

# Studying Surface-Adsorbed Colloidal Particles with Quartz Crystal Microbalance: Hydrodynamic Effects.

I. Reviakine

Centro de Investigación Cooperativa en Biomateriales, Parque Tecnológico de San Sebastián, E-20009 San Sebastián, Spain

and

Department of Biochemistry and Molecular Biology, University of the Basque Country, 48940 Leioa, Spain.

Quartz crystal microbalance (QCM) is widely used for studying soft interfaces in liquid environments. Many of these interfaces are heterogeneous in nature, in the sense that they are comprised of isolated entities adsorbed at a surface. When characterizing such interfaces, one is interested in determining parameters such as surface coverage and size of the surface-adsorbed entities. Currently this information is obtained by fitting QCM data—shifts in resonance frequency,  $\Delta F$ , and bandwidth  $\Delta\Gamma$  (also referred to as dissipation shifts)—with the model derived for smooth, homogeneous films using the film acoustic thickness and shear elastic moduli as fitting parameters. This is the so-called continuum approach. Experimentally, we investigated adsorption of proteins, liposomes, and icosahedral virus particles on inorganic surfaces with QCM and with a combined atomic force microscopy (AFM)-QCM setup. Theoretically, we modeled the QCM response with finite element method (FEM) calculations based on the incompressible Navier-Stokes equation to incorporate hydrodynamic effects.

The results of our studies can be summarized as follows. Experimentally, the relationship between the surface coverage and the frequency shift is not linear. This non-linearity can be modeled with the FEM calculations clarifying the contribution of the solvent to the frequency shift and the origin of dissipation in these heterogeneous films. In particular, our results show that the dissipation in these heterogeneous layers occurs mostly in the solvent and arises due to the motion of the adsorbed particles. In other words, it is not a measure of the elastic properties of the adsorbed particles, but rather of the particle-surface contact.

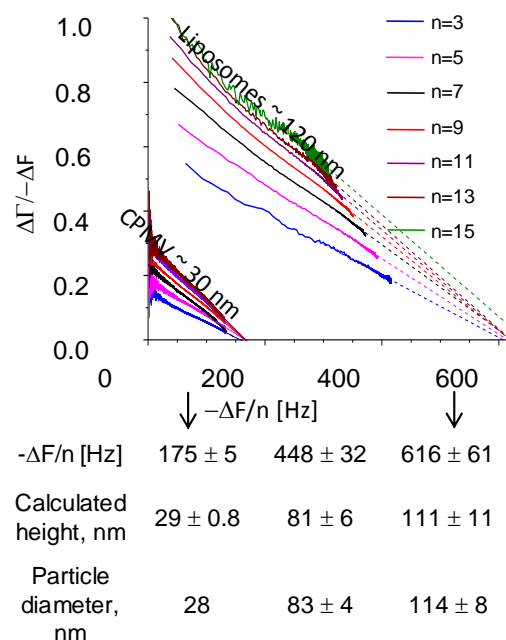


Figure 1: The plot of the  $\Delta\Gamma/-\Delta F$  ratio vs. the frequency shift,  $-\Delta F/n$ , for liposomes and cowpea mosaic virus (CPMV) particles adsorbing on inorganic surfaces. Different overtones are represented by different colors. The ratio decreases with the frequency shift ( $\sim$  surface coverage), but is greater for larger objects. The curves are nearly linear and extrapolate to frequency shifts that can be converted into object heights via the Sauerbrey relationship. These are found to correlate with the crystallographic dimensions of the CPMV particles and liposome sizes measured by dynamic light scattering.

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To directly compare the predictions of the continuum approach with the experimental results, we focus on the ratio between the bandwidth and frequency shifts,  $\Delta\Gamma/\Delta F$  (the  $Df$  ratio). The continuum model predicts that this should increase both with surface coverage and particle size. Instead, we observe that this ratio increases with increasing particle size, but decreases with increasing surface coverage. This behavior is again consistently modeled with the FEM calculations: in other words, this is a hydrodynamic effect.

Finally, we find that the size of the adsorbed colloidal particles can be recovered from a model-independent analysis of the plot of the  $\Delta\Gamma/\Delta F$  ratio vs. the frequency shift on many overtones (Figure 1).

Recent literature on the subject from our and other groups:

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6. Carton, I.; Brisson, A. R.; Richter, R. P. *Analytical Chemistry* **2010**, *82*, (22), 9275-9281.