We have discussed potentiometric and amperometric sensors in the previous homeworks. In this homework, we will focus on two variants of cantilever sensors, namely, classical linear cantilever sensors and a new type of nonlinear cantilever sensors that combines potentiometric and mass-based sensing within a single scheme.

PART I: AMPEROMETRIC SENSORS

Problem 4.1: An electrochemical cell is made of two electrodes with Cadmium ($Cd^{2+}/Cd$) and Antimony ($Sn^{2+}/Sn$). Which metal will be cathode/anode? Write the half-reactions and the equation of the cell. What is the emf of the cell?

Solution:
Since, the standard reduction potential of $Sn^{2+}$ is more positive (less negative), it will act as cathode and $Cd$ will act as anode. The equation of the electrochemical cell is then given by

$$Sn^{2+} + Cd \rightarrow Sn + Cd^{2+}$$

With two half-reactions:

$$Sn^{2+} + 2e^- \rightarrow Sn$$  (Cathode, Sn is reduced following the gain of two electrons)

$$Cd \rightarrow Cd^{2+} + 2e^-$$  (Anode, Cd is oxidized following the loss of two electrons)

Emf of the cell is given by the difference in the reduction potential:

$$E_{cell} = E_{cathode} - E_{anode}$$

$$= -0.136 - (-0.403)$$

$$= 0.267 \text{V}$$

Problem 4.2: Derive the Butler-Volmer equation which describes the following redox reaction,
$R \xrightarrow[k_f]{k_b} O + ne^-$

where $k_f, k_b, \rho_{s,R}, \rho_{s,O}$ are forward reaction rate, backward reaction rate, the surface concentrations of reductant and oxidant, respectively. The constant $n$ refers to the number of electrons exchanged during each reaction.

(a) Write an expression for the current flowing through the electrodes as a balance between forward (reduced to oxidized species) and reverse (oxidized to reduced species) reactions. Assume that the electrode area is $A$.

(b) The forward and backward rate constants are bias dependent and given by

\[
k_f = k_{0,f} e^{-(1-\alpha)n(E-E_0)/k_BT} \\
k_b = k_{0,b} e^{-\alpha n(E-E_0)/k_BT}
\]

Rewrite the current expression in terms of the biases. This is called Butler-Volmer equation. Also, derive an expression for the equilibrium potential, $E_{eq}$ the bias at which the net current is zero. Here, $n$ is the number of electron exchanged per reaction and $\alpha$ is the charge transfer coefficient.

(c) Rewrite equation a) in terms of overpotential, $\eta = E - E_{eq}$ and exchange current,

\[
i_o = qA \left(k_{0,f} \rho_{s,R}\right)^\alpha \left(k_{0,b} \rho_{s,O}\right)^{1-\alpha}
\]

(d) Approximate the current for large $\eta$ (either positive/negative). The resultant expression is called Tafel equation.

(e) What is the meaning of $E_0$ in Butler-Volmer equation?

**Solution:**

\[
a) \quad I = qA \left(k_f \rho_{s,R} - k_b \rho_{s,O}\right)
\]

\[
b) \quad \Rightarrow I = qA \left(k_{0,f} \rho_{s,R} e^{-(1-\alpha)n(E-E_0)} - k_{0,b} \rho_{s,O} e^{-\alpha n(E-E_0)}\right)
\]

This is called Butler-Volmer equation.

At $E = E_{eq}$, $I = 0$
\[ E_{eq} = E_0 + \frac{k_B T}{nq} \ln \left( \frac{k_{0,f} \rho_{s,O}}{k_{0,b} \rho_{s,R}} \right) \]

c) Put \( E = \eta + E_{eq} \) in part b), we get

\[ I = qA \left( k_{0,f} \rho_{s,R} \right)^\alpha \left( k_{0,b} \rho_{s,O} \right)^{1-\alpha} \left( e^{(1-\alpha)nf \eta} - e^{-\alpha n f \eta} \right) \]
\[ = i_o \left( e^{(1-\alpha)nf \eta} - e^{-\alpha n f \eta} \right) \]

d) The Tafel equation is obtained when either oxidation or reduction dominates the reaction. It depends on the potential of the electrode, as follows.

\[ i = i_o e^{\frac{(1-\alpha)nf \eta}{kT}} \quad \eta \gg 0 \]
\[ i = i_o e^{\frac{-\alpha n f \eta}{kT}} \quad \eta \ll 0, \]

The result shows that the current is exponentially dependent on the overpotential.

e) \( E_0 \) refers to the standard reduction potential of the electrode.

Problem 4.3: The current passing through the electrodes with flux recycling is given by

\[ i = q \bar{p} C_{D,SS} \left[ \frac{e^{-f \eta_a} - e^{-f \eta_b}}{1 + e^{-f \eta_a} + e^{-f \eta_b}} \right] \]

Find the expression for a pair of planar electrodes. Assume that the electrode areas are equal.

Solution:
The current expression is given by:

When $A_b = A_a = A$,

$$i = q \bar{p} C_{D,SS} \left\{ \frac{e^{-f_{\eta_b}} - e^{-f_{\eta_A}}}{1 + e^{-f_{\eta_b}} - 1 + e^{-f_{\eta_A}}} \right\} \left( 1 + \left( \frac{C_{D,SS}}{k_0} \right) \left( \frac{1}{A_a} + e^{f_{\eta_A}} + \frac{1}{A_b} + e^{f_{\eta_B}} \right) \right).$$

We get,

Since,

$$i = q \bar{p} C_{D,SS} \left\{ \frac{e^{-f_{\eta_b}} - e^{-f_{\eta_A}}}{1 + e^{-f_{\eta_b}} - 1 + e^{-f_{\eta_A}}} \right\} \left( 1 + \left( \frac{C_{D,SS}}{Ak_0} \right) \left( \frac{e^{f_{\eta_A}} + e^{f_{\eta_B}}}{1 + e^{f_{\eta_A}} + 1 + e^{f_{\eta_B}}} \right) \right).$$

$$C_{D,SS} = \frac{A_b D}{W} = \frac{A_a D}{W} = \frac{AD}{W},$$

we get

$$I_{RD} = q \rho_R \frac{AD}{W} \left\{ \frac{1}{e^{f_{\eta_B}} + 1} - \frac{1}{e^{f_{\eta_B}} + 1} \right\} \left( 1 + \left( \frac{D}{Wk_0} \right) \left( \frac{1}{e^{f_{\eta_A}} + 1} + \frac{1}{e^{f_{\eta_B}} + 1} \right) \right).$$

**Problem 4.4:** The mass of a Virus can be measured by shift in resonant frequency of a cantilever.

(a) A typical virus weights approximately ten atto-gram ($\Delta m = 10 ag$). Assume a Si cantilever sensor with $E = 150GPa$, $\rho = 2300kg/m^3$, $L = 3.3 \mu m$, $W = 1.5 \mu m$. Calculate the
absolute and relative shifts in resonant frequency (ignore damping) due to capture of a single virus molecule?

(b) Recalculate the response for Vaccinia virus (VACV or VV), which large, complex virus, see below. It’s weight is about ten femto-gram \((\Delta m = 10fg)\). Calculate the absolute and relative shift in the resonance frequency.

Hint. Assume the equivalent spring-mass model. Take \(\alpha_1 = 0.85, \alpha_2 = 1\) for these calculations.

Solution:
(a) Change in the resonance frequency of a cantilever due to capture of bio-molecule is simply given by-

\[
\Delta f = -\frac{\Delta m}{2m_0} f_0,
\]

where \(\Delta f\) is the change in resonance frequency, \(\Delta m\) is the mass of captured molecules, \(m_0\) is the initial mass of the cantilever and \(f_0\) is the resonance frequency of the cantilever before capture. Note that, Eq. 1 assumes that there is no change in the stiffness of the cantilever due to capture of molecules. The resonance frequency of a cantilever is simply given by-

\[
f_0 = \sqrt{\frac{k_0}{m_0}}.
\]

where \(k_0\) is the initial stiffness of the cantilever. Using \(m_0 = \alpha_1 \rho WH L\) and \(k_0 = \alpha_2 EWH^3 / 12L^3\), it can be shown that-

\[
\Delta f = -\frac{\Delta m}{2} \sqrt{\frac{\alpha_2 E}{12\rho^3 \alpha_1^3 (WL)^3}},
\]
where \( W \) is the width, \( L \) is the length, \( E \) is the Young’s modulus, \( \rho \) is the density of cantilever. \( \alpha_1 \) and \( \alpha_2 \) are geometrical constants of the cantilever.

Now, put all the numbers together:
For a typical virus, \( \Delta m = 10 \times 10^{-18} g = 10^{-20} kg, E = 150 GPa, \rho = 2300 kg/m^3, W = 1.5 \mu m, L = 3.3 \mu m \) in formula Eq. 3 to get \( \Delta f = -119 Hz \). This frequency shift may be too small to be resolved in a typical experiment.

(b) For a VacciniaVirus, \( \Delta m = 10 \times 10^{-15} g = 10^{-17} kg, \Delta f = -119 kHz \). This frequency shift is easy to detect.

Here’s an example of frequency shift after loading a single Vaccinia virus particle (Gupta, A., D. Akin, and R. Bashir. "Single virus particle mass detection using microresonators with nanoscale thickness." Applied Physics Letters 84.11 (2004): 1976-1978.). There is a 60 kHz decrease in resonant frequency with plan dimension of \( L=3.6 \) um and \( W=1.7 \) um.
Problem 4.5: MEMSLab allows us to calculate changes in the resonant frequency by numerical simulation.

Here we determine the resonance frequency of a cantilever MEMS structure, and understand the impact of increased mass and stiffness on the resonance frequency. In this exercise, we will be using a different simulator, called MEMSLab – also available from nanohub.org. The same nanohub id will work.

Exercise

Consider a cantilever with the following properties for the suspended membrane: \( L=3\mu m, W=1\mu m, \) thickness=40nm thick, Young’s modulus=200 GPa, Poisson ratio=0.31, and density=2000 kg/m\(^3\). The airgap is 100nm. To prevent accidental short, a 10nm insulator has been deposited on the bottom electrode (although it will not play any significant role in the following calculation).

The resonant frequency of this cantilever will change once the biomolecules are captured the sensor surface. We assume that the change in membrane thickness due to biomolecule capture is negligible, but the mass changes by 5%.

Follow the following steps to determine the change in resonance frequency by analyzing the 1V step response of this cantilever before and after the molecule capture.

Simulator setup

- Launch the online tool MEMSLab (https://nanohub.org/tools/cvgraph/)

A) Setting up the input parameters

Input page 1: Electrode geometry: Cantilever
Simulation Type: Numerical Model
3D Poisson: OFF

Input page 2: Transient Analysis: ON
Voltage Type: Step voltage
Run Time: 5e-6s
Voltage: 1V

Input page 3: Length of electrode: 3um
Width of electrode: 1um
Thickness of electrode: 40nm
Air-gap: 100nm
Dielectric thickness: 10nm
Number of grids: 40

Input page 4: Electrode material: Custom
Young’s modulus: 200GPa
Poisson’s Ratio: 0.31
Density: 2000kg/m\(^3\)
Dielectric material: Silicon Nitride
B) Click the simulate button. We observe oscillations at small times in the Capacitance vs. Time plot. These oscillations die down because of damping. For larger time, the capacitance settles to the steady state value. The oscillation frequency corresponds to the natural resonance frequency of the cantilever for the given bias. Find this resonance frequency.

C) Using the “base parameter set”, we now change the mass of the electrode by 5%. To do this, we increase the density by 5%. Comment what will happen to the resonance frequency and why. Verify by simulating the step response that it is indeed the case.

**Solution:**

![Capacitance vs Time graph](image)

Time difference between first two peaks: \(2.0578 \times 10^{-7} \text{s} - 7.0866 \times 10^{-8} \text{s} = 1.349 \times 10^{-7} \text{s}\).

So, natural resonance frequency = 7.41MHz
We see that due to the increased mass (dark blue), the resonance frequency has reduced from the previous case (light blue). Applying a similar approach to problem 1, the frequency is $-7.16\text{MHz}$.

**Part III: Cantilever based Nonlinear NanoBioSensors**

**Problem 4.6: The response of a fixed-fixed suspended nanosensor becomes nonlinear at large displacement**

(a) Derive a relationship for the pull-in voltage, $V_{PI}$

(b) Show that $y/y_0 = 2/3$ at the transition point.

(c) What the degree of spring softening at $0.8y_0$? What about $y = 0.9y_0$?

**Solution:**
(a)-(b)
Fig. 4.6: Schematic of Flexure-FET without the channel.

For this problem, ignore the field effect transistor part and just consider the device as shown in Fig. 4.4. The operation of Flexure-FET is fundamentally governed by the balance of spring and electrostatic forces i.e.,

\[ k(y_0 - y) = \frac{1}{2} \frac{\epsilon_0 A}{y^2} V^2, \]  

where \( k \) is the stiffness, \( y_0 \) is the initial air-gap, \( y \) is the position of the gate (\( M_1 \)), \( \epsilon_0 \) is the permittivity of free space, \( A \) is the area of gate electrode, and \( V \) is the applied voltage. Note that, at pull-in, the mechanical stiffness and electrical stiffness becomes equal i.e.,

\[ k = \frac{\epsilon_0 A}{y^2} V^2. \]  

Use this value of stiffness in Eq. 1 and get-

\[ y_0 - y = \frac{y}{2}, \]

which simplifies to give us the point where pull-in instability (transition point) occurs i.e.,

\[ y_{PI} = \frac{2}{3} y_0. \]  

Use this value of \( y_{PI} \) in Eq. 1 to get the following value for pull-in voltage i.e.,

\[ V_{PI} = \sqrt{\frac{8Ky_0^3}{27\epsilon_0 A}}. \]

(c)

With the increase in voltage, gate not only moves down, but its effective stiffness also changes according to-

\[ K_{eff} = -\frac{d}{dy} (F_s - F_{elec}) = K - \frac{\epsilon_0 A}{y^2} V^2, \]  

Which gets simplified to (using Eq. 1)-

\[ \frac{K_{eff}}{K} = 3 - \frac{2y_0}{y}. \]  

Equation 6 suggests that effective stiffness goes to zero at pull-in i.e., at \( y = y_{PI} = \frac{2}{3} y_0 \). Now, value of \( K_{eff} \) at \( y = 0.8y_0 \) and \( y = 0.9y_0 \) is given by-
\[ \frac{K_{\text{eff}}}{K} (y = 0.8y_0) = 3 - \frac{2}{0.8} = 0.5 \]
and
\[ \frac{K_{\text{eff}}}{K} (y = 0.9y_0) = 3 - \frac{2}{0.9} = 0.77. \]

Stiffness changes rapidly as gate moves down eventually vanishing at pull-in.

**Problem 4.7: A Flexure FET has exponential sensitivity**

**Initial Setup**
- Log on using your Nanohub id.
- Launch the online tool BiosensorLab (https://nanohub.org/tools/senstran/) and select version II
- In the sensor structure, choose Flexure-FET.
- Use the default parameters: \( L = 4\mu m, W = 1\mu m, y_0 = 100nm, H = 40nm, y_d = 5nm \).
- Go to type of simulation to be done and click yes on sensitivity. Choose Response to bio-molecules for the analysis.
- Use the default parameters: \( N_A = 6 \times 10^2 m^{-3}, \epsilon_r = 3.9, V_{DS} = 0.5V \). Change the Young’s modulus of the beam to \( E = 198GPa \) so that \( K = \frac{483EI}{L^3} \approx 8N/m \). Also, change captured molecule density to \( N_s = 8.5e12cm^2 \) which corresponds to 10% change in stiffness. \( N_s = (\Delta K/K) \times (H/3) \times (1/A_tH_t) \) with \( A_t = \pi nm^2 \) and \( H_t = 5nm \). \( A_t \) is the cross-sectional area of the molecule and \( H_t \) is the height of the molecule.
- Click on simulate

**Exercise**

(a) From the position of gate before capture (\( y \) vs. \( V_g \)), calculate the pull-in voltage and confirm it with the analytical result obtained in HW4.6.
(b) From the position of gate after capture (\( y \) vs. \( V_g \)), calculate the position of gate at the same voltage.
(c) From the drain current before and after capture (\( I_{DS} \) vs. \( V_g \)), calculate the ratio of drain current before and after capture at pull-in voltage.

**Solution:**

From the position of gate vs. voltage plot (Fig. 4.7.1), one can easily see that the pull-in voltage is around 8.97V. One may recall that the analytical formula in HW2 gave us a pull-in value of 8.77V. The two values are really close and confirms the validation of analytical results.
From the position of gate vs. voltage (Fig. 4.7), one can easily see that the position of gate after capture is 75.487nm. One may recall that analytical formula in HW2 gave us a position of 77.69nm. The two values are again very close.

![Graph showing position of gate before and after capture](image)

**Fig. 4.7.1:** Position of gate before and after capture of bio-molecules.

(d) From the drain current vs. voltage plots in Fig. 2.4.2 or ratio of drain current before and after capture of bio-molecules plot in Fig. 2.4.3, one can easily see that the drain current changes by 511 due to 10% change in the stiffness. One may recall that the analytical formula predicted this change to be 411. The two values are close at least in order.
Fig. 4.7.2: Drain current before and after capture of bio-molecules.
Fig. 4.7.3: Ratio of drain currents before ($I_{DS1}$) and after ($I_{DS2}$) capture of bio-molecules.