8-1-2008

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Accepted version. *Analytical Chemistry*, Vol. 80, No. 15 (August 2008): 5760-5767. DOI. © 2008 American Chemical Society. Used with permission.

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Analytical Chemistry, Vol 80, No. 15 (August 1, 2008): pg. 5760-5767. DOI.

Abstract: Expressions describing the resonant frequency and quality factor of a dynamically driven, polymer-coated microcantilever in a viscous liquid medium have been obtained. These generalized formulas are used to describe the effects the operational medium and the viscoelastic coating have on the device sensitivity when used in liquid-phase chemical sensing applications. Shifts in the resonant frequency are normally assumed proportional to the mass of sorbed analyte in the sensing layer. However, the expression for the frequency shift derived in this work indicates that the frequency shift is also dependent on changes in the sensing layer's loss and storage moduli, changes in the moment of inertia, and changes in the medium of operation's viscosity and density. Not accounting for these factors will lead to incorrect analyte concentration predictions. The derived expressions are shown to reduce to well-known formulas found in the literature for the case of an uncoated cantilever in a viscous liquid medium and the case of a coated cantilever in air or in a vacuum. The theoretical results presented are then compared to available chemical sensor data in aqueous and viscous solutions.

Polymer-coated microcantilevers have been extensively investigated for use as chemical sensor platforms.[1-4] Microcantilevers have shown high sensitivities in chemical vapor detection. In particular, polymer-coated cantilevers are often utilized in the dynamic (resonant) mode for detection in gas.[2,5-9] Several investigators have analyzed such devices by considering only the mass loading effect of the chemical analyte without consideration of the coating viscoelastic effects.[3,4,10] Others have explicitly included the effects of the coating properties,[2] while assuming operation in a vacuum. In this work, the effects of both the medium and the coating will be taken into account.

Application of microcantilevers to liquid-phase detection has mostly focused on static-mode detection because dynamically driven microcantilevers suffer from low frequency stability in viscous liquid media.[11] The characteristics of uncoated dynamically driven microcantilevers have previously been investigated in viscous liquid media accounting for the properties of the liquid media, including density and viscosity.[12] Recently, work has been done on characterizing the behavior of polymer-coated microcantilevers in a vacuum, which indicated significant chemically induced coating plasticization effects.[1] However, the effects of the polymer coating in a viscous liquid environment have not been studied, which includes plasticization and the properties of the viscous liquid. The present derivation extends previous work on uncoated and coated microcantilevers to obtain generalized formulas for the characteristics of a polymer-coated microcantilever operating in a viscous liquid medium.

Theoretical Analysis

Generalized Equation of Motion

Figure 1 shows the length, *L*, width, *b*, and thickness, h_1, of the microcantilever as well as the polymer layer's thickness, h_2. The deflection function, $w(x,t)$, which represents the vertical displacement along the length of the beam as a function of time is also indicated.

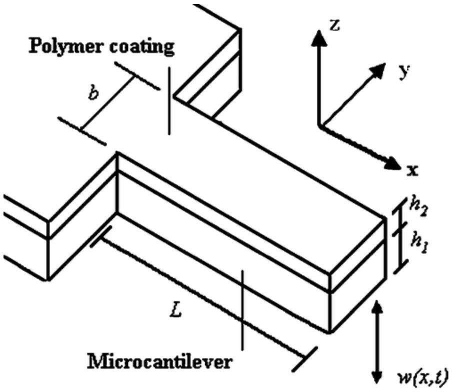

Figure 1. Rectangular microcantilever shown with a polymer layer.

Assuming that the microcantilever is a rectangular beam with $L \gg (h_1 + h_2)$ undergoing small transverse displacements, the equation of motion for a polymer-coated microcantilever operating in a vacuum is given by

$$(EI)^* \frac{\partial^4 w(x,t)}{\partial x^4} + m/L \frac{\partial^2 w(x,t)}{\partial t^2} = F(x) e^{j\omega t} \qquad (1)$$

where $(EI)^*$is the beam's complex flexural rigidity, *m* is the microcantilever and the polymer layer's overall mass, and $F(x)$ is the position-dependent forcing function per unit length operating at an angular frequency of ω. [1] Since the polymer coating is usually viscoelastic, the flexural rigidity is complex and can be calculated by

$$(EI)^* = \left(\sqrt{(EI)'^2 + (EI)''^2}\right) e^{j\theta} \qquad (2)$$

with

$$(EI)' = \left(E_1 I_1 + E_2' I_2\right) \tag{3}$$

and

$$(EI)'' = (E_2'' I_2) \tag{4}$$

E_1 is the Young's modulus of the microcantilever base layer, which is assumed to be purely elastic, E_2' and E_2'' are the storage modulus and loss modulus of the polymer layer, respectively, and I_1 and I_2 are the moments of inertia of the microcantilever base and polymer layer, respectively. For a system with a polymer layer, the moment of inertia can be approximated assuming a time-invariant neutral axis, found by using the Cauchy principal value theorem on the position of the time-variant neutral axis location.[1] The parameter θ in eq 2 is the composite loss angle of the beam and is defined as

$$\theta = \tan^{-1}\left(\frac{h_2 E_2''}{h_1 E_1 + h_2 E_2'}\right) \tag{5}$$

Although not shown explicitly in eqs 2–5, it is noted that the complex modulus of the coating depends on the operating frequency.

When operating in a viscous liquid medium, the medium exerts a force (per unit length) on the microcantilever, $F_{\text{fluid}}(x,t)$, and the equation of motion is

$$(EI)^* \frac{\partial^4 w(x,t)}{\partial x^4} + m/L \frac{\partial^2 w(x,t)}{\partial t^2} = F(x) e^{j\omega t} + F_{\text{fluid}}(x,t) \tag{6}$$

The $F_{\text{fluid}}(x,t)$ has been defined as[12]

$$F_{\text{fluid}}(x) = -g_1 \frac{\partial w(x,t)}{\partial t} - g_2 \frac{\partial^2 w(x,t)}{\partial t^2} \tag{7}$$

where g_1 represents the viscous damping caused by fluid shear and g_2 represents the displaced mass of the fluid per unit length.[10] g_1 and g_2 are defined as[13]

$$g_1 = \frac{\pi}{4}\rho_{\mathrm{L}} b^2 \Gamma_i(Re)\,\omega \qquad (8)$$

and

$$g_2 = \frac{\pi}{4}\rho_L b^2 \Gamma_r(Re) \qquad (9)$$

respectively. Here, ρ_L is the density of the medium and $\Gamma_r(Re)$ and $\Gamma_i(Re)$ are the real and imaginary parts of the hydrodynamic function, $\Gamma(Re)$, of the microcantilever, given by

$$\Gamma(Re) = \Omega(Re)\Gamma_{\mathrm{circ}}(Re) = \Omega(Re)\left(1 + \frac{4jK_1(-j\sqrt{jRe})}{\sqrt{jRe}\,K_0(-j\sqrt{jRe})}\right) \qquad (10)$$

In eq 10, $\Omega(Re)$ is the function used to correct the hydrodynamic function of a beam of circular cross section, $\Gamma_{\mathrm{circ}}(Re)$, to that of a long, thin rectangular beam for which $(h_1 + h_2) \ll b$ and $b \ll L$. [12] K_0 and K_1 are modified Bessel functions of the third kind. The hydrodynamic function is dependent on the Reynolds number,[10] which is a measure of the ratio of inertial forces to the viscous forces acting on the beam, and is defined as

$$Re = \frac{\rho_{\mathrm{L}}\omega b^2}{4\eta_{\mathrm{L}}} \qquad (11)$$

where η_L is the viscosity of the fluid.

Assuming a sinusoidal deflection function, the right-hand side of eq 7 can be written as $(jg_1/\omega - g_2)(\partial^2 w(x,t)/\partial t^2)$. Substitution into eq 6 results in the following equation of motion,

$$(EI)^* \frac{\partial^4 w(x,t)}{\partial x^4} + m_{\mathrm{B}}{}^* \frac{\partial^2 w(x,t)}{\partial t^2} = F(x)\,\mathrm{e}^{j\omega t} \qquad (12)$$

where $m_B{}^*$ is the complex effective mass per unit length given by

$$m_B{}^* = \sqrt{(m/L + g_2)^2 + (g_1/\omega)^2}\, e^{j\varphi} \qquad (13)$$

where

$$\varphi = -\tan^{-1}\left(\frac{g_1/\omega}{m/L + g_2}\right) \qquad (14)$$

Generalized Resonant Frequency

The deflection of the coated microcantilever is composed of an infinite number of harmonic flexural modes. The resonant frequency for the *i*th mode of a coated microcantilever in a viscous liquid medium can be found using the generalized equation of motion, eq 12. It is commonly assumed that the Young's modulus of the base layer is frequency-independent. For the polymer layer, the Young's modulus depends on the frequency. However, a first approximation is to use the polymer properties at the resonant frequency and neglect their variation in the vicinity of the resonant peak. Assuming a frequency-dependent hydrodynamic function, the resonant frequency obtained by solving eq 12 is given by

$$f_{\mathrm{res},i} = \frac{\alpha_i^{\,2}}{2\pi}\sqrt{\frac{k}{M}} \qquad (15)$$

where α_i is the *i*th root of

$$\cos(\alpha_i)\,\cosh(\alpha_i) - 1 = 0 \qquad (16)$$

$$k = \frac{(EI)' - \dfrac{\left(g_1/\omega\right) + \left(\dfrac{\omega}{2}\right)\dfrac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)}{\left(m/L + g_2 + \left(\dfrac{\omega}{2}\right)\dfrac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)}(EI)''}{L^3} \qquad (17)$$

$$M = (m + Lg_2) + \frac{\left((g_1/\omega) + \left(\dfrac{\omega}{2}\right)\dfrac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)}{\left(m/L + g_2 + \left(\dfrac{\omega}{2}\right)\dfrac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)}(g_1/\omega)L \qquad (18)$$

$$\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega) = \frac{\pi}{4}\rho_{\mathrm{L}} b^2 \Lambda_i(Re) \qquad (19)$$

$$\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2) = \frac{\pi}{4}\rho_{\mathrm{L}} b^2 \Lambda_{\mathrm{r}}(Re) \qquad (20)$$

and $\Lambda_r(Re)$ and $\Lambda_i(Re)$ are the real and imaginary components of $\Lambda(Re)$, which is defined as the derivative of the hydrodynamic function. This function can be obtained as

$$\Lambda(Re) = 2\Omega(Re)\left(\frac{\left(K_1\left(-j\sqrt{jRe}\right)\right)^2 - K_2\left(-j\sqrt{jRe}\right)\left(K_0\left(-j\sqrt{jRe}\right)\right)}{\omega\left(K_0\left(-j\sqrt{jRe}\right)\right)^2}\right) + \Gamma_{\mathrm{circ}}(Re)\,\frac{\mathrm{d}}{\mathrm{d}\omega}(\Omega(Re)) \qquad (21)$$

Through the use of an iterative process, eq 15 can be solved. Iterative correction uses an initial guess for ω (for example, the resonant frequency in a vacuum). A value for the Reynolds number can then be calculated, which in turn can be used to update the value of ω.

It can be shown that eq 15 reduces to the well-known expression for the resonant frequency of a coated-microcantilever in a vacuum ($g_1 = g_2 = 0$), given by

$$f_0 = \frac{\alpha_0^{\,2}}{2\pi}\sqrt{\frac{E_1 I_1 + E_2' I_2}{mL^3}} \qquad (22)$$

with $\alpha_0 \cong 1.875$ corresponding to the fundamental flexural mode.[2]

If there are only small dissipative effects from both the polymer and the viscous liquid medium, the resonant frequency simplifies to

$$f_{\mathrm{res}} = f_0 \frac{1}{\sqrt{1 + Lg_2/m}} \qquad (23)$$

This form is analogous to that obtained in ref 12 for an uncoated microcantilever in a viscous liquid medium. When the medium is assumed inviscid, eq 23 can be further simplified to a form analogous to the one presented in ref 14 as

$$f_{\mathrm{res}} = f_0 \frac{1}{\sqrt{1 + L\pi\rho_{\mathrm{L}} b^2/(4m)}} \qquad (24)$$

If both the Young's modulus of the polymer layer and the Reynolds number are assumed frequency-independent near resonance (making the hydrodynamic function frequency-independent), the resonant frequency can be simplified to

$$f_{\mathrm{res},1} = \frac{\alpha_i^2}{2\pi L^2}\sqrt{\frac{(m/L + g_2)(EI)' - (g_1/\omega)(EI)''}{(m/L+g_2)^2 + (g_1/\omega)^2}} \qquad (25)$$

Quality Factor

Operation in a viscous liquid medium drastically decreases the frequency stability of microcantilevers in an oscillator configuration. It also decreases the accuracy of the determination of the resonant frequency using a frequency sweep due to the damping and broadening of the frequency response. Equation 12 can be used to calculate the quality factor of the system. The quality factor is best solved numerically in the general case because the analytical expression is cumbersome to obtain. This is done by solving eq 12 numerically and calculating the upper and lower 3 dB frequencies through an iterative process. In high-loss systems, the lower 3 dB frequency is zero, and the bandwidth can be found using only the upper 3 dB frequency. However, if both the Young's modulus of the polymer layer and the Reynolds number are again considered constant in the range of operational frequencies, the quality factor can be obtained from eq 12 as

$$Q = \left(2\left(1 - \sqrt{1 - \left|\frac{(g_1/\omega)(EI)' + (m/L+g_2)(EI)''}{(m/L+g_2)(EI)' - (g_1/\omega)(EI)''}\right|}\right)\right)^{-1} \qquad (26)$$

Assuming operation in a vacuum, g_1 and g_2 are both zero and eq 26 reduces to the one presented in refs 1 and 2, which incorporates only the viscoelastic losses in the polymer layer:

$$Q_0 = \left(2\left(1 - \sqrt{1 - \frac{(EI)''}{(EI)'}}\right)\right)^{-1} \qquad (27)$$

In low loss media, eq 26 can further be approximated as

$$Q_{\text{approx}} = \frac{(m/L + g_2)(EI)' - (g_1 + \omega)(EI)''}{(g_1/\omega)(EI)' + (m/L + g_2)(EI)''} \qquad (28)$$

For an uncoated cantilever, eq 28 reduces to the estimation of the quality factor in low-loss media from ref 12.

In practical applications, the losses caused by the medium and the polymer coating (i.e., the losses considered in this paper) are normally the dominant terms. However, other losses (thermoelastic losses, clamping losses, acoustic losses, losses from the squeeze film effect, etc...)[10] can be taken into account when calculating the quality factor using the well-known equation for multiple loss systems,

$$\frac{1}{Q_{\text{sum}}} = \sum_i \frac{1}{Q_i} \qquad (29)$$

where Q_i is the quality factor associated with a particular loss source. Equation 29 is based on the assumption that the losses due to various sources are independent of one another.

In a previous paper,[15] the viscoelastic losses in the layer and the viscous losses in the surrounding medium have been considered separately and combined using eq 29 to obtain an approximation of the total quality factor. In the case of low-loss media, the quality factor obtained by using eq 29 with the viscoelastic and viscous losses is

$$Q_{\text{sum}} = \left(\frac{(g_1/\omega)}{(m/L + g_2)} + \frac{(EI)''}{(EI)'}\right)^{-1} \qquad (30)$$

In the present paper, the losses due to the polymer coating and the surrounding medium are not assumed to be independent of one another. In the case of small losses the quality factor may be expressed by eq 28, which is the same as eq 30 if $(g_1/\omega)(EI)''$ is neglected. However, when losses are more significant (e.g., when the medium is highly viscous or the coating losses are large), the accuracy of the approximate quality factor expressions are questionable and a more accurate calculation of the quality factor (based on the generalized model presented here) is warranted.

Effects of Chemical Analyte Sorption into the Coating

Introduction of a chemical analyte into the operational medium will not only change the medium's viscosity and density, but will also affect the characteristics of the coated microcantilever through chemical sorption into the polymer layer. For example, the mass and thickness of the polymer layer will increase; the moment of inertia for both layers will change due to a change in the neutral axis location; and the complex Young's modulus of the polymer layer will change.

While the shifts in the resonant frequency due to some of these effects are negligible in comparison with the overall resonant frequency, they still can be significant with regards to the overall shift in the resonant frequency, Δf_{res}, which is used to determine the chemical concentration of the analyte in the medium.

Assuming only small variations in the properties of the polymer layer due to analyte sorption, the relative shift in the resonant frequency can be found as a function of the change in microcantilever mass, Δm, changes in the storage and loss moduli, $\Delta E_2'$ and $\Delta E_2''$, changes in the moments of inertia, ΔI_1 and ΔI_2, and changes in viscosity and density, which cause changes in the hydrodynamic function, thus Δg_1 and Δg_2 as

$$\frac{\Delta f_{\text{res}}}{f_{\text{res}}} \cong (\lambda_{\text{m}} \Delta m) + \left(\lambda_{E_2'} \Delta E_2' + \lambda_{E_2''} \Delta E_2''\right) + \left(\lambda_{I_1} \Delta I_1 + \lambda_{I_2} \Delta I_2\right) + \left(\lambda_{g_1} \Delta g_1 + \lambda_{g_2} \Delta g_2\right) \quad (31)$$

In eq 31), the λ terms describe the sensitivities to various changes in the system, and are given as

$$\lambda_{\mathrm{m}} = \left(\frac{\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega} g_1/\omega\right)(g_1/\omega)\,(EI)'}{2kLM\left(m/L + g_2 + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)^2} + \frac{\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)(m/L + g_2)\,(EI)''}{2kLM\left(m/L + g_2 + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)^2} - \frac{1}{2M} \right) \quad (32a)$$

$$\lambda_{E_2'} = \frac{I_2}{2kL^3} \quad (32b)$$

$$\lambda_{E_2''} = -\frac{I_2\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)}{2kL^3\left((m/L) + g_2 + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)} \quad (32c)$$

$$\lambda_{I_1} = \frac{E_1}{2kL^3} \quad (32d)$$

$$\lambda_{I_2} = \left(\frac{1}{2kL^3}\right)\left(E_2' - E_2'' \frac{\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)}{\left(m/L + g_2 + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)}\right) \quad (32e)$$

$$\lambda_{g_1} = -\left(\frac{\left((g_1/\omega)\,(EI)'' + (m/L + g_2)\,(EI)''\right)}{2kLM\left(m + Lg_2 + L\left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)\omega} + \left(\frac{L^2}{2M\omega}\right)\frac{\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)}{\left(m + Lg_2 + L\left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)} \right) \quad (32f)$$

and

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$$\lambda_{g_2} = \frac{\left((g_1/\omega) + \left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_1/\omega)\right)\left((g_1/\omega)(EI)' + (m/L + g_2)(EI)'\right)}{2kM\left(m + Lg_2 + L\left(\frac{\omega}{2}\right)\frac{\mathrm{d}}{\mathrm{d}\omega}(g_2)\right)^2} - \frac{L}{2M} \quad (32g)$$

and ω in eqs 32a−g is evaluated at the resonant frequency.

It is noted that the swelling-induced change in the polymer thickness is included in the ΔI terms. All other terms besides those calculated from eq 32a−g (including higher-order terms) have been assumed negligible in deriving eq 31 for small frequency shifts. Also, eq 32d and eq 32e have been shown to make negligible contributions to the frequency shift because of the insensitivity of the neutral axis position to the analyte sorption. (This is similar to what was shown in ref 2, in which swelling effects were neglected.) The effects due to ΔI_1 and ΔI_2 will therefore be disregarded. Variations in the viscosity and density can also affect the resonant frequency as indicated by the Δg_1 and Δg_2 terms in eq 31. However, in practical applications, these shifts are normally assumed accounted for using differential measurement from a reference cantilever, a cantilever of identical geometry and polymer coating thickness which is not sensitive to the analyte. Therefore, changes in the viscosity and density will not be included in the discussion dealing with eq 31. Equations 31 and 32 can then be used to analyze the sensitivity response of coated microcantilever chemical sensors.

Results and Discussion

Simulations

Simulations are performed to illustrate the effects of coating and medium properties on a microcantilever of typical geometry. The polymer layer assumed in these simulations is polyisobutylene (PIB). The Young's modulus for PIB has been previously characterized in ref 16. Figures 2 and 3 show the frequency response of a polymer-coated microcantilever to different aqueous mixtures of glycerol and ethanol, respectively, using both eq 15) for the exact calculation of the resonant frequency and eq 25 for the approximate calculation of the resonant frequency that assumes that both the Young's modulus of the polymer layer and the hydrodynamic function are frequency-independent near resonance. The calculated resonant frequency in air for the 100 × 20 × 2 μm microcantilever coated with 0.5 μm of PIB is 246.54 KHz. The approximation made by eq 25 is found to be valid for systems with thin polymer layers and Reynolds numbers much greater than one. For low Reynolds numbers, *Re*, i.e., high-viscosity or low-density fluid, the results indicate that the hydrodynamic function cannot be considered frequency-independent. Therefore, g_1 and g_2 must be considered frequency-dependent in calculating the resonant frequency for low Reynolds numbers. While ethanol has a higher viscosity compared to water, its lower fluid density leads to the device having an overall higher resonant frequency than that of water, as is shown in Figure 3. This indicates that the resonant frequency is not just dependent on the viscosity, but on the overall Reynolds number.

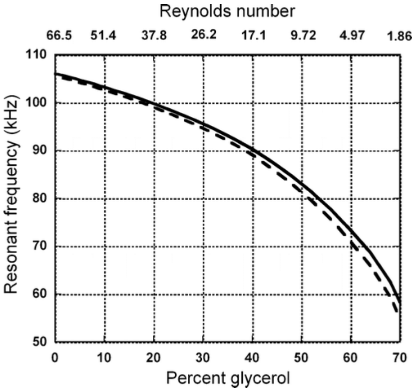

Figure 2. Calculated resonant frequency of a 100 × 20 × 2 μm microcantilever coated with 0.5 μm of PIB in varying mixtures of glycerol (up to 70%, or ~23 cP) using eq 15 (solid line) compared to an approximation (dashed line) calculated using eq 25 which assumes that the Young's modulus and the Reynolds number are frequency-independent. The Reynolds number calculated using this resonant frequency for each varying mixtures of glycerol is shown on the axis above.

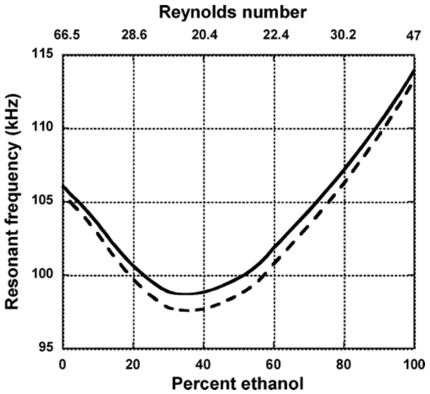

Figure 3. Calculated resonant frequency of a 100 × 20 × 2 μm microcantilever coated with a 0.5 μm of PIB in varying mixtures of ethanol using eq 15 (solid line) compared to an approximation (dashed line) calculated using eq 25, which assumes that the Young's modulus and the Reynolds number are frequency-independent. The Reynolds number calculated using this resonant frequency for each varying mixtures of ethanol is shown on the axis above.

The difference between the calculated quality factor using the upper and lower 3 dB frequencies and that obtained with eq 26 has been observed to be negligible in aqueous solutions of both glycerol and ethanol. Figures 4 and 5 compare the calculated quality factor with that of the low-loss approximation using eq 28 for different aqueous mixtures of glycerol and ethanol, respectively, which assumes the Reynolds number is much greater than one. As expected, eq 28 is shown to be inappropriate for high-viscosity media. The difference between the approximation and the more general model is found to increase as the Reynolds number decreases. In the calculations, it is assumed that the Young's modulus of the coating does not change as a function of the operational medium.

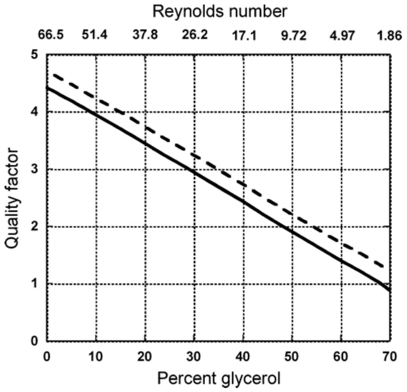

Figure 4. Calculated quality factor of a 100 × 20 × 2 μm microcantilever coated with a 0.5 μm of PIB in varying mixtures of glycerol (up to 70%, or ∼23 cP, solid line)

compared with the small loss approximation Q_{approx} (dashed line) calculated using eq 28.

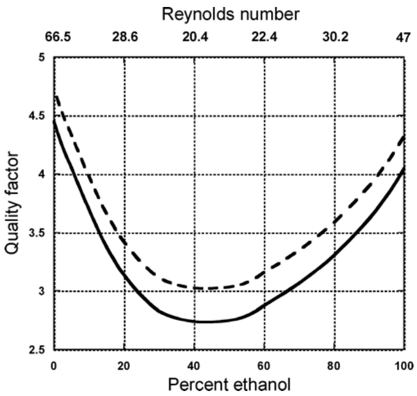

Figure 5. Calculated quality factor of a 100 × 20 × 2 μm microcantilever coated with a 0.5 μm of PIB in varying mixtures of ethanol (solid line) compared with the small loss approximation Q_{approx} (dashed line) calculated using eq 28.

The quality factor also can change as a function of the polymer coating thickness. Figure 6 gives the calculated quality factor of a polymer-coated microcantilever as a function of PIB coating thickness compared to both the approximation that the loss is from only the medium and the approximation that the viscoelastic PIB coating contributes loss, but is independent of the losses caused by the medium. Both approximations are calculated by assuming that the hydrodynamic function is frequency-independent and thus differ slightly from the exact calculation when the polymer layer thickness is zero. The calculated quality factor in air for the 100 × 20 × 2 μm microcantilever coated with 0.5 μm of PIB is 204. Figure 6 indicates that one should include the losses from the polymer coating. It also indicates that there is an optimum coating thickness with regards to the quality factor of ∼1 μm of PIB for this configuration. This behavior is shown for both the exact calculation of the quality factor and the approximation assuming the losses are independent.

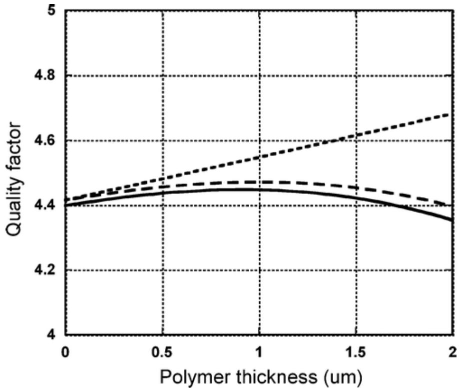

Figure 6. Calculated exact value of the quality factor (solid line) of a 100 × 20 × 2 μm microcantilever coated with varying PIB thicknesses up to 2 μm compared with both the approximation, assuming that the losses caused by the medium and the polymer coating are independent (dashed line) and that the losses are from only the medium (short dashed line). Note both approximations assume a frequency-independent hydrodynamic function and thus differ from the calculated exact value for the quality factor when the polymer layer thickness is zero.

Chemical sorption into the polymer coating is simulated assuming an increase in polymer mass by up to 5% (45.85 pg), a storage modulus decrease by up to 10% (−6.73 MPa), and a loss modulus increase by up to 100% (+102.48 MPa) (Figures 7 and 8). Such a mass uptake, for example, corresponds to an exposure to aqueous solutions of up to 327 mg/L toluene, using the partition coefficient of 140 for toluene in PIB.[2,17] The assumed changes in the polymer moduli represent the effects of coating plasticization and have been deduced from recent related work using guided SH-SAW sensor[17] changes in the shear modulus of PIB upon exposure to different concentrations of toluene. Due to the approximately linear character of the experimental data, the data have been linearized with respect to concentration. These data were obtained for a higher frequency device (100 MHz) and has served in the present simulation for a lower frequency microcantilever device as a guide for choosing the relative variation in the PIB properties, i.e., the percent change, provided that the variations in property values correspond to the same concentration in the coating. The mass sorption is found to cause up to a 42-Hz decrease in the resonant frequency in water, whereas the coating plasticization effects contribute up to an additional 9.9 Hz decrease in the resonant frequency. In 40% glycerol (~3.6 cP), the same mass loading causes up to a 23.9-Hz decrease in the resonant frequency, whereas the coating plasticization effects contribute an additional 11.7-Hz decrease in the resonant frequency. This indicates that the sensitivity to mass loading decreases in higher viscosity (lower *Re*) solutions, whereas the sensitivity to changes in the Young's modulus increase in higher viscosity solutions.

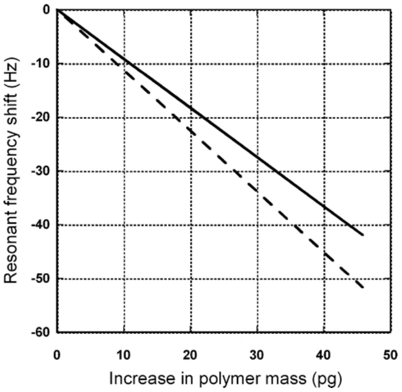

Figure 7. Shifts in the resonant frequency of a 100 × 20 × 2 μm microcantilever coated with a 0.5 μm of PIB in water undergoing mass sorption of up to 45 pg with (dashed line) and without (solid line) coating plasticization effects

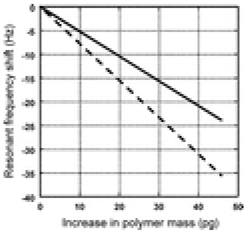

Figure 8. Shifts in the resonant frequency of a 100 × 20 × 2 μm microcantilever coated with a 0.5 μm of PIB in a 40% glycerol mixture undergoing mass sorption of up to 45 pg with (dashed line) and without (solid line) coating plasticization effects.

Comparison to Experimental Data

Recently performed experiments have shown the feasibility of dynamically driven CMOS multilayer microcantilever chemical sensors in liquid environments.[3] With a reference microcantilever to account for the effects of the medium, the response of a 150 × 140 × 8.2 μm CMOS-based microcantilever coated with 0.3 μm of PIB to 350 ppm ethylbenzene was found to result in a shift in the resonant frequency of ~85 Hz. However, the theoretical model used in ref 3 by assuming only mass loading predicted a 63-Hz shift in the resonant frequency. Note that for the present geometry the shearing effects at the edge of the microcantilever can no longer be neglected since the length is not much greater than the width. As a result, theoretical values of g_1 and g_2 obtained from eqs 8 and 9 cannot be used in the present case since the assumptions placed upon the derivation of the equation of motion and the hydrodynamic function will be violated. The values of g_1 and g_2 are thus approximated from the experimental resonant frequency and quality factor. The derived analytical expression for the shift in the resonant frequency can still be used if the values for g_1 and g_2 are calculated empirically.

For this microcantilever geometry in water, the polymer thickness is small compared to the base layer. In this case, $(EI)' \gg (EI)''$ and the resonant frequency and quality factor can be calculated using eq 25 and eq 30, respectively. Assuming that $(EI)'' = 0$, from these two equations, g_1 and g_2 can be approximated, respectively, as

$$g_1 \cong \frac{(m/L + g_2)}{Q}\omega \qquad (33)$$

and

$$g_2 \cong \left(\left(\frac{f_0}{f_{\text{res}}}\right)^2 (1 + 1/Q^2)^{-1} - 1\right) m/L \qquad (34)$$

where the quality factor in water (and dilute analyte solution) was experimentally determined to be $Q = 10$, and the measured resonant frequency in a vacuum and in the liquid were 400 and 200 kHz, respectively.[3]

From eq 34, g_2 is calculated to be roughly three times the mass per unit length of the microcantilever. From eq 33, g_1 is given by

$$g_1 \cong \frac{4}{10}\omega\left(\frac{m}{L}\right) \qquad (35)$$

The changes in the Young's storage and loss moduli used in Figures 7 and 8 were obtained using the response of PIB to the sorption of toluene.[2] Similar coating plasticization caused by ethylbenzene can be assumed using the appropriate partition coefficient of aqueous ethylbenzene in PIB. The maximum ethylbenzene concentration used in ref 3 is 350 ppm. Thus, the maximum amount of coating plasticization will be assumed

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approximately four to five times larger than that of toluene. The change in the mass of the polymer can be calculated as[2]

$$\Delta m = Kh_2 bLC_A \qquad (36)$$

where K is the dimensionless partition coefficient and C_A is the concentration of the analyte in the medium of operation. The partition coefficient for ethylbenzene in liquid for PIB has been experimentally determined as 464.[2,17] The microcantilever used in ref 3 is multilayered with a silicon thickness of 5 μm, a silicon oxide thickness of 2.2 μm, and a silicon nitride thickness of 1 μm. The resulting mass per unit length of the beam is calculated as 2.7181 mg/m. The composite Young's modulus for the beam is set at 112.9 GPa so that eq 15 will produce the experimentally obtained resonant frequency of 200 kHz in water. Since the Reynolds number for this configuration is 6000, the change in g_1 and g_2 can be neglected.

The calculated response of the microcantilever is shown in Figure 9 with only the mass loading and the total differential shift (including plasticization effects). The responses are compared with the experimentally measured resonant frequency shift that also accounts for changes in the medium properties by use of a reference cantilever. For example, for a concentration of 300 ppm ethylbenzene, using eq 31 with only the mass loading effect, the decrease in the resonant frequency due to mass sorption alone is calculated to be 54 Hz. Assuming up to a 50% decrease in the storage modulus and up to a 500% increase in the loss modulus, an additional 10-Hz decrease in the resonant frequency can be accounted for by coating plasticization, which compares well with the measured shift of 64 Hz. Thus, these results illustrate the important fact that to obtain a good prediction of the frequency shift, one must account for the effects of plasticization.

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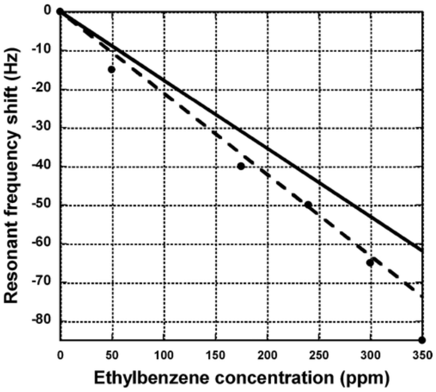

Figure 9. Comparison of experimentally measured values in ref 3 (dots) for the resonant frequency shift of a 150 × 140 × 8.2 μm microcantilever coated with 0.3 μm of PIB to the theoretically calculated frequency shift taking into account first mass sorption (solid line) and then mass sorption and plasticization effects (dashed line). Note that a reference cantilever is used in ref 3 to account for the effects of changes in the medium properties.

Conclusions

Generalized expressions for the resonant frequency and quality factor of a dynamically driven, polymer-coated microcantilever accounting for the effects of the medium and the polymer coating have been presented. It is found that the resonant frequency and quality factor must be calculated taking into account these effects. The resonant frequency was found to be significantly affected by nonmass loading effects. It is also found that the resonant frequency's sensitivity to mass loading and other system properties are dependent on the medium of operation. The generalized expressions obtained in this work simplify to known special cases and can be used to estimate the contribution of nonmass sorption effects in the response of dynamically driven microcantilever chemical sensors.

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