Membrane-enhanced surface acoustic wave analysis of grafted polymer brushes

David A. Brass and Kenneth R. Shull^{a)}*Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, Illinois 60208-3108, USA*

(Received 29 November 2007; accepted 6 February 2008; published online 8 April 2008)

An analysis is developed for the frequency response of a quartz crystal resonator (often referred to as a quartz crystal microbalance) that is modified with a grafted solvent-swollen polymer brush and placed in contact with a membrane capping layer. The shear wave generated at the resonator surface couples into the membrane layer with an efficiency that is strongly dependent on the thickness of the swollen brush layer. As a result, the resonant frequency changes by a maximum amount that is closely approximated by the Sauerbrey shift for the capping layer. The calculated shift substantially decreases for increases in the brush thickness of approximately 10 nm, which gives a net frequency response that is extremely sensitive to the degree of swelling of the polymer brush. An optimum capping layer thickness is determined by balancing the Sauerbrey shift against dissipative effects that weaken the crystal resonance. This optimum membrane thickness depends only weakly on the properties of the membrane material and is in the micron range. Detailed multilayer calculations are presented for the specific case of a poly(ethylene glycol) brush swollen with water and brought into contact with an elastomeric water-permeable membrane. These calculations confirm that the method is sensitive to the properties of the brush layer in the experimentally relevant thickness regime. Connections are also made to conceptually simpler two and three layer models of the acoustic impedance of the material systems that are brought into contact with the resonator. © 2008 American Institute of Physics. [DOI: 10.1063/1.2903880]

I. INTRODUCTION

Quartz crystal resonators (QCRs) are extremely sensitive to surface loading. For example, the quartz crystal microbalance (QCM) takes advantage of the sensitivity of these devices to mass loadings of a picogram¹ or partial monolayer thicknesses in the subnanometer range.² These mass sensing applications are based on the work of Sauerbrey, who in 1959 derived a simple expression for the shift in the resonant frequency Δf_s ,³ attributable to the deposition of a material with a thickness of d_j and density ρ_j onto the QCM surface,

$$\Delta f_s = -\frac{2nf_1^2}{Z_q}\rho_j d_j. \quad (1)$$

Here, f_1 is the fundamental frequency (5 MHz for the quartz crystals used in this paper), Z_q is the acoustic impedance of quartz ($8.84 \times 10^6 \text{ kg m}^{-2} \text{ s}^{-1}$), and n is the order of the harmonic that is being measured. All of the calculations in this paper correspond to the third harmonic ($n=3$) at 15 MHz.

The Sauerbrey equation has numerous restrictions that limit its quantitative applicability. When the loading material is viscoelastic,^{4–8} sufficiently thick,⁹ and/or complex in structure,^{10,11} the Sauerbrey equation will break down. The extent of this breakdown is dependent on the material properties and the thickness of the layer. When the material properties are known, corrections have been established that enable films with thicknesses greater than the supporting crystal to be analyzed.¹² Also, equivalent circuit approaches⁶

such as the Mason equivalent circuit^{13–15} and the Butterworth–van Dyke equivalent circuit^{6,14,16} have been developed to model more complicated loading of the quartz crystal, including multilayer systems with nonuniform mechanical properties.^{17,18}

An understanding of the loading of QCRs in viscous environments^{7,16,19,20} has led to the development of techniques for measuring a variety of processes at the solid/liquid interface, including molecular adsorption^{21,22} and the swelling of polymer brushes.¹⁷ However, polymer adsorption generally results in a shift in the resonant frequency of at most several hundred hertz. This sensitivity can be greatly enhanced by adding a capping layer, as illustrated schematically in Fig. 1. Addition of a suitably chosen capping layer can enhance the sensitivity of the quartz crystal resonator by

FIG. 1. (Color online) Schematic of the PEG brush grafted to the surface of the QCR. The brush (layer 1) is capped by a membrane film (layer 2) and submerged in water (layer 3).

^{a)}Electronic mail: k-shull@northwestern.edu.

a factor of 100.¹⁸ In addition, this capping layer can behave as a semipermeable membrane that allows the transport of water and other chemical species that may affect the structure of the interfacial layer that is being probed. A consequence of the existence of this capping layer is that the complexity of the data analysis is increased.

The sensitivity of QCRs to the loading conditions is determined by the propagation of acoustic shear waves generated by the oscillating crystal. These “surface acoustic waves” are strongly affected by the presence of the capping membrane, and we refer to the accompanying analysis as the “membrane-enhanced surface acoustic wave analysis.” Our primary aim in this paper is to illustrate the power of the method, and to investigate the membrane properties that are most suitable for its application. For illustrative purposes, we focus on the specific case of grafted poly(ethylene glycol) (PEG) brush. While we study the effects of the membrane properties on the response, the most common membrane capping layer is a rubbery poly(styrene-ethylene/butene-styrene) (SEBS) film. The SEBS layer acts as a diffusion barrier for the water and also enhances the sensitivity of the crystal resonator to the degree of swelling of the PEG brush. We begin by summarizing the basic equations for a single layer in Sec. II A. This model is then expanded to include second and third layers in Sec. II B. These models assume a uniform polymer concentration within a layer, which is not the case with a polymer brush. Also, the analytic models get very complicated with the addition of only a few layers. To handle both of these factors, the model is generalized to handle an arbitrary number of layers in Sec. II C. While this generalized approach results in a series of equations that must be numerically solved, the notation is conceptually straightforward, and the generalized multilayer method is in many ways more tractable than the analytic expressions that emerge from the two or three layer models.

The results of our calculations are summarized in Sec. III. In Secs. III A and III B, we provide information that is needed to understand the properties of the PEG brush. The relationship between the measured crystal response and the properties of both the polymer brush and the capping layer are summarized in Sec. III C. The information in these sections is included in order to provide guidance for the optimization of the membrane thickness and its linear viscoelastic properties. In Sec. III D, we describe the propagation of the acoustic shear wave through the entire system in order to give a physical picture of the mechanism by which the membrane enhances the sensitivity to the properties of the polymer brush.

II. BACKGROUND AND THEORY

The piezoelectric character of an AT cut quartz crystal results in a shear oscillation when an alternating electric field is applied across the thickness of the crystal.^{23,24} Mechanical resonances are sensed as peaks in the admittance spectrum that can be measured with a network analyzer. A Lorentzian fit of the conductance peak in the vicinity of a mechanical resonance gives a complex resonant frequency, $f_n^* = f_n + i\Gamma_n$. Here, f_n is the frequency corresponding to the conductance

maximum at the n th harmonic and Γ_n is half the bandwidth of this resonant peak, which acts as a measure of the energy dissipation. (Note that all starred quantities in this paper are complex). Though the quantitative description of these QCRs has been provided elsewhere,^{4,6,9,24} we find it useful in the following sections to review some of the more important equations in order to develop a consistent notation for the parameters used in the analysis.

The presence of material on one side of the QCR produces a shift in its resonant frequency. This complex frequency shift ($\Delta f^* = \Delta f + i\Delta\Gamma$) includes changes in the real component of the resonant frequency and also the bandwidth and is related to the change in the complex impedance associated with the loading of the crystal Z^* ,²⁵

$$\Delta f^* = \frac{if_1 Z^*}{\pi Z_q}. \quad (2)$$

This loading impedance is also defined as the ratio of the interfacial shear stress σ^* to the velocity of the shear wave $\dot{u}^*$,

$$Z^* = \frac{\sigma^*}{\dot{u}^*}. \quad (3)$$

In the case where this loading is by one semi-infinite material, this impedance is the same as the material dependent impedance given below in Eq. (6). In the following sections, we discuss how to obtain the impedance for more complicated loading situations.

A. Single layer on QCR

For a single layer located on the crystal, the impedance of this layer is

$$Z_{1,0}^* = iZ_1^* \tan(k_1^* d_1), \quad (4)$$

where

$$k_j^* = \frac{\omega_n \rho_j}{Z_j^*} \quad (5)$$

is the complex wavenumber for the acoustic shear wave in layer j , with $j=1$ for the simple single layer case considered here. The angular frequency ω_n for the n th harmonic is equal to $2\pi f_n$ and d_j is the thickness of layer j . The two component subscript is used to signify the presence of the layer under a second medium, in this case being air or vacuum, since the total impedance is dependent on the layer geometry. The single subscript for Z_j^* indicates that this acoustic impedance is a material property for layer j , which is related to its density ρ_j and complex shear modulus G_j^* ,

$$Z_j^* = (\rho_j G_j^*)^{1/2}. \quad (6)$$

In some cases, it is convenient to express G_j^* in terms of its magnitude $|G_j^*|$ and loss angle ϕ_j ,

$$G_j^* = |G_j^*| \exp(i\phi_j). \quad (7)$$

When this single layer is sufficiently thin, Eqs. (2)–(6) reduce to the Sauerbrey equation [Eq. (1)]. The Sauerbrey equation represents the leading term in a series expansion of

the tangent function in Eq. (4). A more extensive comparison between the tangent function and expressions obtained by retaining higher order terms in the expansion is given in the Appendix.

Due to the widespread use of the Sauerbrey equation, it is a useful normalization for the predicted values of the frequency shift and bandwidth. Also, normalization by the Sauerbrey frequency shift illustrates in quantitative terms the accuracy of the Sauerbrey equation for different film thicknesses. Combination of Eqs. (2) and (4) gives the following expression for the normalized frequency shift for a single layer:

$$\frac{\Delta f_{1,0}^*}{\Delta f_S} = \frac{\tan(k_1^* d_1)}{k_1^* d_1}. \quad (8)$$

In our notation, $\Delta f_{1,0}^*$ is the complex frequency shift for a single layer (layer 1) since the “second” layer is air or vacuum. Equation (8) can be expanded into a more useful form by writing the complex wave vector in terms of the loss angle and wavelength λ_j for the shear wave in the material corresponding to layer j ,

$$\lambda_j = \text{Re}\left(\frac{2\pi}{k_j^*}\right) = \frac{1}{f_n} \left(\frac{|G_j^*|}{\rho_j}\right)^{1/2} \frac{1}{\cos(\phi_j/2)}. \quad (9)$$

The equivalent expression for the complex wave vector is

$$k_j^* = \frac{2\pi}{\lambda_j} [1 - i \tan(\phi_j/2)]. \quad (10)$$

Combination of Eqs. (8) and (10) with $j=1$ gives the following expression for the normalized complex frequency shift for the single layer case:

$$\frac{\Delta f_{1,0}^*}{\Delta f_S} = \frac{1}{\frac{2\pi d_1}{\lambda_1} [1 - i \tan(\phi_1/2)]} \tan\left\{\frac{2\pi d_1}{\lambda_1} [1 - i \tan(\phi_1/2)]\right\}. \quad (11)$$

From Eq. (11), it is clear that the wavelength is the natural normalization of the film thickness. When plotted against this normalized film thickness, the normalized frequency shift for the single layer case is a function only of the loss angle of the layer at the frequency f_n . The real ($\Delta f_{1,0}/\Delta f_S$) and imaginary ($\Delta \Gamma_{1,0}/\Delta f_S$) portions of this normalized frequency shift are plotted for different loss angles in Fig. 2. At a loss angle of zero (metal or fully elastic film), the divergence in the tangent function gives a corresponding divergence in the frequency shift and dissipation at $d_1 = \lambda_1/4$, a condition that is referred to as the film resonance.^{14,17} As the loss angle approaches zero, dissipation quite sharply peaks at the thickness corresponding to film resonance. The effect is damped but still qualitatively observed for finite values of the loss angle.

The single layer calculations can be used to provide guidance in choosing a capping layer with the appropriate properties since this layer determines the sensitivity that will ultimately be obtained in the experiment. While Eq. (11) and the corresponding plot in Fig. 2 provide a complete picture of the single layer response, the normalizations obscure some

FIG. 2. Normalized frequency shift [part (a)] and change in bandwidth [part (b)] for loading of the resonator by a single layer plotted as a function of the normalized thickness of the layer [Eq. (11)]. Values are shown for loss angles of the layer ranging from 0° to 90° .

of the relationships to film properties that are important in choosing a capping layer. In order to more clearly illustrate these relationships, we use the following form of Eq. (11) that relates the complex frequency shift to the thickness and linear viscoelastic properties of the film:

$$\Delta f_{1,0}^* = -\frac{f_1}{\pi Z_q} [\rho_1 |G_1^*| \exp(i\phi_1)]^{1/2} \times \tan\left\{\omega_n d_1 \left[\frac{\rho_1}{|G_1^*| \exp(i\phi_1)}\right]^{1/2}\right\}. \quad (12)$$

By assuming a density of 1 g/cm^3 (typical density for polymers) and a layer thickness of $1 \text{ } \mu\text{m}$ (typically experimental thickness of capping layers), we obtain the plots in Fig. 3. These show the effects of both the magnitude of the shear modulus and the loss angle. Similar to the frequency shift in Fig. 2, a film resonance is present and appears at a modulus of $\sim 3 \text{ MPa}$ for this membrane thickness. For experiments, we prefer to use a capping layer with a shear modulus that is greater than this in order to give a well-behaved frequency response with minimal dissipation.

B. Two and three layer models

In our experiments, we are interested in the case where a thin hydrated layer exists between a membrane layer and the electrode surface of the QCR. For this reason, we are interested in the impedance of a two layer system, $Z_{1,2}^*$. The impedance with only two layers present is¹⁴

FIG. 3. Frequency shift [part (a)] and change in bandwidth [part (b)] for loading of the resonator by a single layer with a thickness of $1 \mu\text{m}$ and a density of 1 g/cm^3 as a function of the magnitude of the complex modulus of the layer. Values are shown for loss angles of the layer ranging from 5° to 90° .

$$Z_{1,2}^* = \frac{i[Z_1^* \tan(k_1^* d_1) + Z_2^* \tan(k_2^* d_2)]}{1 - \frac{Z_2^*}{Z_1^*} \tan(k_1^* d_1) \tan(k_2^* d_2)}. \quad (13)$$

In our notation, we number the layers outward from the electrode surface of the QCR, so layer 1 is the hydrated layer and

layer 2 is the membrane. Because no third layer is included, Eq. (13) applies to the case where this two layer system exists in air, a condition that we refer to as the “air contact” case in our subsequent discussion.

By following similar steps to those used for the single layer model to convert from impedance to frequency shifts, and normalizing by Δf_{S_2} , the Sauerbrey frequency shift for the capping layer (layer 2), the normalized frequency shift becomes

$$\frac{\Delta f_{1,2}^*}{\Delta f_{S_2}} = \frac{1}{k_2^* d_2} \left[\frac{\frac{Z_1^*}{Z_2^*} \tan(k_1^* d_1) + \tan(k_2^* d_2)}{1 - \frac{Z_2^*}{Z_1^*} \tan(k_1^* d_1) \tan(k_2^* d_2)} \right]. \quad (14)$$

It is evident from this equation that the frequency shift depends in a nontrivial way on the thicknesses and mechanical properties of both layers. Nevertheless, the membrane enhancement effect can be understood quite well from the behavior of this expression.¹⁸ However, the two layer model does not address the potential importance of the liquid layer in which the entire system is immersed. From an experimental viewpoint, this liquid layer is important because it is much easier to control the activity of the water (or, equivalently, the osmotic pressure of the solution) by immersion in a liquid than to rely on the vapor phase transport of water vapor to the membrane surface. In order to adequately describe this “water contact” case, we need a three layer model, where layer 1 is the hydrated brush layer, layer 2 is the membrane, and layer 3 is either pure water or an appropriately chosen aqueous solution. The following expression is obtained by expanding the multilayer model discussed in Sec. II C to obtain the acoustic impedance $Z_{1,2,3}^*$ of this three layer system:

$$Z_{1,2,3}^* = \frac{i \left[Z_1^* \tan(k_1^* d_1) + Z_2^* \tan(k_2^* d_2) + Z_3^* \tan(k_3^* d_3) - \frac{Z_1^* Z_3^*}{Z_2^*} \tan(k_1^* d_1) \tan(k_2^* d_2) \tan(k_3^* d_3) \right]}{1 - \frac{Z_3^*}{Z_2^*} \tan(k_2^* d_2) \tan(k_3^* d_3) - \frac{Z_3^*}{Z_1^*} \tan(k_1^* d_1) \tan(k_3^* d_3) - \frac{Z_2^*}{Z_1^*} \tan(k_1^* d_1) \tan(k_2^* d_2)}. \quad (15)$$

The corresponding expression for the frequency shift, which is normalized by the Sauerbrey frequency shift for the membrane layer (layer 2), is

$$\frac{\Delta f_{1,2,3}^*}{\Delta f_{S_2}} = \frac{\left[\frac{Z_1^*}{Z_2^*} \tan(k_1^* d_1) + \tan(k_2^* d_2) - i \frac{Z_3^*}{Z_2^*} + i \frac{Z_1^* Z_3^*}{Z_2^* Z_2^*} \tan(k_1^* d_1) \tan(k_2^* d_2) \right]}{(k_2^* d_2) \left[1 + i \frac{Z_3^*}{Z_2^*} \tan(k_2^* d_2) + i \frac{Z_3^*}{Z_1^*} \tan(k_1^* d_1) - \frac{Z_2^*}{Z_1^*} \tan(k_1^* d_1) \tan(k_2^* d_2) \right]}. \quad (16)$$

Note that Eqs. (15) and (16) reduce to their two layer counterparts [Eqs. (13) and (14)] when $d_3=0$ or $Z_3^*=0$.

To illustrate the use of Eq. (16), we consider the case where the first layer is a PEG solution, and the second layer is a capping layer consisting of a $1 \mu\text{m}$ SEBS film, with a

loss angle of 15° , shear modulus amplitude of 50 MPa , and a density of 0.987 g/cm^3 . The PEG solution is a simplistic representation of the grafted polymer brush shown in Fig. 1. The Sauerbrey shift for this membrane layer at the third harmonic ($f_n=15 \text{ MHz}$) is -16.75 kHz , as obtained from Eq.

FIG. 4. Frequency shift [part (a)] and change in bandwidth [part (b)] for PEG layers of different solution concentrations under a SEBS membrane layer. Data are included for the “air” case, where layer 3 has an acoustic impedance of zero, and the “water” case, where layer 3 corresponds to a bulk layer of pure water. The numbers on the plot correspond to the volume percentages of PEG in the layer beneath the membrane (layer 1). The two layer model [Eq. (14)] was used to generate the curves for the air case and the three layer model [Eq. (16)] was used to generate the curves for the water case.

(1). This frequency change is observed if the membrane is directly placed onto the bare electrode surface of the quartz crystal. If a low impedance layer exists between the electrode surface and the membrane, the acoustic wave is not completely coupled into the membrane, and the resonant frequency shift is less than the Sauerbrey prediction. The actual value of the frequency is very sensitive to the thickness of this low impedance layer, which in our case is the PEG solution. The third layer is either air, in which the two layer model applies, or a semi-infinite layer of water. Using the calibrations for the PEG solutions shown in Sec. III B, we can vary the assumed PEG concentration in the first layer from 0% to 60% by volume. The relationships between the thickness d_1 of these PEG solution layers and the values for the frequency shift and bandwidth are plotted in Fig. 4. As the solution concentration corresponding to the brush layer increases, curves become less steep and shift to larger values of d_1 . The primary effect of the addition of the third layer, corresponding to the immersion of the system in bulk water, is to shift the curves to slightly lower thicknesses. These differences arise from the transmission of the shear wave into the water layer, an effect that is discussed in more detail in Sec. III D. In all cases, the total increase in bandwidth $\Delta\Gamma$ is less than 20 kHz. This result is significant because it is difficult to accurately measure the frequency shift and dissipation when the crystal is too highly damped. As a general rule, we find that useful experimental data can be obtained when $\Delta\Gamma < 20$ kHz.

C. General multilayer acoustic impedance modeling

Though the two and three layer models provide useful approximations to the behavior of the membrane-enhanced system, it is often useful to further discretize one or more of the layers. In the polymer brush case considered here, we subdivide the first layer in order to utilize a more realistic concentration profile for the polymer brush. The multilayer approach that we utilize is an adaptation of the approach described by Johannsmann² and Domack *et al.*¹⁷ Here, we review this approach and describe its application to our particular system.

Our starting point is a description of the shear displacement field associated with the forward traveling acoustic wave moving away from the crystal surface (+ direction) and the backward traveling wave moving toward the crystal surface (− direction),²

$$u_{(\pm)j}^* = u_{(\pm)j}^{0*} \exp[i(\omega_n t \mp k_j^* z_j)]. \quad (17)$$

Here, u_{+j}^{0*} and u_{-j}^{0*} are the amplitudes of the forward and backward traveling waves at the surface of the layer closest to the quartz, where z_j is defined to be equal to zero.

For the multilayer system, we are again interested in the overall impedance Z^* , which is related to the reflection coefficient r^* and the acoustic impedance of the material that is in direct contact with the electrode surface of the QCR,

$$Z^* = Z_1^* \frac{1 - r^*}{1 + r^*} \quad (18)$$

The reflection coefficient is given the ratio of the backward to forward traveling wave amplitudes at the electrode surface,

$$r^* = \frac{u_{(-)1}^{0*}}{u_{(+)1}^{0*}}. \quad (19)$$

The state of the shear wave throughout the system is dependent on the values of $u_{(+)j}^{0*}$ and $u_{(-)j}^{0*}$, which we express as a two component vector. Since the relative amplitudes of the forward and backward traveling waves at the surface of the quartz crystal are initially unknown, we begin by specifying the boundary condition at the top surface. This boundary condition only requires that the relative amplitudes of the forward and backward traveling waves be correct because calculation of Z^* only requires that we know the ratio of these amplitudes. The air contact and water contact cases are similarly handled, although an extra calibration step is needed for the water contact case because of the presence of the extra layer above the membrane.

For the air contact case, the top layer (layer N) terminates at the air interface, which has a zero impedance. As a result, the wave is completely reflected at this interface, so that $u_{(+)N+1}^{0*} = u_{(-)N+1}^{0*}$. In this case, we use the vector $[1, 1]$ to specify the complex amplitude of the wave at the top of layer N . The amplitudes at the bottom of the quartz surface (layer 1) are related to these top-surface amplitudes by the following matrix multiplication:

$$\begin{bmatrix} u_{(+1),\text{eff}}^{0*} \\ u_{(-1),\text{eff}}^{0*} \end{bmatrix} = [L_1^*][S_{1,2}^*][L_2^*][S_{2,3}^*] \cdots [L_{N-1}^*][T_N^*] \begin{bmatrix} 1 \\ 1 \end{bmatrix}. \quad (20)$$

Here, $[L_j^*]$ is the propagator of the wave through layer j ,

$$[L_j^*] = \begin{bmatrix} \exp(ik_j^* d_j) & 0 \\ 0 & \exp(-ik_j^* d_j) \end{bmatrix}, \quad (21)$$

and $[S_{j-1,j}^*]$ is the propagator of the wave through the interface between layers $j-1$ and j , which is determined from the condition that the stress be continuous across the interface,

$$[S_{j-1,j}^*] = \frac{1}{2} \begin{bmatrix} 1 + (Z_j^*/Z_{j-1}^*) & 1 - (Z_j^*/Z_{j-1}^*) \\ 1 - (Z_j^*/Z_{j-1}^*) & 1 + (Z_j^*/Z_{j-1}^*) \end{bmatrix}. \quad (22)$$

The termination matrix $[T_N^*]$ takes the place of the interface propagator between layer $N-1$ and layer N , and the layer propagator within layer N . The termination matrix has the following form:¹⁸

$$[T_N^*] = \frac{1}{2} \begin{bmatrix} 1 + (Z_{N,0}^*/Z_{N-1}^*) & 0 \\ 0 & 1 - (Z_{N,0}^*/Z_{N-1}^*) \end{bmatrix}. \quad (23)$$

An important aspect of the termination matrix is that it involves the quantity $Z_{N,0}^*$ [see Eq. (4)]. For the air contact (layer N is the membrane), $Z_{N,0}^*$ can be directly measured by directly depositing the membrane layer onto the electrode surface of the QCR.¹⁸ It does not require that the acoustic impedance and thickness of the membrane be independently specified. In the water contact case, the membrane becomes layer $N-1$ and the medium in which it is immersed becomes layer N . In this case, we need to specify both the bulk acoustic impedance and the thickness of membrane layer, thereby adding an extra calibration step described in Sec. III C. In this case, since the water layer is semi-infinite, $Z_{N,0}^*$ reduces to Z_N^* the bulk impedance of water.

The calculated displacements, $u_{(+1),\text{eff}}^{0*}$ and $u_{(-1),\text{eff}}^{0*}$, obtained from Eq. (20) are “effective” displacements because their magnitudes are not physically meaningful. However, the reflection coefficient is accurately given by the ratio these effective displacements,

$$r^* = \frac{u_{(-1),\text{eff}}^{0*}}{u_{(+1),\text{eff}}^{0*}}. \quad (24)$$

Once the reflection coefficient has been determined, the quantitative shear displacements and shear stresses throughout the multilayer sample can be obtained. We begin with the following expression for the magnitude of the displacement amplitude at the resonator surface:²⁶

$$|u_1^{0*}| = \frac{1}{n^2} (1.25 \text{ pm/V}) Q U_{el,0}, \quad (25)$$

where Q is the quality factor of the resonance, n is the harmonic, and $U_{el,0}$ is the peak voltage driving the QCR (typically 315 mV for our experiments). The quality factor is inversely proportional to the bandwidth,²

$$Q = \frac{f_n}{2\Gamma_n}. \quad (26)$$

The overall displacement is given by the sum of the forward and backward traveling waves,

$$u_j^* = u_{(-)j}^* + u_{(+)j}^*. \quad (27)$$

At the crystal surface, we have $u_1^{0*} = u_{(-)1}^{0*} + u_{(+1)}^{0*}$, and the magnitudes of the forward and backward traveling waves at the electrode surface are given as follows:

$$\begin{bmatrix} u_{(+1)}^{0*} \\ u_{(-)1}^{0*} \end{bmatrix} = \frac{|u_1^{0*}|}{(1+r^*)} \begin{bmatrix} 1 \\ r^* \end{bmatrix}. \quad (28)$$

The displacement amplitudes within any layer are given by Eq. (17). The displacements at the bottom of each surface layer (closest to the electrode surface) are given by applying the appropriate propagators,

$$\begin{bmatrix} u_{(+)j}^{0*} \\ u_{(-)j}^{0*} \end{bmatrix} = [S_{j-1,j}^*]^{-1} [L_{j-1}^*]^{-1} \begin{bmatrix} u_{(+)j-1}^{0*} \\ u_{(-)j-1}^{0*} \end{bmatrix}. \quad (29)$$

Because Eq. (29) describes the evolution of the displacement field from low index (small j) layers to higher index (larger j) layers, the propagators appearing are the inverses of the propagators defined in Eqs. (21) and (22),

$$[L_j^*]^{-1} = \begin{bmatrix} \exp(-ik_j^* d_j) & 0 \\ 0 & \exp(ik_j^* d_j) \end{bmatrix}, \quad (30)$$

$$[S_{j-1,j}^*]^{-1} = \frac{1}{2} \begin{bmatrix} 1 + (Z_{j-1}^*/Z_j^*) & 1 - (Z_{j-1}^*/Z_j^*) \\ 1 - (Z_{j-1}^*/Z_j^*) & 1 + (Z_{j-1}^*/Z_j^*) \end{bmatrix}. \quad (31)$$

Finally, the local shear stress can be determined from the fact that the local impedance is the ratio of the shear stress to the shear velocity $\dot{u}^*$.² By accounting for the contributions from the forward and backward traveling waves, we obtain

$$\sigma_j^* = Z_j^* (\dot{u}_{(-)j}^* - \dot{u}_{(+)j}^*) = i\omega_n Z_j^* (u_{(-)j}^* - u_{(+)j}^*). \quad (32)$$

III. CALIBRATIONS AND MODELING

A. Self-consistent mean field theory calculations

In the previous section, we describe a system where a liquid solution of PEG is located beneath a capping layer and submerged in an aqueous environment. As a first approximation, this system can be described by a three layer model where the brush is assumed to be a solution with uniform concentration throughout a region of thickness h_{br} . As shown previously by Milner *et al.*,²⁷ a better approximation to the concentration profile of the polymer brush is the following parabolic profile:

$$\phi_{\text{br}}(z) = \frac{3h_{\text{dry}}}{2h_{\text{br}}} \left[1 - \left(\frac{z}{h_{\text{br}}} \right)^2 \right], \quad (33)$$

where h_{dry} is the dry thickness of the brush, which is equal to the integrated brush volume fraction. While this expression is a very useful approximation in many cases, it fails to ac-

FIG. 5. Self-consistent-field calculations of the osmotic pressure as a function of brush layer thickness for PEG brushes with a molecular weight of 5700 g/mol with dry thicknesses ranging from 1 to 9 nm.

count for subtle yet potentially important effects such as depletion zones near a nonadsorbing surface or tail regions of low polymer concentration at the outer regions of the brush.^{28–31} In addition, we are often interested in cases where the overall thickness of the hydrated layer, which we refer to as h , does not correspond to the thickness of an isolated parabolic brush. For these reasons, we use the numerical self-consistent mean-field (SCF) theory³² implemented as described previously²⁸ to determine the concentration profile of the hydrated layer. In calculations, we assume that the PEG brush has a molecular weight of 5700 g/mol and that h_{dry} varies between 1 and 9 nm, which are values that correspond to the experimentally accessible range.¹⁸

From the SCF calculations, the free energy per unit area U is calculated as a function of h at a fixed value of h_{dry} . The osmotic pressure is then obtained by differentiating this free energy with respect to the layer thickness,

$$\Pi = - \left. \frac{dU}{dh} \right|_{h_{\text{dry}}} . \quad (34)$$

Calculated osmotic pressure curves of the swollen brush for different values of h_{dry} are plotted in Fig. 5. These are the pressures that must be applied to the system in order to obtain a given value of h . The pressure can either be osmotically applied by using PEG solutions in a “wet contact” experiment or as an actual physical pressure.^{18,33} If relatively low pressures in the range of 1000 Pa are applied, the hydrated layer thicknesses are generally in the range of 15–30 nm. As demonstrated in the calculations below, this thickness regime corresponds to the regime where we are most sensitive to the small changes in h . The utility of the membrane enhancement technique as a characterization method arises from this excellent correspondence between the length scales that are probed in the experiment and the length scales that are experimentally relevant.

B. PEG calibration experiments

Impedance calibrations of PEG solutions were performed by flooding the QCR surface with 650 μl of PEG (1000 and 6800 g/mol, Scientific Polymers Products, Inc.; 70 kg/mol, synthesized in house) solutions in water, with polymer volume fractions ranging from 0 to 0.6. Measured values for the frequency shift Δf_{br} and change in the band-

FIG. 6. Measured values of the frequency shift ($-\Delta f_{\text{br}}$, open symbols) and shift in bandwidth ($\Delta \Gamma_{\text{br}}$, closed symbols) for PEG solutions of different concentrations. The dashed lines are the quadratic fits given by Eq. (35).

width $\Delta \Gamma_{\text{br}}$ are plotted as a function of the polymer volume fraction in Fig. 6. The dashed lines in these figures are the following polynomial fits:

$$\Delta f_{\text{br}}(\text{kHz}) = -1.24 - 2.54\phi_{\text{PEG}} - 7.71\phi_{\text{PEG}}^2, \quad (35)$$

$$\Delta \Gamma_{\text{br}}(\text{kHz}) = 1.24 + 7.99\phi_{\text{PEG}} + 8.71\phi_{\text{PEG}}^2.$$

These values directly give the complex impedance of the PEG solutions by application of Eq. (2). These values can also be directly related to the complex viscosity of PEG solutions through the following expression:

$$\Delta f_{\text{br}}^* = \Delta f_{\text{br}} + i\Delta \Gamma_{\text{br}} = \frac{if_1}{\pi Z_q} \sqrt{i\omega_n \rho_{\text{br}} \eta_{\text{br}}^*}, \quad (36)$$

where η_{br}^* is the complex viscosity of the PEG solutions and ρ_{br} is the corresponding solution density. For pure water ($\phi_{\text{PEG}}=0$), the complex viscosity is real and one expects $-\Delta f = \Delta \Gamma = 1.24$ kHz, which is in good agreement with the experimental data.

As ϕ_{PEG} increases, the magnitude of the complex viscosity increases and the solutions gradually become more elastic. For sufficiently high molecular weights, the response is independent of the molecular weight itself. In our case, we obtain nearly identical results for PEG solutions with molecular weights of 6.8 and 70 kg/mol. This result is attributable to the fact that at these high oscillation frequencies, we are probing the higher order Rouse modes characteristic of local segmental motions within the polymers. This result justifies our use of PEG solutions as calibration standards for the determination of the local acoustic impedance within the hydrated polymer brush layer. We assume that this local impedance is equal to the acoustic impedance of a PEG solution with the same PEG composition.

C. Acoustic wave modeling

The merits of using the full SCF brush profile in the calculations are illustrated in Fig. 7. Part (a) of this figure shows a comparison of three brush profiles for $h=36$ nm. The total brush coverage is the same in each case with $h_{\text{dry}}=8$ nm. The simplest of these profiles has a constant brush volume fraction between $z=0$ and $z=h$. The second profile has the parabolic form of Eq. (33) with $h_{\text{br}}=h$. The third is

FIG. 7. (a) PEG concentration profiles of a brush grafted to the surface of a QCR with $h_{\text{dry}}=8$ nm. Uniform, parabolic [Eq. (33)], and numerically calculated SCF profiles are included. (b) Relationship between the calculated resonant frequency shift and the overall thickness of the hydrated brush layer for the three types of concentration profiles from part (a) with h_{dry} fixed at 8 nm in each case. The membrane has a thickness of $1.15 \mu\text{m}$, $\phi = 15^\circ$, $|G^*|=50$ MPa, and a density of 1 g/cm^3 , and the system is assumed to be submerged in pure water.

the full SCF profile, which closely approximates a parabolic function but with a value for h_{br} that is not necessarily equal to h . In Fig. 7(b), we show the calculated frequency shift for each of the three types of concentration profiles as a function of the total hydrated layer thickness h . For the uniform and parabolic profiles, the parameters are adjusted so that h_{dry} remains fixed at 8 nm as h is allowed to vary. The constant volume fraction for the uniform case is h_{dry}/h and h_{br} is equal to h for the parabolic case. The calculated frequency shifts for the parabolic and SCF profiles are in quantitative agreement only for the case where the membrane is just coming into contact with the brush [point c in Fig. 7(b)].¹⁸ At higher values of h , a layer of nearly pure water exists between the membrane and the brush—an effect that is captured only by the full SCF calculation. While this effect can be accounted for by adding a separate layer of pure water to the parabolic profile, we use the full SCF calculation in the remainder of our calculations. This approach is most accurate and enables other effects, such as interactions with the brush and membrane itself, to be incorporated into the model.

In order to quantify the sensitivity of the membrane-enhanced technique to details of the brush structure, we introduce four parameters to characterize the calculated relationships between Δf^* and h . The first is the maximum magnitude of Δf , which we refer to as Δf_{max} . The second is $\Delta\Gamma_{\text{max}}$, which is the corresponding maximum in the change in bandwidth. This quantity describes the maximum dissipation and is closely related to the minimum Q -factor for the

FIG. 8. Relationship between the calculated resonant frequency shift [part (a)] and increase in bandwidth [part (b)] for SCF-calculated brush profiles with h_{dry} ranging from 0 to 9 nm and with identical membrane properties to those listed in Fig. 7. The system is assumed to be submerged in pure water.

resonator [see Eq. (26)]. The third is a sensitivity factor, $\partial\Delta f/\partial h|_{\text{max}}$, which gives the maximum sensitivity of a measurement to changes in the hydrated layer thickness. The final parameter is the qualitative estimate of the range of hydrated thicknesses over which a reasonable sensitivity to this thickness is obtained. A large portion of this region has a slope similar to the frequency shift sensitivity factor. The optimal capping layer will produce a large Δf_{max} and $\partial\Delta f/\partial h|_{\text{max}}$ while minimizing $\Delta\Gamma_{\text{max}}$. In order for useful experimental data to be obtained, it is important that the oscillator not be too highly damped. Empirically, we find that reliable data are obtained at the third harmonic ($f_n = 15$ MHz) when $\Delta\Gamma_{\text{max}}$ is less than 20 kHz.

In Figs. 8–11, we present a series of calculated relationships between the resonant frequency shift, change in bandwidth, and the thickness of the hydrated brush layer. The assumed capping layer thickness in each case is $1.15 \mu\text{m}$, which was experimentally found to give a sensitive system that is not overly damped. The first parameter investigated was the dry brush thickness, which was altered between 0 and 9 nm and shown in Fig. 8. These calculations correspond to a SEBS capping layer with a density of 0.987 g/cm^3 , $|G^*|=50$ MPa, and a loss angle of 15° , which are values that correspond to the capping layer used in our experiments. The calculated values of our four metrics are shown in Table I. In each case, a maximum sensitivity of $\sim 2 \text{ kHz/nm}$ is obtained, although our sensitivity range increases to larger values of h as h_{dry} increases. In all cases, $\Delta\Gamma_{\text{max}}$ is low enough so that a sufficiently sharp resonance is obtained so that Δf and $\Delta\Gamma$ can be accurately measured.

FIG. 9. Frequency shift [part (a)] and change in bandwidth [part (b)] as a function of the hydrated layer thickness for a PEG brush with $h_{\text{dry}} = 8$ nm in contact with different membrane layers, each having a thickness of $1.15 \mu\text{m}$. The membrane properties are listed in Table II and the system is assumed to be submerged in pure water.

Figure 9 shows the range of responses that are obtained by using a range of very different material types as the capping layer. Representative moduli, densities, and loss angles

FIG. 10. Frequency shift [part (a)] and change in bandwidth [part (b)] as a function of the hydrated brush layer thickness for a PEG brush with $h_{\text{dry}} = 8$ nm in contact with a SEBS membrane. The membrane properties are the same as in Fig. 7 but calculations for the full range of loss angles are included. The system is assumed to be immersed in pure water.

FIG. 11. Frequency shift [part (a)] and change in bandwidth [part (b)] as a function of the hydrated brush layer thickness for a PEG brush with $h_{\text{dry}} = 8$ nm in contact with a SEBS membrane. The membrane properties are the same as in Fig. 7 but with membrane thicknesses ranging from 0.25 to 1.5 μm . The system is assumed to be immersed in pure water.

were chosen for these materials^{7,34} with the specific values listed in Table II. The membrane thickness was fixed at $1.15 \mu\text{m}$ and h_{dry} was fixed at 8 nm. The results of these calculations are summarized by the metrics listed in Table III. The metal layer experiences the greatest magnitude of frequency shift primarily because its high density gives it the largest Sauerbrey shift [see Eq. (1)]. This increased value of Δf_{max} comes at the expense of a higher value of $\Delta \Gamma_{\text{max}}$, however. In fact, it would be very difficult to accurately measure the resonance with a metal film of this film thickness. This issue can easily be avoided by using a thinner metal film since Δf_{max} and $\Delta \Gamma_{\text{max}}$ are generally correlated with one another.

The essential message of the data included in Fig. 9 and Tables II and III is that the technique can work quite well

TABLE I. Metrics describing the sensitivity of the $1.15 \mu\text{m}$ SEBS membrane (Fig. 8) to changes in the thickness of the hydrated brush layer.

Dry brush height h_{dry} (nm)	Δf_{max} (kHz)	$\Delta \Gamma_{\text{max}}$ (kHz)	$\left. \frac{\partial \Delta f}{\partial h} \right _{\text{max}}$ (kHz/nm)	Sensitivity range (nm)
0	-22.04	11.28	1.81	0–23
1	-22.60	13.61	1.89	4–25.5
3	-22.85	14.15	1.93	9–32
5	-22.95	14.11	2.08	13.5–36
7	-23.06	14.00	2.06	17–40
8	-23.10	13.93	2.08	18.5–42
9	-23.13	13.86	2.10	20–44

TABLE II. Properties of the materials used as capping layers.

Material	Density ρ (g/cm ³)	Shear modulus magnitude $ G^* $ at 15 MHz	Loss angle ϕ (deg)	Wavelength λ (μ m)	Sauerbrey frequency 1.15 μ m Δf_s (kHz)
Metal ^a	2.7	940 GPa	0	1244	-52.69
Glassy polymer ^a	1	47 GPa	3	457.2	-19.51
SEBS (rubbery polymer)	0.987	50 MPa	15	15.13	-19.26
25% SEBS gel in mineral oil ^b	0.875	13 MPa	51	8.83	-17.07
Mineral oil ^b	0.838	2.2 MPa	88	4.75	-16.35

^aApproximate material properties taken from Ref. 7 by using the density of aluminum.^bMaterial properties taken from Ref. 34.

with any type of membrane material, provided that the membrane thickness is optimized. Elastomeric membranes such as the SEBS film are mechanically robust, are very easy to prepare, and are sufficiently permeable to water so that the hydrated layer can equilibrate with a solution that is placed on the other side of the membrane. A potentially complicating feature of elastomeric membranes is that the loss angles are nonzero and may be difficult to accurately measure. Fortunately, the specific value of the loss angle does not substantially affect the measured values of the frequency shift and dissipation. This aspect of the system behavior is illustrated in Fig. 10, where the calculations of Fig. 7 for $h_{\text{dry}}=8$ nm are repeated but with membrane loss angles spanning the complete range from 0° to 90°.

The maximum measurable frequency shift is directly related to the thickness of the capping layer. This result is illustrated in Fig. 11. Here, we again use the $h_{\text{dry}}=8$ nm calculations from Fig. 7 as a baseline, but we include a range of capping layer thicknesses from 0.25 to 1.5 μ m. The thickness dependence is easy to understand and directly arises from the Sauerbrey frequency shift obtained from Eq. (1). The arrows in Fig. 11(a) represent the Sauerbrey frequency shifts for each of the seven capping layer thicknesses after the addition of the extra 1.24 kHz shift obtained when the system is immersed in water [Eq. (36) with $\eta_{\text{br}}^*=0.001$ Pa s and $\rho_{\text{br}}=1$ g/cm³]. This simple calculation gives a good approximation of the response when the shear wave emanating from the electrode surface is completely coupled into the

capping layer. Also, we generally observe in our calculations that the dissipation is maximized for hydrated layer thicknesses where the sensitivity as given by $\partial\Delta f/\partial h$ is also maximized. For this reason, it is especially important to keep $\Delta\Gamma_{\text{max}}$ at a value that is not too high. As mentioned above, a good rule of thumb is that $\Delta\Gamma_{\text{max}}$ be less than 20 kHz. This consideration also limits the value of the membrane thickness that can be utilized in the experiments because $\Delta\Gamma_{\text{max}}$ generally correlates with Δf_{max} . For the calculations shown in Figs. 8–11, we find that $\Delta\Gamma_{\text{max}}$ is between $0.5\Delta f_{\text{max}}$ and Δf_{max} with $0.7\Delta f_{\text{max}}$ being a typical value. Membranes with thickness in the micron regime provide a high Δf_{max} while also giving values for $\Delta\Gamma_{\text{max}}$ that are low enough for the experiment to be successfully performed.

D. Acoustic shear wave amplitudes

While the Sauerbrey equation gives a simple estimate of Δf_{max} , the range of hydrated layer thicknesses where the sensitivity is maximized depends in a nontrivial way on the spatial dependence of the acoustic impedance. In order to illustrate this effect in more detail, we calculate the depth dependence of the shear wave amplitude, as described in Sec. II C. In Fig. 12, we plot the normalized shear amplitude as a function of distance from the electrode surface for a brush with $h_{\text{dry}}=8$ nm. Three different values of the hydrated layer thickness are included in these calculations. The membrane and brush profile in these calculations is identical to that used to generate the SCF curve (solid line) in Fig. 7(b). The thicknesses for parts (a)–(c) in Fig. 12 correspond to the respective labels (a, b, and c) in Fig. 7(b). For $h=72$ nm [Fig. 12(a)], the shear wave has largely decayed by the time it reaches the membrane layer. As a result, the experiment is relatively insensitive to the presence of the membrane layer and the magnitude of Δf is quite low. For $h=25$ nm [Fig. 12(c)], we see the opposite situation, where the shear wave is completely coupled into the SEBS capping layer and a large value of Δf is obtained. This value of h corresponds to the thickness where the membrane is just coming into contact with the brush, which has a volume fraction profile given by the dashed line in each plot in Fig. 12. An intermediate situation is observed for $h=36$ nm [Fig. 12(b)]. In this case, the shear wave slowly decays in the region of space occupied by

TABLE III. Metrics describing the sensitivity of membrane materials (Fig. 8) to changes in the thickness of the hydrated brush layer.

Material	Δf_{max} (kHz)	$\Delta\Gamma_{\text{max}}$ (kHz)	$\left.\frac{\partial\Delta f}{\partial h}\right _{\text{max}}$ (kHz/nm)	Sensitivity range (nm)
Metal	-57.15	40.04	7.68	16–32
Glassy polymer	-21.80	12.73	1.88	19.5–42
SEBS (rubbery polymer)	-23.10	13.93	2.08	18.5–42
25% SEBS gel in mineral oil	-19.24	13.09	1.46	18.5–41
Mineral oil	-6.61	6.77	0.29	18.5–42

FIG. 12. Normalized magnitude of the acoustic shear wave as it travels through the system corresponding to the SCF brush in Fig. 7. Calculations are for $h=72$ nm [part (a)], $h=36$ nm [part (b)], and $h=25$ nm [part (c)] corresponding to the three labeled points in Fig. 7(b). The calculated PEG concentration profile for each case is shown as the dashed line in each plot.

the PEG brush and much more rapidly decays in the region between the brush and the membrane that is nearly pure water.

A more complete picture of the behavior of this intermediate situation is shown by the data in Fig. 13, where we plot the absolute magnitudes of the shear displacement amplitude, shear velocity, and shear stress for a typical value of the peak voltage of 315 V for the parameters corresponding to Fig. 12(b). Several features are immediately evident from these plots. First, the displacement amplitudes are very small, which decay from a maximum value of $0.29 \text{ \AA}$ at the electrode surface. Second, while the displacement and velocity decay in a very nonuniform manner throughout the whole system, the decay in the shear stress is nearly linear. For a given stress level, the spatial variation in the displacement amplitude is greatest in the regions where the acoustic impedance is the lowest, i.e., in the region of nearly pure water for values of z between 25 and 36 nm. This low impedance layer behaves as a slip layer that decreases the displacement that is actually transferred to the membrane.^{10,35}

IV. CONCLUSION

The response of a QCR to loading by a nonuniform medium is a complicated process that generally requires a nu-

FIG. 13. The displacement [part (a)], velocity [part (b)], and shear stress [part (c)] for the acoustic wave as it travels through the system corresponding to the data shown in Fig. 12(b).

merical analysis. We have applied this analysis to the specific case of a grafted polymer brush in contact with a membrane capping layer. By appropriate choice of the membrane, it is possible to design an experiment that is extremely sensitive to the degree of swelling of the polymer brush. In this paper, we have applied the analysis to the specific case of a PEG brush that is grafted to the gold electrode surface of the resonator. Our work and the most important conclusions emerging from it are summarized as follows.

- The parameters needed in the analysis, including the overall acoustic impedance of the membrane layer and the local acoustic impedance within the brush layer, are all obtained from calibration experiments.
- The experiment is sensitive to details of the polymer volume fraction profile within the swollen polymer brush. In our case, we use self-consistent-field theory to calculate the concentration profile of the polymer brush. These calculated concentration profiles are used with the calibration experiments to determine the complete spatially dependent acoustic impedance throughout the entire system.
- The optimal membrane thickness for these experi-

ments is $\sim 1 \mu\text{m}$ and is not strongly dependent on the membrane properties. Compliant elastomeric membranes that allow the brush structure to equilibrate by the transport of water through the membrane are particularly convenient.

- The resonant frequency shift is strongly dependent on the thickness of the hydrated layer within the experimentally relevant thickness regime (typically tens of nanometers).

ACKNOWLEDGMENTS

This work was supported by NIH (R01 DE14193) and NSF (DMR-0525645).

APPENDIX A: SERIES EXPANSION OF THE SINGLE LAYER FREQUENCY SHIFT

The tangent function of Eq. (8) can be expanded as a Taylor series that gives the following expression for the normalized complex frequency shift:

$$\frac{\Delta f_{1,0}^*}{\Delta f_s} = \sum_{n=1}^N \frac{B_{2n}(-4)^n(1-4^n)}{(2n)!} (k_1^* d_1)^{2(n-1)}, \quad (\text{A1})$$

where B_{2n} are the even Bernoulli numbers. The expansion to $N=5$ is

$$\begin{aligned} \frac{\Delta f_{1,0}^*}{\Delta f_s} = 1 + \frac{1}{3}(k_1^* d_1)^2 + \frac{2}{15}(k_1^* d_1)^4 + \frac{17}{315}(k_1^* d_1)^6 \\ + \frac{682}{31185}(k_1^* d_1)^8. \end{aligned} \quad (\text{A2})$$

For a SEBS layer with $\phi_1=15^\circ$, a comparison of the full tangent and Taylor expansions for $N=1-5$ is shown in Fig. 14. As shown, the Taylor expansion to $N=3$ fully describes the features of the tangent function. There are very small additional improvements by further expanding the Taylor series in this region of the curve.

APPENDIX B: CORRELATION WITH THE WHITE AND SCHRAG APPROACH

The multilayer model used throughout this paper is a modified version of the model previously developed by Domack *et al.*¹⁷ In the case of a two layer system where the top layer is a semi-infinite expanse ($d_2 \rightarrow \infty$), this model is equivalent to the model described by White and Schrag⁷ for an elastic film in a viscous medium. The form of the model described by White and Schrag is obtained by expanding all complex quantities into their real and imaginary components. The following expressions relate the parameters from the White and Schrag model (K , L , Q , P , c , and d) to the parameters that we have used:

$$\frac{(-L + iK)}{(Q + iP)} = \frac{[iZ_1^* \sin(k_1^* d_1) + Z_2^* \cos(k_1^* d_1)]}{Z_1^* \cos(k_1^* d_1) + iZ_2^* \sin(k_1^* d_1)}, \quad (\text{B1})$$

$$c - 1 + di = iZ_1^*, \quad (\text{B2})$$

$$c + 1 + di = -iZ_2^*.$$

FIG. 14. The frequency shift produced by a single material film normalized by the Sauerbrey frequency shift on a QCR. Values are shown for a film with a 15° loss angle. The curves shown are the approximations of different orders of the Taylor expansion of the tangent function with the solid line being the tangent function.

- G. G. Guilbault and J. M. Jordan, *Crit. Rev. Anal. Chem.* **19**, 1 (1988).
- D. Johannsmann, *Springer Series on Chemical Sensors and Biosensors: Piezoelectric Sensors* **5**, 49 (2007).
- G. Sauerbrey, *Z. Phys.* **155**, 206 (1959).
- C. E. Reed, K. K. Kanazawa, and J. H. Kaufman, *J. Appl. Phys.* **68**, 1993 (1990).
- D. Johannsmann, K. Mathauer, G. Wegner, and W. Knoll, *Phys. Rev. B* **46**, 7808 (1992).
- D. Johannsmann, *Macromol. Chem. Phys.* **200**, 501 (1999).
- C. C. White and J. L. Schrag, *J. Chem. Phys.* **111**, 11192 (1999).
- S. J. Martin, H. L. Bandey, R. W. Cernosek, A. R. Hillman, and M. J. Brown, *Anal. Chem.* **72**, 141 (2000).
- E. Benes, *J. Appl. Phys.* **56**, 608 (1984).
- M. Urbakh, V. Tsionsky, E. Gileadi, and L. Daikhan, *Springer Series on Chemical Sensors and Biosensors: Piezoelectric Sensors* **5**, 111 (2007).
- R. Lucklum, C. Behling, P. Hauptmann, R. W. Cernosek, and S. J. Martin, *Sens. Actuators, A* **66**, 184 (1998).
- C. S. Lu and O. Lewis, *J. Appl. Phys.* **43**, 4385 (1972).
- W. P. Mason, *Piezoelectric Crystals and their Application to Ultrasonics* (Van Nostrand, Princeton, NJ, 1950).
- V. E. Granstaff and S. J. Martin, *J. Appl. Phys.* **75**, 1319 (1994).
- T. Nakamoto and T. Moriizumi, *Jpn. J. Appl. Phys., Part 1* **29**, 963 (1990).
- S. J. Martin, V. E. Granstaff, and G. C. Frye, *Anal. Chem.* **63**, 2272 (1991).
- A. Domack, O. Prucker, J. Ruehe, and D. Johannsmann, *Phys. Rev. E* **56**, 680 (1997).
- D. A. Brass and K. R. Shull, *Langmuir* **22**, 9225 (2006).
- H. L. Bandey, A. R. Hillman, M. J. Brown, and S. J. Martin, *Faraday Discuss.* **107**, 105 (1997).
- J. Goubaidouline, J. Reuber, F. Merz, and D. Johannsmann, *J. Appl. Phys.* **98**, 014305 (2005).
- S. Storri, T. Santoni, M. Minunni, and M. Mascini, *Biosens. Bioelectron.* **13**, 347 (1998).
- J.-W. Benjamins, K. Thuresson, and T. Nylander, *Langmuir* **21**, 149 (2005).
- J. F. Nye, *Physical Properties Of Crystals: Their Representation by Tensors and Matrices* (Clarendon, Oxford, 1985).
- D. A. Buttry and M. D. Ward, *Chem. Rev. (Washington, D.C.)* **92**, 1355 (1992).

- ²⁵F. Eggers and T. Funck, *J. Phys. E* **20**, 523 (1987).
- ²⁶D. Johannsmann and L.-O. Heim, *J. Appl. Phys.* **100**, 094505 (2006).
- ²⁷S. T. Milner, T. A. Witten, and M. E. Cates, *Europhys. Lett.* **5**, 413 (1988).
- ²⁸K. R. Shull, *Macromolecules* **29**, 2659 (1996).
- ²⁹M. W. Matsen, *J. Chem. Phys.* **122**, 144904 (2005).
- ³⁰A. P. Gast, *Langmuir* **12**, 4060 (1996).
- ³¹H. Orland and M. Schick, *Macromolecules* **29**, 713 (1996).
- ³²M. W. Matsen, *J. Phys.: Condens. Matter* **14**, R21 (2002).
- ³³A. Flory, D. A. Brass, and K. R. Shull, *J. Polym. Sci., Part B: Polym. Phys.* **45**, 3361 (2007).
- ³⁴F. N. Nunalee and K. R. Shull, *Langmuir* **22**, 431 (2006).
- ³⁵C. Neto, D. R. Evans, E. Bonaccorso, and H. J. Butt, and V. S. J. Craig, *Rep. Prog. Phys.* **68**, 2859 (2005).