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Studying adsorbent dynamics on a quartz crystal resonator using its nonlinear electrical response

Sourav K. Ghosh, Victor P. Ostanin, Ashwin A. Seshia*

University of Cambridge Nanoscience Centre, 11 J J Thomson Avenue, Cambridge, Cambridgeshire CB3 0FF, United Kingdom

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ABSTRACT

The quartz crystal resonator has been traditionally employed in studying surface-confined physisorbed films and particles by measuring dissipation and frequency shifts. However, theoretical interpretation of the experimental observations is often challenged due to limited understanding of physical interaction mechanisms at the interfaces involved. Here we model a physisorbed interaction between particles and gold electrode surface of a quartz crystal and demonstrate how the nonlinear modulation of the electric response of the crystal due to the nonlinear interaction forces may be used to study the dynamics of the particles. In particular, we show that the graphs of the deviation in the third Fourier harmonic response versus oscillation amplitude provide important information about the onset, progress and nature of sliding of the particles. The graphs also present a signature of the surface–particle interaction and could be used to estimate the interaction energy profile. Interestingly, the insights gained from the model help to explain some of the experimental observations with physisorbed streptavidin-coated polystyrene microbeads on quartz resonators.

1. Introduction

Studying the interaction of surface-adsorbed films and particles with the surface is of interest from both theoretical and applied standpoints. The knowledge of intermolecular forces between the surface and adsorbents is fundamental to the field of nanotribology [1] and has applications in varied fields of biosensing, drug discovery and drug delivery [2]. The measurement of such interaction forces can also play a crucial role in studying the selectivity of functionalised surfaces in bioanalytics and rapid screening technologies [3]. However, direct measurements of interaction forces with conventional techniques such as centrifuge [4] and the atomic force microscope (AFM) [5], although insightful, are technically demanding and expensive, and therefore unsuitable for routine use. By virtue of their principle of operation, the acoustic techniques using in-plane shear oscillations, such as the quartz crystal microbalance (QCM) (also known as thickness-shear mode resonator) and shear-horizontal surface acoustic wave (SH-SAW) devices, provide a more convenient way of measuring interaction of the surface with the adsorbed layers. It has been demonstrated that the dissipation and frequency shifts data from the QCM can be used to measure the slippage effects in molecularly thin films [6,7], to study the mechanical microcontacts of adsorbed microparticles [8] and to measure the dissipation at the interface of adsorbed discrete biomolecular particles (globular proteins and virus) [9]. However, the mechanisms of interaction at the substrate–adsorbent, adsorbent–ambient and substrate–ambient interfaces are often not entirely understood and this limits reliable interpretation of the dissipation and frequency shift data. Moreover, it is not known that the QCM technique can be used to study the adsorbent dynamics on the surface, such as desorption and sliding, or determine the activation energy of dissociation of surface–adsorbent interactions. In this paper we present how the quartz resonator can be employed to study these phenomena and parameters by analysing its nonlinear electrical response in presence of the adsorbents. The initial results from modelling and experiments suggest that this technique may be used in conjunction with the QCM technique, i.e. dissipation and frequency shift data, to get a better understanding of the surface–adsorbent interactions and adsorbent dynamics. Although a quartz crystal is used as the resonator in this demonstration, the concepts may be applied to other resonator configurations with in-plane oscillation and suitable transduction method in place.

2. Adsorbent-induced nonlinear response

The shear forces in an oscillating thickness-shear mode (TSM) AT-cut quartz crystal due to an applied electrical voltage are transduced into electrical charge by virtue of the piezoelectric effect. The time derivative of this charge represents an electrical current that is recorded as the response of the crystal to the drive voltage.

* Corresponding author.
E-mail address: aas41@cam.ac.uk (A.A. Seshia).

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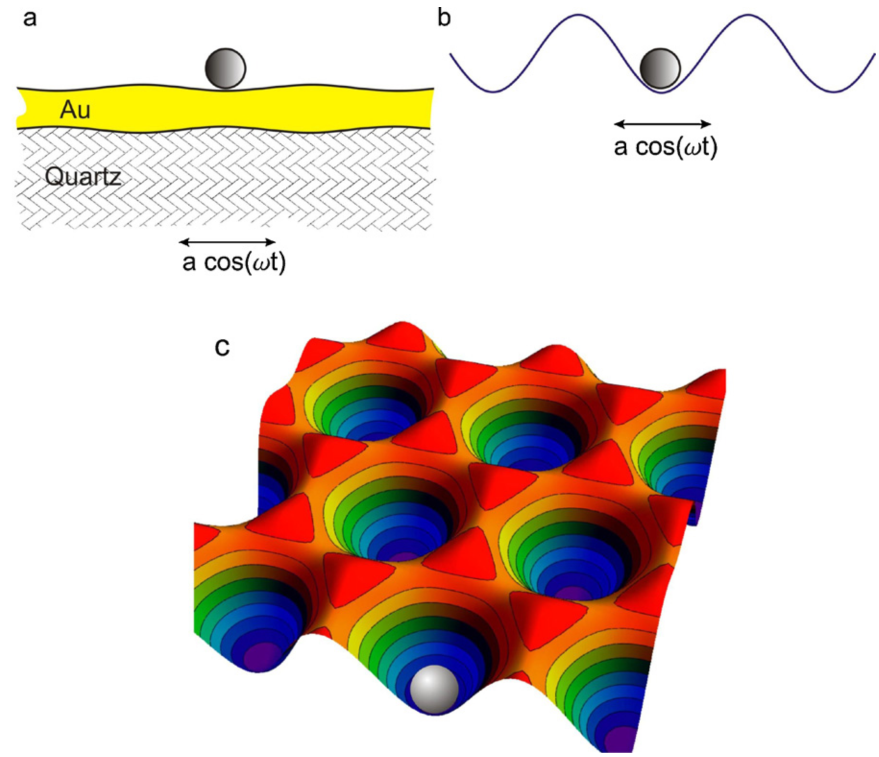

Fig. 1. (a) A particle on a gold electrode of a quartz crystal resonator. (b) The particle in a simplified one-dimensional periodic potential of the surface–particle interaction. (c) The particle in a 2D periodic potential of the Au(1 1 1) surface–particle interaction, the particle having a single point of contact.

The electrical current in response to a harmonic electrical voltage is also predominantly harmonic. Mechanical interactions between the adsorbents and the crystal surface result in modification of the bulk shear forces and consequent distortion of the electrical response. Hence, the electrical current comprises Fourier harmonic components (i.e. multiples of the drive frequency, which is typically close to the fundamental resonant frequency of the resonator). Since even harmonics are not transduced in a TSM AT-cut quartz (as internal charges produced by stress are cancelled against each other), deviation in magnitude of electrical current is observed at odd harmonics, with the relative deviation being significant at third and higher odd harmonics. This deviation can be measured in practice to detect the presence of surface-bound particles [10,11]. To be able to understand this nonlinear modulation of the electrical current due to the surface–adsorbent interactions, we have attempted to model the case of a particle physisorbed on a gold electrode of a quartz crystal resonator with a single point of contact (Fig. 1a). The particle here is essentially treated as a point mass.

3. Modelling surface–adsorbent interaction

3.1. With one-dimensional interaction potential

To begin with, the following simplified one-dimensional periodic interaction potential is assumed between the adsorbent particle and the surface (Fig. 1b). The assumption of a periodic potential is justified since the interaction force changes as a function of position of the particle relative to the crystal lattice of the surface.

$$U(x) = -u \cos(x(t)) \tag{1}$$

Here u is the depth of potential and $x(t)$ is the displacement (along the surface) of the point of contact of the particle with respect to the lattice equilibrium point at an instant t. To get a simpler form, the period of lattice is assumed as 2π. When the crystal is driven at frequency f and amplitude A, the interaction potential function also oscillates with the surface. If we assume for simplicity 100% slippage (case of a heavy particle), we have $x(t) = A\cos(2\pi ft)$. Thus, the interaction shear force on the crystal is given by

$$\begin{aligned} F(x(t)) &= \frac{\partial U(x(t))}{\partial x} = u \sin(x(t)) = u \sin(A\cos(2\pi ft)) \\ \Rightarrow F(x(t)) &= u\left(A \cos(2\pi ft) - \frac{1}{6}A^3 \cos(2\pi ft)^3 + \frac{1}{120}A^5 \cos(2\pi ft)^5 - \ldots\right) \end{aligned} \tag{2}$$

It is clear from Eq. (2) that the interaction shear force is not a harmonic function in f and should therefore comprise higher Fourier harmonics of f. However, the even harmonics are absent due to symmetricity of the function $F(x(t))$. The first three odd harmonics are presented in Eq. (3).

$$\begin{aligned} H_1(A) &= \frac{\omega}{\pi}\int_0^T F(x(t))\exp(j\omega t)dt = A - \frac{A^3}{8} + \frac{A^5}{192} - \ldots; \\ H_3(A) &= \frac{\omega}{\pi}\int_0^T F(x(t))\exp(3j\omega t)dt = -\frac{A^3}{24} + \frac{A^5}{384} - \ldots; \\ H_5(A) &= \frac{\omega}{\pi}\int_0^T F(x(t))\exp(5j\omega t)dt = \frac{A^5}{1920} - \ldots \end{aligned} \tag{3}$$

Here $\omega = 2\pi f$ and the depth of potential u is set to be 1 unit. Variation of these harmonics with oscillation amplitude is presented in Figure S-1 (Supporting Information).

This anharmonic (or nonlinear) interaction shear force modifies the shear forces in the bulk quartz and results in increase in the magnitude of the higher odd Fourier harmonic components in the electrical response. For example, the increase in the third Fourier harmonic of the response is given by $6\pi f\tau\alpha H_3(A)$, where α is the enhancement due to proximity to third overtone resonance of the quartz crystal, τ is the force-to-charge transduction factor for AT-cut quartz and $6\pi f$ is the factor for conversion of charge into current at frequency $3f$. The third overtone resonance frequency typically lies several tens of kilohertz above $3f$.