A formalism is presented which predicts the influence of laterally heterogeneous slip (for instance, induced by nanoscopic air bubbles) on the shift of the resonance frequency and bandwidth of quartz crystal resonators immersed in liquids. The lateral heterogeneities are decomposed into their Fourier components. The distribution of slip lengths provides a boundary condition, giving rise to a small, secondary flow field. There are several reasons for why the shifts in frequency and half-band-half-width often are not exactly the same, even if the liquid is perfectly Newtonian. First, there may be additional channels of dissipation such as coupling to the holder or emission of compressional waves. These effects would tend to make the shift in the half-band-half-width larger than the negative frequency shift because compressional waves withdraw energy from the resonator. A finite imaginary part of the viscosity, \( \eta' \), would have the same effect (see eq 4). Experimentally, one frequently finds the opposite effect: the shift in the half-band-half-width is smaller than the negative frequency shift.

Effects of Laterally Heterogeneous Slip on the Resonance Properties of Quartz Crystals Immersed in Liquids

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Introduction

Quartz crystal resonators are well-known tools for the determination of film thickness. According to the Sauerbrey equation, a film deposited on the crystal surface decreases the resonance frequency according to

\[
\frac{\delta f}{f_0} = \frac{-m_t}{m_q} = \frac{-2f_0}{Z_q}m_t
\]

where \( \delta f \) is the frequency shift, \( f = nf_0 \) is the frequency, \( n \) is the overtone order, \( m_t \) is the areal mass density of the film, \( m_q = Z_q/(2f_0) \) is the areal mass density of the quartz plate, \( f_0 \) is the fundamental frequency, and \( Z_q = 8.8 \times 10^8 \) kg m\(^{-2}\) s\(^{-1}\) is the acoustic impedance of a T-cut quartz. According to the Sauerbrey equation, the frequency shift scales as the overtone order, \( n \). Equation 1 is the basis of the quartz crystal microbalance (QCM).

In the 1980s, it was recognized that the QCM can also be operated in liquids, provided that the rather strong damping can be overcome. The presence of a Newtonian liquid also gives rise to a frequency shift. In this case, the Kanazawa equation holds:

\[
\delta f = \frac{-f_0}{\pi Z_q} \sqrt{\pi f_0 \rho \eta}
\]

Introduction


d of eq 2, which is

\[
\frac{\delta f}{f_0} = \frac{\delta f + i\delta \Gamma}{f_0} = \frac{iZ_q}{\pi Z_q}G = \frac{i}{\sqrt{2\pi Z_q}} \sqrt{\rho \eta} = \frac{i}{\sqrt{2\pi Z_q}} \sqrt{\rho \eta} \]

Here, \( Z_i = (\rho G)^{1/2} \) is the acoustic impedance of the liquid and \( G = i\omega \eta \) is the complex shear modulus.

Equation 3 predicts that the shift in the bandwidth is equal and opposite to the frequency shift. If one can be sure to deal with a strictly Newtonian liquid, this prediction can be used to check for certain artifacts. The intrinsic relaxation times of water are in the gigahertz range. If, on the other hand, the liquid under study is viscoelastic, the complex viscosity, \( \eta''(\omega) = \eta(\omega) - i\eta'(\omega) \), can be explicitly derived from the shift of frequency and bandwidth by the relation

\[
\eta''(\omega) = \eta'(\omega) - i\eta'(\omega) = \frac{-\pi Z_q}{iZ_q} \delta f = \frac{\delta f}{\rho f_0^2} \frac{-\delta \Gamma}{2\delta f} \]

There are several reasons for why the shifts in frequency and half-band-half-width often are not exactly the same, even if the liquid is perfectly Newtonian. First, there may be additional channels of dissipation such as coupling to the holder or emission of compressional waves. These effects would tend to make the shift in the half-band-half-width larger than the negative frequency shift because compressional waves withdraw energy from the resonator. A finite imaginary part of the viscosity, \( \eta''(\omega) \), would have the same effect (see eq 4). Experimentally, one frequently finds the opposite effect: the shift in the half-band-half-width is smaller than the negative frequency shift.


According to a heuristic basis, one can decompose the frequency surface. It behaves like a thin film in the Sauerbrey sense. Located in the crevices moves rigidly with the crystal according to the laws of physics, one often derives a function proportional to $n^{1/2}$ and $n^{3/2}$, respectively (Figure 2). The experiments can be well represented by functions of the form

$$\frac{\delta f}{f_0} = -\frac{1}{\pi Z_q} \sqrt{n_f \rho \eta} (1 + B n)$$

with one single dimensionless parameter, $B$. We propose laterally heterogeneous slip as the source of these deviations of the experimental data from the Kanazawa line.

The occurrences of slip at solid—liquid interfaces as well as its physical reasons have been intensely discussed in the recent literature.\(^8\)–\(^\text{11}\) Various cases need to be distinguished: First, sliding often occurs between solid surfaces under large lateral stress.\(^\text{12}\) This is a nonlinear phenomenon, which is much different from what we consider here. Second, slippage and even plug flow is common for polymer—solid interfaces because the entanglement network provides for a very high viscosity in the bulk. Since this network does not include the substrate, the rate of shear strain at the surface often is much larger than that in the bulk. This phenomenon also is outside the scope of this paper. With regard to simple fluids, surface slip was considered the exception rather than the rule for a long time, because the interaction between the molecules and the surface should be about as strong as the interaction between the molecules.\(^\text{13}\) It is not easy to see why the near-surface region should have a decreased viscosity. There is a class of experiments where the slip of monolayers of simple liquids has been investigated with the QCM.\(^\text{14},\text{15}\) For monolayers, the local van der Waals pressure is small, which generates a situation much different from the case of the bulk.

Even though this thought result came as somewhat of a surprise, it is now widely accepted that slip does occur at the solid—liquid interfaces under certain conditions. At low frequencies, this kind of slip has been experimentally investigated with the surface force apparatus\(^\text{16–18}\) as well as with dynamic colloidal probe experiments.\(^\text{8,19}–\text{21}\)


\(^13\) See, for example: Larson, R. G. The Structure and Rheology of Complex Fluids; Oxford University Press: 1999; Chapter 1.5.2.


\(^16\) Kamacheva, E. Prog. Surf. Sci. 1998, 58, 75–120.


A number of researchers have also investigated high-frequency slip with quartz crystal resonators. There is agreement that—first order in the slip length—slip increases the frequency, which looks like a negative Sauerbrey mass. This makes sense intuitively: if the plane of extrapolated zero-shear is located inside the crystal, this has the same consequences as a hypothetical film with a negative thickness. Daikhin et al. have experimentally investigated the adsorption of pyridine onto gold and could explain their results if they assumed that the adsorbate introduced slip. Ferrante and co-workers have investigated the slip in a variety of different liquids and found that the slippage was larger in liquids of low viscosity. Thompson et al. have also looked into the question of whether trapped gas can explain the apparent negative Sauerbrey mass by virtue of its reduced density alone and concluded that this is not the case. Most recently, Ellis and Hayward determined the slip values for a number of different polar and nonpolar liquids with the QCM and found agreement with the literature values within 1 order of magnitude.

A physical picture has emerged where there are several sources of slip. One potential explanation of slip is the formation of small gas bubbles at a surface which is not wetted well by the liquid. Actually, the formation of gas bubbles may be viewed as wetting of the surface by the gas. The comparison of the effects of hydrophobic and hydrophilic liquids indicates that this mechanism is at work in our experiments, as well, even though we do not claim that it is the only one. It is well-known that wetting on rough surfaces is a process which does not proceed in a laterally homogeneous way. The valleys and crevices of the surface are wetted first due to capillary condensation. Note that, in this case, the wetting phase is a gas rather than a liquid. One could term the phenomenon “inverse capillary condensation” in the sense that the crevices are the dry parts of the surface. If one adopts the view that gas bubbles are the source of slip, laterally heterogeneous slip is a natural consequence. The dry parts of the surface are expected to slip, whereas the wet parts should obey a no-slip condition.

As a first attempt for modeling, one might argue that one can average over the heterogeneities and use the average slip length for viscoelastic modeling in the usual way. However, this picture does not explain our findings. The same is true for the more complicated expressions and the boundary conditions provided in detail below. We start out from the general equation

\[ \frac{\delta f^*}{f_0} = \frac{\delta f + i \delta \Gamma}{f_0} = i \frac{Z_{\text{load}}}{\pi Z_q} = i \frac{(\delta)}{\pi Z_q v_s} \]  

where \( Z_{\text{load}} \) is the impedance at the surface of the quartz. \( Z_{\text{load}} \) is the ratio of stress, \( \langle \alpha \rangle \), and lateral speed at the surface, \( v_s \). \( Z_{\text{load}} \) is not a material constant. For liquids, one has \( Z_{\text{load}} = Z_i \) and the Kanazawa relation results. For films, one has \( Z_{\text{load}} = i \omega \mu_{ij} \) leading to the Sauerbrey equation. Note that we use the stress balance at the interface to derive the frequency shift rather than the integrated kinetic energy and the integrated dissipation. Urbakh and Daikhin have used the latter approach. In the following, we calculate the average stress above a planar and a structured surface on the basis of the Navier–Stokes equation and the boundary conditions provided in detail below.

We assume that the Reynolds number is much less than unity and nonlinearities can therefore be neglected. We can decompose the flow field into its Fourier components and solve the linearized hydrodynamic equations for each Fourier component separately. The Navier–Stokes equation is given by

\[ \rho \frac{dv}{dt} - \eta \nabla^2 v + \nabla p = 0 \]  

where \( v \) is the speed, \( \rho \) is the density, \( \eta \) is the viscosity, and \( p \) is the pressure. The lateral motion occurs along the x-direction at an angular frequency, \( \omega \). The surface normal is \( \mathbf{z} \). The fluid is assumed to be incompressible, leading to volume conservation as expressed by

\[ \frac{dv_x}{dx} + \frac{dv_z}{dz} = 0 \]

Note that, under conditions of incompressibility, the pressure, \( p \), is not a true pressure but rather a variable which always assumes a value ensuring volume conservation.

Smooth Surfaces and Pure Shear. A smooth, laterally oscillating surface with a no-slip boundary condition

induces a pure shear flow, whose $x$-component varies along the $z$-direction according to

$$v_{ps}(x, z, t) = v_s \exp(i(\omega t - k z))$$  \hspace{1cm} (10)

with $k = (-i \omega \rho \eta)_{\|} = k' - ik'' = (1 - i)/\delta$ being the wave vector of shear sound and $v_s$ the lateral speed of the substrate. The index $ps$ stands for “pure shear”. The shear gradient $dv/dz$ is proportional to $v_s/\delta$, with $\delta$ being the penetration depth of the shear wave in the liquid:

$$\delta = \sqrt{\frac{2 \eta}{\omega \rho}}$$  \hspace{1cm} (11)

The stress exerted by the quartz onto the liquid is given by

$$\sigma = -\eta \left( \frac{\partial v_x}{\partial z} + \frac{\partial v_y}{\partial x} \right) \bigg|_{z=0} = i \eta k v_s = \frac{1 + i}{\sqrt{2}} \sqrt{\rho \omega \eta} v_s$$  \hspace{1cm} (12)

From eq 12, one derives the Kanazzawa equation (eq 3) by noting that $\partial^2/\partial z^2 = i/(z Z_p) \partial v_z$.

**Structured Surfaces and Secondary Flow Fields.**

For a structured surface, the field $v_{ps}$ does not fulfill the boundary conditions. Before treating the boundary conditions in detail, we introduce a secondary flow field, $v(x, z, t)$, and write $v_{tot} = v_{ps} + v$. Even without specifying the boundary conditions, certain statements on this field can be made: Since we assume linear hydrodynamics, the field $v(x, z, t)$ can be decomposed into the Fourier series $v(x, z, t) = \sum v_i(x) \exp(i q x) \exp(i \omega t)$. The index $q$ denotes the wave vector of the respective Fourier component. Each component $v_i(x) \exp(i q x) \exp(i \omega t)$ must satisfy linear hydrodynamics: We omit the index $q$ from $v_i$ in the following. For the flow field with the lateral wave vector $q$ along the $x$-direction, we use the ansatz

$$v_i(x, z) = v_{i0} \cos(q x) \exp(-\alpha z)$$

$$v_j(x, z) = 0$$

$$v_z(x, z) = v_{z0} \sin(q x) \exp(-\alpha z)$$

$$p(x, z) = p_0 \sin(q x) \exp(-\alpha z)$$  \hspace{1cm} (13)

where $\alpha$ is a complex decay constant. Inserting this ansatz into eqs 8 and 9, we arrive at the following system of linear equations:

$$i \omega \rho v_{i0} \cos(q x) - \eta (-q^2 + \alpha^2) v_{i0} \cos(q x) + q p_0 \cos(q x) = 0$$  \hspace{1cm} (14a)

$$i \omega \rho v_{i0} \sin(q x) - \eta (-q^2 + \alpha^2) v_{i0} \sin(q x) - q p_0 \sin(q x) = 0$$  \hspace{1cm} (14b)

or equivalently:

$$[i \omega \rho + (q^2 - \alpha^2) \eta] v_{i0} + |q| p_0 = 0$$

$$[i \omega \rho + (q^2 - \alpha^2) \eta] v_{i0} + |\alpha| p_0 = 0$$  \hspace{1cm} (15)

Equation 15 is a linear homogeneous equation system which only has a solution if the determinant vanishes

$$-(i \omega \rho + (q^2 - \alpha^2) \eta) \alpha^2 + (i \omega \rho + (q^2 - \alpha^2) \eta) q^2 = 0$$  \hspace{1cm} (16)

Using $i \omega \rho \eta = -k^2$, this reads

$$(-k^2 + q^2 - \alpha^2)(q^2 - \alpha^2) = 0$$  \hspace{1cm} (17)

Equation 17 has the following two solutions:

$$\alpha_I = \sqrt{q^2 - k^2} = \sqrt{q^2 + 2i \delta^2}$$

$$\alpha_{II} = q$$

The plus sign has been used in the upper line in order to ensure that the wave decays at infinity. $\alpha_I$ and $\alpha_{II}$ correspond to two separate modes. The two modes have the amplitudes $v_{i0I}$ and $v_{i0II}$. The parameter $v_{z0}$ is fixed by eq 14c. For mode I, we find

$$v_{i0I} = -\frac{q}{\alpha_I} v_{z0I}$$  \hspace{1cm} (19)

For mode II, one has

$$v_{i0II} = -v_{z0II}$$  \hspace{1cm} (20)

We now use the boundary condition of the $z$-component at the surface ($v_z(z=0) = 0$) to fix the relative amplitudes of modes I and II. The condition of vanishing vertical flow at the surface implies that

$$[v_{i0I} + v_{z0II}] \sin(q x) = 0$$  \hspace{1cm} (21)

Using eqs 19 and 20, this leads to

$$v_{z0II} = -\frac{q}{\alpha_I} v_{z0I} = -(1 + 2i(q \delta)^2) v_{z0I}$$  \hspace{1cm} (22)

$v_{z0I}$ is the only free amplitude. For simplicity, we term it $v_0$ in the following. $v_0$ is fixed by the $x$-component of the boundary condition. The $x$-component of the flow field is given by

$$v_x(x, z) = v_0 \left[ \exp(-\alpha z) - \frac{q}{\alpha_I} \exp(-q z) \right] \cos(q x)$$  \hspace{1cm} (23)

If the $q$-vector is perpendicular to the direction of shear (that is, along the $y$-direction), the situation is simpler. We make the ansatz

$$v_x(x, z) = v_0 \cos(q y) \exp(-\alpha z)$$

$$v_j(x, z) = 0$$

$$v_z(x, z) = 0$$

$$p(x, z) = 0$$  \hspace{1cm} (24)

where, again, $\alpha$ is a complex decay constant. Inserting this ansatz into the Navier–Stokes equation (eq 8), we find

$$i \omega \rho v_0 \cos(q y) = -q^2 v_0 = 0$$  \hspace{1cm} (25)
or equivalently

$$[i \omega \rho + (q^2 - \alpha^2) \eta]v_0 = 0 \quad (26)$$

Remembering that \(i \omega \rho / \eta = -k^2\), eq 26 is solved by

$$\alpha_i = \sqrt{q^2 - k^2} = \sqrt{q^2 + 2i\delta^2} \quad (27)$$

If the \(q\)-vector is perpendicular to the direction of shear, there is just one mode, the amplitude of which again is determined by the boundary condition of the lateral flow component.

**Boundary Condition with Finite Slip.** Up to eq 27, our calculation is equivalent to the small-roughness calculation done by Urbakh and Daikhin.\(^{37,38}\) In the following, we use a different boundary condition because we claim that slip, rather than roughness, determines the deviations from the Kanazawa line. For the lateral wave vector \(q\) along the \(x\)-direction, the boundary condition reads

$$v_x(x, z)|_{z=0} = b(x) \frac{dv_{tot,x}(x, z)}{dz} \bigg|_{z=0} \quad (28)$$

where \(b(x)\) is the slip length. We again decompose the variability of the slip length into its Fourier components and only consider a certain wave vector, \(q\):

$$\Delta b(x) = \Delta b_{q,q} \cos(qx) \quad (29)$$

where \(\Delta b_{q,q}\) is the amplitude of the slip length variation at the wave vector \(q\). For reasons of continuity, the wave vector \(q\) used here must be the same as the wave vector \(q\) in the flow field (eq 13). Again, we omit the index \(q\) from \(\Delta b_{q,q}\) in the following. According to eq 29, the average of \(\Delta b\) is zero. We have moved the reference plane to a position such that the average slip length is zero; that is, we eliminated uniform slip from our analysis. The reference plane is slightly displaced with respect to the quartz surface. We only consider fluctuations of the slip length around its average.

Inserting eqs 29 and 23 into eq 28, we find

$$v_x(x, z)|_{z=0} = \Delta b_0 \cos(qx) \left\{ \frac{d}{dz} v_s(x, z) - ikv_s \exp(-ikz) \right\} \bigg|_{z=0} \quad (30)$$

A complication has appeared: In the form of eq 23, \(v_x(x, z)\) contains the factor \(\cos(qx)\). As a consequence, eq 30 contains both a term proportional to \(\cos(qx)\) and a term proportional to \(\cos^2(qx)\). It cannot be fulfilled with a secondary flow field of the form given in eq 23. This problem can be stated in another way: since \(\cos^2(qx) = \frac{1}{2}(1 + \cos(2qx))\), eq 30 contains terms with different wave vectors, which are 0, \(q\), and 2\(q\). The boundary condition couples different Fourier components to each other. There is no one-to-one correspondence between the Fourier components of the surface heterogeneity and the Fourier components of the flow field. Equation 30 can only be fulfilled with a secondary flow field containing multiple Fourier components:

$$v_x(x, z) \approx v_0^{(0)} \exp(-\alpha_i^{(0)} z) + v_0^{(1)} \left\{ \exp(-\alpha_i^{(1)} z) - \frac{q}{\alpha_i^{(1)}} \exp(-qz) \right\} \cos(qx) + v_0^{(2)} \left\{ \exp(-\alpha_i^{(2)} z) - \frac{2q}{\alpha_i^{(2)}} \exp(-2qz) \right\} \cos(2qx) \quad (31)$$

We now deal with the three amplitudes \(v_0^{(0)}, v_0^{(1)},\) and \(v_0^{(2)},\) where the superscripts indicate the wave vector. In principle, one should include an infinite number of Fourier components. However, it turns out that the stress resulting from the higher components eventually averages out. It suffices to consider three components only. For the complex decay constants, eq 18 becomes

$$\alpha_i^{(j)} = \sqrt{jq^2 - k^2}, \quad j = 0, 1, 2 \quad (32)$$

Inserting eq 31 into eq 30, we find

$$v_0^{(0)} + v_0^{(1)} \left\{ 1 - \frac{q}{\alpha_i^{(1)}} \right\} \cos(qx) + v_0^{(2)} \left\{ 1 - \frac{2q}{\alpha_i^{(2)}} \right\} \cos(2qx) \approx$$

$$\Delta b_0 \cos(qx) \left\{ -\alpha_i^{(0)} v_0^{(0)} + \left\{ -\alpha_i^{(1)} + \frac{q^2}{\alpha_i^{(1)}} \right\} v_0^{(1)} \cos(qx) + \left\{ -\alpha_i^{(2)} + \frac{4q^2}{\alpha_i^{(2)}} \right\} v_0^{(2)} \cos(2qx) - ikv_s \right\} \cos(qx) \quad (33)$$

Using the trigonometric identities \(\cos^2(qx) = (1 + \cos(2qx))/2\) and \(\cos(qx) \cos(2qx) = (\cos(qx) + \cos(3qx))/2\) and collecting the coefficients to the various wave vectors, one finds a set of the following three equations:

$$v_0^{(0)} = -\frac{1}{2} \Delta b_0 v_0^{(1)} \left( \alpha_i^{(1)} - \frac{q^2}{\alpha_i^{(1)}} \right)$$

$$v_0^{(1)} \left\{ 1 - \frac{q}{\alpha_i^{(1)}} \right\} =$$

$$-ik \Delta b_0 (v_0^{(0)} + v_s) + \frac{1}{2} \Delta b_0 v_0^{(2)} \left( \alpha_i^{(2)} - \frac{4q^2}{\alpha_i^{(2)}} \right) \quad (34)$$

$$v_0^{(2)} \left\{ 1 - \frac{2q}{\alpha_i^{(2)}} \right\} = -\frac{1}{2} \Delta b_0 v_0^{(1)} \left( \alpha_i^{(1)} - \frac{q^2}{\alpha_i^{(1)}} \right)$$

where the relation \(\alpha_i^{(0)} = ik\) has been used. Solving this equation set, we obtain

$$v_0^{(0)} = \frac{1}{2} i \Delta b_0^2 k (\alpha_i^{(1)} + q) v_s$$

$$v_0^{(1)} = \frac{i \Delta b_0 k (\alpha_i^{(1)} + q) v_s}{(\alpha_i^{(1)} - q)} \quad (35)$$

$$v_0^{(2)} = \frac{i \Delta b_0^2 k (\alpha_i^{(1)} + q) \alpha_i^{(2)}}{2(\alpha_i^{(2)} - 2q)} v_s$$

We again write down the full form of the secondary flow field induced by the laterally heterogeneous slip at the surface.
\[ v_x = \frac{1}{2} i \Delta b_x^2 k (\alpha_1(1) + q) v_s \exp(-i k z) - \frac{i \Delta b_x k \alpha_1(1)}{(\alpha_1(1) - q)} \left[ \exp(-\alpha_1(1) z) - \frac{q}{\alpha_1(1)} \exp(-q z) \right] \cos(q x) + \frac{i \Delta b_k k \alpha_2(2) (\alpha_1(1) + q)}{2(\alpha_1(1) - 2 q)} \left[ \exp(-\alpha_1(2) z) - \frac{2q}{\alpha_1(2)} \exp(-2 q z) \right] \cos(2 q x) \]

(36)

\[ v_z = - \frac{i \Delta b_z k \alpha_1(1)}{(\alpha_1(1) - q)} v_s - \frac{q}{\alpha_1(1)} \exp(-\alpha_1(1) z) + \frac{i \Delta b_z k \alpha_2(2) (\alpha_1(1) + q)}{2(\alpha_1(1) - 2 q)} v_s - \frac{2q}{\alpha_1(2)} \exp(-\alpha_1(2) z) + \frac{2q}{\alpha_1(2)} \exp(-2 q z) \sin(2 q x) \]

This secondary flow field solves linear hydrodynamics and the partial-slip boundary conditions. For uniform slip or a no-slip condition (\(\Delta b_0 = 0\)), this secondary flow field vanishes. The secondary flow field is now fully specified, and we can proceed to the calculation of the shear stress induced at the interface. Importantly, we only have to consider the space-averaged stress. This much simplifies the equations. Only the component of the flow field independent of \(x\) does not average out. We have

\[ \langle \sigma \rangle = -i \frac{\vartheta}{\pi Z_q} \left\{ \frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} \right\} \bigg|_{z=0} = -i \frac{\partial}{\partial z} (v_x(0) \exp(-i k z)) \bigg|_{z=0} = -\frac{1}{2} \Delta b_0^2 \eta k^2 (\alpha_1(1) + q) v_s \]

(37)

According to eq 7, the secondary flow component induces a complex frequency shift

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} = \frac{i}{\pi Z_q} \langle \sigma \rangle \bigg|_{z=0} = -i \frac{1}{2 \pi Z_q} \Delta b_0^2 \eta k^2 (\alpha_1(1) + q) \]

(38)

where the index \(s\) indicates the part of the shift related to slip. In the large-\(q\) limit (\(q \gg k, \alpha_1(1) \sim q\), this result is approximated by

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} \approx -i \frac{1}{2 \pi Z_q} \Delta b_0^2 \eta k^2 q = - \frac{\Delta b_0^2}{2 \pi Z_q} \frac{\eta}{\delta^3} q \frac{\delta}{\delta^2} \]

(39)

where \(k^2 = -2i/\delta^2\) has been used. For large \(q\), the secondary flow field only affects the frequency shift and the effect scales as \(n\).

In the limit of a large lateral scale (\(q \ll k, \alpha_1(1) \sim i k\)), eq 38 approximates to

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} \approx \frac{\Delta b_0^2 \eta k^3}{2 \pi Z_q} = \frac{1 + i \eta}{\pi Z_q} \delta \frac{\Delta b_0^2}{\delta^2} \]

(40)

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} \approx \frac{1 + i}{\pi Z_q} \sqrt{\frac{\rho \eta \Delta b_0^2}{2 \delta^2}} \]

(41)

The boundary condition reads

\[ \Delta b_0 \cos(q y) \approx \frac{\Delta b_0}{\pi Z_q} \eta \frac{\Delta b_0^2}{\delta^2} q \delta = \frac{1 + i}{\pi Z_q} \sqrt{\frac{\rho \eta \Delta b_0^2}{2 \delta^2}} \]

(42)

Collecting the coefficients to the different Fourier components and solving this equation system, one finds

\[ v_x^{(0)} = \frac{1}{2} i \Delta b_0^2 k \alpha_1(1) v_s \]

(43)

\[ v_x^{(1)} = -i \Delta b_0 k v_s \]

For the calculation of the stress, we again only need the component independent of \(x\).

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} = \frac{i}{\pi Z_q} \langle \sigma \rangle = -i \frac{1}{2 \pi Z_q} \Delta b_0^2 \eta k^2 (\alpha_1(1) + q) \]

(44)

In the large-\(q\) limit (\(q \gg k, \alpha_1(1) \sim q\), this result is approximated by

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} = -i \frac{1}{2 \pi Z_q} \Delta b_0^2 \eta k^2 q = - \frac{\Delta b_0^2}{2 \pi Z_q} \frac{\eta}{\delta^3} q \delta = \]

(45)

Apart from a numerical factor of \(1/2\), eq 45 is the same as eq 39.

In the small-\(q\) limit, we find

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} = \frac{\Delta b_0^2 \eta k^3}{2 \pi Z_q} = - \frac{1 + i}{\pi Z_q} \delta \frac{\Delta b_0^2}{\delta^2} \]

(46)

Equation 46 happens to be the same as eq 40.

We now focus on the small-\(q\) limit. As eqs 40 and 46 show, the frequency shift in this limit does not depend on \(q\). The above discussion was limited to one single \(q\)-vector. However, as long as \(q\) is smaller than \(\delta^{-1}\), we may consider a random superposition of all Fourier components, rather than a single component, and use the mean-square variability of the slip length, \(\langle \Delta h^2 \rangle\), instead of \(\Delta b_0^2\). Replacing the amplitude squared by the mean square introduces a factor of 2. With these substitutions, we find

\[ \frac{\delta f_s + i \delta \Gamma_s}{f_0} = - \frac{1 + i}{\pi Z_q} \sqrt{\frac{\rho \eta \Delta b_0^2}{2 \delta^2}} \]

(47)
Effects of Laterally Heterogeneous Slip

Table 1. Parameters Obtained by Fitting eq 49 to the Experimental Data Shown in Figures 2, 4, and 5

<table>
<thead>
<tr>
<th>Liquid</th>
<th>(\rho) (g/cm(^3))</th>
<th>(\eta) (cP)</th>
<th>(\eta) (_{\text{max}}) (cP)</th>
<th>(\Delta h_{\text{rms}}) (nm)</th>
<th>(k_f) (cP/(\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water #1</td>
<td>0.997</td>
<td>0.89</td>
<td>1.000</td>
<td>11.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Water #2</td>
<td>0.997</td>
<td>0.89</td>
<td>1.003</td>
<td>9.5</td>
<td>0.11</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.790</td>
<td>1.074</td>
<td>1.229</td>
<td>12.0</td>
<td>0.10</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.785</td>
<td>2.038</td>
<td>2.338</td>
<td>17.8</td>
<td>0.13</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.865</td>
<td>0.56</td>
<td>0.570</td>
<td>&lt;7</td>
<td>&lt;8</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.778</td>
<td>0.894</td>
<td>0.873</td>
<td>&lt;8</td>
<td>&lt;8</td>
</tr>
</tbody>
</table>

\(\Delta h_{\text{rms}}\) is given by

\[
\Delta h_{\text{rms}} = \left( \frac{\Delta b^2}{\delta^2} \right)^{1/2}
\]

where \(\delta = (\nu/\pi \rho_0 \sigma_0)^{1/2}\) is the penetration depth of the shear wave at the fundamental. The experiments can then be represented by functions of the following form:

\[
\frac{\Delta f}{f_0} = \frac{1}{x Z_0} \sqrt{\frac{\eta \rho_0 \sigma_0}{\nu_0}} \left( 1 + \frac{2(\Delta b^2)}{\delta^2 n^2} \right) = -A \sqrt{n} \left( 1 + \frac{2(\Delta b^2)}{\delta^2 n^2} \right)
\]

\[
\frac{\Delta \Gamma}{f_0} = \frac{1}{x Z_0} \sqrt{\frac{\eta \rho_0 \sigma_0}{\nu_0}} \left( 1 - \frac{2(\Delta b^2)}{\delta^2 n^2} \right) = A \sqrt{n} \left( 1 - \frac{2(\Delta b^2)}{\delta^2 n^2} \right)
\]

where \(A = (\pi \rho_0 \sigma_0)^{1/2}(x Z_0)\). Equation 49 is the central result. By fitting the experimental data with eq 49, one can simultaneously obtain the Newtonian viscosity of the liquid, \(\eta\), and the root-mean-square variability of the slip length, \(\Delta h_{\text{rms}} = (\Delta b^2)^{1/2}\), of the electrode—liquid interface. Note that fluctuations of slip decrease the frequency on high overtones, which contrasts to the fact that uniform slip increases the frequency.

Experimental Section

To investigate the effect of slip on the resonance parameters, frequency and bandwidth were measured while the resonator was in contact with a number of liquids with different wetting properties (Table 1). The first set of liquids is hydrophilic, while the second is hydrophobic. The measurements were performed with 5 MHz gold-coated AT-cut quartz crystals (Maxtek, Santa Fe Springs, CA) as received at room temperature (25 °C). The gold electrode used here is rather hydrophobic. The contact angle of water is ~65°. The crystal was mounted in the cell at least 1 day before the measurement in order to obtain a stable baseline free of stress-related drifts. The frequency and the bandwidth shift of the resonator in air were taken as reference for the measurements in liquids. PRIoR to the experiments with the hydrophilic liquids, the quartz was cleaned with ethanol and water, while, prior to the experiments with the hydrophobic liquids, the quartz was washed with acetone, ethanol, and water and dried with nitrogen. The crystal remained in the holder during cleaning. The surface roughness of the electrode was measured by atomic force microscopy (AFM) in tapping mode with a Nanoscope IIIa instrument (DI, Santa Barbara, CA).

Figure 3 presents typical AFM images of the electrode surface as well as cross-sectional profiles. Small gold grains with a size of ~50 nm are observed. This feature is typical of the surface morphology of thin gold films created by vacuum evaporation. Note that the morphology of gold films depends on the substrate, which was optically polished crystalline quartz here. The root-mean-square (rms) roughness, \(R_m\), was smaller than 3 nm for all of the images up to scan areas of 50 \(\mu\)m \(\times\) 50 \(\mu\)m. The peak-to-peak variation is ~9 nm.

It has been reported that crystal surfaces with a roughness of ~15% of the penetration depth can be considered to be hydrodynamically smooth.\(^7\) The penetration depth, \(\delta\), is ~238 and ~57 nm for water at 5 and 95 MHz, respectively. The surface roughness fulfilled this criterion for all of the liquids at all overtones orders. While we cannot strictly rule out an influence of topographical roughness on the shifts of resonance frequency and bandwidth, we consider this influence to be small. In particular, geometric roughness cannot explain a dissipation that is less than what is predicted by the Kanazawa relation (eq 9).

Results and Discussion

Hydrophilic Liquids. First, we investigated the response of quartz resonators to the presence of hydrophilic liquids. Since the gold surface is hydrophobic, one expects the formation of small air bubbles\(^8\) and a concomitant slip. Figure 2 shows two data sets for water. Parts a and b show the frequency shift, \(\Delta f\), and the bandwidth shift, \(\Delta \Gamma\), versus the square root of the overtone order. The results are very similar for the two surfaces. The frequency shift is always larger than the bandwidth shift, that is, \(\Delta f + \Delta \Gamma < 0\), as shown in part d. To further emphasize that the data are well fitted by eq 49, we have plotted the quantities \(\Delta f - \Delta f = 2\Delta n^{1/2}\) and \(\Delta f + \Delta \Gamma = -4\pi(\Delta b^2)\delta m^{1/2}\) in parts c and d. The derived viscosity and the mean-square slip length fluctuations (which are the only fit parameters) are provided in Table 1. The reference literature values in Table 1 are from ref 41. The slip length fluctuations were also converted to fluctuations of the interfacial friction coefficient, \(\Delta k_f\), via the relation\(^11\)

\[
\langle \Delta b^2 \rangle^{1/2} \approx \Delta b = \frac{\eta}{k_f} \Delta k_f \sim \frac{\eta}{k_f} \Delta k_f
\]

In the last approximation, it was assumed that the interfacial friction coefficient is of the same order of magnitude as its fluctuations.

Figure 4 shows experimental data taken with quartz #2 in contact with three different hydrophilic liquids, which are water, ethanol, and 2-propanol. The response of the crystal is similar for these three liquids. The frequency shift is always larger than the shift in bandwidth, that is, \(\Delta f + \Delta \Gamma < 0\). Equation 49 fits the data well. The fit parameters are again provided in Table 1.

One of the three liquids, 2-propanol is the least hydrophilic. This liquid should therefore wet the gold surface best, and one would expect it to have the smallest slip length. However, the contrary is the case. Note, however, that the slip length is the ratio of the viscosity and the interfacial friction coefficient. Not only is 2-propanol the liquid with the largest slip length, but it is also the most viscous fluid. The friction coefficient, \(k_f\), calculated by eq 50 in fact is similar for the three liquids.

Hydrophobic Liquids. For comparison, we further investigated the response of quartz crystal resonators in hydrophobic liquids. Hydrophobic liquids wet the gold surface well and therefore should not lead to gas bubbles and slip. Figure 5 shows two data sets taken with crystal #2 in contact with toluene and cyclohexane. In this case, the frequency shift is not always larger than the shift in bandwidth. Clearly, eq 49 cannot fit the data. Actually, there still is a slight downward curvature of the quantity \(\Delta f + \Delta \Gamma\), but its magnitude is much less than that for the hydrophilic liquids. The measured viscosity is ~0.570 and ~0.873 cP for toluene and cyclohexane, respectively, which is very close to the literature values (Table 1).

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Our principal results are that lateral heterogeneity of the slip condition is important for the analysis of data obtained with the QCM. The values which we obtain make sense because the slip is larger for a hydrophilic liquid on a hydrophobic surface than for a hydrophobic liquid on a hydrophobic surface. We did not go through special measures in order to characterize the gold surface very well or to ensure the reproducibility of surface preparation. This is a challenge for gold surfaces, because they instantaneously adsorb organic molecules when exposed to solvent vapor. In particular, we do not quantitatively compare our slip lengths to the slip lengths obtained in ref 30 because these authors used hydrophilic gold surfaces. We can however confirm the results of Craig et al.19 and Neto et al.,21 who said that the slip length strongly depends on the viscosity, whereas the interfacial friction coefficient $k_f$ shows less variability. This suggests that the interfacial friction coefficient is the more fundamental parameter.

Conclusions

The frequency shift and the bandwidth shift of quartz crystal resonators immersed in simple liquids often follow a law given by

$$\delta f = -An^{1/2}(1 + Bn)$$

and $\delta \Gamma = An^{1/2}(1 - Bn)$ (eq 6). The term $Bn$ describes a deviation from the well-known Kanazawa relation. It is straightforwardly determined by fitting the function $-2Bn^{1/2}$ (with the single fit parameter $B$) to the sum of the frequency shift and the bandwidth shift, $\delta f + \delta \Gamma$.

The dissipation on high harmonics deviates to values lower than what is predicted by the Kanazawa relation. Also, the deviations in frequency and bandwidth go in parallel. This finding cannot be explained by any of the current models for the influence of either roughness or slip. We propose laterally heterogeneous slip created by nanoscopic air bubbles as an explanation. The calculation confirms the functional form of the deviations as described above if, first, the rms fluctuation of the slip length is smaller than the decay depth of the shear waves, $\delta$, and, second, the lateral size of the dry patches is larger than $\delta$. These are very realistic assumptions. For such a situation, the term $B$ turns out to be equal to $2\langle \Delta b \rangle^2/b_0^2$, where $\langle \Delta b \rangle^2$ is the mean-square fluctuation of the slip length and $b_0$ is the decay length on the fundamental frequency.

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