Amplitude Change of a Quartz Crystal Microbalance

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The vibrational amplitude change of a quartz crystal microbalance was measured for different surfaces and under different gases. As pressure \( p \) increases, the amplitude has a tendency to decrease, roughly proportional to the square root of \( p \), experimentally. We found that the amplitude change versus \( p \) has a form of \( A/\sqrt{p} \) rather than \( (1/A)\sqrt{p} \). The latter does not fit well in the high-pressure range. The proportionality constant depends on neither the roughness nor the surface area of the quartz crystal resonator. We insists that fitting to \( (1/A)\sqrt{p} \) in the high-pressure range may be misinterpreted as an excessive decrease in \( A \) implying slippage or friction.

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I. INTRODUCTION

The quartz crystal microbalance technique has been widely used to measure an added mass in adsorption or chemical reaction experiments [1, 2]. While the frequency change \( \delta f \) of the quartz crystal transducer, which is proportional to the added mass, has a clear physical meaning, the amplitude change \( \delta A \) has some ambiguous points, and it is difficult to measure its absolute value.

The relation between the frequency change \( \delta f \) and the added mass was suggested by Stockbridge [3]:

\[
-\delta f = \frac{4f_0^2 \Delta m}{R_q S},
\]

where \( f_0 \) is the original resonance frequency, \( \Delta m \) the mass adsorbed, \( R_q \) the transverse acoustic impedance (8.862 \times 10^6 kg/m^2), [4] and \( S \) the surface area of quartz. In addition, \( f \) is affected by the viscosity of the surrounding gas (viscous loading effect) and the pressure of the gas (the hydrostatic pressure effect).

In terms of the quality factor \( Q \), the added mass does not affect the \( Q \) change unless it has sliding motion on the quartz surface. Only the viscous loading effect causes a change in \( Q \), \( \delta (1/Q) \):

\[
\delta (1/Q) = 4\sqrt{\eta \rho \omega /2},
\]

where \( \eta \) is the viscosity, \( \rho \) the density of the gas, and \( \omega = 2\pi f \) [3]. These relations are based on the fluid dynamics. The fluid dynamics are based on statistical mechanics, assuming that the mechanical motions are shorter than the mean free path of the gas, with a statistical approximation. In fact, the viscosity itself is a macroscopic quantity. However, the vibrational amplitude \( A \) of the quartz crystal transducer is on the order of 10 nm [5], and the mean free path of gas molecules could be on the order of 1 \( \mu \)m for low-pressure conditions. We discuss whether Stockbridge's macroscopic and statistical approach is valid in nanoscale kinetics.

The Krim group has published many papers related with the amplitude change of the quartz crystal microbalance [6–8]. Mainly, they used an active oscillator circuit to vibrate the quartz transducer with its resonance frequency \( f \). The electrical output signal from the oscillator circuit is designed to be proportional to the mechanical vibration of the quartz transducer, and the amplitude of the signal is assumed to be proportional to the mechanical \( Q \) value of the quartz transducer. The excessive amplitude changes were interpreted as "slippage or frictional motion" of the adsorbed molecules on the substrate. To make clear the amplitude change effect, we studied the amplitude changes for various quartz crystal resonator (QCR) surfaces under adsorptive and non-adsorptive conditions.

II. EXPERIMENT

In order to identify the reason for the amplitude change, we prepared three samples with different rough-
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III. RESULTS AND DISCUSSION

The amplitude $A$ and the resonance frequency $f$ of the quartz transducers were measured as a function of pressure $p$. Figure 1 shows representative data for $A$. The QCR was coated with carbon nanotube (CNT) bundles, and $A$ was measured as function of the $O_2$ pressure, $p$, at $T = 293$ K. In Figure 1(a), the measured data were plotted and fitted to a fitting curve

$$\frac{1}{A} = \frac{1}{A_0} + \beta \sqrt{p}, \quad (3)$$

where $1/A_0 = 3.92 \, \text{V}^{-1}$ and $\beta = 0.041$ are fitting parameters. If we accept the ideal gas law and if $Q$ is proportional to $A$, Eq. (2) is equivalent to Eq. (3). The fitting curve (solid line) does not seem to fit well over the entire pressure range. The deviation from the fitting curve in the high-pressure range could be attributed to slippage of the adsorbed thin film [6,7]. However, it is obvious that the temperature was room temperature, and no adsorption was expected at this temperature.

On the other hand, in the $p$ versus $A$ plot, as shown in Figure 1(b), the fitting curve

$$A = A_0 - b\sqrt{p}, \quad (4)$$

appears to provide a satisfactory fit. In general, the $A$ is believed to be proportional to $Q$ [6,9,10]. Therefore, $A$ should be fitted to the curve in Figure 1(a), following Eq. (2), but the curve in Figure 1(b) seems to fit better, and it did for all the data we measured. The resultant fitting parameter $b$ was $0.234 \pm 0.01$ for $O_2$ on a CNT bundle.

Table 1 shows a summary of the fitting results with Eqs. (3) and (4). While the fitting to Eq. (4) gives consistent values of $b$, the fitting result with Eq. (3) gives inconsistent values of $\beta$. Especially, three $\beta$ values for

<table>
<thead>
<tr>
<th>gas substrate</th>
<th>$T$ (K)</th>
<th>$f$ (MHz)</th>
<th>$A_0$</th>
<th>$b \times 10^3$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ Ag</td>
<td>79.8</td>
<td>5</td>
<td>0.244</td>
<td>2.4 $\pm$ 0.1</td>
<td>0.0428</td>
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<tr>
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<tr>
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<td>0.238</td>
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responding to the mass of 0.26 $\mu$g of graphite powder. The carbon nanotube (CNT) substrate was also prepared in the same manner. For the Ag substrate, we used an as-prepared commercial QNT coated with Ag electrode.

Fig. 1. Amplitude $A$ of CNT-coated quartz was measured as a function of the $O_2$ pressure $p$ at $T = 293$ K. (a) The measured data were fitted to a fitting curve ($1/A = 1/A_0 + \beta \sqrt{p}$). The fitting curve (solid line) does not seem to fit well. (b) The fitting to $A = A_0 - b\sqrt{p}$ seems good.

Table 1. Summary of fitting results.

Figures: [Diagram of amplitude $A$ versus pressure $p$ for different gas substrates.]

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Fig. 2. Adsorption isotherm measurements were done with different supply voltages at $T = 80$ K. The adsorbate was O$_2$, and the adsorbent was graphite. The amplitude $A$ and the frequency $f$ were measured, simultaneously. The amplitude $A$ was fitted to (a) Eq. (4) and (b) Eq. (3). The inset shows the change in $f$, indicating the adsorption behavior.

O$_2$/graphite are entirely different numbers that depend on the $A_0$. Judging from the $A_0$ dependency of $\beta$, we believe that the fitting with Eq. (3) should be modified to the form $1/(A - A_0) = 1/A_0^2 + \beta \sqrt{p}$ to make $\beta$ independent of $A_0$. It is noticeable that $b$ for O$_2$ gas does not depend on the temperature or on the substrate within the measurement accuracy. In the case of N$_2$ gas, the difference in the $b$ values originates from the difference in $f$, as one might expect from an analogy with the Eq. (2).

A naive idea held that the pressure dependency of the amplitude depended on the roughness of the substrate. Therefore, the rough surface coated with CNT bundles or graphite powder was expected to have greater $b$ compared with the value for the Ag surface. Our experimental result, however, shows that damping due to the gas environment does not depend on the surface roughness. It is noticeable that the fitting parameter $b$ is independent of the temperature. This behavior looks plausible considering Eq. (2) because $\rho$ is inversely proportional to $T$ for the ideal gas model and because $\eta$ is roughly proportional to $T$ (for instance, $\eta \approx 59$ and 201 $\mu$Poise at $T = 80$ and 292 K, respectively [11]). By comparing the He and the O$_2$ data in Table 1, one sees that Eq. (2) works roughly because the $\eta$ of He is similar to that of O$_2$, $\rho$ of He is 8 times smaller than that of O$_2$ and $\beta$ of He is 3 times smaller.

In order to check the linearity of our instrument, adsorption isotherm measurements were done with different supply voltages at $T = 80$ K, as shown in Figure 2. The adsorbate was O$_2$, and the adsorbent was graphite. The amplitude $A$ and the frequency $f$ were measured simultaneously. As the temperature was unstable, the frequency data show unrealistic wiggles at low pressures, as shown in the inset. However, the amplitude data are more stable because the amplitude is not sensitive to the temperature. The two $A$ versus $p$ curves correspond to different supply voltages. As the amplitude was increased with higher supply voltage from 0.19 (+) to 0.28 V [□] in Figure 2(a), the frequency $f$ was also raised to 5 Hz, as shown in the inset. Though the two amplitude data sets started from different values of $A$ when $p = 0$, each data set $\delta A$ looks very similar, but with different offsets, as shown in Figure 2(a). The solid lines in this graph shows fitting curves to Eq. (4). The fitting parameters $b$ are the same (2.4 ± 0.1) within experimental
The amplitude $A$ was measured with different gases. (a) shows $1/A$ changes as a function of $O_2$ pressure and (b) shows that of He gas at the same temperature $T = 79.8$ K. The inset shows the frequency change for $O_2$ adsorption accuracy. However, in the $1/A$ plot (Figure 2(b)), each $\beta$ has a totally different value (0.34 and 0.75). According to Eq. (2), $\beta$ should be invariant for an offset $A_0$ change. We insist that there should be a correction parameter in Eq. (2) to fit the experimental raw data. It is noticeable that the amount of amplitude change $A - A_0$, is independent of $A_0$.

We happened to observe a strange behavior for $N_2$ adsorption on Ag in the condensation region, as shown in Figure 3. The temperature was 78.3 K. The same data were fitted to (a) Eq. (4) and (b) Eq. (2). The inset shows the simultaneously measured frequency changes. Neither fittings worked well in the high-pressure range. The deviations from the fitting curves (solid lines) in the high-pressure range can be attributed to a slippage behavior, as the Krim group insisted [6, 7, 10]. As the pressure was increased, the deviation became large and then decreased. In the desorption process ($p$ decreasing), this behavior seems to be reproduced. In a preliminary test at room temperature, this QCR seemed to be normal. With repetitive measurements, this behavior was reproduced. However, we found that this QCR was not soldered tightly to the electric wire inside the sample can and that this anomaly occurred only for this QCR. Therefore, the anomaly can be interpreted as follows: The adsorbed film filled the bad electric connection gap, the rf signal transmission changed.

On the other hand, Figure 4 shows changes in the values of $A$ for a Ag-coated QCR as functions of (a) $O_2$ and (b) He gas pressure at $T = 79.8$ K. These two sets of data were obtained successively under the same conditions. In Figure 4(b), two data sets, one measured with $p$ increasing and the other with $p$ decreasing, are depicted together; both lie on a curve and are barely distinguishable. In Figure 4(a), the $1/A$ fitted to Eq. (3) shows a behavior similar to that shown in Figure 1. While in case of Figure 1, the temperature was high and no adsorption was expected, the temperature for Figure 4(a) was low, and the clear adsorption was evidenced by the $-\delta f$ versus $p$ data, as shown in the inset. When we replaced $O_2$ with He, which is not expected to be adsorbed, the $1/A$ data could be fitted well by using Eq. (3), as shown in Figure 4(b). However, considering the $p$ range less than 250 Torr, these data are not enough to conclude that Stockbridge's model is valid in this sample. One possible clue why only the He data fit Eq. (2) well is that He is an inert gas that is more ideal gas-like than the other sample gas.

**IV. CONCLUSIONS**

We found that the amplitude $A$ change versus $p$ had a form of $\delta A = -b\sqrt{p}$ rather than $\delta(1/A) \propto \sqrt{p}$. The latter did not work well in the high-pressure range. The proportionality constant $b$ depended on neither the roughness nor the surface area of the QCR. We insist that an excessive decrease in $A$ compared to $\delta(1/A) \propto \sqrt{p}$ in the high-pressure range should not be misinterpreted as a slippage or friction.

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