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

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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 reasonably well.

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 nanotribology¹ and has applications in varied fields of biosensing, drug discovery and drug delivery². The measurement of such interaction forces can also play a crucial role in studying the selectivity of functionalized surfaces in bioanalytics and rapid screening technologies³. However, direct measurements of interaction forces with conventional techniques such as centrifuge⁴ 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 microparticles⁸ 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 modeling 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.

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. The electrical current in response to a harmonic (single frequency) 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 (Figure 1a). The particle here is essentially treated as a point mass.

Figure 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(111) surface-particle interaction, the particle having a single point of contact.

MODELING SURFACE-ADSORBENT INTERACTION

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 (Figure 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.

$$U(x) = -u \cos(x(t)) \quad (1)$$

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 $x(t) = A \cos(2\pi f t)$. Thus, the interaction shear force on the crystal is given by

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

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.

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

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 $3f$.

With two-dimensional (2D) interaction potential. Since the gold electrodes are usually evaporated onto the quartz crystals, Au(111) is the expected orientation of the gold crystal lattice. Due to hexagonal symmetry, the 2D interaction potential of a particle physisorbed on Au(111) with a point contact is expected to have a functional form similar to the classical 2D periodic potential for methyl-thiol on Au(111)¹² developed by Jeon et al, and this can be represented as in eq 4, where u is the depth of a potential well and λ is the period of potential. λ should remain the same in both cases, being equal to the lattice period of Au(111), i.e. 0.288 nm, but u could differ depending on the electronic and phononic interaction between the particle and the surface at the point of contact. Figure 1c presents the particle in this 2D potential.

$$U(x, y) = -\frac{u}{9} \left[2 \left(2 \cos \left(2\pi \frac{x}{\lambda} \right) \cos \left(\frac{2}{\sqrt{3}} \pi \frac{y}{\lambda} \right) + \cos \left(\frac{4}{\sqrt{3}} \pi \frac{y}{\lambda} \right) \right) + 3 \right] \quad (4)$$

The angle between the direction of oscillation of the surface and an axis of the hexagonal potential influences the particle dynamics. The unknown angle between these two directions is modeled by applying a rotational transformation to the abovementioned potential function by an angle β (shown in Figure 2a with $\beta = 37^\circ$). Hence, eq 4 is modified with $x = X \cos(\beta) + Y \sin(\beta)$ and $y = -X \sin(\beta) + Y \cos(\beta)$.

Figure 2. (a) Positions of minima of the potential before and after rotation by an angle $\beta = 37^\circ$. (b) Sliding of the particle on the oscillating surface ($d_b = 5 \mu\text{m}$ and $\beta = 37^\circ$).

When the surface is driven by a pure sinusoidal in-plane oscillation of frequency f and amplitude A along the X axis (see Figure 2a), the interaction potential also oscillates with it. To investigate the response at different amplitudes of oscillation, A is increased linearly from 0 to $A_{\max}$ in time $T_{\max}$. The force acting on the particle, parallel to the surface, is obtained by differentiating the potential function as shown below.

$$\begin{aligned} F_x(t) &= \frac{\partial}{\partial x} U(X(t) - X_d(t), Y(t), \beta) \\ F_y(t) &= \frac{\partial}{\partial y} U(X(t) - X_d(t), Y(t), \beta) \end{aligned} \quad (5)$$

Here, $(X(t), Y(t))$ denotes the position of the particle's point of contact on the surface and $X_d(t) = A_{\max} t \sin(2\pi f t) / T_{\max}$ the displacement of the surface. The describing differential equations for the particle are then given as follows.

$$\begin{aligned} (2/7)m_b \ddot{X}(t) &= -(2/7)\gamma \dot{X}(t) - F_x(t) \\ (2/7)m_b \ddot{Y}(t) &= -(2/7)\gamma \dot{Y}(t) - F_y(t) \end{aligned} \quad (6)$$

Here, m_b is the mass of the particle and γ the coefficient of viscous resistance of air, which approximated by the Stokes' Law is given by $\gamma = 6\pi\eta_a(d_b/2)$, where η_a is the dynamic viscosity of air and d_b the diameter of the particle. The factor $2/7$ is used since the centre of mass of a sphere pivoted on a surface moves only $2/7$ th of the distance moved by the surface¹³.

The equations 5 and 6 are solved using Mathcad 14.0 assuming the following values: $u = 0.5$ eV (similar to that reported in thiolate-Au literature^{12, 14}); $f = 14.3$ MHz; $A_{\max} = 1.73$ nm (equal to 6 lattice distance of Au(111)); $T_{\max} = 3000 / f = 210$ μ s; $\eta_a = 1.98 \times 10^{-5}$ Pa.s at 300 K; $\rho_b = 1$ gm/cc (similar to that of most biological particles).

Figure 2b presents the resulting motion of the particle (i.e., its point of contact on the surface) with (0,0) as the initial position. The positions of minima of the potential are shown in dots. This particular simulation assumed $d_b = 5$ μ m and $\beta = 37^\circ$. The choice of β is made keeping in mind the hexagonal symmetry of the potential, such that most generic

features of the kinetics are revealed. It can be observed from Figure 2b that as the surface oscillates, the particle oscillates about the positions of the minima of the potential and the positions of the saddle points on the boundary of the potential wells (ref. Figure 1c), intermittently jumping from one potential well to another. This is expected since the gradient of the potential is zero at these places. The saddle points can be points of stability depending on the oscillation frequency of the surface. The video of particle motion from this model (supporting video Vid1.avi) illustrates the motion of the particle with further clarity. The graphs and videos for multiple runs of the simulation show that the motion becomes chaotic at higher surface oscillation amplitude.

The shear force on the surface, which is equal to the force on the particle, is given by $F_x(t) = -(2/7)[\gamma\dot{X}(t) + m_b\ddot{X}(t)]$ (from eq 6). The third Fourier harmonic of $F_x(t)$ is then numerically computed, multiplied by the force-to-charge conversion factor for an AT-cut quartz¹⁵ and by a factor of amplitude enhancement due to proximity to the third overtone resonance, and then differentiated to compute the third Fourier harmonic current or the $3f$ current. This $3f$ current is due to the interaction at the interface and contributes to the deviation in the $3f$ response of the quartz resonator. The subsequent figures (Figure 3 to Figure 6) present the results from a simulation with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$. The responses are multiplied by 3000 to be able to compare with the results for multiple particles model presented later. Physically, this may be assumed as the case of 3000 particle moving synchronously. Figure 3a shows the displacements of the particle along X and Y and the magnitude of the $3f$ current against the oscillation amplitude of the surface.

Figure 3. (a) X and Y displacements of particle and the magnitude of the $3f$ current against the oscillation amplitude, with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$. (b) X and Y displacements of the particle and the phase of $3f$ current against oscillation amplitude, with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$.

The abrupt shifts in the X and Y displacements indicate jumps of the particle. It can be noted that the particle makes its first jump out of a potential well ($X \approx 0.5\lambda$), when the oscillation amplitude is approximately half the period of potential (or half the lattice period λ in this case), i.e., close to the distance between the potential minima and the boundary. This indicates close to 100% slip between the particle and the surface. It is interesting to note that the magnitude of $3f$ current increases till the particle jumps off the potential well after which it sharply decreases. This is found to repeat at every jump with the magnitude of the $3f$ current (and its fluctuation) decreasing with the increase in oscillation amplitude, possibly due to greater damping (velocity dependent) at higher amplitudes. Moreover, the particle slides over multiple potential wells averaging out the shear forces. Figure 3b shows that the particle-jumps also have a correlation with the remarkable stepwise shifts in the phase of the $3f$ current. However, the particle-jumps are found to have even better correlation with the shifts in the real and imaginary components of the $3f$ current. It can be observed from Figure 4a that the real component of the $3f$ current remains almost stable and close to zero when the particle oscillates inside the potential well and sharply increases at the instant of the particle-jump from the well. However, the imaginary component of the $3f$ current (Figure 4b) grows until the point of particle-jump, and then quickly reverses in sign. This may be explained as follows. Electric power supplied to the crystal can be presented in complex domain notation as $\bar{P} = (1/2)\bar{V} \cdot \dot{\bar{I}}$. With voltage taken as the reference and the voltage maximum amplitude remaining constant, the real power consumed over a period is thus proportional to the real component of current. Hence, the real component of the current due to the surface-particle interaction gives a measure of the overall energy consumed by the network (surface-particle system) over a period due to the interaction. Similarly, the reactive power (the imaginary component) is proportional to the imaginary component of current. Hence, the imaginary component of the current due to the surface-particle interaction gives a measure of the energy flowing to and from the network. When the particle oscillates inside the potential well, the potential gradient or the force of surface-particle coupling is relatively small. As a result, the overall energy consumed by the system is negligible. So, as observed in Figure 4, the $3f$ real component of current is negligible. Only the $3f$ imaginary component is present due to the energy flowing to and from the system, and grows as this bidirectional energy flow increases with higher surface oscillation amplitude. As the particle approaches point of jump, the potential gradient or the surface-particle coupling force gets steeper resulting in the observed increase in the $3f$ real component of current at the points of jumps.

The instantaneous change of phase of the particle oscillation at the points of jumps explains the change of sign of the $3f$ imaginary component of current. However, it might be interesting to study the above observations with detailed analytical and numerical treatment.

Figure 4. (a) X and Y displacements of particle and the real component of the $3f$ current against the oscillation amplitude, with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$. (b) X and Y displacements of the particle and the imaginary component of $3f$ current against oscillation amplitude, with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$.

Particle dynamics and period of potential. The above results lead to an interesting observation that the magnitude, phase, real and imaginary components of the $3f$ current (due to the surface-particle interaction) provide important information on the dynamics of the particle on the surface. This includes initiation of particle sliding and its jumps over multiple wells of a periodic surface-particle interaction potential. Moreover, for a given damping constant, the oscillation amplitude corresponding to the first jump gives an estimate of the period of the interaction potential.

Characteristic dependence on drive frequency. It needs to be noted that the characteristics of these graphs (both displacement and $3f$ components) for a given particle, interaction potential and damping depends on the drive frequency. The particle mass, interaction function and damping determine the resonant frequency of the particle along the drive (in a potential well). The resulting motion of the particle depends on how the particle resonant frequency compares with the drive frequency. For example, for a $5.6 \mu\text{m}$ particle with the potential function and damping assumed in the model, the resonant frequency along X at the initial instant is given by $f_{res} = (1/2\pi)\sqrt{\partial/\partial x(F_x(0))/m_b} = 4 \text{ MHz}$, whereas the drive frequency is 14.3 MHz . A higher drive frequency, such as 100 MHz (Supplementary Figure S-2) or a lower drive frequency such as 1 MHz (Supplementary Figure S-3) gives completely different graphs. However, the initiation of the particle jumps is still found to be associated with the sudden increase in the $3f$ real component and change in sign of the $3f$ imaginary component. Comparisons between Figure S-2 and Figure S-3 indicate that the magnitude of these changes is larger for higher drive frequencies ($\sim 50\text{-}100 \mu\text{A}$ for 100 MHz drive and $\sim 2 \text{ nA}$ for 1 MHz drive). It is interesting to note that for drive frequencies higher than the said resonant frequency of 4 MHz (both 14.3 MHz and 100 MHz) the particle jump occurs at oscillation amplitude equivalent to approximately half the period of potential. The corresponding amplitude is larger for drive frequencies lower than the said resonant frequency (more than twice the period of potential with 1 MHz drive frequency), and once the jump initiates, the particle slides over large number of lattice periods unlike in the former case. Therefore appropriate choice of drive frequency is important to study the dynamics of a given particle. Similarly, for a given drive frequency and damping, these graphs provide a signature of the particle and surface-particle interaction.

Distinctive patterns of $3f$ and $1f$ currents. The results for the $1f$ current due to the surface-particle interaction are similar and may be interesting to consider for theoretical interest. However, it is challenging to record this $1f$ current in practice since, at the drive

frequency (or $1f$), the baseline response (typically many tens of milliamperes) is significantly higher than $1f$ response from the surface-particle interaction (few microamperes). $1f$ components (due to the surface-particle interaction) have not been discussed above. However, it may be interesting to observe the interdependence between the real and imaginary components of the first and third Fourier harmonics of the current due to the surface-particle interaction. Figure 5 presents this. It is interesting to note from Figure 5a that the real components of $3f$ and $1f$ do not tend to be high simultaneously, i.e., statistically one is low when the other is high and vice versa. However, the imaginary components of $3f$ and $1f$ show good correlation (Figure 5b). The pattern of imaginary versus real components of $1f$ (Figure 5c) is strikingly unconventional and the same for $3f$ (Figure 5d) gives a distinctive ‘anchor’ shape. It is interesting to note that these patterns are found to change with drive frequency and surface-particle interaction potential. With a better understanding of the dependence of the shape of these patterns on the particle size, drive frequency and surface-particle interaction, these patterns could potentially serve as signatures of the surface-particle interaction or particle size for a given drive frequency. This calls for studies with more elaborate analytical and numerical treatments.

Figure 5. (a) Real components at $3f$ and $1f$. (b) Imaginary components are $3f$ and $1f$. (c) Real and imaginary components at $1f$. (d) Real and imaginary components at $3f$.

Multiple particles on a two-dimensional (2D) interaction potential. The model for a single particle in a 2D periodic potential presented above is extended here for multiple particles that are not all synchronous in motion. Evaporation creates patches of gold Au(111) with the angular direction of the crystal lattice randomly varying across the surface area of quartz. This gives an arbitrarily different β (angle between the direction of an axis of the hexagonal potential and the direction of oscillation of the surface) for each particle. To model such a case, the $3f$ current is first evaluated for a single particle for each of the following values of β : 0° , 7.5° , 15° , 22.5° , 30° , 37.5° , 45° and 52.5° , and then averaged and multiplied by the number of particles (3000 in this case). Due to hexagonal symmetry of the periodic potential, the case of $\beta = 60^\circ$ is equivalent to the case of $\beta = 0^\circ$. The different values of β considered here represent the eight equiangular divisions of the angle 60° . The averaging is done assuming that equal number of particles experiences the different crystal orientations under consideration and that all the particles experience equal oscillation amplitude of the crystal.

Coherence in particle motion. The results obtained for ‘asynchronous’ multiple particles are almost similar to those in the case of a single particle or ‘synchronous’ multiple particles presented earlier. The graphs of averaged magnitude (Figure 6a) and averaged phase (Figure 6b) of $3f$ current correlate well with the jumps in averaged displacements, with the first peak of $3f$ magnitude and first step jump in $3f$ phase again occurring at approximately half the period of potential. Here again, the averaged real and imaginary $3f$ current components give important details of how the real and active power components vary with particle-jumps (Figure S-4). However, one distinct difference is that the magnitude of increase in the $3f$ response (magnitude, real or imaginary component) at the first jump dies down much more quickly than the case where $\beta = 37.5^\circ$ for all particles. This is because the interaction forces for multiple particles moving randomly at various angular directions at higher amplitudes tend to average out. However, distinct phase steps remain intact, only slightly smoothed. Therefore, the $3f$ response (magnitude, real or imaginary component) also gives an index of the coherence (or randomness) in the motion of the particles.

Figure 6. (a) X and Y displacements for a single particle and the magnitude of 3f current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ (all averaged over various crystal orientations). (b) X and Y displacements for a single particle and the phase of 3f current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ (all averaged over various crystal orientations).

EXPERIMENTAL VALIDATIONS

Thickness-shear mode (TSM) AT-cut quartz crystals were functionalized with a self-assembled monolayer (SAM) of hydroxyl terminated thiol and streptavidin-coated polystyrene microbeads (SCPM) were physisorbed onto them as described in the ‘Materials and Methods’ section. The crystals were driven in air close to their fundamental resonant frequency (14.3 MHz) at increasing amplitude from 0.035 V rms to 3.5 V rms and the $3f$ response was recorded, first with clean electrodes and subsequently with electrodes adsorbed with SCPM. The schematics of instrumentation used for these experiments and the detail on how the measurements were made are presented in Figure S-5. A microscopic video of the motion of the particles was simultaneously recorded.

A significant increase in $3f$ response was observed with adsorbed particles, confirming the above modeling estimates and previously reported results¹⁰. Interestingly, the real and imaginary components of the $3f$ response from the crystals with adsorbed particles revealed ‘wiggles’ (representative result shown in Figure 7a), which were absent in the $3f$ response from clean crystals. These ‘wiggles’ resembled the oscillations in $3f$ real and imaginary components of the model at the points of particle-jumps (Figure 4 and Figure S-4 discussed earlier). Figure S-6 presents a representative complete $3f$ response recorded.

Figure 7. (a) 3f real and imaginary components of current with streptavidin-coated polystyrene microbeads show ‘wiggles’ resembling the oscillations in these components observed from modeling. (b) Magnitude of 3f current due to surface-particle interaction from model and experiment plotted as a functional of inferred QCM displacement.

Representative experimental data of deviation in the $3f$ response from a crystal with approximately 1800 SCPM is presented and discussed here. Figure 7b shows the magnitude of the deviation in the $3f$ response after physisorption of SCPM onto the crystals, i.e. the magnitude of the $3f$ current due to the interactions at the surface-particle interface. The first peak in this graph is found to correspond in time to the initiation of sliding of the particles as observed in the recorded microscopic video, confirming the finding of the model.

Estimating period of potential. The oscillation amplitude corresponding to the peak is found to be 3 nm. Hence, using the inferences from the model, the period of potential can be estimated as 6 nm. This value is justifiable since it compares well with the length of the streptavidin-hydroxylated-thiol linker (~ 6 nm)¹⁶. The magnitude of the $3f$ current and the oscillation amplitude at the peak estimated from the model is fitted with the same observed from this representative data to estimate the depth of the surface-particle interaction potential as described below.

Estimating depth of potential. The period of the interaction potential was taken as $\lambda = 6$ nm, as estimated from above. Now assuming an initial value of the depth of potential $u = 0.5$ eV, simulations were run iteratively (gradually increasing u) to fit the magnitude of the first peak of the $3f$ current from the model with the same from the above representative data from the experiment. A deeper potential for a given period results in a steeper potential gradient and therefore a higher magnitude of the first peak. A reasonable agreement was found for $u = 47.836$ eV (Figure 7b). This value of depth of potential can be justified for streptavidin-coated polystyrene microbeads as discussed in Supporting Information Section S1. To improve the estimation of u , experiments may be carried out with the same surface-particle interaction at a few different drive frequencies (with the fundamental resonant frequency of the chosen crystal always close to the drive frequency) and the said fitting may be done. Averaging of the depths of potential values obtained could then provide a better estimate of u . Hence, both depth and period of the potential, the two important parameters of the surface-particle interaction energy profile, can be estimated from comparing the deviation in the $3f$ response with attached particles with the same estimated using the presented model.

Comparison of $3f$ response from model and experiment. The surface of the thiol monolayer is not atomically smooth as assumed in the model (the ideal case) due to various factors, such as the roughness of the quartz substrate, defects on the gold surface and imperfections in monolayer formation (like multi-layering and island formation). Microscopic video confirms that some beads after onset of sliding often get trapped in these

defects or imperfections. The shear forces of interactions between the bead and the surface for these trapped beads are stronger than that between sliding beads and the surface, and often do not dissociate even at relatively higher amplitudes. As a result, although a reasonable agreement is found between the experiment and the model until the peak or initiation of sliding as observed in Figure 7b, the graphs diverge at higher amplitudes with the magnitude of $3f$ response from experiments higher than that from the model. Moreover, since the said imperfections are not reproducible from one sensor to the other, the shape of the graph of $3f$ response against oscillation amplitude after the peak is not reproducible in experiments from one sensor to the other.

SCPM dynamics. The representative experimental video recorded under microscope (supplementary video Vid2.avi) reveals stick and slip motion of the SCPM particles supporting observation from the representative video (Vid1.avi) and the $3f$ graphs from the model. The experimental video also shows that the motion become increasingly random at higher amplitudes supporting the observation of chaotic behaviour at higher amplitudes in the model.

Signature of surface-particle interaction. We have seen from modeling results that the graphs of deviation in $3f$ response (magnitude, phase, real or imaginary components) against oscillation amplitude in presence of adsorbed particles on a surface oscillating at a given frequency gives a signature of the surface-particle interaction. Interestingly, experiments with physisorbed SCPM show that the graph of $3f$ imaginary versus $3f$ real current components present an ‘anchor’ shape similar to that observed from the model (Figure 5d discussed earlier). Figure S-7 is a representative result showing such an ‘anchor’ shape.

DISCUSSION AND CONCLUSION

In this work a physisorbed surface-particle interaction for atomic-size particles on Au(111) surface of a quartz resonator has been modeled and the resulting deviation in the $3f$ response of the crystal is estimated. It is found that the graphs of the magnitude, phase and real and imaginary components of this deviation versus oscillation amplitude correlate well with the particle-jumps and give important information on the initiation, progress and nature of sliding. These graphs and those of the real versus imaginary components of the $3f$ response (deviation) provide a signature of the surface-particle interaction. The insights gained from the model are used to interpret the experimental observations with streptavidin-coated polystyrene microbeads on a quartz resonator, both electrical measurements and microscopic videos. Although a simplistic model such as the one presented here does not capture the

complex reality in its entirety, yet the striking similarities in the qualitative features in particle dynamics and nonlinear response from the model and the experiment are thought inspiring. Moreover, using the qualitative similarities, the graph of magnitude of the $3f$ response (deviation) versus oscillation amplitude from the model can be fitted with that from the experiment for quantitative estimation of the depth and period of the interaction potential. Thus, the nonlinear modulation data from a quartz resonator, if used in conjunction with the conventional dissipation and frequency shift measurements, could potentially provide more holistic information on the surface dynamics of adsorbed particles and the surface-particle interaction. This could have important applications in varied fields, such as nanotribology, biosensing and drug discovery. The significance of the approach thus calls for further theoretical work for better understanding of some of the non-trivial features of the presented graphs. It will also be interesting to carry out further experiments with different particle sizes, drive frequencies and surface-particle chemistries, in air and different liquid medium, and analyse the results by extending the presented model.

MATERIALS AND METHODS

Functionalising quartz crystals. AT-cut quartz crystals of fundamental resonant frequency 14.3 MHz (Lap-Tech Inc., Bowmanville, Ontario, Canada) were cleaned successively in acetone, isopropanol (IPA) and argon plasma (250 W for 20 s) and washed in an ultra-pure absolute ethanolic solution. The cleaned crystals were left immersed overnight in 1 mM ethanolic solution of hydroxyl-terminated polyethylene glycol (OH-PEG) thiol ($\text{HS}-(\text{CH}_2)_{11}-(\text{EG})_3\text{-OH}$, TH 002-02, Prochimia, Sopot, Poland). On the following day, the unbound thiols were washed thoroughly, with ultra-pure absolute ethanol and Milli-Q water (Millipore Corp.) and the crystals were dried in N_2 flow. Baseline measurements ($3f$ response) were taken with the dry functionalised crystals.

Adsorbing the microbeads onto crystals. A 10 μL solution of 5.6 μm SCPM (Bangs Laboratories, Inc., Fishers, IN, US) in Milli-Q water was placed on each functionalised crystal for 1 hr for the SCPM to diffuse to the surface. The streptavidin on the SCPM bound to the hydroxyl ends of the thiol on the crystal via physisorbed or weak electrostatic interactions. The crystals with physisorbed SCPM were then carefully dried in a slow N_2 flow.

The number of physisorbed SCPM was counted under an optical microscope. The experiment was video recorded under the microscope.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text.

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16. X-Ray crystallographic studies suggest that diameter of a streptavidin complex is 5 nm, and the length of a OH-(CH₂)₁₁-SH thiol is approximately 1 nm. Hence, the length of a streptavidin-hydroxylated-thiol linker is approximately 6 nm.

Supporting Information for “Studying adsorbent dynamics on quartz crystal resonator using nonlinear electrical response”

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Figure S-1. The variations of the first (H1), third (H3) and fifth (H5) Fourier harmonics of the shear interaction force at the surface-particle interface with oscillation amplitude.

Figure S-2. Particle dynamics at 100 MHz of surface oscillation. **(a)** X and Y displacements for a single particle and the 3f real component current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$. **(b)** X and Y displacements for a single particle and the 3f imaginary component current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$.

Figure S-3. Particle dynamics at 1 MHz of surface oscillation. **(a)** X and Y displacements for a single particle and the 3f real component current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$. **(b)** X and Y displacements for a single particle and the 3f imaginary component current against oscillation amplitude for 3000 particles with $d_b = 5.6 \mu\text{m}$ and $\beta = 37.5^\circ$.

Figure S-4. (a) Averaged X and Y displacements for a single particle and the averaged real component of $3f$ current against oscillation amplitude for 3000 particles with $d_b = 5.6\mu\text{m}$. (b) Averaged X and Y displacements for a single particle and the averaged imaginary component of $3f$ current against oscillation amplitude for 3000 particles with $d_b = 5.6\mu\text{m}$.

S1. Depth of physisorbed potential between surface and microbead

It is known that each streptavidin monomer has one electronic charge¹. Let r_1 , r_2 , r_3 and r_4 respectively be the distance of the net electronic charges at the centres of the four monomers of a streptavidin molecule from the surface. It is assumed that a streptavidin-hydroxylated-thiol linker is approximately 6 nm long. It is also assumed that one streptavidin monomer (r_1) is attached to the microbead and one (r_4) is physisorbed to the surface, while the other two are free (parallel to the surface). Hence, the distances of net charges from the surface can be given as: $r_1 = 1.5$ nm, $r_2 = 3.0$ nm, $r_3 = 3.0$ nm and $r_4 = 4.5$ nm. Hence, the electrostatic potential due to one linker is given by

$$u = \frac{q_e^2 \epsilon}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_4} \right) = 2.24 \text{ eV} \quad (\text{S1})$$

where electronic charge is give by $q_e = 1.602 \times 10^{-19}$ coulomb, permittivity of free space $\epsilon_0 = 8.85 \times 10^{-12}$ farad/m and relative permittivity of air $\epsilon = 1$. The electrostatic potential from 21 linkers then gives a reasonable agreement with the depth of potential estimated by fitting the modeling estimates with the experiments ($u = 47.836$ eV) discussed in the main article. This number of 21 is within the estimate (33 for a $5.6 \mu\text{m}$ streptavidin-coated polystyrene microbead) reported earlier².

Figure S-5. Schematics of instrumentation: A 33220A Agilent function generator was used to generate an AC signal. This signal was amplified and fed through a low pass filter to remove undesired harmonic distortions to act as the input drive signal across the quartz crystal electrodes. The transduced output signal was received by an SR844 lock-in amplifier (Stanford Research Systems) that recorded the complex (amplitude and phase) 3f signal. A passive frequency tripler was used to generate the reference signal for the lock-in. Additionally, two quadrature receivers were employed to detect the complex 1f voltage and the quartz output current. The experiment was controlled and the data was captured and processed using a computer.

Figure S-6. Wiggly jumps in $3f$ response (real and imaginary) for an AT-cut thickness-shear mode crystal adsorbed with streptavidin-coated polystyrene microbeads. The jumps correspond to sliding of the particles.

Figure S-7. Characteristic anchor shape in the $3f$ imaginary versus $3f$ real response for AT-cut thickness-shear mode crystal adsorbed with streptavidin-coated polystyrene microbeads.

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