

# Thursday Morning, November 13, 2014

## Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: 317 - Session QC+AS+BI+MN-ThM

### Fundamentals and Method Development of QCM

**Moderator:** Ralf Richter, CIC biomaGUNE & MPI for Intelligent Systems, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology

8:40am **QC+AS+BI+MN-ThM3 High-Frequency Contact Mechanics Studies with a QCM.** *Diethelm Johannsmann*, Clausthal University of Technology, Germany **INVITED**

Studying particulate objects with a QCM is challenging with regard to interpretation, but also of outstanding interest. Potential samples would be (bio-) colloids, vesicles, granular matter, bacteria or technical multi-contact interfaces. The analysis must build on the small-load approximation, which states that the shifts in resonance frequency and resonance bandwidth are proportional to the in-phase and the out-of-phase component of the area-averaged stress at resonator surface. For realistic modeling, a numerical code is needed which predicts this stress field from the geometry and all materials parameters involved. There is such a model in two dimensions, building the finite element method.

On a simpler level, the behavior of particles on a resonator surface can also be understood from the coupled resonance model. The particles in contact form small resonators of their own, where the “particle resonance frequency” is determined by the mass and the stiffness of the contact. If the particle resonance frequency in the range of frequencies amenable to the QCM one observes a coupled resonance, meaning that the shifts of resonance frequency and resonance bandwidth themselves form a resonance curve when plotted versus overtone order. Depending on whether the particle resonance frequency is higher or lower than the QCM frequency, the frequency shift can be positive or negative. From the particle resonance frequency, one can assess the stiffness of the contact between the particle and the surface.

The detailed investigation of the coupled resonance picture reveals a problem. though. FEM models of the corresponding geometries reveal two coupled resonance, occurring at different frequencies. They corresponding to a rotation of the particle about the point of contact (the “rocking mode”) and a rotation about the center of mass (the rotational mode”). The problem complicates the interpretation of experimental data, but it points to an intriguing analogy between QCM experiments a vibrational spectroscopy. A QCM experiment amounts to a vibrational spectroscopy on surface-attached colloids.

The last part of the talk is concerned with a novel sensing dimension of the QCM, which is the dependence of frequency and bandwidth on amplitude. Such dependences are ubiquitous in contact mechanics experiments and can be understood in terms of partial slip. The contacts behave nonlinearly. Nonlinear behavior can also be observed in liquids, where it is caused by the nonlinear term in the Navier-Stokes equation. The nonlinear term drives a steady flow of liquid along the direction of oscillation towards the center of the plate.

9:20am **QC+AS+BI+MN-ThM5 Study of Water Adsorption and Capillary Bridge Formation for SiO<sub>2</sub> Nanoparticle Layers by Means of a Combined In Situ FT-IR Reflection Spectroscopy – QCM-D Set-up.** *Boray Torun, C. Kunze*, University of Paderborn, Germany, *C. Zhang, T.D. Kühne*, Johannes Gutenberg University Mainz, Germany, *G. Grundmeier*, University of Paderborn, Germany

During the past decade nanoparticles attracted a great deal of attention and found many applications in various fields ranging from pigments and antibacterial agents to highly effective catalysts. In this context, the handling and processing of nanoparticle powders play an important role. In contrast to macroscopic particles, nanoparticle flow properties are mainly governed by the particle-particle interactions. The forces determining these interactions strongly vary not only with the material properties but also with surface chemical composition as well as the environmental conditions. Hence, a fundamental understanding of the processes and forces involved plays a key role for the prediction of nanoparticle powder behavior.

In the presented study<sup>[1]</sup>, water adsorption and capillary bridge formation within a defined layer of SiO<sub>2</sub> nanoparticles was studied by means of a novel *in-situ* analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier

transformation infrared reflection absorption spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change ( $\Delta f$ ) and changes in the contact mechanics, indicated by dissipation changes ( $\Delta \Gamma$ ), whereas on the other hand FT-IRRAS allowed for the characterization of the adsorbed water structure. Employing peak deconvolution to the OH-signal in the region of 3400 cm<sup>-1</sup>, “ice-like” and “liquid-like” water structures could be clearly identified.

Combined measurements show that for a monolayer of monodisperse SiO<sub>2</sub> particles with a diameter of about 250 nm the adsorption of water leads to a linear increase in dissipation for relative humidity (RH) values up to 60%. Subsequently, the strong increase in dissipation between 60% and 80% RH was attributed to the actual liquid bridge formation. This result was supported by the predominant growth of “liquid-like” water during the bridge formation phase indicated by the corresponding FT-IR data. Furthermore, for RH > 90% a decrease in dissipation was detected indicating the merging of capillaries and the onset of a water film formation. Overall, our results indicate that combined *in-situ* QCM-D and FT-IRRAS analysis enables the qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

[1] Torun, B. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 7377-7384

9:40am **QC+AS+BI+MN-ThM6 On the Role of Acoustic Streaming in Particle Detachment Events at a QCM Surface.** *Rebekka König, A. Langhoff, D. Johannsmann*, Clausthal University of Technology, Germany

A steady flow of liquid was observed above the surface of a quartz crystal microbalance (QCM) under conditions, where the oscillation amplitude exceeded 10 nanometers. The streaming flow occurs parallel to the displacement vector and is directed towards the center of the plate. It is expected to have applications in acoustic sensing, in microfluidics, and in micromechanics in a wider sense. The flow is caused by the nonlinear term in the Navier-Stokes equation, which can produce a nonzero time-averaged force from a periodic velocity field. Central to the explanation are the flexural admixtures to the resonator's mode of vibration. Unlike pressure-driven flows, the acoustically driven steady flow attains its maximum velocity at a distance of a few hundred nanometers from the surface. It is therefore efficient in breaking bonds between adsorbed particles and the resonator surface. As a side aspect, the flow pattern amounts to a diagnostic tool, which gives access to the pattern of vibration. In particular, it leads to an estimate of the magnitude of the flexural admixtures to the thickness-shear vibration.

[1] R. König, A. Langhoff, D. Johannsmann, *Physical Review E* **2014**.

11:00am **QC+AS+BI+MN-ThM10 QCM for Particle Sizing and Beyond.** *Adam Olsson, I.R. Quevedo, D. He, M. Basnet, W. Lee, N. Tufenkji*, McGill University, Canada **INVITED**

The dissipative energy loss of a quartz crystal microbalance (QCM) sensor is typically ascribed to the viscoelastic nature of the adsorbed material. While such an interpretation is suitable for thin homogeneous films, it is not *a priori* valid for discrete objects. As demonstrated recently, dissipation due to nanoparticle deposition can be described by the relative movement of the particles attached to the oscillating sensor surface. This particular dissipation behavior of nanoparticles gives rise to new experimental approaches to study colloidal transport, particle-surface interactions and particle properties.

In this presentation, we focus on QCM-D as a method to determine the size of deposited nanoparticles. The approach involves analysis of the change in dissipation per attached mass (i.e., the “ $\Delta D/\Delta f$ -ratio”) to predict a hypothetical full particle surface coverage that can be used to calculate an effective layer thickness of the particulate film; and this quantity, in turn, can be related to the average particle diameter. To validate the approach, we determined particle sizes using various types of nanoparticles with diameters ranging from ~ 5 nm to ~ 110 nm and compared the results with sizes obtained from dynamic light scattering (DLS) and transmission electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and the sensor surface. Hence, if the particle size is known, the approach can also be used to investigate the strength of the nanoparticle-surface interaction.

We will also describe our ongoing work where we are studying the QCM-D response to the deposition of anisotropic bacteriophage to determine their orientation on the surface. Bacteriophages are viruses that bind to and infect bacteria with high specificity and, thus, can be exploited in antimicrobial and biosensor applications. One challenge in functionalizing surfaces with bacteriophages is to control their orientation such that their binding sites remain exposed to the ambient medium. By studying how dissipation changes with phage surface coverage, it is possible to identify at which surface coverage phage-phage interaction occurs. This event compromises

the phages ability to bind to bacteria, as evidenced by subsequent bacterial “capture” experiments and imaging, and thus is crucial for the performance of QCM-D based biosensors that utilize bacteriophage as a biorecognition element.

11:40am **QC+AS+BI+MN-ThM12 Full Experimental Proof of the Relationship between the Intrinsic Viscosity of DNA and the Acoustic Ratio of SAW and TSM Sensors**, *Achilleas Tsortos*, IMBB-FORTH, Greece, *G. Papadakis*, NCSR-Demokritos, Greece, *E. Gizeli*, IMBB-FORTH & Univ. of Crete, Greece

Acoustic wave sensors are extensively used in biotechnology and biophysics in order, for example, to detect molecules in a solution, study an antibody-antigen interaction or the hybridization of DNA. Today, data analysis includes (a) the use of the Sauerbrey equation, in order to calculate the mass of the molecules attached on the surface of the acoustic device by use of frequency data and (b) the use of complicated mathematical models of the assumed ‘film’ formed by the attached molecules. In the second case information such as the rigidity modulus and viscosity of the ‘film’ can be calculated and comments can be made on the softness (viscoelasticity) of the added layer.

Here, we present an entirely different approach. Based on a theory developed earlier<sup>1,2</sup> we correlate the acoustic ratio  $R$ , to the intrinsic viscosity  $[\eta]$  of the attached molecule. The acoustic ratio is the ratio of the amount of energy loss per attached unit mass – this is given as  $(\Delta D/\Delta F)$  in the TSM acoustic mode notification, or as  $(\Delta A/\Delta Ph)$  in the SH-SAW mode and is readily obtained in each experiment. The *intrinsic* viscosity on the other hand, is a hydrodynamic quantity directly related to the size and shape of a biomolecule and can be determined independently through viscometry. In this study we present collected experimental data from a variety of case studies proving for the first time the semi-empirically assumed relationship  $R \sim [\eta]$  in a general form. Data are presented for various shapes and sizes of DNA and other systems of biological interest. The case is made for two acoustic modes (thickness shear and surface horizontal) and for various frequencies in the range of 5-155 MHz.

Our analysis presents a paradigm shift and challenge; we claim that (label-free) structure probing is a much more improved method offering higher flexibility in design and interpretation of experimental assays. Detecting and monitoring in real time processes that involve structural changes but not necessarily mass changes and/or ‘film’ formation is a novel concept that can be readily applied in anything from DNA, RNA hybridization and detection of mutations to molecular machines (e.g. DNA Holliday junction) and protein/DNA/RNA interactions in the broad areas of biophysics, structural DNA nanotechnology and diagnostics.

Acknowledgement: the REGPOT-InnovCrete/EU-FP7 (Contract No. 316223) for financial support.

References:

1. A. Tsortos, et al., *Biophys. J.* 2008, 94:2706
2. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836

12:00pm **QC+AS+BI+MN-ThM13 Characterization of the Conformation of Linker-Suspended Proteins at Surfaces through Acoustic Ratio Measurements**, *Electra Gizeli*, IMBB-FORTH & Univ. of Crete, Greece, *D. Milioni*, IMBB-FORTH, Greece, *G. Papadakis*, NCSR-Demokritos, Greece, *A. Tsortos*, IMBB-FORTH, Greece

Characterization of protein shape and orientation following surface binding is an area of great interest in biophysics with many applications in chemistry and nano/biotechnology. Techniques such as ellipsometry and AFM have been extensively used for providing such information. A lot of effort has also been put with acoustic sensors; results in this case though depend greatly on the data interpretation model employed. An important question is always the preservation of protein integrity/form.

In this work we employ acoustic devices based on a QCM geometry at 35 MHz. The acoustic ratio  $\Delta D/\Delta F$ , i.e., the dissipation over frequency change of the shear wave has been employed in our analysis. We have previously shown<sup>1</sup> that as a tool, this ratio provides valuable information regarding the conformation of surface attached DNA molecules; we have also employed this approach in the design of DNA assays for diagnostic purposes, including detection of sequence targets in real samples<sup>2</sup>.

Here we expand this methodology in proteins; streptavidin is used as a case study for characterizing spherical protein immobilization on an acoustic device. Good control of the binding mode was achieved by changing the distance of the protein from the surface, ranging from zero (direct physisorption) to several nm, using anchor molecules. In this way we can manipulate the degree of surface interference to the protein structure. Our results clearly show that direct protein adsorption is a multistep process resulting in very low acoustic ratio, in agreement with the literature. However, we show for the first time that suspending the protein away from the surface from a single point through a variable-length linker, gives an

entirely different picture; the process is a single-step event, as judged from D-F plots, and the resulting acoustic ratio is much higher (order of magnitude) than that obtained in physisorption. The effect of the linker length on the apparent acoustic ratio is analyzed. This approach gives more reliable and different information regarding the protein shape than do simple physisorption protocols and interpretation models involving notions such as ‘film’ formation etc.

References:

1. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836; A. Tsortos et al., *Biophys. J.* 2008, 94:2706
- G. Papadakis et al., *Anal. Chem.* 2012, 84:1854; G. Papadakis et al., *Scientific Rep.* 2013, 3:2033

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