PHYSICAL REVIEW E **78**, 031604 (2008)

Resonant frequency and dissipation factor isotherms of adsorbed molecules on solid-liquid interfaces probed by quartz crystal microbalance

Jiajie Fang and Da-Ming Zhu[*]
Department of Modern Physics, University of Science and Technology of China, Hefei, China 230027
and University of Missouri-Kansas City, Kansas City, Missouri 64110, USA

(Received 23 April 2008; published 15 September 2008)

Changes in the resonant frequency Δf and the dissipation factor ΔD of a quartz crystal microbalance due to adsorption of molecules onto the electrode surface in solutions at different concentrations have been numerically analyzed. It has been found that the contribution from the solution due to the variation of the concentration can mask the overall behaviors of the Δf and ΔD isotherms. However, if the solution is sufficiently dilute or the contribution of the solution can be characterized accurately, the corrected Δf and ΔD, as a function of the solution concentration, will reveal characteristic features of the adsorption processes for the adsorbed films. Specifically, steplike behaviors will be displayed in Δf isotherms, which correspond to layer formation and layer-by-layer growth of the films, but the onsets of the steps usually do not coincide with the layer completion. Oscillatory behaviors will be revealed in ΔD isotherms if the adsorbed molecular layer is soft at low concentration and becomes rigid near layer completion.

DOI: 10.1103/PhysRevE.78.031604 PACS number(s): 68.43.−h, 68.08.−p, 68.15.+e

I. INTRODUCTION

The adsorption of atoms or molecules on an interface is ubiquitous and controls many physical, chemical, and biological processes [1,2]. One simple yet effective approach to study adsorption phenomena is to probe the response of adsorption versus some parameters which are directly related to the chemical potentials of the adsorbates at a constant temperature, generating so-called adsorption isotherms [3–19]. When adsorption occurs in a gaseous or vacuum environment, the chemical potentials of the adsorbates are directly related to the vapor pressures of their vapor phases under equilibrium. Thus, vapor pressure isotherms have been widely used in characterizing the adsorption processes and have proven to be highly sensitive for detecting subtle changes in the properties of adsorbed films on various substrates [13–16]. Novel phenomena, such as layer-by-layer growth and wetting and nonwetting of adsorbed films, have been revealed unambiguously from the results of vapor pressure isotherm measurements [17–22].

For adsorption occurring on a solid-liquid interface, the adsorbed film is sandwiched in between two condensed phases. The situation is often complicated by the presence of the bulk liquid covering the solid substrate, which renders many experimental surface study techniques difficult to use. In the case of the physisorption of neutral molecules, the chemical potential of the adsorbed film is determined mainly by the concentration of the adsorbates in solution; thus, the adsorption isotherms will usually be measured against the concentration. Among several techniques, quartz crystal microbalance (QCM) has been widely applied to isotherm measurements and in studies of adsorption both in gaseous phases and in solutions in recent years [23–36]. The technique is based on the piezoelectric property of a quartz crystal, which can oscillate in a thickness shear mode at a resonant frequency with an extraordinarily high quality factor and is very sensitive for detecting small amounts of mass deposited on the electrode surface and changes in an adsorbed film when operated in vacuum or in a gaseous environment [23–25]. When used in solution, the technique suffers from the fact that the interactions between the adsorbed film and the solution generate significant energy dissipation to the oscillation, which broadens the resonant peak and results in a reduced sensitivity for detecting the adsorbed entities. On the other hand, the broadening of the resonant peak provides an additional parameter for characterizing the property of the adsorbed film, although detailed relationships between the dissipation factor and the microstructure of the adsorbed film remain to be worked out [28–36]. The changes of the resonant frequency and the dissipation factor of a QCM operated in solution are found to be sensitive to the viscoelastic profile, rather than the adsorbed mass, of the adsorbed film on the interface [30,36]. In a recent study of macromolecules adsorbed on the gold-plated electrode surface of a QCM, the measured frequency shift as a function of the concentration of the adsorbed molecules shows a steplike behavior in the concentration of the adsorbed molecules, reminiscent of the layer formation seen in the adsorption in the vapor phase [26,27]. However, it is not entirely clear if the features observed in the resonant frequency isotherm in solution can be interpreted in the same way as that for features displayed in vapor pressure isotherms.

In this work, we have numerically analyzed the changes of the resonant frequency Δf and the dissipation factor ΔD of a QCM adsorbed with molecules in solutions of different concentration using a continuum mechanics model. The results of the calculation show that usually the contribution from the solution to the viscoelastic response measured by the QCM is important. If the viscosity of the solution as a function of the concentration can be characterized accurately, so that the contribution from the solution can be appropriately subtracted off, the corrected Δf and ΔD as a function of

---

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

the concentration in solution will reveal the intrinsic features associated with layer formation and multilayer growth of a film. The calculated results show that in this case Δf isotherms will reveal characteristic features of adsorption such as steplike behavior associated with the layer formation and layer-by-layer growth; ΔD isotherms may display a broad bump associated with the completion of an adsorbed layer and an oscillatory variation associated with the layer-by-layer growth behavior of multilayer films. These results are consistent with the currently available experimental data.

II. METHODS AND MODELS

As molecules adsorbed on the electrode surface of a QCM submerged in solution, the adsorbed film with a varying concentration profile from layer to layer is sandwiched between a solid substrate and a bulk liquid. A detailed derivation of the changes in the resonance frequency Δf and ΔD from the wave equation for bulk shear waves propagating in a homogeneous viscoelastic medium has been worked out by Rodahl and Kasemo [29]. The acoustic response of the QCM adsorbed with two layers in a homogenous liquid medium was further calculated by Voinova *et al.*, which treats the solution as a semi-infinite Newtonian fluid [34] and assumes that each adsorbed layer can be described by a Voight-based viscoelastic model with distinct viscosity η_j and shear modulus μ_j and no slippery boundary condition at the boundaries. These results have been extended to the case in which the adsorbed molecules form multilayers with a varying viscoelastic profile in the layers normal to the interface [36]:

$$\Delta f \approx -\frac{1}{2\pi\rho_q h_q}\left[\frac{\eta_b}{\delta_b}+\sum_{j=1}^{n}\left(\rho_j-\rho_b\frac{\eta_b}{\eta_j}\frac{1}{(\mu_j/\eta_j\omega)^2+1}\right)\omega\Delta h_j\right], \tag{1}$$

$$\Delta D \approx \frac{2}{\omega\rho_q h_q}\left[\frac{\eta_b}{\delta_b}+\sum_{j=1}^{n}\left(\frac{\rho_b\eta_b\omega}{\eta_j}\right)\frac{\mu_j}{\eta_j\omega}\frac{1}{(\mu_j/\eta_j\omega)^2+1}\Delta h_j\right], \tag{2}$$

where $\delta_b = (2\eta_b/\rho_b\omega)^{1/2}$ is the viscous penetration depth in solution, Δh_j is the thickness of the jth adsorbed layer; ρ_b and η_b are the density and the viscosity of the solution, respectively; ρ_q and h_q are the density and thickness of the quartz crystal electrode, respectively. In the calculated results presented below, the third overtone of a 5-MHz frequency is assumed. The results can be scaled if other frequencies or overtones are used. In Eqs. (1) and (2), the densities of the solution and the adsorbed film, and the parameters which describe the viscoelastic properties of the solution and the film, all depend on the concentration of the adsorbates in solution. The first terms in these equations involving η_b/δ_b are the contributions directly from the solution, which are the same as those in the case of a bulk liquid covering the surface of the QCM derived by Kawazana and Gordon [28]. In principle, the contribution described by this term can be characterized independently by measuring the viscosity of the solution as a function of the concentration of adsorbed molecules. It is known that for solutions dissolved with macromolecules at low concentration, typically below the semidilute concentration, the viscosity of the solution usually displays a linear dependence on the concentration [37]. At higher concentrations where macromolecules start to tangle together, the viscosity rises more rapidly with concentration, its dependence on the concentration having been described as a power law with an exponent roughly equal to 3.5 [37]. The typical semidilute concentrations for many solutions of macromolecules are found to be around 10%. Since the effects from the solution on Δf and ΔD are not the main focus of this study, we consider the cases where the saturated concentration of adsorbates in solution is below 10%, the typical semidilute concentration [37]. Thus, the concentration dependence of the viscosity of the solution in these cases can be expressed as

$$\eta_b = [1 + \alpha c/c_0 + \alpha(10c/c_0)^3]\eta_w, \tag{3}$$

where c and c_0 are the concentration and the saturated concentration of adsorbates in solution, η_w is the viscosity of the pure solvent, and α is a coefficient. The concentration dependence of the viscosity of the adsorbed molecular layers at the interface should take the same form as Eq. (3), except that the concentration may vary from layer to layer; thus, the term c/c_0 should be replaced with θ_j, the coverage of the adsorbed molecules in the jth layer, and $\theta_j = 1$ corresponds to the completion of the adsorbed layer. The relationship between the concentration and the shear modulus μ_j of the adsorbed layers can be quite complicated; it may depend not only on the concentration, but also on the configuration of the molecules, as well as the measuring speed [38]. For certain types of polymers dissolved in water, the studies found that the appearance of elasticity occurs at concentration much higher than the semidilute concentration. Theoretical modelings have predicted that a concentration dependence semiflexible polymers solution follows a power law with an exponent of around 2–3 [39]. Without knowing what exactly relationship between the concentration and the elastic modulus of the adsorbed layers should be used in calculating the viscoelastic responses, we have varied the ratio $\mu/\eta\omega$ and found that as $\mu/\eta\omega < 0.1$, the shear modulus of the adsorbed layers has almost no effect on the frequency shift of a QCM, and as $\mu/\eta\omega > 0.1$, an order of magnitude increase of this ratio results in a less than 3% increase of the resonant frequency shift, but the effect of the elastic modulus of the adsorbed layer to the dissipation factor can be quite large [36]. In this work, we assumed that the concentration dependence of the shear modulus of the adsorbed layers follows a power-law —i.e., $\mu \cong \beta\theta^3$, where β is a coefficient. The difference between the coverage dependence of the shear modulus and the viscosity of the film is that at the low-coverage limit, μ approaches zero, while η approaches the value of the solvent. At higher concentration, $\mu/\eta \sim \beta/\alpha$, which is a constant. It should be noted that the assumptions used in the calculation may not be completely appropriate when the viscosity and the shear modulus of an adsorbed layers become high, but on the other hand, in the limit where the viscosity and the shear modulus of an adsorbed film are high, the Δf and ΔD measured by a QCM should be reduced to that described by the Sauerbrey equation [23]. So the results of the calculation should reveal the intrinsic behavior of molecules adsorbed on a solid-liquid interface [23].

The most important factor which determines Δf and ΔD as a function of the concentration might actually be the growth behaviors of the adsorbed film as the concentration in solution varies, according to Eqs. (1) and (2). The growth behaviors are determined mainly by the interactions between the adsorbed molecules and substrate and between the adsorbed molecules and solvent [40–42]. The purpose of this work is to explore that for a given growth mode of adsorbed molecules whether or not the resonant frequency and the dissipation factor isotherms reveal the characteristic behaviors of the growth behaviors. For this purpose, we used the Langmuir model of adsorption [43] and the Brunauer-Emmett-Teller (BET) model of adsorption for calculating Δf and ΔD for the growth of monolayer and multilayer films, respectively [44]. The results of the calculations are then compared with the detailed features presented in these two adsorption models.

III. RESULTS AND DISCUSSIONS

A. Growth of a liquidlike monolayer

The first step to investigate the viscoelastic response measured by a QCM in solution is to check if the characteristic behavior of a monolayer growth can be revealed in the Δf and ΔD isotherms. For this purpose, we used the Langmuir adsorption model to describe the film growth mode. The model assumes that surface adsorption sites are equally active and each site can adsorb only one molecule and a dynamic equilibrium exists in free molecules in solution and the adsorbed molecules on the surface [43]. The change of surface coverage θ of the adsorbed molecules is governed by a balance of the rates of adsorption and desorption of the molecules, which yields the equilibrium coverage at a given concentration:

$$\theta_{eq} = c/(c + k^{-1}). \tag{4}$$

The ratio between adsorption and desorption coefficients, $k = k_a/k_d$, determines the variation of the coverage versus the concentration in solution. The coverage approaches 1, which corresponds to a complete monolayer of adsorbed molecules, at high concentration. The characteristics of Langmuir growth are a rapid rise in the coverage at the low concentration, followed by a plateau in the coverage, indicating the completion of a monolayer.

If the adsorbed layer is liquidlike—i.e., $\mu/\eta\omega \ll 1$—then there should be no change in the dissipation factor—i.e., $\Delta D = 0$—as shown in Eq. (2); the adsorption causes resonant frequency shift only. Figure 1 is a resonant frequency Δf isotherm of the adsorption of molecules with $k = 4.3\times 10^3$ and a linear coefficient $\alpha = 10^2$ based on the Langmuir growth mode. The calculated results show that $-\Delta f$ rises rapidly at the low concentration and then reaches a plateau. As the concentration further increases, the viscosity of the solution rises, resulting in a rapid rise in $-\Delta f$. In this calculation, the saturated concentration was assumed to be 1%. The results indicate that even in this low concentration, the changes in resonant frequency due to the concentration change can completely mask changes due to the additional adsorption of the molecules on the interface. As was described above, if the concentration dependence of the viscosity of a solution can be characterized independently, the first term in Eq. (1), which is purely due to the contribution from the solution, can be subtracted off from the measured Δf. Also plotted in Fig. 1 is the Δf isotherm with the first term η_b/δ_b being subtracted off. The solution-corrected Δf isotherm displays a rapid rise and a gradual approaching of a saturated value, closely resembling the actual growth behavior of a Langmuir growth mode. It should be noted that the η_b/δ_b term represents the contribution of a bulk solution without an adsorbed film. As the interface is covered by an adsorbed layer, due to the acoustic attenuation through the adsorbed layer, the effect from the covering solution is reduced, so the actual contribution from the solution should be less than that described by the term involving η_b/δ_b. Thus, the subtraction actually over corrects the contribution from the solution. This is why when the η_b/δ_b term is subtracted from Δf, it shows a slight drop at the higher concentration, as can be seen in Fig. 1.

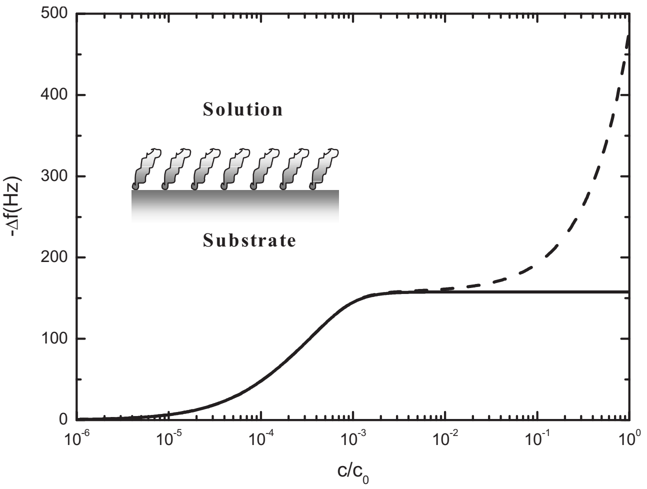

FIG. 1. Calculated resonant frequency shift due to the adsorption of molecular film in water at room temperature using the Langmuir model with the ratio of adsorption and desorption coefficients $k = 4.3\times 10^3$. The viscosity of the adsorbed film versus concentration is described by Eq. (3) with the coefficient $\alpha = 100$. The dashed line is the total resonant frequency shift; the solid line is the resonant frequency after the η_b/δ_b term being subtracted off. The inset is an illustration of the adsorption on the interface.

For the adsorption of molecules on a homogenous substrate, the shape of the adsorption isotherm contains information about adsorption kinetics. A larger ratio of the adsorption and desorption coefficients k produces a more rapid rise in the coverage of adsorbed molecules at the low concentration. An important question is whether or not such a correlation still holds in Δf isotherms measured using a QCM. Figure 2(a) plots the Langmuir adsorption isotherms with the value of k chosen to be 4.3×10^2, 4.3×10^3, and 4.3×10^4, respectively. Figure 2(b) is the calculated Δf dependence on the concentration in solution using the adsorption isotherm in Fig. 2(a) and assigning $\alpha = 10^3$ to determine the viscosity of

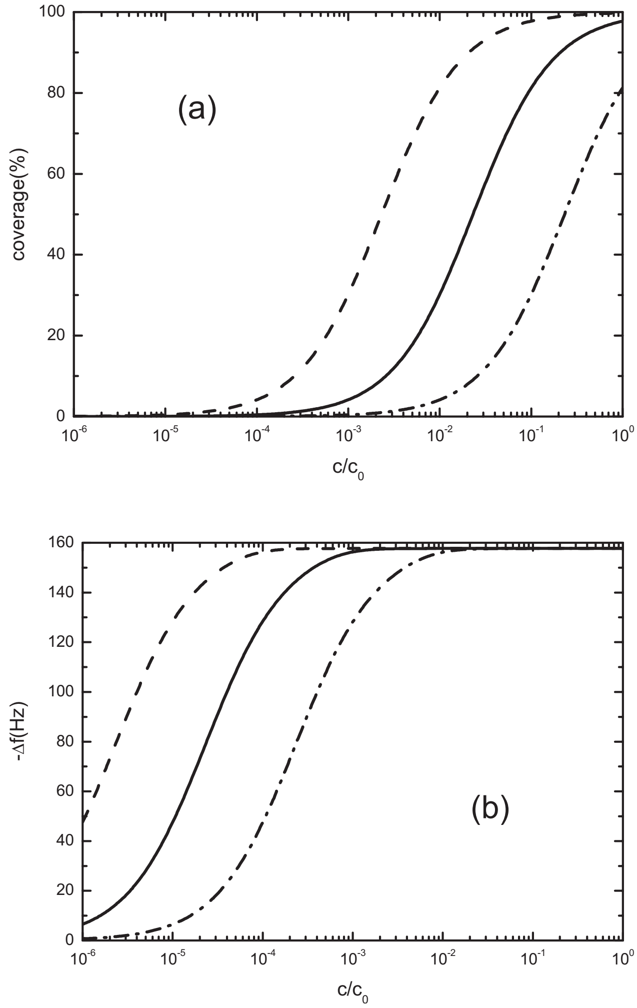

FIG. 2. (a) Illustration of Langmuir adsorption isotherms (a) and their corresponding Δf isotherms with k chosen to be 4.3×10^2, (dot-dashed line), 4.3×10^3 (solid lines), and 4.3×10^4, (dashed lines), respectively. The viscosity of the adsorbed film versus concentration can be described by Eq. (3) with the coefficient $\alpha = 10^3$.

the adsorbed layer. It can be seen from the figures that, in comparison to the adsorption isotherms, the Δf isotherms maintain their overall shapes, but shift towards lower concentrations. This is because Δf is determined by the viscosity contrast between the adsorbed layer and the solution [30,36]; a small amount of molecular adsorption at the low concentration can result in a $-\Delta f$ which is close to that due to the adsorption of a complete layer, so the Δf plateau appears at relatively low concentrations.

The coefficient of the linear relationship between the viscosity and the coverage of the adsorbed layer also affects the shape of the Δf isotherms. Plotted in Fig. 3 are Δf isotherms calculated using $\alpha = 10^2, 10^3, 10^4$, respectively, with $k = 4.3\times 10^3$. It is interesting to note that the linear coefficient in the viscosity relation has a similar effect as that of the ratio of the adsorption kinetics coefficient k. A larger coefficient in the layer coverage dependence of the layer's viscosity produces a larger viscosity contrast between the adsorbed layer and that of the solution at a given concentration, an effect similar to that of the adsorption/desorption ratio of coefficients k. Although the η_b/δ_b-term-corrected Δf isotherms maintain the shape of the true adsorption isotherms, care needs to be exercised in interpreting the onset of layer completion based on the Δf isotherms.

B. Growth of a solid-liquid monolayer

If the adsorbed layer is solidlike—i.e., $\mu/\eta\omega \geqslant 1$—both Δf and ΔD will vary with the concentration of the adsorbed molecules in the solution. To calculate Δf and ΔD isotherms, one needs to know the relationship between the shear modulus of the adsorbed layers on the concentration of the adsorbed molecules. As was described above, we assume that in the low-concentration limit the shear modulus of the adsorbed layer has a linear dependence on the concentration—i.e., $\mu \cong \beta\theta^3$, where β is a coefficient. Figures 4(a) and 4(b) show the calculated Δf and ΔD versus the concentration of molecules with $k = 4.3\times 10^3$ and at the high-concentration

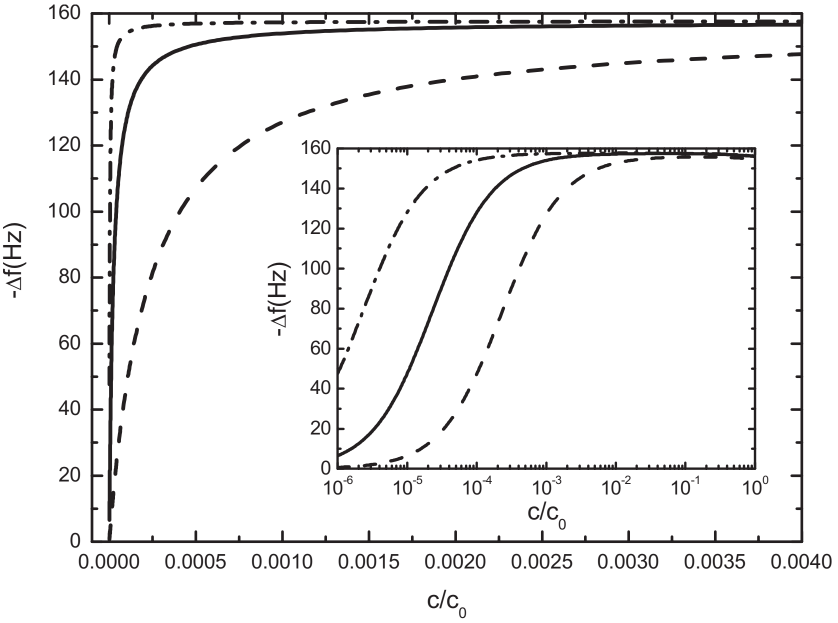

FIG. 3. Numerically calculated Δf isotherms for different linear coefficients used in determining the viscosity dependence of the adsorbed film and the concentration of adsorbed molecules. The inset is a semilogarithmic plot of the same figure. The linear coefficients α chosen for using Eq. (3) are 10^2 (dashed lines), 10^3 (solid lines), and 10^4 (dot-dashed lines), respectively. The ratio of adsorption and desorption coefficients used in the Langmuir adsorption model in the calculation is $k = 4.3\times 10^3$.

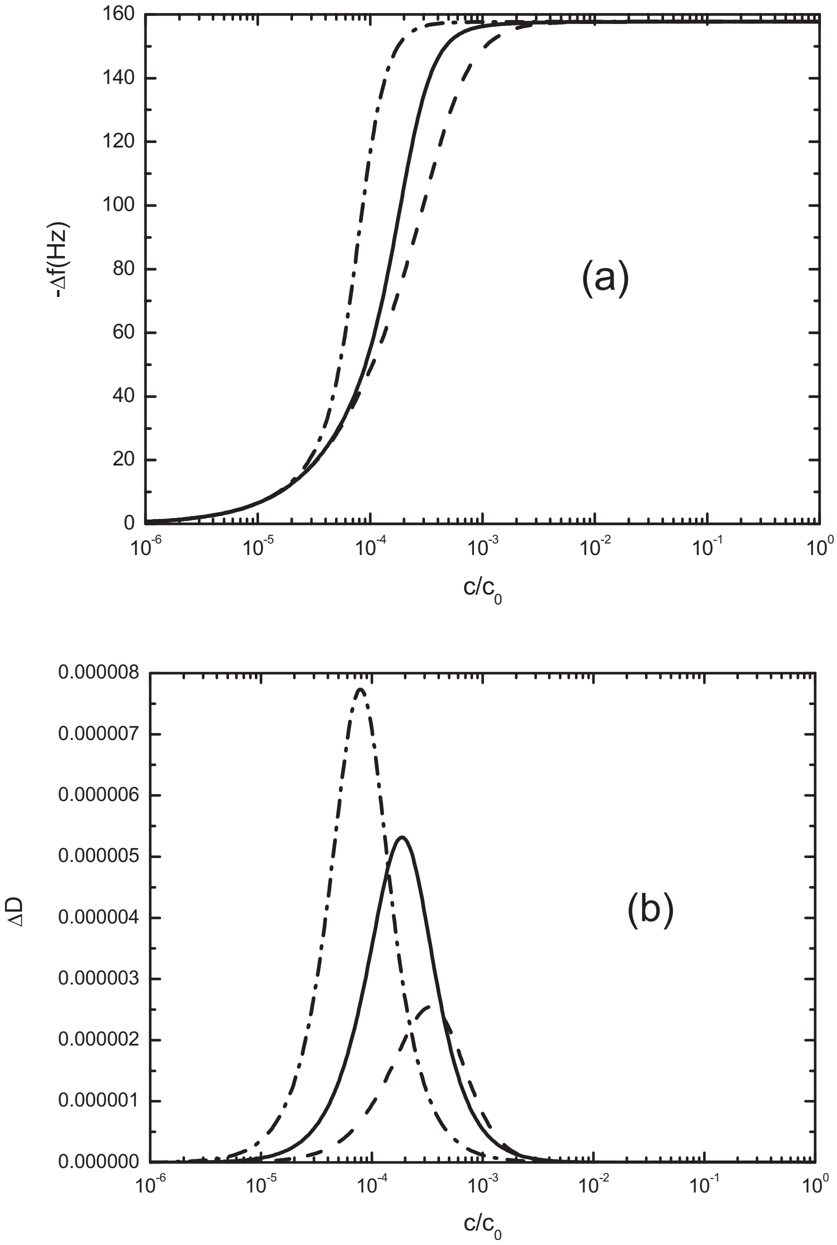

FIG. 4. Numerically calculated (a) Δf and (b) ΔD versus the concentration of the molecules adsorbed on a surface in a Langmuir growth mode with $k=4.3\times 10^3$, $\alpha=10^2$, and at the high-concentration limit, $\mu/\eta\omega=0.5$ (dashed line), 2 (solid line), 10 (dot-dashed line), respectively.

limit $\mu/\eta\omega=0.5,2,10$, respectively, at a constant frequency. The overall shapes of the Δf isotherms for solidlike films are similar to those of liquidlike films. As shown in the figure, a larger value of the shear modulus further increases the viscoelastic contrast between the adsorbed layers and the solution, shifting the Δf isotherms further towards lower concentrations.

The general trend of the ΔD isotherm is governed by the factor $(\mu/\eta^2\omega^2)/[(\mu/\eta\omega)^2+1]$, which is proportional to μ at low concentration and η^{-1} at high concentration where $\mu/\eta\omega$ is a constant. As the concentration of the adsorbed molecules increases from low coverage, the interaction between the adsorbed molecules and the solvent molecules increases, and so does the energy dissipation. As the adsorbed layer approaches completion, the solvent molecules are squeezed out of the layer and the layer becomes more rigid, resulting in a decrease in the energy dissipation. So it is expected that the dissipation factor will rise initially, reach a peak, and then gradually decrease at higher concentration. Such a trend of decreasing ΔD at a higher concentration has been recently observed experimentally (see Fig. 5 in Ref. [27]). It should be noted that although the linear relationship may be reasonable at low concentration, the dependence of the shear modulus of an adsorbed layer on the concentration of the adsorbates can be complicated at higher concentration. But in the limit where the shear modulus of the adsorbed layer becomes large so that adsorbed layer becomes rigid, Δf is reduced to that described by the Sauerbrey equation and ΔD approach zero [23]. So the actual rise in the Δf isotherms may be more abrupt and the bump in the ΔD isotherm may appear at lower concentration.

C. Growth of multilayer films

The growth behaviors of multilayer films on a solid-liquid interface can be described by a well-known model proposed

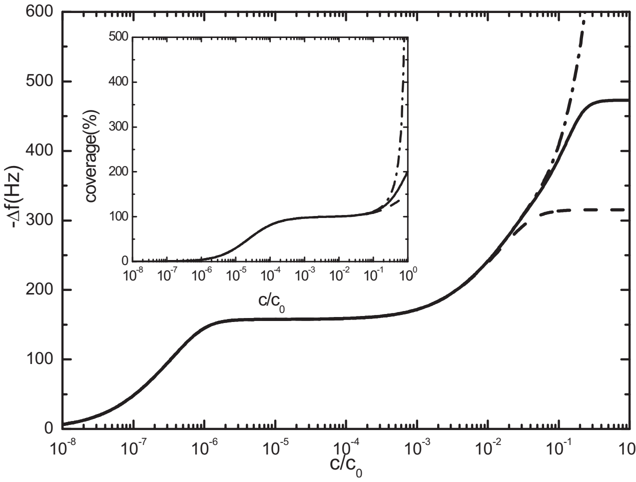

FIG. 5. Numerically calculated Δf isotherms for liquid like adsorbed films for $k=4.3\times10^4$, $\alpha=10^2$, with maximum number of layers that can form to be 2 (dashed line), 3 (solid line), and infinity—i.e., completely wetting case (dot-dashed line). The inset shows the corresponding BET adsorption isotherms.

by BET, who treated the adsorption using a lattice gas model which allows the molecules to occupy a three-dimensional array of sites above the solid surface [44]. In this model, the equilibrium condition which equalizes the adsorption rate and desorption rate in each molecular layer, at a given relative concentration c/c_0, determines the concentration profile in the adsorbed layers [44]. If the thickness of the adsorbed layers cannot exceed a maximum number n, the coverage of the adsorbed layers can be expressed as [44]

$$\theta=\frac{kx}{1-x}\left[\frac{1-(n+1)x^n+nx^{n+1}}{1+(k-1)x-kx^{n+1}}\right], \qquad (5)$$

where $x=c/c_0$ is the ratio of the solution concentration and the saturated concentration, and k is the ratio of adsorption and desorption coefficients. If the maximum number of layers allowed is infinite, which corresponds to the case of complete wetting, the above equation is reduced to

$$\theta=\frac{kx}{(1-x)[1+(k-1)x]}. \qquad (6)$$

Using either Eq. (5) or Eq. (6) for finite-layer multilayers or infinite-layer systems, and choosing a value for the parameter k, the concentration profile of the adsorbed layers and its variation with the solution concentration can be determined. Following the procedure used in calculating the isotherms for Langmuir adsorption, the concentration dependence of Δf and ΔD for BET adsorption were calculated. Figure 5 is a plot of the calculated Δf isotherms for liquidlike adsorbed films with the maximum number of layers that can form limited to 2, 3, and infinite (complete wetting case). The inset is the corresponding BET adsorption isotherms. The results demonstrate that Δf isotherms follow the adsorption of the molecules and display the same features as in the BET isotherms. The number of maximum layers and the wetting behaviors can be identified in the Δf isotherms. Figure 6 shows the calculated Δf as a function of the concentration of the adsorbed molecules in solution for a liquidlike adsorbed layer with $\mu=0$ and solidlike adsorbed layer $\mu/\eta\omega=2$. Again, the features displayed in the adsorption isotherms can all be seen in the Δf isotherms, and the features in the isotherms for solidlike adsorbed films are simply shifted towards lower concentration comparable to that of liquidlike films. Figure 7 shows the numerically calculated ΔD isotherms. ΔD increases with the concentration and displays a maximum in the process of the first-layer formation, as demonstrated in the ΔD isotherms for Langmuir growth. In the multilayer regime, the number of layers formed increases rapidly with the concentration, the oscillatory variations in ΔD from different layers overlap, producing a rapid increase in the energy dissipation. The drop in the dissipation at close to the saturation concentration is due to the assumption of formation of a multilayer rigid solid film at that concentration and has been observed in the studies of adsorption of polyelectrolyte molecules [45]. Due to the interactions between the adsorbed molecules and the solvent molecules, the adsorbed multiplayer film, especially the top layers, are probably always diffusive in solution. Apparently, a continuum mechanics model is not adequate in describing viscoelastic properties of layers of molecular thickness. A better approach would probably require a molecular dynamics calculation which can deal with solid and liquid phases in each layer to account for the details of the Δf and ΔD isotherms.

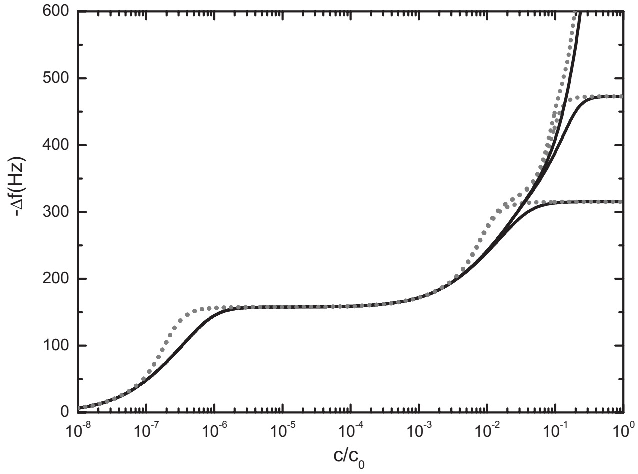

FIG. 6. Numerically calculated Δf isotherms for liquidlike ($\mu=0$) multilayer films with maximum number of layers that can form to be 2, 3, and infinity (solid lines) and the corresponding solidlike ($\mu/\eta\omega=2$) multilayer films (dotted lines) of the same thickness. All other parameters used in the calculation are the same as those in Fig. 5. The solidlike multilayer films show more prominent steps corresponding to layer formation, with the onsets of the plateaus shifted towards lower concentrations.

IV. CONCLUSIONS

We have numerically analyzed the characteristics of resonant frequency and the dissipation factor isotherms of adsorption of molecules onto the surface of the electrode of the

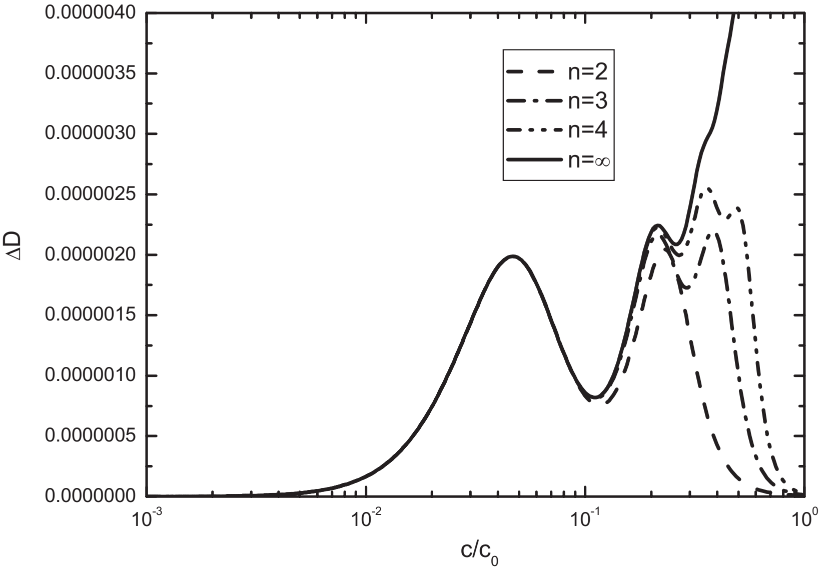

FIG. 7. Numerically calculated ΔD isotherms of multilayer growth. The numbers indicate the maximum number of layers allowed to form in the BET model used in the calculation. ΔD displays maxima associated with the formation of each layer. The maxima for the formation of layers beyond the first one overlap each other.

QCM in solution as a function of concentration. The solution contribution corrected resonant frequency isotherms follow the behaviors of adsorption isotherms and thus can be used for characterizing the adsorption properties of the molecules. The dissipation factor isotherms reveal oscillatory behaviors which correspond to layer formation and layer completion for adsorbed layers based on the simple Langmuir and BET adsorption models. The analysis presented here shows that the resonant frequency and the dissipation factor isotherms can be powerful tools for characterizing and studying the adsorption behaviors of the molecules on a solidlike interface.

ACKNOWLEDGMENTS

We would like to thank Dr. Paul Rulis for his critical review of this manuscript. This work is support in part by a grant 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, *Polymers at Interfaces*, 1st ed. (Cambridge University Press, Cambridge, England, 1993), and references therein.
[2] H. Taub, G. Torzo, H. J. Lauter, and S. F. Fain, Jr., *Phase Transitions in Surface Films II*, Vol 267 of *NATO Advanced Study Institute, Series B: Physics* (Plenum, New York, 1991).
[3] A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, Phys. Rev. B **31**, 7643 (1985).
[4] M. Drir, H. S. Nham, and G. B. Hess, Phys. Rev. B **33**, 5145 (1986).
[5] Y. Larher, F. Anger, and Y. Maurice, J. Chem. Soc., Faraday Trans. 1 **83**, 3355 (1987).
[6] A. D. Migone, A. Hofmann, J. G. Dash, and O. E. Vilches, Phys. Rev. B **37**, 5440 (1988).
[7] J. Ma, D. L. Kingsbury, F. Liu, and O. E. Vilches, Phys. Rev. Lett. **61**, 2348 (1988).
[8] M. T. Alkhafaji and A. D. Migone, Phys. Rev. B **45**, 8767 (1992).
[9] M. T. Alkhafaji, P. Shrestha, and A. D. Migone, Phys. Rev. B **50**, 11088 (1994).
[10] Y. M. Liu, P. S. Ebey, O. E. Vilches, J. G. Dash, M. Bienfait, J.-M. Gay, and G. Coddens, Phys. Rev. B **54**, 6307 (1996).
[11] D.-M. Zhu, A. Zambano, A. Migone, and S. Harrington, Phys. Rev. E **63**, 011404 (2001).
[12] D. S. Rawat and A. D. Migone, Phys. Rev. B **75**, 195440 (2007).
[13] S. Talapatra, V. Krungleviciute, and A. D. Migone, Phys. Rev. Lett. **89**, 246106 (2002).
[14] S. Talapatra and A. D. Migone, Phys. Rev. Lett. **87**, 206106 (2001).
[15] A. J. Zambano, S. Talapatra, and A. D. Migone, Phys. Rev. B **64**, 075415 (2001).
[16] M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsky, M. Muris, M. R. Johnson, T. Wilson, M. DePies, and O. E. Vilches, Phys. Rev. B **70**, 035410 (2004).
[17] H. S. Youn and G. B. Hess, Phys. Rev. Lett. **64**, 443 (1990); **64**, 918 (1990).
[18] J. Z. Larese and Q. M. Zhang, Phys. Rev. B **51**, 17023 (1995).
[19] H. S. Youn, X. F. Meng, and G. B. Hess, Phys. Rev. B **48**, 14556 (1993).
[20] G. B. Hess, M. J. Sabatini, and M. H. W. Chan, Phys. Rev. Lett. **78**, 1739 (1997).
[21] P. Pfeifer, Y. J. Wu, M. W. Cole, and J. Krim, Phys. Rev. Lett. **62**, 1997 (1989).
[22] P. Taborek and J. E. Rutledge, Phys. Rev. Lett. **71**, 263 (1993).
[23] G. Sauerbrey, Z. Phys. **155**, 206 (1959).
[24] V. E. Bottom, *Introduction to Quartz Crystal Unit Design* (Van

Nostrand Reinhold, New York, 1982).
[25] M. Rodahl, F. Hook, A. Krozer, P. Brzezinski, and B. Kasemo, Rev. Sci. Instrum. **66**, 3924 (1995).
[26] B. Wu, K. Wu, P. Wang, and D.-M. Zhu, J. Phys. Chem. C **111**, 1131 (2007).
[27] K. Wu, B. Wu, P. Wang, Y. Hou, G. Zhang, and D.-M. Zhu, J. Phys. Chem. B **111**, 8723 (2007).
[28] K. K. Kanazawa and J. G. Gordon, Anal. Chem. **57**, 1770 (1985).
[29] M. Rodahl and B. Kasemo, Sens. Actuators, A **54**, 448 (1996).
[30] A. Domack, O. Prucker, J. Ruhe, and D. Johannsmann, Phys. Rev. E **56**, 680 (1997).
[31] A. Domack and D. Johannsmann, J. Appl. Phys. **80**, 2599 (1996).
[32] D. Johannsmann, Macromol. Chem. Phys. **200**, 501 (1999).
[33] F. Hook, B. Kasemo, T. Nylander, C. Fant, K. Sott, and H. Elwing, Anal. Chem. **73**, 5796 (2001).
[34] M. V. Voinova, M. Rodahl, M. Jonson, and B. Kasemo, Phys. Scr. **59**, 391 (1999).
[35] D.-M. Zhu, K. Wu, B. Wu, P. Wang, J. J. Fang, Y. Hou, and G. Zhang, J. Phys. Chem. C **111**, 18679 (2007).
[36] D.-M. Zhu, J. J. Fang, B. Wu, and X. B. Du, Phys. Rev. E **77**, 031605 (2008).
[37] P. G. De Gennes, Macromolecules **9**, 587 (1976); **9**, 594 (1976); P. Gupta, C. Elkins, T. E. Long, and G. L. Wilkes, Polymer **46**, 4799 (2005).
[38] B. Hinner, M. Tempel, E. Sackmann, K. Kroy, and E. Frey, Phys. Rev. Lett. **81**, 2614 (1998).
[39] H. Tanaka, T. Miura, K. Takagi, and T. Nishi, Proc. IEEE **3**, 1325 (1990).
[40] J. Krim, J. G. Dah, and J. Suzanne, Phys. Rev. Lett. **52**, 640 (1984).
[41] M. P. Nightingale, W. F. Saam, and M. Schick, Phys. Rev. B **30**, 3830 (1984).
[42] Q. M. Zhang, H. K. Kim, and M. H. W. Chan, Phys. Rev. B **33**, 413 (1986).
[43] I. Langmuir, J. Am. Chem. Soc. **41**, 868 (1919).
[44] S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).
[45] G. Liu, J. Zhao, Q. Sun, and G. Zhao, J. Phys. Chem. B **112**, 333 (2008); G. Liu, S. Zou, and L. Fu, *ibid.* **112**, 4167 (2008).