



Towards vibrational spectroscopy on surface-attached colloids performed with a quartz crystal microbalance

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ABSTRACT

Colloidal spheres attached to a quartz crystal microbalance (QCM) produce the so-called “coupled resonances”. They are resonators of their own, characterized by a particle resonance frequency, a resonance bandwidth, and a modal mass. When the frequency of the main resonator comes close to the frequency of the coupled resonance, the bandwidth goes through a maximum. A coupled resonance can be viewed as an absorption line in acoustic shear-wave spectroscopy. The known concepts from spectroscopy apply. This includes the mode assignment problem, selection rules, and the oscillator strength. In this work, the mode assignment problem was addressed with Finite Element calculations. These reveal that a rigid sphere in contact with a QCM displays *two* modes of vibration, termed “slipping” and “rocking”. In the slipping mode, the sphere rotates about its center; it exerts a tangential force onto the resonator surface at the point of contact. In the rocking mode, the sphere rotates about the point of contact; it exerts a torque onto the substrate. In liquids, both axes of rotation are slightly displaced from their ideal positions. Characteristic for spectroscopy, the two modes do not couple to the mechanical excitation equally well. The degree of coupling is quantified by an oscillator strength. Because the rocking mode mostly exerts a torque (rather than a tangential force), its coupling to the resonator’s tangential motion is weak; the oscillator strength consequently is small. Recent experiments on surface-adsorbed colloidal spheres can be explained by the mode of vibration being of the rocking type.

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1. Introduction

The quartz crystal microbalance is well known to the scientific community as a film thickness monitor [1] and, further, as a tool to study of soft layers beyond gravimetry [2,3]. Central to the advanced QCM is the ability to determine the resonance bandwidth in addition to resonance frequency and to compare shifts of frequency and bandwidth between overtones [4]. The models of stratified viscoelastic layer systems on a QCM surface are well-established [5,6].

Many samples of practical interest are not stratified layers. This includes particles [7–9], cell layers [10], vesicles [11], viruses [12,13], and bacteria [14–16]. Generally speaking, the prediction of the shifts in frequency and bandwidth (Δf and $\Delta \Gamma$) induced by structured samples is challenging. Numerical methods are required [17]. There is one group of heterogeneous samples, though, which is amenable to analytical description. If the particle of interest contacts the resonator surface across a sufficiently narrow contact (a “point contact”), and if, further, neighboring contacts are elastically independent from each other, the only parameters of relevance are the tangential force and the torque. Since the zone of deformation is small, one can define a tangential displacement and an angle of rotation, to be evaluated far away from the

deformed zone (Fig. 1A). The deformed region in the following is called “the contact”. The fact that the contact is localized is critical to the analysis.

In the past, the complications arising from the motion of the external object being a superposition of translation and rotation have often been avoided by choosing the external objects so heavy that they were clamped in space by inertia [18,19]. Large spheres do not follow the MHz oscillation of the resonator, they undergo neither rotation nor translation. The angle of rotation then is zero; the displacement between the two sides of the contact is equal to the displacement of the resonator surface, given as $u_0 \cos(\omega t)$ with u_0 the amplitude of oscillation. Dividing force by displacement, one obtains the contact’s tangential stiffness.

The arguments below are concerned with situations, where the external object is too small to be clamped in space. Most bio-colloids fall into that class. The prospect of being able to measure the stiffness of a link between a bio-colloid and a solid substrate has attracted much interest. The situation evidently becomes more complicated than for large immobile spheres, but as long as the object is stiff, translation and rotation can be accounted for with suitably modified equations.

Particles in the micron-size range give rise to a phenomenon known since 1985, which is the “coupled resonance” [20]. (Coupled resonances were known before, but they were put into the context of QCM-based sensing by Dybwad at that time.) An introduction to coupled resonances

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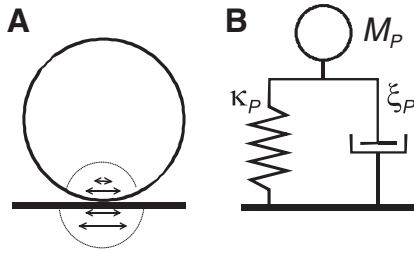


Fig. 1. A: Sketch of a contact between a sphere and the resonator surface. It is essential that the contact is smaller than the sphere and, also, is smaller than the wavelength of sound. Only the region close to the contact (dashed circle) is deformed. Together with the deformed region of the substrate, it forms a Hookean spring. B: Mechanical equivalent circuit. Viscous dissipation is accounted for by a dashpot.

is given in Section 2. It turns out that a coupled resonance amounts to an absorption line in shear-wave spectroscopy. A particle linked to the surface has its own frequency of vibration. With a QCM, one can do vibrational spectroscopy on surface-attached colloids. The conceptual analogies between coupled resonances and shear-wave spectroscopy are far-reaching. Keywords are mode-assignment, modal mass, modal stiffness, homogeneous linewidth, heterogeneous linewidth, degeneracy, selection rules, and oscillator strength. These terms can all be applied to shear-wave spectroscopy. The oscillator strength, in particular, is non-trivial. The oscillator strength is needed to explain experimental results.

A complication not appreciated by Dybwad was the fact that there are (at least) two dynamic variables, which are the position of the particle along the direction of surface displacement and the angle of rotation into the same direction. The conjugate variables are a tangential force and a torque. Because there are two dynamic variables, there are two coupled resonances. Dybwad's model misses this aspect. He depicts the geometry as one-dimensional. The way he draws his central diagram alludes to rotation, but he does not elaborate. The following discussion closes this gap.

2. Coupled resonances

Central to the prediction of the frequency shift is the small-load approximation, which states that the complex frequency shift ($\Delta\tilde{f} = \Delta f + i\Delta\Gamma$, with Γ the half-bandwidth at half-height) is proportional to the load impedance, Z_L . The load impedance is the area-averaged ratio of stress and velocity at the resonator surface. We have:

$$\frac{\Delta\tilde{f}}{f_F} = \frac{\Delta f + i\Delta\Gamma}{f_F} \approx \frac{i}{\pi Z_q} \left\langle \frac{\tilde{\sigma}_0}{\tilde{v}_0} \right\rangle_{\text{area}} = \frac{i}{\pi Z_q} \tilde{Z}_L \quad (1)$$

A tilde denotes a complex variable and an index 0 denotes a complex amplitude of a time-harmonic variable. Γ (the half-bandwidth) is related to the widely used “dissipation factor” [21], D , by the relation $D = 2\Gamma/f$. f_F is the fundamental frequency, $Z_q = 8.8 \cdot 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$ is the acoustic wave impedance of AT-cut quartz. σ is the tangential stress, v is the tangential velocity, and $Z_L \leq \tilde{\sigma}_0/\tilde{v}_0$ is the load impedance (the ratio of stress and velocity). Angle brackets denote an area average.

For discrete contacts, the load impedance can be expressed as $N_P/A F_0/\tilde{v}_0 = N_P/A Z_{\text{mech}}$ with N_P the number of particles and A the active area, F_0 the amplitude of the periodic force exerted at the contact, and Z_{mech} the mechanical impedance of the sphere in contact with the surface (the force-to-velocity ratio, see below). In the following discussion, we exploit the electromechanical analogy. The sphere-plate assembly can be modeled by a mechanical equivalent circuit as depicted in Fig. 1B. The force exerted by an arrangement of dashpots, springs, and point-masses follows from the mechanical impedances of the individual elements and certain rules of how to add impedances together. These

rules are the analogs of the Kirchhoff rules in electrical engineering. There is a complication with regard to the mechanical Kirchhoff rules: In mechanical circuits, impedances are additive if the elements are placed in parallel, while inverse impedances are additive if the elements are placed in series. In this regard, the rules differ from electricity, where impedances are additive for elements arranged in series. The mechanical impedances entering the problem are $i\omega M_P$, (originating from a rigid point-mass M_P), $\kappa_P/(i\omega)$ with κ_P the spring constant of a Hookean spring, and ξ_P , where ξ_P is the drag coefficient of a dashpot. κ_P , ξ_P , and M_P will have to be interpreted as a modal stiffness, a modal damping, and a modal mass later on. The meaning of these parameters depends on the mode of vibration. At this point, we assume κ_P , ξ_P , and M_P to be the same for all spheres, that is, we ignore heterogeneity. Also, κ_P and ξ_P might depend on frequency, but we treat them as constant for simplicity. κ_P is also called “contact stiffness” in the following. Note that this definition pertains to an individual contact (as opposed to the stiffness of an interface between rough surfaces).

Representing a particle in contact with the resonator surface by an equivalent circuit as in Fig. 1B, one finds the load impedance as

$$\begin{aligned} \tilde{Z}_L &= \frac{N_P}{A} \left(\left(\frac{\kappa_P}{i\omega} + \xi_P \right)^{-1} + (i\omega M_P)^{-1} \right)^{-1} = \frac{N_P}{A} \left(\left(\frac{\tilde{\kappa}_P}{i\omega} \right)^{-1} + (i\omega M_P)^{-1} \right)^{-1} \\ &= \frac{N_P}{A} \frac{i\omega M_P \tilde{\kappa}_P}{\tilde{\kappa}_P - \omega^2 M_P} \end{aligned} \quad (2)$$

In step 2, the spring constant and the drag coefficient were subsumed under a single complex spring constant, $\tilde{\kappa}_P$, given as $\tilde{\kappa}_P = \kappa_P + i\omega\xi_P$. Inserting Eq. (2) into Eq. (1), one finds

$$\frac{\Delta\tilde{f}}{f_F} = \frac{N_P - \omega M_P}{A} \frac{\tilde{\kappa}_P}{\pi Z_q \tilde{\kappa}_P - \omega^2 M_P} = \frac{N_P - \omega M_P}{A} \frac{\kappa_P + i\omega\xi_P}{\pi Z_q \kappa_P + i\omega\xi_P - \omega^2 M_P} \quad (3)$$

Eq. (3) can be simplified by introducing the “particle resonance frequency”, $\tilde{\omega}_P$, as

$$\tilde{\omega}_P^2 = 4\pi^2 \tilde{f}_P^2 = \frac{\tilde{\kappa}_P}{M_P} = \frac{\kappa_P}{M_P} + \frac{i\omega\xi_P}{M_P} = \omega_P^2 + i\omega\gamma_P \quad (4)$$

In the last step, the damping factor was introduced, which is defined as $\gamma_P = \xi_P/M_P$. γ_P has dimensions of frequency. If the damping of the coupled resonance is small (only then), $\gamma_P/(2\pi)$ is equal to the bandwidth of the coupled resonance (see Fig. 2). One can then write $\tilde{\omega}_P \approx \omega_P + i\gamma_P/2$ close to the resonance. To see that, write

$$\tilde{\omega}_P = \omega_P \sqrt{1 + \frac{i\omega\gamma_P}{\omega_P^2}} \approx \omega_P \left(1 + \frac{i\omega\gamma_P}{2\omega_P^2} \right) \approx \omega_P + \frac{i\gamma_P}{2} \quad (5)$$

Taylor-expansion of the square root was used in step 2; $\omega \approx \omega_P$ was used in step 3. For narrow resonances, the imaginary part of the complex resonance frequency is equal to half the bandwidth (see, for example, Section 4.1.3 in Ref. [22]). Note, however, that coupled resonances often are highly damped. γ_P should therefore not be viewed as the bandwidth.

Inserting Eq. (4) into Eq. (2) and using the small load approximation (Eq. (1)), one finds

$$\frac{\Delta\tilde{f}}{f_F} = \frac{N_P - \omega M_P}{A} \frac{\tilde{\omega}_P^2}{\tilde{\omega}_P^2 - \omega^2} \quad (6)$$

Δf and $\Delta\Gamma$ plotted versus ω form a resonance curve on their own, hence the name “coupled resonance”. The real and the imaginary parts of Eq.

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