Quantitative Rheometry of Thin Soft Materials using the Quartz Crystal Microbalance with Dissipation (QCM-D)

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Abstract: In the inertial limit, the resonance frequency of the quartz crystal microbalance (QCM) is related to the coupled mass on the quartz sensor through the Sauerbrey expression that relates the mass to the change in resonance frequency. However, when the thickness of the film is sufficiently large, the relationship becomes more complicated and both the frequency

and damping of the crystal resonance must be considered. In this regime, a rheological model of the material must be used to accurately extract the adhered film's thickness, shear modulus, and viscoelastic phase angle from the data. In the present work we examine the suitability of two viscoelastic models, a simple Voigt model (***Physica Scripta*** 1999, 59, 391-396) and a more realistic power-law model (***Langmuir*** 2015, 31, 4008), to extract the rheological properties of a thermo-responsive hydrogel film. By changing temperature and initial dry film thickness of the gel, the operation of QCM was traversed from the Sauerbrey limit, where viscous losses do not impact the frequency, through the regime where the QCM response is sensitive to viscoelastic properties. The density-shear modulus and the viscoelastic phase angle from the two models are in good agreement when the shear wavelength ratio, d/λ_n, is in the range of 0.05-0.20, where d is the film thickness and λ_n is the wavelength of the mechanical shear wave at the n^{th} harmonic. We further provide a framework for estimating the physical properties of soft materials in the megahertz regime by using the physical behavior of polyelectrolyte complexes. This provides the user with an approximate range of allowable film thicknesses for accurate viscoelastic analysis with either model, thus enabling better use of the QCM-D in soft materials research.

Introduction

For nearly 70 years the piezoelectric oscillation of a quartz resonator has been used as an ultra sensitive mass sensor, utilizing the Sauerbrey relationship between the resonant frequency and the mass per unit area deposited on the crystal.[1] This relationship has enabled the quartz crystal microbalance (QCM) to be a mainstay of vacuum science.[2,3] In the 1980's Kanazawa and co-workers demonstrated that QCM operation in liquids was possible,[4] opening opportunities for QCM to contribute to many electrochemical[5–7] and biological[8–10] investigations. However, the frequency change due to coupled mass at the crystal surface only provides a partial description of the adhered layer, especially if it is viscoelastic in nature. Viscous losses associated with the material lead to energy dissipation of the crystal, providing additional information regarding the adhered film. The dissipation is obtained from the half width at half maximum (Γ) of the

conductance peak at the resonance condition, which is proportional to the energy transfer from the resonator to the medium with which it is in contact.[11,12] Therefore, measuring Γ offers access to rheological information of the system.[13–16] The QCM's high sensitivity has already enabled a breadth of informative work on characterizing soft materials[6,17–25], yet many QCM investigations would benefit further if its capabilities as a high-frequency rheometer were made clearer.

The commercialization of instrumentation developed by Kasemo and co-workers has enabled the proliferation of rheological characterization of thin soft materials based on the measurement of the resonant frequency and dissipation of the QCM at multiple harmonics.[26] Values of the dissipation obtained with the QCM-D (Quartz Crystal Microbalance with Dissipation) instrument are generally reported in terms of a dissipation factor, D, which is directly proportional to Γ at each harmonic, n, via Eq. 1.[14] In the present work we use D and Γ interchangeably as they are the same parameter.

$$D_n = 2\Gamma_n / f_n \tag{1}$$

The viscoelastic nature of many biological[27,28] and polymeric[16,29–31] materials at surfaces has been determined with the QCM-D, but these results are tied to the model used to describe the viscoelastic properties of the film.[8,32] A viscoelastic model is needed because the QCM response for a thin film at a given resonant harmonic depends on three quantities (the film's mass/area, and the real and imaginary parts of the complex modulus at the resonant frequency), but only two quantities are measured at each harmonic (the resonant frequency and dissipation). As a result, information needs to be obtained at multiple harmonics, with some assumption made regarding the frequency dependence of the viscoelastic properties of the film. A commonly employed model is the Voigt model, where the storage modulus is assumed to be frequency independent, whereas the loss modulus is assumed to scale linearly with the frequency.[32] Data are typically reported at a reference harmonic, n_{ref}, which is generally either 1 (corresponding to a frequency of 5 MHz for the commonly used quartz crystals with a fundamental resonance frequency of 5 MHz) or 3 (a frequency of 15 MHz for a 5 MHz crystal). In the Voigt model, the

properties at different resonant harmonics are therefore related as follows:

$$G'_n = G'_{n_{ref}} = |G^*_{n_{ref}}| \cos(\phi_{n_{ref}})$$

$$G''_n = \frac{n}{n_{ref}} G''_{n_{ref}} = \frac{n}{n_{ref}} |G^*_{n_{ref}}| \sin(\phi_{n_{ref}})$$

Here $|G^*_n|$ is the magnitude of the complex modulus and ϕ is the viscoelastic phase angle, which is defined to be 0° for perfectly elastic materials and 90° for Newtonian liquids. As pointed out by Reviakine *et al.*, these assumptions are not rheologically consistent, and only observed in real materials in some specific and highly unusual situations.[15] A more realistic and generally useful model is a power-law model, where the storage and loss moduli are both assumed to be power-law functions of the frequency, with the phase angle related directly to the value of the power-law exponent. This power-law model is simpler to apply, and introduces very little error into the physical properties extracted from an appropriately designed QCM experiment.[33] It has been applied to investigations of polyelectrolyte complexation[5,16] and the curing of thermosets.[16] Mathematically the power-law model assumes:

$$|G^*_n| = |G^*_{n_{ref}}| n^{\phi/90}$$

In the present work, we illustrate the use of this approach to swelling measurements of thin layers of a crosslinked gel, comparing results obtained with the Voigt (V) and the power-law (R) models. In the process of this comparison, we delineate regimes of QCM operation where the Sauerbrey relationship applies and where deviation from Sauerbrey is significant enough to allow viscoelastic characterization of thin films.

Experimental Methods

Materials and sample preparation: A random copolymer of N-isopropylacrylamide (NIPAAm) and 2-(N-ethylperfluorooctane sulfonamido)ethyl acrylate (FOSA) with 5 mol % FOSA as reported previously[34,35] was used as the hydrogel with hydrophobic associations of FOSA producing nano-aggregates that provided physical crosslinks when hydrated.[35] These hydrogels exhibit volume phase transition of an LCST-type with a midpoint of 17 °C in the bulk[35] and 20 °C in thin films.[36] Changing the temperature from 35 °C to 5 °C increased the swelling % (Eq. 8) of the films from 50 and 350 %. This large change in the water content of the hydrogel significantly impacted its rheological properties. The dried copolymer was dissolved in dioxane at 1.0 and 1.75 wt% for spin coating on the silica-coated quartz sensors (QSX-335, Q-Sense). These sensors had a diameter of 14 mm, thickness of 0.37 mm, and fundamental resonant frequency of 5 MHz. The sensors were cleaned by sonication in toluene, isopropanol, and DI water. Immediately prior to film casting, the sensors were further cleaned by ultraviolet-ozone (UVO CLEANER®, Model 42, Jelight Company Inc.) for 90 s. The copolymer-dioxane solutions were spun coat at 2500 rpm for 30 s onto the quartz sensors. After 1 h at ambient conditions, the films on the sensors were annealed for 18 h at 150 °C and 27 torr vacuum.

The hydrogel films on the quartz sensor were characterized using QCM-D (Q-Sense E1) and SE (J.A. Woollam, M-2000UI) at the same time using the ellipsometry module (Q-Sense, Biolin Scientific). The thickness of the dry copolymer was determined using Δf relative to the uncoated sensor in air with an assumed density of 1000 kg/m^3. Simultaneous measurement with SE provided an optical route to also determine the copolymer film thickness using an optical stack for the sensors consisting of gold (optically opaque), titanium, TiO_2, and silica from bottom to top. The ellipsometric angles of the sensors were fit using the protocol described previously for these QCM-D sensors.[37] These thicknesses were then fixed to fit for the thickness of the copolymer or hydrogel that was coated on the sensor with the optical properties of the copolymer and hydrogel, which were both well described by the Cauchy model. The thickness determined from the Sauerbrey expression based on the frequency shift from the blank crystal agreed within 3% of the thickness obtained from ellipsometry for the dry copolymer film.

For the swelling measurements, the coated sensor was first exposed to liquid water at 25 °C and allowed to equilibrate. The temperature was subsequently raised to 35 °C and allowed to equilibrate for 1 h. Then the temperature was decreased in 1-2 °C increments each hour until 5 °C was reached, with a total of 24 temperature steps. The frequency and dissipation of the bare sensor in water at each temperature was used as the reference for calculating Δf_n and ΔD_n. This reference state allowed for the viscosity and density changes in the water with temperature as well as the effect of temperature itself to be removed from the data.

The QCM-D data were fit using two different protocols that relate the viscoelastic properties of the film to the oscillator response. The Voigt Extended Viscoelastic model was used in conjunction with the standard Q-Tools software (Q-Sense), which is based on the model refined by Voinova and co-workers.[32] The frequency and dissipation changes were recursively fit to this model to minimize the mean square error between the prediction and measured values. A flowchart of these fit procedures are shown in the SI in Figures S3. The same input parameters/assumptions were used with a different viscoelastic model that is based on a self-consistent description of the complex modulus as developed by Shull and co-workers.[16,33] The fits from both models can be used to determine the shear modulus, phase angle and thickness of the hydrogel. Additional details about these two models are further explained in the subsequent Theory section.

Polyelectrolyte complexes were synthesized as reported previously.[38] Briefly, 10 wt% of poly(4-vinylpyridine) was quaternized with iodomethane at 10 % excess in DMSO. This cationic polymer was precipitated with equimolar poly(styrenesulfonate) in excess deionized water. The precipitates were washed with deionized water until the solution conductivity reached $\approx$ 50 $\mu S/cm$, followed by overnight drying at 60 ^{o}C. 1.5 g of the dried complex was dissolved in 15 ml of 1.7 M KBr to form the coacervate phase. The coacervate was directly spin coated onto the QCM crystal before swelling measurements in KBr solutions up to 1.0 M at 0.1 M increments.

Theory & Modeling of QCM Operation

For sufficiently rigid and/or thin adhered layers, the frequency will be directly related to mass through the Sauerbrey expression, such that details of the viscoelasticity of the material are not relevant to describe QCM operation.[39] The point for quantitative failure of the Sauerbrey expression can be described in terms of the ratio d/λ_n, which is the film thickness (d) normalized by the shear wavelength of the mechanical oscillation (λ_n) in the medium at the n^{th} overtone or harmonic, occurring roughly for $d/\lambda_n \approx 0.05$.[33] For sufficiently thick viscoelastic films, d/λ_n can approach 0.25 leading to to an increase in frequency may be observed with increasing mass[39], counter to the even qualitative directionality of the Sauerbrey expression.[16,32,40–42] This film resonance effect also leads to a very large increase in Γ (equivalently D), making the parameter difficult to measure accurately. Film resonance is most pronounced at $d/\lambda_n = 0.25$, but its effects become significant from $d/\lambda_n = 0.20$.[33] Therefore the regime where viscoelastic details can be measured accurately should be in the range of $d/\lambda_n = 0.05 - 0.20$. Film resonance effects are less pronounced for more dissipative (less elastic, $\phi > 45°$) films, such that viscoelastic properties can be measured for $d/\lambda_n = 0.25$ or even larger.

In order to understand the challenges with analyzing the behavior of a viscoelastic film on the QCM, it is first necessary to understand the effect of viscoelasticity on the QCM response. As mentioned earlier, the presence of viscoelastic character in the film results in an increased Γ, however, measuring a change in Γ does not necessarily mean that the viscoelastic properties have changed. This is simply due to the fact that changes in areal density (i.e. thickness) also changes Γ, and therefore, a rheological model must be used which takes into account both frequency and dissipation shifts to paint an accurate picture. The sensitivity of the QCM to viscoelasticity arises from deviations to the Sauerbrey expression, the magnitude of which depends on the quantities d/λ_n and ϕ. The shear wavelength of a mechanical oscillation in a medium further depends on the following expression:

$$\lambda_n = \frac{1}{f_n}\left[\frac{|G_n^*|}{\rho}\right]\frac{1}{cos(\phi/2)} \tag{2}$$

where ρ is the density, $|G_n^*|$ is the magnitude of the complex shear modulus, ϕ is the viscoelastic phase angle of the medium and n is the order of the overtone. Since viscoelastic information can only be calculated in a limited range of d/λ_n, typically 0.05-0.20, Eq. 2 presents a challenge since $|G_n^*|$ and ϕ are material parameters of interest to begin with. This issue is addressed later in the manuscript.

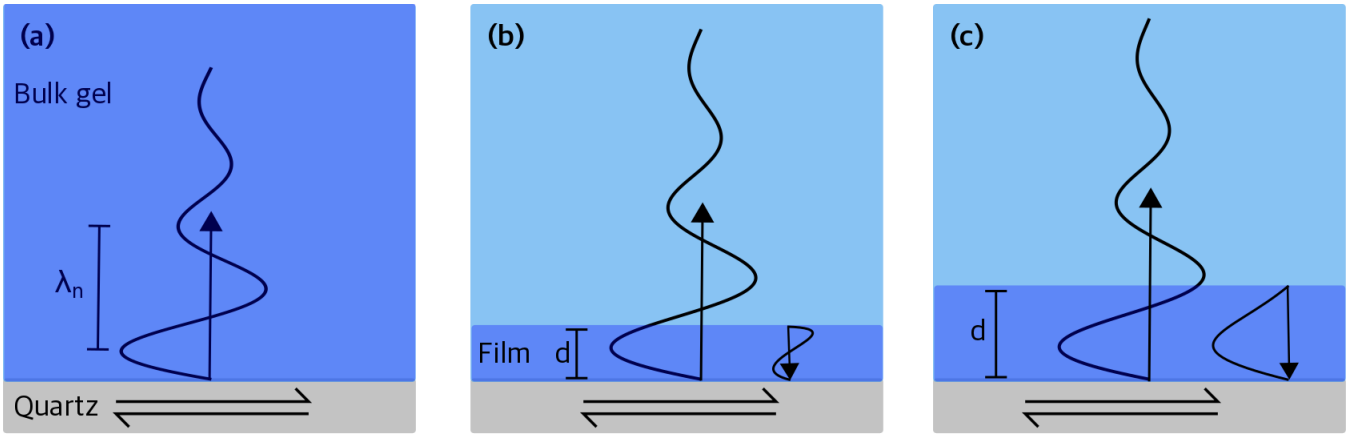

Figure 1: Propagation of the shear wave generated from AC driven quartz-sensor surface into a sample consisting of a hydrogel film immersed in water. For sufficiently thick films, (a) the wave decays through the hydrogel without encountering an interface for reflection, which probes the "bulk" properties. For thinner films, the hydrogel-water interface is encountered by the shear wave, which can result in (b) partial wave reflection from the interface to slightly decrease the crystal frequency ($0.05 < d/\lambda_n < 0.25$) or (c) coupling of the reflected wave with the propagating wave that effectively increases the crystal frequency (film resonance, $d/\lambda_n \approx 0.25$). Note that this figure is not drawn to scale, and the shear wave is exaggerated.

The description of the shear wave propagation can be expressed in 3 limiting cases as pictorally illustrated in Figure 1. If the hydrogel is sufficiently thick, the shear wave decays completely within the adhered layer of the material (Figure 1a). This case can be considered equivalent to bulk measurement of the hydrogel where the response does not depend upon the fluid in contact with the hydrogel.[14,16] In this limit the QCM response is described simply by the following two equations:

$$\Delta f_n = \frac{-f_1}{\pi Z_q}(\rho|G_n^*|)^{1/2}\sin(\phi/2) \tag{3}$$

$$\Delta \Gamma_n = \frac{f_1}{\pi Z_q}(\rho|G_n^*|)^{1/2}\cos(\phi/2) \tag{4}$$

where Z_q is the acoustic shear impedance ($8.84 \times 10^6\,\mathrm{kg/m^2s}$ for AT-cut quartz) and f_1 is the fundamental frequency. Note that the change in the QCM-D dissipation factor is related to $\Delta\Gamma$ as $\Delta D_n = 2\Delta\Gamma_n/f_n$. Therefore, bulk materials are described by two equations with two unknowns, and this scenario works very well for viscous liquids ($\phi > 60^o$) in which the quartz crystal can simply be exposed to or immersed in. Note that in this case the wave is eventually completely damped in the bulk medium and thus no thickness information exists.

A more common case is when the shear wave propagates through the adhered layer and then fully decays in the bulk solvent, thus both the film and the aqueous phase contribute to the crystal response. A shear wave encountering the hydrogel-water interface splits into a transmitted wave and a reflected wave (Figure 1b). The reflected wave generally slightly decreases the oscillation frequency at the sensor.[41] However, it is possible for the reflected shear wave to couple with the outbound shear wave to effectively increase the oscillation frequency at the sensor surface from the addition of these two transverse waves (Figure 1c). The condition under which the shear wave is coupled to the reflected wave is known as film resonance and is a result of approaching the quarter wave condition ($d/\lambda_n = 0.25$).

For a film of thickness d and density ρ deposited on the crystal, deviation from Sauerbrey can be quantified in terms of two quantities: $\Delta f_n/\Delta f_{sn}$ and $\Delta\Gamma_n/\Delta f_{sn}$. Here, Δf_{sn} is the expected Sauerbrey shift, $\Delta f_{sn} = (2nf_1^2\rho d)/Z_q$, and Δf_n and $\Delta\Gamma_n$are the experimentally measured shifts at the n^{th} harmonic. If the film is sufficiently thin, i.e., in the Sauerbrey limit, then $\Delta\Gamma_n \approx 0$ and $\Delta\Gamma_n/\Delta f_{sn} \approx 0$. Similarly, no deviation from Sauerbrey is expected here, so $\Delta f_n/\Delta f_{sn} \approx -1$. If the film swells, d increases and viscoelastic properties begin to take effect, resulting in $\Delta\Gamma_n/\Delta f_{sn} > 0$ and $\Delta f_n/\Delta f_{sn} < -1$. This behavior is described fully by the QCM master equation (Eq. 7). Figure 2 plots the deviation from Sauerbrey for materials with differing viscoelastic character ($\phi = 15^o, 30^o, 45^o$), and identifies the different regimes of QCM operation. We now define two quantities, r^* and D_n^*, which will be prove to be insightful for understanding the QCM response. We will refer to the properties of the film and the liquid with the subscripts f and l, respectively. An asterisk denotes a complex quantity and the subscript n denotes the harmonic order, as usual.

$$r^* = \left(\frac{\rho_\ell G^*_{n\ell}}{\rho_f G^*_{nf}} \right)^{1/2} \tag{5}$$

$$D^*_n = \frac{2\pi d}{\lambda_n} \left(1 - i \tan\left(\phi_n/2\right)\right) \tag{6}$$

Here, r^* is the ratio of the film properties relative to the properties of the overlaying liquid medium, and D^*_n is a complex quantity whose value depends on d/λ_n and ϕ. With these two quantities, the entire QCM response can be described by the following equation:

$$\frac{\Delta f_n + i\Delta\Gamma_n}{\Delta f_{sn}} = -\frac{\tan(D^*_{nf})}{D^*_{nf}} \left[\frac{1 - (r^*)^2}{1 + ir^* \tan(D^*_{nf})} \right] \tag{7}$$

Written in this form it is more appreciable that there is no net response for the case where the film and liquid medium have identical properties ($r^* = 1$), and that the QCM response for a film in air is recovered for $r^* = 0$ (see DeNolf *et al.*).[33] The method of solving Eq. 7, and all related nuances have been reported elsewhere for films in air[33] and for films in a liquid environment.[16] The MATLAB code to solve Eq. 7 (or equivalent expressions of it) using the power-law assumption for experimentally determined frequency and dissipation shifts is provided in the Supporting Information.

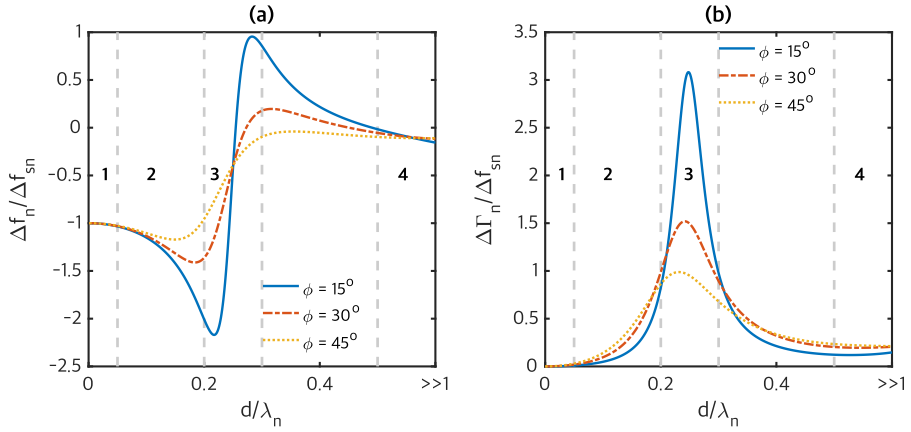

Figure 2: Impact of d/λ_n on the deviation from the Sauerbrey limit for elastic films ($\phi = 15^o$) to viscoelastic films ($\phi = 45^o$). Four regimes of operation are delineated: (1) Sauerbrey, (2) viscoelastic, (3) near film resonance, and (4) bulk-like (Eq. 3 and 4 apply). These plots are obtained from Eq. 7 with $r^* = 0$, that is, a film in air.

Results & Discussion

Measuring the swelling ratio of stimulus responsive soft materials is usually a simple yet insightful experiment. The swelling behavior can be modulated using pH[43], temperature[36], light[44] or electrochemical[45] stimuli, and these approaches have been exploited to construct soft materials for a variety of coating and biomedical applications.[46] Typically, a change in the swelling ratio results from the ingress or egress of water from the material, corresponding with a change in the mechanical properties due to the increase or decrease in crosslink density. Measuring these changes for thin soft materials is challenging since the traditional tensile tests or dynamic mechanical analysis cannot be performed. A further complication is that often the *in-situ* behavior of responsive coatings or gels are of interest, which is where the utility of QCM becomes invaluable since it is capable of monitoring subtle viscoelastic changes with a fine time resolution. Furthermore, few other mechanical testing methods can adequately characterize materials ranging in properties from Newtonian liquids to glassy solids. Given these advantages, the QCM is an attractive material characterization platform. Since films utilized in QCM experiments can have a range of thicknesses, especially if the material is responsive, it is most convenient to define a swelling % for comparison across samples and materials. We define the swelling % of a film with thickness d and density ρ using Eq. 8:

$$Swelling\,\% = \frac{d\rho - (d\rho)_{dry}}{(d\rho)_{dry}} \times 100 \tag{8}$$

Here, $(d\rho)_{dry}$ is the areal mass of the film after removal of all water.

In the present work, a thermo-responsive hydrogel based on a random amphiphilic copolymer enables change in the swelling % with temperature. Such a large change in the swelling % is expected to span orders of magnitude in modulus, which coupled with the change in thickness, traverses d/λ_n from the Sauerbrey limit to the viscoelastically sensitive regime. Our aim is to quantify the value of d/λ_n beyond which the Sauerbrey relationship starts to deviate, and from which point on viscoelastic information can be obtained.

Characterization of PNIPAAm-FOSA Hydrogels

One challenge with experimentally exploring predictions associated with the shear wavelength is the wide parameter space in d/λ_n that requires widely varying thickness and/or rheological properties, which is difficult to obtain without a multitude of samples. Here a thermoresponsive hydrogel based on a random amphiphilic copolymer enables large changes in the swelling and mechanical behavior with temperature. As the film swells, it traverses from the Sauerbrey limit to the viscoelastically sensitive regime, and ultimately into film resonance conditions as d/λ_n approaches 0.25. To systematically elucidate this d/λ_n landscape, we begin with two films of initial areal densities of 52 and 100 mg/m^2. For simplicity we assume that the film density is $1 g/cm^3$, and thus simply refer to the two films as 52 and 100 nm. Probing the properties of these two films, which are a factor of two in thickness apart, across a large temperature range allows us to systematically observe the QCM response. We are interested in learning how well the swelling behavior of these gels compare to the behavior of PECs, and comparing results from the Voigt model (V) and the power-law model (R). We now make a note about the nomenclature to be used in the remainder of the manuscript. Since obtaining mechanical properties from QCM experiments require data from two harmonics, we refer to the V model solutions as $n/n+2$, with n being the harmonic order. For example, we primarily focus on the $3^{rd}/5^{th}$ harmonic combinations in this section. The R model uses the frequency shifts of two harmonics and the dissipation shift of another harmonic to solve for material properties. This is denoted as, for example, a 3:5,5 calculation which uses Δf_3, Δf_5 and $\Delta\Gamma_5$.

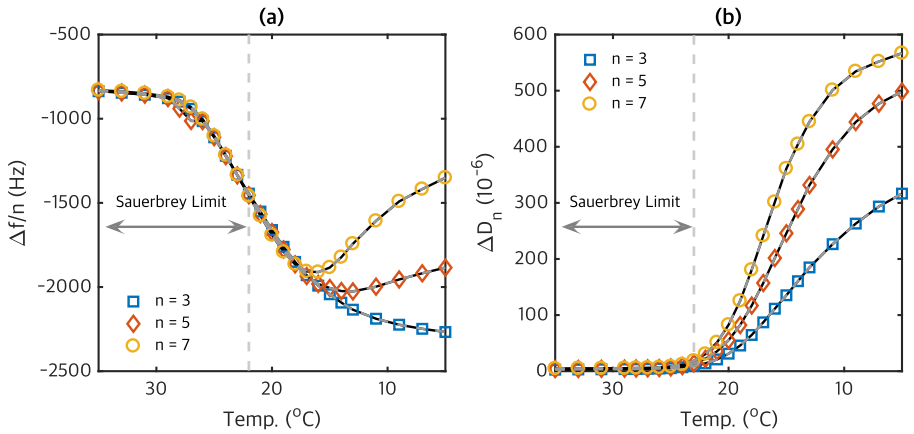

Figure 3: Δf_n and ΔD_n in water for the 100 nm initial dry film. The x-axis is reversed to highlight that the hydrogel was cooled incrementally starting from 35 °C. The solid black lines are fits using the Voigt model and the gray dashed lines are predictions using the power-law model. The Sauerbrey limit applies to the left of the gray dashed lines, where the dissipation is too small. The shifts for the 52 nm film is provided in Figure S2. Note that for both the models examined there is no significant difference in the goodness of the fit for $\Delta f_n$and ΔD_n.

Figure 3 plots the frequency and dissipation shifts for the 100 nm dry film. At high temperatures, the dissipation is small and the frequency shifts obey the Sauerbrey relationship. At lower temperatures, the film swells and d/λ_n increases until film resonance effects cause an uptick in the frequency shift with increasing mass. It is important to note that the effect of temperature on the resonance of the crystal can introduce some error in Δf_n for very thin films, so it is important to use a reference (blank) crystal to subtract these effects from the measured signal as described in the Experimental Section. Figure 4 plots the mechanical behavior of the two films as a function of temperature using both the V and R models. At cooler temperatures, there is a good agreement between the two models for the modulus and phase angle for both films. However, as the temperature increases and the film becomes stiffer as a consequence of deswelling, the QCM response approaches the Sauerbrey limit where no viscoelastic information can be obtained. The temperature above which the Sauerbrey limit applies in this case is above 22^o C for the 100 nm film and 19^o C for the 52 nm film. Interestingly, Figure 4 shows that the Voigt model attempts to fit the frequency and dissipation shifts even in the Sauerbrey regime, and provides quite reasonable answers for the 52 nm film– by chance. While it is tempting to believe the Voigt solutions in the Sauerbrey regime for the 52 nm film, by considering the 100 nm film response one should quickly dismiss it. This thicker film remains in the viscoelasti-

cally sensitive regime over a larger range of temperature, where again we find good agreement between the two models, but its response becomes non-physical at high temperatures where an increasing modulus and a decreasing phase angle is expected. This simple comparison between films of two thicknesses highlights the danger of attempting to model QCM data in the Sauerbrey limit where only the frequency shift can be used to calculate the areal mass. Both models, however, are in good agreement for the swelling behavior, which was independently measured via ellipsometry (Figure S1).

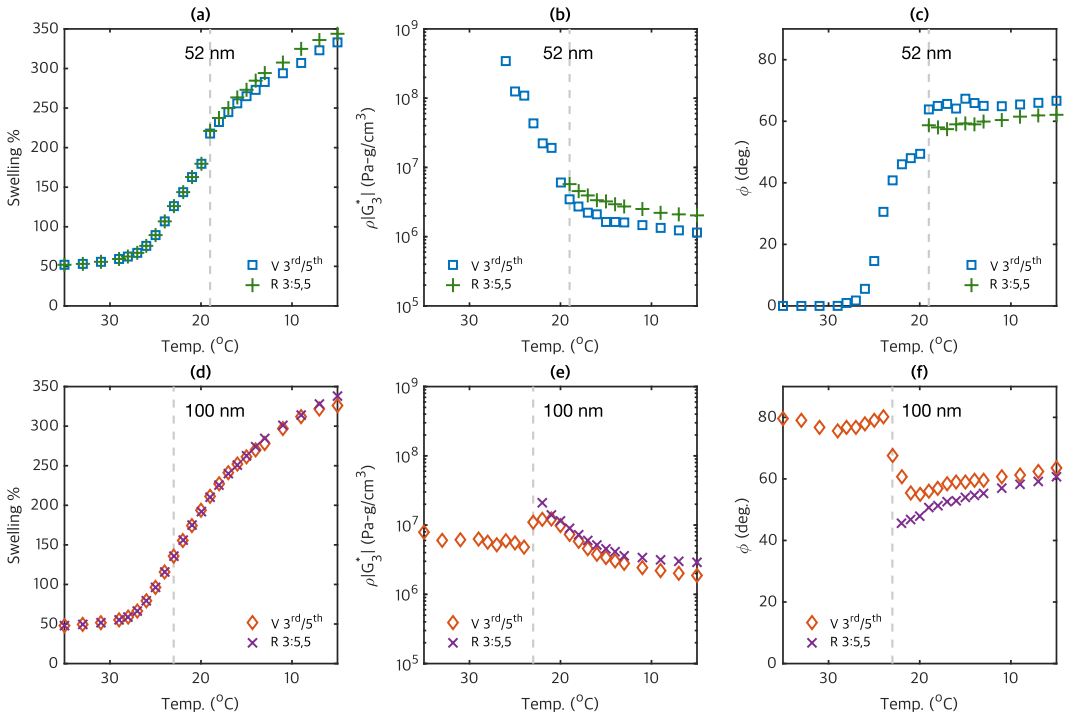

Figure 4: Comparison of the Voigt (V) and power-law (R) models for (a) swelling, (b) modulus and (c) phase angle of the 52 nm dry film. (d) Swelling, (e) modulus and (f) phase angle of the 100 nm dry film. The Sauerbrey limit applies to the left of the gray dashed lines. Note that the moduli calculated correspond to 15 MHz (n=3).

We have described that d/λ_n must be in the 0.05-0.20 range for optimal viscoelastic data. This illustrated in Figure 5 where d/λ_n remains below 0.05 for a significant portion of the temperature range, and as expected, it remains in the Sauerbrey regime for a slightly larger temperature window for the thinner film. The results of this section highlight the need to be in the correct thickness regime for a film such that $0.05 < d/\lambda_n < 0.2$. Since the Voigt model aways provides excellent fits to the measured frequency and dissipation shifts, it is up to the experimentalist to

determine whether the solved modulus and phase angle make physical sense in light of d/λ_n and in the context of the material being investigated. This assessment is a challenge without a robust framework to provide guidance on when to trust the modulus determined from the Voigt model.

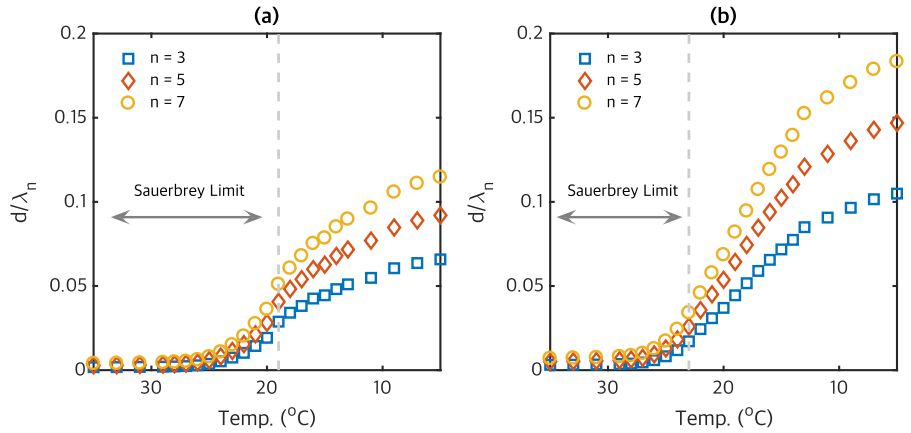

Figure 5: Changes in d/λ_n for hydrogels of (a) 52 nm and (b) 100 nm initial dry thickness. The rough temperature range over which the Sauerbrey limit applies is highlighted.

PECs as Model Systems

Polyelectrolyte Complexes (PECs) consist of oppositely charged macromolecules that associate due to the large entropy gain from counter ion release. In the dry state these complexes form glassy solids, but when immersed in salt solutions, the ion pairs formed between the polycation and polyanion can be broken causing water ingress into the complex.[38] Thus, the swelling ratio of the complex can be controlled by choosing the solution ionic strength. At even higher salt concentrations, the solid complexes form a viscous coacervate phase. Addition of more salt leads to dissolution of the coacervate phase into a single phase solution with properties very close to that of water. This salt responsive behavior of PECs falls on a continuum of mechanical properties from glassy solids to Newtonian liquids, where the physical properties are primarily dependent on the amount of water in the material– a phenomenon that is reminiscent of many soft materials.[38] However, in most cases the entire range of mechanical properties are not accessible on the same materials system. For example, gels with well defined hydrophobic domains similar to the copolymer being investigated in this work, or covalently crosslinked systems,

typically have an upper limit to the swelling ratio. Our recent work quantified the entire mechanical spectrum associated with strong polyelectrolyte complexation using the QCM, such that the whole range of physical properties were comparable on a single mechanical testing platform.[38] This allowed data from from the liquid-like coacervates to be directly comparable to those from glassy complexes without any caveats. Since PECs span the entire mechanical spectrum, they are an excellent model system to elucidate how the physical properties of soft matter are related.

$$\phi = -9.5 \times ln(\rho|G_3^*|) + 200 \tag{9}$$

Figure 6a illustrates the mechanical spectrum associated with PECs, providing an empirical relationship (Eq. 9) between the shear modulus and the viscoelastic phase angle. Importantly, Eq. 9 illustrates that a simple log-linear expression describes soft materials that is swollen by water at this high frequency. This expression is also followed by polyethylene oxide solutions[47], protein-oxometalate complexes[16], and polyelectrolyte complexes,[5,38] demonstrating the generality of this relationship for a broad variety of soft matter at the megahertz frequency.

Eq. 9 displays how the physical behavior of soft materials are coupled in terms of the modulus and the phase angle. The question now becomes how to identify where on the mechanical spectrum a given material lies. Since the swelling behavior of a coating or a film is quite simple to measure accurately using ellipsometry or the QCM via the Sauerbrey relationship, we speculate it could serve as a basis of comparison. Again, we turn to the behavior of a model PEC. Figure 6b plots the shear modulus versus swelling of poly(styrene sulfonate) complexed with methyl quaternized poly(4-vinylpyridine), which varies log-linearly with swelling. We assume that the fit to the data would follow an expression of the form:

$$\rho|G_3^*| = \rho_o|G_3^*|_o e^{-S \times Swelling\%} \tag{10}$$

where $\rho_o|G_3^*|_o$ is the density-shear modulus of the dry glassy material at the third crystal harmonic (15 MHz), and S is a sensitivity factor. $\rho_o|G_3^*|_o$ is typically $\approx 2 \times 10^9$ Pa-g/cm^{3}for glassy

polymers. The value of S determines how sensitive the modulus is to changes in swelling, and is ≈ 0.03 for polyelectrolyte complexes swollen by water. Note that between Eq. 9 and 10, S is the single parameter whose value quantifies changes in physical properties over the entire swelling range. If the swelling % of a soft material is now known, Eq. 9 and 10– provide an estimation of the material's properties at $n = 3$ (15 MHz). We speculate that Eq. 9 is quite general and describes a wide variety of soft materials– an assumption we seek to investigate in the context of the physically crosslinked gel in this manuscript. While we expect that Eq 10 is more material specific, we nevertheless suspect that it is a smart approximation for films swollen in water from an initially glass-like state. Note that in Eq. 9 and 10 we have used mechanical properties at $n = 3$ (15 MHz).

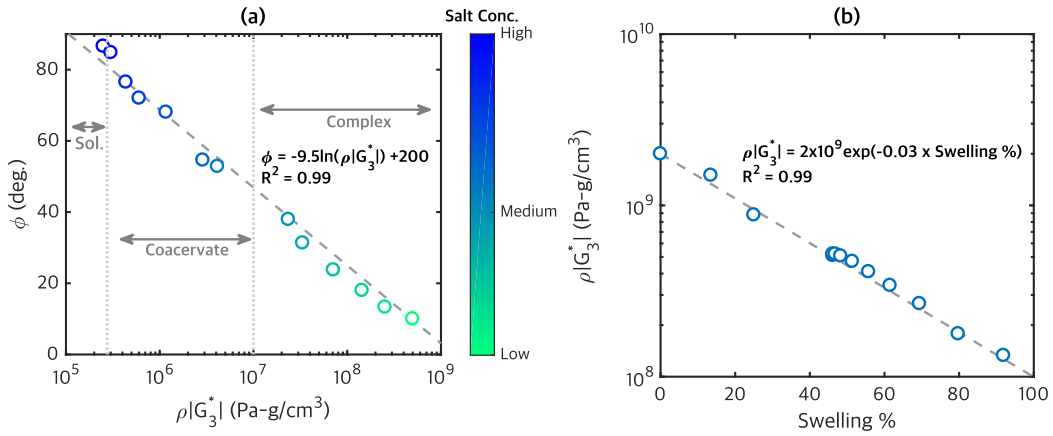

Figure 6: (a) Influence of salt concentration on the mechanical spectrum of polyelectrolyte complexation . The QCM was used to elucidate the continuous transition from solid complex to coacervate to a single phase solution.[38] Note that in this MHz regime, water has a $\rho|G^*|$ of 10^5 Pa-g/cm^3 and ϕ of 90°. Glassy films have $\rho|G^*| \approx 10^9$ and $\phi < 10°$. (b) The effect of swelling on the density shear-modulus of poly(styrene sulfonate) and methyl quaternized poly(4-vinylpyridine) polyelectrolyte complex. Dashed lines are Eq. 9 and 10. Some data were reproduced from ref. 38 with permission.

We now proceed to comparing the behavior of the physically crosslinked gels of the present work to the behavior of PECs. Figure 7a plots the properties of PNIPAAm-FOSA gels on the spectrum of mechanical properties which may be assumed by soft materials at the megahertz frequency. We find that Eq. 9 excellently describes the relationship between ϕ and $\rho|G^*_3|$. Just as salt allowed movement along Eq. 9 for PECs, temperature allows the same movement for the PNIPAAm-FOSA gels. A high temperature results in a high modulus and a low ϕ, while

a low temperature results in a low modulus and a high ϕ. Next, Figure 7b plots the swelling-modulus behavior of the 52 nm and 100 nm films. At lower swelling ratios (< 200 %) the PNIPAAm-FOSA films begin to be described by Eq. 10. Figure 7 leads us to several important conclusions about the high frequency responsive behavior of soft materials. The relationship between ϕ and modulus is not arbitrary, i.e., a material cannot have a high modulus and a very large ϕ simultaneously. In this respect, Figure 7a is quite general. However, the relationship between the swelling ratio and the modulus is more material specific. In this particular case, we find that the swelling ratio and the modulus starts to deviate from Eq. 10 as the temperature is decreased. Yet, since polymer glasses have a modulus of around $\approx 2 \times 10^9$ Pa at 15 MHz, it is reasonable to expect that such a material would approximately follow Eq. 10, at least initially. Indeed we find that at lower swelling ratios PNIPAAm-FOSA gels approach the behavior of PECs, while at large swelling ratios there is significant deviation, where $|G^*|$ must necessarily plateau at a value at least as large as the value for pure solvent ($\approx 10^5$ Pa for water at 15 MHz). Nevertheless, PECs provide a guide for approximating materials properties at a specific swelling % up to 175 % nearly quantitatively. More importantly, by generalizing soft materials properties using Figure 7 we have now enabled one to calculate the parameter d/λ_n using Eq. 2 for a film of thickness d if the approximate swelling % (Eq. 8) is known. Therefore, a more guided and quantitative approach may now be taken to aim for $0.05 < d/\lambda_n < 0.20$.

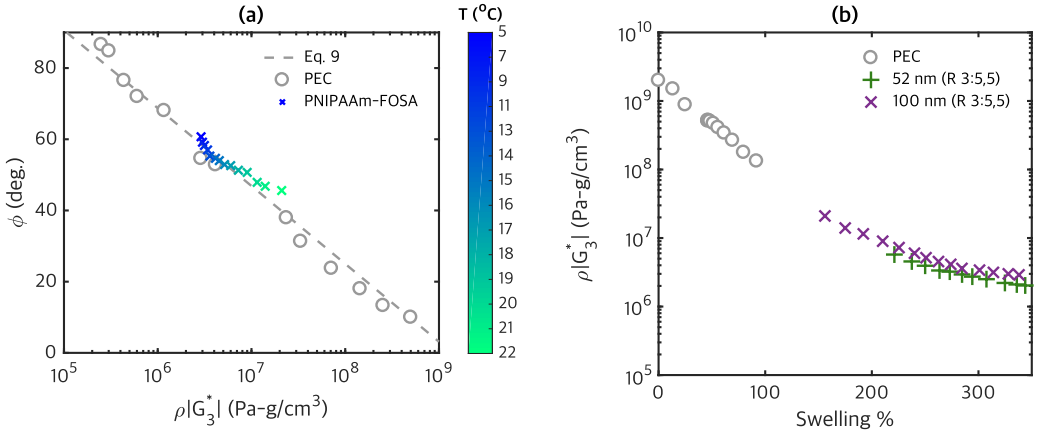

Figure 7: (a) Movement of the 100 nm film properties on the mechanical spectrum (Eq. 9) as a function of temperature, and (b) the swelling-modulus behavior of the 100 nm and 52 nm film in comparison to Eq. 10. Gray data points were reproduced from Figure 6 and ref. 38.

Optimal Film Thickness for QCM-D Rheology

The QCM is a highly versatile and inexpensive fixed frequency rheometer which can be used to probe thin soft materials *in-situ*. In this context, the QCM has tremendous potential to elucidate the responsive behavior of advanced coatings and soft materials. While the simplicity of experiments and the quality of data are advantageous, the correct analysis of those data requires a good understanding of QCM response in terms of d/λ_n. Recall that λ_n requires knowledge of the material properties to which the crystal is in contact (Eq. 2). This is challenging for casual QCM users since it in not immediately intuitive what the appropriate thickness must be for a material with a particular modulus and phase angle. A typical consequence of this in literature is that users often attempt to fit data for films that are too thin, and where the QCM is not sensitive to viscoelasticity. However, there are quantitative thickness limits to QCM operation which must be met in order to obtain meaningful data. Recall that modeling QCM data requires the frequency and dissipation shifts from two harmonics, and let us then consider the case of $n = 3, 5$. The optimal thickness window in this scenario would be where both the harmonics deviate from the Sauerbrey limit, yet the Γ of the higher harmonic remains low enough such that it is still measurable. The maximum Γ that is accurately measurable is about 10 kHz. Thus, to obtain data that is sensitive to viscoelasticity and can be solved by either the V model or the R model, d/λ_3 must be at least around 0.05 and Γ_5 must be less than 10 kHz. Figure 8 lists the range of thickness which satisfy both of these requirements for $n = 3, 5$ and $n = 5, 7$ at all relevant mechanical properties. Note that no thickness range is provided for $\phi > 70^o$ since it is recommended that the bulk limit (3 and 4) be used here, if possible. For the reader interested in exploring QCM experiments in more detail we point to a breadth of work[5,9,16,31,38,48], and the excellent book by Johannsmann[49].

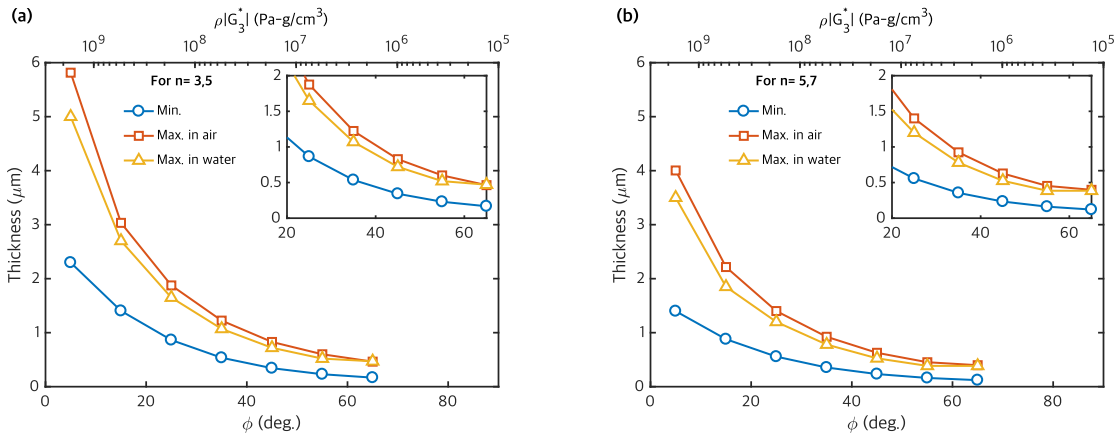

Figure 8: Recommended thickness ranges for accurate QCM rheology for films with a particular modulus and/or phase angle in air or water using (a) $3^{rd}/5^{th}$ and (b) $5^{th}/7^{th}$ harmonic combinations. The insets show zoom-ins of the thickness for ϕ between 20^o and 65^o. Thickness upper bounds are calculated by limiting the dissipation of the higher harmonic in each case to 10 kHz. Thickness lower bounds are calculated by setting the minimum deviation from Sauerbrey limit of the lower harmonic in each case to be 2% ($d/\lambda_n \approx 0.05$). The density is assumed to be 1 g/cm^3 here, therefore these thickness ranges are approximate.

Based on the results of this work, the authors now make some general recommendations for taking a more guided approach to QCM-D rheology:

- If the swelling % of a film in water is known relative to its dry thickness, then Eq. 9 and Eq. 10 can be used to approximate the mechanical properties, which can subsequently be used to identify the optimal thickness range using Figure 8. While Eq. 9 appears to be quite general in describing the fixed frequency response of soft materials, we find that Eq. 10 is more material specific (as it is expected to be). However, Eq. 10 still provides a good approximation for mechanical properties at lower swelling ratios for initially glass-like films.

- Figure 8 is agnostic of materials chemistry and/or mechanism of responsiveness (pH, ionic strength, temperature, etc.). It only requires the user to have an approximate knowledge of the modulus and/or phase angle of their material in the megahertz regime. For reference, at this frequency water has $\rho|G_3^*| = 10^5$ Pa-g/cm^3 and $\phi = 90^o$, gels (or hydrated soft materials) typically have $\rho|G_3^*| \approx 10^8 - 10^6$ Pa-g/cm^3 and $\phi = 25^o - 70^o$, and glassy materials have $\rho|G_3^*| \approx 10^9$ Pa-g/cm^3 and $\phi < 10^o$.

- For glassy films (e.g. polystyrene, $\phi \approx 3^o$), 4-5 μm thick films provide enough dissipation change to be modeled accurately. For soft viscoelastic films (e.g. gels, $\phi \approx 45^o$), 0.5-1.2 μm films are a good start. For viscous liquids (e.g. polymer solutions) Eqs. 3 and 4 can be solved simultaneously at a single harmonic, n, to obtain $\rho|G_n^*|$ and ϕ by exposing the crystal to the liquid-like medium.

- For best results, harmonics $n = 3, 5, 7$ are recommended for modeling. Higher order harmonics should be used with caution since coupling of anharmonic resonances with the main resonance peak may lead to erroneous observation of Δf and $\Delta\Gamma$. Modeling with $n = 1$ is discouraged due to insufficient energy trapping.[49]

- Films should be as smooth and homogeneous as possible.

Conclusion

In the present work a thermo-responsive hydrogel undergoing large swelling changes was used to probe the three distinct regimes of QCM operation. At high temperatures the film was stiff and deswollen and the Sauerbrey limit applied. As the film was cooled, it swelled significantly and the film thickness, modulus and phase angle could be calculated using the Voigt (V) and the power-law (R) model. At even higher swelling ratios, the film neared resonance conditions where an uptick in the frequency could be observed with increasing mass, contrary to the Sauerbrey relationship. Both models accurately predicted this behavior and were able to calculate the film properties with good agreement. However, the Voigt model was found to provide modulus and phase angles even in the Sauerbrey limit where no viscoelastic information exists in the QCM response. While in the case of the 52 nm dry film the Voigt model appeared to provide reasonable values even in the Sauerbrey limit, it failed to replicate those values for the 100 nm film. Therefore, it is imperative for QCM users to avoid fitting frequency and dissipation shifts in the Sauerbrey limit. To that end, we demonstrated that a minimum value of ≈0.05 is needed for the film thickness normalized by the shear wavelength (d/λ_n) for the QCM to be sensitive to viscoelastic properties. However, often some prior knowledge about the material

being investigated is required to accurately calculate d/λ_n, since the shear wavelength depends upon the film's modulus and phase angle. We provided a quantitative relationship between the modulus and the phase angle (Eq. 9) and the swelling % and modulus (Eq. 10) which could be used to approximate material properties at a specific swelling ratio, ultimately allowing one to approximate d/λ_n. These relationships were enabled by quantifying the mechanical behavior of polyelectrolyte complexes, whose properties span the entire mechanical spectrum from low viscosity fluids to glassy solids. While dependence between swelling and modulus can be material specific, the behavior of polyelectrolyte complexes serves as a good approximation nonetheless, especially at lower swelling ratios. Finally, we provided thickness ranges as a function of the mechanical properties of materials being investigated where the QCM response would be sensitive to viscoelasticity. This should provide QCM users an initial guess as to what thickness regime to aim for to obtain meaningful viscoelastic data.

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Author Contributions

CGW performed PNIPAAm-FOSA QCM experiments and the Voigt modeling. KS performed data analysis according to the power-law model and performed all experiments related to polyelectrolyte complexes. CGW and KS contributed equally to the manuscript preparation. BDV

and KRS conceived of the general framework of the experiments and supervised the work. CCW provided insights on data analysis. RAW encouraged CGW to investigate the thermo-responsive materials and helped supervise the work. All authors discussed the results and contributed to the final manuscript.

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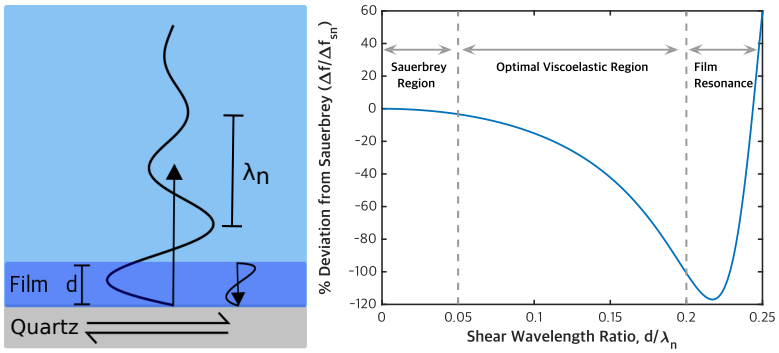
λn
Film
d
Quartz
60
40
20
0
-20
-40
-60
-80
-100
-120
0
0.05
0.1
0.15
0.2
0.25
Sauerbrey Region
Optimal Viscoelastic Region
Film Resonance
% Deviation from Sauerbrey (Δf/Δf_sn)
Shear Wavelength Ratio, d/λ_n

Figure 9: TOC