Feature Article

Viscoelastic analysis of organic thin films on quartz resonators

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SUMMARY: By analyzing the frequency shifts and bandwidths of coated quartz resonators the viscoelastic coefficients of the coatings may be derived. The paper gives an overview of the experimental procedure and the data analysis. Some examples of the application of this technique in the range of soft condensed matter are described. The swelling and plasticization of polymer films in solvent vapor was monitored in-situ. We reported on measurements of the acoustic thickness of polymer brushes, the thickness of which varies with the solvent quality. The acoustic thickness is significantly larger than the optical thickness because the dilute outer portions of the swollen layer affects the acoustic behavior of the brush much more than the optical behavior. Sandwiching polymer layers between quartz plates and rigid overlayers expands the range of the applicability of the technique at the end of low film thicknesses, because the rigid overlayer adds inertia to the composite film and therefore enhances the stress acting on the layer of interest. Finally, the combination with optical birefringence measurements in Fabry-Perot configuration gives access to the stress-birefringence inside the polymer film. Normal stress components proportional to the square of the oscillation amplitude have been measured for the first time.

I. Introduction

The structure and dynamics of polymers on the mesoscopic scale has increasingly come into the focus of scientific interest in the past years. This development has been partly stimulated by the widespread tendency towards miniaturization. There is also a genuine scientific interest in polymers at this length scale because the mesoscopic scale coincides with many intrinsic length scales of polymers such as the radius of gyration, the hydrodynamic screening length, the domain size in block copolymers, the persistence length of stiff main chains, and many others.

Mechanical dynamical studies on the mesoscopic scale, however, are difficult. The standard mechanical dynamical equipment does not achieve the required mechanical precision. To date, most investigations have been carried out with the surface forces apparatus (SFA) where two crossed cylinders are approached to each other. The dynamical behavior of polymers confined to the space between the cylinders can be probed by either modulating their distance or by shearing them with respect to each other. Although similar efforts are reported for atomic force microscopes, this technique is still in its infancy, the most prominent problem being the ill-defined contact area.

A somewhat complementary approach consists of analyzing the resonance spectrum of quartz crystals. In the context of quartz crystal microbalances where frequency shifts are converted to deposited mass, viscoelastic effects were widely perceived as an impediment to accurate mass determination. When the viscoelastic constants of the coating are known, correction for the viscoelastic effects is possible. This correction is particularly important for thick films and for soft materials such as rubber polymers.

If, on the other hand, sufficient information can be gathered from the spectrum of resonances, the viscoelastic constants may actually be derived from quartz measurements. This additional information becomes accessible by (a) measurement of the resonance frequency as well as the resonance bandwidth and (b) comparison of the resonant behavior on several harmonics. The technique is particularly suited for the investigation of fast dynamics in the MHz range.

The fundamental laws governing the behavior of quartz crystals in contact with viscoelastic media have been described as early as 1948 by Mason in his book “Piezoelectric Crystals and their Applications to Ultrasonics”. Mason does not, however, make reference to the study of thin films. The interest in quartz resonators was for a long time (and still is in terms of commercial application) governed by frequency control. The effects of temperature, pressure, aging, and driving voltage were analyzed in great detail. Full three-dimensional modeling was undertaken. In particular, it was recognized that the oscillation can be confined to the central portion of the quartz by using key-hole-shaped electrodes, edge profiling, or the use of...
plane-convex quartz plates\cite{13}. However, to our knowledge no full three-dimensional modeling including a viscoelastic medium in contact with the resonator has been undertaken so far.

Sauerbrey realized in 1964 that the frequency shift induced by a thin film deposited on a quartz resonator can be used to determine the film’s mass\cite{8}. Monolayer sensitivity is readily achieved. Quartz crystal microbalances are today routinely employed for this purpose in the thin films and coatings industry\cite{10}.

The interest in quartzes immersed in liquids originated from electrochemistry, where the electrode current was correlated with the mass transfer\cite{17–19}. Unfortunately, the simple Sauerbrey relation does not necessarily apply in liquids. It was then realized that the resonance bandwidth contains very valuable information as well\cite{20, 21}. Even in air or vacuum, where damping is small, the bandwidth can be used to probe dissipative processes on the quartz surface\cite{22}. In liquids, the viscous drag results in a frequency shift, which is a priori not separable from the effect of deposited mass. However, for an ideal liquid the viscosity leads to an increase in bandwidth twice as large as the frequency shift which in principle allows for a separate determination of mass and viscosity. Reed and Kanazawa were the first to provide a full modeling of coated quartzes including viscous dissipation\cite{23}.

The extension of the viscoelastic model to viscoelastic films and multilayers follows the matrix formalism known from the optics of multilayered media\cite{24}. Surface and interface anomalies are analyzed by treating these regions as separate layers in an appropriate multilayer configuration. A particularly interesting situation occurs for films with a thickness of one quarter of the wavelength of sound. Under this condition – termed film resonance – the bandwidth as a function of film thickness goes through a maximum and the frequency increases when the film mass is further increased\cite{25, 26}. The film resonance is a very salient feature because it allows for the inversion of the equations in order to derive the film’s viscoelastic properties\cite{26, 27}. There are other configurations which also allow the derivation of viscoelastic constants.

This paper reviews various experimental situations and corresponding procedures of data analysis. In Section II some experimental aspects are discussed. Section III summarizes the theoretical formalism and gives the equations for certain special cases of interest to the experimentalist. In Section IV some examples of the use of quartz resonators in soft condensed matter physics are presented.

II. Experimental aspects

In the electronics industry as well as in the context of microweighing applications, quartz resonators are usually integrated into oscillator circuits. While this is a cheap and convenient configuration for determining resonance frequencies, it is not the method of choice for viscoelastic analysis. Important additional information is gained through the use of network analyzers instead of oscillator circuits. With network analyzers the impedance spectrum $Z(o)$ is passively determined. The advantages of this procedure are:

- Both frequency and bandwidth are accessible.
- Different harmonics can be sequentially addressed.
- Undesired anomalies including skewed resonance curves or distorted resonances due to the interference of anharmonic sidebands are directly detected. While in some cases the problems can be overcome by proper analysis, the problematic modes have to be excluded from analysis in other cases. Still, it is very important to recognize the problem which is often impossible with oscillator circuits.

Fig. 1 displays examples of a good set of raw data as well as data from a high overtone with inferior data quality. In the latter case an oscillator circuit would hardly yield reliable results. Depending on the network analyzer available, the speed of measurement may be lower for passive measurements than for oscillator circuits. Data traces such as the ones shown in Fig. 1 are taken in about 10 s. With the use of modern network analyzers this time can be much reduced. Note, however, that the quartz resonators themselves may display time dependent behavior such as slow response or overshooting on the time scale of fractions of a second when they are subjected to

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{resonance_curves.png}
\caption{AC electrical conductance of a quartz resonator around its 3rd and its 35th harmonic. The frequency and the bandwidth are obtained by fitting Lorentzians to the conductance. For the 3rd harmonic the fit (dashed line) cannot be graphically distinguished from the data (straight line). For high harmonics, anharmonic sidebands interfere with the resonance of interest and ultimately limit the useful frequency range.}
\end{figure}
rapidly varying environmental conditions. These effects are particularly severe when the process of interest is accompanied by gradients of temperature or pressure.

If the data taken on different harmonics are compared, the use of overtone quartzes is highly advisable. These have two optically polished, flat surfaces. The number of accessible overtones critically depends on the parallellity of the two surfaces. For good quartz blanks the overtone spectrum can be examined to well beyond \( n = 20 \).

Mounting is a critical issue. Special attention has to be paid to mounting in liquid cells. Here the resonator has to be attached to the holder all around its rim in order to prevent electrical contact between the two electrodes. The front electrode should be connected to the electric ground. Usually the influence of mounting is largely reduced by energy trapping \(19)\), whereby the oscillation is confined to the central portion of the quartz. For overtone quartzes this is achieved by using keyhole-shaped electrodes. Frequently this mode of energy trapping is only efficient on higher harmonics. On the fundamental mode the use of plane-convex quartzes is preferable. For this reason data from low harmonics (the fundamental in particular) have frequently to be discarded. In practice, the use of harmonics higher than about \( n = 7 \) has turned out to be a viable procedure.

A second drawback with regard to the use of low harmonics is piezoelectric stiffening which is proportional to the inverse overtone order (see Theory Section). Piezoelectric stiffening introduces a separate term into the equivalent circuit ("\( Z_a \)" in Fig. 2a) which severely complicates the analytic treatment. Also, the acoustic behavior of the quartz is affected by the electric boundary conditions via piezoelectric stiffening, which introduces undesirable complications \(28, 29)\). These effects are negligible on high harmonics. Piezoelectric stiffening can be reduced by lateral field excitation \(30)\). However, the electric field across the quartz is weak in this case, resulting in problems of sensitivity.

At the high frequency end of the resonance spectrum mixing of anharmonic sidebands with the resonance of interest ultimately limits the accessible range (Fig. 1, bottom). Since mode mixing strongly depends on the bandwidth, it becomes more severe in the presence of viscous overlayers.

An interesting alternative to the conventional mode of mounting and contacting is the use of electrode-less quartzes excited across an air gap \(30)\). For narrow gaps the electrical amplitude is large enough to determine the resonance frequency although there certainly is a loss of sensitivity. Also, due to piezoelectric stiffening the resonance frequency depends on the width of the air gap. The most attractive feature of this mode is the elimination of electrodes, which are a major source of complication in the viscoelastic analysis (see Theory Section). Also, since this is the simplest possible geometry, it should be a good starting point for full three-dimensional modeling. The elimination of electrodes, on the other hand, also eliminates energy trapping and the oscillation is no longer confined to the central portion of the quartz blank. Mounting has to be done as gentle as possible. Suspending the quartz on an air cushion is one possibility. It turns out that the blank may also be directly placed on the lower metal plate without much affect on its resonance properties because due to the natural roughness of the metal plate the mechanical contact is limited to a few point-like contacts. The elastic interaction across these point contacts is so weak that its influence on the resonance properties is tolerable.

A final word of caution is appropriate with regard to temperature \(14)\), hydrostatic pressure \(31)\), mechanical stress \(32)\), and the driving voltage. All these factors affect the resonance frequency (potentially with memory effects) and have to be monitored with care. The temperatures dependence can to some degree be optimized by proper choice of the crystal cut, where the so-called "AT-cut" has a low temperature-frequency coupling at room temperature.

### III. Theory

#### III A. Equivalent circuit models

There are a number of different ways to model loaded quartz crystals. One popular description is given by equivalent circuits \(13, 25, 26, 33, 34)\). Here the quartz plate is treated as laterally infinite with all waves propagating along the surface normal. Since the model is essentially one-dimensional, the quartz plate can be represented by an acoustic transmission line coupled to an electrical port. The resulting "Mason equivalent circuit" is shown in Fig. 2a. In this three-port network the quartz plate is operated as a transducer with external shear stress acting across its surface. The piezo-effect is modeled as a transformer with force-to-voltage ratio \(\Phi \phi\) depends on the geometry and the piezoelectric coefficient. It is assumed that only the \(x_2\)-component of the stress tensor and only displacements along the \(x\)-direction are present. With this restriction all quantities become scalars and tensor indices may be dropped.

When the quartz plate is operated as a resonator, there are no external forces and the circuit is closed across the acoustic ports. In vacuum this amounts to just short-circuiting them (Fig. 2b). The impedance at the electric port then shows resonant behavior close to the poles of the tangent. The exact definition of the resonance frequency is somewhat ambiguous. Here we use the series resonance frequency, which is given by the condition \(\text{Im}(Z_e) = 0\), where \(Z_e\) is the impedance of the acoustic branch. In experiment this frequency corresponds to the maximum
of the real part of the admittance ("conductance") across the electric port.

The circuit shown in Fig. 2b can be further simplified by applying the Norton transformation\(^{33}\) and linearizing the trigonometric functions around the resonance. One arrives at the Butterworth-van Dyke (BVD) equivalent circuit (Fig. 2c) which is widely used in electronics.

In practice the quartz is usually loaded, for instance by electrodes and/or the layers of interest. Loading by layered systems is accounted for by adding elements to the circuit as shown in Fig. 2d. An arbitrary number of layers can be included provided that the thickness, the acoustic impedance, and the velocity of sound are known. The resonance frequencies are derived by calculating the impedance \(Z_a\) of the acoustic branch and numerically searching the zeros of this function (cf. Fig. 4). This procedure is an exact treatment of the one-dimensional problem. Although it can of course not include effects related to the finite width of the quartz blanks, it does capture a number of non-trivial effects. For example, it shows that the Sauerbrey constant (Section III C) slightly depends on the harmonic used for measurement.

A conceptually different (but equivalent) approach is depicted in Fig. 2e. Here the load is represented as a sin-
ingle generalized impedance $Z'$. The generalized impedance is defined as

$$Z' = \frac{\sigma}{\partial u/\partial t}$$

(1)

with $\sigma$ the shear stress, $u$ the particle displacement, and $\partial u/\partial t$ the particle velocity. Note that in this definition the impedance is normalized to unit area, which is not usually done in electric circuits. For a single acoustic wave in a bulk medium, the generalized impedance $Z'$ equals the conventional acoustic impedance $Z$

$$Z = \rho v = \sqrt{\rho G}$$

(2)

with $\rho$ the density, $v$ the velocity of sound, and $G = G' + iG''$ the shear modulus. In the presence of reflected waves the stress $\sigma$ is the sum of the shear stresses exerted by all waves. In this sense, $Z'$ is not a material constant but depends on geometry. In a geometry with shear waves traveling in both directions, one obtains

$$Z' = \frac{\sigma}{\partial u/\partial t} = \frac{G(\partial u/\partial x)}{\partial u/\partial t} - \frac{Gk(u_+ - u_-)}{i\omega(u_+ + u_-)}$$

$$= \sqrt{\rho G} \frac{1 - r}{1 + r} = Z \frac{1 - r}{1 + r}$$

(3)

with $u_+$ and $u_-$ the amplitudes of waves traveling forward and backward, $r = u_+/u_-$, the normalized amplitude of the reflected wave at the quartz surface (reflection coefficient), and $Z = (\rho G)^{1/2}$ the acoustic impedance of the film at the quartz surface. $Z$ is understood as a material constant, not as a generalized impedance in the sense of Eq. (1). For arbitrary multilayers the reflection coefficient $r$ is calculated with the matrix formalism known from optics, where the acoustic impedance $Z$ takes the role of the refractive index. Continuous viscoelastic profiles can be divided into discrete slabs of small width and treated with the same matrix formalism. Alternatively, one can calculate the impedance of the equivalent network shown in Fig. 2d. The impedance $Z'$ in Fig. 2e is the same as the impedance obtained by applying the Kirchhoff rules to the equivalent circuit. The formulation given in Eq. (3) is closer to the wave picture and potentially a little closer to intuition.

Loading induces a frequency shift $\delta f = f - f_{\text{ref}}$ relative to the unloaded quartz. When the term $Z_s$ is neglected and the trigonometric functions are linearized around the poles of the tangent a simple relation results:

$$\delta f = \frac{i f_0}{\pi} \frac{Z'}{Z_s}$$

(4)

with $\delta f' = \delta f + i\delta \Gamma'$ the shift of the complex resonance frequency $f' = f + i\Gamma'$, $2\Gamma$ the bandwidth, $Z_s = 8.8 \cdot 10^6 \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}$ the acoustic impedance of AT-cut quartz, and $f_0$ the fundamental frequency.

The neglect of the term $Z_s$ ("piezoelectric stiffening") is justified for harmonics higher than about $n = 7$. Note that $Z_s \propto \omega^{-2}$. On low harmonics $Z_s$ induces a frequency dependent correction to Eq. (4). Another caveat to be mentioned with regard to Eq. (4) is the linearization of trigonometric functions. For the viscoelastic analysis presented below the trigonometric functions are frequently Taylor-expanded to third order. For a correct treatment of these effects the linearization leading to Eq. (4) has to be dropped and a full perturbation treatment is necessary (Section III C).

An important feature appears when the reflection coefficient $r$ in Eq. (3) approaches $-1$. This is, for example, the case when the sample is a homogeneous film with a thickness $d_l$ equal to a quarter of the wavelength of sound $\lambda$. In this case the bandwidth $2\Gamma$ of the resonance becomes large and the frequency shift $\delta f$ changes sign (Fig. 3). Note that a positive frequency shift $\delta f$ would correspond to a negative apparent mass of the film if naively interpreted in the picture of the quartz crystal microbalance. An acoustic model is required to correctly analyze the behavior of quartz resonators, once the film thickness is comparable to the wavelength of sound. A situation where $r$ in Eq. (3) is close to $-1$ has been termed "film resonance" because the film itself forms a resonator which has an eigenfrequency close to the driving resonator’s frequency. When the two coupled resonators (quartz and film) have similar frequencies, transfer of energy into the film is most efficient and the damping of the quartz resonance reaches a maximum. Film resonances are unambiguously identified when the frequencies and bandwidths are measured on several harmonics. The condition $d_l \approx \lambda/4$ will only be fulfilled on those harmonics where the wavelength approximately matches four times the film thickness. These harmonics have large
bandwidths and the frequency shift changes sign for harmonics lower and higher than the ones exactly on the film resonance.

III B. Explicit equations for various configurations

1) Semi-infinite liquid medium

For a quartz immersed in a liquid, the generalized impedance $Z'$ equals the acoustic impedance. From Eq. (4) one obtains

$$\delta f' = \frac{i f_0}{\pi Z_q} \sqrt{\rho_1 G_t} = \frac{(i-1)}{\sqrt{2}} \frac{f_0}{\pi Z_q} \sqrt{\rho_1 \omega \eta_1}$$

with $\eta_1$ the viscosity of the liquid. Quartz resonators can be used to measure viscosity\(^{20}\). In practice, torsional resonators operating similarly, but at lower frequencies have been used more often than AT-cut quartz plates. Similar information can be obtained by measurements of ultrasound reflectivity\(^{40}\). Note, however, that small longitudinal contributions may severely affect the measurements. Contrary to shear waves, longitudinal waves do not decay in liquids and may be reflected at the surfaces of the container leading to large artifacts\(^{39,41}\).

2) Single viscoelastic film

If the acoustic load is a film in air or vacuum, the coefficient of reflection $r$ in Eq. (3) can be calculated analytically\(^{25,26}\). One finds the relation

$$\delta f' = \frac{i f_0}{\pi Z_q} Z' = - \frac{f_0}{\pi Z_q} Z_i \tan(k_i d_i)$$

$$= \frac{f_0}{\pi Z_q} \sqrt{\rho_1 G_t} \tan\left(\sqrt{\rho_1 / G_t} \omega d_i\right)$$

where $k_i$ is the wavenumber in the film and $d_i$ the film thickness. The pole of the tangent corresponds to the film resonance (Fig. 3).

In practice, the quantitative agreement between experiment and Eq. (6) turns out to be poor. The general features are, however, well discernible. The origin of the discrepancies between theory and experiment is not quite clear at present. There are indications that coupling to anharmonic sidebands is significantly increased close to the film resonance\(^{42}\). One can infer the viscoelastic properties without quantitative fitting from the frequency of the pole of the tangent. The condition at the film resonance is

$$k_i d_i = 2\pi f_i / \sqrt{\rho_1 G_t} d_i = p\pi/2, \quad p = 1, 3, 5, \ldots$$

with $k$, the wavenumber and $f_i$ the frequency at the film resonance.

For polymers one usually observes only the lowest film resonance ($p = 1$) because the higher film resonances are overdamped. Setting $p = 1$ in Eq. (7) one finds

$$G_t' \approx 16\rho_1 f_i^2 d_i^2$$

For rubbery polymer films and frequencies in the MHz range the film resonance typically occurs in the thickness range of some microns.

For very thin films it is useful to expand Eq. (6) around $d_i = 0$ (“linear regime”). Using $\tan(x) \approx x$ one finds the classical Sauerbrey equation\(^{38,43}\).

$$\frac{\delta f}{f} \approx - \frac{2 f_0}{Z_q} m_t$$

with $m_t = \rho_t d_i$ the mass per unit area. Here and in the following, the quantity $m$ always denotes a mass normalized to area. The Sauerbrey equation is valid for films much thinner than the wavelength of sound. Rigorous treatment of the term $Z_i$ in Fig. 2d and the finite electrode thickness (Section III C) introduces some modifications to this equation even for molecularly thin films.

For films which are thinner but not much thinner than a quarter of the wavelength of sound, one can Taylor-expand Eq. (6) to third order (“cubic regime”). Using $\tan(x) \approx x + 1/3 x^3$ one finds

$$Z' = \frac{f_0}{Z_q} \left[1 + J'_i (\omega) \frac{m_i^2 \omega^2}{3 \rho_1}\right]$$

with $J'_i = J'_i - i J''_i = 1/G_t$ the shear compliance.

Because the tangent was expanded to third order, Eq. (4) must not be straightforwardly applied using $Z'$ as in Eq. (10). The full perturbation (Section III C) yields

$$\frac{\delta f'}{f} \approx \frac{2 f_0}{Z_q} m_t \left(1 + \left[ J'_i (\omega) \frac{4\pi^2 m_i^2}{3 \rho_1} + C \right] f^2 \right)$$

$$\approx \frac{2 f_0}{Z_q} m_t - \frac{2 f_0}{Z_q} \left[ J'_i (\omega) \frac{4\pi^2 m_i^2}{3 \rho_1} + C \right] n^2$$

where $n$ is the overtone order. When plotting the normalized frequency shift $\delta ff / n^2$, one can read the film’s elastic compliance from the slope. For soft films in the absence of electrodes the term $C$ may be neglected. In this case Eq. (11) is easily evaluated with respect to the film’s compliance. With electrodes present the term $C$ depends on the electrode thickness and has to be determined in a separate calibration experiment.

Since Eq. (11) is to be understood as a complex equation, both $J'_i$ and $J''_i$ can be obtained by plotting $\delta f f / n^2$ and $\delta f f / n^2$ versus $n^2$ and reading the slope. From the intercept with the $y$-axis one can also read the film’s mass $m_t$. This mass is a better approximation to the true film mass than the one obtained from the Sauerbrey equation (Eq. (9)) because the elastic corrections have been accounted for.
A certain complication arises because the elastic compliance \( J_l(\omega) \) usually depends on frequency itself. Fortunately, the frequency dependence is smooth in most cases of interest and power laws like \( J_l(\omega) \propto J_l(\omega_0)^{a(\omega/\omega_0)^b} \) and \( J_r(\omega) \propto J_r(\omega_0)^{c(\omega/\omega_0)^d} \) are good approximations. For polymers in the MHz range, the exponents \( a \) and \( b \) typically are between 0 and \(-1/2\). \( J_r \) and \( J_r \) are then determined by fitting the resulting slightly curved lines (rather than a straight line) to the data as shown in Fig. 8. Although the assumed exponents \( a \) and \( b \) do of course affect the results, the dependence is rather weak. The frequency dependence of \( J_l \) must still be kept in mind as a caveat with regard to the numerical accuracy of the derived compliance.

The experimental consideration here considered is impractical for the measurement of the viscoelasticity of ultrathin films because the film is located at an antinode of the standing wave, where the stress exerted on the film is small. As a consequence, the viscoelastic contribution in Eq. (11) is proportional to the third power of the film’s mass. In practice, the sensitivity for viscoelastic properties is lost for films thinner than about 50 nm. For the investigation of thinner films these have to be sandwiched between the quartz and an overlayer, which could either be a second coating or a liquid of known viscosity.

3) Viscoelastic film in a liquid environment

For a film immersed in a liquid one finds

\[
Z' = Z_{l(\omega)} \left( \frac{Z_l + Z_i}{Z_l + Z_i} \right) \exp(2ik_d d_l) \left( \frac{Z_l - Z_i}{Z_l + Z_i} \right)
\]

(12)

where the indices \( f \) and \( l \) denote the film and the liquid, respectively. The denominator becomes large when \( Z_l \gg Z_i \) and \( \exp(2ik_d d_l) \approx -1 \). This is again the condition for a film resonance.

For thin films linear expansion of \( \exp(2ik_d d_l) \) about \( d_l = 0 \) yields \( 44)\)

\[
\begin{align*}
\delta f' &= \frac{f}{\pi Z_k} \left[ \frac{Z_l - Z_l'}{Z_l} \right] \\
\delta f'' &= \frac{f}{\pi Z_k} \left[ \frac{1 - \frac{2\pi \rho \eta}{f}}{\sqrt{2}} - 2\pi m \left( 1 - \frac{\rho}{\rho_l \eta_l} \right) \right]
\end{align*}
\]

(13)

The first term in square brackets is related to the viscosity of the liquid (cf. Eq. (5)). The second term describes a shift induced by the film \( 45, 46) \). As long as the viscosity of the ambient medium remains constant, quartz resonators can be used as microbalances even in liquid environments. This mode of measurement has been widely used in electrochemistry and for sensoric applications \( 47, 48) \). Note, however, that the factor relating mass and frequency shift contains the film’s elastic modulus.

For soft films, this correction may be appreciable. Conversely, if the film’s mass has been determined independently, Eq. (13) may be used to actually derive the film’s elastic properties. Interestingly, the elastic properties enter linearly into the frequency shift. In principle, this should allow measurements on films which are only a few monolayers thick.

A caveat to be mentioned here is the possible influence of surface roughness. The influence of roughness is two-fold: firstly, liquid trapped in crevices will appear as a rigid mass \( 49) \). Secondly, geometric asperities will deviate the flow of liquid and increase the viscous dissipation \( 50, 51) \). These rather complicated hydrodynamic issues are beyond the scope of this review.

For thin polymeric adsorbates with an internal viscoelastic profile \( G(z) \), Eq. (12) also holds in the integral sense

\[
\delta f' = \frac{f}{\pi Z_k} \left[ \frac{iZ_l - \omega \rho \int_0^\infty G(z) - G_w \, dz}{Z_l} \right]
\]

(14)

For polymeric adsorbates the variation of the shear modulus is much stronger than the variation of density. If the density is taken as constant, one arrives at

\[
\delta f' = \frac{f}{\pi Z_k} \left[ \frac{iZ_l - \omega \rho \int_0^\infty G(z) - G_w \, dz}{G(z)} \right]
\]

(15)

In analogy to the “ellipsometric moment” in optics \( 52, 53) \) the integral can be called the “acoustic moment” of the viscoelastic profile. It is the central observable in polymer adsorption as long as the adsorbed layer is much thinner than the wavelength of sound \( 54) \).

The frequency dependence of the generalized impedance from Eq. (12) may be quite complex. To third order in \( \omega \) the impedance is

\[
Z' = Z_l(\omega) + i\rho m \left( \frac{Z_l(\omega) - Z_i(\omega)}{Z_l(\omega)} + \omega^2 m^2 Z_l(\omega) - 2Z_l(\omega) + 3Z_i(\omega) \right)
\]

(16)

where the frequency dependence of the impedance \( Z_l(\omega) \) has been explicitly included to remind the reader that dispersion may in general not be neglected. When the ambient medium is a Newtonian liquid, the relation \( Z_l = (i\omega \rho \eta_l)^{1/2} \) holds. Collecting terms up to third order in \( \omega \), Eq. (16) reads

\[
Z' = \sqrt{i\omega \sqrt{i\omega \eta_l} + i\rho m + \omega^2 m J_l(\omega) \rho \eta_l} \rho_l
\]

\[
+ \omega^3 m^2 J_l(\omega) \sqrt{i\omega \eta_l} \rho_l + i\omega^3 m^2 J_l(\omega) \rho l
\]

(17)

In principle, investigations on several harmonics with different frequencies \( \omega \) should yield additional informa-
tion. Unfortunately, the dependence of the frequency shift on the overtone order is so complex that Eq. (17) can only be exploited if additional information (such as the viscosity of the medium) is available with sufficient accuracy.

4) Two-layer systems

Two-layer systems are still amenable to analytic treatment. Since they are important both for proper treatment of electrodes and for the sandwich configuration, we present the full results. In the latter configuration, the (thin) film of interest is covered by a second, rigid overlay the only purpose of which is to advantageously affect the properties of the composite system such that the viscoelastic properties of the middle layer become accessible. For a two-layer system the impedance $Z'$ is

$$Z' = i \frac{Z_t \tan(k_d d) + Z_m \tan(k_m d_m)}{1 - Z_t/Z_m \tan(k_d d) \tan(k_m d_m)}$$

(18)

where the indices $t$ and $m$ denote the top and the middle layer, respectively. A film resonance is again predicted when the denominator becomes small, i.e., when

$$\frac{\tan(k_m d_m)}{Z_m} = \frac{\cot(k_m d)}{Z_t}$$

(19)

This compares to the film resonance condition for the case of a single film, which is $\tan(k_d d_t) = \infty$. Since the term on the right-hand side can be much less than infinity for a sufficiently thick overlay, the condition for film resonance is shifted towards lower thicknesses. Linearizing Eq. (19) one arrives at

$$\frac{\omega d_m}{G_m} = \frac{1}{\omega m_t}$$

(20)

which is the resonance condition for a rigid mass $m$ elastically suspended on a spring with the spring constant $G_m/d_m$.

Expanding Eq. (18) to third order in $\omega$ yields

$$Z' \approx i \left[ \omega (m_t + m_m) + \frac{\omega^3}{3} \left( \frac{J_m}{\rho_m} (m_m^2 + 3m_m^2) + \frac{J_f}{\rho_f} m_f^2 \right) \right]$$

(21)

The case of the thin overlayer ($m_l \ll m_m$) is treated in detail in Section III C. In the sandwich configuration ($m_m \ll m_t$) one can neglect higher powers of $m_m$. One then has

$$Z' \approx i \left[ \omega (m_t + m_m) + \frac{\omega^3}{3} \left( m_m \frac{J_m}{\rho_m} 3m_m^2 + \frac{J_f}{\rho_f} 3m_f^2 \right) \right]$$

(22)

Due to the overlayer, the viscoelastic effects now scale linearly with thickness of the film in the middle. The viscoelastic effects related to the finite shear compliance are much enhanced by the overlayer.

III C. Perturbation analysis for frequency shifts on quartz plates with electrodes

In order to rigorously simulate the behavior of quartz resonators within the equivalent circuit model, one has to numerically search for the zeros of the impedance of the acoustic branch in Fig. 2d. Fig. 4 shows the results of such a model calculation. The general finding is that the normalized frequency shift $\delta f / f$ follows laws like

$$\delta f / f \approx \mu_0 + S_n n^2$$

(23)

for high enough overtone order $n$. The offset $\mu_0$ and the slope $S_n$ are quantities to be interpreted with regard to viscoelastic parameters. The deviation from this law at low harmonics is caused by the term $Z_t$ (Fig. 2a). With the term $Z_t$ neglected, the functional form of Eq. (23) can be analytically derived by a perturbation analysis. The perturbation analysis also clarifies the significance of the slope $S_n$ in Eq. (23). Since the non-trivial viscoelastic effects occur in third order ($\tan(x) \approx x + 1/3 x^3$) the perturbation must be carried out to third order and Eq. (4) does not capture the behavior correctly. The condition for the (series) resonance is

$$Z_s = 0$$

(24)

where $Z_s$ is the impedance of the acoustic branch. From Fig. 2d one sees that the condition $Z_s = 0$ amounts to
where the relation \( \sin(2\alpha) = 2\tan(\alpha)/(1 + \tan^2(\alpha)) \) has been used. \( Z_0 \) and \( Z_{ak} \) are the general impedances according to Eq. (3) on the front and the back side of the quartz blank. We are interested in the behavior close to the poles of the tangent where

\[
k_\alpha = \frac{n\pi}{2h} (1 + \epsilon), \quad n = 1, 3, 5, ...
\]

with \( \epsilon = -\Delta f / f \) a small quantity and \( n \) the overtone order. Using \( \tan(x + n\pi/2) = -\cot(x) \) and neglecting \( Z_K \), Eq. (25) reads

\[
0 = \frac{iZ_q}{2} \left( \cot \left( \frac{n\pi}{2} \frac{1 + \epsilon}{2} \right) + \tan \left( \frac{n\pi}{2} \frac{1 - \epsilon}{2} \right) \right) \\
+ \frac{\left( Z_0 \tan \left( \frac{n\pi}{2} \frac{1 + \epsilon}{2} \right) - iZ_q \right) \left( Z_{ak} \tan \left( \frac{n\pi}{2} \frac{1 - \epsilon}{2} \right) - iZ_q \right)}{\left( -2iZ_q + (Z_0 + Z_{ak}) \tan \left( \frac{n\pi}{2} \frac{1 - \epsilon}{2} \right) \right) \tan \left( \frac{n\pi}{2} \frac{1 + \epsilon}{2} \right)} \tag{27}
\]

For the empty quartz blank both \( Z_0 \) and \( Z_{ak} \) vanish and Eq. (27) is solved by \( \epsilon = 0 \). In the case of non-zero loads, the loads are expanded to third order in frequency \( \omega \) (Eq. (10), (21), or (22)). The small quantity \( \epsilon \) is then written as \( \epsilon = \epsilon^{(1)} + \epsilon^{(2)} + \epsilon^{(3)} \). In first order perturbation, \( \epsilon \) in Eq. (27) is substituted by \( \epsilon^{(1)} \). Eq. (27) is then linearized and solved with regard to \( \epsilon^{(1)} \). For the second order approximation, \( \epsilon \) is replaced by \( \epsilon^{(1)} + \epsilon^{(2)} \), where the solution from first order perturbation is used for \( \epsilon^{(2)} \). Eq. (27) then again is linearized and solved with regard to \( \epsilon^{(2)} \). The third order approximation proceeds analogously. The total normalized frequency shift is then given by \( \delta f / f = \epsilon^{(1)} + \epsilon^{(2)} + \epsilon^{(3)} \).

1) Single film on one quartz surface

For a single film on one quartz surface, the quantity \( Z_0 \) in Eq. (24) is replaced by

\[
Z_0 \approx im \omega \left[ 1 + J_i(\omega) \frac{m^*_f \omega^2}{3\rho_f} \right] \tag{28}
\]

The impedance at the back side \( Z_{ak} = 0 \). The perturbation analysis yields

\[
0 = Z_0 - \frac{iZ_q}{\sin(2k_\alpha h)} + \frac{(iZ_q \tan(k_\alpha h) + Z_0)(iZ_q \tan(k_\alpha h) + Z_{ak})}{(2iZ_q \tan(k_\alpha h) + Z_0 + Z_{ak})} \\
- \frac{\Phi^2}{\cos(C_{0q})} \frac{iZ_q(1 + \tan^2(k_\alpha h))}{2\tan(k_\alpha h)} \\
+ \frac{(iZ_q \tan(k_\alpha h) + Z_0)(iZ_q \tan(k_\alpha h) + Z_{ak})}{(2iZ_q \tan(k_\alpha h) + Z_0 + Z_{ak})} \tag{25}
\]

Fig. 5. Normalized frequency shifts \( \delta f / f \) vs. \( f^2 \) for a 300 nm film of poly(isobutylene) spin-cast onto a bare quartz blank and determined with the resonator suspended on an air cushion. The slope \( S_c \) can be evaluated with respect to the film’s elastic compliance according to Eq. (11) with \( C = 0 \). Systematic errors from electrodes have been eliminated. On the other hand, the resonance excitation across an air gap has raised the noise level

\[
\frac{\delta f}{f} = -\frac{m_r}{m_q} + \left( \frac{m_r}{m_q} \right)^2 - \pi^2 n^2 \left( \frac{m_r}{m_q} \right)^3 \left( Z_{ak}^2 - Z_q^2 \right)
\]

\[
\approx -2f_m Z_q + \left( \frac{2f_m Z_q}{Z_q^2} \right)^2 - \frac{2f_m Z_q}{Z_q^2}
\]

\[
- \frac{2f_m Z_q}{Z_q^2} \left( J'_i(\omega) \frac{4\pi^2 m_r^3}{3\rho_f} - \frac{4\pi^2 m_r^3}{3Z_q^3} \right) \tag{29}
\]

where the relation \( m_r = Z_q / (2f_m) \) has been used. \( m_q \) here is the mass of the quartz per unit area.

The quadratic and the cubic term independent of frequency result from the fact that the inverse frequency of resonance \( 1/f_c \) is proportional to the total mass \( m_q + m_r \). If the film has the same impedance as the AT-cut quartz, one has

\[
\frac{\delta f}{f} = \frac{m_r}{m_q} + \frac{1}{1 + m_r/m_q} - 1
\]

\[
\approx -\frac{m_r}{m_q} + \left( \frac{m_r}{m_q} \right)^2 - \left( \frac{m_r}{m_q} \right)^3 \tag{30}
\]

These terms are corrections to the Sauerbrey relation (Eq. (9)). If the acoustic impedance of the film differs from the impedance of AT-cut quartz, \( \delta f / f \) depends on the overtone order. The term \( C \) in Eq. (11) is identified as \( C = -4/3 \pi^2 m_r^3 / Z_q^3 \).

Eq. (30) assumes that there are no electrodes present. In the absence of evaporated electrodes, the resonances have to be excited externally across an air gap. Fig. 5 shows data from a 300 nm film of poly(isobutylene) taken in that configuration. Due to the increased electrode spacing and the correspondingly lower electric fields the signal-to-noise ratio is significantly decreased compared to the conventional procedure. The slope \( S_c \) is still well determined and analyzed with regard to the elastic compliance.
2) Two symmetric films (bare electrodes)

For symmetric films (bare electrodes) \( Z_{a} \) and \( Z_{b} \) are replaced by

\[
Z_{a} = Z_{b} \approx \text{i}m_{s} \omega \left[ 1 + J_{p}^{1}(\omega) \frac{m_{s}^{2} \alpha_{1}^{2}}{3p_{l}} \right]
\]

where the abbreviations \( \mu_{e} = m_{e}/m_{o} \), \( \mu_{s} = m_{s}/m_{o} \), \( \alpha = Ze_{j}/Z_{l}^{2} - 1 = (J_{j}/\mu_{o})Z_{j} - 1 \), and \( \alpha_{1} = Ze_{j}/Z_{l}^{2} - 1 = (J_{j}/\mu_{o})Z_{j} - 1 \) have been used.

The above equation assumes that the frequency shift is referenced to the bare quartz blank without electrodes. When the frequency shift is referenced to the quartz with electrodes, one arrives at the following modification

\[
\frac{\delta f}{f} \approx \mu_{e} \left[ -1 + 2\mu_{e} - 4\mu_{s}^{2} + 8\mu_{s} \right]
\]

where the abbreviations \( \mu_{e} = m_{e}/m_{o} \), \( \mu_{s} = m_{s}/m_{o} \), \( \alpha = Ze_{j}/Z_{l}^{2} - 1 \), and \( \alpha_{1} = Ze_{j}/Z_{l}^{2} - 1 \) have been used.

3) Film on symmetric electrodes

In Eq. (29) it was assumed that there were no electrodes underneath the film of interest. Unless one excites the resonance across an air gap, this is not the case in experiment. For a film on electrodes the impedance \( Z_{e} \) is given by (Eq. (21))

\[
Z_{e} \approx \left[ \omega(m_{e} + m_{o}) + \frac{\alpha_{1}^{2}}{3} \right]
\]

\[
\cdot \left[ \frac{J_{p}^{1}}{\rho_{e}} (m_{e}^{2} + 3m_{o}^{2}m_{e} + 3m_{o}m_{e}^{2} + \frac{J_{p}^{1}}{\rho_{l}} m_{e}^{2}) \right]
\]

The perturbation analysis yields

\[
\frac{\delta f}{f} \approx -2\mu_{e} + (2\mu_{s})^{2} - (2\mu_{s})^{3}
\]

\[
+ \mu_{e} \left[ -1 + 2\mu_{e} - 12\mu_{s}^{2} + 32\mu_{s}^{3} \right]
\]

\[
+ \mu_{s} \left[ -1 + 16\mu_{e}^{2} - 24\mu_{s}^{2} + 80\mu_{s}^{3} \right]
\]

\[
+ \mu_{s} \left[ -1 + 8\mu_{e} - 40\mu_{s}^{2} + 160\mu_{s}^{3} \right]
\]

\[
+ \alpha \pi^{2} \left[ \alpha_{1}^{2} \left[ -2 + 3\mu_{s}^{2} \right] \right]
\]

\[
+ \mu_{e} \alpha \left[ \alpha_{1}^{2} \left[ 32/3 \mu_{s}^{2} \right] \right]
\]

\[
+ \mu_{s} \alpha \left[ \alpha_{1}^{2} \left[ -12\mu_{e}^{2} - 260/3 \mu_{s}^{3} \right] \right]
\]

\[
+ \mu_{s} \alpha \left[ \alpha_{1}^{2} \left[ 4\mu_{e} - 50\mu_{s}^{2} + (1120/3)\mu_{s}^{3} \right] \right]
\]

\[
+ \mu_{s} \alpha \left[ \alpha_{1}^{2} \left[ -1/3 + (8/3)\mu_{e} - (40/3)\mu_{s}^{2} + (160/3)\mu_{s}^{3} \right] \right]
\]

The expression is quite analogous to the one obtained for a single film.

\[
\frac{\delta f}{f} \approx \mu_{e} \left[ -1 + 2\mu_{e} - 4\mu_{s}^{2} + 8\mu_{s} \right]
\]

The term in curly brackets relating frequency shift and film mass is called the "Sauerbrey constant" in this context. The values for gold electrodes with a thickness of 100 nm on a quartz blank with a fundamental frequency of 4 MHz are \( \zeta = -0.856 \) and \( \mu_{s} = 0.0017 \). When one plots \( \delta f \) vs. \( n \) according to \( \delta f = \mu_{s} + S_{n} n^{2} \) one finds a positive slope \( S_{n} \), which is not related to the film's viscoelastic properties. The latter can only be determined after the effect from the electrodes has been subtracted.

Since the mass of the film is a priori unknown, the effect of the electrodes has to be determined before the
experiment by successively increasing the electrode thickness and determining the slope \( S_S(m_e) \) as a function of the electrode mass (Fig. 6). One finds a smooth functional dependence \( S_S(m_e) \), which can be well fitted by third order polynomials in mass \( m_e \). Since the electrode mass is not known in absolute terms, the connection to the Langmuir-Blodgett layer is derived from the existing electrodes. The encircled data points correspond to the deposition of 40 and 80 Langmuir-Blodgett layers of a hairy-rods polyglutamate \(^{55,56}\). The elastic compliance experiment by successively increasing the electrode had flexible side chains attached to the rigid a-helical core. (30% octadecyl side chains, 70% methyl side chains). These side chain regions are rather fluid which explains the fact that the shear modulus is lower than expected for stiff rods. 

The reader is reminded that viscoelastic dispersion has not been explicitly accounted for in the above derivation. With viscoelastic dispersion present the quantities \( \zeta_e \) and \( \zeta_s \) are functions of frequency. When plotting \( \delta f/\delta t \) vs. \( n^2 \) one no longer expects straight lines, but slightly curved lines instead. The appropriate power laws have to be used for fitting. The derived viscoelastic constants slightly depend on the power laws assumed for dispersion.

**IV. Examples**

1) **Solvent vapor induced plastification of polymer films**

The occurrence of the film resonance is most directly demonstrated experimentally by investigating the solvent vapor induced swelling and softening of polymer films. Fig. 7 shows data taken on a 1.6 \( \mu \)m film of poly(isobutylene), which had been applied to the quartz surface by spin-casting\(^{57}\). At \( t = 0 \) a vessel with toluene was placed into the sample chamber. The vessel only had a small hole making contact with the sample chamber so that the toluene vapor pressure in the sample compartment increased only slowly with time. The kinetics displayed in Fig. 7 reflects the increase in vapor pressure. The intrinsic swelling kinetics after a jump in vapor pressure would be much faster.

The general features of the film resonance – a maximum in bandwidth and an antisymmetric feature in the frequency shifts – are clearly seen. However, the quantitative agreement with the theory is rather unsatisfactory. In later investigations, coupling to anharmonic sidebands was identified as the most likely source of the discrepancies\(^{57}\). Given these shortcomings, it is generally impossible to separate vapor-induced thickening and vapor-induced softening from the resonance shifts alone. To circumvent this problem the film thickness was independently determined with ellipsometry. With the film thickness as an input parameter to the fit, the film’s compliance is readily determined. In this particular case, the elastic effects are so strong, that the analysis can proceed without recursion to perturbation theory and Eq. (6) can be directly used for fitting. The softening is in line with the expectations from the physics of glass forming polymers\(^{57}\) and the literature values for poly(isobutylene)\(^{58}\).

![Normalized frequency shifts \( \delta f/\delta t \) vs. time during swelling of a 1.6 \( \mu \)m film of poly(isobutylene) in toluene vapor. Film resonances occur when the film thickness equals a quarter of the wavelength of sound](image_url)

Fig. 7. Normalized frequency shifts \( \delta f/\delta t \) and normalized bandwidths \( \delta f/\delta t \) vs. time during swelling of a 1.6 \( \mu \)m film of poly(isobutylene) in toluene vapor. Film resonances occur when the film thickness equals a quarter of the wavelength of sound.
The viscoelastic measurements on the dry polymer film may also serve as an example for the use of the cubic approximation (Eq. (10)) to derive the viscoelastic parameters. Fig. 8 shows a plot of the normalized frequency shift $\delta f/f$ vs. $f^2$ (i.e. $n^2$) and specifically addresses the issue of viscoelastic dispersion. The different lines correspond to different power laws according to $J'(f) = J'(20 \text{ MHz}) \times (f/20 \text{ MHz})^x$. The dependence of the derived value for $J'(f = 20 \text{ MHz})$ on the assumed power law is rather weak.

### 2) Swollen polymer brushes

Polymeric adsorbates in a liquid environment are a challenging task for viscoelastic characterization. Such polymeric ad-layers on dispersed particles are widely used in the paints and coatings industry to prevent particle aggregation and flocculation. Polymer brushes which are systems of linear chains attached to the substrate at one end are particularly popular because the polymer statistics ensures that the interaction between two swollen brushes is always repulsive. The contact between two particles is to be viewed as a dynamic process, which involves both hydrodynamic interactions and viscoelasticity. The viscoelastic properties of the brushes are therefore a highly relevant topic for both fundamental research and application.

In the experiments described in ref. a polystyrene brush grown by the grafting-from technique was investigated in cyclohexane. Fig. 9 sketches the experimental setup. The collapsed thickness of the brush is 70 nm. In solvent the brush swells to a thickness of about 400 nm. The solvent quality in the polystyrene/cyclohexane system monotonously increases with temperature.

The $\theta$-condition, where segment attraction and excluded volume effects are of equal magnitude occurs at about $34 ^\circ \text{C}$. Previous theoretical and experimental studies have shown that the collapse of the brush with decreasing solvent quality proceeds rather continuously, which contrasts to the behavior of bulk polymer.

Fig. 10 shows the frequency shift and the bandwidth on 10 harmonics as a function of temperature. Since the solvent quality increases with temperature, the brush thickness increases with temperature as well. One clearly
observes a sequence of film resonances (see Eq. (12) and the subsequent discussion in the Theory Section). On the high harmonics with a short wavelength of shear sound, the resonances occur at low temperatures (low thickness).

Viscoelastic modeling is as usual complicated by the fact that both the thickness and the shear stiffness change with the degree of swelling. These two effects cannot be disentangled from the resonance shifts alone. Also, the viscoelastic profile is not expected to be a rectangular box, but instead to display a rather smooth transition from a dense (and stiff) region at the bottom of the brush to a dilute, soft part at the outer edge.

However, additional information is available. Firstly, the thickness of the brush can be independently determined with ellipsometry. Ellipsometry yields an “equivalent optic thickness” whose geometric interpretation again depends on the functional form of the segment density profile $\rho(z)$. Secondly, the relation between segment density and shear modulus can be calibrated with the same setup using bulk polymers. This calibration assumes that bulk polymers behave similarly to the brush material. Given that the MHz modulus is a rather local property, this seems to be a reasonable assumption.

With this additional input fitting becomes feasible. Interestingly, the acoustic thickness derived from fitting is larger than the optical thickness derived from ellipsometry. The reasons for this discrepancy is to be sought in the drastically different magnitudes of acoustic and optical contrast. The refractive index varies by only a few percent, whereas the acoustic impedance varies by orders of magnitude. The incremental reflectivity $r_i$ at a small impedance step is given by $r_i = (Z_1 - Z_2)/(Z_1 + Z_2) = \Delta Z/(2Z)$. In optics the impedance, i.e., the refractive index, does not vary much and one has gotten used to the relation $r_i \propto \Delta n$. In acoustics the denominator must not be dropped and $r_i \propto \Delta Z/Z$. Therefore, the dilute outer portions of the brush with a low impedance make a fairly large contribution to the overall reflectivity of the brush-solvent interface. The acoustic wave travels fairly far into the dilute outer portions of the brush. The difference between acoustic and optical thickness highlights the necessity to probe the viscoelastic properties of soft materials with inherently viscoelastic means of investigation. Using the optical thickness to estimate the range of viscoelastic action of a brush results in serious errors. The situation is somewhat reminiscent of the difference between the optical and the hydrodynamic thickness of polymer layers, the latter often being substantially larger than the former.$^{74,75}$.

3) Experiments in sandwich geometry

A major advantage of quartz resonators is the fact that there is no need for a second surface to induce shear. The sample shears under its own inertia. Due to this technical advantage one does not worry about dust grains or asperities forming mechanical bridges. This fact, on the other hand, limits the applicability of the technique to ultrathin films. As the film mass decreases, the film’s inertia decreases as well. The viscoelastic term in Eq. (10) scales as the third power of mass. A certain compromise can be found by depositing a second layer onto the film of interest, thereby increasing the inertia. If the second layer is stiffer than the layer of interest, the elastic compliance of the composite resonator is dominated by the thin layer in the middle and the latter becomes accessible to experiment. The analysis proceeds according to Eq. (18) – (21). In particular, Eq. (21) shows that there is now a viscoelastic term linear in the film’s mass $m_n$.

Fig. 11. Normalized frequency shifts $\delta f/f$ and normalized bandwidths $\delta f/f$ vs. $f^2$ for a 125 nm film of POBDSMS (see text) covered with an SiO$_x$ layer to increase the inertia (“sandwich configuration”). A film resonance is observed. At a temperature of about $T = 70^\circ$C one clearly observes the melting transition. (From ref.$^{78}$)
Here we present an example of a film resonance observed for a composite system with sandwich geometry (Eq. (18) and (19)). The sample investigated was a 125 nm spin-cast film of the polymer poly(oxybisdimethylsilylene) (POBDMS for short\textsuperscript{76,77}) which undergoes a melting transition at around 70°C. A 200 nm film of SiO\textsubscript{x} was evaporated onto the polymer film. Fig. 11 shows the frequency shifts and bandwidths on the first 13 harmonics as a function of temperature. The film resonance is clearly observed\textsuperscript{78). Around 70°C there is a qualitative change induced by melting. Quantitative fitting of Eq. (18) is, as often found with film resonances, difficult. The data were therefore analyzed by reading the frequency of the film resonance from Fig. 11 and converting it to a mechanical compliance according to Eq. (20) (Fig. 12). Apart from determining the elastic coefficient, this procedure allows to determine the melting point. These experiments should be possible for layers much thinner than 100 nm.

4) Stress-induced birefringence

Dynamic investigations on polymer melts are often greatly assisted by measuring internal stresses via the stress-induced birefringence\textsuperscript{79–81). The stress-optics law states that the birefringence tensor is proportional to the tensor of deviatoric stresses

$$
\Delta n_{ij} = C \Delta \sigma_{ij}
$$

with $C$ the stress-optic coefficient. Using an experimental setup where the polymer film is part of a Fabry-Perot resonator, it is possible to measure stress birefringence in films coated onto quartz resonators\textsuperscript{82). Fig. 13 shows the setup. A semitransparent gold layer was evaporated onto a spin-cast 2.3 μm film of poly(methyl methacrylate) (PMMA). The resulting structure acts as a Fabry-Perot cavity with sharp dips in the reflectivity at discrete angles of incidence which are the coupling angles of the various waveguide modes. When the refractive index inside the cavity changes – for instance due to shear stress – the coupling angles change as well. By modulating the amplitude of oscillation and referencing the lock-in detector to the modulation, one can easily detect shear-induced variations in the refractive index down to $\delta n \approx 10^{-5}$. Fig. 14 shows the modes (static reflectivity $R$) and the differential signal $\Delta R$ obtained when modulating the oscillation amplitude. The changes in reflectivity depend on whether the quartz was sheared parallel or perpendicular to the plane of incidence.

When observing $\Delta R$ at a fixed angle on the slope of one of the modes and frequency-sweeping the function generator, one obtains $\Delta R(\omega)$ as a function of resonator frequency. As expected, $\Delta R(\omega)$ displays the quartz resonance. When investigating $\Delta R$ as a function of driving voltage one finds a square dependence ($\Delta R \propto V^2$). The observed effects appear to be of second order in shear stress. Effects linear in stress are in fact symmetry-forbidden in the given configuration. The observed stresses are normal stresses acting perpendicular to the direction of shear\textsuperscript{83,84). Normal stress in the $z$-direction may also increase the thickness of the film in addition to changing the refractive indices. From the angular shift of the optical modes one can assess the magnitude of the normal stresses. For the given data one arrives at $\Delta \sigma_{11}/\gamma_1^* = (0 \pm 3)$ GPa, $\Delta \sigma_{22}/\gamma_2^* = (0.6 \pm 0.2)$ GPa, and $\Delta \sigma_{33}/\gamma_3^* = (6 \pm 3)$ GPa, where the “1”-direction is in the plane of the film.
We see great potential in particular in combining the copy, or the surface forces apparatus, with quartz crystal with other techniques such as ellipsometry, surface plasmon spectroscopy, scanning force microscopy, or the surface forces apparatus. These results are in line with qualitative phenomenological models which state that the quantity \( \Delta \sigma / \sigma \) should be of the same order of magnitude as the shear modulus. To our knowledge, this is the first time that normal stresses have been determined for a thin film under conditions where the shear strain is only 3%.

**Outlook**

A wealth of information about thin films can be obtained by analyzing the resonance spectra of coated quartz resonators. The step towards the elastic properties of molecularly thin films still remains a challenge. By rigorously modeling the quartz blanks as three-dimensional bodies one can hope to overcome the present limitations of one-dimensional modeling and extend the applicability of the standard technique to layers only a few nanometers thick. We see great potential in particular in combining the quartz crystal with other techniques such as ellipsometry, surface plasmon spectroscopy, scanning force microscopy, or the surface forces apparatus.

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