Spreading of liquids and soft solids on a rigid surface in a surrounding liquid medium is investigated by utilizing the lateral sensitivity of the quartz crystal microbalance (QCM). While the QCM has been used extensively to study systems with spatial variations in the direction normal to the crystal's electrodes, few studies have exploited the QCM's ability to sense changes in loading in the plane of the electrodes. We propose equations to describe the predicted response of the QCM to a generalized viscoelastic material spreading at the QCM surface at the expense of the surrounding liquid medium. Several experimental examples are given in order to support the validity of the proposed equations, including situations where the spreading material is a Newtonian liquid, a viscoelastic liquid, or one of two viscoelastic solids. The first viscoelastic solid is a physically cross-linked gel based on a styrene/ethylene–butene/styrene triblock copolymer in mineral oil, and the second is a cross-linked poly(ethylene glycol) hydrogel.

The widespread use of the quartz crystal microbalance (QCM) can be attributed to its excellent sensitivity to the properties of liquid and soft solid materials with which it is brought into contact. This sensitivity arises from the coupling between the mechanical, shear oscillation of the crystal and its electrical response at frequencies close to resonance. This coupling depends on the details of the shear wave propagation into the material with which the QCM is in contact. For most liquid and soft viscoelastic materials, the decay length of this shear wave is on the order of 100 nm; so in these cases, the QCM is truly a surface-sensitive technique. This surface sensitivity is responsible for a wide range of applications in biology and electrochemistry, where the QCM is often used to sense material that is absorbed to the crystal surface from solution.

The material property that determines the response of the QCM is the complex acoustic impedance of the loading material.

In many cases, the acoustic impedance varies with the distance from the crystal surface, and models accounting for this depth dependence must be utilized in order to interpret the data. QCM studies of adsorption from aqueous solution are one example of this type of approach. In these cases, it is almost always appropriate to assume that the system is homogeneous along the crystal surface. In this paper, we are interested in the opposite situation, where spatial heterogeneities exist primarily in the lateral direction. In particular, we study a spreading contact area of one material surrounded by another at the QCM surface. Lin and Ward have investigated one such system, involving droplets of one Newtonian liquid growing in another. In this paper, we extend their work by investigating the more general case of a viscoelastic material spreading across the QCM surface that is immersed in a Newtonian liquid. We begin with a background section outlining the equations necessary to describe the response of the QCM to this general loading condition. The initial section is followed by a discussion of compressional waves, which often complicate the analysis when the QCM is operating in a liquid environment. In the Results and Discussion section, several experimental examples are given to test the validity of the generalized equations for both Newtonian liquids and viscoelastic materials submerged in a Newtonian liquid.

BACKGROUND

QCM Loading by Soft Materials. We begin with the general assumption of a homogeneous surface coverage of one side of the QCM. The response of the QCM to such a load can be generalized in terms of a complex frequency shift in the crystal's resonant frequency, \( \Delta f_n^* \), which has the following form:

\[
\Delta f_n^* = \Delta f_n + i \Gamma_n
\]

(1)

where the real part of the complex frequency shift, \( \Delta f_n \), is the change in resonant frequency and the imaginary part, \( \Gamma_n \), is the change in dissipation. The subscript \( n \) is used to denote the...
existence of multiple harmonic frequencies. In our experiments, we operate at the third harmonic \((n = 3)\) of crystals with a fundamental frequency of 5 MHz (i.e., \(f_1 = 5\) MHz and \(f_2 = 15\) MHz). The complex frequency shift is linearly related to the complex acoustic impedance, \(Z^*\), of the loading material:

\[
\Delta f^*_n = \frac{j}{\pi} \frac{Z^*}{Z_q} \quad (2)
\]

where \(Z_q = (\rho_q \mu_q)^{1/2}\) is the acoustic impedance of the quartz. Here, \(\rho_q\) is the density of quartz \((2.65 \text{ g/cm}^3)\) and \(\mu_q\) is the shear modulus of quartz \((2.95 \times 10^{10} \text{ Pa})\).

For a semi-infinite material, that is, one that is much thicker than the decay length of the acoustic shear wave in the material, \(Z^* = (\rho_0 G^*)^{1/2}\), where \(\rho_0\) and \(G^*\) are the density and complex shear modulus of the viscoelastic material. \(G^*\) is conveniently defined by its magnitude, \(|G^*|\), and phase angle, \(\phi\), such that \(G^* = |G^*| e^{i\phi}\). Therefore, the complex frequency shift of the QCM can be rewritten in terms of the material properties of a viscoelastic loading material as follows:

\[
\Delta f^*_n = \frac{j}{\pi Z_q} (\rho_0 |G^*|)^{1/2} e^{i\phi/2} \quad (3)
\]

**Radial Sensitivity.** Because of the nonuniform shear displacement profile at the surface of the QCM, eq 3 must be modified if the loading material is in contact with only a portion of the quartz crystal. The QCM surface vibration is primarily confined to the area defined by the electrodes so that the shear displacement is largest at the center and decays to zero in a roughly Gaussian manner toward the perimeter of the electrodes. Thus, the active area of the QCM is defined by the smaller of the two electrodes deposited on either side of the quartz crystal. A Gaussian expression of the following form is often used to describe the distribution of the shear displacement amplitude, \(u\), across the QCM as a function of radial position, \(r\):

\[
u(r) = u_{\text{max}} \exp\left(-\beta \left(r^2/r_0^2\right)\right) \quad (4)
\]

where \(u_{\text{max}}\) is the maximum amplitude at the center of the electrodes \((r = 0)\), \(r_0\) is the radius of the smaller electrode, and \(\beta\) is a factor that determines the sharpness of the Gaussian curve. The value of \(\beta\) is generally around 1, though it is dependent on both the overtone order and the loading condition of the QCM.

The sensitivity of the QCM is related to the energy imparted into the loading material from the vibrating quartz crystal, and this energy scales as the square of the surface shear displacement, \(u^2(r)\). The sensitivity of the QCM is therefore maximized at the center, an effect that is often referred to as energy trapping. In our experiments, the loading is not uniformly imposed on the crystal, as assumed by eq 3, but is instead confined to a circular area of radius \(a\) that is centered at \(r = 0\). The overall response of the QCM is determined by the ratio of the loaded area, \(A\), to the active area \(A_0\). Here \(A = \pi a^2\) and \(A_0 = \pi r_0^2\). It is possible to define a sensitivity factor, \(K_s\), so that the response of the crystal as given by eq 3 is multiplied by a factor \(K_s A/A_0\). The value of this multiplicative factor is obtained as the ratio of the integrated squared surface shear displacement across the contacted area to the same integral evaluated over the entire surface of the quartz crystal:

\[
K_s A/A_0 = \frac{2\pi r^2 (r)}{A_0} - 1 - \exp\left(-2\beta \frac{A}{A_0}\right) \quad (5)
\]

where \(r_0\) is the radius of the entire quartz crystal, which is assumed to substantially exceed the value of \(r_0\). Inclusion of the radial sensitivity factor given by eq 5 into the expression for \(\Delta f^*_n\) yields the following, more general expression:

\[
\Delta f^*_n = -\left(1 - \exp\left(-2\beta \frac{A}{A_0}\right)\right) \frac{j}{\pi Z_q} (\rho_0 |G^*|)^{1/2} e^{i\phi/2} \quad (6)
\]

For small contact areas, \(K_s\) reduces to \(2\beta\), and \(\Delta f_n^*\) and \(\Delta \Gamma_n\) both increase linearly with the contact area. When \(A/A_0\) is large, \(K_s A/A_0\) approaches unity and the QCM equations describing the response to uniform crystal loading are recovered.

**Liquid Loading.** We can now consider the situation where the upper electrode of the QCM is submerged in a viscoelastic liquid (material 1) and then probed with a second viscoelastic material (material 2), which is in contact with the QCM over an area, \(A\). The change in complex frequency of the QCM upon loading by material 2 is now dependent on the properties of both materials 1 and 2 because of the changing acoustic impedance, \(\Delta Z^*\), sensed by the QCM. Equation 2 must be modified as follows:

\[
\Delta f^*_n = -\left(1 - \exp\left(-2\beta \frac{A}{A_0}\right)\right) \frac{j}{\pi Z_q} \frac{\Delta Z^*}{Z_q} \quad (7)
\]

where \(\Delta Z^* = Z^*_2 - Z^*_1\). Furthermore, eqs 6 and 7 can be expanded to yield expressions for \(\Delta f_n^*\) and \(\Delta \Gamma_n\) that include the physical properties of both materials 1 and 2:

\[
\Delta f_n = -\left(1 - \exp\left(-2\beta \frac{A}{A_0}\right)\right) \frac{j}{\pi Z_q} \{ |G^*_2|^{1/2} \sin(\phi_2/2) - (\rho_2 \mu_2)^{1/2} \sin(\phi_2/2) \} \quad (8)
\]

\[
\Delta \Gamma_n = -\left(1 - \exp\left(-2\beta \frac{A}{A_0}\right)\right) \frac{j}{\pi Z_q} \{ |G^*_2|^{1/2} \cos(\phi_2/2) - (\rho_2 \mu_2)^{1/2} \cos(\phi_2/2) \} \quad (9)
\]

where we have utilized the trigonometric relationship \(e^{i\phi/2} = \cos(\phi/2) + i \sin(\phi/2)\). Note that if \(\Delta Z^* = 0\), the QCM will detect no change in its environment. Furthermore, if \(\Delta Z^* < 0\), the resonant frequency will **increase** while the change in dissipation will **decrease**, which is opposite of the QCM response in air when

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In the sections below, eqs 8 and 9 will appear in various forms depending on the particular system studied. For example, if materials 1 or 2 are Newtonian liquids, the QCM equations can be simplified to include viscosities instead of complex shear moduli.

**Compressional Waves.** An interesting but often complicating feature of the QCM under liquid loading conditions is the presence of longitudinal waves normal to the surface of the quartz. These so-called “compressional waves” have been reported and studied by a number of investigators. Compressional waves arise primarily from a conservation of mass in the liquid at the QCM surface. Due to the radial distribution of shear wave amplitudes at the surface of the QCM, there is a velocity gradient at the surface of the oscillating crystal. To satisfy the Navier–Stokes equations for fluid velocity, the in-plane velocity gradient of the liquid dictates that a velocity component must also exist in the direction normal to the QCM surface. This out-of-plane velocity oscillates at the same frequency as the quartz, resulting in a longitudinal pressure wave.

Unlike shear waves, longitudinal waves do not rapidly decay as they travel through a viscous medium. Thus, compressional waves can travel away from the QCM surface, reflect at some interface, and then return to the quartz. Depending on the phase of the returning wave, interference occurs, which manifests itself as a disturbance in the QCM response on the order of tens of hertz. This interference can be observed by moving a smooth, solid plate that is parallel to the crystal surface up and down in the surrounding liquid. The periodicity of the QCM response to the interfering compressional waves will be inversely proportional to the velocity of the moving plate. Alternatively, the liquid above the QCM can simply be allowed to evaporate. In this case, the air–liquid interface acts as the reflecting surface for the compressional waves; so as the liquid evaporates, the interface moves toward the crystal and results in periodic interference.

Experimentally, it is generally desirable to reduce the effects of compressional waves, either by eliminating the reflecting surface or by ensuring that the surface remains stationary. For instance, liquid experiments can often be done in a closed environment to prevent evaporation. Alternatively, a stationary reflecting plate can be inserted into the liquid to prevent changing interference conditions. In many of the contact mechanics experiments described in this paper, there is a moving interface that travels through the liquid. Fortunately, in all of those cases, the indenter is hemispherical in shape, so the longitudinal waves are scattered in many directions and the interference attributed to compressional waves is greatly reduced.

The significance of compressional waves in the experiments described below can be summarized in Figure 1. The large plot shows the effects of compressional wave interference on the resonant frequency of the QCM ($f_0 = 15$ MHz) for a reservoir of water allowed to evaporate. The noise is on the order of $\pm 20$ Hz in contrast to a stability of less than 1 Hz in air. The inset shows the noise level for the same water reservoir with a hemispherical Kraton gel traveling through the liquid toward the QCM surface. Here, the noise has been reduced 10-fold to $\pm 2$ Hz. The response of the dissipation is comparable to that of the resonant frequency in both conditions.

**EXPERIMENTAL SECTION**

**Polymer Systems.** Many of the experiments discussed below involve the use of H2O, which was deionized and provided by our own campus facilities. 2-Ethylhexanol was purchased from Sigma-Aldrich (104-76-7, St. Louis, MO). Poly(styrene) (PS) was synthesized by anionic polymerization and had a weight average molecular weight, $M_w$, of 193,000. Solutions of PS in chloroform (CX1058-6, EMD Chemicals, Inc., Gibbstown, NJ) were prepared at polymer concentrations of 0.05, 0.10, 0.15, and 0.20 g/cm$^3$.

Kraton G purchased commercially is a triblock copolymer with PS end blocks and a midblock composed of a random distribution of poly(ethylene) (PE) and poly(1-butene) (PB). The total molecular weight of the polymer is ~170,000, with the PE/PB midblock comprising ~70% of the polymer by mass. To form gels, the Kraton polymer was mixed with light mineral oil (33079-1L, Sigma-Aldrich) at concentrations of 0.10, 0.15, 0.20, and 0.25 g/cm$^3$. The mixtures were heated to 175 °C for 1 h and then allowed to cool, resulting in the formation of elastic gels. The thermally reversible nature of the gels provides a means for easily fashioning them into any desired shape. For this study, hemispherical gels were formed in a mold of cross-linked poly(dimethyl siloxane) (Sylgard 184, Dow Corning, Midland, MI). The radius of curvature for each of the gels was 6 mm.

Poly(ethylene glycol) (PEG) hydrogels were synthesized as described previously. Briefly, solutions of PEG homopolymer ($M_w = 8000$), terminated with polymerizable acrylic end groups, were prepared in phosphate-buffered saline at a concentration of 0.15 g/cm$^3$. A photoinitiator, 2,2′-dimethoxy-2-phenylacetophenone, was added to the polymer solutions. Drops of the
solutions were placed on a hydrophobic surface and irradiated with a UV lamp for at least 2 min, which polymerized the acrylic groups to form chemically cross-linked hemispherical hydrogels. The gels had a mean radius of curvature of 3.1 mm and an average Young’s modulus of 70 kPa.

**QCM Methodology.** Quartz crystals with circular gold electrodes and fundamental resonant frequencies of 5.0 MHz were purchased from Maxtek, Inc. (149257-1, Santa Fe Springs, CA). In all cases described below, the crystals were oscillated at their third harmonic frequency ($f_3 = 15.0$ MHz) due to enhanced stability over the fundamental resonant frequency as a result of better energy trapping. In some instances, the quartz crystals were coated with polystyrene films (~100 nm thick) prior to mechanical testing by spin casting from dilute solutions in toluene (244511-1L, Sigma-Aldrich). The quartz crystals were designed to fit into a specialized holder, which provided good electrical contact to the gold electrodes as well as a rigid mounting of the crystal (CHC-100, Maxtek, Inc.). The geometry of the holder was such that the crystal could easily be flooded with any desired liquid to a depth of several millimeters. The crystal holder was connected to a network analyzer (250B-1, Saunders & Associates, Phoenix, AZ) that measured the complex admittance across the QCM. The control of the network analyzer and the collection of data were managed by a software program designed by Prof. Diethelm Johannsmann (QTZ, Resonant Probes, Goslar, Germany).

For QCM experiments involving drops of one liquid submerged in another, the drops were deposited from above using a flat-ended syringe. Images of the droplets were recorded using a low-magnification microscope (Zoom 6000, Navitar, Inc., Rochester, NY) connected to a CCD camera (KP-M2AN, Hitachi Kokusai Electric, Inc.). For experiments involving hemispherical polymer gels, a contact mechanics geometry modeled after the work of Johnson, Kendall, and Roberts (JKR) was employed. This geometry, which in this paper involves bringing a hemispherical soft material into contact with a flat, rigid substrate, will be referred to herein as the JKR geometry. In a typical JKR experiment, a gel was attached to a glass slide connected to a piezoelectric inchworm motor (IW-702-00, Burleigh Instruments, Fishers, NY) that was used to move the gel into contact with the QCM surface. The compressive and tensile forces between the gel and the QCM were measured with a load transducer (FTD-G-50, Schaevitz Sensors, Hampton, VA), while the displacement of the motor was recorded with a fiber-optic motion sensor (RC62-GLMORV, Philtec, Annapolis, MD). A microscope and CCD camera were used to capture images of the interfacial contact between the gel and the QCM, though visualization was not possible in the case of the PEG hydrogels immersed in water because of poor optical contrast. The motion of the motor and the collection of load, displacement, and image data were automatically controlled using a LabVIEW software program. In a typical contact experiment, the polymer gel was pressed into the QCM at a rate of 1–3 μm/s up to a maximum compressive load. The direction of the motor was then reversed, and the gel was pulled away from the QCM surface.

In all cases described below, the crystals were oscillated at their fundamental resonant frequencies of 5.0 MHz. The QCM was submerged in a fluid at a rate of 1 m/s up to a maximum compressive load. The direction of the motor was then reversed, and the gel was pulled away from the QCM surface.

**RESULTS AND DISCUSSION**

In the following sections, we apply eq 7 to contact studies in a variety of materials systems. In all cases, the top half of the QCM was first submerged in a Newtonian liquid, which was either water or mineral oil. A second Newtonian liquid or viscoelastic material was then immersed in the first Newtonian liquid and brought into contact with the surface of the crystal. Results for each type of material combination are described below.

**Two Newtonian Liquids.** We begin with the simple case of a growing drop of 2-ethylhexanol centered on the QCM and surrounded by water, as illustrated in Figure 2a. In this example, no additional coatings were applied to the QCM, so the upper gold electrode was the exposed surface. Though 2-ethylhexanol is less dense than water, droplets of the former are stable at the gold–water interface due to the adhesion of 2-ethylhexanol to gold. Equations 8 and 9 can be simplified to predict the response of the QCM to this particular loading condition. Since water and 2-ethylhexanol are both Newtonian liquids, the phase angle of the complex shear modulus for both liquids is 90°. Furthermore, $G^* = G'' = 2\sigma_d\eta_d$, resulting in the following equation:

$$-\Delta\sigma_n = \Delta\Gamma_n = \left(1 - \exp\left(-\frac{2\beta A}{A_d}\right)\right)\frac{f_3}{Z_{\eta_d}^{1/2}}\left(\rho_{2EH}\eta_{2EH}\right)^{1/2} - \left(\rho_{H2O}\eta_{H2O}\right)^{1/2}$$

(10)

where $\eta_{2EH}$ and $\eta_{H2O}$ are the Newtonian viscosities of 2-ethylhexanol and water, respectively. Equation 10 is similar to an equation proposed by Lin and Ward for liquid–liquid systems on the QCM. It can be used to illustrate an important point concerning the resolution of the QCM: if the product $\rho_\eta$ is the same for both liquids ($\Delta\sigma_n = 0$), there will be no change in the resonant frequency or dissipation of the QCM as the droplet of liquid 2 grows. Conversely, if $\rho_\eta$ for liquid 2 is much greater than that for liquid 1 ($\Delta\sigma_n \gg 0$), the effects due to the displacement of liquid 1 become negligible. Accordingly, 2-ethylhexanol droplets in water offer a nice model system because there is an intermediate degree of contrast.

Figure 3 is a plot of $\Delta\sigma_n$ and $\Delta\Gamma_n$ versus fractional contact area as a droplet of 2-ethylhexanol grows at the gold–water interface.

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In this and all of the following experiments described in this paper, the third harmonic frequency is used instead of the fundamental resonant frequency due to better stability of the resonance, which is generally ascribed to better energy trapping. The lines are modified to account for a viscoelastic material growing in water, as follows:

\[ \Delta f_{u} = - \left( 1 - \exp \left( -2\beta A/A_{0} \right) \right) \frac{f_{1}}{\pi \Delta Z_{q}} \left( \rho_{u} \left( G^{*} \right)^{1/2} \sin \left( \phi/2 \right) \right. \]
\[ \left. - \left( f_{u} \rho_{H_{2}O} / \rho_{H_{2}O} \right)^{1/2} \right) \]  
(11)

\[ \Delta \Gamma_{u} = \left( 1 - \exp \left( -2\beta A/A_{0} \right) \right) \frac{f_{1}}{\pi \Delta Z_{q}} \left( \rho_{u} \left( G^{*} \right)^{1/2} \cos \left( \phi/2 \right) \right. \]
\[ \left. - \left( f_{u} \rho_{H_{2}O} / \rho_{H_{2}O} \right)^{1/2} \right) \]  
(12)

Chloroform is a good solvent to work with in this case because it is immiscible with water. Also, it is more dense than water (\( \rho_{c} = 1.47 \) g/cm\(^3\)), so it is easy to form droplets of chloroform at the gold–water interface.

In Figure 4, we plot the change in dissipation of the QCM as droplets of PS solutions grow at the QCM–water interface. Lines are drawn using eq 12 with the appropriate viscoelastic parameters held constant and \( \beta = 1.00 \).

Viscoelastic Liquid in a Newtonian Liquid. In this section, we again study droplets of one liquid growing in another at the QCM surface, as in Figure 2a, but in this case the droplets are viscoelastic. The surrounding liquid is still water, but the droplets are solutions of PS in chloroform. Thus, eqs 8 and 9 must be modified to account for a viscoelastic material growing in water, as follows:

Figure 3. Changes in QCM resonant frequency (circles) and dissipation (squares) vs fractional contact area as a droplet of 2-ethylhexanol grows at the gold–water interface. Lines representing eq 10 are shown for two different values of \( \beta \).

Figure 4. Change in QCM dissipation vs fractional contact area as droplets of PS solutions grow at the QCM–water interface. Lines are drawn using eq 12 with the appropriate viscoelastic parameters held constant and \( \beta = 1.00 \).

Viscoelastic Solid in a Newtonian Liquid: Part I. We now examine the situation where the QCM is submerged in a Newtonian liquid and probed by a solid gel, where an increasing gel–QCM contact area comes at the expense of an identical liquid–QCM contact area, as shown in Figure 2b. For the loading condition of a viscoelastic solid in a Newtonian liquid, eqs 11 and 12 are again valid. To study such a system, we turn to Kraton gels contacting a PS-coated QCM, where the interface is now submerged in water.

Figure 5a shows conductance versus frequency curves for the QCM submerged in water with and without a small interfacial...
contact area between a Kraton gel and the crystal. Upon gel loading, the peak conductance decreases, the resonant frequency decreases, and the half-width at half-maximum of the curve, $\Gamma_3$, increases. However, these features are quite subtle in comparison to the changes seen for gel contact in air, shown in Figure 5b. In the liquid immersion experiments, one material establishes interfacial contact with the QCM at the expense of another, and if the two have similar viscoelastic properties, the QCM response will be quite small. However, the viscosity of mineral oil is so much larger than that of water (by a factor of $\sim 25$) that the QCM can resolve the effects of Kraton gel loading in water reasonably well.

Figure 6a shows the interfacial contact area as a function of the normal displacement in a JKR experiment between a Kraton gel with a concentration of 0.15 g/cm$^3$ and a PS-coated QCM that is submerged in water. Initially, the contact area grows as the displacement increases. Then, when a certain maximum compressive load is reached, the direction of the motor changes and the displacement decreases as the gel is pulled away from the QCM.

Figure 6b shows the QCM response to the contacting Kraton gel during the same experiment. Qualitatively, the resonant frequency decreases and the dissipation increases with increasing displacement. Another feature to note about Figure 6b is that the data are a bit noisy. There are at least two sources of this noise: the first involves compressional waves, which were discussed in Compressional Waves. However, this phenomenon only accounts for a few hertz of noise as the gel moves through the water. The other source of noise, which seems to be dominant, is that the resonance of the QCM is not as sharp once the crystal becomes heavily damped. As the sharpness of the resonance decreases, the QCM software has a more difficult time fitting the admittance curves, resulting in data that appear noisy. Still, the signal-to-noise ratio in these samples is sufficiently high that a quantitative analysis is warranted.

In Figure 7, both $\Delta f_3$ and $\Delta \Gamma_3$ are plotted against $A/A_0$ for four different concentrations of Kraton gels. Only the loading portions (increasing contact area) of the data are shown. Fits to the curves using eqs 11 and 12 are provided, where $|G^*|^{1/2} \sin(\phi/2)$ and $|G^*|^{1/2} \cos(\phi/2)$ are the adjustable parameters, respectively. The other variables are held constant as follows: $\beta = 1.00$, $f_1 = 5.0$ MHz, $f_2 = 15.0$ MHz, $\rho_0 = 0.84$ g/cm$^3$, $\rho_{\text{gel}} = 1.0$ g/cm$^3$, and $\mu_{\text{gel}} = 1.0$ mPa-s. Values obtained for $|G^*|$ and $\phi$ from this procedure are plotted as a function of the polymer concentration in the gel in Figure 8, where we also include values obtained for the case where the gels were not immersed in water but were brought directly into contact with a QCM in air. While the air and water values of these parameters are close to one another, the gels in water exhibit an enhanced dissipation, with larger values of both $\Delta f_3$ and $\Delta \Gamma_3$. 

![Figure 5](image1.png)  
**Figure 5.** Change in the conductance across the QCM upon loading by a hemispherical Kraton gel with the crystal (a) initially submerged in water and (b) in air.

![Figure 6](image2.png)  
**Figure 6.** (a) Fractional contact area and (b) changes in resonant frequency and dissipation as a function of advancing and receding displacement over the course of a JKR-QCM contact experiment in water for a 0.15 g/cm$^3$ Kraton gel.
The reasons for this discrepancy at this point are unclear but may be due to subtle differences in the nature of the gel–QCM interface. A very thin modified layer at this interface will change the response of the QCM, so that properties within the contact zone can no longer be considered to be uniform in the direction normal to the crystal surface. These effects may be responsible for the fact that different values of $\beta$ are needed to fit the data in Figures 3 and 4, and we are currently designing experiments to probe this issue in more detail.

During a contact cycle between a Kraton gel and a PS-coated QCM, a thin film of mineral oil is transferred to the PS substrate after gel detachment. Quantitatively, the presence of this transferred oil film is manifested in the fact that the resonant frequency of the QCM does not return to zero after the gel contact experiment, as can be seen in Figure 6b. For the case of a thin, viscoelastic film created at the interface between the QCM and a semi-infinite, viscoelastic liquid, Johannsmann proposed the following QCM response in terms of a complex frequency shift:

$$\Delta f^* = -\frac{2f f_s \rho_f}{Z_q} \left( 1 - \frac{\rho G'_l}{\rho G'_f} \right)$$  \hspace{1cm} (13)$$

where “l” subscripts refer to the semi-infinite liquid and “f” subscripts refer to the film. In the case of a mineral oil film submerged in water, both the film and the liquid are Newtonian, so $G'_l$ and $G'_f$ can be replaced with $2\eta f_l$ and $2\eta f_f$, respectively. Making these substitutions and adding the prefactor to account for a fractional contact area, we find that there is no predicted change in dissipation and the change in resonant frequency is given by

$$\Delta f_n = -\left( 1 - \exp\left( -2\beta A A_0 \right) \right) \frac{2f f_s \rho_f}{Z_q} \left( 1 - \frac{\rho f_l}{\rho f_f} \right)$$  \hspace{1cm} (14)$$

Equation 14 is nearly the same as the prediction for the change in resonant frequency of the QCM loaded by a thin film in air. The submersion of the film in a liquid medium acts as perturbation to the system, represented by the last term in eq 14, which involves a ratio of densities and viscosities. Since the viscosity of mineral oil is so much larger than that of water, the perturbation accounts for less than 5% of the total frequency shift.

Figure 9 plots the thickness of oil films transferred to the QCM versus polymer concentration for Kraton gels that have been loaded and subsequently removed from the QCM surface. The thickness values are calculated using eq 14 with $\beta = 1.0$, $f_f = 5.0$ MHz, $f_l = 15.0$ MHz, $\eta_f = 1.0$ g/cm$^3$, $\eta_l = 1.0$ mPa·s, $\rho_f = 0.84$ g/cm$^3$, and $\rho_l = 26$ mPa·s. The relevant contact area of the films is taken to be the maximum contact area established between each Kraton gel and the QCM during a contact experiment. In Figure 9, the filled symbols represent transfer in air and the open symbols represent transfer in water. The general trend of the data is that the transferred oil films decrease in thickness with increasing polymer concentration. Clearly, within the scatter of the data from multiple experiments, the presence of the water does little to affect the thickness of the transferred oil film. This result can be explained in the context of an argument that was presented previously, where the osmotic pressure of the Kraton...
gels was set equal to the disjoining pressure of the transferred oil films in order to relate film thickness to polymer concentration. It was shown that the film thickness is predicted to be only weakly related to the Hamaker constant, $A_{\text{Ham}}$, of the mineral oil film at the PS–air or PS–water interface ($t \sim (-A_{\text{Ham}})^{1/3}$). The similarity in the oil thickness data for the air and water cases is consistent with this weak dependence on the Hamaker constant, which will differ for the PS–oil–air and PS–oil–water systems.

**Viscoelastic Solid in a Newtonian Liquid: Part II.** In this paper, we have studied several systems that resulted in increased acoustic impedance at the surface of the QCM or, in terms of eq 7, systems where $\Delta Z^*$ is positive. As mentioned previously, any soft material studied in air will result in an increase in $Z^*$. However, when the QCM is immersed in a liquid, there is the possibility of a negative change in $Z^*$. This section describes QCM experiments involving a PEG hydrogel in water and in mineral oil to give examples of cases where $\Delta Z^*$ is close to zero or even negative.

In terms of the QCM response, a gel submerged in its own solvent is interesting because there may not be a clear physical boundary defining the interface between the gel and the liquid. Instead, there may be somewhat of a gradient in polymer concentration at the interface increasing from zero in the pure liquid to some bulk value within the gel. Furthermore, since the density and viscosity of the gel’s solvent and the surrounding liquid are the same, the ability of the QCM to resolve the presence of the gel will depend solely on the polymeric contribution to the gel’s acoustic impedance. To illustrate this resolution issue, Figure 10 plots $\Delta f_3$ and $\Delta \Gamma_3$ for a PEG hydrogel contacting the QCM in water. For clarity, only the compressive loading portions of the curves are shown. While it was not possible to directly measure contact areas for this system, areas can be calculated from the load and displacement data since Hertzian (nonadhesive) contact is observed.

As the fractional contact area between the PEG hydrogel and the QCM increases, both $\Delta f_3$ and $\Delta \Gamma_3$ increase, but only by tens of hertz. By contrast, the compression of a Kraton gel into the QCM submerged in water at similar forces leads to changes in frequency and dissipation of many hundreds of hertz, as shown in Figure 6b. These data indicate that the limit of the QCM’s ability to resolve changes in loading is being approached because the rheological properties of water and dilute PEG hydrogels are very similar at high frequencies ($\Delta Z^* \approx 0$).

The example of a PEG hydrogel in water offers the first illustration in this paper of a system where the loading condition of the QCM is changing, yet $\Delta Z^*$ is very close to zero. We can also explore the possibility of a negative $\Delta Z^*$ by submerging the same PEG/QCM interface in mineral oil. Figure 11 shows compressive load, $\Delta f_3$ and $\Delta \Gamma_3$ versus displacement during the loading portion of a JKR-QCM contact test. Zero displacement is defined as the point where the load begins to increase. As the displacement increases and the gel is pressed into the QCM, the resonant frequency increases while the dissipation decreases. These trends are in the opposite direction of other examples involving an increasing contact area between a gel and the QCM, and

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they are a result of the fact that the acoustic impedance at the QCM surface is actually decreasing as the hydrogel replaces the much more viscous mineral oil. Therefore, a negative ΔZ* has been observed.

Another interesting feature of Figure 11 is that the QCM begins to respond to the approaching hydrogel before the load increases. A reasonable explanation for this behavior that is consistent with previous observations is that there is a water layer at the surface of the gel that is detected by the QCM before mechanical contact is established between the PEG and the crystal surface. The fact that the QCM is sensitive to details of contact that are beyond the sensitivity of bulk mechanical probes, such as those found in the JKR geometry, provides a strong validation for our efforts to incorporate the two techniques for a more thorough analysis of a contact mechanics experiment.

CONCLUSIONS

In this paper, the use of the QCM as a contact mechanics sensor for soft materials has been extended to situations where the interfacial contact region is submerged in water or some other liquid. This advance has the potential to greatly impact the study of adhesion and wetting of materials in liquids due to the sensitivity of the QCM to surface mechanical properties. Our results can be summarized as follows:

1. Equations designed to model the response of the QCM to a growing fractional contact area submerged in a liquid were proposed for a Newtonian liquid, a viscoelastic liquid, and a viscoelastic solid. Experimental examples of each system were provided, confirming the plausibility of the proposed equations.

2. The parameter β, which is a shape factor in the Gaussian distribution of shear amplitudes on the QCM surface, was found to be 1.64 in a system of 2-ethylhexanol droplets growing on the QCM submerged in water. This result indicates that β, which is generally close to 1.0 in less highly damped systems, may depend on the loading condition of the QCM.

3. Contact mechanics studies of Kraton gels in water with the QCM exhibited features similar to analogous experiments in air. The transfer of mineral oil to PS during contact experiments led to similar oil film thicknesses in both cases.

4. Contact mechanics studies of PEG hydrogels in water and mineral oil were used to illustrate the resolution of the QCM for cases when the application of a load results in nearly no change or even negative changes in the acoustic impedance sensed by the crystal. Furthermore, when submerged in mineral oil, the approaching PEG hydrogel was sensed by the QCM well before mechanical loading was established, leading to the conclusion that these gels have a liquidlike layer at their surface.

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