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: Spontaneous reaction vs. forced oxidation-reduction reaction

An electrochemical cell is made of two electrodes with Cadmium \((Cd^{2+}/Cd)\) and Antimony \((Sn^{2+}/Sn)\). Which metal will be cathode/anode? What is the emf (potential difference) of the cell?

Problem 4.2: Derive the Butler-Volmer equation which describes the following redox reaction,

\[ R \stackrel{k_f}{\rightarrow} k_b \rightarrow O + ne^- \]

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

\[ k_f = k_{0,f} e^{(1-\alpha) n \frac{(E-E_0)}{k_B T}} \]

\[ k_b = k_{0,b} e^{-\alpha n \frac{(E-E_0)}{k_B T}} \]
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?

**Problem 4.3: Beating the diffusion limit in an amperometric sensor.**

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

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

**PART II: LINEAR CANTILEVER SENSORS**

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

(a) A typical virus weights approximately ten atto-gram ($\Delta m = 10ag$). Assume a Si cantilever sensor with $E = 150$GPa, $\rho = 2300$kg/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.
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:  $L=3\text{um}$, $W=1\text{um}$, thickness=$40\text{nm}$ thick, Young’s modulus=$200\text{ GPa}$, Poisson ratio=$0.31$, and density=$2000\text{ kg/m}^3$. The airgap is $100\text{nm}$. To prevent accidental short, a $10\text{nm}$ 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
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.

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, $V_{pl}$

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

(c) What the degree of spring softening at $y = 0.8y_0$ ? What about $y = 0.9y_0$?
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/](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 biomolecules capture for the analysis.
- Use the default parameters: \( N_A = 6 \times 10^{22} m^{-3}, \epsilon_r = 3.9, V_{DS} = 0.5V \). Change the Young's modulus of the beam to \( E = 198GPa \) so that \( k = 483EI/L^3 \approx 8N/m \). 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 \((y \text{ vs. } V_g)\), calculate the pull-in voltage and confirm it with the analytical result obtained in HW4.6.
(b) From the position of gate after capture \((y \text{ vs. } V_g)\), calculate the position of gate at the same voltage.
(c) From the drain current before and after capture \((I_{DS} \text{ vs. } V_g)\), calculate the ratio of drain current before and after capture at pull-in voltage.