PHYSICAL REVIEW E **77**, 031605 (2008)

Viscoelastic response and profile of adsorbed molecules probed by quartz crystal microbalance

Da-Ming Zhu,[1,2,*] Jiajie Fang,[1,2] Bing Wu,[1] and Xianbin Du[1]
[1]*Department of Modern Physics, University of Science and Technology of China, Hefei, China*
[2]*Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA*
(Received 7 December 2007; published 12 March 2008)

The acoustic responses of molecular films with continuous viscoelastic profiles adsorbed on solid-liquid interfaces probed by quartz crystal microbalance (QCM) are analyzed using a continuum mechanics model. The numerically calculated results show that the shift of resonant frequency and the change of dissipation factor of a QCM are determined mostly by the change of viscoelastic profile of the layers in solution adjacent to the quartz-solution interface due to the adsorbed molecular film. For films with the same amount of absorbed mass, the changes in resonant frequency and the dissipation factor vary approximately linearly with the width of the film-solution interface in the profiles. Other viscoelastic properties of the adsorbed films are also affected by the profiles.

DOI: 10.1103/PhysRevE.77.031605 PACS number(s): 68.43.−h, 68.08.−p, 68.15.+e

I. INTRODUCTION

Although the adsorption of molecules on a solid-liquid interface plays an essential role in determining the physical, chemical, and biological processes occurring on that interface, a quantitative study of the phenomena is complicated by the presence of the liquid covering the solid surface [1–9]. Because the adsorption occurs in a condensed phase, the interactions between the adsorbates and the solvent molecules are strong, and, in many cases, cannot be neglected as in the case of the study of adsorption of molecules in vacuum or gaseous environments [10]. The strong interaction between the adsorbates and the solvent molecules also tends to disturb the adsorbed layers, resulting in a diffusive interface between the adsorbed layer and the solution with an appreciable interface width [11–28]. Hence the concept of a sharp interface, which is often implied in the description of adsorption of molecules on substrates in vacuum or in gaseous environments, may not be applicable to the case of adsorption of molecules on solid-liquid interfaces, and the results obtained using the experimental techniques that are traditionally used for studying adsorption on solid-vapor interfaces require some caution in the interpretation.

Quartz crystal microbalance (QCM) is a simple and sensitive experimental technique that has been used in studies of a wide variety of adsorption phenomena on solid surfaces, including film growth modes, wetting and superfluid transitions in adsorbed films, and frictions at atomic scales [29–34]. The essential component of the technique is a thin quartz disk which is excited to oscillate in a thickness shear mode at resonant frequency by applying an alternating electric field across the electrodes on opposite sides of the crystal. A small amount of mass deposited on the electrodes of the quartz crystal induces a decrease in the resonant frequency [29,30]. Due to the high-quality (Q) factor of the resonance, which is typically about 10^5 or better, QCM is sensitive enough to detect mass deposition on the surface with a resolution typically in the range of nanograms.

In recent years, QCM has been increasingly used in probing molecular films deposited on solid-liquid interfaces. Much information on the adsorption behaviors of various molecules on different solid-liquid interfaces has been obtained using the technique [35–42]. However, some results obtained using QCM are inconsistent with those obtained using other techniques. For example, the adsorbed masses determined from the resonant frequency shift of QCMs are often found to be several times larger than that actually adsorbed [37,42]. Several recent studies have analyzed the response of a QCM operated in solution using a continuum mechanics model, and have elucidated several issues related to the characteristic features displayed by QCMs in probing adsorption of molecules on solid-liquid interfaces [38–43], but understanding these features quantitatively has yet to be achieved.

In this work, we have analyzed the acoustic response of adsorbed molecular films with continuous viscoelastic profiles probed by a QCM using the same mechanics model employed in recent studies. We assume that the viscoelastic profile is a direct consequence of the density or the concentration profile of molecules in the adsorbed film in the direction normal to the interface. We have numerically calculated the viscoelastic response due to the adsorption of such films probed by the QCM. The numerically calculated results show that, instead of being directly related to the mass of adsorbed molecules, the resonant frequency shift and the dissipation factor change of a QCM are affected mostly by the changes of the viscoelastic profile of the layers on the quartz crystal-liquid interface due to the adsorption of the molecules. An adsorbed film with a profile which contains a long tail intruding into the solution can result in a significant change in the viscoelastic responses probed by the QCM.

II. METHOD AND MODEL

The method we used in this work is a modified slab model which treats the density or the concentration of adsorbed molecules varying from layer to layer in describing the viscoelastic responses of an adsorbed film on the electrode sur-

---

[*] Author to whom correspondence should be addressed. zhud@umkc.edu

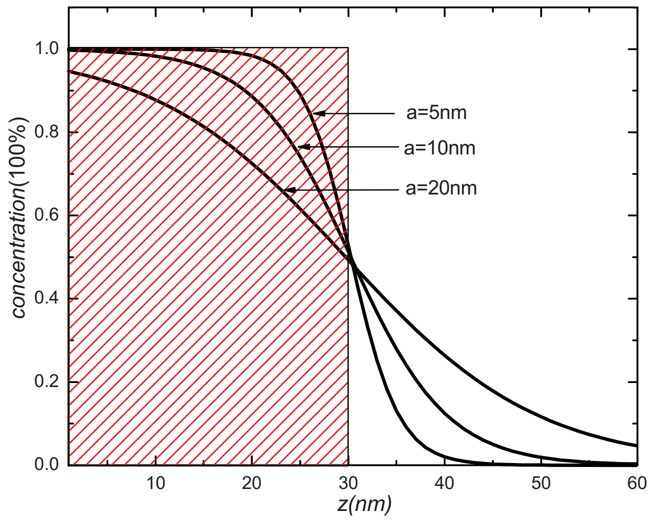

FIG. 1. (Color online) Illustration of continuous concentration (or density) profiles of the adsorbed molecules in films. The shaded region represents a box profile which has a sharp film-solution interface. Different lines represent profiles with different interface width a. The total amount of adsorbed molecules for these profiles is the same.

face of a QCM. In the slab model, the adsorbed molecules are considered to form a homogeneous layer with a box profile of density ρ, and shear modulus and viscosity being μ and η, respectively, situated in between the solid electrode surface and a semi-infinite fluid [42,43], as illustrated in Fig. 1. The shaded region represents a box shaped profile of the adsorbed film. Assuming that the adsorbed layer can be described by a Voight-based viscoelastic model and using "no-slip" boundary conditions [43], the changes of the resonant frequency and the dissipation factor due to the adsorption can be expressed as

$$\Delta f = \mathrm{Im}\left(\frac{\beta}{2\pi\rho_q h_q}\right), \tag{1}$$

$$\Delta D = \mathrm{Re}\left(\frac{\beta}{\pi f \rho_q h_q}\right), \tag{2}$$

where

$$\beta = \kappa\xi \frac{1 - A\exp(2\xi h)}{1 - A\exp(2\xi h)}, \tag{3}$$

$$A = \frac{\kappa\xi + \kappa_b\xi_b \tanh(\xi_b h_b)}{\kappa\xi - \kappa_b\xi_b \tanh(\xi_b h_b)}, \tag{4}$$

$$\kappa = \eta - i\frac{\mu}{\omega}, \quad \xi = \sqrt{-\frac{\rho\omega^2}{\mu + i\omega\eta}}, \tag{5}$$

$$\kappa_b = \eta_b, \quad \xi_b = \sqrt{\frac{i\rho_b\omega}{\eta_b}}. \tag{6}$$

In the above equations, h is the thickness of the adsorbed layer, ρ_b, η_b, are the density and the viscosity of the solution, respectively, h_b is the thickness of the solution, and ρ_q and h_q are the density and thickness of quartz crystal electrode, respectively. A calculation of Δf and ΔD as a function of the film thickness using Eqs. (1) and (2) finds that the resonant frequency decreases linearly with the thickness h, a result described by the well-known Sauerbrey equation [38], until h becomes close to the viscous penetration depth $\delta = (2\eta/\rho\omega)^{1/2}$. The resonant frequency and the dissipation factor reach saturation values when the film is thicker than a few times the penetration depth. For films in the thick limit, $h \to \infty$, $\exp(2\xi h) \to \infty$, Eq. (4) is reduced to

$$\frac{1 - A\exp(2\xi h)}{1 + A\exp(2\xi h)} \approx -1,$$

and $\beta \approx -\kappa\xi$. Then

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\sqrt{\frac{\rho}{2}}\left(\eta\omega\sqrt{\frac{\sqrt{\mu^2+\eta^2\omega^2}+\mu}{\mu^2+\eta^2\omega^2}} - \mu\sqrt{\frac{\sqrt{\mu^2+\eta^2\omega^2}-\mu}{\mu^2+\eta^2\omega^2}}\right), \tag{7}$$

$$\Delta D \approx \frac{1}{\pi f \rho_q h_q}\sqrt{\frac{\rho}{2}}\left(\eta\omega\sqrt{\frac{\sqrt{\mu^2+\eta^2\omega^2}-\mu}{\mu^2+\eta^2\omega^2}} + \mu\sqrt{\frac{\sqrt{\mu^2+\eta^2\omega^2}+\mu}{\mu^2+\eta^2\omega^2}}\right). \tag{8}$$

If the shear viscosity of the adsorbed film is zero, the above equations are reduced to

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\sqrt{\frac{\rho\omega\eta}{2}}, \tag{9}$$

$$\Delta D \approx \frac{1}{\rho_q h_q}\sqrt{\frac{2\rho\eta}{\omega}}, \tag{10}$$

which are the results obtained by Kawazana and Gordon, and by Rodahl *et al.* for QCM operating in a bulk Newtonian liquid [37,38]. The viscoelastic response of a film with a thickness below the viscous penetration depth probed by a QCM as a function of the shear modulus and the viscosity have been further analyzed by Voinova *et al.* [43]; the results show a strong film resonance as the sound velocity determined by the shear modulus of the adsorbed layer matches the resonant frequency of the QCM [43].

However, the density of an absorbed film, in general, varies from molecular layer to molecular layer. It has been shown that, in the case of adsorption from vapor phases, the layer density of a multilayer film varies from the bottom to the top layers [44,45]. For molecular layers adsorbed in solutions, this variation of the layer density may become bigger, due to the strong interaction between the adsorbates and the solvent molecules. The variation in the layer density for a film composed of macromolecules may be even more dramatic since the interactions can change the molecular configurations; the molecular segments can be stretched out or get compressed in the adsorbed layers and the adsorbed molecules are often mixed with solvents. Therefore, it is more appropriate to describe the layer density of an adsorbed molecular film on a solid-liquid interface in terms of a continuous concentration profile which gradually diminishes over a distance that can be substantially larger than the average film thickness. Currently, it is not known what exact form this density profile should be in general. Attempts have been made to describe the profile in terms of a Gaussian, a simple exponential or hyperbolic functions, and an error function [11,39,44–48]. For polymers adsorbed in a diluted solution and the interface is saturated, the variation of the polymer density may follow a power law profile [49]. To keep the calculation simple, we adopt a hyperbolic-tangent function to describe the concentration profile:

$$c = c_b + (c_0 - c_b)\{1 - \tanh[(z-b)/a]\}/2, \tag{11}$$

where z is the coordinate in the direction perpendicular to the solid-liquid interface, c_0 is the concentration of a saturated layer which corresponds to the closest packed structure of the adsorbed molecules on the surface, c_b is the concentration of the molecules in solution, a is a parameter which describes the width of the film-solution interface, and b is a parameter which gives approximately the average thickness of the adsorbed film. As will be shown below, the viscoelastic responses are sensitive to the width of the film-solution interface. However, the main conclusions obtained in this work should not depend on the explicit form of the profile. The total amount of molecules adsorbed can be evaluated by integrating over the concentration profile. Figure 1 illustrates several continuous concentration profiles of adsorbed films of different interfacial width a (b varies slightly) but of the same amount of adsorbed molecules.

The local viscoelastic properties, such as viscosity and shear modulus, of each adsorbed layer depend on the concentration of the molecules in the layer. Assuming a linear relationship between the viscoelastic property and the concentration of the molecules in the layer, the profiles of the shear modulus and the viscosity take similar forms to that of concentration profiles:

$$\mu = \mu_0\{1 - \tanh[(z-b)/a]\}/2, \tag{12}$$

$$\eta = \eta_b + (\eta_0 - \eta_b)\{1 - \tanh[(z-b)/a]\}/2, \tag{13}$$

where η_0 and μ_0 are the viscosity and shear modulus of the adsorbed layer with saturated concentration, and η_b the viscosity of the solution. Here, we consider the shear modulus of the solution to be zero; a and b are the same as that in the concentration profile.

In the calculation, we consider that the adsorbed film thickness is much less than the viscous penetration depth. Following the same approach used by Voinova *et al.* [43], the adsorbed film with a continuous viscoelastic profile is divided into a large number of discrete slabs, each has a small width Δh_j and satisfies $\xi_j \Delta h_j \ll 1$, the viscosity $\eta(z_j)$ and the shear modulus $\mu(z_j)$ of each layer are determined by Eqs. (12) and (13). Assuming no slipping between adjacent layers, the acoustic response of a QCM with an adsorbed layer immersed in a Newtonian bulk liquid can be expressed as

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\left\{\frac{\eta_b}{\delta_b} + \sum_{j=1}^{n}\left[\rho\omega - 2\left(\frac{\eta_b}{\delta_b}\right)^2 \frac{\eta(z_j)\omega^2}{\mu^2(z_j) + \eta^2(z_j)\omega^2}\right]\Delta h\right\}, \tag{14}$$

$$\Delta D \approx \frac{2}{\omega\rho_q h_q}\left\{\frac{\eta_b}{\delta_b} + \sum_{j=1}^{n}\rho_b\omega\frac{\eta_b\mu(z_j)\omega}{\mu^2(z_j) + \eta^2(z_j)\omega^2}\Delta h\right\}. \tag{15}$$

The first terms in Eqs. (14) and (15) are due to the presence of the solution above the adsorbed film. If the changes in resonant frequency and the dissipation factor are measured with references to that in the presence of the solution but without adsorption, the terms involving η_b/δ_b are dropped out in Eqs. (14) and (15).

III. RESULTS AND DISCUSSION

A. Liquidlike adsorbed layer

For a liquidlike adsorbed film, its shear modulus $\mu = 0$. Equations (14) and (15) are reduced to

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\sum_{j=1}^{n}\omega\left(\rho - \rho_b\frac{\eta_b}{\eta(z_j)}\right)\Delta h_j, \tag{16}$$

$$\Delta D \approx 0. \tag{17}$$

The resonant frequency shift is due to the difference between the mass density of the adsorbed molecules and that of the solvent molecules scaled by the ratio of the viscosities of the solution and the adsorbed molecules. The mass densities of most organic molecules do not differ significantly from that of aqueous solution, but the viscosity of an aqueous solution dissolved with organic molecules can vary dramatically. If we assume that $\rho \sim \rho_b$, Eq. (16) becomes

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\sum_{j=1}^{n}\omega\rho_b\left(1 - \frac{\eta_b}{\eta(z_j)}\right)\Delta h_j.$$

It can be seen from this equation that the resonant frequency shift is determined by the profile of $\eta(z)$. For those molecular layers in which the concentration of the adsorbates is low but the viscosity of the layer due to the adsorbates is appreciably higher than that of the solution, they contribute significantly to the frequency shift. Since the viscosity of an aqueous solution usually is small, the adsorbated film with a spread-out interfacial density profile can satisfy the condition $\eta_b/\eta < 1$ in a region with thickness much larger than the average film thickness. In other words, the resonant frequency shift of a QCM in probing the adsorption in solution actually measures the change of the viscosity profile caused by the adsorption of the molecules; i.e., the thickness in the solution that QCM probes is the length scale normal to the interface over which the viscosity has been significantly increased due to the adsorption. Figure 2 plots the numerically calculated $\Delta f/\Delta f_0$ versus the width of the interface a for adsorbed films with

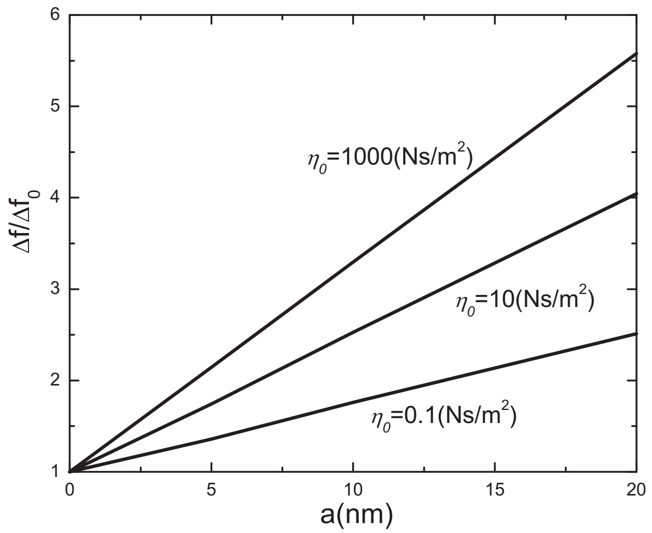

FIG. 2. Numerically calculated $\Delta f/\Delta f_0$ of liquidlike layers vs the width of the interface a for adsorbed films with the same amount of adsorbed molecules [Eq. (12) is used in describing the viscosity profile; b varies slightly in order to keep the total amount of adsorbates constant].

the same amount of adsorbed molecules [Eq. (13) is used for describing the viscosity profile, b slightly varies in order to keep the total amount of adsorbates constant]. In the calculation, we assumed that a 5 MHz QCM is used in its third harmonics ($\omega \approx 10^8$ rad/s), and the density and the viscosity of the solution are equal to that of pure water ($\rho = 1.0$ g/cm; $\eta = 10^{-3}$ Ns/m^2). Δf_0 is the shift for an adsorbed layer of 30 nm thickness with a box profile ($a = 0$ nm). As shown in the figure, $\Delta f/\Delta f_0$ increases approximately linearly with the interfacial width a, demonstrating that a larger interfacial width leads to a larger resonant frequency shift for the same amount of molecules adsorbed. This mechanism explains why the masses of adsorbed molecular films in solution determined using the resonant frequency shift of QCM are often found to be much larger than that actually adsorbed.

For a multilayer film, the density of the bottom layer is close to that corresponding to a closely-packed structure. η_0 in the viscosity profile [Eq. (13)] represents the viscosity of this layer. The range over which the viscosity profile affects the viscoelastic responses probed by a QCM is also determined by the value of η_0; a larger η_0 increases the number of layers that satisfy the condition $\eta_0/\eta \ll 1$. Figure 3 plots the numerically calculated $-\Delta f$ versus η_0/η_b for adsorbed films with a box profile ($a = 0$, $b = 30$ nm) and with a continuous profile of $a = 5$ nm and $b = 30$ nm. This is the same as the calculated results shown in Fig. 2, where the viscosity of the solution is assumed to be the same as that of water (10^{-3} Ns/m^2). For an adsorbed film with a boxed profile, the resonant frequency shift rises from zero at small η_0/η_b and then quickly saturates, indicating that Δf does not depend on the viscosity of the saturated layer η_0 as long as the viscosity is appreciably larger than that of the solution. For a film with a continuous profile, the resonant frequency shift continues to rise with η_0/η_b.

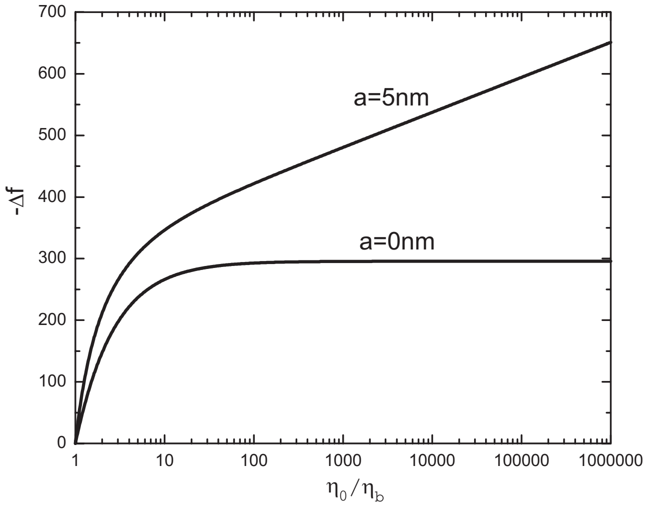

FIG. 3. Numerically calculated resonant frequency shift Δf as a function of the saturated viscosity η_0 of liquidlike adsorbed layers with a box viscous profile ($a = 0$ nm; $b = 30$ nm) and with a continuous viscous profile ($a = 5$ nm; $b = 30$ nm).

B. Solidlike adsorbed layer

For a solidlike adsorbed layer, $\mu > 0$, the changes in the resonant frequency and the dissipation factor can be expressed as

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\sum_{j=1}^{n}\left(\rho - \rho_b \frac{\eta_b}{\eta(z_j)} \frac{1}{\left(\frac{\mu(z_j)}{\eta(z_j)\omega}\right)^2 + 1}\right)\omega \Delta h_j,$$

$$\Delta D \approx \frac{2}{\omega\rho_q h_q}\sum_{j=1}^{n}(\rho_b\eta_b\omega)\left(\frac{1}{\eta(z_j)\omega}\right)^2 \frac{\mu(z_j)\omega}{\left(\frac{\mu(z_j)}{\eta(z_j)\omega}\right)^2 + 1}\Delta h_j$$

$$\approx \frac{2}{\omega\rho_q h_q}\sum_{j=1}^{n}\left(\frac{\rho_b\eta_b\omega}{\eta(z_j)}\right)\frac{\mu(z_j)}{\eta(z_j)\omega}\frac{1}{\left(\frac{\mu(z_j)}{\eta(z_j)\omega}\right)^2 + 1}\Delta h_j.$$

The differences between the solidlike and the liquidlike behaviors of an adsorbed film probed by a QCM are entirely determined by the factor $\mu/(\eta\omega)$, which in general varies along the direction normal to the interface. Under the same assumption that the viscoelastic profile varies linearly with the concentration profile of the adsorbates, the ratio of the viscosity and the shear modulus of each layer should be approximately a constant, i.e., $\mu(z)/\eta(z) \sim \mu_0/\eta_0$. If $\mu_0/(\eta_0\omega) \ll 1$, the responses between the solidlike and liquidlike adsorbed layers are indistinguishable. On the other hand, if $\mu_0/(\eta_0\omega) \gg 1$, the adsorbed film behaves like a rigid solid; the changes in the resonant frequency becomes proportional to the mass of those layers that behave like a solid; there is no change in the dissipation factor. One peculiar feature displayed in the viscoelastic response of a solidlike film probed by QCM is the dependence of response on the probing frequency. At a lower frequency the response is more sensitive to the viscoelastic flow properties of the layer,

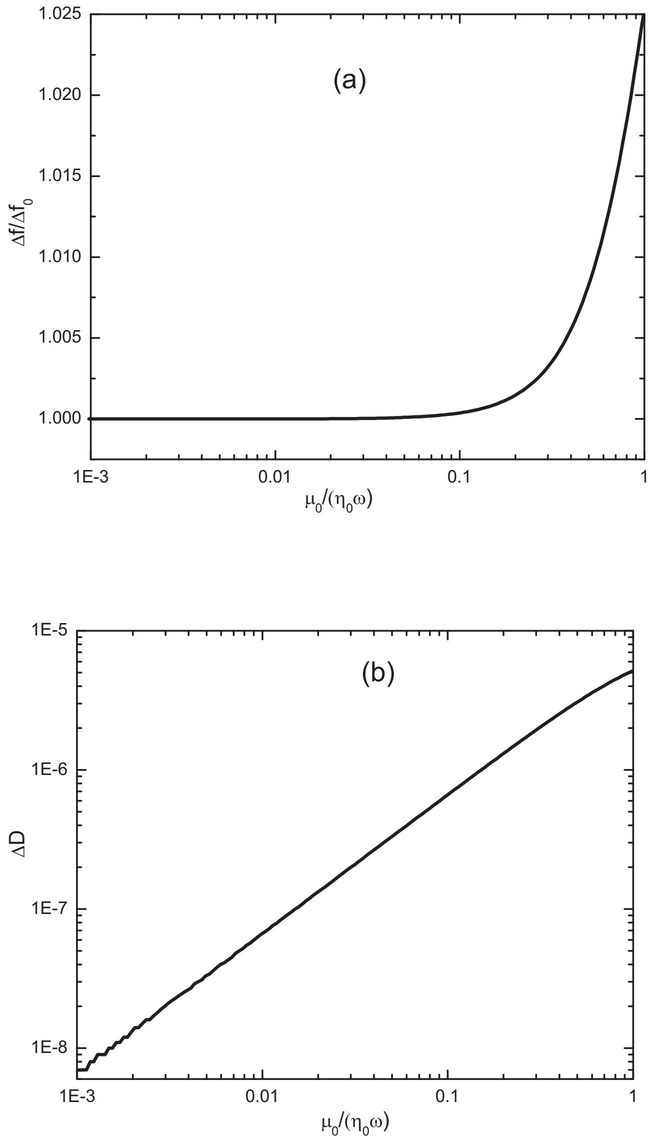

FIG. 4. (a) Numerically calculated $\Delta f/\Delta f_0$ vs $\mu_0/(\eta_0\omega)$ for adsorbed solidlike layers with profile parameters $a=5$ nm and $b=30$ nm. (b) Numerically calculated dissipation factor D vs $\mu_0/(\eta_0\omega)$ of a film with the same profile as that in (a).

while, at the high frequency limit, the whole layer behaves like a rigid solid. Figure 4 is a plot of $\Delta f/\Delta f_0$ versus $\mu_0/(\eta_0\omega)$ for an adsorbed film with profile parameters $a=5$ nm and $b=30$ nm. The frequency dependence of the factor $\mu/(\eta\omega)$ also shows that results obtained at different harmonic overtones do not simply scale with the Sauerbrey relation [29]. The resonant frequency shifts at higher harmonic overtones are smaller than that obtained at lower overtones, after having taken into account the overtone number. This frequency dependence in the normalized frequency shift has been observed experimentally [42], and can be explained as due to a continuous viscoelastic profile of the adsorbed film.

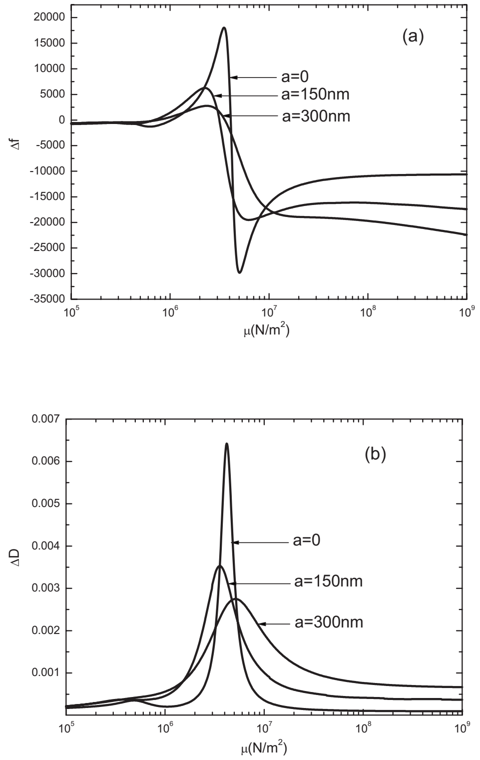

FIG. 5. (a) Numerically calculated resonance frequency shift Δf of a QCM as a function of the shear modulus of an adsorbed film of thickness $h=1$ μm and the viscosity $\eta=0.002$ (Ns/m^2) deposited in water. (b) Numerically calculated dissipation factor change ΔD as a function of the shear modulus of the same film deposited under the same condition as in (a).

C. Film resonance and film-solvent profile

For a homogeneous film in contact with a fluid, the film itself forms a resonator if the film thickness h matches a quarter of wavelength of the sound ($h\sim\lambda/4$). When the eigenfrequency of the film resonator and the resonant frequency of the QCM matches the energy transfer from the QCM to the film is most efficient, so the damping of the quartz resonance reaches a maximum and the resonant frequency shift of the QCM changes from negative to positive as the film eigenfrequency changes from above to below the resonant frequency of the QCM. This “film resonance” behavior has been illustrated by the results from the numerical calculation based on the slab model with a box profile of the adsorbed layers [43].

Since the frequency of film resonance depends sensitively on the thickness of a film, a continuous viscoelastic profile in the film would result in a distribution of the effective film thickness and, thus, smear out the film resonance. To illustrate this effect, the changes of the resonant frequency and the dissipation factor are calculated for adsorbed films of average film thickness $b=1$ μm as a function of the film-solution interface width a. Figure 5 displays the calculated film resonance for an adsorbed film in water with viscoelastic parameter $\eta_0=0.002$ (Ns/m^2). It is obvious that for a continuous viscoelastic profile, the larger the interface width, the less pronounced the resonance. This characteristic behavior may explain the broad “film resonance” observed in the temperature dependence of the frequency shift and the change of the dissipation factor of a polymer film [39].

IV. SUMMARY

We have numerically analyzed the acoustic responses of adsorbed molecular films with continuous concentration profiles on a solid-liquid interface probed by quartz crystal microbalance (QCM). The analysis uses a continuum mechanics model and assumes a hyperbolic tangent profile for the film-solution interface. The calculated results show that viscoelastic properties of the adsorbed films depend strongly on the width of the film-solvent interfaces. With a nonzero interface width, the viscoelastic responses probed by the QCM also depend on the magnitudes of viscosity and shear modulus in the profile over the entire film. Also, the "film resonance" is broadened due to the diffusive nature of the film-solution interface. These calculated results explain a number of experimental observations in the studies of macromolecules adsorbed on solid-liquid interfaces. The analysis assumes a linear relationship between the viscoelastic properties of the adsorbed layers and the concentration of the adsorbed molecules in the layers. The actual viscosity of a layer can rise much more rapidly with the concentration for many macromolecule systems as the concentration reaches the semidiluted value [50]. In these cases, the effects of a continuous concentration profile of the adsorbed films would be larger than what has been presented in here.

ACKNOWLEDGMENTS

This research was supported by an award from Research Corporation (D-M.Z.), and by a grant from National Science Foundation of China (Project No. 10574116) and by the Commission of Education of China Oversea Visiting Student Program (J.F.).

---

[1] G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, in *Polymers at Interfaces*, 1st ed. (Cambridge University Press, Cambridge, England, 1993).

[2] S. Alexander, J. Phys. (France) **38**, 983 (1977).

[3] P. G. de Gennes, Macromolecules **13**, 1069 (1980).

[4] S. T. Milner, Science **251**, 905 (1991).

[5] C. Walldal and S. Wall, Colloid Polym. Sci. **278**, 936 (2000).

[6] F. Caruso and H. Mohwald, J. Am. Chem. Soc. **121**, 6039 (1999).

[7] T. Oya, T. Enoki, A. Y. Grosberg, S. Masamune, T. Sakiyama, Y. Takeoka, K. Tanaka, G. Wang, Y. Yilmaz, M. S. Field, R. Dasari, and T. Tanaka, Science **286**, 1543 (1999).

[8] K. C. Daoulas, A. F. Terzis, and V. G. Mavrantzas, J. Chem. Phys. **116**, 11028 (2002).

[9] L. G. MacDowell and M. Muller, J. Chem. Phys. **124**, 084907 (2006).

[10] H. Taub, G. Torzo, H. J. Lauter, and S. F. Fain, Jr., in *Phase Transitions in Surface Film II*, NATO Advanced Study Institute, Series B: Physics (Plenum, New York, 1991).

[11] S. T. Milner, T. A. Witten, and M. E. Cates, Macromolecules **21**, 2610 (1988).

[12] M. Manciu and E. Ruckenstein, Langmuir **20**, 6490 (2004).

[13] S. Forster, E. Wenz, and P. Lindner, Phys. Rev. Lett. **77**, 95 (1996).

[14] C. Marzolin, P. Auroy, M. Deruelle, J. P. Folkers, L. Leger, and A. Menelle, Macromolecules **34**, 8694 (2001).

[15] G. Romet-Lemonne, J. Daillant, P. Guenoun, J. Yang, and J. W. Mays, Phys. Rev. Lett. **93**, 148301 (2004).

[16] P. Venema and T. Odijk, J. Phys. Chem. **96**, 3922 (1992).

[17] C. Wu and J. Gao, Macromolecules **32**, 1704 (1999).

[18] P. Auroy, L. Auvray, and L. Leger, Macromolecules **24**, 2523 (1991).

[19] P. Auroy, Y. Mir, and L. Auvray, Phys. Rev. Lett. **69**, 93 (1992).

[20] P. Auroy and L. Auvray, J. Phys. II **3**, 227 (1993).

[21] Y. Mir, P. Auroy, and L. Auvray, Phys. Rev. Lett. **75**, 2863 (1995).

[22] C. Marzolin, P. Auroy, M. Deruelle, J. P. Folkers, L. Leger, and A. Menelle, Macromolecules **34**, 8694 (2001).

[23] H. Motschmann, M. Stamm, and C. Toprakcioglu, Macromolecules **24**, 3681 (1991).

[24] R. Maassen, E. Eisenriegler, and A. Bringer, J. Chem. Phys. **115**, 5292 (2001).

[25] A. Chakrabarti and R. Toral, Macromolecules **23**, 2016 (1990).

[26] J. B. Field, C. Toprakcioglu, R. C. Ball, H. B. Stanley, L. Dai, W. Barford, J. Penfold, G. Smith, and W. Hamilton, Macromolecules **25**, 434 (1992).

[27] T. Cosgrove, T. G. Heath, J. S. Phipps, and R. M. Richardson, Macromolecules **24**, 94 (1991).

[28] J. M. H. M. Scheutjens and G. J. Fleer, J. Phys. Chem. **83**, 1619 (1979); **84**, 178 (1980).

[29] G. Sauerbrey, Z. Phys. **155**, 206 (1959).

[30] V. E. Bottom, *Introduction to Quartz Crystal Unit Design* (Van Nostrand Reinhold Co., New York, 1982).

[31] A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. B **31**, 7643 (1985).

[32] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **71**, 263 (1993).

[33] J. Krim, D. H. Solina, and R. Chiarello, Phys. Rev. Lett. **66**, 181 (1991).

[34] M. Rodahl, F. Hook, A. Krozer, P. Brzezinski, and B. Kasemo, Rev. Sci. Instrum. **66**, 3924 (1995).

[35] B. Wu, K. Wu, P. Wang, and Da-Ming Zhu, J. Phys. Chem. C **111**, 1131 (2007).

[36] K. Wu, B. Wu, P. Wang, Y. Hou, G. Zhang, and Da-Ming Zhu, J. Phys. Chem. B **111**, 8723 (2007).

[37] K. K. Kanazawa and J. G. Gordon, Anal. Chem. **57**, 1770 (1985).

[38] M. Rodahl and B. Kasemo, Sens. Actuators, A **54**, 448 (1996).

[39] A. Domack, O. Prucker, J. Ruhe, and D. Johannsmann, Phys. Rev. E **56**, 680 (1997).

[40] A. Domack and D. Johannsmann, J. Appl. Phys. **80**, 2599 (1996).

[41] D. Johannsmann, Macromol. Chem. Phys. **200**, 501 (1999).

[42] F. Hook, B. Kasemo, T. Nylander, C. Fant, K. Sott, and H. Elwing, Anal. Chem. **73**, 5769 (2001).

[43] M. V. Voinova, M. Rodahl, M. Jonson, and B. Kasemo, Phys. Scr. **59**, 391 (1999).

[44] Da-Ming Zhu and J. G. Dash, Phys. Rev. Lett. **60**, 432 (1988).
[45] Da-Ming Zhu and J. G. Dash, Phys. Rev. B **38**, 11673 (1988).
[46] J. Zittartz, Phys. Rev. **154**, 529 (1967).
[47] J. Q. Broughton, A. Bonissent, and F. F. Abraham, J. Chem. Phys. **74**, 4029 (1981).
[48] W. A. Curtin, Phys. Rev. Lett. **59**, 1228 (1987).
[49] S. Metzger, M. Muller, K. Binder, and J. Baschnagel, J. Chem. Phys. **118**, 8489 (2003).
[50] P. G. de Gennes, Macromolecules **9**, 594 (1976).