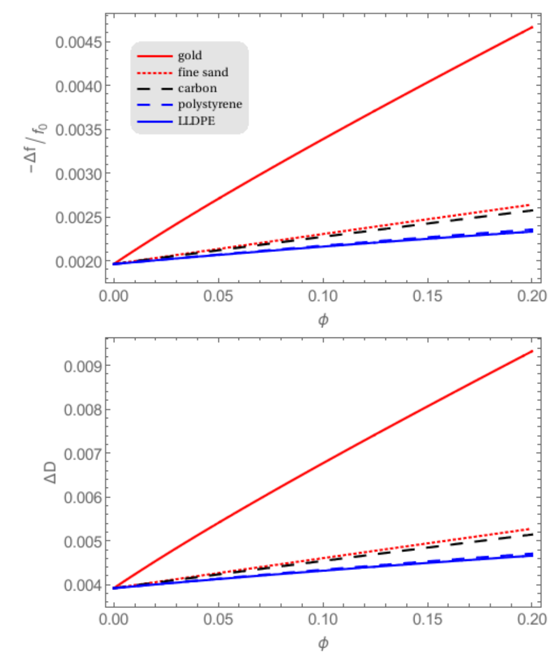
QCM-D

- **Our results:**

Dispersion equation for the 3-layers rigid/viscoelastic films (on top – gas or viscous/viscoelastic fluid)

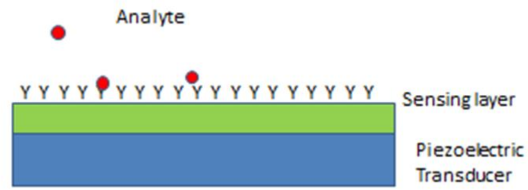
Analytical results: calculated shift in the resonance frequency and the dissipation – a generalization of Sauerbrey relation for viscoelastic materials in wet conditions (vapours or liquids)

Figure 6



Numerical calculations QCM Δf/f (ϕ), Δf/f (h),
Microparticles and thin viscous/viscoelastic coatings in wet / underliquid conditions

Modeling of QCM-D: analytical results



Viscoelastic corrections to the measured mass M of the soft layer under Newtonian liquid:

$$M_S = M\left\{1 - \frac{\eta_L \rho_L \omega}{\rho} \frac{G''}{G'^2 + G''^2}\right\}$$

Soft layer under Newtonian bulk liquid:
the total shift in the resonance frequency is a sum of the frequency shift due to the surface mass $M = \rho \cdot h$, contribution of bulk liquid Δf_L and corrections due to the layer viscoelasticity $G^* = G' + iG''$

$$\Delta f - \Delta f_L \approx -\frac{h\rho\omega}{2\pi\rho_q h_q}\left\{1 - 2\left(\frac{\eta_L}{\delta_L}\right)^2 \frac{J''}{\rho}\right\} \qquad J'' = \frac{G''}{G'^2 + G''^2}$$

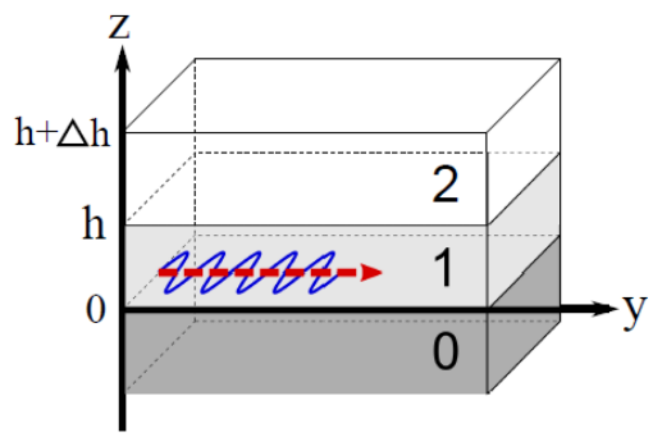
The change in the dissipation factor:

$$\Delta D - \Delta D_L \approx \frac{h\rho\omega}{f\rho_q h_q}\left\{2\left(\frac{\eta_L}{\delta_L}\right)^2 \frac{J'}{\rho}\right\} \qquad J' = \frac{G'}{G'^2 + G''^2}$$

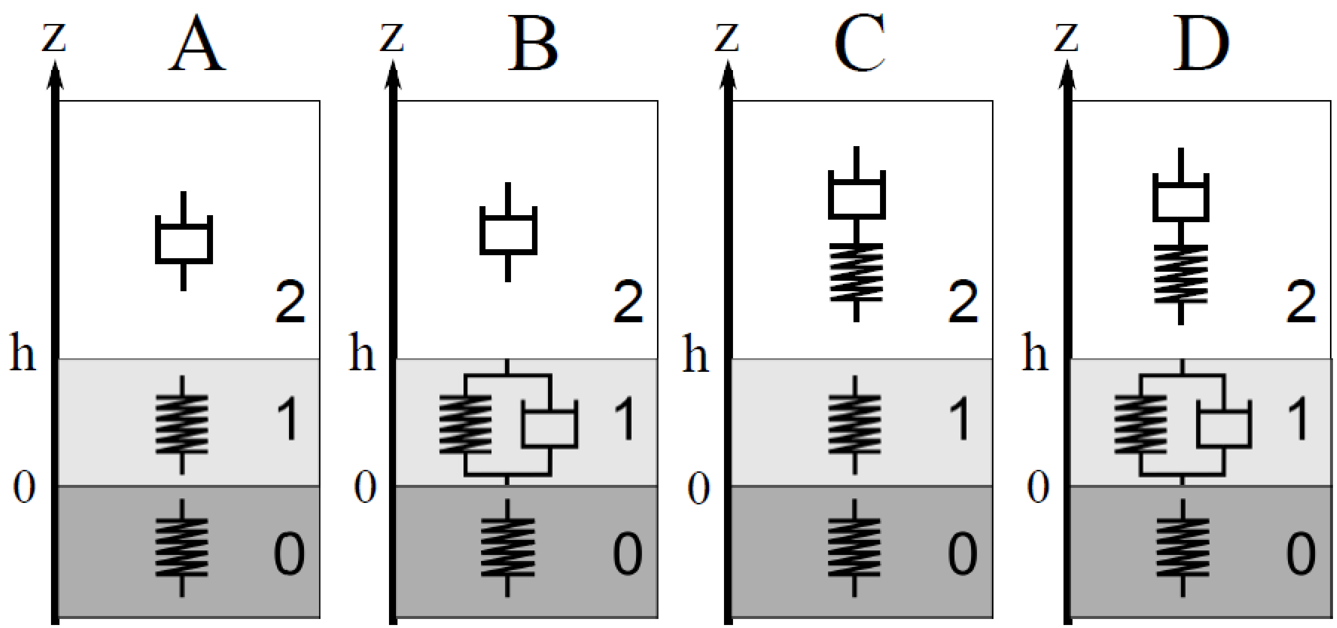
Modeling SH-SAW sensors: soft film dynamics in fluids

- The system geometry: layered viscoelastic films of thickness h under viscous fluid
- Mechanical properties of films: density ρ and viscoelastic moduli μ* (Voight/Maxwell models)
- Top medium: gas,

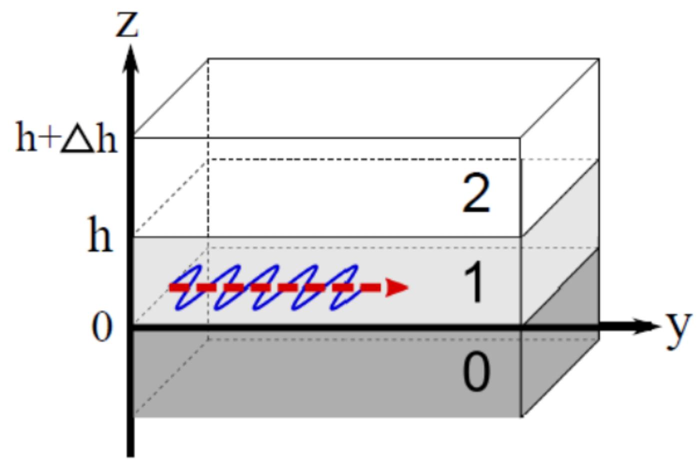
  vapours or viscous fluid



Viscoelasticity schemes for the 3-layer system: combined Voight/Maxwell models



SH-SAW dispersion equation



$$\kappa = \frac{\mu_1^* \xi_1}{\mu_0} \frac{F_- - e^{2\xi_1 h} F_+}{F_- + e^{2\xi_1 h} F_+},$$

$$F_\pm = \mu_1^* \xi_1 \pm \mu_2^* \xi_2 \tanh(\Delta h \xi_2).$$

$$\kappa = \sqrt{k^2 - \frac{\omega^2}{v_0^2}}. \qquad \xi_i = \sqrt{k^2 - \omega^2 \frac{\rho_i}{\mu_i^*}}$$

SH-SAW sensor experimental measurables

- Phase velocity shift

$$\frac{\Delta v}{v_0} \approx -\mathrm{Re}\left(\frac{\kappa^2}{2k^2}\right)$$

- Attenuation coefficient

$$\Gamma \approx -\mathrm{Im}\left(\frac{\kappa^2}{2k}\right)$$

Analytical Results of Modeling

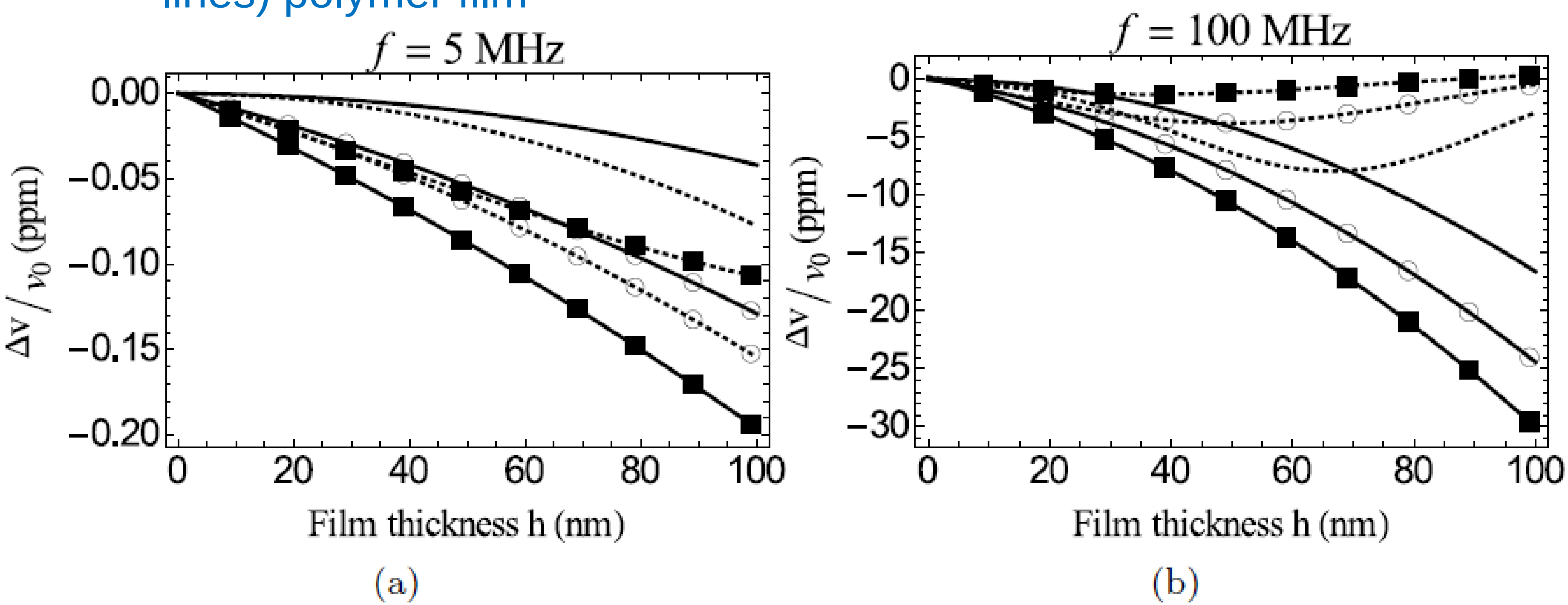
$$\frac{\Delta v}{v_0} \approx \frac{v_0^2}{2\mu_0^2}\left\{\rho_2 G' + (G''^2 - G'^2)\frac{1}{v_0^2} + [h\rho_1]\rho_2(G'K_1 - G''K_2)\right\}$$

$$\Gamma \approx \frac{v_0 \omega \rho_2}{2\mu_0^2}\left\{G'' - \frac{2G'G''}{\rho_2 v_0^2} + [h\rho_1](G''K_1 + G'K_2)\right\}$$

Dynamics of SH-SAWs

Numerically calculated phase velocity shift :

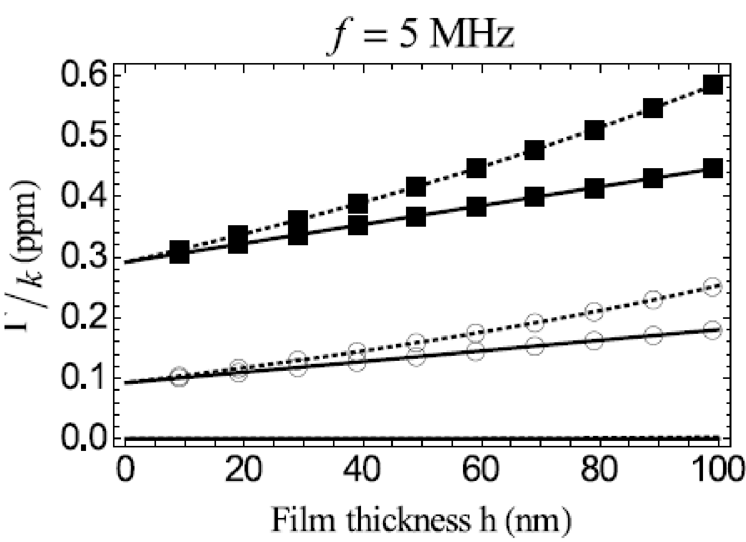
- **THE ROLE OF FILM SOFTNESS / frequency**
- Quartz substrate covered by a rigid (solid lines) or soft (dashed lines) polymer film



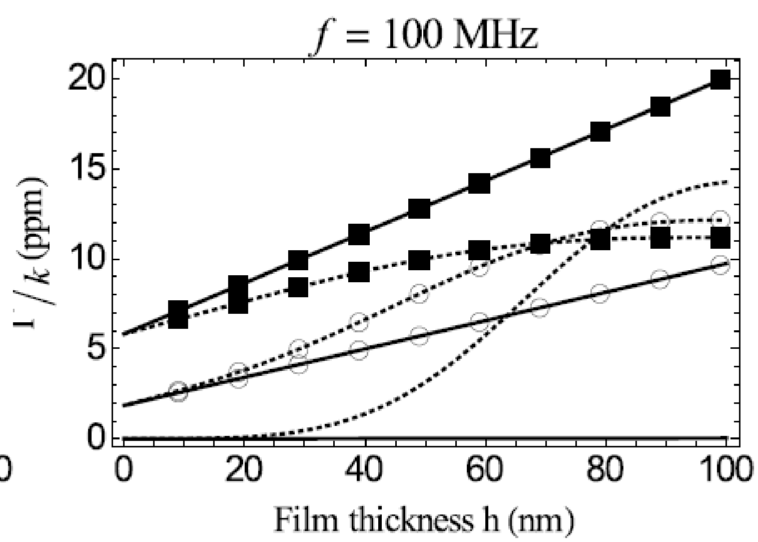
Numerical analysis (SH-SAW sensors)

- **Calculated attenuation coefficient**

Quartz covered by a rigid (solid lines) or soft (dashed lines) polymer film



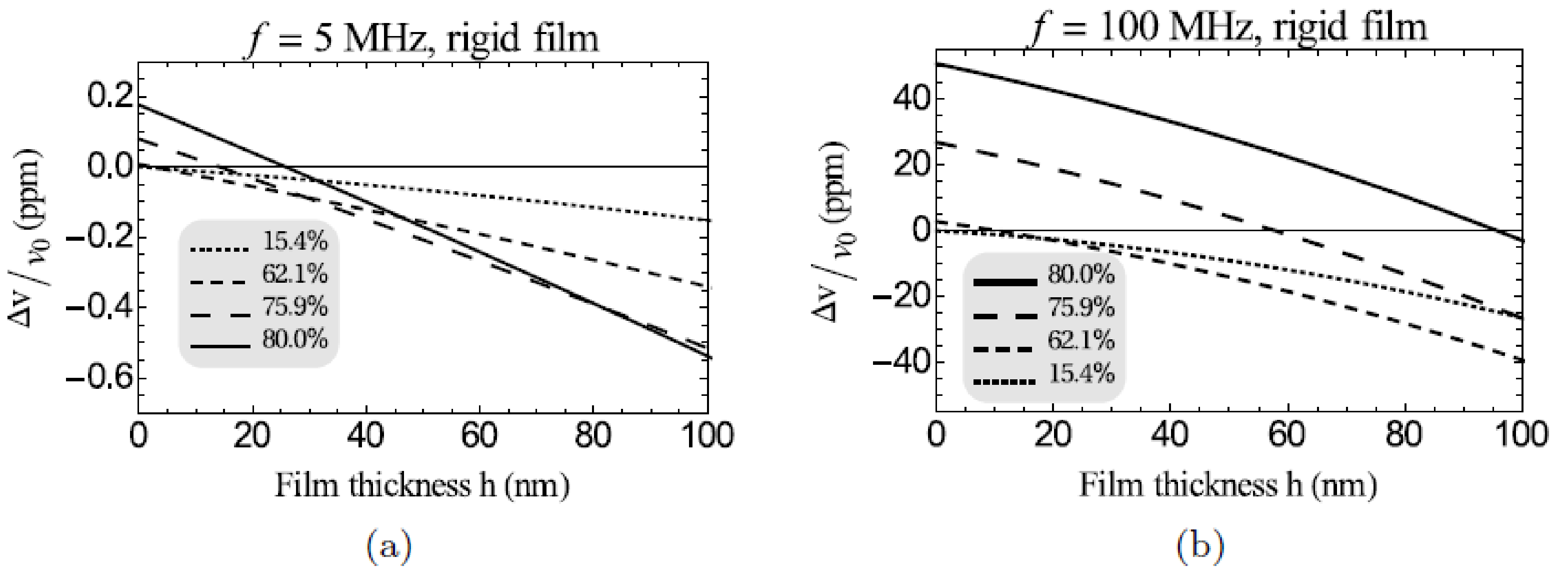
(a)



(b)

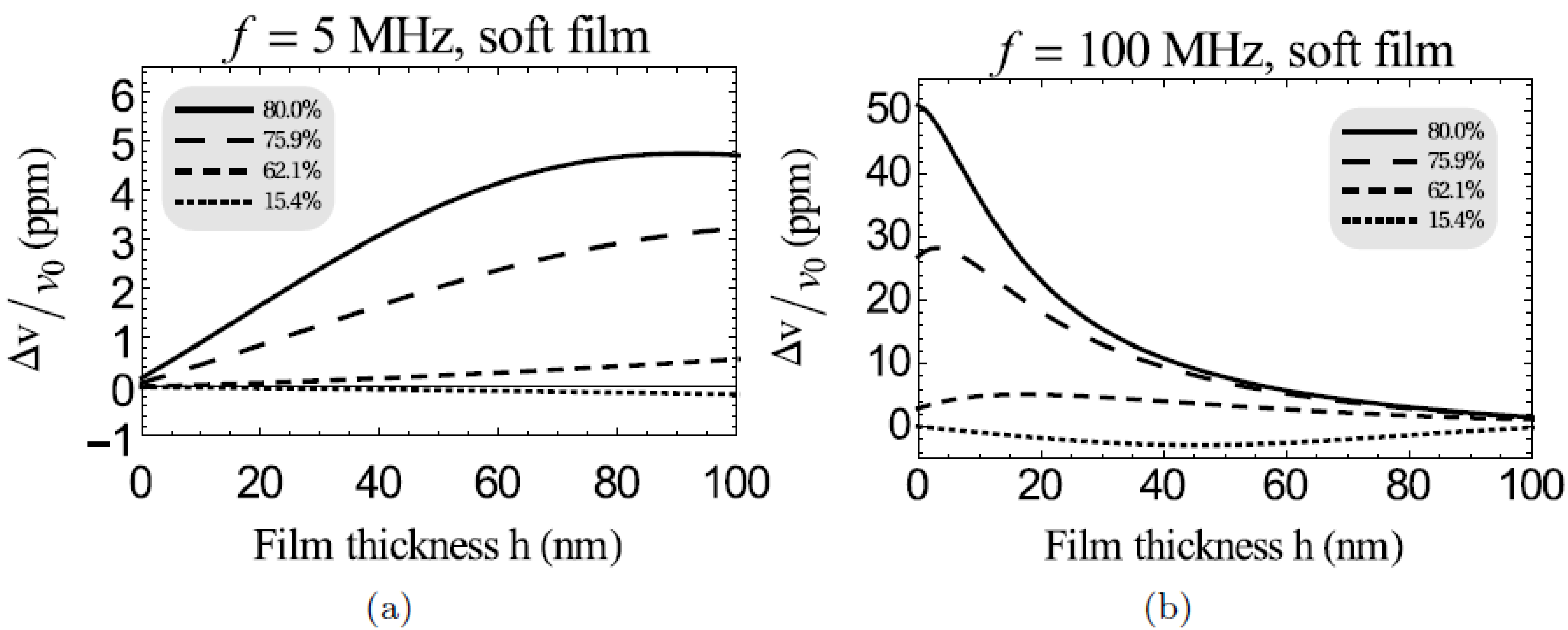
Calibration of SAW-sensors

Velocity shifts for a rigid film in glycerol/water mixtures



Calibration of SAW-sensors

Velocity shifts for a soft film in glycerol/water mixtures



Main results

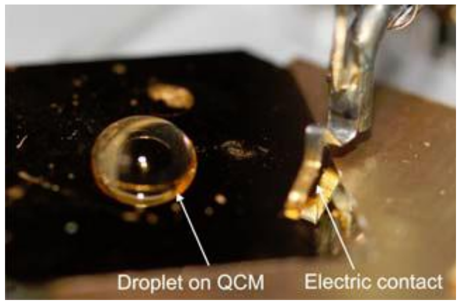
- We developed a rigorous physical theory of coated QCM-D and SH-SAW sensors operated in gas, vapours or liquid environments
- The generalization of the Saurbrey relation for the viscoelastic film coating in wet conditions is derived
- Analytical formulae for the experimentally measurable sensors characteristics are obtained

The importance of the results

- The developed general theory provides a rigorous support to the experimental acoustical sensors research and gives the correction of the measured mass due to the viscous or viscoelastic effects
- The theory is a powerful analytical tool allowing researchers to quantify the results of experiments with viscoealstic coatings performed in wet conditions and to calibrate the sensors
- The results are used as a mathematical basis for modeling and devices software to analyze the experimental data in particular in environmental and biomedical research

OUTLOOK

Theoretical support of experiments with QCM-D and SAW sensors **integrated in microfluidic** and **LOCs systems**



Picture: Lederer et al. **A HIGH FUNDAMENTAL FREQUENCY QUARTZ CRYSTAL BIOSENSOR INTEGRATED INTO AN ELECTRO-WETTING-ON-DIELECTRICS BASED LAB-ON-A-CHIP.(2010)**

Future research.

New nano materials: Graphene-GO coated SAW and QCM sensors

Environmental applications example:

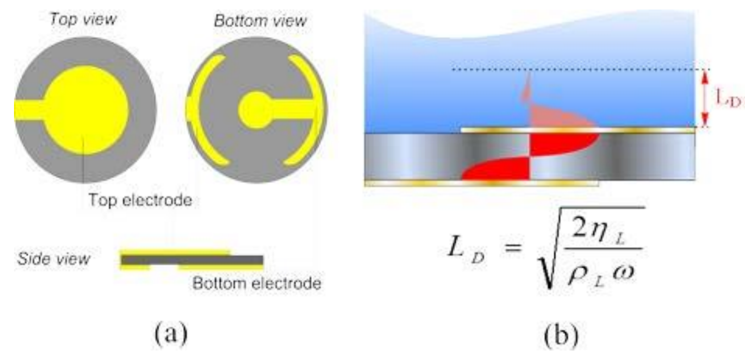
- Detecting formaldehyde *) both in industrial and in-door environment
- Detecting VOC
- Challenge: Humidity influence
- Innovation: Controlling SAWs with graphene**) : theoretical analysis

*) Zhihua, Liang, Kaixin, Weiwei, Characterization of quartz crystal microbalance sensors coated with graphene films, Procedia Eng. 2012

**) Bandhu, Nash. Controlling the properties of SAW with graphene. Nano Research 2016

Future research: Interaction of graphene with water

QCM coated with graphene films in water and nonpolar liquids: Challenges:



Studying graphene – liquid interactions

Underliquid measurements

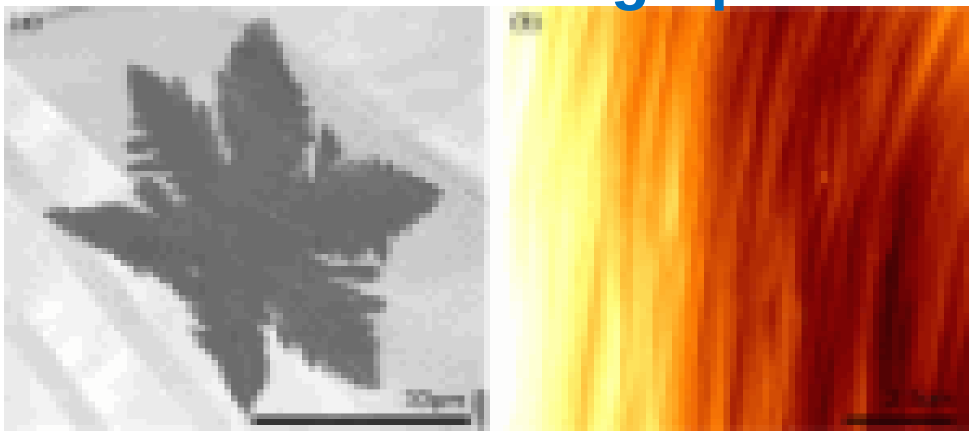
Swelling of graphene

Complex multistage behavior of absorption of water vapour in graphene

Image source: From: Mazzocco et al.Proceedings of NanoTech 2012

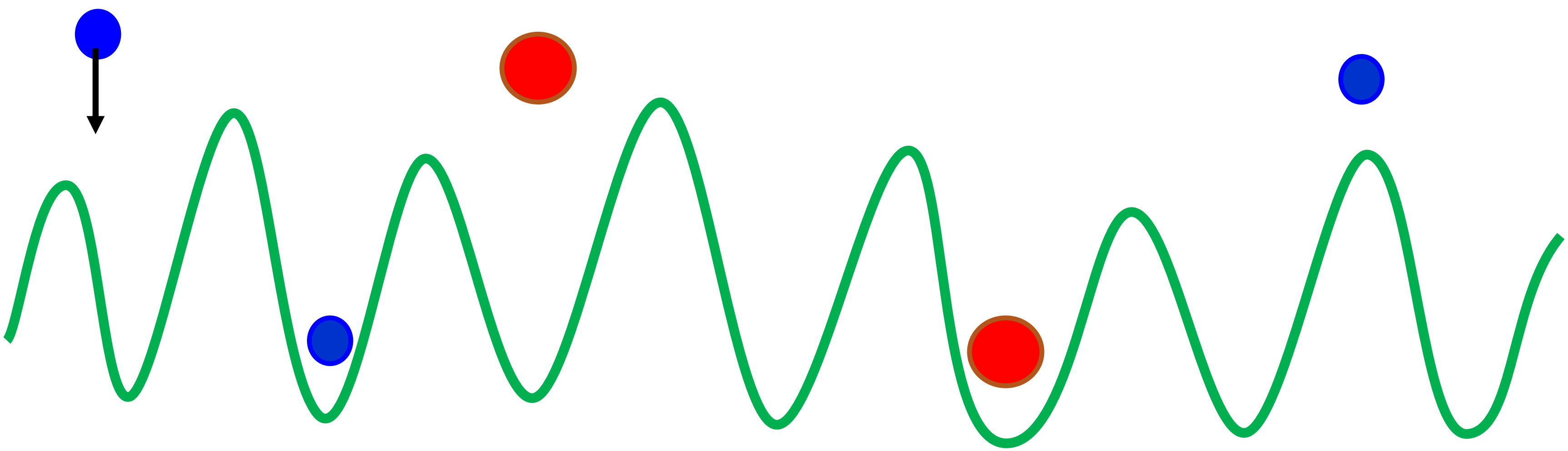
Perspective research:

Probing with QCM interfacial mass variation during adsorption of water and biomolecules on graphene surface



Ripples on graphene flake (AFM)

SEM and AFM images of graphene flake: N.Kakenov et al. Weighing graphene with QCM to monitor interfacial mass changes. Appl Phys Lett 2016



Recommendations

Dissiminate
COST Action results:
Movie release

R&D project

Integrated sensors activity

Theoretical modeling +

New lab&field experiments

Applications: Air/ocean pollution
Soil and water quality control

Picture: Georgy Dmitriev 'Mediterrenian view'

Acknowledgments

To Anton Vikström, PhD student,

Chalmers University of Technology

To COST Action TD1105

THANK YOU FOR YOUR KIND ATTENTION!