Studying mechanical microcontacts of fine particles with the quartz crystal microbalance

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The vibration of the QCM changes the micromechanical contact between QCM surface and particles. There is an instantaneous and a long-term effect. Instantaneously, the oscillation induces partial slip. Under an oscillating load, part of the contact ruptures, which decreases the effective stiffness of the contact. In addition, there are long-term memory effects. The vibration of the QCM can lead to a consolidation and an increased coupling. However, it can also break the contact and even lead to detachment. Particles deform the PS surface and induce damage due to inertial forces.

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1. Introduction

Micromechanical contacts are important from the fundamental point of view and in many applications. The mechanical interaction between fine particles determines the flow of granular materials. It is relevant for the cleaning of surfaces, for example in semiconductor industry and the dispersion of powders to aerosols, e.g. in asthma treatment. Problems in lubricating microcontacts make commercial applications and are experimentally demanding. Therefore, a simple alternative technique is desired.

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1. Introduction

Micromechanical contacts are important from the fundamental point of view and in many applications. The mechanical interaction between fine particles determines the flow of granular materials. It is relevant for the cleaning of surfaces, for example in semiconductor industry and the dispersion of powders to aerosols, e.g. in asthma treatment. Problems in lubricating microcontacts make commercial application MEMS devices with sliding surfaces very difficult [1]. Furthermore “Acousto-lubrication” is being investigated as a potential mechanism to promote dry lubrication of MEMS devices [2–4].

An understanding of friction and adhesion between solid bodies has to be based on the knowledge of microcontacts. Therefore, micromechanical contacts have been studied extensively [5,6]. Still, a fundamental understanding is lacking, due to at least two reasons. First, all experiments in which a certain property of microcontacts (for example the adhesion force) is determined show wide distributions rather than a single value. Adhesion forces vary by typically a factor of two to ten even within relatively monodisperse powders [7–11]. Even when measuring the adhesion force between smooth silicon oxide particles taken from one batch adhesion forces differed by a factor two from one pair of particles to the next [12]. As a cause of this variation surface roughness and surface heterogeneity have been suggested [13–18]. Roughness can cause a significant change in the contact area between two particles, depending on the precise location of the contact. Heterogeneity in chemical composition or molecular structure at different length scales can cause a different energy of adhesion and thus can cause a variation in the effective adhesion force depending on the precise location of contact.

Second, direct measurements of adhesion forces, or rolling and sliding friction of particles are technically demanding, expensive, and of limited applicability. This includes experiments with the centrifuge [19] and the atomic force microscope (AFM) [20], the two most widely used techniques. Though both techniques have provided us with valuable insights, they also have their limits. With the centrifuge contact times are long and after detachment no further experiments can be carried out with the same particle. In the case of AFM experiments, each individual particle has to be attached to the end of a microcantilever. The direction of contact is predetermined and not free to adjust. Both techniques are not applicable for routine applications and are experimentally demanding. Therefore, a simple alternative technique is desired.

A promising method could be the quartz crystal microbalance (QCM). Usually the QCM is applied to measure the mass per unit area
of homogeneous thin films. The resonance frequency decreases if the mass is increased. However, for contacts between a QCM and particles with a size in the micron range, the frequency increases [21]. The frequency increase is closely related to the stiffness of the contact and may therefore be used to probe this stiffness.

In this paper we describe experiments with glass particles of variable size on a QCM. The aim is to evaluate the potential of QCMs to measure the nature and strength of microcontacts with particles. Therefore we analysed the influence of inertia and surface adhesion of the particles on the response of a QCM. Surface effects are more important for small particles, while for the large particles inertia should dominate. Inertia and adhesion were varied in two ways: first, we carried out experiments with particles of 5, 10, 15, and 20 μm diameter. In this way the inertial mass was varied by a factor 64. Second, the particles were deposited onto 160 nm-thick films of polystyrene (PS) which had been spin-coated onto the QCM surface. After analysing the physisorbed particles, the sample was annealed at 150 °C. This led to the formation of a PS meniscus, which increased the limits. If the spheres are tightly coupled to the crystal, they behave in essentially the same way as a well-characterized modelled as a pair of coupled resonators [21,26]. As derived in Ref. [21,26], the solution for weak-coupling limit. One can go from the weak-coupling limit to the strong-coupling limit. When further increasing \( f \), the negative frequency shift decreases in magnitude to reach the value given by Eq. (2) for \( f \to \infty \).

We show in the Supporting information that Eq. (3) reduces to the Sauerbrey equation in the limit of tight contacts (\( k \to \infty \)). The supporting information also shows that the “weak-coupling limit” is obtained in the limit \( k \to 0 \). The following relation holds:

\[
\Delta f = \frac{\pi Q f_0}{120} \left( \frac{M}{2\pi Q f_0} \right)^{1/2}
\]

(3)

Here, \( f_0 \) is the resonance frequency without particles. Eq. (3) differs from the form given in Ref. [21] in the prefactor \( N \). The original work was concerned with a single particle, while this work was carried out with ensembles. We justify the factor \( N \) in Appendix A.

As discussed in Appendix A, the solution for \( k/m \approx K/M \) entails intricacies, which we avoid by limiting the discussion to the cases, where the sphere is either tightly coupled to the crystal (\( k/m \gg K/M \), as shown in Appendix A, the minus sign applies before the square root in Eq. (3)) or loosely coupled to the crystal (\( k/m \ll K/M \), plus sign before the square root). The tight-coupling limit is basically equivalent to the Sauerbrey regime. \( \Delta f \) is negative and proportional to the areal mass density \( N m/A_0 \) (Eq. (2)). The particles move with the crystal and increase its mass.

Weak-coupling is less well understood. For fixed values of \( M \), \( K \), and \( m \), the resonance frequency first increases weakly with increasing \( K \) due to the additional effective spring. When the coupling constant approaches the resonance condition, \( k \to 4\pi f_0^2 m \), the frequency increases steeply. For the example of a QCM with a fundamental resonance frequency at 6 MHz this is shown in Fig. 1A. In this regime, the data have to be analysed with care because both solutions of Eq. (3) may be visible in an experiment. However, for a large bandwidth, they may or may not be resolved. What appears as a broad resonance in the experiment, may actually be a superposition of two peaks. At \( k \gg m(2\pi f_0)^2 \) the minus sign in Eq. (3) applies and the frequency shift turns negative. This is the “strong-coupling regime”. When further increasing \( k \), the negative frequency shift decreases in magnitude to reach the value given by Eq. (2) for \( k \to \infty \).

We show in the Supporting information that Eq. (3) reduces to the Sauerbrey equation in the limit of tight contacts (\( k \to \infty \)). The supporting information also shows that the “weak-coupling limit” is obtained in the limit \( k \to 0 \). The following relation holds:

\[
\Delta f = \frac{f-f_0}{f_0} \approx \frac{N k}{\pi Q f_0} \frac{1}{A_0 d_Q}
\]

(4)

Here, \( f_0 = 2Q f_0/d_Q \) is the frequency of the fundamental (\( f_0 = 6 \text{ MHz in our case} \)). \( Q_0 = 8.8 \times 10^6 \text{ kg m}^{-2} \text{s}^{-1} \) is the acoustic impedance of an AT-cut quartz. \( f_0 \) is the resonance frequency of the unloaded state. \( \omega = 2\pi f \) is the angular frequency with \( f \) being the resonance frequency including a possible load. In principle, Eq. (4) is implicit in frequency, because \( f \) appears on both sides (\( \Delta f = f - f_0, \omega = 2\pi f \)). However, \( \Delta f \) is so small that one may safely replace \( 2\pi f \) by \( 2\pi f_0 \), which turns Eq. (4) into an explicit equation.

The weak-coupling limit is of paramount importance in the context of this paper. In the limit of weak-coupling, the frequency shift is positive and proportional to the stiffness of the contact. There is an intuitive explanation to the increase in frequency. One has to realize that the inertia clamps particles in space at high frequencies. A large sphere contacting the crystal across a narrow bridge cannot possibly follow the crystal’s MHz oscillation. The sphere behaves like an immobile wall. Given that the contact exerts a restoring force onto the crystal, the overall stiffness of the composite resonator increases and the frequency increases accordingly. Only if the contact is very stiff, does the sphere follow the crystal’s motion. This is the strong-coupling limit. One can go from the weak-coupling limit to the strong-coupling limit by annealing an existing contact. This was done here by heating a glass-forming substrate to a temperature above the glass transition temperature \( T_g \).

\[
\Delta f = N \left( \frac{1}{2\pi f_0} \left[ \frac{1}{M} + \frac{k_f}{K} + \frac{k_1}{M} \right] \right) \left( \sqrt{\frac{K}{M} + \frac{k}{M} + \frac{k_1}{M}} - 4\frac{K}{M} \right)^{1/2} - f_0
\]

(5)
shift we convolute the frequency shift given by Eq. (3) with the probability \( P \):

\[
\Delta f(\Delta k) = \int_0^\infty p(\Delta k) \Delta f(\Delta k) \, d\Delta k
\]

Please note that \( \int_0^\infty p(\Delta k) \, d\Delta k = 1 \). Three examples obtained with \( \Delta k = 11938 \) N/m and \( \Delta k = 1000, 2000, \) and 3000 N/m are plotted in Fig. 1C. In each curve three regimes can be distinguished:

- First, for weak-coupling, the frequency increases with increasing mean coupling constant.
- Then the frequency decreases and turns negative between the maximum and the minimum. This regime spans a larger and larger range on the \( \Delta k \) axis the higher the variation \( \Delta k \). Maximum and minimum get less and less pronounced with increasing \( \Delta k \).
- After the minimum \( \Delta f(\Delta k) \) increases again in the strong-coupling regime.

The higher \( \Delta k \) the smoother the curves. Please note that the sharp positive and negative peaks in Eq. (3) are reduced by orders of magnitude.

### 2.3. Amplitude dependence of frequency and bandwidth

A particularly interesting feature in high-frequency contact mechanics is the ease, by which nonlinear mechanical behaviour is experimentally observed and quantified. As discussed in the introduction, adhesion is usually quantified by the force (or, alternatively, the energy) needed to break a contact. Such a measurement occurs deep in the nonlinear regime of the stress–strain relation. The frequency shift as predicted by Eq. (4), on the other hand, refers to small stress and strain, that is, to the linear portion of the stress–strain curve. Measurements of \( \Delta f \) may occur at amplitudes of oscillation well below 0.1 nm and linear behaviour is indeed expected at this level.

At first glance, the measurement of an adhesion force and the measurement of a shear stiffness in the linear regime have little to do with each other. However, in high-frequency mechanics, linear behaviour and rupture are both limiting cases of a more general scenario termed “partial slip”. In the small–amplitude limit, partial slip approaches elastic behaviour, while at large amplitudes, partial slip turns into “gross slip”. “Gross slip” here denotes sliding, which implies detachment, should there be a force pulling vertically onto the particle. Evidently, the transition between stick and slip always is continuous if one looks at very short time scales. However, the cascade of local rupture events usually is so fast that it can only be detected with equipment accessing short time scales such as the QCM.

Nonlinear phenomena can be accessed with the QCM, as long as the nonlinearities are small. As long as \( \Delta f/f_0 \ll 1 \), the QCM is only weakly perturbed and – in consequence – behaves only weakly nonlinear (if nonlinear at all). Central to the analysis is the assumption that the motion of the crystal stays close to sinusoidal, even in the presence of the load. The load changes the resonance frequency and the bandwidth, but it does not disrupt the periodic motion altogether.

Going through details, one finds the relation [29,30]

\[
\frac{\Delta f(u_0)}{f_0} = -\frac{1}{\pi^2 Z_0 \omega_0^2} (F_f(t) \cos(\omega t))_{\text{time}}
\]

\[
\frac{\Delta \Gamma(u_0)}{f_0} = -\frac{1}{\pi^2 Z_0 \omega_0^2} (F_f(t) \sin(\omega t))_{\text{time}}
\]

\( \Delta f \) is the shift in the half bandwidth at half height (“bandwidth”, for short). Angular brackets denote an average. \( u_0 \) is the amplitude of motion, \( \omega = 2\pi f \approx 2\pi f_0 \) is the angular frequency. \( F_f \) is the tangential force, where a restoring force has negative sign. Eq. (7) can be cast into complex form as \( \Delta f + i \Delta \Gamma = -2fF_f \exp(\omega t)_i/(\pi^2 Z_0 \omega_0 u_0) \).

### 2.2. Distributions of contact stiffnesses

It is realistic to assume that the coupling constants between particles and a surface are also widely distributed rather than having one precise value. For a semi-quantitative approach we take the coupling constants to be distributed like a normal Gaussian:

\[
P(k) = \frac{1}{\Delta k \sqrt{2\pi}} \exp \left[ -\frac{(k - \bar{k})^2}{2 \Delta k^2} \right]
\]

Here, \( P(k) \, dk \) is the probability to find a coupling constant in the interval \( k, k + dk \). \( \bar{k} \) is the mean coupling constant and \( \Delta k \) characterizes the width of the distribution. As examples, Fig. 1B shows three distributions of coupling constants around the mean value of \( k = 11938 \) N/m for \( \Delta k = 1000, 2000, \) and 3000 N/m. This particular value of \( \bar{k} \) was chosen because with \( m = 8.4 \times 10^{-12} \) kg it leads to a resonance frequency of 6 MHz.

How does the observed frequency shift depend on the mean coupling constant at a given variation \( \Delta k \)? To calculate the frequency
In essence, the QCM operates like a lock-in amplifier. ∆Γ and ∆Γ* pick out the in-phase and the out-of-phase component of the force, respectively. If force and displacement are linearly related, \( F_{\parallel} = ku = k_0u_0 \cos(\omega t) \), Eq. (7) reduces to Eq. (4). Here, \( u = u_0 / \cos(\omega t) \), where \( u(t) \) is the lateral displacement between the centre of the sphere and the substrate. The frequency is independent of amplitude. Should, however, the force depend nonlinearly on displacement, the frequency will become amplitude-dependent. This situation is known from the theory of pendulum. Here, the restoring force is proportional to the sine of the angle rather than the angle itself. For this reason, pendulum clocks run slower than expected if the amplitude of motion is too large.

Under certain conditions, the time average in Eq. (7) can be converted into a weighted average over the displacement between the sphere and substrate, \( u \). For ∆Γ, one has

\[
\Delta \Gamma(u_0) = - \frac{2f}{\pi nA_Z u_0} \left( F_{\parallel}(t) \cos(\omega t) \right)_{\text{time}}
\]

\[
= - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{2} F_{\parallel}(t) \cos(\omega t) dt + \frac{T}{2} F_{\parallel}(t) \cos(\omega t) dt \right]
\]

\[
= - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{T} F_{\parallel}(u, u_0) + F_{\parallel}(u, -u_0) \right] \frac{u}{u_0} \left( 1 - (u/u_0)^2 \right)_{\text{displacement}}
\]

\[
\Delta \Gamma(u_0) = - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{2} F_{\parallel}(t) \sin(\omega t) dt \right]
\]

\[
= - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{T} F_{\parallel}(u, u_0) + F_{\parallel}(u, -u_0) \right] \frac{u}{u_0} \left( 1 - (u/u_0)^2 \right)_{\text{displacement}}
\]

The frequency shift is a weighted average of the sum of \( F_{\parallel} \) and \( F_{\parallel} \). \( F_{\parallel} \) and \( F_{\parallel} \) are the forces experienced during decreasing and increasing displacement, respectively. Note that the motion occurs laterally. “Increasing displacement” is movement to the right. Evidently, symmetry requires \( F_{\parallel}(u) = -F_{\parallel}(-u) \). \( T = 1/f \) is the time for one vibration. For the shift in bandwidth, ∆Γ, the outcome of the calculation is:

\[
\Delta \Gamma(u_0) = - \frac{2f}{\pi nA_Z u_0} \left( F_{\parallel}(t) \sin(\omega t) \right)_{\text{time}}
\]

\[
= - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{T} F_{\parallel}(t) \sin(\omega t) dt \right]
\]

\[
= - \frac{1}{\pi nA_Z u_0} \left[ \frac{T}{T} F_{\parallel}(u, u_0) + F_{\parallel}(u, -u_0) \right] \frac{u}{u_0} \left( 1 - (u/u_0)^2 \right)_{\text{displacement}}
\]

The shift in bandwidth is an integral over the difference of \( F_{\parallel} \) and \( F_{\parallel} \), that is, ∆Γ is proportional to the area under the hysteresis loop (Fig. 2). In line 4, we made use of the relation \( \cos(\omega t) = u/u_0 \). The minus sign before \( F_{\parallel} \) is a consequence of the exchange of integration boundaries.

If the forces are a function of displacement only (that is, \( F_{\parallel} = F_{\parallel}(u) \), as opposed to \( F_{\parallel}(u, u_0) \)) Eqs. (8) and (9) can be explicitly inverted. They turn into Volterra integral equations of the first kind. For these particular equations, analytical solutions are known [31]. A similar formalism has been used in atomic force microscopy, where the interaction forces between the tip and the substrate are derived from shifts of the resonance frequency of the cantilever [32–34]. However, in contact mechanics, the forces usually depend on the position as well as amplitude and the inversion of Eqs. (8) and (9) requires further assumptions.

In the context of this paper, we limit ourselves to a qualitative discussion, based on graphical representations of the force-displacement relation as shown in Fig. 2. Panel A shows the purely elastic case. There is no hysteresis and ∆Γ therefore vanishes. \( F_{\parallel} \) and \( F_{\parallel} \) are both equal to \( ku \). Inserting the relation \( F_{\parallel} = F_{\parallel} = ku \) into Eq. (8), one recovers Eq. (4). Panel B shows viscoelastic coupling, still obeying linear behaviour. There is a viscous component to the force, \( F_{\parallel} = \xi du/dt \) (\( \xi \) the drag coefficient) and the area under the curve is not zero. Also, since the viscous force depends on the speed, the force at any given position depends on the amplitude of motion, \( u \). Eq. (9) therefore cannot be directly inverted. In this particular case, one can relate the drag coefficient \( \xi \) to the bandwidth ∆Γ using viscoelastic behaviour as an input to the model. The result is \( \Delta \Gamma = N \xi k/(nA_Z u_0) \). For a proof, start from Eq. (4), replace ∆Γ by ∆Γ and further replace \( k \) by \( \xi \).

Panel C in Fig. 2 shows the case of partial slip in the Mindlin sense [35,36]. In the context of QCM experiments, partial slip has been described in detail in Ref. [37]. When exerting a lateral force onto a sphere-plate contact, there is a stress singularity at the rim of the contact area. The high local stress leads to a ring-shaped area, inside which the surfaces slide relative to each other. With increasing lateral force, the sliding portion of the contact zone increases in size, until the entire contact finally slips (“gross slip”). The quantitative description of partial slip goes back to Mindlin [36]. He assumes that sliding sets in once the local tangential stress exceeds the product of the normal stress with the static friction coefficient, \( \mu_s \). For oscillatory loading, the lateral displacement, \( u(t) \), and the lateral force, \( F_{\parallel}(t) \), are related by [37]

\[
\frac{F_{\parallel}(t)}{\mu_s F_{\parallel}} = - \left[ \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} - 2 + \frac{\mu_s}{\sqrt{3}} \left( 1 + \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} \right) \right]^{1/2} \frac{1}{3} \theta \frac{1}{\lambda S}
\]

\[
\frac{F_{\parallel}(t)}{\mu_s F_{\parallel}} = - \left[ \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} - 2 + \frac{\mu_s}{\sqrt{3}} \left( 1 + \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} \right) \right]^{1/2} \frac{1}{3} \theta \frac{1}{\lambda S}
\]

\[
\frac{F_{\parallel}(t)}{\mu_s F_{\parallel}} = - \left[ \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} - 2 + \frac{\mu_s}{\sqrt{3}} \left( 1 + \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} \right) \right]^{1/2} \frac{1}{3} \theta \frac{1}{\lambda S}
\]

\[
\frac{F_{\parallel}(t)}{\mu_s F_{\parallel}} = - \left[ \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} - 2 + \frac{\mu_s}{\sqrt{3}} \left( 1 + \frac{F_{\parallel}(0)}{\mu_s F_{\parallel}} \right) \right]^{1/2} \frac{1}{3} \theta \frac{1}{\lambda S}
\]

\[
\Delta \Gamma \approx \frac{k}{\pi nA_Z u_0} \left( 1 - \frac{1-u_0}{6} \right)
\]

\[
\Delta \Gamma \approx \frac{k}{\pi nA_Z u_0} \left( 1 - \frac{1-u_0}{6} \right)
\]

\[
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\]
energy outperforms just about all other engineering materials. This happens because the integrated area of slipping contact keeps increasing with increasing load. Only after partial slip turns into “gross slip” is this situation reversed. Gross slip in the context of railway tracks implies large scale movement of the entire structure, which requires enormous forces.

The peculiar behaviour of “granular contacts” is evident in the QCM results. For Mindlin microslip in the small-amplitude limit, the area under the hysteresis loop depends cubically on amplitude [35]. The dissipated energy becomes large because the sliding portion of the contact increases with amplitude. Dividing the dissipated energy by \( u_f^2 \) (Eq. (9)) one finds that \( \Delta \Gamma \) increases roughly linearly with amplitude. This situation is found in experiments after the contact is first established (black squares in Fig. 6). For Coulomb-type friction, on the other hand, the size of the hysteresis loop scales either linearly with amplitude (dynamic friction) or does not depend on amplitude at all (static friction). In both cases, \( \Delta \Gamma \) decreases with amplitude. In experiments, this situation is encountered after annealing (green upper triangles in Fig. 6).

3. Materials and methods

3.1. QCM

Throughout this work, AT-cut quartz crystals with a fundamental resonance frequency of 6 MHz and a thickness of 0.27 mm were used (China National Scientific Instruments and Material Corp., Hangzhou, China). The blanks were optically polished and had a diameter of 25.4 mm. After cleaning in an ultrasonic ethanol bath, a 2 nm-thick adhesive layer of chromium followed by a 100 nm-thick gold layer with a diameter of 10 mm was evaporated on the quartz surface. This gold electrode was electrically grounded during experiments. On the back side, a gold electrode of 7 mm diameter and 200 nm thickness was deposited. It was connected to a Network Analyzer (Agilent E5100A 10 kHz–180 MHz). Outside the active area of about 7 mm diameter the oscillating amplitude decays exponentially [40].

The gold electrodes had an average root-mean-square (rms) roughness of \( r_{rms} = 1.1 \) nm or below. Roughness was determined from \( 5 \times 5 \) \( \mu \)m images recorded by atomic force microscopy in tapping mode (Dimension 3100, Veeco Instruments, cantilever tapping mode, OMLCAC 160 TS-W2, Silicon).

The amplitude of oscillation was adjusted via the drive level of the network analyzer. If not otherwise mentioned we recorded the 3rd harmonic at 18 MHz because it was more stable than the 1st harmonic. To calculate the amplitude of the motion of the quartz crystal resonator, \( u_0 \), we used [41]:

\[
u_0 = \frac{4d_{33}^2}{n^2}QU_{\text{rel}}
\]

Here, \( d_{33} = 3.1 \times 10^{-12} \) m/V is the piezoelectric strain coefficient, \( Q \) is the quality factor, \( n \) is the overtone order (in our case \( n = 3 \)), and \( U_{\text{rel}} = 0.317 \times 10^{12} \) (dBm)/20) V is the driving voltage. \( Dl \) is the drive level in units of dBm (as shown on the interface of the network analyzer).

3.2. Polystyrene films

Polystyrene (PS) with \( M_w = 11700 \) g/mol was dissolved in toluene (20 g/l.). To remove any dust, the solution was filtered through Millipore filters of 0.2 \( \mu \)m (Millipore MILLIPORE, Syringe Driven Filter Unit, hydrophobic PTFE) before the polymer was spin-coated onto gold electrodes at 1600 rpm for 60 s. Afterwards, samples were annealed for 15 min at 150 °C in a preheated oven. After annealing, the sample was left to cool down to room temperature. The film thickness was in the range of \( 160 \pm 20 \) nm as calculated from the QCM response with the Sauerbrey equation. The thickness measured
with the QCM was verified by ellipsometry measurements (Ellipsometer EP3–SE, Nanofilm, Germany). The quality of the surface coating was assessed by estimating the roughness of the PS film by tapping mode atomic force microscopy as described above. The mean value of rms roughness for PS coated gold was 0.78 nm (5 × 5 μm² image). The advancing contact angles of 5 μL water drops were measured to be 81° for bare gold and 99° for PS coated gold.

3.3. Borosilicate particles

Spherical borosilicate glass particles (Duke Scientific Corporation, California, USA) with mean diameters of 5, 10, 15, and 20 ± 1 μm were used as received. Without taking the quartz out, the particles were deposited on the polymer surface. Therefore, a thin metal-wire, washed before with THF and dried with nitrogen or left in a vacuum oven to dry, was used to pick-up several hundreds of the particles from the bulk. They were placed on the quartz surface by shaking. In order to deposit them in the centre of the quartz, the particles were deposited through a 1 mm diameter hole of an aluminum film used to cover the holder. The smaller the particle-diameter was, the stronger the tendency of the particles to agglomerate. For the 5 μm particles agglomeration was unavoidable while for 20 μm particles practically no agglomeration was observed. The surface with deposited particles was imaged by a video camera connected to the microscope (Fig. 3). The images were analysed by Image Pro Plus software (Media Cybernetics, Inc. Silver Spring, MD, USA) to determine the number of particles. The mean density of particles was 33,200, 12,900, 8700, 3200 particles per cm² for 5, 10, 15 and 20 μm particles, respectively. The microsphere density is roughly 2500 kg/m³ (Duke Scientific Corporation data sheet).

3.4. AFM adhesion measurements

In order to measure the adhesion force between particles and PS coated surface, the colloidal probe technique was used. According to Kappl et al. [42], borosilicate glass spheres with 10 μm diameter were attached with epoxy glue (UHU plus endfest 300, UHU, Buehl, Germany) to the ends of AFM tipless rectangular silicon cantilevers (Schaefer Technologie, Langen, Germany, length 350 μm, 2.0 μm thick, resonant frequency 21 kHz). The spring constant of the cantilevers was determined by the reference spring method [43,44]. The reference cantilever was calibrated using the thermal noise method introduced by Hutter and Bechhoefer [45]. For adhesion force measurements all results were taken using force-volume-mode. The force curves were taken from a grid of 32 × 32 points, within a scan area of 500 × 500 nm.

3.5. Video system

To reduce the influence of mechanical vibration, the whole setup was placed on an active vibrations isolation table (Newport Corporation, Irvine, CA, USA). In order to estimate the adhesion force between particles and surfaces, the QCM holder was turned upside down, facing downwards (Fig. 4). As a result, particles fell off as soon as the adhesion force was overcome by their weight and vibrational motion. A stereomicroscope (Leica MS 5) with a 1× objective and a five-step magnification changer (0.63×, 1.0×, 1.6×, 2.5×, 4.0×) was used. The upright microscope was altered to an

![Fig. 3. Representative video images of 5 (A), 10 (B), 15 (C) and 20 μm (D) diameter glass particles on polystyrene films on a QCM.](image-url)
inverted configuration. A digital camera (Watex WAT-202D) was connected to the system by means of a C-Mount-Adapter (0.63×). The QCM was illuminated with a fibre optic ring light source attached to the microscope. Magnifications of 0.63 and 1.6 were applied, showing a field of view of 1 cm and 0.4 cm respectively. With the higher magnifications the position of an individual particle was imaged. We were able to distinguish three different behaviours: 1) no movement of the particles, 2) lateral motion, and 3) particles fall off.

4. Results and discussion

After depositing a PS film on the gold electrode the resonance frequency of the QCM decreased according to the mass density of the film. No significant change of the resonance frequency with the driving amplitude was observed up to amplitudes $u_0$ of 10 nm (Fig. 5). Between 10 and 16 nm a slight increase of the resonance frequency was observed, which is small compared to the changes observed with particles.

4.1. 20 μm particles

When depositing particles with a diameter of 20 μm on a PS coated surface the resonance frequency always increased (Fig. 6A). Here and in the following, all frequency shifts are referenced to the PS coated crystals prior to the deposition of spheres. Unless stated otherwise, Δ$f$ was determined in the limit of small amplitudes (<0.5 nm) where a partial slip is of negligible influence. From optical microscopy, the areal number density $N/A_0$ in the particular experiment shown in Fig. 6A was determined to be about 30 particles/mm².

We would like to point out that van der Waals forces are completely sufficient to keep the particles at the surface. Generally, the van der Waals force between a sphere and a planar surface is given by

$$F_{vdW} = \frac{A_H R}{6D^2}$$

where $D$ is the distance and $R$ is the particle radius. Estimating the Hamaker constant $A_H$ for PS-air-silica to be $2 \times 10^{-20}$ J and the distance at contact to be 0.17 nm, the van der Waals attraction keeping the particle at the PS surface is 1.1 μN. The gravitational force is $4\pi R^2 g \rho/3 \approx 0.1$ nN, with $g = 9.81$ m/s² and $\rho = 2500$ kg/m³. Unless the particle is separated by at least a distance $D = \sqrt{A_H/(8\pi R^2 \rho)}$, it will remain attached to the surface. The critical fall off distance is $D = 1.8 \times 10^{-13}$ m²/R and we estimate this distance to be 18 nm.

Right after the first deposition of particles (Fig. 6A, black squares) Δ$f$ increased by 350 Hz. Such an increase of the resonance frequency after the addition of particles has been observed before [21]. This system is in the weak-coupling regime. Quantitative analysis of the frequency shift with Eq. (4) yields a surprisingly high value for the spring constant, $k$. Particle counting using video microscopy yielded a particle density $N/A_0$ of the order of 30 particles/mm². With $\Delta f \approx 350$ Hz (first sweep), Eq. (4) leads to a spring constant of $k \approx 6000$ N/m. This value can be compared to the Hertz theory. For a Hertzian contact one expects a lateral spring constant of about [37]

$$k = G \frac{a}{E^*}$$

where $G$ is the shear modulus, $E^*$ is an effective modulus, $G$ is the shear modulus, and ν is Poisson’s number. Note that Eq. (14) assumes a semi-infinite substrate and neglects roughness. The contact radius, $a$, as predicted from Hertz theory is

$$a = \sqrt{\frac{F}{\pi E}}$$

$$E^* = \frac{1}{4} \left( \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \right)$$

Here, $a$ is the radius of contact. The indices 1 and 2 label the contacting materials, $G^*$ is an effective modulus, $G$ is the shear modulus, and $\nu$ is Poisson’s number. From optical microscopy, $G^*$ can be compared to Hertz theory is

$$a = \sqrt{\frac{F}{\pi E}}$$

$$E^* = \frac{1}{4} \left( \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2} \right)$$

Here $F_1$ is the adhesion force (estimated as 1.1 μN above), $E$ is Young’s modulus, and $E^*$ is the reduced Young’s modulus. Using $E = 2 (1+\nu) G$ and $\nu \approx 1/3$, one finds that $E^* \approx 6/5 G^*$. In the following, we assume the glass beads to be much stiffer than polystyrene, that is, we neglect the second terms in Eqs. (14) and (15) ($G_2 \approx E_2 \approx \infty$). For polystyrene at MHz frequencies, the shear modulus has been determined to be about 2 GPa [46]. Inserting these values, one finds a lateral spring constant of about 1000 N/m, which is a factor of 6 lower than the experimental value. In order to match the experimental value of 6000 N/m, one would have to use a shear modulus of 25 GPa, which is highly unrealistic. The contact radius according to the Hertz theory is 110 nm, which is less than the thickness of the polystyrene film. While the finite thickness may be of some influence in principle, it is hard to see how the correction should amount to a factor of 6. Unexpectedly high values for the spring constant as derived from the Hertz theory have been found before [47]. The discrepancy has often surpassed a factor of 10. While we have no rigorous explanation at hand, we believe that the result can...
be understood on a qualitative level, assuming a multi-asperity contact. We provide arguments in Appendix B.

In the first sweep, the oscillation amplitude was increased from \( h_0 = 0.1 \text{ nm} \) to 4 nm. Video microscopy did not reveal significant movement of the particles. Less than 5% of the particles fell off or moved on the surface. In the second sweep, the resonance frequency increased by 2.5 kHz relative to the clean PS film. This indicates a tighter coupling. We interpret this “consolidation” of the particle-PS contact in the following way: neither the particle nor the PS surface are perfectly homogeneous. During the first sweep, the particles rotate and oscillate and in this way they obtain an optimum binding position. In the third sweep (Fig. 6A, red circles) only a slight decrease in the resonance frequency was observed. No changes were detected by video microscopy. The mean coupling constant shifts back to slightly lower values.

That consolidation is a major effect is supported by the AFM adhesion force measurements. Adhesion varied from one position to another by a factor of \( 2-3 \). Furthermore, the absolute value of 30–70 nN is relatively low. We use the model of Johnson et al. [48] for an estimation of the adhesion. The adhesion force between an elastic sphere and a planar surface is \( F = 3 \mu W R^2 \), where \( W \) is the work of adhesion per unit area. With \( W = 0.03 \text{ N/m} \) and \( F = 70 \text{ nN} \) an effective radius of the sphere can be estimated to be 0.5 \( \mu \text{m} \). This is much lower than the actual radius and indicates that surface roughness reduced the contact area significantly.

The partial slip length is read from the \( \Delta f \)-versus-amplitude by fitting a straight line to the data at low amplitudes and extrapolating this line to \( \Delta f = 0 \) according to Eq. (11). The straight lines in Fig. 3B and C show these extrapolations. For the particles with 20 \( \mu \text{m} \) diameter, the partial slip length is of the order of 0.6 nm. With an adhesion force of \( F_i = 1.1 \mu \text{N} \) and a spring constant of \( k = 6000 \text{ N/m} \), one finds an apparent static friction coefficient of \( \mu_0 \approx F_i/(k h_0) \approx 0.3 \). While this value is in the expected range, \( \mu_0 \) derived from \( \lambda_0 \) and the Mindlin model has occasionally also been found to be somewhat larger than unity [47]. This may well go back to a short-coming of the Mindlin model. However, \( \mu_0 \), being larger than one may also be a consequence of the fast oscillation. This would imply, that the induction of partial slip takes time and is less efficient at MHz frequency than it would be in conventional macroscopic experiments.

At this point we slightly digress on the possibility of a rotation of the sphere under the force of inertia. The Mindlin model assumes that the bulk of the sphere remains at rest. It neither translates, nor rotates. Evidently, this is not fully realistic. One expects a slight periodic rotatory component to the motion, in which case our experiments would probe the rolling friction rather than the Mindlin microslip. The deformation pattern in the contact zone would consist of mixed, rather than pure shear. Finite element calculations [2] show that, firstly, the amplitude of rotation is very small. The pattern of deformation mostly is a shear deformation. However, if the moduli of the two contacting materials are different, there still is a vertical stress component at the rim of the contact area. This fact is well-known from fracture mechanics [49]. For a hard–soft contact, shear-induced crack propagation always entails a normal tensile stress, termed “mode II crack opening” in this context. The essence of the Mindlin model (partial slip) certainly remains correct even for mode II crack opening, but the details may need refinement.

In the following step, the quartz crystal (including the particles) was annealed at 150 °C for 15 min in a preheated oven. After annealing and cooling the frequency decreased to \( \Delta f = -6.9 \text{ kHz} \) (Fig. 6A, green upper triangles). Following the Dybwad model, one concludes that the contacts are now in the tight-coupling regime. Annealing leads to the formation of a PS meniscus and binds the
particles stronger to the quartz. Meniscus formation was confirmed by atomic force microscopy. Under the control of an optical microscope a particle was removed from the surface with the tip of an AFM. Subsequently, the PS surface was imaged in tapping mode. The remaining meniscus had a height of 200–400 nm and diameter 3–6 μm (Fig. 7).

Using the Sauerbrey equation, one can check whether the weight of the particles as determined by microgravimetry matches the number density from particle counting. The latter was 30 particles/mm². If we assume that the particles are tightly bound, we can calculate a density of 26 particles/mm² from Eq. (2) from the shift in resonance frequency. One could conclude that roughly 80% of the particles are tightly bound to the QCM surface and follow its movement. In the framework of Fig. 1, the system would be on the far left in the strong-coupling regime. We would, however, like to point out that this is no unique conclusion. The system could also be in the intermediate regime with k being slightly above the resonance point.

In the following sweeps leading to the aged state (blue lower triangles), the resonance frequency gradually increased until the same state as before temperature annealing was reached. We interpret this increase as a reduction of the mean coupling constant. Actually, the frequency shift remained below −4 kHz, as long as the amplitude sweeps did not exceed 3 nm. It required the highest possible amplitude of 4 nm (in this particular experiment) to bring the system back to the initial value observed before annealing.

After annealing we did not detect any particle movement or detachment by video microscopy. This observation excludes a frequency shift due to mass loss. Therefore we conclude that the bond between the particles and the PS surface was reduced again to the level of the binding strength before annealing. With a decreasing mean coupling constant the system went from negative frequency shifts in the strong-coupling regime to positive frequency shifts in the weak-coupling regime.

4.2. 15 μm particles

A similar behaviour was observed with 15 μm particles. In the example shown in Fig. 6A, the frequency increased by 360 Hz upon the addition of particles. It further increased by 390 Hz in the second sweep. Afterwards, it remained constant as long as the oscillation amplitude did not exceed 5 nm. No particle movement or loss of particles was observed by video microscopy. Annealing caused Δf to become negative (−1.9 kHz). For the 20 μm particles, we attribute the decrease of the resonance frequency to a tight-coupling of the particles and the accompanying increase in effective mass. In contrast to the larger particles, the resonance frequency did not change in all following sweeps, even when increasing the amplitude to 10 nm. Video microscopy showed no indication of particle movement or loss.

To explain the fact that the 15 μm particles were not decoupled by resonating at high amplitude, we first calculated the force acting on the particle. Assuming that particles move with the quartz surface, their position is \( u_0 \cos(\omega t) \). The force required to oscillate the particle is \( F_{osc} = -m \omega^2 u_0 \cos(\omega t) \) (Fig. 8). The peak force is \( 4\pi R^3 \rho u_0 \omega_0 \Delta \). It increases with the third power of the particle radius. This has to be compared to the force binding the particles to the surface. This binding force is expected to grow proportional to R, though it is not clear how the binding between the particle and the PS surface is broken. One might argue that in the absence of elastic strain the adhesion force is proportional to the contact area. For a given film thickness with \( h \ll R \), the contact area is approximately given by \( \pi a^2 \), where \( a \) is the contact radius. Here, we neglect the influence of the meniscus. With \( a^2 = 2hR - h^2 \approx 2Rh \) the contact area scales increase proportional to R. Thus, the oscillation force due to the inertia of the particle increases with \( R^3 \) while the binding to the PS is expected to increase only with \( R \). For large particles the oscillation force is more likely to detach the particles, while for small particles the binding force should dominate.

One might also argue via the torque. To detach the particle from its meniscus it would need to roll up onto the film. The maximal torque leading to it is \( (R - h) 4\pi R^3 \rho u_0 \omega_0 \Delta \approx 4\pi R^3 \rho u_0 \omega_0 \Delta \). Adhesion resists rolling. To roll, the torque \( \tau_{adh} \) has to be overcome. Assuming that the adhesion force scales with the contact area, the resistance is proportional to \( a^2 = (2hR)^{3/2} \). Again, large particles should detach more easily under an oscillating lateral force than small particles.

The experiments with the 15 μm particles revealed a problem intrinsic to the Dybwad model, which complicates quantitative interpretation. Comparing the number of particles per unit area observed by microscopy with the mass per unit area derived from the Sauerbrey equation, we often find the latter to be much smaller than expected. The difference amounted to up to a factor of 5. Within the semi-quantitative model (Fig. 1), this is explained by the system being in the intermediate regime between strong and weak coupling. When \( k \) is around the resonance condition (\( k \approx \omega^2 m \)), quantitative analysis is difficult.

4.3. 10 μm particles

The deposition of 10 μm particles caused the frequency to increase by 280 Hz (Fig. 6C, black squares). Increasing the oscillation amplitude up to 5 nm caused no optical detectable changes, although the frequency decreased by 75 Hz in the second sweep. \( \Delta f \) remained stable after the second sweep. The red circles in Fig. 6C show the third sweep. In contrast to the larger particles, annealing caused an increase of \( \Delta f \) to a value of \( \Delta f \approx +450 \) Hz, rather than a decrease. Evidently, annealing in this case was not sufficient to reach the strong-coupling regime. \( k \) increased, pushing the system towards the resonance condition (thereby increasing \( \Delta f \)). However, the increase did not carry the system beyond the resonance condition.

Sweeps with a maximum amplitude of about 6 nm caused a further small increase of \( \Delta f \) by about 50 Hz. Increasing the amplitude...
to 10 nm caused particle loss and a decrease of $\Delta f$ down to 285 Hz. Further increasing the amplitude to 16 nm left the sample unchanged.

### 4.4. 5 $\mu$m particles

The smallest particles used caused a decrease of the frequency by $\Delta f \approx -200$ Hz (Fig. 6D). Three amplitude sweeps did not change the frequency. After annealing, the frequency decreased down to $\Delta f \approx -400$ Hz. Aging the sample at high amplitudes further decreased the frequency down to $-600$ Hz. These particles are in the strong-coupling regime.

#### 4.5. Mindlin microslip versus Coulomb-type friction

An interesting result showing up in all measurements is the dependency of the bandwidth on the amplitude. Upon deposition of the particles, the bandwidth increased with amplitude as predicted by the Mindlin model (Eq. (11)). This has been observed before [37,50]. After annealing, on the contrary, $\Delta f$ decreased with amplitude, which is a novel finding. We have argued in the theory section that such a decrease of $\Delta f$ with amplitude can be understood in the frame of Coulomb-type friction. Mathematically speaking, $\Delta f$ decreasing with amplitude implies that the area inside the hysteresis loop increases less-than-quadratically with amplitude. This is for instance, the case with peaks in dissipation around the turning points of the oscillation. Evidently, the detailed mechanism cannot be inferred from measurements of the bandwidth alone. Still, the result is quite characteristic.

#### 4.6. Surface damage by the particles

When the particles move with the surface of the QCM the forces reach values of up $F = m D_0 \omega^2$. For the 20 $\mu$m particles with $m = 10$ ng, $\omega_0 = 113$ MHz, and $D_0 \approx 20$ nm peak forces are 2.7 mN. This can lead to high local stresses in the polymer. Taking a contact area of 1 $\mu$m² for example leads to a stress of the order of 3 GPa. Such a stress is able to damage a polymer. For this reason we investigated if the polymer was deformed by the glass particles.

As a first control, particles were placed on an annealed PS coated surface without quartz stimulation. After 24 h, the particles were carefully removed and the surface was imaged with an AFM. Particles left barely visible marks on the surface. Fig. 9 shows an example of an AFM tapping mode image of structural changes on the PS coated gold after removing a 20 $\mu$m particle which had been in contact with the PS for 24 h at room temperature.

![AFM tapping mode image of structural changes on the PS coated gold after removing a 20 $\mu$m particle which had been in contact with the PS for 24 h at room temperature.](image)

With typical values for the parameters ($A_H = 2 \times 10^{-20}$ J, $D_0 = 0.17$ nm, $\rho = 2500$ kg/m³) we obtain $v_e \approx 6$ mm/s. In our experiment the particles fall off once gravitation is stronger than the van der Waals forces. For a particle radius of 10 $\mu$m we get a fall off distance of $D = 18$ nm. The time of one jump can be estimated to be $\tau = D / D v_e \approx 3$ $\mu$s. With a spacing of 0.5 $\mu$m between the elongated marks a horizontal velocity of 0.16 m/s is estimated.

For 5 $\mu$m particles no detectable changes were found.

#### 4.7. Conclusions

Changes in the resonance frequency caused by particles on a QCM surface can be interpreted by a balance of the coupling strength and inertial forces. For strong-coupling and low mass the particles move with the vibrations of the QCM and add effective mass. This leads to a decrease of the resonance frequency. For lower coupling and high mass the particles are not able to follow the movement of the QCM surface. They effectively add a spring and increase the resonance frequency.

For a semi-quantitative interpretation we have to take into account that the particles show a distribution of coupling constants rather than a single, precisely defined value. Introducing a distribution of coupling constants and convoluting it with the frequency shift $\Delta f$ predicted by the Dybwad Eq. (3) three regimes can be distinguished: (1) for low mean coupling constants $\bar{k}$, the frequency increases with increasing $\bar{k}$ until it reaches a maximum. (2) After the maximum $\Delta f$...
decreases and turns negative to reach a minimum. (3) Further increasing $R$ leads to a gradual increase of $\Delta f$ until it has reached a value in which the mass increase dominates. The vibrations of the QCM can drastically change the micro-mechanical contact between QCM surface and particles. It can lead to a consolidation and an increased coupling. It can also break the contact and even lead to detachment.

From standard QCM experiments alone a quantitative determination of interaction forces of particles with surfaces does not seem to be possible. One reason is that the frequency shift is not a unique function of the coupling constant. For any measured frequency shift, different coupling constants are possible.

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Appendix A. Extension of the Dybwad model to many spheres

Dybwad’s treatment applies to a single sphere. The extension of the model to many spheres results in a rather complicated set of equations. The difficulty goes back to the presence of more than one periodic solution to the equation of motion. Such a situation is well-known from the theory of the coupled pendulum. For the coupled pendulum there are two solutions, which are given by either a symmetric or an antisymmetric motion of the two arms. In the Dybwad model, there are two such modes as well. If the angular resonance frequency of the crystal, $(K/M)^{1/2}$ and the angular frequency of the coupled resonator $(k/m)^{1/2}$ are the same, these are the symmetric (sphere moves in parallel to the crystal surface) and the antisymmetric (sphere moves antiparallel to the crystal surface) solutions. However, $(K/M)^{1/2}$ and $(k/m)^{1/2}$ are usually not the same. In most cases of practical interest one has either $k/m \gg K/M$ or $k/m \ll K/M$. For such a situation, the modes are localized. One mode is a thickness-shear displacement of the crystal. The sphere closely follows the motion of the top surface. The other mode is given by an immobile crystal. The sphere moves relative to the top surface. Importantly, only the former mode is experimentally observed because only this mode induces a surface polarization inside the electrodes. It therefore suffices to investigate how the presence of the sphere shifts the frequency of this mode.

In the context of the QCM, a similar situation has been encountered before for the thickness-shear mode of a viscoelastic film resonance [51]. A thick viscoelastic film deposited on a quartz crystal has a resonance frequency of its own. The resonance condition is $df = \lambda/4$, with $df$ the film thickness and $\lambda$ the wavelength of sound. This “film resonance” constitutes a “coupled resonance” in much the same way as the sphere-plate contact. If the resonance frequency of the coupled resonance is the same as the resonance frequency of the resonator, one finds two modes. The existence of two such modes has also been observed experimentally.\footnote{Oliver Wolff, private communication.}

The extension of the Dybwad model to numerous coupled spheres leads to cumbersome complications because every new sphere introduces another periodic solution to the equation of motion.
creates a new mode. As in vibrational spectroscopy, the number of modes increases with number of coupled particles. Again: the presence of more than one periodic solution to the force balance equation is by no means an artefact, it has been observed. Simplification is possible by limiting one’s attention to cases, where the frequencies of the coupled resonances are either much larger or much smaller than the frequency of the resonator (weak-coupling limit and strong-coupling limit). Then all modes are localized and it suffices to consider the experimentally observable mode only.

There is a formalism adapted to this situation termed “small load approximation” (SLA) [52,53]. Other authors use the word “surface impedance concept” [54]. One can show that the frequency shift of the crystal is given by [55]:

$$\Delta f + i \Delta \gamma \approx \frac{i}{f_0} \frac{Z_i}{\eta Z_q} \approx \frac{i}{\eta Z_q} \frac{\sigma}{\text{area}}$$  \hspace{1cm} (17)

$$Z_i = \sigma u$$ \text{is the “load impedance”, \(\sigma\) is the tangential stress at the crystal surface, \(u\) is the lateral speed at the crystal surface and angle brackets \(\langle \rangle\) denote an average. The “load” here may consist of any object perturbing the crystal’s motion. Well-known loads are the thin film in the Sauerbrey sense and the viscous liquid as described in Refs. [56,57]. Other types of loads might be layers of biological cells, adsorbed vesicles, a sand pile, a froth, or liquid droplets. Any type of load can be modelled within the small load approximation, provided that the stress induced at the crystal surface, \(\sigma\) can be calculated. Within the small load approximation, \(N\) identical spheres behave similar to a single sphere. The presence of \(N\) spheres just amounts to a prefactor of \(N\) on the right-hand-side of Eq. (3). Again, the SLA requires that the stress obeys \(\sigma = \frac{Z_q}{\text{area}}\), that is, that the load is small. This is not the case when \(k/m = K/M\).

If the sample consists of small spheres, the shifts of frequency and bandwidth are [27]

$$\Delta f + i \Delta f \approx \frac{N}{A q} \frac{m \omega}{\eta Z_q} \frac{1}{\omega^2 + \eta \omega} \approx \frac{N}{A q} \frac{m \omega}{\eta Z_q} \frac{1}{\omega^2 + \eta \omega} \hspace{1cm} (18)$$

with the angular resonance frequency of a particle \(\omega_c^2 = k/m\). The force constant providing for the link between the sphere and the sensor surface was considered to be complex, that is, \(k\) was replaced by \(k + i\omega \gamma\), with \(\gamma\) as a damping coefficient.

There are two benefits to the use of the small load approximation. Firstly, Eq. (18) is simpler than Eq. (3). It avoids the two solutions. Also, the strong-coupling (Sauerbrey) limit and the weak-coupling limit can be derived simply by using \(\omega_c \gg \omega_0\) (Sauerbrey limit) and \(\omega_c \ll \omega_0\) (weak-coupling limit) [58]. Second, Eq. (18) encompasses dissipative processes, which lead to an increase in bandwidth. Again, Eq. (18) is algebraically distinct from Eq. (3) but it leads to a rather similar phenomenology.

Appendix B. On the lateral stiffness of multi-asperity contacts

There are two reasons why a multi-asperity contact between a sphere and plate would be stiffer under a shear load than a single contact. The first argument has to do with the fact that the vertical load carried by a contact scales as the cube of the contact radius, \(a^3\) (cf. Eq. 15), while the lateral spring constant scales as \(a\) (cf. Eq. 14). A similar result has been found in bioadhesion. The phenomenon is termed contact splitting [59]. Here, the difference in scaling occurs between vertical load \((-a^3)\) and rupture force \((-a)\). Contact splitting is exploited by some animals in order increase the dry adhesion between their feet and the object they need to stick to.

In order to make the argument more quantitative, we make simplifying assumption: the contact is made across a finite number \(N_c\) of identical nanoscopic contacts; the contacts are not elastically coupled to each other, all individual contacts behave according to Hertz theory, all have the same radius of curvature, \(R_c \approx R\). Then all the share the vertical load equally between them, and they all contribute equally to the lateral stiffness. Further, we assume \(E^* \approx G^*\) in Eqs. (14) and (15). The combination of Eqs. (14) and (15) now reads

$$k = -N_c G^* a = N_c G^* \left( \frac{F_c R_c}{N_c G^*} \right)^{1/3} = \frac{N_c}{2} \left( \frac{G^*}{N_c} \right)^{2/3} \left( \frac{R_c}{N_c} \right)^{1/3} \hspace{1cm} (19)$$

This scaling analysis predicts that the lateral contact stiffness increases with the number of contacts. Note however, that the contacts have to elastically independent. The assumptions certainly are not fully correct for a contact between rough surfaces. Elastic coupling between the contacts, in particular [60] may change the outcome of this calculation.

A second reason, why roughness may increase the lateral stiffness of a contact has to do with the distribution of loads. As the analysis by Mindlin shows, the distribution of local stress in the contact zone shows sharp peaks at the rim of the contact zone. When distributing the vertical load between numerous small nano-contacts, some of these nano-contacts will be situated further away from the centre than the rim of equivalent single-asperity contact. Roughness “spreads out” the distribution of the load-carrying contacts. Since the local stress increases with distance from the centre, the more distant contacts do more efficiently support lateral stress than the central contacts. This contrasts to vertical load. The vertical load is strongest in the centre. The situation resembles beam bending, where hollow rods resist bending stronger than full rods of the same cross-sectional area. Moving the supporting material away from the neutral plane stiffens the respective element.

Both these arguments are qualitative. Hopefully, they can be substantiated by a more rigorous treatment in the future.

Appendix C. Derivation of the Sauerbrey limit and the elastic loading limit from Eq. (3)

For notational brevity, we write the derivation down for a single particle \((N = 1)\). The derivation for many particles is recovered by replacing \(m\) with \(Nm\) and \(k\) with \(Nk\). We first derive the Sauerbrey Limit, which is found for stiff contacts \((k \rightarrow \infty)\):

$$2 \omega_c^2 = 8 \pi^2 \left( f_0 + \Delta f \right)^2 \approx$$

\[= \left( \frac{K}{M} + \frac{k}{m} + \frac{k}{m} \right) \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{(M+m)}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{Mm} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]

\[= \frac{K}{M} + k \frac{M+m}{Mm} \left( \frac{k}{M} + \frac{k}{m} \right)^2 - 4 \frac{k}{M} \]
$M_{tot}$ was inserted for $M + m$ in line 3. $\sqrt{1 + \varepsilon} \approx 1 + \varepsilon / 2$ was used in line 5. $k \rightarrow \omega$ was used in line 8. In the following, we make use of $\omega^2 = kM / M_0$ and $1 / (1 + \varepsilon) \approx 1 - \varepsilon$:

$$2\omega^2 + 4\omega \Delta \omega + 2 \Delta \omega^2 = 2\omega^2 \frac{M + m}{M + m} = 2\omega^2 \frac{1}{1 + m/M}$$

$$\omega^2 + 2\omega \Delta \omega \approx \omega_0^2 \left(1 - \frac{m}{M}\right)$$

$$\Delta \omega \approx \frac{-m}{M} \frac{1}{2\sqrt{\omega_0^2 q}}$$

$$\omega_0 = \frac{1}{k} \frac{\varepsilon}{\varepsilon + 2}$$

$$M = A \omega_0^2 q_0$$

$\sqrt{1 + \varepsilon} \approx 1 + \varepsilon / 2$ was used in line 3. The term quadratic in $k$ was omitted in line 4.

References


